Encoding Electronic and Biological Function in Hierarchical Soft Materials

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Abstract

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Developing materials with comparable structural complexity and programmed hierarchy as those found in nature is a grand challenge in materials science. One way to synthesize soft materials with these complex architectures is to use bottom-up self-assembly of nanoscale building blocks, mimicking how organisms grow tissues with specific functions from peptides, carbohydrates, lipids, inorganic crystals, and nucleic acids. In this context, this work explores the encoding of small molecules to engage in specific interactions to drive their assembly into ordered structures for applications in energy and medicine. For targets in energy, organic molecules were programmed to template deposition of functional inorganic materials in hierarchical hybrid structures. In the first system, aromatic surfactants were studied as additives during electrodeposition of layered cobalt hydroxide to tune the interlayer spacing and microstructure of thin film supercapacitor electrodes. One specific surfactant was discovered to induce curvature of the inorganic layers resulting in the deposition of multi-walled organic-cobalt hydroxide nanotubes. The nanotubular architecture was found to provide high surface area and global orientation of the inorganic layers perpendicular to the current collecting substrate for efficient electron transport. The organic molecules used to template the structure also enhanced the stability of the hybrid material in the harsh environments necessary for energy storage function. A second hybrid system was investigated based on a series of aromatic cations as intercalants in layered organic-lead iodide perovskite thin films, which are of interest as solar cell active layers. Layered perovskites are inherently more environmentally stable than their three-dimensional counterparts, but they suffer from poor photovoltaic performance due to orientation of the semiconducting layers parallel to the
substrate and the typically insulating organic cations between the layers. By introducing aromatic cations with tunable intramolecular interactions, enhanced out-of-plane conductivity and photovoltaic performance was achieved without compromising environmental stability. A different organic-inorganic hybrid system investigated in this work took inspiration from natural biomineralization processes. In this system supramolecular peptide amphiphile (PA) nanofibers were encoded with amino acids that could bind or nucleate gold nanoparticles to form conductive nanowires. The conductivity was found to be highly dependent on the pathway for gold metallization of the PA fibers. When spray coated in a thin layer on plastic substrates the hybrid nanowires demonstrated high transparency and conductivity, ideal for transparent conducting electrodes in flexible touch screens or solar cells. Finally for biomedical applications this work investigated 3D printing to order supramolecular assemblies into patterned hydrogels with programmed alignment via shear during extrusion. The attractive and repulsive interactions between individual PA molecules and between multiple PA assemblies were critical for determining the viscosity and printability of the aqueous inks. 3D printed hydrogels composed of aligned PA fibers were found to exhibit anisotropic ionic transport, programmable actuation, and directed cell outgrowth. In order to target potential bioelectronic functions in future systems, the 3D printing technique was extended to aqueous inks composed of semiconducting chromophore amphiphile (CA) nanofibril assemblies based on carbonyl bridged triarylamine aromatic cores. By incorporating hydrogen bonding motifs on the periphery of the CA aromatic core, \( \pi \)-orbital overlap between molecules was increased leading to higher conductivity. The addition of the biopolymer alginate to the ink not only allowed for shear alignment of the supramolecular CA fibrils during 3D printing, which results in further enhancement of the electronic transport, but also imparts durability to the material during cyclic bending. The soft organic scaffolds and organic-templated hybrid materials investigated in this work demonstrate the structural complexity that can be achieved via programmed molecular self-assembly, in some cases combined with
additive manufacturing. These synthetic materials are reminiscent of hierarchical structures found in nature, and can be further explored in the future for novel functions in electronics, sustainability and healthcare.
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List of Abbreviations

AFM  Atomic Force Microscopy
Ag NW  Silver Nanowire
ATRP  Atom-Transfer Radical Polymerization
Au NC  Gold Nanocrystal
Au NW  Gold Nanowire
BRE  Bio-Recognition Element
Cox  Oxide Capacitance
CA  Chromophore Amphiphile
CB  Chlorobenzene
CBT  Carbonyl-Bridged Triarylamine
CBT-al  Carbonyl-Bridged Triarylamine Alkyne
CBT-am  Carbonyl-Bridged Triarylamine Amide
CPD  Critical Point Drying
Cryo-TEM  Cryogenic Transmission Electron Microscopy
CV  Cyclic Voltammetry
dN−I  Average cationic nitrogen to peripheral-iodide distance
DA  Decanoic Acid
DCM  Dichloromethane
DEGMA  Diethylene Glycol Methyl Ether Methacrylate
DIC  N, N′-diisopropylcarbodiimide
DIEA  Diisopropylethylamine
DIW  Direct Ink Writing
DMEM  Dulbecco’s Modified Eagle Medium
<table>
<thead>
<tr>
<th>Acronym</th>
<th>Full Form</th>
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<tbody>
<tr>
<td>DMF</td>
<td>Dimethylformamide</td>
</tr>
<tr>
<td>DMSO</td>
<td>Dimethyl Sulfoxide</td>
</tr>
<tr>
<td>DRC</td>
<td>Dendron Rodcoil</td>
</tr>
<tr>
<td>E$_{S_1}$</td>
<td>Energy of S$_1$ exciton peak</td>
</tr>
<tr>
<td>EDL</td>
<td>Electric Double-Layer</td>
</tr>
<tr>
<td>EDLC</td>
<td>Electric Double-Layer Capacitance</td>
</tr>
<tr>
<td>EDS</td>
<td>Energy Dispersive X-ray Spectroscopy</td>
</tr>
<tr>
<td>EIS</td>
<td>Electrochemical Impedance Spectroscopy</td>
</tr>
<tr>
<td>ESI-MS</td>
<td>Electrospray Ionization Mass Spectrometry</td>
</tr>
<tr>
<td>EtOH</td>
<td>Ethanol</td>
</tr>
<tr>
<td>Fmoc</td>
<td>9-Fluorenylmethoxycarbonyl</td>
</tr>
<tr>
<td>FTO</td>
<td>Fluorine doped Tin Oxide</td>
</tr>
<tr>
<td>FWHM</td>
<td>Full-Width at Half-Maximum</td>
</tr>
<tr>
<td>GBL</td>
<td>$\gamma$-butyrolactone</td>
</tr>
<tr>
<td>GIWAXS</td>
<td>Grazing-Incidence Wide-Angle X-ray Scattering</td>
</tr>
<tr>
<td>GIXS</td>
<td>Grazing Incidence X-ray Scattering</td>
</tr>
<tr>
<td>HAADF</td>
<td>High-Angle Annular Dark-Field</td>
</tr>
<tr>
<td>HAP</td>
<td>Hydroxyapatitie</td>
</tr>
<tr>
<td>HBTU</td>
<td>2-(1H-Benzotriazol-1-yl)-1,1,3,3-tetramethyluronium hexafluorophosphate</td>
</tr>
<tr>
<td>HF</td>
<td>High Frequency</td>
</tr>
<tr>
<td>HOMO</td>
<td>Highest Occupied Molecular Orbital</td>
</tr>
<tr>
<td>HPLC</td>
<td>High Performance Liquid Chromatography</td>
</tr>
<tr>
<td>ID</td>
<td>Inner Diameter</td>
</tr>
<tr>
<td>IPA</td>
<td>Isopropanol</td>
</tr>
<tr>
<td>I$_{SD}$</td>
<td>Source-Drain Current</td>
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ITO  Indium Tin Oxide
I-V  Current-Voltage Curve
LC-MS  Liquid Chromatography-Mass Spectrometry
LCST  Lower Critical Solution Temperature
LED  Light Emitting Diode
LUMO  Lowest Unoccupied Molecular Orbital
MeOH  Methanol
MW  Molecular Weight
NBA  2-Naphthalenebutyric Acid
NBAA  N,N'-methylenebisacrylamide
NMP  N-methyl-2-pyrrolidone
NMR  Nuclear Magnetic Resonance
OEGMA_{500}  Oligo(ethylene glycol) Methyl Ether Methacrylate
OM  Optical Microscopy
PA  Peptide Amphiphile
PCE  Power Conversion Efficiency
PDMS  Polydimethylsiloxane
PEDOT  Poly(3,4-ethylenedioxythiophene)
PEDOT:PSS  Poly(3,4-ethylenedioxythiophene) Polystyrene Sulfonate
PEGSH  Poly(ethylene glycol) Methyl Ether Thiol
PEO  Poly(ethylene oxide)
PET  Poly(ethylene terephthalate)
PI  Polyimide
POM  Polarized Optical Microscopy
PPO  Poly(propylene oxide)
PXRD  Powder X-ray Diffraction
PyAA  1-Pyreneacetic Acid
PyBA  1-Pyrenebutyric Acid
PyHA  1-Pyrenehexanoic Acid
RT    Room Temperature
SAED  Selected Area Electron Diffraction
SAXS  Small-Angle X-ray Scattering
SEM   Scanning Electron Microscopy
STEM  Scanning Transmission Electron Microscopy
TBAP  Tetrabutylammonium Perchlorate
TCE   Transparent Conducting Electrode
TEM   Transmission Electron Microscopy
TFA   Trifluoroacetic Acid
TGA   Thermogravimetric Analysis
THF   Tetrahydrofuran
UPS   Ultraviolet Photoelectron Spectroscopy
$V_G$ Gate Voltage
WAXS  Wide-Angle X-ray Scattering
XPS   X-ray Photoelectron Spectroscopy
XRD   X-ray Diffraction
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Chapter 1

Introduction

1.1 Anisotropic Hierarchical Structures in Nature

Through millions of years of evolution, nature has solved many great engineering challenges. From tough yet lightweight structural components to critical tissues for movement and fluid flow, the intricately ordered structures found in nature serve as a source of awe and inspiration.\(^1,2\) Since the early 20th century, these biological materials have been studied to derive the structure and properties relationship that defines their unique function.\(^3-7\) One of the key incites was that many biological materials are structured hierarchically, where the structural elements of a tissue themselves have structure.\(^8,9\) In human compact bone, for example, cells are embedded in a composite matrix of collagen fibrils and hydroxyapatite (\(\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2\)) nanocrystals. Individual collagen molecules have glycine residues every third amino acid that induce folding into tropocollagen triple helices (\(\sim 300\) nm long and \(\sim 1.5\) nm diameter).\(^10,11\) The hydroxyapatite crystals (roughly 50 nm x 25 nm x 3 nm) are distributed uniformly along the length of the collagen fibrils with the crystallographic \(c\) axis parallel to collagen fibril alignment (Figure 1.1a).\(^12,13\) The final levels of hierarchy are mineralized collagen fibrils bundled into fibers and arranged in lamellar concentric arrays to form hollow cylinders with diameters \(\sim 100\) \(\mu\)m.\(^14\) These structures, called osteons, surround the bone’s nerves and blood vessels allowing for vascularization and repair, while remaining tough and lightweight.

Tendons are another tissue type based on collagen fibril assembly that exhibit outstanding mechanical properties due to the many levels of structural hierarchy.\(^2\) In this case,
Figure 1.1: Hierarchical structures in nature. (a) Compact bone is composed of aligned collagen triple helices and hydroxyapatite nanocrystals. Mineralized collagen fibrils are bundled into fibers that are arranged in a geometrical pattern to form osteons, that surround blood vessels. (b) In bamboo, aligned cellulose fibers are embedded in a lignin-hemicellulose matrix that are arranged in hollow prismatic cells. Reproduced from Ref. 14.

the assembled fibrils (~500 nm diameter) are not mineralized but are bound together by proteoglycans into aligned bundles called fascicles (~100 µm diameter) that are further arranged into parallel tendon fibers (~500 µm diameter). Even more complex anisotropic and hierarchical ordering is observed in cardiac tissue and in the human brain. Other extraordinary phenomena in nature that are possible only due to hierarchical structuring include the exceptional dry adhesive properties of gecko feet, the high tensile strength and great extensibility of silk, and the mechanical efficiency of bamboo in terms of mechanical properties per unit weight. Geckos have specialized toe pads organized in a ~500 µm lamellar texture; each lamellae consists of arrays of ~5 µm keratin protein filaments called setae,
that split into smaller, rounded ∼200 nm protrusions at their ends called spatulae.\textsuperscript{19,20} The spatulae-tipped footpads greatly enhance the surface density of contact points, maximizing the weak van der Waals contact forces to allow for robust adhesion to even molecularly smooth surfaces.\textsuperscript{21} In spider and silkworm silk fibers, peptide chains consisting of alternating blocks of hydrophobic and hydrophilic amino acids assemble into semicrystalline fibrils with amorphous hydrophilic regimes and nanoconfined 2-5 nm $\beta$-sheet crystals stabilized by hydrogen bonds.\textsuperscript{20,22} Upon stretching, the $\beta$-sheet nanocrystals act as reinforcing crosslinking regions to transfer the load between extended polypeptide chains.\textsuperscript{23} The result is a material that has a higher tensile strength than steel even though it is composed of soft organic building blocks and stabilized by mechanically inferior hydrogen bonds.\textsuperscript{23,24} The elite mechanical efficiency of bamboo is due to the highly ordered honeycomb cellular structure with aligned cellulose fibrils reinforcing an intertwined hemicellulose and lignin matrix (Figure 1.1b).\textsuperscript{14,25} On the nanoscale, cellulose polysaccharide chains bundle into hexagonal or rectangular fibers with crystalline (ordered hydrogen bonding) and amorphous (irregular hydrogen bonding) domains.\textsuperscript{26} A further level of hierarchy is achieved through a radial gradient of the fiber density so that the reinforcement is highest where the stresses are largest at the outer periphery.\textsuperscript{25,27} In many of these examples, the anisotropy of the fibrous components is key in developing the link between multiple length scales of the hierarchy and the resulting function of the biomaterial.

In contrast to traditional synthetic materials design where the focus is on creating new compounds, biological systems employ relatively few polymeric and ceramic building blocks (e.g. proteins or polysaccharides, and calcium salts or silica). Rather, it is the specific arrangement of hard and soft materials in complex architectures with order over multiple length scales that results in their remarkable properties. It is clear then, that developing new functional materials will require careful chemical design of the organic component as well as control of the nano-, micro- and macroscale structural order.
1.2 Biomineralization on Organic Scaffolds

One particularly rich subset of hierarchically structured materials found in nature are bio-synthesized minerals. Shells, teeth, vestibular otoliths and skeletal bones all have highly ordered complex architectures designed to exhibit specific material properties that are critical for protection, predation, motility and ultimately, survival (Figure 1.2). In general, there are two processes for biogenic mineralization. “Biologically induced” mineralization occurs in many bacterial and algae species, where minerals such as calcium carbonate precipitate as a result of the reaction between biogenic gases (e.g. reduction of CO$_2$ during algal photosynthesis) and metal ions present in the surrounding environment (e.g. calcium ions in supersaturated seawater). These minerals typically display random crystal orientations and faceting consistent with those precipitated from inorganic solutions in a laboratory setting. “Organic matrix-mediated” biominerals, on the other hand, can be much more complex with levels of hierarchical order, anisotropy and compartmentalization that are currently impossible to fabricate synthetically. In this case, the genetic code of the organism controls the construction of a precise organic matrix to induce localized crystallization of minerals with a specific polymorph, orientation and microstructure. Often the minerals that form are far from what would be expected to crystallize at equilibrium and are the basis for their unique properties.

Therefore, many studies have aimed at understanding the chemistry and structure of the organic scaffolds that direct the unusual nucleation and growth phenomena observed in biominerals. For example, the exquisite nanostructured patterns of diatom frustules have been attributed to a specific set of highly phosphorylated polycationic peptides called silaffins, that attract silicic acid and induce colloidal gel formation of silica nanospheres which are used as precursors for the intricate exoskeleton structures. Notably, it was found that only the phosphorylated, zwitterionic form of the silaffins led to silica nanosphere formation in vitro, due to the electrostatic self-assembly into aggregates that act as templates for
Figure 1.2: Biominerals follow the traditional materials paradigm. Biological synthesis conditions lead to unique structures with a wide range of properties and applications that ultimately lead to survival of the organism.

biosilica deposition. The chiton radula, or rasping tongue, has similarly complex biomineral features that are heavily controlled by the organic matrix macromolecules. Each tooth in the radula is capped with a hard magnetite layer deposited on a fibrous chitin polysaccharide framework. Acidic proteins decorate the chitin matrix and bind specific metal ions that are thought to strengthen the interface between the fibers and magnetite crystals. While there is still much to learn about the interactions between the organic matrix and the surrounding mineral phases, these studies lay the foundation for designing new hybrid materials based on organic templated synthesis.

Most research on bio-inspired materials so far has addressed structural applications, e.g. tough and lightweight composites. More recently, however, there has been a growing interest in applying biomimetic mineralization strategies in the fields of energy and sustainability. In one study, researchers grew gold nanoparticles inside amyloid (protein) fibril
hydrogels via protein-assisted nucleation. Upon solvent exchange and drying by supercritical CO₂, the resulting aerogels demonstrated the high porosity and large internal surface area that is ideal for potential applications in pressure sensing and in continuous flow catalysis. Another unconventional biomineralization strategy involves genetic engineering of the M13 virus coat proteins to present specific peptide sequences on the viral capsid surface for nucleating or binding specific inorganic particles. The M13 virus platform has been used for a variety of energy devices from cobalt oxide or iron phosphate based battery electrodes to titanium dioxide photoanodes for solar cells. These examples highlight the rich potential for using bio-programmable organic templates to organize functional inorganic materials at the nanoscale.

1.3 Supramolecular Chemistry for Anisotropic Assemblies

One way to build organic scaffolds with programmed function is through supramolecular chemistry. In broad terms, supramolecular chemistry is any interaction beyond the covalent bonds that define a molecule, e.g. hydrogen bonding, electrostatic interactions, solvophobic forces, π-π interactions, metal coordination and van der Waals forces. Though these noncovalent interactions are weaker than covalent bonds, they are the driving force for hierarchical structure and effective function in both electronic and biological materials. Life itself is based on these interactions with prominent examples of self-organization ranging in size from DNA double helices to ligand-receptor binding and protein folding to cell cytoskeletons and full tissues. Further, the dynamic nature of these bonds allows for exquisite properties like self-healing and restructuring based on environmental cues. The cytoskeleton of living cells exhibits this behavior when protein monomers assemble into filaments and depolymerize dynamically to allow for cell migration, attachment and division.

To mimic the complex systems found in nature, much effort has been devoted towards creating functional supramolecular polymers. Leveraging one or more noncovalent inter-
actions, each molecular building block is encoded with information to assemble into a desired shape with a specific conformation, thereby realizing the target function (Figure 1.3). Often, the function is derived from anisotropy in the supramolecular assemblies.\textsuperscript{53,54} One-dimensional assemblies, e.g. fibers and tubes, can entangle to form crosslinked hydrogels\textsuperscript{55} or can be aligned to display preferential ionic and electronic transport.\textsuperscript{56} Two-dimensional assemblies, e.g. sheets and wide ribbons, can act as membranes\textsuperscript{57} or form layered thin films with non-linear optical properties.\textsuperscript{53,58}

Peptide-based assemblies are particularly rich for designing anisotropic supramolecular materials due to their multitude of secondary bonding motifs, including $\alpha$-helices, $\beta$-sheets, turns and hydrophobic interactions. A number of peptide sequences have been identified that self-assemble into fibrous structures, including (RADA)$_4$ and KLVFF.\textsuperscript{59,60} More recently, researchers developed a twelve amino acid collagen mimetic peptide with sticky ends to induce assembly of long nanofibers with the characteristic triple helix conformation of collagen.\textsuperscript{61} They found that the self-assembled nanofibers formed temperature dependent hydrogels and could be broken down by collagenase at a rate similar to natural collagen.

Covalent conjugation of a hydrophobic component to a peptide sequence adds another handle for controlling the size and shape of self-assembled structures. The hydrophobic component renders the molecules amphiphilic, and as a result, these structures follow Israelachvili’s rules of amphiphilic self-assembly in water.\textsuperscript{62} In general, this broad class of molecules are referred to as peptide amphiphiles (PAs).\textsuperscript{63,64} Early efforts on lipidated peptides were motivated by interest in studying bioactivity in artificial cell membranes.\textsuperscript{65–67} Later, an aliphatic tail was conjugated to an amino acid sequence with the ability to form ordered intermolecular hydrogen bonds.\textsuperscript{68} This resulted in the assembly of high aspect ratio nanofibers (10 nm in diameter, many microns in length) that are reminiscent of the filamentous extracellular matrix in living tissues. Based on this initial work, numerous PA molecules have been synthesized that assemble into a variety of anisotropic shapes, includ-
Figure 1.3: Specific interactions between monomers induce aggregation into supramolecular polymers. (a and b) A random-coil polymer formed by quadruple hydrogen bonding between ureidopyrimidinone monomers. (c and d) Peptide amphiphile molecules assemble into nanofibers by hydrophobic collapse and $\beta$-sheet hydrogen bonding. (e and f) A twisted ribbon assembly from substituted oligo(phenylene vinylene) monomers with programmed quadruple hydrogen bonding and chirality. (g and h) A monomer with an electron-donating hexabenzocoronene core and both hydrophobic alkyl chains and hydrophilic ethylene glycol chains that form bilayers and assemble into nanotubes. Reproduced from Ref. 52.

The typical fiber-forming PA consists of three distinct regions: (i) an aliphatic tail to drive hydrophobic collapse, (ii) a $\beta$-sheet forming peptide sequence that induces long-range order and directed hydrogen bonding along the fiber axis, and (iii) a charged amino acid headgroup to impart solubility in water. A fourth region containing a bioactive epitope can be added at the end of the charged domain to target a specific biological function. The PA nanofiber platform
has been used in a wide range of biomedical applications from orthopedics\textsuperscript{72–74} and cancer therapies\textsuperscript{75–77} to vascularization\textsuperscript{78–80} and neurology.\textsuperscript{81–83}

![Figure 1.4: The general structure of a PA molecule (center) that can be programmed to self-assemble into a wide range of supramolecular nanostructures. Reproduced from Ref. 64.](image)

Introducing electronic components into anisotropic supramolecular assemblies is also of great interest for synergistic biologic-electronic therapies as well as for soft and flexible electronic devices. Two examples have been demonstrated within PA nanofibers; in one, the conducting polymer poly(3,4-ethylenedioxythiophene) (PEDOT) was oxidatively polymerized inside the nanofiber core\textsuperscript{84} and in the second, diacetylene units on the aliphatic tail were crosslinked by UV irradiation to form a covalently conjugated backbone along the nanofiber axis.\textsuperscript{85} These materials maintained robust nanofiber assemblies, though the measured conductivity values were modest. The same set of design rules for peptide amphiphile self-assembly can also be extended to molecules with aromatic hydrophobic components. In this case, water solubility is still promoted by charged carboxylates or amines, but the hydrophobic collapse is driven by the aromatic core, and the assembly anisotropy is derived from $\pi-\pi$ stacking and dipole-dipole interactions.\textsuperscript{86–88} These molecules have been termed chromophore amphiphiles (CAs) since the aromatic cores have delocalized $\pi$ electrons and
often absorb visible light. Aggregates of CAs in water can form fibers, ribbons, helices and sheets, and can be entangled to form hydrogels via changes in pH or addition of salts.\textsuperscript{88–90} Charge screening by salts leads to crystallization of the CA molecules and enhances the electronic coupling.\textsuperscript{90–92} By introducing a catalyst and sacrificial electron donor, the CA hydrogels demonstrated electrode-free photocatalytic H\textsubscript{2} production under illumination.\textsuperscript{86,88–90} These studies lay the foundation for anisotropic, electronically active supramolecular polymers in aqueous and physiologically-relevant environments.

### 1.4 Templating of Synthetic Organic-Inorganic Hybrid Materials

Combining the biomineralization strategies discussed in Section 1.2 with the supramolecular chemistry approaches outlined in Section 1.3 is a promising route towards developing synthetic organic-inorganic hybrid materials with unique functions. In contrast to composites that have components mixed at the micron to millimeter scale, hybrid materials generally involve organic and inorganic constituents co-assembled at the nanometer or molecular level (Figure 1.5). Often this arrangement leads to fundamentally different physics rather than just a summation of the properties of two components.\textsuperscript{53,93} Early work on functional hybrid materials from supramolecular templates focused on synthesizing semiconducting superlattices\textsuperscript{94} for solar energy conversion and organoceramics for catalytic functions\textsuperscript{95} and artificial bone.\textsuperscript{96}

Based on these initial studies, more complex organic templates were developed with explicit nanostructures prior to mineralizing them with inorganic phases. For applications in electronics, one particularly interesting organic template is the network of twisted nanoribbons formed from dendron rodcoil (DRC) molecules.\textsuperscript{97} These molecules consist of three covalent blocks: a branched hydrophilic component (dendron), a rigid aromatic segment (rod), and a flexible aliphatic chain (coil). When dissolved in ethyl methacrylate, these molecules assemble into 10 nm wide, 2 nm thick and several microns long twisted ribbons
that can gel the solution above DRC concentrations of $\sim$1 wt%. In the presence of soluble cadmium nitrate and hydrogen sulfide gas, the DRC ribbons template the precipitation of semiconducting cadmium sulfide nanohelices on their surfaces.\textsuperscript{98,99} The DRC gels were also used to disperse zinc oxide (ZnO) nanocrystals for ultraviolet lasing applications.\textsuperscript{100} In this study, the wide face of the DRC ribbons was more effective for binding and stabilizing crystals dispersions than flexible, thin polymers like poly(vinyl alcohol). Further, the high aspect ratio ribbons could align the ZnO crystals in an external electric field, which allowed for a lower threshold pulse energy for ultraviolet photoluminescence compared to randomly oriented crystals.\textsuperscript{100}

There has also been a large effort on using supramolecular assemblies for templating synthetic biominerals. The PA nanofiber assemblies discussed previously were originally
developed to mimic collagen fibrils for hydroxyapatite (HAP) mineralization in synthetic bone. In the initial study, the PA molecules were synthesized with phosphoserine and aspartic acid residues to present a negatively charged surface for establishing a local calcium ion supersaturation. After the PA fibers were assembled on a TEM grid, calcium and phosphate precursors were added on each side of the carbon film, and HAP crystals were observed on the nanofiber surfaces. Interestingly, the c-axes of the HAP crystals were oriented along the long axes of the PA nanofibers, mimicking natural HAP-collagen fibril alignment, and suggesting that the PA fibers were controlling the crystallographic orientation. In a subsequent study, Newcomb et al. found that only PAs that assembled into cylindrical nanofibers, rather than thin ribbons, directed crystal growth of the HAP c-axis down the long axis of the template. Additionally, when the cylindrical nanostructures were prepared in a gel composed of aligned fiber bundles, the ability to mineralize oriented crystals was maintained throughout the macroscopic construct. Similar studies of PA nanofiber templates with specifically adapted peptide sequences have also been investigated for bio-inspired silica and magnetite mineralization, as well as for silver nanoparticle nucleation in anti-microbial coatings.

An orthogonal approach for synthesizing hybrid materials is through electrodeposition. Traditionally, metal or metal oxides are deposited from a solution containing metal precursors on to a substrate by applying a voltage. This usually results in flat thin films of metals or metal oxides with standard crystal habits. To synthesize hybrid materials with unique properties using this technique, the electrodeposition bath can be augmented with organic molecule templates. The first attempts to template inorganic structures during electrodeposition used liquid crystalline phases to induce nanoporosity or added anionic surfactants to tune the basal spacing of layered materials. This work inspired the design of electronically active, p-type surfactant molecules that could be incorporated in between layers of inorganic n-type semiconductors during electrodeposition. The resulting electrodeposited hybrid films had flake microstructure composed of alternating layers of 1 nm
thick ZnO and 2-3 nm thick conjugated surfactant molecules, forming nanoscale p-n junctions. This material exhibited excellent photodetector metrics (e.g. large gain, wide dynamic range, and high detectivity) and showed no degradation over 8 months. Further investigations on these electrodeposited hybrids explored preferential orientation of the layers by careful design of the organic surfactant and surface chemistry of the substrate. In sum, these examples highlight the promise of using synthetic organic templates to guide assembly of functional inorganic materials with complex architectures and unique properties.

1.5 3D Printing Hydrogel Materials

Hydrogels are three-dimensional solids composed primarily of water molecules dispersed in a network of crosslinked polymer chains or colloidal particles. Great advances have been made in hydrogel engineering and theory over the last 20 years for applications in both energy and medicine. Specific examples include contact lenses, localized drug delivery vehicles, tissue engineering scaffolds, stimuli responsive materials, filtration absorbents, and flexible electrodes and electrolytes for energy conversion and storage devices. The network components can be either synthetic or biologically-derived materials that have random polymer entanglements or a defined hierarchical structure. While nanoscale structure can be encoded through specific chemical interactions, controlling the shape and hierarchical order on a macroscopic length scale remains a challenge in hydrogel engineering. Therefore, new processing methods are necessary to generate additional levels of order that would enhance the function of hydrogel materials.

Three-dimensional (3D) printing is a rapidly expanding technology that produces 3D solid objects from a digital file, allowing for fabrication of intricate shapes and infill patterns that are not achievable by traditional manufacturing methods. Originally, 3D printers were developed for prototyping with cheap thermoplastic materials, but have recently expanded to other more functional materials like metals, ceramics and hydrogels. In the hydrogel
context, 3D printing can be used for precisely placing and orienting constituent materials with designed pore sizes, geometry and patterns. These attributes could allow for programmed electronic and biological signaling as well as enhanced molecular and ionic transport or compartmentalization of multiple synergistic components.

**Figure 1.6:** Types of 3D printing technologies. Extrusion and inkjet printing depends on materials that can rapidly solidify upon exiting the nozzle. Laser sintering and stereolithography use light for local heating or photoinduced polymerization, respectively, to solidify the material. Reproduced from Ref. 123.

Extrusion printing is a subset of 3D printing (Figure 1.6). In contrast to stereolithography printers, where patterns of light trigger solidification of a precursor material, extrusion printers dispense “inks” through a syringe that must rapidly solidify upon leaving the nozzle to retain the patterned shape. A wide range of solidification mechanisms have been investigated including evaporation, thermal solidification, ionic and physical crosslinking, UV polymerization, embedded printing and shear thinning pastes. The ability to print multiple inks simultaneously and the extensive customization afforded by extrusion printers makes them ideal for building soft, hydrogel materials. There have been many recent reports of hydrogel extrusion printing for targets in biomimetic tissue scaffolds, soft robotics and soft energy materials. This field is still in its in-
fancy but holds great promise for game changing applications in personalized regenerative medicine and soft, flexible bioelectronic devices.

1.6 Thesis Overview

This thesis is based on the directed assembly of soft and hybrid materials into functional hierarchical structures for energy and medicine applications. Taking inspiration from biology, small molecules programmed with specific interactions are used as building blocks to construct bulk macroscopic materials with unique properties. Understanding the effect of molecular structure, intermolecular attractive and repulsive forces, and the processing conditions are all critical for achieving materials with the desired function.

The work begins with the rational design of small amphiphilic molecules for precipitating and crystallizing inorganic semiconducting materials into ordered layered phases. In Chapter 2, the addition of surfactant molecules during electrodeposition of cobalt hydroxide films for energy storage electrodes is explored. One specific surfactant molecule with programmed $\pi-\pi$ stacking interactions leads to the formation of concentric multiwalled nanotubes growing perpendicular from the substrate surface. The hierarchical structure of nanotubes growing monolithically from the substrate demonstrates superior electrochemical performance and stability over similar layered cobalt hydroxide films electrodeposited with surfactants lacking the $\pi-\pi$ stacking interaction. The results indicate that very small changes to the molecular design have significant impact on the resulting thin film morphology and electrode performance.

A similar strategy is applied to photovoltaic materials in Chapter 3, where small organic cations are added to the lead halide perovskite precursor solutions to crystallize layered perovskite thin films. Layered perovskites have much better environmental stability than their three-dimensional analogues but suffer from poor device efficiency due to the traditionally resistive organic layers between the lead halide sheets. To address this shortcoming, organic
cations with varying aromatic substituents are systematically studied to enhance the out-of-plane conductivity through the organic layers. The strong influence on the conductivity from the supramolecular $\pi$-stacking geometry and intramolecular hydrogen bonding of the organic cation is described.

Chapter 4 takes inspiration from natural biomineralization processes to decorate organic PA nanofibers with electronically conductive Au particles. Two pathways are studied; one attaching pre-synthesized Au nanoparticles onto the organic nanofibers and a second using direct mineralization of Au salts onto the nanofiber surface. The Au coated fibers are then applied in a thin layer on a transparent plastic substrate and evaluated as materials for flexible transparent conductive electrodes in optoelectronic devices.

In Chapter 5, the focus moves towards processing of the PA nanofiber assemblies into patterned macroscopic hydrogels with programmed alignment using 3D printing. The effect of pH and PA fiber-to-fiber interactions on the viscosity of the nanofiber inks is analyzed, along with a study detailing the necessary salt concentration and valency for solidifying the extruded ink into a robust hydrogel. Using x-ray diffraction and optical birefringence measurements, the optimal printing parameters for aligning the PA nanofibers during extrusion are determined. Finally, some of the unique properties of these anisotropic hydrogels are highlighted, including enhanced ionic and electronic conductivities, directed cell outgrowth and muscle-inspired actuation.

The 3D printing technique for aligning supramolecular nanostructures in hydrogels is extended in Chapter 6 to semiconducting chromophore amphiphile (CA) fibrillar assemblies. Additional hydrogen bonding motifs on the outside of the aromatic core of the CA molecule are studied as a strategy to increase the $\pi$-orbital overlap along the axis of the filaments compared to fibrils composed of molecules with only the aromatic core driving the one-dimensional assembly. Significant differences in the optoelectronic properties, gel morphology and stiffness are observed as a result of the additional attractive interaction encoded in the
hydrogen bonding molecule. However, due to the low viscosity of the solutions containing these assemblies, the biopolymer alginate is added to the ink to allow for shear alignment during extrusion. The alginate in this hybrid covalent polymer-supramolecular polymer ink has drastic effects on the bundling properties of the CA fibrils and imparts enhanced mechanical properties to the 3D printed xerogels. The gels exhibit anisotropic electron transport along the direction of extrusion and a strong resistance to cracking when compared to films solely composed of CA fibrils without alginate.

Chapter 7 discusses the next steps for progressing on the work detailed in Chapters 2 through 6, and proposes further studies that could lead to enhanced performance of hybrid materials used in energy storage, photovoltaic and conductive nanowire applications. In the context of 3D printable hydrogels, additional experiments and future targets are suggested along with a general outlook on the promise of this technology.
CHAPTER 2

Oriented Hybrid Organic-Co(OH)$_2$ Nanotubes for Energy Storage Electrodes

2.1 Objectives and Significance

In energy storage materials, large surface areas and oriented structures are key architecture design features for improving performance through enhanced electrolyte access and efficient electron conduction pathways. Layered hydroxides provide a tunable materials platform with opportunities for achieving such nanostructures via bottom-up syntheses. These nanostructures, however, can degrade in the presence of the alkaline electrolytes required for their redox-based energy storage. We report here on a layered Co(OH)$_2$-organic hybrid material that forms a hierarchical structure consisting of microns-long, 30 nanometer diameter tubes with concentric curved layers of Co(OH)$_2$ and 1-pyrenebutyric acid. The nanotubular structure offers high surface area as well as macroscopic orientation perpendicular to the substrate for efficient electron transfer. Using a comparison with flat films of the same composition, we demonstrate that the superior performance of the nanotubular films is the result of a large accessible surface area for redox activity. We found that the organic molecules used to template nanotubular growth also impart stability to the hybrid when present in the alkaline environments necessary for redox function.

2.2 Background

Over the past decade there has been great interest in energy storage materials partly motivated by consumer demand for portable electronics and electrified vehicles.\textsuperscript{140–142} Su-
percapacitors are a promising class of electrochemical energy storage devices that can exhibit superior power capabilities and cycling lifetimes over traditional batteries.\textsuperscript{143,144} However, conventional supercapacitors that store energy through electric double-layer capacitance (EDLC) in symmetric carbon-based electrodes have only limited energy density compared to currently used batteries. There has been growing interest recently in asymmetric supercapacitors that utilize high-performance EDLC anodes,\textsuperscript{145,146} in conjunction with faradaic cathodes that undergo redox reactions and thus have much larger energy densities.\textsuperscript{147–149} Among the materials investigated for cathodes, cobalt(II) hydroxide (Co(OH)$_2$) is a particularly promising candidate due to its high theoretical specific capacity and electrical conductivity.\textsuperscript{150–152} This metal hydroxide is known to form a crystalline layered structure that facilitates ion transport, and in the presence of an oxidizing potential and hydroxide ions it will transform into a cobalt(III) oxyhydroxide (CoOOH) phase.\textsuperscript{153} This charging transformation is easily reversible in a discharge process that reduces the oxyhydroxide back to the original cobalt hydroxide. This redox reaction offers the potential for high energy storage density and rapid charge/discharge cycles, the two attributes that define a supercapacitive material. While the operating voltage window for Co(OH)$_2$ electrodes is limited to $\sim 0.5$ V, solid-state asymmetric supercapacitor devices utilizing Co(OH)$_2$-based cathodes and EDLC anodes have demonstrated stable potential windows of 1.2 and 1.8 V.\textsuperscript{154,155} This electrode pairing balances the high capacity and small voltage window of Co(OH)$_2$ with the low capacity and large voltage window of EDLC materials.

In an effort to increase the specific capacity of Co(OH)$_2$ electrodes, previous work has focused on the synthesis of high surface area nanostructures\textsuperscript{155,156} and strategies to increase the interlayer spacing of Co(OH)$_2$ with various types of intercalated anions.\textsuperscript{153} In addition to optimization of specific capacity, one of the critical challenges in the use of this material in supercapacitor devices is its inherent instability in alkaline electrolytes necessary for the redox reaction. Dissolution of layered cobalt hydroxide in the alkaline environment leads to
re-precipitation of a different phase known as $\beta$-Co(OH)$_2$, which lacks intercalated anions. This is accompanied by a change in microstructure that may compromise performance.\(^{157-159}\) Direct observation of this degradation in nanostructured Co(OH)$_2$ electrodes is particularly challenging due to the common use of additives to create an electrically conductive network between energy storage particles and the current collection substrate. An important advance in this area would be to generate additive-free cobalt hydroxide electrodes with high capacity to conduct and store charge. The absence of additives is crucial to observe and understand mechanisms of degradation during charging and discharging cycles. In this work, we describe a one-pot electrodeposition process for the synthesis of hybrid organic-Co(OH)$_2$ electrodes without additives. In-situ synthesis of inorganic-organic hybrids has been an area of great interest as a strategy to generate unique morphologies, inspired by biomineralization processes.\(^{53,94,160-165}\) Electrodeposition can lead to synthesis of high surface area hybrid nanostructures with tunable interlayer spacing and controllable orientation of the inorganic layers with respect to the substrate.\(^{107-110}\) Applying this technique to Co(OH)$_2$ materials can yield high specific capacity electrodes with direct conduction pathways through the inorganic layers allowing for additive-free operation.

### 2.3 Results and Discussion

#### 2.3.1 Electrodeposition Morphologies

We first synthesized hybrid layered nanostructures on stainless steel substrates by electrodeposition in a water/dimethyl sulfoxide solution of cobalt nitrate (Co(NO$_3$)$_2$) and 1-pyrenebutyric acid (PyBA) surfactant. Cathodic reduction of nitrate ions increases the local pH near the surface of the steel working electrode, resulting in the deposition of Co(OH)$_2$. We selected PyBA as an amphiphile with a carboxylate group that could bind to the Co(OH)$_2$ layers and an aromatic core that could form attractive intermolecular interactions such as $\pi-\pi$ stacking. We found that this synthetic procedure promotes the growth of nanotubular
structures perpendicular to the substrate using cross-section scanning electron microscopy (SEM) (Figure 2.1a). Analysis of transmission electron microscopy (TEM) images shows outer diameters of the tubes ranged from 22 to 46 nm with an average of 30 nm, while the inner diameters were measured to be 12 ± 2 nm. TEM further reveals that the nanotubes are composed of alternating layers of PyBA and cobalt hydroxide with a periodicity of about 3 nm (Figure 2.1b, left and top right). The cross-section for each tube shows equal number of layers on both sides, suggesting a concentric tube structure. High-angle annular dark-field scanning transmission electron microscopy (HAADF STEM) depicts the inorganic cobalt hydroxide layers as bright rings when viewed down the long axis of the hybrid tubes, further verifying the concentric arrangement (Figure 2.1b, bottom right). Subtracting the ∼4.7 Å thickness of a single Co(OH)₂ sheet from the interlayer periodicity derived from x-ray scattering (vide infra), we calculate an interlayer gap width of 25.2 Å between Co(OH)₂ sheets.¹⁵⁵,¹⁶⁶ Since the length of a single PyBA molecule is 1.3 nm,¹⁰⁸ we suggest that the PyBA molecules are not interdigitated and arrange instead in a bilayer structure. The bilayer structure would of course facilitate interactions between Co ions and carboxylate anions while still allowing π-π overlap among aromatic cores of the amphiphiles (Figure 2.1c and d).

We observe the same nanotubular morphology for films deposited on lightweight and flexible substrates such as graphite foil and carbon fiber paper (Figure 2.2). While a solvothermal synthesis has been recently reported to homogeneously nucleate Co(OH)₂ nanotubes of similar diameters,¹⁶⁷ our work is the first example of Co(OH)₂ nanotubes of high curvature heterogeneously nucleated on a substrate.

To understand the nucleation and growth of the hierarchical tubular structure, we studied the changes in morphology using top-down and cross-sectional SEM as well as grazing incidence X-ray scattering (GIXS) (Figure 2.3). These techniques were used to characterize the structure at 5 minute intervals throughout the deposition. Three general stages of growth were observed: an initial flat dense film, a flake-like intermediate structure, and finally the
Figure 2.1: Structural characterization of layered hybrid nanostructure. (a) Cross-sectional SEM image of Co(OH)$_2$/PyBA nanotubes growing perpendicular to substrate. (b) Bright-field TEM images (left and top-right) and high angle annular dark field STEM image (bottom right) of Co(OH)$_2$/PyBA nanotubes. (c) Schematic of concentric nanotubes emerging from flakes. (d) Schematic of layered ordering within a nanotube composed of inorganic Co(OH)$_2$ tubes and bilayers of PyBA.

perpendicularly oriented tubular structure. While small variations in reactant concentration and deposition bath pH affect the deposition time necessary for each growth stage to occur, the morphological transition from flat film to flakes to tubes was observed in all cases (Figure 2.4, Table 2.1, Methods Section 2.5). Therefore, to normalize for variations in film area, we have divided the three growth stages in terms of film mass.

The first stage of growth, in the 0-10 µg/cm$^2$ range, typically occurs within the first 5 minutes of deposition, and is comprised of a flat dense film of $\sim$100 nm thickness (Figure 2.3a,
Figure 2.2: SEM images of Co(OH)$_2$/PyBA nanotubes electrodeposited on carbon fiber paper (a, b) and graphite foil (c, d).

b). The GIXS pattern exhibits very weak lamellar ordering oriented parallel to the substrate, with a periodicity of $\sim$2.9 nm (Figure 2.3c, Figure 2.5, Methods Section 2.5). Once the film grows to an areal density over 10 µg/cm$^2$, rounded protrusions begin to appear on top of the flat film. Between 20-40 µg/cm$^2$, discrete flakes grow vertically from these rounded structures on the flat dense base layer (Figure 2.3d and e). This is the typical structure for electrodeposited Co(OH)$_2$ thin films with organic surfactants previously reported in the literature$^{107}$ as well as in the Zn(OH)$_2$ studies from our group.$^{108-110}$ The GIXS pattern for the flake-dominant films shows a stronger lamellar ordering compared to dense films, with nearly isotropic (00$l$) rings corresponding to a d-spacing of 2.99 nm (Figure 2.3f, Figure 2.6).
Figure 2.3: Structural evolution of the hybrid with increasing film mass. (a) Representative top-down SEM image, (b) cross-sectional SEM image and (c) 2D GIXS pattern of a 0-10 µg/cm² film. (d) Representative top-down SEM image, (e) cross-sectional SEM image and (f) 2D GIXS pattern of a 20-40 µg/cm² film. (g) Representative top-down SEM image, (h) cross-sectional SEM image and (i) 2D GIXS pattern of a 50-100 µg/cm² film. Emergence of π-π stacking is visible with preferential orientation parallel to the substrate. A small β-Co(OH)_2 impurity peak is also apparent (See Figure 2.8 and Methods Section 2.5). All samples shown here were coated with 10 nm Au/Pd before imaging.

However, an interesting structure emerged during the final stage of growth consisting of tubes nucleated out of the ridges on top of the flakes (at film masses over 40 µg/cm²). To
Figure 2.4: SEM images of Co(OH)$_2$/PyBA films at varying deposition bath concentrations. (a) 75% [NO$_3^-$] after 60 min, (b) 150% [NO$_3^-$] after 90 min, (c) 50% [PyBA] after 60 min, and (d) 150% [PyBA] after 120 min.

Table 2.1: Deposition bath concentrations for samples in Figure 2.4.

<table>
<thead>
<tr>
<th>Sample</th>
<th>[Co$^{2+}$]</th>
<th>[NO$_3^-$]</th>
<th>[PyBA]</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>0.1 M</td>
<td>0.15 M</td>
<td>1.25 mM</td>
</tr>
<tr>
<td>B</td>
<td>0.1 M</td>
<td>0.3 M</td>
<td>1.25 mM</td>
</tr>
<tr>
<td>C</td>
<td>0.1 M</td>
<td>0.2 M</td>
<td>0.625 mM</td>
</tr>
<tr>
<td>D</td>
<td>0.1 M</td>
<td>0.2 M</td>
<td>1.875 mM</td>
</tr>
</tbody>
</table>

To our knowledge, our work is the first example of oriented metal hydroxide nanotubes grown on a substrate. At around 100 µg/cm$^2$ (~60 minutes of deposition time), the tubes were observed to grow to a few micrometers in length and 30 nm in diameter (Figure 2.3g and h). Since the Au/Pd coating process used for SEM imaging can result in mechanical damage of the film and partial fracture of the tubes, images of uncoated full-length tubes are provided in Figure 2.7. The lamellar d-spacing for the tubular films remains invariant at 2.99 nm, but the film transforms in time into a hierarchical structure with long range percolation.
of the electronically conductive redox-active phase parallel to the steel substrate normal (Figure 2.3i, 2.6 and 2.8). This is clearly shown by SEM and TEM images revealing radial lamellar ordering that is perpendicular to the long axes of the tubes (Figure 2.1b and 2.3h).

Figure 2.5: Line cut of the 2D-GIXS pattern in Figure 2.3c. A constrained mask on the GIXS pattern was set to $\Phi$ values of 70-90° to increase the signal-to-background ratio, since the majority of the (001) ordering was parallel to the substrate at this growth stage and there was high fluorescence from the stainless steel substrates.

We also observed a reflection at $q \sim 1.65 \text{ Å}^{-1}$ with preferential orientation parallel to the substrate that does not correspond to lamellar ordering (Figure 2.9). Since this reflection corresponds to a spacing of 3.8 Å, consistent with a $\pi-\pi$ stacking distance, we expect the PyBA molecules to be stacked with their face normal vectors perpendicular to the substrate and parallel to the long axes of the tubes (Figure 2.1d). Additionally, to get an ensemble measurement of tube diameters over the entire electrodeposited film we performed further analysis on the 2D GIXS profile. Upon close inspection of Figure 2.3i, new oscillations in the scattering profile are observed in the low $q$ region (see Figure 2.10 for expanded view). These peaks correspond to form factor scattering associated with regular tube diameters.
Figure 2.6: Line cuts of the (001) peak in the 2D-GIXS pattern depicted in Figure 2.3f and i. A constrained mask on the GIXS pattern was set to Φ values of 70-90° to increase the signal-to-background ratio, since the majority of the (00l) ordering was parallel to the substrate at this growth stage and there was high fluorescence from the stainless steel substrates.

Figure 2.7: SEM images of an uncoated Co(OH)$_2$/PyBA nanotubular film from (a) a top-down view, (b) a cross-sectional view, and (c) a 30° view, showing the preferential nanotube orientation perpendicular to the substrate.

across the substrate. Applying a solid cylinder form factor model with a first order Bessel function (Figure 2.11, Methods Section 2.5), we calculated an average tube diameter of 27.5 nm, in agreement with the average measurement from TEM imaging.

To investigate the tube formation pathway in our system, we collected a series of high magnification electron micrographs on samples at different stages of tube growth (Fig-
Figure 2.8: Line cut of the 2D-GIXS pattern depicted in Figure 2.3i over $\Phi$ values of 0-90°. The tube form factor oscillations, the (001) peak for the impurity $\beta$-Co(OH)$_2$ phase and the $\pi-\pi$ stacking peaks are highlighted in purple.

Figure 2.12. SEM images of samples at the initial stage of tube growth suggest that these tubes may be nucleated by curling of cobalt hydroxide sheets protruding from the ridges on the edge of the flakes (Figure 2.12a). The ridged flake edges are likely a result of non-uniform growth fronts during electrodeposition, similar to dendritic growth observed in electrodeposition of metals. HAADF STEM images of the same sample show the epitaxial relationship between the layered structures in the flake and the multilayer structure in the curled protrusion (Figure 2.12b). We observe in the STEM projection a line of low contrast that runs perpendicular to the flake layers and leads to the base of the curled protrusion, consistent with commonly observed projections of screw dislocations in layered materials. We hypothesize that such screw dislocations may drive the nucleation of the nanotubes. Additionally, the curvature of the curled multilayered protrusions is similar to that of the final
Figure 2.9: Line cut of the apparent \( \pi-\pi \) peaks in the 2D-GIXS pattern depicted in Figure 2.3i, with a constraint of \( 1.55 \text{ Å}^{-1} < q < 1.75 \text{ Å}^{-1} \). The decrease in signal intensity as \( \Phi \) increases from 90° to 180° shows the preferential orientation of \( \pi-\pi \) stacking parallel to the substrate.

tubes, suggesting that the inner diameter of the tubes is defined at the initial nucleation step. One possible explanation for the induced curvature of the multilayered protrusions is internal mechanical stress between layers with different growth rates as described by Bavykin et al.\(^{170}\) TEM and HAADF STEM images show that there are step edges along the tube axis in single layer increments (Figure 2.12c). Addition of concentric layers after initial tube formation would explain the variation in number of layers and tube outer diameters while maintaining the inner diameter. Our observations on the nanotube growth pathway reveal that screw dislocations in the layered flakes may result in epitaxial nucleation of curved multilayer sheets that close into concentric tubes.

To understand the role of the pyrene surfactant in directing structure, we synthesized hybrid samples with other carboxylic acid containing amphiphiles. We investigated molecules with no aromatic core, a smaller aromatic core and different alkyl linker lengths (see Figure 2.13 and Methods Section 2.5). These molecules yielded layered hybrid materials with
Figure 2.10: 2D GIXS pattern from Figure 2.3i. Enlarged to more clearly show the oscillations for $q < \sim 0.2 \text{ Å}^{-1}$ that are associated with the scattering form factor of tubes. A detailed analysis and description of this form factor is presented in the Methods Section 2.5

Figure 2.11: Correlation between the observed minima for the scattering intensity and the expected minima locations from the Bessel function of the first order. The first three points are derived from a GISAXS pattern, while the other five are from GIWAXS of the same sample. See Methods Section 2.5 for analysis details.

flat film or flake morphologies but failed to generate tubular structures across the range of electrodeposition parameters tested. This indicates that the molecular structure of PyBA
Figure 2.12: Growth pathway for hybrid nanotubes. (a) Top-down SEM image and (b) HAADF STEM image of nanotubes at the initial growth stage. Arrow in (b) marks the axis of a possible screw dislocation. (c) TEM and HAADF STEM images of full-length tubes. Arrows in (c) indicate the step edge of the Co(OH)$_2$ layers.

plays a crucial role in driving the curvature for tubular growth with macroscopic order parameter. In particular, decanoic acid (DA) was further explored as a control amphiphile with similar molecular length to PyBA but without attractive intermolecular $\pi-\pi$ interactions.
When Co(OH)$_2$ is electrodeposited with DA, only flat films are observed even after 90 minutes of deposition time and similar film masses (Figure 2.13g). The lamellar nanostructure is still strongly apparent in the Co(OH)$_2$/DA GIXS patterns (Figure 2.14), with layer orientation parallel to the substrate and a d-spacing of 2.7 nm, consistent with previous reports from our group on Zn(OH)$_2$/DA hybrids. When DA molecules intercalated in the hybrid are exchanged for PyBA, the resulting film has a flat morphology but the same d-spacing as the nanotubular films (see Methods Section 2.5 and Figure 2.15). As discussed later, this material is useful for isolating the effects of the tubular nanostructure versus a flat lamellar morphology on energy storage capacity.
Figure 2.13: Electrodeposition of Co(OH)\textsubscript{2} hybrids with other surfactants. SEM images and XRD patterns for electrodeposited Co(OH)\textsubscript{2} films with PyAA (a, b), PyHA (c, d), NBA (e, f), and DA (g, h). Small impurity peaks from nitrate-intercalated \(\alpha\)-Co(OH)\textsubscript{2} are observed at \(2\theta = 5.2^\circ\) for PyAA and NBA, with a larger \(\alpha(001)\) peak for PyHA. These were observed across all samples and could not be reduced without decreasing the hybrid lamellar ordering simultaneously.
Figure 2.14: GIXS pattern of electrodeposited Co(OH)$_2$/DA flat film. Strong lamellar orientation parallel to the substrate is observed.
Figure 2.15: Characterization of PyBA-exchanged DA film. (a) SEM image of a DA film that has been exchanged with PyBA. (b) Cross-sectional SEM image of exchanged film. (c) XRD pattern of the film showing lamellar ordering with a d-spacing of 3.0 nm, the same d-spacing as hybrid films that were deposited with PyBA. (d) UV-vis absorbance spectrum of an aqueous 1 M KOH solution used for dissolving surfactants from a PyBA-exchanged DA film. Quantification of PyBA in this solution shows that 40% of the film mass can be attributed to PyBA, indicating that the majority of DA originally in the film has been exchanged with PyBA (see Methods Section 2.5).
2.3.2 Electrochemical Performance

To evaluate the electrochemical performance of the hybrid films, we performed galvanostatic charge/discharge measurements using a three-electrode setup in 1 M KOH electrolyte (Figure 2.16a, b). As commonly described in the literature, the faradaic reaction responsible for energy storage in Co(OH)$_2$ is the following:

$$\text{Co(OH)}_2 + \text{OH}^- \leftrightarrow \text{CoOOH} + \text{H}_2\text{O} + e^- \quad (1)$$

We used specific capacity as the metric of energy storage capabilities which seems appropriate in the context of recent perspectives on performance assessment for redox-based supercapacitor materials.\textsuperscript{147,148} The often-used specific capacitance metric is included as well to facilitate comparison to previous literature, but we note that it does not provide an accurate representation of energy storage capabilities for any nonlinear voltage profiles in galvanostatic charge-discharge testing. Galvanostatic charge/discharge on nanotubular Co(OH)$_2$/PyBA films was carried out at gravimetric current densities ranging from 2 A/g to 20 A/g (Figure 2.16a). We observe that the coulombic efficiency for galvanostatic cycling exceeds 94% after an initial 20 cycles at 2 A/g, indicating high reversibility of the redox charge storage reactions (Figure 2.17). The specific discharge capacity ranges from 63.4 mAh/g to 31.6 mAh/g at 2 A/g and 20 A/g, respectively (Figure 2.16b). When only the active material mass (Co(OH)$_2$ only) is considered, the specific capacity ranges from 137 mAh/g to 68.3 mAh/g (see Figure 2.18, Table 2.2 and Methods Section 2.5 for calculation of Co(OH)$_2$ mass). These values are comparable to Co(OH)$_2$ electrodes similarly deposited as thin films on non-porous substrates without conductive additives.\textsuperscript{106,171–176} We note that many previous reports on Co(OH)$_2$ electrodes utilize nickel foam current collectors, which result in thinner layers of active material for the same mass loading and may also contribute to storage
capacity due to the redox activity of Ni(OH)$_2$ formed from the current collector in alkaline conditions.$^{177,178}$

**Figure 2.16:** Electrochemical characterization of hybrid films. (a) Galvanostatic charge/discharge profiles for a tubular Co(OH)$_2$/PyBA film at different current densities. (b) Specific capacity and capacitance values for the charge/discharge curves in (a). (c) Cyclic voltammograms of a nanotubular Co(OH)$_2$/PyBA film and a flat Co(OH)$_2$/PyBA film in 1 M KOH at 10 mV/sec scan rate. (d, e) Specific charge capacity calculated from CV of nanotubular film compared to that of flat film in (d) 1 M KOH and in (e) 0.1 M TBAP/acetonitrile. (f) b-value analysis of nanotubular and flat films from CV in 1 M KOH. (g) Nyquist impedance plot of nanotubular and flat films in 1 M KOH.

To investigate the effects of the hierarchical microstructure on performance while retaining the nanoscale interlayer spacing, we exchanged the intercalated DA molecules of a Co(OH)$_2$/DA flat film for PyBA and the resulting film was cycled for comparison with the nanotubular films. The exchanged flat film has the same interlayer spacing as the nanotubular films, but yields a peak specific capacity of 14.0 mAh/g versus the 40.6 mAh/g for nanotubular films at 10 A/g current density (Figure 2.19). We observe a decrease in capacity of the nanotubular film to 18.5 mAh/g over 10000 cycles, which we believe is linked
Figure 2.17: Coulombic efficiency of nanotubular film under galvanostatic charge/discharge cycling at 2 A/g in 1 M KOH.

Figure 2.18: Thermogravimetric analysis (TGA) of Co(OH)$_2$/PyBA nanotubular films.

to changes in surface area and morphology during charging and discharging (Figure 2.20). In comparison, the flat film only retains 1.5 mAh/g capacity over 10000 cycles. For reference, the as-deposited Co(OH)$_2$/DA films also reveal significantly lower specific capacity than that of the nanotubular films, which indicates that film morphology is the dominant factor in electrochemical performance (Figure 2.21). Future work needs to be focused on the stabilization of the nanostructure during charge/discharge cycles, which may be accom-
Table 2.2: Co(OH)$_2$ hybrid film masses before and after calcination for 6 different samples.

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Bare substrate mass (g)</th>
<th>Substrate + deposited film mass (g)</th>
<th>Substrate + deposited film mass post-calcination (g)</th>
<th>Film mass change (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PyBA-a</td>
<td>1.1687760</td>
<td>1.1690200</td>
<td>1.1688860</td>
<td>-54.9</td>
</tr>
<tr>
<td>PyBA-b</td>
<td>1.1694284</td>
<td>1.1696953</td>
<td>1.1695493</td>
<td>-54.7</td>
</tr>
<tr>
<td>PyBA-c</td>
<td>1.1708271</td>
<td>1.1710234</td>
<td>1.1709224</td>
<td>-51.4</td>
</tr>
<tr>
<td>DA-a</td>
<td>1.1664314</td>
<td>1.1667035</td>
<td>1.1665631</td>
<td>-51.6</td>
</tr>
<tr>
<td>DA-b</td>
<td>1.0944348</td>
<td>1.0945184</td>
<td>1.0944752</td>
<td>-51.7</td>
</tr>
<tr>
<td>DA-c</td>
<td>1.1265958</td>
<td>1.1267226</td>
<td>1.1266556</td>
<td>-52.8</td>
</tr>
</tbody>
</table>

Average mass % loss for Co(OH)$_2$/PyBA film: -53.7

Average mass % loss for Co(OH)$_2$/DA film: -52.0

plished by incorporating a secondary electronically conductive phase that could minimize non-uniform charging and mitigate structural degradation. Additionally, to fabricate a full device with large energy and power density, a high-performance anode is necessary to match the capacity and rate capability of the Co(OH)$_2$ nanotubular electrode.\textsuperscript{155,179}

![Figure 2.19](image-url)  

Figure 2.19: Specific capacity and capacitance over 10000 galvanostatic charge/discharge cycles at 10 A/g for a nanotubular Co(OH)$_2$/PyBA film (blue) and a flat Co(OH)$_2$/PyBA film (black).
Figure 2.20: Structure of Co(OH)$_2$/PyBA films after 100 charge/discharge cycles in 1 M KOH. (a) SEM image of degraded nanotubular film after cycling. (b) XRD patterns of nanotubular film before cycling (black) and after cycling (red).

Figure 2.21: Specific capacity and capacitance over 1000 galvanostatic charge/discharge cycles at 10 A/g for a flat Co(OH)$_2$/DA film.

To probe the nature of the increased capacity of the nanotubular films, we performed potentiostatic and kinetic electrochemical characterization on both the nanotubular films and the Co(OH)$_2$/PyBA flat films (Figure 2.16c-g). Cyclic voltammetry (CV) performed on
samples immersed in 1 M KOH shows redox peaks consistent with typical Co(OH)$_2$ materials (Figure 2.16c).\textsuperscript{156,180} We measured the specific charge capacity of each film type with CV in both aqueous 1 M KOH and 0.1 M tetrabutylammonium perchlorate (TBAP) in acetonitrile to quantify the contribution of the electric double-layer (EDL) on the total specific capacity of each material (Figure 2.16d, e, and Figure 2.22). Since the redox activity of Co(OH)$_2$ is limited in non-aqueous solutions such as acetonitrile, we expect only adsorption of the ClO$_4$\textsuperscript{-} anions to contribute to energy storage. The EDL contribution to specific capacity is less than 0.2\% of the total charge storage measured in 1 M KOH for both nanotubular and flat films, demonstrating that the capacity measured in alkaline electrolytes is almost entirely due to redox reactions. We also observe that the capacity for nanotubular films is approximately three to four times higher than that of the flat films for both redox- and EDL-based storage. This indicates that the majority of the increased capacity of the nanotubular hybrid results from higher surface area accessible to the ions in solution required for redox and EDL storage. Furthermore, to investigate if the decrease in capacity is due to diffusion limitations in the flat film, we collected a series of cyclic voltammograms at different sweep rates. A power law relationship between the current and the sweep rate gives the equation:

\[ i = av^b \]  

(2)

where \( i \) is the measured current, \( v \) is the sweep rate, and \( a \) and \( b \) are adjustable parameters. For current response governed by semi-infinite diffusion limitation within the electrode, \( b \) approaches a value of 0.5, while capacitive current response would exhibit \( b \) values near 1.\textsuperscript{148,179,181–183} The slopes of the log-log plots of the peak cathodic current versus the sweep rate give the \( b \)-values for nanotubular and flat films (Figure 2.16f). Both morphologies show linear behavior with \( b \)-values near 1 for sweep rates up to 100 mV/sec, corresponding to a charging time of 4.5 seconds. This indicates that the current response is predominately capacitive in nature and therefore diffusion limitation does not account for the lower capacity.
of the flat film. Thus, the EDL measurements and \( b \)-value analysis suggest that the increased capacity of the nanotubular film is a result of higher accessible surface area. Fittings of the Nyquist plot from electrochemical impedance spectroscopy (EIS) show similar series resistances (3.3 \( \Omega \)) but significantly larger resistance in the high frequency (HF) loop for the flat film (4.34 \( \Omega \)) compared to that of the nanotubular film (1.35 \( \Omega \)) (Figure 2.16g, 2.23). We hypothesize that this larger HF loop is due to lower electronic conductivity perpendicular to the current collector in the flat film. The results of the EDL capacity measurements and the \( b \)-value analysis highlight the importance of high surface area morphologies, while EIS experiments demonstrate that the oriented tubes may facilitate more efficient electron transport parallel to the macroscopic normal of the electrode.

![Cyclic voltammograms of nanotubular and Co(OH)$_2$/PyBA flat films in 0.1 M TBAP/acetonitrile electrolyte at a 10 mV/sec sweep rate. The potential is calibrated to the ferrocene redox couple.](image)

**Figure 2.22:** Cyclic voltammograms of nanotubular and Co(OH)$_2$/PyBA flat films in 0.1 M TBAP/acetonitrile electrolyte at a 10 mV/sec sweep rate. The potential is calibrated to the ferrocene redox couple.
Figure 2.23: Modified Randles circuits used for fitting Nyquist impedance plots for (a) nanotubular films and (b) Co(OH)$_2$/PyBA flat films, consisting of resistors and constant phase elements (CPE). CPE are used for representing double-layer capacitance and redox capacitance in the films.

2.3.3 Stability During Immersion in Alkaline Electrolyte

One of the often-overlooked challenges in using Co(OH)$_2$ as an electrochemical energy storage material is the fundamental instability of this layered hydroxide phase in typical electrolyte conditions near pH 14. In the case of Co(OH)$_2$, it has long been understood that the anion-intercalated $\alpha$-Co(OH)$_2$ polymorph undergoes dissolution and re-precipitation into the $\beta$-Co(OH)$_2$ phase, which we have also observed for electrodeposited nitrate-intercalated $\alpha$-Co(OH)$_2$ films (Figure 2.24).$^{158,184}$ This phase and morphology change led to a $\sim$88% loss
of specific capacity (Figure 2.25). This demonstrates that the stability of electrode materials in their electrolytes is key to ensuring a reasonable “shelf life” of peak performance for energy storage devices.

![Image](image-url)

**Figure 2.24:** Degradation of nitrate-intercalated $\alpha$-Co(OH)$_2$ films in 1M KOH electrolyte. (a) SEM image of electrodeposited $\alpha$-Co(OH)$_2$ film with characteristic flake microstructure. (b) SEM image of the film in (a) after immersion in 1M KOH for 24 hours, resulting in platelet morphology. (c) XRD patterns of the samples in (a) and (b). We note that the primary (001) peak exhibited after immersion in 1 M KOH corresponds with a d-spacing of 4.3 Å and indicates the presence of $\beta$-CoOOH rather than $\beta$-Co(OH)$_2$, which we attribute to dissolved oxygen as discussed above.

A similar dissolution and re-precipitation phenomenon occurs for our electrodeposited layered Co(OH)$_2$ films intercalated with organic anions. Upon immersion of Co(OH)$_2$/PyBA
films in aqueous 1 M KOH, we observe dissolution of the nanotubes and re-precipitation to a platelet morphology within 24 hours (Figure 2.26a, b). The (001) peak of the resulting phase in the x-ray diffraction (XRD) pattern corresponds to a 4.3 Å d-spacing, indicating formation of oxidized $\beta$-CoOOH as opposed to $\beta$-Co(OH)$_2$ (Figure 2.26e). This oxidation may be attributed to dissolved oxygen in the 1 M KOH solutions, as immersion in 1 M KOH sparged and sealed under inert Ar atmosphere results in formation of only $\beta$-Co(OH)$_2$ (Figure 2.27). The Co(OH)$_2$/DA films show an analogous decomposition, dissolving and reforming as $\beta$-CoOOH platelets within 24 hours (Figure 2.26f, g, j). We found that the intercalated PyBA and DA molecules are highly soluble in alkaline solutions as observed by mass decrease of hybrid films after immersion and by quantification of the dissolved molecules in the solutions via absorption spectroscopy (see Methods Section 2.5 and Figure 2.28). Therefore, we conclude that the change in morphology can be attributed to both the dissolution of the intercalated species and the Co(OH)$_2$ layers upon exposure to alkaline electrolytes.

To address the dissolution of organic moieties from the lamellar galleries, we used a high concentration (25 wt%) of deprotonated PyBA as an electrolyte additive (see Methods Section 2.5). The high concentration of surfactant in the external electrolyte prevents the
dissolution of the intercalated surfactants out of the hybrid film. This in turn slows the
dissolution of the inorganic Co(OH)$_2$, increasing the overall stability of the hybrid. When
immersing a Co(OH)$_2$/PyBA nanotube film into an aqueous solution of 1 M KOH with con-
centrated PyBA (1 M KOH/25 wt% PyBA) for five days, the film retained a nanotubular
morphology as well as lamellar XRD peaks (Figure 2.26c, e). To prove that the stabilization
effect is in fact due to suppression of PyBA intercalant dissolution, we immersed another
Co(OH)$_2$/PyBA film in a 1 M KOH solution with similarly concentrated deprotonated DA
(1M KOH/25 wt% DA) for five days. This resulted in dissolution of PyBA from the hy-
brid film and complete decomposition to $\beta$-CoOOH (Figure 2.26d, e). We also immersed
Co(OH)$_2$/DA films in both PyBA and DA solutions to probe if suppression of intercalant dis-
solution is a general strategy for stabilization of Co(OH)$_2$ hybrids. We found that immersion
in the concentrated PyBA solution induces intercalant exchange, resulting in an expanded
(001) d-spacing of 3.0 nm and stabilization of the hybrid over five days (Figure 2.26h, j). In
contrast, immersion in a concentrated DA solution for five days resulted in complete decom-
position to $\beta$-CoOOH (Figure 2.26i, j). These results indicate that simply concentrating the
cycling electrolyte with the corresponding intercalated surfactant for a hybrid film is insuffi-
cient for stabilization and that only specific molecules provide stability to Co(OH)$_2$ hybrids
in alkaline environments. We hypothesize that $\pi-\pi$ interactions of the aromatic core of the
surfactant contribute to the stability of the Co(OH)$_2$/PyBA hybrid over the Co(OH)$_2$/DA
analogue.

To demonstrate the effectiveness of this stabilization method, we measured the first cycle
discharge capacity of Co(OH)$_2$/PyBA nanotubular films as a function of time immersed in
alkaline electrolytes with and without surfactant additives (Figure 2.29). Following immer-
sion in 1 M KOH, 1 M KOH/25 wt% DA, and 1 M KOH/25 wt% PyBA, the films were
galvanostatically cycled at 2 A/g in their respective electrolytes. Electrochemical measure-
ments performed on as-deposited nanotubular films in these electrolytes indicate that the
surfactant additives do not significantly affect the cycling behavior of the hybrid material (Figure 2.30). Consistent with the structural stabilization observed in Figure 2.26, only the alkaline electrolyte with concentrated PyBA successfully preserved the initial specific capacity of nanotubular films. In 1 M KOH and 1 M KOH/25 wt% DA, the nanotubular films lost more than 80% of the specific capacity of pristine nanotubular films after 24 hours of immersion. We attribute this loss in performance to the dissolution and reprecipitation of the nanotubular hybrid into $\beta$-CoOOH platelets (Figure 2.26b, d, e). Interestingly, the nanotubular film immersed for 120 hours in an electrolyte containing PyBA exhibited a specific capacity of 57.5 mAh/g, while the films immersed in electrolytes without PyBA exhibited specific capacities of ~4.5 mAh/g. These results suggest the possibility of stabilizing hybrid nanostructures, with their respective organic components in the electrolyte, prior to electrochemical cycling. Future experimental and computational work in this area could identify additional strategies to stabilize organic-inorganic electroactive hybrids in harsh chemical environments.
Figure 2.26: Stability of layered Co(OH)$_2$ materials in pH 14 solutions with concentrated surfactant electrolyte additives. SEM images of Co(OH)$_2$/PyBA films (a) as deposited, (b) after immersion in 1M KOH for 24 hours, (c) after immersion in 1M KOH/25 wt% PyBA for 5 days, and (d) after immersion in 1M KOH/25 wt% DA for 5 days. (e) XRD patterns of samples shown in (a)-(d). SEM images of Co(OH)$_2$/DA films (f) as deposited, (g) after immersion in 1M KOH for 24 hours, (h) after immersion in 1M KOH/25 wt% PyBA for 5 days, and (i) after immersion in 1M KOH/25 wt% DA for 5 days. (h) XRD patterns of samples shown in (f)-(i). For (e) and (j), tick marks indicate (00$l$) peaks of the layered structures, while * denotes the (001) peak of the $\beta$-CoOOH degradation product.
Figure 2.27: Stability of Co(OH)$_2$/PyBA films in Ar-sparged electrolyte. (a) XRD pattern, (b) SEM image, and (c) specific capacity of a nanotubular film after immersion for 5 days in Ar-sparged 1 M KOH. Large $\beta$-Co(OH)$_2$ platelets are present in the degraded film. The specific capacity of the immersed film was calculated from the first cycle discharge capacity during galvanostatic cycling at 2 A/g in 1 M KOH.
Figure 2.28: Absorbance spectroscopy on immersion and cycling electrolytes of Co(OH)$_2$/PyBA films. (a) Calibration curve for quantifying PyBA dissolved into various electrolytes. (b) Absorbance spectra for different electrolytes after immersion for at least 24 hours.
Figure 2.29: Specific capacity of nanotubular hybrid films after immersion in alkaline electrolytes for varying lengths of time. Samples were immersed in 1 M KOH (purple), 1 M KOH/25 wt% DA (blue), and 1 M KOH/25 wt% PyBA (red) prior to galvanostatic cycling at 2 A/g current density.

Figure 2.30: Electrochemistry of nanotubular Co(OH)$_2$/PyBA films in concentrated surfactant electrolytes. (a) CV at 10 mV/s and (b) galvanostatic cycling at 10 A/g in 1 M KOH/25 wt% PyBA electrolyte (blue) and in 1 M KOH/25 wt% DA (red). We note that there is an increase in the separation of the Co(OH)$_2$ redox peaks in KOH/DA. This may be due to a hydrophobic DA bilayer on the surface of the electrode resulting in slower diffusion kinetics. (c) Flow curves for 1M KOH and KOH/surfactant electrolytes. These viscosities are orders of magnitude below typical aqueous polymer electrolytes, which are allowed to dry to a solid-like gel.$^{154,155}$
2.4 Conclusion

We synthesized concentric cobalt hydroxide-organic hybrid nanotubes perpendicular to a metallic substrate. We demonstrated that the superior electrochemical performance of the nanotubular films is the result of a large accessible surface area for redox activity and showed that diffusion limitations do not exist for charging times as fast as five seconds. Finally, we discovered a pathway to increase the stability of these hybrid architectures under the harsh conditions necessary to achieve high performance in energy storage devices or other potential electrochemical applications. Our work demonstrates that organic molecules in these hybrids can not only template complex architectures, but also stabilize materials at the solid-liquid interfaces critical to their functions.

2.5 Materials and Methods

**Electrochemical synthesis**

Electrochemical synthesis of PyBA-Co(OH)$_2$ hybrid samples was carried out in 10 mL solutions (5:5 (v/v) DMSO/ultrapure H$_2$O, DMSO obtained from Sigma Aldrich) of 0.1 M Co(NO$_3$)$_2$·6H$_2$O (Alfa Aesar, 99.999% metals basis) and 1.25 mM 1-pyrenebutyric acid (Sigma Aldrich) in an undivided cell vial using a three-electrode set-up (Metrohm Autolab PGSTAT128N) with a Co counterelectrode (Alfa Aesar, 1 mm thick foil, 99.95% metals basis) and a Ag/AgCl reference electrode (BASi model RE-5B). Solutions were heated in an oil bath to 80°C, pH adjusted slowly with 0.1 M aqueous KOH to pH $\sim$5.2 (Hanna HI 1131B pH electrode) and sparged for 20 min with Ar gas before depositions were started. Synthesis of the nitrate-intercalated $\alpha$-Co(OH)$_2$ was carried out at room temperature with 10 mL aqueous solutions of 0.1 M Co(NO$_3$)$_2$·6H$_2$O in the same undivided vial with a three-electrode set-up with a Pt wire counterelectrode and a Ag/AgCl reference electrode.
Freshly abraded 1 cm x 2 cm 304 stainless steel substrates (McMaster Carr) were used as working electrodes and positioned upright in the cell. Pyrolytic graphite foil (MTI) and carbon paper (Toray TGP-H-030, 5% waterproofed) were used as received for flexible working electrode substrates. A pulsed deposition procedure was used for hybrid samples, with alternating 30 second pulses of -0.8 V and 0 V vs. reference for 5 to 90 minutes. While pulsing is not required for tube growth, it allows for equilibration of pH and reactant concentrations which minimizes formation of undesired Co(OH)$_2$ phases (Figure 2.31). Nitrate-intercalated $\alpha$-Co(OH)$_2$ samples were deposited at a constant potential of -1.0 V vs reference for 1 minute to achieve similar mass loadings as the hybrid films.

Figure 2.31: Characterization of a Co(OH)$_2$/PyBA film electrodeposited for 60 minutes with a constant potential of -0.8 V vs. Ag/AgCl (i.e. without 30 second pulses). (a) Representative SEM image of non-pulsed nanotubular films. (b) XRD pattern showing much weaker lamellar signal compared to pulsed samples shown previously. A significant $\alpha$-Co(OH)$_2$ impurity peak is apparent, likely due to the higher pH at the electrode interface that arises without pulsing the deposition.

Deposited films were thoroughly rinsed with water and allowed to air dry at room temperature. Samples for the cross-sectional SEM images were deposited on 0.001” thick substrates, while samples for electrochemical and x-ray characterization, as well as all other SEM characterization were deposited on 0.031” thick substrates for more facile handling.
Materials characterization

SEM imaging was performed using a Hitachi SU8030 SEM. Au/Pd coated samples for SEM imaging were sputtered with 10 nm of Au/Pd using a Denton III Desk Sputter Coater. Bright-field TEM images were taken with a JEOL 2100F microscope at 200 kV and a Hitachi HT7700 microscope at 120 kV. Dark-field STEM images were taken with a Hitachi HD-2300 microscope at 200 kV. Samples were scraped off from the substrate with a razor blade and the powder was then applied on copper TEM grids. XRD data was obtained using Mo Kα x-rays from a two-circle diffractometer with a rotating anode generator and multilayer optic monochromator, using energy filters to exclude fluorescence signal from the stainless steel substrate and cobalt in the films. 2D-GIXS data was obtained at beamline 8-ID-E at the Advanced Photon Source, Argonne National Laboratory, using a photon energy of 7.35 KeV and an incident angle of 0.1°.

All substrates were weighed before and after depositions, subtracting the pre-deposition mass from the post-deposition mass to obtain the film mass. All substrate masses were measured with a Mettler Toledo UMX2 microbalance. Surface areas of the deposited films were measured in ImageJ from photographs of the front and back of the electrodes. Typical mass loadings for samples used in electrochemical characterization ranged between 75 and 100 µg/cm².

All electrochemical characterization was performed in a three-electrode set-up with a Pt counterelectrode and a Hg/HgO reference electrode (CH Instruments, model CHI152). EDL measurement was performed using the same three-electrode setup with 0.1 M tetra-butylammonium perchlorate (TBAP) in acetonitrile as the electrolyte and a non-aqueous AgNO₃ reference electrode (BASi, MW-1085). CV, galvanostatic charge/discharge, and EIS measurements were carried out using a Metrohm Autolab PGSTAT128N equipped with a FRA32M module. Specific charge capacity measurements derived from CV were integrated from the total current passed in the negative voltage sweep direction at 10 mV/sec. EIS
measurements were performed at 0.25 V vs. Hg/HgO after a 10 minute potential equilibra-
tion step, with a 5 mV perturbation and frequencies ranging from 50 kHz to 10 mHz. For
the immersion studies, the concentrated surfactant electrolytes were prepared as described
in the Methods Section 2.5. The storage capacities for the immersed films were normalized
with the original hybrid film masses prior to immersion.

**Relative concentration independence of tube formation**

We conducted a series of time-resolved morphological studies described in Figure 2.3 at
different initial deposition bath concentrations to explore the range of compositional window
for the nanotubular growth. We found that moderate changes to the precursor composition
does not greatly affect the ability of nanotubes to form, but rather the amount of deposition
time it takes to nucleate the tubes. Table 2.1 shows the compositions we have tested. For
example, nanotubes were observed after 60 minutes at both 75% and 150% of the original
nitrate concentration (Figure 2.4a and b, respectively). To maintain a constant Co^{2+} con-
centration, CoCl₂ was substituted to reduce nitrate concentration while KNO₃ was added
to raise nitrate concentration. Raising the nitrate concentration accelerates the deposition,
because more hydroxide ions are being produced at the surface of the working electrode
leading to more rapid precipitation of the hybrid Co(OH)₂ structure. For PyBA concentra-
tions between 50% and 150% of the original 1.25 mM, all films had at least partial nanotube
formation after 90 minutes. At lower concentrations of PyBA, some pure flake structures
were formed, presumably because there was insufficient PyBA intercalation to induce nan-
otube formation (Figure 2.4c). At higher concentrations, nanotube formation was observed
after about 120 minutes (Figure 2.4d). This may be due to the increased concentration of
PyBA molecules inhibiting nitrate reduction at the electrode surface, effectively acting as a
passivating layer.
Synthesis of 1-pyrenehexanoic acid and 2-naphthalenebutyric acid

Unless otherwise specified, all reagents were used without further purification. Monomethyl adipate, triethylamine, pyrene, 2-bromonaphthalene, thionyl chloride, iodine and succinic anhydride were obtained from Sigma-Aldrich; diethyl ether, dichloromethane (DCM), hexanes, sodium hydroxide, hydrochloric acid (HCl), magnesium turnings, tetrahydrofuran (THF), and ethyl acetate (EtOAc) were obtained from Fisher Scientific; trifluoroacetic acid (TFA) was obtained from Alfa Aesar; triethylsilane was obtained from Acros Organics. Anhydrous solvents were degassed on a Vacuum Atmospheres 103991 system. Proton NMR spectra were performed on a Varian Inova 500 or Agilent DD MR-400 with working frequencies of 500 and 400 MHz, respectively. Carbon NMR spectra were obtained using a Bruker Avance III 500 spectrometer, with working frequency of 125.6 MHz for $^{13}$C nuclei. Chemical shifts are reported in parts per million (ppm) and referenced to the residual nondeuterated solvent frequencies (CDCl$_3$: $\delta$ 7.26 ppm for $^1$H, $\delta$ 77.36 ppm for $^{13}$C, DMSO-D$_6$: $\delta$ 2.62 for $^1$H and 40.45 ppm for $^{13}$C). High-resolution mass spectra were recorded on an Agilent Model 6210 LC-TOF multimode ionization (MMI).

The 1-pyrenehexanoic acid (PyHA) was synthesized using the scheme illustrated in Figure 2.32a.

1-Pyreneoxohexanoic methylester (PyCOHAME). Monomethyl adipate (2.04 mL, 13.8 mmol) was dissolved in DCM (15 mL) and triethylamine (1.67 mL, 12.0 mmol) was added. The flask was put in an ice bath and thionyl chloride (0.872 mL, 12.0 mmol) was injected into the solution. The reaction was stirred for 10 minutes and the solvent was evaporated under vacuum. The crude material was dissolved in diethyl ether and the precipitate filtered. The ether washings were placed in a Schlenk flask and the ether was removed under vacuum. Pyrene (2.30 g, 9.99 mmol) was then added and the flask was degassed by three vacuum/nitrogen cycles before injecting anhydrous DCM (20 mL) under nitrogen. The flask was placed in an ice bath and immediately after, titanium (IV) chloride (1.32 mL, 12.0
Figure 2.32: Synthesis of (a) 1-pyrenehexanoic acid and (b) 2-naphthalenebutyric acid.

mmol) was injected dropwise. The cooling bath was then removed and the reaction was left stirring for 30 minutes before quenching it by adding the solution to a solution of saturated sodium bicarbonate (100 mL) and filtering the entire mixture over celite, then washing the celite pad with DCM (250 mL). The DCM washings were placed in a separatory funnel to remove water. The solvent was then evaporated under vacuum and the product was purified by column chromatography (DCM) to give a yellow solid (2.52 g, 64%). $^1$H NMR (400 MHz; CDCl$_3$): $\delta$ 8.88 (d, $J$ = 9.4 Hz, 1H), 8.32 (d, $J$ = 8.0 Hz, 1H), 8.26 (dd, $J$ = 7.6, 1.8 Hz, 2H), 8.23-8.17 (m, 3H), 8.10-8.05 (m, 2H), 3.67 (s, 3H), 3.25 (t, $J$ = 7.2 Hz, 2H), 2.42 (t, $J$ = 7.3 Hz, 2H), 1.94-1.88 (m, 2H), 1.85-1.80 (m, 2H). $^{13}$C NMR (126 MHz; CDCl$_3$): $\delta$ 204.9, 174.2, 134.1, 132.9, 131.5, 130.9, 129.94, 129.84, 129.66, 127.4, 126.76, 126.60, 126.4, 125.4, 125.1, 124.7, 124.4, 51.9, 42.5, 34.3, 25.0, 24.7. HRMS calc m/z 344.1412, found 344.1320.

1-Pyrenehexanoic methylester (PyHAME). PyCOHAME (1.23 g, 3.60 mmol) was dissolved in trifluoroacetic acid (6.00 mL, 78.4 mmol) and triethylsilane (1.50 mL, 9.00 mmol) was added dropwise before stirring the reaction for 1 h. The solvent was then removed under
vacuum and the crude was washed with hexane (200 mL) to give a relatively pure yellow solid (0.792 g, 67%). $^1$H NMR (400 MHz; CDCl$_3$): $\delta$ 8.27 (d, $J = 9.3$ Hz, 1H), 8.18-8.15 (m, 2H), 8.11 (dd, $J = 8.5$, 2.3 Hz, 2H), 8.02 (d, $J = 2.3$ Hz, 2H), 7.99 (dd, $J = 9.8$, 5.4 Hz, 1H), 7.86 (d, $J = 7.8$ Hz, 1H), 3.67 (s, 3H), 3.35 (t, $J = 7.8$ Hz, 2H), 1.88 (dt, $J = 15.4$, 7.7 Hz, 2H), 1.74 (dd, $J = 15.4$, 7.6 Hz, 2H), 1.56-1.50 (m, 2H). $^{13}$C NMR (126 MHz; CDCl$_3$): $\delta$ 174.5, 137.2, 131.8, 131.3, 130.1, 128.9, 127.8, 127.55, 127.51, 126.9, 126.1, 125.42, 125.38, 125.15, 125.11, 124.99, 123.7, 51.8, 34.4, 33.7, 31.8, 29.6, 25.2. HRMS calc m/z 330.1620, found 330.1630.

**1-Pyrenehexanoic acid (PyHA).** PyHAME (1.00 g, 3.04 mmol) was dissolved in methanol (30 mL) and 6 M NaOH (5.00 mL, 30.0 mmol) was then added and the solution was refluxed for 6 h (or until TLC indicates full hydrolysis of methyl ester) before removing the solvent under vacuum. Acidification with 4 M HCl (10 mL) gave a yellow precipitate, which was filtered and washed with DCM (100 mL), collected and dried (0.600 g, 79%). $^1$H NMR (499 MHz; THF): $\delta$ 8.36 (d, $J = 9.3$ Hz, 1H), 8.18 (t, $J = 6.9$ Hz, 2H), 8.15-8.13 (m, 2H), 8.07-8.03 (m, 2H), 7.99 (t, $J = 7.6$ Hz, 1H), 7.92 (d, $J = 7.8$ Hz, 1H), 3.61 (d, $J = 19.9$ Hz, 30H), 3.40 (t, $J = 7.8$ Hz, 2H), 2.29-2.26 (m, 2H), 1.92-1.88 (m, 2H), 1.76-1.68 (m, 20H), 1.60-1.55 (m, 2H). $^{13}$C NMR (126 MHz; DMSO): $\delta$ 175.4, 137.9, 131.8, 131.3, 130.1, 128.9, 128.4, 128.1, 127.4, 127.0, 125.84, 125.66, 125.15, 125.10, 124.4, 34.6, 33.5, 32.2, 29.6, 25.4. HRMS calc m/z 316.1463, found 316.1472.

The 2-naphthalenebutyric acid (NBA) was synthesized using the scheme illustrated in Figure 2.32b.

**2-Naphthaleneoxobutyric acid (NCOBA).** A flask containing 2-bromonapthalene (5g, 24.2 mmol) and freshly polished magnesium (0.860 g, 36.0 mmol) was degassed by three vacuum/nitrogen cycles before injecting anhydrous THF (30 mL). Iodine (0.254 g, 1.00 mmol) was then added and the flask was heated until the color of iodine disappeared. The flask was placed in an ice-bath as necessary to prevent violent boiling of THF. Once
cool to room temperature, the Grignard reagent was cannulated into a degassed solution of succinic anhydride (2.89 g, 28.9 mmol) in anhydrous THF (20 mL) and left stirring for 30 minutes. Aqueous NaOH (6 M, 1 mL) was then added and the reaction diluted in water (100 mL) and extracted with ethyl acetate (50 mL). The aqueous layer was collected and acidified with 4 M HCl (10 mL), then extracted with ethyl acetate (50 mL). The organic layer was collected and the solvent was removed under vacuum. The product was purified by column chromatography (10% MeOH/DCM) to afford a white solid (2.00 g, 36%). ¹H NMR (499 MHz; CDCl₃): δ 8.52 (d, J = 0.4 Hz, 1H), 8.05 (dd, J = 8.6, 1.7 Hz, 1H), 7.97 (d, J = 7.9 Hz, 1H), 7.92-7.88 (m, 2H), 7.63-7.55 (m, 2H), 3.49-3.46 (m, 2H), 2.90-2.88 (m, 2H). ¹³C NMR (126 MHz; CDCl₃): δ 198.2, 176.6, 136.1, 134.1, 132.8, 130.2, 129.9, 128.95, 128.89, 128.2, 127.2, 124.1, 33.7, 28.1. HRMS calc m/z 228.0786, found 228.0789.

2-Naphthalenebutyric acid (NBA). NCOBA (0.560 g, 2.45 mmol) was dissolved in trifluoroacetic acid (3.00 mL, 39.2 mmol) and triethylsilane (0.980 mL, 6.12 mmol) was added dropwise before stirring the reaction for 1 h. The solvent was then removed under vacuum and the product was purified by column chromatography (10% MeOH/DCM) to afford a white solid (0.430 g, 82%). ¹H NMR (499 MHz; CDCl₃): δ 7.80 (dd, J = 12.3, 8.0 Hz, 3H), 7.63 (s, 1H), 7.48-7.42 (m, 2H), 7.34 (dd, J = 8.4, 1.4 Hz, 1H), 2.85 (t, J = 7.6 Hz, 2H), 2.42 (t, J = 7.4 Hz, 2H), 2.11-2.05 (m, 2H). ¹³C NMR (126 MHz; CDCl₃): δ 180.0, 139.0, 133.9, 132.4, 128.4, 127.95, 127.79, 127.5, 127.0, 126.3, 125.6, 35.5, 33.6, 26.4. HRMS calc m/z 214.0994, found 214.0989.

Electrodeposition of Co(OH)₂ hybrids with other surfactants

Electrochemical synthesis of layered Co(OH)₂ materials with other organic surfactants were carried out in a similar electrodeposition procedure with a three-electrode set-up in 10 mL DMSO/H₂O solutions. The surfactants tested were 1-pyreneacetic acid (PyAA), 1-pyrenehexanoic acid (PyHA), 2-naphthalenebutyric acid (NBA), and decanoic acid (DA).
The deposition conditions were systematically varied to tune the surfactant solubility and the deposition rate in an effort to enhance the synergistic self-assembly of the hybrid material. The surfactant concentrations ranged from 0.25 to 3 mM while the Co(NO$_3$)$_2$ concentrations were varied from 25 to 200 mM. The DMSO/H$_2$O ratio was varied from 5:5 to 7:3, depending on the solubility of the surfactant (e.g. 6:4 and 7:3 were used for lower solubility surfactants like PyHA). The solution temperature was tested between 70-80°C and pulsed depositions (-0.8 V vs Ag/AgCl Ref.) were carried out for 30-210 minutes. Representative SEM images and XRD patterns for the hybrid films of each surfactant with film masses near 100 µg/cm$^2$ are provided in Figure 2.13.

**2D-GIXS azimuthal angle ($\Phi$) analysis**

For the 2D-GIXS analysis referenced in this work, the angle $\Phi$ refers to the azimuthal angle in the $q_{yz}$ plane of the detector. This angle determines the orientation of crystalline order with respect to the film’s substrate. For peaks localized at $\Phi = 90^\circ$, the associated lattice planes are oriented parallel to the substrate. Peaks localized at $\Phi = 0^\circ$ or $180^\circ$ are associated with lattice planes oriented parallel to the substrate normal and thus perpendicular to the substrate. Line cuts in this work refer to integrated signal intensities of 2D-GIXS data, and may be plotted with respect to $q$ or $\Phi$.

The small oscillations at $q < 0.2$ Å$^{-1}$ are a result of the nanotubular scattering form factor, as later described in the following section and Figure 2.10. A small $\beta$-Co(OH)$_2$ (001) peak is observed at $q = 1.30$ Å$^{-1}$, which indicates the presence of non-intercalated Co(OH)$_2$ as a minor impurity phase. We expect that this impurity phase is a result of high pH localized at the substrate-film interface, which can convert PyBA-intercalated Co(OH)$_2$ to $\beta$-Co(OH)$_2$. This $\beta$-Co(OH)$_2$ is the more stable Co(OH)$_2$ phase at higher pH values. Two peaks are observed at $q = 1.62$ Å$^{-1}$ and 1.68 Å$^{-1}$, which correspond to d-spacings of 3.88 Å
and 3.73 Å respectively and are expected to be the result of \( \pi-\pi \) stacking of the PyBA (see Figure 2.9 for orientation of this \( \pi-\pi \) stacking).

**Scattering analysis on the tube size**

We used the lateral intensity profiles from the grazing incidence X-ray scattering patterns to estimate the average diameter of the nanotubes. The measured scattering profiles have significant background from substrate fluorescence – therefore we identified the minima in the scattering profiles and compared against the theoretical form factor minima from a cylindrical model instead of fitting the entire curve to the core-shell cylindrical model.

The scattering form factor of an infinitely long cylindrical object is described as:

\[
F = 4\pi r^2 (\Delta \rho) \cdot \left( \frac{J_1(qr)}{qr} \right)
\]  

(3)

Here \( r \) denotes the radius of the cylinder, \( \Delta \rho \) the electron density difference, \( q \) the scattering vector magnitude defined as \( q = (4\pi \sin \theta)/\lambda \) where \( \theta \) is half of the total scattering angle and \( \lambda \) is the wavelength, and \( J_1 \) the Bessel function of order 1. As the scattering intensity is proportional to the square of the form factor, minima for the scattering intensities occur where \( J_1 = 0 \).

Figure 2.11 shows the correlation between the observed minima of the scattering patterns and the roots of \( J_1 \). The lateral intensity profiles for both GISAXS and GIWAXS were laterally averaged over 100 pixels above the sample horizon. The linear fit of the correlation provides the average radius of the nanotubes, which is estimated to be 13.6 nm, giving 27.3 nm for the diameter.

**Determination of active material mass by thermogravimetric analysis**

To determine the mass of Co(OH)$_2$ active material deposited on each film, the mass percentage of Co(OH)$_2$ in the Co(OH)$_2$/PyBA hybrid films must first be determined. Ther-
mogravimetric analysis was performed to determine the organic content of hybrid films, with the assumption that there is negligible mass loss by the inorganic Co(OH)$_2$ material during heating to moderate temperatures (Figure 2.18). Several films were scraped from their substrates and collected for analysis using a Mettler-Toledo TGA/SDTA 851 instrument. TGA was performed in air with a 5°C/min ramp rate. The TGA curve presented in Figure 2.18 has been subtracted with a blank curve collected under identical conditions with an empty pan to correct for buoyancy effects. A ~50% mass loss is observed in the 200-300°C range, which is attributed to PyBA combustion. Co(OH)$_2$ active material mass percentage is thus estimated to be ~50% in the hybrid material.

Due to the difficulty of collecting enough material for accurate mass quantification with TGA, several films were left on their substrates and calcined for more accurate mass determination. Films of Co(OH)$_2$/PyBA and Co(OH)$_2$/DA hybrids were deposited on stainless steel substrates, heated to 310°C with a 5°C/minute ramp rate, and held at 310°C for 10 minutes before cooling to room temperature. The masses of these substrates before and after calcination are summarized in Table 2.2.

Assuming that any mass change of the underlying substrate is negligible compared to the mass changes of the deposited films, the mass percentage losses of the Co(OH)$_2$/PyBA and Co(OH)$_2$/DA films are -53.7% and -52.0% respectively. The Co(OH)$_2$ active material mass percentages for Co(OH)$_2$/PyBA and Co(OH)$_2$/DA films are thus calculated to be 46.3% and 48.0% respectively.

**Absorbance spectroscopy on immersion and cycling electrolytes**

UV-vis absorbance spectroscopy was used to characterize the extent of PyBA dissolution out of the nanotubular films during soaking or cycling in 1 M KOH. The PyBA concentration was calibrated using standards of known concentration and applying Beer-Lambert’s law (Figure 2.28a). In Figure 2.28b, absorbance spectra of various electrolytes used for soaking
and cycling are plotted along with a 50 μM PyBA standard curve. After normalizing the spectra of each film for electrolyte volume, we determined the PyBA mass in the electrolyte and compared to the total film weight. For immersion or cycling of a nanotubular film in 1 M KOH for 24 hours, we found the PyBA mass constitutes roughly half of an average film and concluded that approximately all of the organic content dissolves out, corroborating the data in Table 2.2. We further confirmed the mass change calculated from UV-vis by weighing the films after immersion. We found that the mass change can be solely attributed to the dissolution of the PyBA, and thus conclude that any dissolved Co(OH)$_2$ species reprecipitate as β-CoOOH.

To verify complete dissolution of PyBA, we immersed a sample cycled in 1 M KOH into fresh 1 M KOH and observed negligible PyBA absorbance. Furthermore, we deduced that it is the basicity of the KOH rather than the ionic strength or liquid phase of the electrolyte that dissolves the PyBA out of the structure when comparing to 1 M KCl and pure deionized water controls.

**Exchange of PyBA into DA-intercalated hybrid**

Flat Co(OH)$_2$/DA films with similar mass to that of the nanotubular films were produced with 60-90 minute pulsed depositions (30 second alternating pulses of 0 V and -0.8 V vs. Ag/AgCl). These films were immersed in 0.5 mL volume solutions of 1 M KOH/25 wt% PyBA for twelve hours. XRD and 2D-GIXS patterns of these films show that the d-spacing expands from the 2.7 nm characteristic of the original Co(OH)$_2$/DA films to the 3.0 nm that is observed for the Co(OH)$_2$/PyBA nanotubular films. To determine if any DA remains in these PyBA-exchanged films, the films were submerged into individually aliquoted aqueous 1 M KOH solutions. Subsequent quantification of their PyBA content by UV-vis absorbance spectroscopy of the KOH solutions and comparison to the measured mass loss after the KOH immersion indicates that nearly all mass loss can be attributed to PyBA dissolved out of
the films. Since all intercalated surfactants are expected to dissolve out of the film into the KOH solution, we deduce that negligible DA remains with the PyBA-exchanged hybrid.

**Preparation of 1 M KOH/25 wt% surfactant solutions**

To prevent neutralization of the aqueous 1 M KOH solutions when adding large amounts of acidic surfactants, 0.75 g and 2 g of PyBA and DA powders respectively were added to separate conical tubes and neutralized with equimolar amounts of KOH using aqueous 1 M KOH solutions. ~30 mL of ultrapure water was added to each tube followed by mixing with vortexing and sonication. The resulting solutions were lyophilized to produce dry powders of deprotonated surfactants. 1 M KOH was then added to each tube in sufficient quantities to produce 1 M KOH/25 wt% surfactant solutions (approximately 1 molal PyBA and 1.6 molal DA).

**Viscosity measurements on surfactant solutions**

Flow curves for each surfactant solution were measured with an MCR 302 rheometer (Anton Paar) operating in a cone-plate configuration with 50 mm diameter, 1° angle fixture (CP 50-1) and 0.1 mm gap. The viscosity was measured as a function of the applied shear rate from 1 to 1000 s⁻¹. All experiments were performed at 25°C.
Chapter 3
Enhanced Out-of-Plane Conductivity in Hybrid Layered Perovskites through Organic Cation Design

3.1 Objectives and Significance

Layered perovskites with the formula \((R-NH_3)_2PbI_4\) have excellent environmental stability but poor photovoltaic function due to the preferential orientation of the semiconducting layer parallel to the substrate and the typically insulating nature of the \(R-NH_3^+\) cation. Here we report a series of these \(n = 1\) layered perovskites with the form \((\text{aromatic-O-linker-NH}_3)_2\text{PbI}_4\) where the aromatic moiety is naphthalene, pyrene or perylene and the linker is ethyl, propyl or butyl. These materials achieve enhanced conductivity perpendicular to the inorganic layers due to better energy level matching between the inorganic layers and organic galleries. The enhanced conductivity and visible absorption of these materials led to a champion power conversion efficiency of 1.24%, which is the highest value reported for any \(n = 1\) layered perovskite, and it is an order of magnitude higher efficiency than any other \(n = 1\) layered perovskite oriented with layers parallel to the substrate. These findings demonstrate the importance of leveraging the electronic character of the organic cation to improve optoelectronic properties and thus the photovoltaic performance of these chemically-stable low \(n\) layered perovskites.

3.2 Background

Two-dimensional organic-inorganic layered perovskites based on the lead halide framework have demonstrated many of the attractive optoelectronic properties and translational
The structure of these layered perovskites can be generally viewed as the periodic splitting of the three-dimensional structure along a particular crystallographic plane, most commonly along the (100) plane, to form a layered structure. Chemically, this is accomplished by substituting a bulky organic cation \((R-NH_3^+)\) for the interstitial A-site cation according to the formula \((R-NH_3)_2Pb_{n}X_{3n+1}A_{n-1}\). In these structures, \(n\) corner-sharing \(PbX_4^{2-}\) octahedra span the thickness of the inorganic layer where \(n\) is modulated by tuning the ratio of the small interstitial A site cation to the bulky organic cation \((n = 1\) shown in Figure 3.1a). These 2D semiconducting inorganic layers are separated by bulky organic cations, which are typically insulating and thus isolate the inorganic layers both physically and electronically.

In the modern photovoltaic literature, the role of the organic cation has been primarily structural, and the optoelectronic properties of these materials have been designed through the compositional tuning of inorganic layers (varying \(X\) and \(n\)) and processing conditions. To date, these studies have achieved remarkable results with a reported power conversion efficiency (PCE) of 12.5% for a layered perovskite where \(n = 4\), \(R = \text{butylammonium iodide}\), and \(A = \text{methylammonium iodide}\). In this example, the inorganic layers were oriented perpendicular to the bottom contact through a hot-casting technique to mitigate the negative impact of the insulating butyl groups on conductivity between the inorganic layers. Even though the introduction of hydrophobic cations into these \(n > 1\) layered perovskites has been shown to improve stability compared to three-dimensional perovskites, most examples still utilize methylammonium iodide as the A-site cation, which is known to be intrinsically unstable under atmospheric conditions. Furthermore, it is still unclear if the orientation control of the hot-casting technique is applicable to all cations in layered perovskites or for low \(n\) layered perovskites in general.
In this work, we study layered perovskites of the n = 1 variety where X = I. These n = 1 layered perovskites do not contain an A-site cation and are thus considerably more stable than the n > 1 variety. These materials, however, present new challenges due to their wide bandgap and, in all but one example, their inorganic layers prefer orientation parallel to the substrate. This orientation therefore requires conduction of excited-state-carriers perpendicular to the inorganic layers and through typically insulating organic layers (out-of-plane conductivity) to reach the electrodes. If enhanced out-of-plane conductivity can be achieved in these materials, it would obviate the need to reorient the inorganic layers with respect to the substrate surface in photovoltaic devices.

Recent layered perovskite studies have utilized well-known organic moieties such as butylammonium, benzylammonium, and phenylethylammonium or other commercially available molecules where the desired optoelectronic properties were achieved through tuning of the inorganic lattice and post-synthetic modification. However, preceding research of layered perovskites as photovoltaic materials, a number of investigators studied optoelectronic properties and functions with cations containing conjugated moieties such oligothiophene, pyrene, anthryl, naphthalene, and phenyl. Much of this earlier work investigated the charge-transfer of photo-excited carriers between the inorganic and organic layers and explored electroluminescent properties. Their work showed the contribution that the organic chromophores can have on the optoelectronic properties and applications of these materials. They also demonstrated how the alignment of the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) energy levels of the organic and inorganic layers can affect charge transfer between them in the hybrid. Since this work predated interest in these materials as photovoltaic active layers, it primarily considered charge transfer from inorganic-to-organic layers or vice versa as a single event. However, charge transfer in a photovoltaic active layer requires many charge transfer events across many organic-inorganic interfaces through the thickness of the device. Using inspira-
tion from this pioneering work in organic-inorganic layered perovskites as well as our own work on hybrid systems where the organic components serve both structural and electronic functions,\textsuperscript{53,95,108} we report here on efforts to enhance photovoltaic performance in $n = 1$ layered perovskite through organic cation design.

In this work, we utilize the electronic and structural properties of custom-synthesized organic cations to achieve enhanced optoelectronic properties and device performance. We have synthesized organic cations containing various aromatic moieties and have explored how the electronic properties and structural arrangement of the cation within the organic galleries contribute to overcoming the chief limitation of $n = 1$ layered perovskites, which is their poor out-of-plane conductivity. Specifically, we have synthesized $n = 1$ layered perovskites with the formula (aromatic-O-linker-$\text{NH}_3^+$)$_2\text{PbI}_4$ for which bulky cations are synthesized to contain the aromatic groups naphthalene, pyrene, or perylene and the linkers ethyl, propyl or butyl conjugated through an ether bond (Figure 3.1a and b). We have investigated the impact of the HOMO and LUMO alignment of the organic cation and the inorganic layer as well as the structural arrangement of the organic cations within the organic layer on out-of-plane conductivity and optical properties of these layered perovskite materials. Guided by our findings we fabricated photovoltaic devices and analyzed their performance.

\textbf{3.3 Results and Discussion}

\textbf{3.3.1 Synthesis and Characterization of Organic Salts}

We report here on a modular synthetic approach which enabled the development of a homologous series of organic ammonium iodide salts that varied in both electronic character of the aromatic moiety and length of aliphatic linker. This approach facilitates the study of how the energy levels of the aromatic moieties and packing of the organic cations affect the optoelectronic properties of the resulting layered perovskites. Specifically, we synthesized six aromatic ammonium iodide salts with the general form aromatic-O-linker-$\text{NH}_3^+$I where
Figure 3.1: (a) \( n = 1 \) layered perovskites of the form \((R-NH_3)_2PbI_4\) showing alternating organic and inorganic layers that align parallel to the substrate. (b) Modular molecular design of the ammonium iodide cation consisting of an aromatic core joined by an ether bond to an alkyl linker of variable length. (c) Energy levels of typical \( n = 1 \) layered perovskites (gray) with values specific to \((\text{butyl-NH}_3)_2\text{PbI}_4\) compared to the energy levels of the conjugated organic ammonium iodide salts of interest: perylene-O-ethyl-NH\(_3\)I, pyrene-O-propyl-NH\(_3\)I, and naphthalene-O-propyl-NH\(_3\)I. HTL and ETL refer to hole and electron transport layers.

The aromatic moiety is naphthalene, pyrene, or perylene and the linker is ethyl, propyl or butyl. The aromatic moieties were chosen based on reported HOMO and LUMO levels for
the non-functionalized aromatic core in relation to the HOMO and LUMO levels reported for typical \( n = 1 \) lead iodide layered perovskites with aliphatic cations. To synthesize these ammonium iodide salts, hydroxyl-naphthalene, pyrene or perylene were conjugated to either the protected bromo-ethyl, propyl or butyl amine under basic conditions. Following purification, the protecting groups were cleaved and the resulting amine protonated with hydroiodic acid to form the final ammonium iodide salt (see publication for full synthetic details). Once synthesized, the HOMO and LUMO levels of the ammonium iodide salts were determined by ultraviolet photoelectron spectroscopy (UPS) and optical absorption experiments. These are plotted with respect to the HOMO and LUMO levels reported for the reported \( n = 1 \) layered perovskite \( (\text{CH}_3(\text{CH}_2)_3\text{NH}_3)_2\text{PbI}_4 \) in Figure 3.1c.

### 3.3.2 Crystal Growth and Optical Properties

The six aromatic cations with structure aromatic-O-linker-NH\(_3\)I were successfully crystallized with lead (II) iodide into the desired (100) type \( n = 1 \) layered perovskite. Single crystals were prepared through vapor diffusion of dichloromethane (DCM) into \( \gamma \)-butyrolactone (GBL) solutions of 2:1 molar ratio of organic ammonium iodide salt: lead (II) iodide. We will refer to the resulting perovskites using an abbreviated formula of the general type (aromatic-O-linker-NH\(_3\))\(_2\)PbI\(_4\). Here we report on seven \( n = 1 \) layered perovskites including (naphthalene-O-ethyl-NH\(_3\))\(_2\)PbI\(_4\), (naphthalene-O-propyl-NH\(_3\))\(_2\)PbI\(_4\), (naphthalene-O-propyl-NH\(_3\))\(_2\)PbI\(_4\)\(\cdot\)(C\(_4\)H\(_6\)O\(_2\))\(_{0.5}\), (pyrene-O-ethyl-NH\(_3\))\(_2\)PbI\(_4\), (pyrene-O-propyl-NH\(_3\))\(_2\)PbI\(_4\), (pyrene-O-butyl-NH\(_3\))\(_2\)PbI\(_4\), and (perylene-O-ethyl-NH\(_3\))\(_2\)PbI\(_4\). The structures of these layered perovskites were determined using single crystal X-ray diffraction. Crystallographic details are provided in Table 3.1. Note that naphthalene-O-propyl-NH\(_3\)I can form two distinct layered perovskites. The first has the anticipated form and stoichiometry (naphthalene-O-propyl-NH\(_3\))\(_2\)PbI\(_4\) and the second contains GBL within the lattice (naphthalene-O-propyl-NH\(_3\))\(_2\)PbI\(_4\)\(\cdot\)(C\(_4\)H\(_6\)O\(_2\))\(_{0.5}\). This was the only structure in this work that contained solvent.
molecules within the unit cell, and this structure could not be produced in thin film. All other layered perovskites were crystallized in thin film by spin-casting and annealing the same stoichiometric ratios dissolved in a 1:1 volume ratio of dimethylformamide (DMF) and dimethyl sulfoxide (DMSO). Grazing-incidence wide-angle X-ray scattering (GIWAXS) was used to verify that the same crystallographic phase was obtained in thin film as observed in single crystals.

Optical absorption spectroscopy was used to determine the energy of the $S_1$ exciton peak ($E_{S1}$) in thin film samples of each layered perovskite (Table 3.1 and Figure 3.2). These $n = 1$ layered perovskites have characteristically large exciton binding energy in the range of 250-500 meV that results from the dielectric confinement of the 2D-inorganic layer.\textsuperscript{206} The large binding energy is apparent in the absorption spectra with a pronounced lowest energy electronic transition which is assigned to the $S_1$ exciton followed by a broader absorption onset typically assigned to the bandgap absorption (Figure 3.3). The precise determination of the bandgap of these materials can be difficult to ascertain from the absorption spectra at room temperature. Thus, we used the $E_{S1}$ transition as an indication of bandgap energy for these materials since this absorption has been shown to produce photocurrent and is thus important to photovoltaic performance.\textsuperscript{207}

A wide range of $E_{S1}$ values (2.27 eV to 2.57 eV) have been observed for the layered perovskites investigated here. Increasing $E_{S1}$ values are correlated with increasing distortion of the $\text{PbI}_4^{2-}$ octahedra compared with the ideal, lowest energy arrangement in which Pb-I-Pb bond angles along the central plane of the inorganic layer are 180° (Figure 3.4).\textsuperscript{208,209} The role that the organic cation plays in dictating octahedral distortion and thus the optical properties of layered perovskites has been previously linked to the position of the positively charged ammonium cation with respect to the negatively charged inorganic lattice.\textsuperscript{208} Our materials generally follow this previously-defined model, except for (naphthalene-O-propyl-NH$_3$)$_2$PbI$_4$, which has the highest $E_{S1}$ despite having moderate penetration of the ammonium cation into
Table 3.1: Crystal data for \( n = 1 \) layered perovskites of the form (aromatic-O-linker-NH\(_3\))\(_2\)PbI\(_4\).

<table>
<thead>
<tr>
<th>Precursor Salt</th>
<th>(naphthalene-O-ethyl)(_2)PbI(_4)</th>
<th>(naphthalene-O-propyl)(_2)PbI(_4)</th>
<th>(naphthalene-O-propyl-NH(_3))(_2)PbI(_4)</th>
</tr>
</thead>
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<tr>
<td>empirical formula</td>
<td>((C_\text{aromatic-O})_2)PbI(_4)</td>
<td>((C_\text{aromatic-O})_2)PbI(_4)</td>
<td>(\text{C}<em>\text{H}</em>\text{O}(C_\text{aromatic-O})_2)PbI(_4)</td>
</tr>
<tr>
<td>formula weight (g/mol)</td>
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<td>1119.39</td>
<td>1162.37</td>
</tr>
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<td>crystal system</td>
<td>Monoclinic C</td>
<td>Monoclinic P</td>
<td>Triclinic</td>
</tr>
<tr>
<td>space group</td>
<td>(\text{C}_\text{c})</td>
<td>(\text{P}_{2_1/\text{c}})</td>
<td>(\text{P})</td>
</tr>
<tr>
<td>unit cell/dimension</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>a, Å</td>
<td>12.5228(17)</td>
<td>23.0465(10)</td>
<td>12.4131(3)</td>
</tr>
<tr>
<td>b, Å</td>
<td>12.4688(17)</td>
<td>8.8619(4)</td>
<td>12.5652(4)</td>
</tr>
<tr>
<td>c, Å</td>
<td>39.555(6)</td>
<td>8.2792(4)</td>
<td>23.8888(7)</td>
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<td>90, 95.2934(19), 90</td>
<td>101.10, 104.07, 90.71</td>
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<td>(E_{S1}) (eV)</td>
<td>2.39(^1)</td>
<td>2.57(^1)</td>
<td>2.35(^2)</td>
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<table>
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<tr>
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<th>(pyrene-O-ethyl)(_2)PbI(_4)</th>
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<th>(pyrene-O-buty1)(_2)PbI(_4)</th>
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<tr>
<td>empirical formula</td>
<td>((C_\text{H}_\text{aromatic-O})_2)PbI(_4)</td>
<td>((C_\text{H}_\text{aromatic-O})_2)PbI(_4)</td>
<td>(\text{C}<em>\text{H}</em>\text{O}(C_\text{H}_\text{aromatic-O})_2)PbI(_4)</td>
</tr>
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<td>formula weight (g/mol)</td>
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<td>1267.48</td>
<td>1293.83</td>
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<td>crystal system</td>
<td>Monoclinic C</td>
<td>Monoclinic C</td>
<td>Monoclinic C</td>
</tr>
<tr>
<td>space group</td>
<td>(\text{C}_\text{c})</td>
<td>(\text{C}_\text{c})</td>
<td>(\text{C}_{2_1/\text{c}})</td>
</tr>
<tr>
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<td></td>
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</tr>
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<td>53.3048(16)</td>
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<tr>
<td>b, Å</td>
<td>12.4019(3)</td>
<td>8.4895(2)</td>
<td>6.1727(2)</td>
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<td>c, Å</td>
<td>48.3623(3)</td>
<td>9.4484(2)</td>
<td>12.565(4)</td>
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<td>90, 94.9469(13), 90</td>
<td>90, 90.318(2), 90</td>
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<tr>
<td>(E_{S1}) (eV)</td>
<td>2.38(^1)</td>
<td>2.27(^1)</td>
<td>2.40(^1)</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Precursor Salt</th>
<th>(perylene-O-ethyl)(_2)PbI(_4)</th>
</tr>
</thead>
<tbody>
<tr>
<td>empirical formula</td>
<td>((C_\text{aromatic-O})_2)PbI(_4)</td>
</tr>
<tr>
<td>formula weight (g/mol)</td>
<td>1339.54</td>
</tr>
<tr>
<td>crystal system</td>
<td>Monoclinic P</td>
</tr>
<tr>
<td>space group</td>
<td>(\text{P}_{2_1/\text{c}})</td>
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<tr>
<td>unit cell/dimension</td>
<td></td>
</tr>
<tr>
<td>a, Å</td>
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<td>b, Å</td>
<td>8.8638(3)</td>
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<td>c, Å</td>
<td>8.7113(3)</td>
</tr>
<tr>
<td>(\alpha, \beta, \gamma), deg</td>
<td>90, 94.282(2), 90</td>
</tr>
<tr>
<td>(E_{S1}) (eV)</td>
<td>2.41(^1)</td>
</tr>
</tbody>
</table>

\(^1\) Energy of \(S_1\) exciton determined by optical absorption of thin films in transmission mode.

\(^2\) Energy of \(S_1\) exciton determined by optical reflectance spectroscopy on finely powdered crystals.

Structures solved with direct methods using SHELXL and refined with least squares minimization using the SHELXS refinement package. Additional crystallographic detail provided in supporting information.
Figure 3.2: UV-Vis absorption spectra for layered perovskite films with the $S_1$ exciton peak labeled for perovskite phases (a) (naphthalene-O-ethyl-NH$_3$)$_2$PbI$_4$, (b) (naphthalene-O-propyl-NH$_3$)$_2$PbI$_4$, (c) (pyrene-O-ethyl-NH$_3$)$_2$PbI$_4$, (d) (pyrene-O-propyl-NH$_3$)$_2$PbI$_4$, (e) (pyrene-O-butyl-NH$_3$)$_2$PbI$_4$, (f) (perylene-O-ethyl-NH$_3$)$_2$PbI$_4$.

the inorganic lattice (Figure 3.5). Recently, low octahedral distortion has been observed in an $n = 1$ layered perovskite containing tertiary ammonium groups. In this structure, substitution on the ammonium group may increase the distance between the cationic nitrogen and the negatively charged inorganic lattice. In our materials, we have observed that $E_{S1}$ values increase linearly with decreasing average cationic nitrogen to peripheral-iodide distance ($d_{N-I}$) (Figure 3.6a). As $d_{N-I}$ decreases, the electrostatic interaction between the cationic nitrogen and negatively-charged inorganic lattice increases, resulting in octahedral distortion and a higher $E_{S1}$. The structural features of the organic cation must dictate $d_{N-I}$ and thus influence the resulting electrostatic interaction. Understanding and harnessing the
Figure 3.3: Annotated UV-Vis absorption spectra showing the two distinct characteristics of \( n = 1 \) lead iodide layered perovskite absorption spectra. A sharp excitonic absorption (red) is followed by a low cross section region of the spectrum followed by the bandgap absorption onset (blue). Precise determination of the bandgap is challenging from room temperature optical absorption so we track the \( S_1 \) exciton instead.

structural properties of the organic cation to influence \( E_{S1} \) and the bandgap of the layered perovskite will be crucial to the further development of these materials.

Figure 3.4: Octahedral distortion affects the bandgap (and \( S_1 \) exciton transition) in these materials. (a) as the Pb-I-Pb bond angles along the central plane decrease from the maximum 180° as a result of octahedral tilting, the bandgap in these materials is raised. (b) We observe the expected correlation between octahedral tilting and bandgap (measured by \( S_1 \) exciton energy) in the seven layered perovskites in this work.
Figure 3.5: The energy of the $S_1$ exciton is plotted against the penetration distance of the nitrogen of the ammonium cation into the mean plane formed by the peripheral iodine of the octahedra.

As mentioned previously, the $E_{S1}$ values observed for the seven layered perovskites investigated here span 0.3 eV, a significant range for $n = 1$ layered perovskites. In most of these layered perovskites, the alkyl linker to the ammonium cation adopts an extended conformation within the organic galleries. However, this does not occur in (pyrene-O-propyl-NH$_3$)$_2$PbI$_4$ where we observe an intramolecular hydrogen bond between the ammonium cation and the ether linkage (Figure 3.6b). This intramolecular hydrogen bond hinders the extended conformation of the alkyl linker resulting in just a 0.22 Å increase in the inorganic-to-inorganic layer spacing from (pyrene-O-ethyl-NH$_3$)$_2$PbI$_4$ to (pyrene-O-propyl-NH$_3$)$_2$PbI$_4$. This is compared to a 1.77 Å spacing increase from (pyrene-O-propyl-NH$_3$)$_2$PbI$_4$ to (pyrene-O-butyl-NH$_3$)$_2$PbI$_4$. The intramolecular hydrogen bond observed in (pyrene-O-propyl-NH$_3$)$_2$PbI$_4$ also appears to affect the $d_{N-I}$, resulting in the longest observed $d_{N-I}$ and correspondingly the lowest $E_{S1}$ of 2.27 eV. Interestingly, when crystallized as a thin film, the same pyrene-O-propyl-NH$_3$I molecule that creates (pyrene-O-propyl-NH$_3$)$_2$PbI$_4$ can form a different perovskite phase with a higher $E_{S1}$ of 2.53 eV (Figure 3.7). This high $E_{S1}$ phase has a larger inorganic-to-inorganic layer spacing than (pyrene-O-propyl-NH$_3$)$_2$PbI$_4$, suggesting
Figure 3.6: (a) Energy of the $S_1$ exciton vs. average distance between the nitrogen cation and the peripheral iodides of the inorganic layers ($d_{N-I}$) (left); (naphthalene-O-propyl-NH$_3$)$_2$PbI$_4$ structure showing with dashed lines the four different N-I distances used to calculate $d_{N-I}$ (right). Crystal structures showing intramolecular hydrogen bonding (if present) for (b) (pyrene-O-propyl-NH$_3$)$_2$PbI$_4$, (c) (naphthalene-O-propyl-NH$_3$)$_2$PbI$_4$·(C$_4$H$_8$O$_2$)$_{0.5}$, and (d) (naphthalene-O-propyl-NH$_3$)$_2$PbI$_4$. Intramolecular hydrogen bonding in the crystal structure acts to increase $d_{N-I}$ and reduce $E_{S1}$.

that the alkyl linker in this phase adopts a more extended conformation. This conformation may decrease the $d_{N-I}$ and thus raise $E_{S1}$ compared to (pyrene-O-propyl-NH$_3$)$_2$PbI$_4$ which contains an intramolecular hydrogen bond.
Figure 3.7: Two crystal phases can form during spin coating of thin films with the pyrene-O-propyl-NH$_3$I molecule. The first (pyrene-O-propyl-NH$_3$)$_2$PbI$_4$ (red line) has been crystallized and the structure is reported in this work but there is another high bandgap phase (blue line) which appears in thin film. (a) PXRD of two thin film phases showing a larger d-spacing in the unknown phase and (b) UV-Vis absorption of the two thin film materials.

As noted previously, the naphthalene-O-propyl-NH$_3$I molecule can form both (naphthalene-O-propyl-NH$_3$)$_2$PbI$_4$ and (naphthalene-O-propyl-NH$_3$)$_2$PbI$_4$(C$_4$H$_6$O$_2$)$_{0.5}$. These perovskites demonstrate a similar structural trend to the two layered perovskites formed by the pyrene-O-propyl-NH$_3$I molecule. The propyl linker in (naphthalene-O-propyl-NH$_3$)$_2$PbI$_4$ adopts an extended conformation and the material exhibits a high $E_{S1}$ of 2.57 eV (Figure 3.6c). The second layered perovskite, (naphthalene-O-propyl-NH$_3$)$_2$PbI$_4$(C$_4$H$_6$O$_2$)$_{0.5}$, has a lower $E_{S1}$ of 2.35 eV, and in two of the four molecules within
the asymmetric unit of the crystal structure the propyl linker is disordered between two conformations. In one, it adopts an extended conformation, but in the other it exhibits the same type of intramolecular hydrogen bond observed in \((\text{pyrene-O-propyl-NH}_3)_2\text{PbI}_4\) (Figure 3.6d). In both \((\text{naphthalene-O-propyl-NH}_3)_2\text{PbI}_4\cdot(\text{C}_4\text{H}_6\text{O}_2)_{0.5}\) and \((\text{pyrene-O-propyl-NH}_3)_2\text{PbI}_4\), the propyl linker can form a six-membered intramolecular ring when the ammonium cation hydrogen bonds to the aromatic ether. When this intramolecular hydrogen bonding occurs, it reduces the optical bandgap by increasing \(d_{\text{N-I}}\) within the structure. These results demonstrate the structural role that the organic cation can play in dictating the optical properties of the resultant perovskite and suggest new strategies to tune the optoelectronic properties by influencing \(d_{\text{N-I}}\) through intramolecular bonding and steric control.

3.3.3 Out-of-Plane Conductivity

To investigate how the electronic character of the organic cation affects out-of-plane conductivity, we measured the relative out-of-plane conductivity along the layered axis of single crystals for all of the layered perovskites reported in this work (except \((\text{naphthalene-O-propyl-NH}_3)_2\text{PbI}_4\cdot(\text{C}_4\text{H}_6\text{O}_2)_{0.5}\) due to the small sizes of crystals) as well as three aliphatic control crystals \((\text{butyl-NH}_3)_2\text{PbI}_4\), \((\text{hexyl-NH}_3)_2\text{PbI}_4\), and \((\text{octyl-NH}_3)_2\text{PbI}_4\). These measurements were carried out using the devices described in Figure 3.8a, which used single crystals in order eliminate the effects of grain boundaries on conductivity. These measurements were performed on multiple devices per crystal as well as multiple crystals of the same layered perovskite (Table 3.2). The conductivity results show that the median conductivity spans close to four orders of magnitude, and the results are summarized in Figure 3.8b (under illumination) and Figure 3.9 in the dark (see Table 3.3 for numerical data). Generally, layered perovskites containing aliphatic cations were found to have the lowest conductivity, followed closely by the naphthalene-containing layered perovskites. Layered perovskites with
pyrene and perylene cations were found to have substantially higher conductivity than those containing aliphatic moieties. This trend in conductivity mirrors the better alignment of energy levels between perylene and pyrene and the inorganic lattice (Figure 3.1c). This result indicates that the electronic character of the aromatic moieties within the organic galleries can be utilized to enhance out-of-plane conductivity in these materials.

Table 3.2: Summary of conductivity experiments including the number of crystals measured per layered perovskite and the total number of devices measured across all the crystals per layered perovskite. Also included are the minimum and maximum crystal thicknesses for each layered perovskite.

<table>
<thead>
<tr>
<th>Perovskite Sample</th>
<th>Number of crystals measured</th>
<th>Total number of devices</th>
<th>Min. crystal thickness (µm)</th>
<th>Max. crystal thickness (µm)</th>
</tr>
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<tbody>
<tr>
<td>(naphthalene-O-ethyl-NH₃)₂PbI₄</td>
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<td>104.48</td>
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<tr>
<td>(naphthalene-O-propyl-NH₃)₂PbI₄</td>
<td>11</td>
<td>16</td>
<td>5.24</td>
<td>29.53</td>
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<tr>
<td>(pyrene-O-ethyl-NH₃)₂PbI₄</td>
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<td>9</td>
<td>2.12</td>
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<tr>
<td>(pyrene-O-propyl-NH₃)₂PbI₄</td>
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<td>10</td>
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<tr>
<td>(pyrene-O-butyl-NH₃)₂PbI₄</td>
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</tbody>
</table>

Table 3.3: Numerical out-of-plane conductivity values reported for both under illumination and in the dark measurements (names abbreviated for clarity).

<table>
<thead>
<tr>
<th>Perovskite Sample</th>
<th>Under Illumination Conductivity (S/m)</th>
<th>In Dark Conductivity (S/m)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Pyrene-Ethyl (7)</td>
<td>Pyrene-Ethyl (4)</td>
</tr>
<tr>
<td>Min</td>
<td>5.4E-05</td>
<td>2.3E-05</td>
</tr>
<tr>
<td>Q1</td>
<td>7.24E-05</td>
<td>2.64E-05</td>
</tr>
<tr>
<td>Median</td>
<td>2.22E-04</td>
<td>4.04E-05</td>
</tr>
<tr>
<td>Q3</td>
<td>2.71E-04</td>
<td>4.98E-05</td>
</tr>
<tr>
<td>Max</td>
<td>6.00E-04</td>
<td>5.24E-05</td>
</tr>
</tbody>
</table>

In the design of these molecules we included a variable linker length to study the effect of spacing between aromatic moieties and inorganic layers on out-of-plane conductivity. When
Figure 3.8: (a) Schematic representation of the layered perovskite indicating the direction of conductivity measurements (left), and schematic of the device used to measure the out-of-plane conductivity with a colorized SEM of a single crystal drop-cast on a silicon wafer cleaved to reveal the cross section (right) (note the crystal is flat over its width (0.5 mm) and makes intimate contact with the substrate). (b) Conductivity of nine different $n = 1$ layered perovskites with either an aliphatic cation or cation containing naphthalene, pyrene, or perylene. Higher conductivity is observed for the pyrene and perylene samples which possess better energy level alignment with the inorganic lattice. FTO refers to fluorine-doped tin oxide.
Figure 3.9: Out-of-plane conductivity measured in the dark. Enhanced conductivity is observed in samples with better energy level matching of the aromatic moiety to the inorganic layer.

Comparing the three aliphatic controls and (naphthalene-O-propyl-NH₃)₂PbI₄ we found that their conductivities are on the same order of magnitude with a slight trend towards lower out-of-plane conductivity with increasing inorganic-to-inorganic layer spacings (Figure 3.10). Interestingly, a different trend was observed for layered perovskites containing pyrene. In this subset of layered perovskites, (pyrene-O-ethyl-NH₃)₂PbI₄ and (pyrene-O-butyl-NH₃)₂PbI₄ have effectively the same high conductivity of 4 x 10⁻⁵ S/m, while the conductivity of (pyrene-O-propyl-NH₃)₂PbI₄ is 2 x 10⁻⁶ S/m which is considerably lower. This indicates that there is an additional structural aspect that is more significant than just the spacing between
the inorganic layer and the aromatic core. Examination of crystal structures for the three pyrene-containing layered perovskites indicates that in the higher conductivity (pyrene-O-ethyl-NH$_3$)$_2$PbI$_4$ and (pyrene-O-butyl-NH$_3$)$_2$PbI$_4$ the organic cations exhibit edge-to-face type $\pi$-stacking interactions when viewed down the layered axis across the van der Waals gap (Figures 3.11a and b). However, for the lower conductivity (pyrene-O-propyl-NH$_3$)$_2$PbI$_4$, an edge-to-edge arrangement was observed in the crystal structure (Figure 3.11c).

Figure 3.10: Trend between median out-of-plane conductivity and layered spacing for four layered perovskites measured in this study. From smallest to largest layered spacing these are (butyl-NH$_3$)$_2$PbI$_4$, (hexyl-NH$_3$)$_2$PbI$_4$, (octyl-NH$_3$)$_2$PbI$_4$, and (naphthalene-O-propyl-NH$_3$)$_2$PbI$_4$.

Similar to the pyrene-containing layered perovskites, there is a significant difference in out-of-plane conductivity between the two naphthalene-containing layered perovskites. The lowest conductivity sample of all the layered perovskites measured was (naphthalene-O-propyl-NH$_3$)$_2$PbI$_4$ which has a conductivity of 1 x 10$^{-8}$ S/m, while (naphthalene-O-ethyl-NH$_3$)$_2$PbI$_4$ has a significantly higher conductivity of 3 x 10$^{-7}$ S/m. In the higher conductivity (naphthalene-O-ethyl-NH$_3$)$_2$PbI$_4$ we observe edge-to-face type interactions (Figure 3.11d), whereas in the lower conductivity (naphthalene-O-propyl-NH$_3$)$_2$PbI$_4$ the structure reveals a staggered edge-to-edge stacking. This trend between the type of packing across the van der Waals gap and out-of-plane conductivity is the same as in the pyrene-containing layered
Figure 3.11: Crystal structures of \( n = 1 \) layered perovskites ranked from left to right by highest out-of-plane conductivity to lowest where the structures in panels a and b have similar conductivity values: (a) (pyrene-O-ethyl-NH\(_3\))\(_2\)PbI\(_4\), (b) (pyrene-O-butyl-NH\(_3\))\(_2\)PbI\(_4\), (c) (pyrene-O-propyl-NH\(_3\))\(_2\)PbI\(_4\), (d) (naphthalene-O-ethyl-NH\(_3\))\(_2\)PbI\(_4\), and (e) (naphthalene-O-propyl-NH\(_3\))\(_2\)PbI\(_4\). The stacking of aromatic cores is highlighted with dashed lines within the organic galleries and the square inserts show a view down the layered axis from the perspective of an eclipsed aromatic core (viewing direction is denoted by the black arrow in the crystal structures).

perovskites. Lastly, (perylen-O-ethyl-NH\(_3\))\(_2\)PbI\(_4\) shows edge-to-edge type interactions (see Figure 3.12) although it has the highest recorded out-of-plane conductivity of all the layered perovskites studied here. We attribute this to a better energy level alignment with the inorganic lattice compared to materials containing the pyrene, naphthalene, or aliphatic cations.

The results described above suggest that in addition to the electronic character of the aromatic moiety, their structural arrangement within the organic galleries plays a role in the observed out-of-plane conductivity. Specifically, edge-to-face interactions across the van der Waals gap yield enhanced conductivity compared to edge-to-edge interactions. This is likely
Figure 3.12: Crystal structure of (perylene-O-ethyl-NH$_3$)$_2$PbI$_4$ showing edge-to-edge type stacking across the van der Waals gap. This compound had the highest reported conductivity, likely due to better matched HOMO/LUMO levels rather than ideal $\pi$ stacking geometry. Due to better orbital overlap of the aromatic moieties and thus more efficient out-of-plane charge transport. This observation implies that future efforts to improve conductivity need to focus on controlling the spatial arrangements of electronically active cations within the perovskite crystal. Finding strategies to further enhance orbital overlap, possibly through face-to-face interactions, may further improve out-of-plane conductivity.

3.3.4 Device Fabrication and Photovoltaic Performance

Given that poor out-of-plane conductivity is the chief limitation to the application of $n = 1$ layered perovskites in photovoltaic devices, the higher-conductivity layered perovskites in this work should exhibit enhanced photovoltaic device performance. Photovoltaic performance is of course also affected by optical absorption, crystallinity, and morphology of the active layer. Thus, we chose to focus on (pyrene-O-propyl-NH$_3$)$_2$PbI$_4$ for photovoltaic devices since it has the lowest energy $S_1$ exciton and therefore its absorption better matches the solar spectrum. Although this layered perovskite did not have the highest conductivity,
it offered the best balance of properties for photovoltaic performance. As noted previously, thin films of (pyrene-O-propyl-NH$_3$)$_2$PbI$_4$ can crystallize into two different phases, and thus we selected annealing conditions (140°C for 1 minute) that resulted in exclusive formation of (pyrene-O-propyl-NH$_3$)$_2$PbI$_4$ rather than the higher E$_{S1}$ phase.

Our best reproducible device architecture (Figure 3.13a) using (pyrene-O-propyl-NH$_3$)$_2$PbI$_4$ achieved a power conversion efficiency (PCE) of 1.16 ± 0.08% with a champion device performance of 1.24% (Figure 3.13b). These devices had a $V_{oc}$ of 1.07 V, $J_{sc}$ of 2.48 mA/cm$^2$, and fill factor of 0.44 across 4 devices. To our knowledge, this is the highest reported PCE for an n = 1 layered perovskite solar cell. This result is noteworthy given that grazing-incidence wide-angle X-ray scattering (GIWAXS) of our thin films shows a clear preferential orientation of the inorganic layers parallel to the substrate (Figure 3.13c), while the previously-reported highest-efficiency n = 1 device had inorganic layers oriented perpendicular to the substrate.$^{196}$ Furthermore, our device is an order of magnitude higher efficiency than any other reported n=1 layered perovskite with the inorganic layers oriented parallel to the substrate. With respect to charge transport layers, a low work function PEDOT:PSS formulation was used for better energy level alignment with the active layer, and no electron transport layer was added because the pyrene-O-propyl-NH$_3$I molecule forms a native electron-transporting capping layer on the top surface of the active layer.

The PCE of our devices using (pyrene-O-propyl-NH$_3$)$_2$PbI$_4$ is at least an order of magnitude higher than control devices with (butyl-NH$_3$)$_2$PbI$_4$ as the active layer using the same device architecture (Table 3.4). The (butyl-NH$_3$)$_2$PbI$_4$ device required a charge transport layer to achieve photovoltaic function because butylammonium iodide does not form an electron-transporting capping layer on the surface of the active layer, unlike (pyrene-O-propyl-NH$_3$)$_2$PbI$_4$. Thus, to compare the two layered perovskites, we added a thin layer of 1-propoxypyrene on both (pyrene-O-propyl-NH$_3$)$_2$PbI$_4$ and (butyl-NH$_3$)$_2$PbI$_4$ active layers to mimic the native electron transport layer on the (pyrene-O-propyl-NH$_3$)$_2$PbI$_4$ active
Figure 3.13: (a) Energy levels of the layers in the (pyrene-O-propyl-NH$_3$)$_2$PbI$_4$ layered perovskite solar cell. (b) I-V curve for the champion device with 1.24% efficiency (only forward sweep is shown for clarity but the average includes forward and reverse curves where little hysteresis was observed). (c) GIWAXS of (pyrene-O-propyl-NH$_3$)$_2$PbI$_4$ crystallized on a PEDOT:PSS-coated substrate. (d) AFM height and phase images for (pyrene-O-propyl-NH$_3$)$_2$PbI$_4$ crystallized on PEDOT:PSS. (e) Photograph showing the difference in appearance of three substrates dipped in water: the 3D perovskite with the formula (CH$_3$NH$_3$)$_2$PbI$_3$ and the n = 4 layered perovskite with the formula (butyl-NH$_3$)$_2$(CH$_3$NH$_3$)$_3$Pb$_4$I$_{13}$ turn yellow instantly revealing chemical degradation whereas the n = 1 layered perovskite (pyrene-O-propyl-NH$_3$)$_2$PbI$_4$ retains its original color.

layer. These control devices demonstrate that 1-propoxypyrene functions as an electron transport for layered perovskite active layers, and that in this device architecture (pyrene-O-propyl-NH$_3$)$_2$PbI$_4$ performs significantly better than (butyl-NH$_3$)$_2$PbI$_4$ as a photovoltaic active layer.

As previously discussed, GIWAXS was utilized to compare the orientation of the crystalline domains in these thin films. In both (pyrene-O-propyl-NH$_3$)$_2$PbI$_4$ and the (butyl-
Table 3.4: Photovoltaic parameters comparing the (pyrene-O-propyl-NH$_3$)$_2$PbI$_4$ to the control (butyl-NH$_3$)$_2$PbI$_4$ perovskite with 1-propoxypyrene and PCBM overlayers.

<table>
<thead>
<tr>
<th>Perovskite Sample</th>
<th>Overlayer</th>
<th>$J_{sc}$ (mA/cm$^2$)</th>
<th>$V_{oc}$ (V)</th>
<th>Fill Factor</th>
<th>Efficiency (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(pyrene-O-propyl-NH$_3$)$_2$PbI$_4$</td>
<td>native capping layer</td>
<td>1.58</td>
<td>1.12</td>
<td>0.40</td>
<td>0.70</td>
</tr>
<tr>
<td>(pyrene-O-propyl-NH$_3$)$_2$PbI$_4$</td>
<td>1-propoxypyrene</td>
<td>1.32</td>
<td>1.04</td>
<td>0.34</td>
<td>0.46</td>
</tr>
<tr>
<td>(pyrene-O-propyl-NH$_3$)$_2$PbI$_4$</td>
<td>PCBM</td>
<td>1.31</td>
<td>0.88</td>
<td>0.35</td>
<td>0.40</td>
</tr>
<tr>
<td>(butyl-NH$_3$)$_2$PbI$_4$</td>
<td>1-propoxypyrene</td>
<td>0.15</td>
<td>0.39</td>
<td>0.50</td>
<td>0.30</td>
</tr>
<tr>
<td>(butyl-NH$_3$)$_2$PbI$_4$</td>
<td>PCBM</td>
<td>0.05</td>
<td>0.26</td>
<td>0.30</td>
<td>0.004</td>
</tr>
</tbody>
</table>

NH$_3$)$_2$PbI$_4$ (Figure 3.14), the films were found to be crystalline and oriented with the 2D layers parallel to the substrate. We analyzed the orientation of the thin films using Herman’s orientation factor, $S$.\textsuperscript{211} An $S$ value of 1 indicates perfect parallel orientation of domains, $S = 0$ indicates isotropic domains, and $S = -0.5$ indicates perfect perpendicular orientation of domains. By analyzing data along the azimuthal angle $\chi$ from 0 to 90° within the $q$ range of the (600) peak of (pyrene-O-propyl-NH$_3$)$_2$PbI$_4$ we found that $S = 0.95$, and within the $q$ range of the (002) peak of (butyl-NH$_3$)$_2$PbI$_4$ we found that $S = 0.97$. This indicates strong alignment of the layered axis parallel to the substrate for both thin films (see Methods Section 3.5 for details). When analyzed by atomic force microscopy, thin films of (pyrene-O-propyl-NH$_3$)$_2$PbI$_4$ exhibit significant roughness and small grain sizes (Figure 3.13d). This is potentially caused by the low diffusivity of the bulky organic cation during the annealing process. The small grain size observed with this technique may explain some of the azimuthal peak broadening observed in GIWAXS.

Importantly, the active layer in these devices is chemically-stable. Although the complete devices suffer from limited stability in atmospheric conditions due to reactions between the active layer and the cathode material, the active layer itself is exceptionally stable; it can withstand immersion in water for several minutes without any decomposition to lead (II) iodide (Figure 3.15). This property is unique when compared to the prototypical 3D perovskite (CH$_3$NH$_3$)PbI$_3$ and the $n = 4$ layered perovskite (butyl-NH$_3$)$_2$(CH$_3$NH$_3$)$_3$Pb$_4$I$_{13}$ (Figure 3.13e and 3.16).
Figure 3.14: 2D-GIWAXS images of (a) (pyrene-O-propyl-NH$_3$)$_2$PbI$_4$ and (b) (butyl-NH$_3$)$_2$PbI$_4$ layered perovskites. (c) and (d) show the line cut mask and line cut area for the (pyrene-O-propyl-NH$_3$)$_2$PbI$_4$ data from $0 < \chi < 90$ and $0.75 < q < 0.9$, and (e) shows the integrated line cut from this area of the image. (f) shows a similar line cut from the (002) peak of the (butyl-NH$_3$)$_2$PbI$_4$ perovskite.

3.4 Conclusion

The out-of-plane conductivity in chemically stable $n = 1$ layered perovskites has been increased by several orders of magnitude using aromatic cations in the organic layers to better
Figure 3.15: (a) X-ray characterization of thin films of \((\text{pyrene-O-propyl-NH}_3)_2\text{PbI}_4\) before DI water immersion and after 30 s and 5 min of water immersion, along with (b) corresponding photographs. Note that there is no appearance of the lead (II) iodide in the X-ray signature. Slight reduction in intensity is due to slow dissolution of film into water.

Figure 3.16: Comparison of dipping the 3D methylammonium lead triiodide (left), \(n = 4\) layered perovskite \((\text{Butyl-NH}_3)_2\text{Pb}_4\text{I}_{13}(\text{CH}_3\text{NH}_3)_3\) (center) and \(n = 1\) \((\text{pyrene-O-propyl-NH}_3)_2\text{PbI}_4\) (right). Perovskites containing the methylammonium cation are degraded as soon as immersed (center frame was taken immediately after immersion). The \(n = 1\) compound remains intact even after several minutes.

match their energy levels with those of inorganic layers. When used in photovoltaic devices these layered perovskites yielded the highest reported power conversion efficiency (1.24%) for a \(n = 1\) layered perovskite. We showed that both intramolecular hydrogen bonding and supramolecular \(\pi\)-stacking interactions between in the organic cations can result in narrower bandgaps and greater out-of-plane conductivity. Our results suggest that there is great
potential for functional improvement in chemically stable layered perovskites by focusing on design of the molecular and supramolecular structure of the organic layers.

3.5 Materials and Methods

Material characterization

NMR spectra ($^1$H and $^{13}$C) where collected on a 400 MHz Agilent DD MR-400 system. Deuterated solvents (dimethyl sulfoxide and chloroform) were purchased from Sigma Aldrich and all chemical shifts are reported from spectra internally referenced to the solvent residual. Peaks reported in $^{13}$C spectra are those achieving 3 I/s or greater and are clearly resolved from residual solvent or in peak-peak overlap.

High-resolution mass spectrometry was acquired using an Agilent 6210 LC-TOF high-resolution time of flight mass spectrometer with an Agilent 1200 series LC pump stack and Autosampler. Electrospray ionization was used in all cases.

Ultraviolet Photoelectron Spectroscopy (UPS) data was used to determine the HOMO level of the perovskite crystals and the organic molecules alone. UPS data was collected using a Thermo Scientific ESCALAB 250Xi with a -8.0 V sample bias and a He I ($h\nu = 21.2$ eV) source. The spectrum width of UPS data is related to the work function, $\phi$, according to the equation $\phi = h\nu - BE$. The edges of the spectrum were fit in order to determine the binding energy. In the inelastic cutoff region, the intercept between the tangent to the main peak and a linear fit to the background level was used as the edge of the spectrum. At the Fermi edge, the onset of the peak was determined as energy at which the intersection between the local tangent to the spectrum and a linear fit to the background level occurs. The difference in energy between the Fermi edge and the inelastic cutoff region was then subtracted from the incident energy (21.2 eV) in order to determine the HOMO level of the material.
Single crystal preparation for structure evaluation and conductivity measurements

All single crystal samples were prepared using vapor diffusion of dichloromethane into γ-butyrolactone (GBL) solutions containing 2:1 molar ratio of organic ammonium iodide salt: lead (II) iodide. The concentration of GBL solution was critical to obtain high quality samples for both single crystal X-ray diffraction and for electrical measurements (Table 3.5). In all cases, plate-like crystals which ranged in color from yellow to red appeared in ca. 24 hrs. These plate-like crystals form due to preferential crystal growth along the 2D inorganic galleries. To measure conductivity along the layered axis of these plate-like crystals, they were separated from their mother liquor and washed before being drop-cast on a freshly cleaned unpatterned FTO substrates (Solaronix, 15 Ω/square).

Table 3.5: Crystallization conditions: Crystals were prepared by adding 200 µl of the following GBL solutions to individual 4 mL glass vials. These glass vials were then placed in a larger outer container containing dichloromethane. The initial concentration of the precursor solution was important to achieve large and good quality crystals.

<table>
<thead>
<tr>
<th>Perovskite Crystal</th>
<th>Solvent</th>
<th>Anti-solvent</th>
<th>Starting solution concentration (wt%)</th>
<th>Time crystals appeared (hrs)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(naphthalene-O-ethyl-NH$_3$)$_2$PbI$_4$</td>
<td>GBL</td>
<td>DCM</td>
<td>35</td>
<td>24</td>
</tr>
<tr>
<td>(naphthalene-O-propyl-NH$_3$)$_2$PbI$_4$</td>
<td>GBL</td>
<td>DCM</td>
<td>5-10</td>
<td>24</td>
</tr>
<tr>
<td>(naphthalene-O-propyl-NH$_3$)$_2$PbI$_4$(C$_4$H$_6$O$<em>2$)$</em>{0.5}$</td>
<td>GBL</td>
<td>DCM</td>
<td>40</td>
<td>1</td>
</tr>
<tr>
<td>(pyrene-O-ethyl-NH$_3$)$_2$PbI$_4$</td>
<td>GBL</td>
<td>DCM</td>
<td>1</td>
<td>36</td>
</tr>
<tr>
<td>(pyrene-O-propyl-NH$_3$)$_2$PbI$_4$</td>
<td>GBL</td>
<td>DCM</td>
<td>0.5-1</td>
<td>48</td>
</tr>
<tr>
<td>(pyrene-O-butyl-NH$_3$)$_2$PbI$_4$</td>
<td>GBL</td>
<td>DCM</td>
<td>10</td>
<td>12</td>
</tr>
<tr>
<td>(perylene-O-ethyl-NH$_3$)$_2$PbI$_4$</td>
<td>GBL</td>
<td>DCM</td>
<td>0.25-1</td>
<td>24</td>
</tr>
<tr>
<td>(butyl-NH$_3$)$_2$PbI$_4$</td>
<td>GBL</td>
<td>DCM</td>
<td>60</td>
<td>4</td>
</tr>
<tr>
<td>(hexyl-NH$_3$)$_2$PbI$_4$</td>
<td>GBL</td>
<td>DCM</td>
<td>60</td>
<td>4</td>
</tr>
<tr>
<td>(octyl-NH$_3$)$_2$PbI$_4$</td>
<td>GBL</td>
<td>DCM</td>
<td>35</td>
<td>48</td>
</tr>
</tbody>
</table>

The following procedures were followed to prepare devices for conductivity measurements. These procedures were utilized to ensure minimal disturbance to the crystals and particularly the crystal faces and to ensure good electrical contact with the FTO substrate. First, six 4 mL glass vials were prepared with the following solvents. To vials 1 and 2, 800 µL of chlorobenzene (CB) and 200 µL of GBL were added and mixed. To vial 3, 1800 µL of CB and 200 µL of GBL were added. To Vial 4, 1950 µL CB and 50 µL GBL added and to
Vials 5 and 6 2000 µL of CB was added. This gradient to less and less GBL prevented the precipitation of precursor solution without causing noticeable degradation of the crystals. To wash the crystals, a 1000 µL micropipette tip was used. First, the tip of the pipet tip was cut off to create a larger opening of ca. 5 mm. The pipet was set at 500 µL volume. The piped tip was first placed into the crystallization solution and 500 µL of solvent and crystals extracted. The pipet was then held vertically for ca. 20 s until the dense crystals had settled to the bottom. The tip of the pipet was then placed just under the surface of the first wash vial and the crystals allowed to fall from the pipet solution into the wash vial with minimal transfer of the crystallization solution. This transfer process was repeated from vial to vial to progressively clean the crystals. In rare cases, precipitate was visible after a transfer step. This usually resulted from too much of the previous solution being transferred with the crystals. If this was observed, then that sample was discarded over fear that this would lead to defects on the crystal surface that would affect the conductivity measurement. Once the crystals were transferred to the final wash solution, they were put onto a substrate within 2 hrs. Right before device preparation, 5 µL of GBL was added to this solution. This small amount of GBL helps the crystals adhere and recrystallize at the interface of the substrate affording good adhesion and more reproducible conductivity measurements. After this GBL was added, a pipet was prepared in the same way as previously described and the crystals were transferred to un-patterned FTO by briefly touching the tip of the pipette to the FTO and dragging the meniscus around the surface. The crystals were then allowed to dry for 10 min. After drying, good quality and large crystals were selected by polarized optical microscopy.

Small square gold pads of 113 µm x 113 µm x 50 nm were then thermally evaporated on top of the crystals through a TEM shadow mask (Electron Microscopy Sciences T200-Cu) and conductivity was measured on the single crystal samples in a 2-electrode geometry (Signatone probe station, Agilent 4155C semiconductor parameter analyzer). The conductivity was
then measured through the thickness of the crystals and normalized by pad area and crystal thickness. Out-of-plane conductivity was measured both with the microscope lamp turned to full power (MLC-150C illuminator - 150W EKE halogen lamp) and in the absence of any light. The conductivity was calculated using the linear region of the I-V curve (voltage sweep from -5 to 5 V) and parameterized based on individual device thicknesses. The thickness of each device was determined by optical profilometry (Zygo 3D Optical Profiler and Bruker Contour GT-K). The averages of multiple devices per crystal and across several crystals was taken to determine the out-of-plane conductivity of a given structure (Table 3.2).

Crystal structure determination

Single crystal X-ray data were collected at room temperature on a Kappa Apex 3 diffractometer. For control crystals with previously-reported structures, partial data sets were collected for unit cell determination (between 60 and 90 frames) to validate against the previously reported structures. For all other crystals, a complete data set was collected for structure solution and refinement. In all cases the face-indexing tool in Apex 3 was utilized to verify the direction of the layered axis for electrical measurements (Figure 3.17). Using Olex2, crystal structures were solved using ShelXS structure solution program using direct methods and refined using ShelXL refinement package using least squares minimizations. The inorganic lattice was refined anisotropically without restraints. The organic cations were refined anisotropically with the exception of hydrogen atoms which were placed in idealized positions. Additional restraints to the bond lengths and thermal ellipsoids for the organic cations were applied where necessary. Structural information for seven layered perovskites in this work is provided in Table 3.1.
Figure 3.17: Unit cell parameters as determined by APEX 3 using either Difference Vectors or Fast Fourier Transform and Face Indexing Tool in APEX 3 showing that the layered axis is perpendicular to the plate.

Substrate preparation

Glass and patterned ITO substrates (Thin Film Devices, 20 Ω/square) were cleaned by sequential sonication in hexane, soapy water, milli-q water, and a 1:1:1 mixture of
isopropanol, acetone, and methanol. After drying, clean substrates were treated for 20 minutes in a UV-ozone cleaner (Bioforce Nanosciences). Poly(3,4-ethylenedioxythiophene) polystyrene sulfonate in toluene (PEDOT:complex) (Ossila) was filtered through a 0.2 µm PTFE filter before spin-coating at 5000 RPM with a 5000 RPM/second ramp rate for 30 seconds. PEDOT:complex (Ossila) films were then annealed at 120°C for 10 minutes in a nitrogen-filled glovebox. Poly(3,4-ethylenedioxythiophene) polystyrene sulfonate in water (PEDOT:PSS) (Heraeus) was filtered through a 0.45 µm nylon filter before spin-coating at 5000 RPM with a 1000 RPM/second ramp rate for 60 seconds. PEDOT:PSS (Heraeus) films were then annealed at 150°C for 20 minutes in a nitrogen-filled glovebox.

Perovskite thin film preparation

Thin film samples other than those intended for device active layers were prepared by spin-casting 2:1 molar ratios of organic ammonium iodide salt: lead (II) iodide (TCI Chemical) dissolved in 20-30 wt% in 50 vol% DMF 50 vol% DMSO onto freshly cleaned glass slides at 2000 RPM. With respect to solubility, we found that a combination of DMF and DMSO as a solvent mixture was very helpful in dissolving the poorly soluble bulky organic cations in our layered perovskite materials. From this solvent mixture, we spin-coated and annealed crystalline thin films of each of the layered perovskite materials. Each of the layered perovskites crystallized easily in thin films except for that containing the perylene derivative. These substrates were then annealed on a hotplate at 110°C for 30 min. The resulting thin films were characterized by powder X-ray diffraction (PXRD) (Scintag XDS2000 using Cu Kα radiation at 40 kV and 1-20 mA current), ultraviolet-visible absorption spectroscopy (Perkin Elmer LAMBDA 1050) and by grazing incidence wide angle X-ray scattering (GIWAXS) (Beamline 8-ID-E Advanced Photon Source, Argonne National Laboratory). GIWAXS was performed with beam energy 10.92 keV and with 0.14° incidence angle. From the line cuts we performed Herman’s orientation factor analysis on the (600) peak of (pyrene-O-propyl-
\( \text{NH}_3\text{PbI}_4 \) and the \((002)\) peak of the \((\text{butyl-NH}_3)_2\text{PbI}_4\) perovskite. In this analysis, we define

\[
S = \frac{1}{2}(3f_\perp - 1)
\]

where \(f(\chi)\) is the normalized linecut intensity. We normalize the linecut intensity,

\[
\int_0^{\frac{\pi}{2}} f(\chi) d\chi = 1
\]

and in the case of the \((\text{butyl-NH}_3)_2\text{PbI}_4\) perovskite we perform a flat background subtraction due to higher background intensity in that data.

**Device fabrication**

We designed the layers of our photovoltaic devices as shown in Figure 3.13a. The devices in this study were fabricated in a nitrogen-filled glovebox. Pyrene-O-propyl-NH\(_3\)I and lead iodide were dissolved at a 2:1 molar ratio in a 25 wt% solvent mixture of 50 vol% DMF 50 vol% DMSO and heated for 30 minutes at 65°C. For optimized \((\text{pyrene-O-propyl-NH}_3)_2\text{PbI}_4\) devices, the active layer was spin cast onto PEDOT:PSS-coated, patterned ITO substrates for 25 seconds at 4000 RPM with a ramp time of 7 seconds. The active layer was then annealed for 1 minute at 140°C. 50 nm silver contacts were thermally evaporated onto the substrates at a pressure of \(< 10^{-6} \text{ mbar}\) using a shadow mask to define 4 mm\(^2\) devices. Finally, devices were tested in air on a Newport solar simulator with a Keithley 2400 sourcemeter with a voltage ramp rate of 0.2 V/s.
CHAPTER 4

Mineralized Nanofibers for Bio-inspired Electronics

4.1 Objectives and Significance

Nanostructured electrodes are of great interest for improving the efficiency and functionality of energy conversion and storage systems. One bottom-up method to achieve nanoscale order of the inorganic materials in these electrodes is by using organic templates programmed with precise structural and chemical information. Taking inspiration from natural biomineralization processes, we report here on the synthesis of metal-coated supramolecular nanofibers for use in flexible transparent conductive electrodes. We demonstrate two routes for metallizing PA nanofibers with gold and highlight the improved performance using direct mineralization on the nanofiber surface compared to conjugation of pre-synthesized nanoparticles. The filamentous supramolecular templates can be spray-coated on flexible plastic substrates to form thin transparent electrodes or can be patterned via extrusion printing into metallized hydrogel filaments. The three-dimensional metallized hydrogels offer the possibility for hierarchical structuring of multiple inorganic species with nanoscale localization.

4.2 Background

The use of biological templates to organize functional inorganic phases at the nanoscale is a promising alternative route for developing new energy materials. Peptide based materials in particular, provide an attractive platform for inorganic functionalization due to the diversity of binding mechanisms and secondary structures that can be accessed by directly
programming the amino acid sequence.\textsuperscript{212,213} High binding affinity peptides have been developed for a wide range of inorganic materials including calcium phosphate, zinc sulfide, and silver nanoparticles, among many others.\textsuperscript{214–217} Further, leveraging interactions that drive protein folding such as $\alpha$-helices and $\beta$-sheets, researchers have demonstrated assembly of supramolecular peptide fibers, tubes and sheets.\textsuperscript{218–221} Combining the specific binding interactions with defined architectures is the basis for hierarchical mineralized tissues in biology.

Recently there has been growing interest in extending the chemistry from biomineral formation to nanostructured materials for energy devices. Synthetic peptide nanofiber templates have been used to mineralize iron phosphate and gold nanoparticles for Li-ion battery electrodes and chiroptical plasmonics, respectively.\textsuperscript{222,223} Belcher and coworkers have demonstrated the genetic engineering of surface peptides presented on M13 bacteriophages for templating of multi-material nanowires in battery and solar cell electrodes.\textsuperscript{44–46} One application that has been less explored is the use of mineralized peptide templates for flexible, transparent conducting electrodes (TCEs). The current state-of-the-art materials for flexible TCEs are silver nanowires (Ag NWs), which have demonstrated excellent conductivity and mechanical durability during bending.\textsuperscript{224,225} However, atmospheric corrosion of Ag leads to large increases in sheet resistance over time.\textsuperscript{226,227} While much work has focused on passivation layers and composite films, an alternative approach is using Au nanowires (Au NWs) as the conductive component that are inert to oxidation in air.\textsuperscript{228} Synthesizing high aspect ratio Au NWs remains a challenge, though, so using peptide nanofiber scaffolds to template Au NW growth is a promising strategy to realize high aspect ratio, air-stable metal nanowires.

Our lab has previously demonstrated the use of PA nanofiber templates for mineralization of biologically relevant minerals like hydroxyapatite and magnetite.\textsuperscript{68,101,103} More recently, we demonstrated the nucleation of Ag nanoparticles with fairly regular spacing along PA nanofibers using aldehyde chemistry.\textsuperscript{104} In this work we use a simple, tri-lysine terminated PA to bind citrate capped Au nanoparticles or to attract Au(OH)$_4^-$ ions in solution and slowly
reduce them to metallic gold. These reactions occur both on nanofiber coated substrates and in 3D hydrogels composed of PA nanofibers. Using 3D printing we can pattern the nanofiber hydrogel templates prior to metallization allowing for electronically conductive, hierarchically structured composite materials.

4.3 Results and Discussion

4.3.1 Metallizing PA Nanofibers with Au

We first synthesized a known PA molecule (K3 PA) with the sequence (palmitoyl)-VVVAAAKKK. We chose this molecule because the valine and alanine residues encode for cylindrical micelles via $\beta$-sheet hydrogen bonding and the lysine residues present a positive surface charge at neutral pH to bind negatively charged species in solution. To drive the assembly of high aspect ratio nanofibers, we dissolved K3 in milli-Q water and annealed solutions at 80°C before slow cooling overnight. We investigated two pathways for Au functionalization, one using attachment of pre-synthesized Au nanocrystals and one using Au salts for direct precipitation on the surface of the nanofibers (Figure 4.1).

For Path 1, we synthesized $\sim 5$ nm Au nanocrystals with citrate ligands forming a negative corona that would electrostatically bind to positively charged K3 fibers. To determine the processing conditions that optimize Au nanocrystal binding, a range of concentrations and incubation times were tested (Figure 4.2). We found that the timing was of little importance; whether the Au was left on for 1 min or 5 min (or in other trials, as little as 30 sec and as much as 10 min) approximately the same binding was observed. The TEM inset shown for Path 1 in Figure 4.1 was allowed to sit with the gold solution for $\sim 2$ min. Concentration, on the other hand, had a dramatic impact on the nanocrystal binding. At low concentration, there is no binding to the fibers, and the nanocrystals prefer to dry with each other rather than attached to the fibers. At middle concentration ($\sim 0.1$ µM) the Au attaches nicely to the fibers with little excess gold left behind after washing, and at higher concentrations the
Figure 4.1: PA nanofiber metallization pathways. Path 1 utilizes independently synthesized Au nanocrystals to bind electrostatically to PA nanofibers. Path 2 uses direct mineralization of Au$^{3+}$ to Au$^{0}$ at the nanofiber surface from lysine reduction. TEM images show K3 PA fibers before and after mineralization for Path 1 and 2.

The same attachment is observed but more Au is left on the grids after washing. It is worth noting that the Au nanocrystals appear to reach a binding limit on the PA fibers, with full coverage of nanocrystals that are close-packed but often not touching one another along the fibers. This is likely caused by the electrostatic repulsion between the negatively charged ligand spheres of the Au nanocrystals.

The second path under study (Path 2) is direct mineralization, where the Au salts are placed in solution with the PA fibers, allowing gold nanostructures to nucleate and grow directly on the PA fibers. In this pathway, the amines on the lysine residues serve as the reducing agent to form Au$^{0}$ from the Au species in solution, while also creating a local supersaturation of Au near the fiber surface for directed precipitation. Since the amine oxidation potential is higher than the reduction potential of Au, the lysine residues donate electrons and initiate the Au$^{0}$ deposition. We note that the pH of the Au salt solution is
Critical for controlling the metallization reaction. By tuning the pH, the dominant Au species in solution can be selected based on the hydrolysis chemistry of H\(\text{AuCl}_4\):

\[
\text{Au(OH)}_n\text{Cl}_{4-n} + \text{OH}^- \leftrightarrow \text{Au(OH)}_{n+1}\text{Cl}_{3-n} + \text{Cl}^- \quad \text{where } n = 0-3
\] (1)

At pH ~10, the dominant hydrolysis product is \(\text{Au(OH)}_4^-\), which has the lowest tendency to be reduced compared to the chlorinated Au complexes.\(^{229,230}\) This is key because it slows the rate of reduction and allows for controlled precipitation of Au on the nanofiber surface. If the reaction proceeds without the initial pH adjustment, we observe homogeneous nucleation of large Au aggregates in solution as well as precipitation on the fibers (Figure 4.3a, b). The pH adjusted Au salt solution is added to a mildly acidic K3 solution (pH 5-6) which ensures

**Figure 4.2:** Au nanocrystal binding to K3 nanofibers as conditions change, with varying concentration along the vertical axis and varying time along the horizontal axis.
the lysine residues are protonated and rapidly bind the negatively charged \( \text{Au(OH)}_4^- \) before a more reactive Au species forms. The TEM inset for Path 2 in Figure 4.1 shows the results of the direct mineralization path after 5 days. It is worth noting that the number of amines does not directly correspond to the amount of reduced Au, suggesting that there is some other method of Au reduction occurring, but our results suggest that the amines initiate and direct the Au reduction to occur on the nanofibers.

In contrast to the Au NC functionalization, there was an extended time dependence for directly metallizing Au salts on PA fiber surfaces. We observed that after 1 day of incubation, small nucleates on the fiber surfaces were visible, that steadily grew to discrete \( \sim 5 \) nm diameter particles by day 3 (Figure 4.3c,d). After 7 days, a conformal coating around the nanofibers was present and by day 14, the coating had grown thicker such that fibers were \( \sim 30 \) nm in diameter (Figure 4.3e,f). The solution of these final thick fibers had a distinct gray hue.

We performed selected area electron diffraction (SAED) and x-ray photoelectron spectroscopy (XPS) on samples metallized for 7 days to characterize the deposited material. In SAED, we observed two broad rings at 4.29 and 8.47 nm\(^{-1}\) corresponding to the (111) and (311) planes of nanocrystalline gold, respectively (Figure 4.4a). From XPS, we measured a peak at 84.1 eV which matches well with Au\(^0\). These results indicate that the deposited species is polycrystalline metallic Au.

### 4.3.2 Transparent Conductive Electrodes from Au-PA Hybrid Materials

To compare the conductivity of the two synthetic pathways, we aerosol spray coated 1 mM K3 solutions onto poly(ethylene terephthalate) (PET) substrates and then soaked the substrates in either Au NC solutions for 5 minutes or \( \text{Au(OH)}_4^- \) solutions for 14 days to achieve the metallized structures outlined above. We measured the sheet resistance of the deposited films with a 4-point probe and compared them to commercial indium tin
Figure 4.3: Time study of Au deposition on K3 fibers. Direct mineralization reaction without H\text{AuCl}_4 pH adjustment after (a) 1 day and (b) 3 days. Direct mineralization reaction with Au(OH)$_4^-$ after (c) 1 day, (d) 3 days, (e) 7 days and (f) 14 days.

oxide (ITO) and Ag NW electrodes. We found that for both Path 1 and Path 2 films the sheet resistance was over 100 M\text{\Omega}/sq, which is around 6 orders of magnitude higher than the commercial products (Figure 4.5a). We did find in 2-probe measurements that there was an increase in conductivity over pure K3 fibers suggesting some conduction through the deposited Au but it is severely limited (Figure 4.5a, inset). In an effort to remove the ligand shells from the Au NCs and potentially sinter the deposited Au particles, we treated the metallized films in an Ar/O$_2$ plasma for 1 to 5 minutes. While this only decreased the sheet resistance to $\sim$85 M\text{\Omega}/sq for the Path 1 films, we measured a drastic decrease to 665\text{\Omega}/sq for the Path 2 films. We found that when connected in series to a blue LED, that sufficient current could pass through the Path 2 films to power the LED, while the Path
Figure 4.4: Structure characterization of directly mineralized Au-K3 fibers after 7 days. (a) SAED sample area (top) and diffraction pattern (bottom) and (b) XPS spectra confirming deposition of nanocrystalline metallic Au.

1 films completely blocked current flow. Upon inspection of the Path 2 films in Scanning Electron Microscopy (SEM), we observed a near monolayer coating of the metallized fibers from the spray coating and mineralization procedure (Figure 4.5b). Further, we measured over 80% transmittance across the visible light spectrum for the Path 2 films, demonstrating their potential use in flexible, transparent conducting electrodes (Figure 4.5c).

To understand why we saw such large differences in the plasma treated films, we collected TEM images before and after the plasma procedure (Figure 4.6). To achieve any measurable conductivity in the Path 1 films, thick coatings had to be prepared (Figure 4.6a). These coatings did show approximately an order of magnitude increase in conductivity after plasma treatment for 5 minutes but images of the treated material showed a globular network of Au rather than the fibrous starting material (Figure 4.6c). In this case, the PA molecules were likely ablated along with the ligand sphere of the nanocrystals. For plasma treatment less than 5 minutes we still observed fibers but the conductivity of the films was lower. For the Path 2 material, we only needed to plasma treat for 2 minutes to measure the large reduction in sheet resistance. From TEM images, the fibers were still present after treatment but
Figure 4.5: Au metallized K3 fibers for transparent conductive electrodes. (a) Sheet resistance from 4-point probe measurements of Au-PA hybrid materials synthesized from Path 1 and 2, and before and after plasma treatment. Values for commercial ITO and Ag NW electrodes are provided for reference. Inset: 2-point probe IV curve of Au nanocrystals on K3 fibers and K3 fibers alone. Pictures are of Au-PA films connected in series to a blue LED with a 3 V potential. (b) SEM image and (c) absorbance of spray coated and directly mineralized Au-PA film.

there was not a noticeable difference in the structure (Figure 4.6b, d). At junctions between the fibers there may be ‘nanowelding’ of the gold coatings (red arrows) which could lead to better percolation of the conductive network. Additionally, x-ray diffraction (XRD) patterns show a notable sharpening of the (111) peak after plasma treatment, suggesting sintering of the deposited Au particles to larger grain sizes, which could also explain the enhanced conductivity values.
4.3.3 Printing PA Hydrogels for Patterned Mineralization

To further demonstrate the utility of the organic template method, we have also pursued routes to orthogonal mineralization so that circuit components could be designed with multiple materials by controllably mineralizing specific species in programmed locations. So far, these efforts have been focused on the nanocrystal (Path 1) routes, primarily due to the much faster mineralization time, but we expect that the same processes will also work for direct mineralization routes (Path 2). For these studies the PAs are deposited through 3D printing of the annealed fibers onto substrates that have been treated with a divalent salt so the PA solution gels upon contact with the substrate. In Figure 4.7, the PA gels were printed into the letter corresponding with their charge: i.e. K3 was printed as a “K” and the corresponding negatively charged PA, (palmitoyl)-VVVAEEEEE (E3), was printed as an “E.” These gels are then submerged in a solution containing the oppositely charged gold nanocrystal, and over the course of hours the nanocrystals are electrostatically attracted to
and bind to the gels, resulting in an increase in color of the gel after 6 hours. The E print is
fainter because the initial concentration of the positively charged nanocrystals is lower than
that of the negatively charged nanocrystals present in the K print (which can be seen from
the 0 hour pictures).

Figure 4.7: Orthogonal mineralization of printed hydrogels. (a) Negative Au nanocrystals
on positively charged K3 PA. (b) Positive Au nanocrystals on negatively charged E3 PA.

We also found that the conductivity of the mineralized printed gels had an increased
conductivity compared to randomly aligned dropcast gels (Figure 4.8). This suggests that
the hierarchical structure of aligned PA fibers within the printed filaments optimize charge
transport in the direction of alignment. This feature could be useful for other bio-inspired
circuits were directed electron transport is desired.

We demonstrated that by changing the nanoparticle ligand shell that we can selectively
attach particles to specific PA gels, but we also extended the direct mineralization concept
to other metals. For this we chose to explore the mineralization of PA fibers with MnO₂, a
semiconducting material relevant for aqueous based energy storage electrodes. To bind and
mineralize the positive Mn²⁺ species in solution, we used a negatively charged PA molecule
(E3) and a modified synthesis route. In this method, the E3 fibers are soaked in MnCl₂ salt
overnight to localize the metal ions near the fiber surface. Then a reducing agent, NaBH₄
is added to reduce the Mn²⁺ ions to Mn⁰ metal. Finally, the metallized fibers are soaked
in deionized water to allow for oxidation of the Mn$^0$ back to MnO$_2$ by dissolved oxygen in the aqueous solution (Figure 4.9a). With this route, we successfully mineralized E3 fibers with inorganic material as shown in High Angle Annular Dark Field (HAADF) Scanning Transmission Electron Microscopy (STEM) imaging in z-contrast mode (Figure 4.9b). From STEM Energy Dispersive Spectroscopy (EDS) imaging we found that the inorganic species was Mn and using XPS we confirmed that the deposited Mn species was MnO$_2$ with the 642.9 eV peak (Mn $2p_{3/2}$) corresponding to Mn$^{4+}$ oxidation state (Figure 4.9c, d).

To study the kinetics of the mineralization reaction we collected a series of TEM images at increasing time points after the NaBH$_4$ reductant was added. We found that from 10-16 hours of incubation time the evolution of MnO$_2$ deposition changed the most (Figure 4.10). At 10 hours reduction time, discrete particles were noticeable on the surface of the PA fibers, and at 12 hours a conformal coating was obtained. By 14 hours, the nanoparticles on the surface continued to grow leading to bumpy surface, which led to an overgrowth and merging of the fibers at 16 hours. From this study, we demonstrated the application of the direct mineralization process for other energy-relevant materials, and that the extent of mineralization can be controlled by reaction time.

**Figure 4.8:** (a) IV curves of K3 fibers alone and metallized with Au nanocrystals in a drop-cast randomly oriented film and a printed aligned filament. SEM images of Au nanocrystal K3 gels prepared as (b) a dropcast film and (c) a printed filament.
Figure 4.9: MnO$_2$ mineralization on PA fibers. (a) Scheme for mineralizing MnO$_2$ on negatively charged PA surface. (b) Z-contrast mode HAADF-STEM image of MnO$_2$ particles nucleated on E3 fibers. (c) STEM EDS spectral mapping of manganese signal (cyan) from MnO$_2$ particles on PA fibers. (d) XPS spectra of MnO$_2$ mineralized PA fibers, with peak at 642.9 eV corresponding to the Mn 2p$_{3/2}$ spin orbital.

Figure 4.10: Kinetics of MnO$_2$ mineralization. Time series of TEM samples prepared at (a) 10 hours, (b) 12 hours, (c) 14 hours, and (d) 16 hours of reduction time. MnO$_2$ thickness and coverage increase with reductant treatment time with small discrete nuclei at 10 hours growing larger and eventually merging.
4.4 Conclusion

This work highlights the importance of pathway dependence for Au deposition on soft templates. By using a bio-inspired metallization process directly onto PA fibers we achieved thicker and more conductive coatings compared to Au functionalization using ligand-capped Au nanocrystals. The nanofiber templates can be spray coated onto transparent plastic substrates and mineralized to form flexible transparent conducting electrodes. Further, 3D printing the nanofiber scaffolds at higher concentrations to form a hydrogel can be used to localize mineralization or metallization reactions for patterning specific components and also to enhance device performance with nanoscale alignment.

4.5 Materials and Methods

E3 (C16VVVAAE) and K3 (C16VVVAAK) PAs were synthesized using solid phase peptide synthesis on a Rink amide MBHA resin, using standard 9-Fluorenylmethoxycarbonyl (Fmoc) protected amino acids in N,N-dimethylformamide (DMF) with diisopropylethylamine (DIEA) and 2-(1H-Benzotriazol-1-yl)-1,1,3,3-tetramethyluronium hexafluorophosphate (HBTU). The PAs were cleaved from the resin using TFA and purified by prep-scale high performance liquid chromatography (HPLC) using a Phenomenex column.

Gold nanocrystals were synthesized using a procedure for gold seeds from Murphy et al. In brief, 0.5 mL of a 0.01 M stock solution of HAuCl$_4$ (aq.) and 0.5 mL of a 0.01 M stock solution of trisodium citrate (aq.) were added to a vial containing 18 mL of water while stirring. 0.5 mL of freshly-prepared 0.1 M NaBH$_4$ was added to the vial and allowed to stir for $\sim$30 sec, during which the color changed from pale yellow to orange. The solution was left undisturbed at room temperature for 2 hours, during which the color changed to orange-red. The nanocrystals were used within 48 hours without purification.
Positively charged gold nanocrystals were synthesized according to the procedure adapted from Millstone et al.\textsuperscript{232} for 13.1 nm particles. Briefly, in a 250 mL three-neck round bottom flask containing a stir bar, 50 mL of 1 mM HAuCl\textsubscript{4} (aq.) was heated to a strong reflux (\sim 1 drop per second). Next, 5 mL of 33.1 mM of trisodium citrate (aq.) was injected into the refluxing gold solution, changing color to red-purple within 1 min. The reaction was held at reflux for 5 min before removing the heat; after cooling the nanocrystals were stored at 4°C. The native citrate ligands were exchanged for poly(ethylene glycol) methyl ether thiol (PEGSH) by centrifuging 1 mL at a time at 14500 rcf for 10 min, carefully removing the lightly colored supernatant with a pipet, and adding another 1 mL of original gold nanocrystal solution. This was repeated three times, resulting in \sim 3x concentration of gold nanocrystals, which were then redissolved in 50 µL PEGSH and 950 µL water. This was placed on a shaker at room temperature for 4 hours. The nanocrystals were then washed another 2 times by centrifuging and redissolving in water. Separately, thiocholine was prepared by dissolving acetylthiocholine in water and dilute HCl, heating for \textgreater 3 days at 50°C, and removing the liquid under vacuum, resulting in a gel that was redissolved in water. Immediately before use tris(2-carboxyethyl)phosphine was added to the thiocholine solution to reduce any disulfide bonds that had formed. The PEGSH ligands were exchanged for the thiocholine through the same procedure as described for the citrate to PEGSH exchange, without changing the nanocrystal concentration.

Direct mineralization was accomplished by adding sodium hydroxide to a solution of 10 mM HAuCl\textsubscript{4} (aq.) until the pH reaches 10 by pH paper, at which point the predominant species in solution is Au(OH)\textsubscript{4}^- and is accompanied by a notable solution color shift from dark yellow to light yellow. This solution is then added to an annealed solution of K3 fibers and allowed to incubate under mildly shaking at room temperature and in the dark for 1-14 days.
TEM images were collected on a Hitachi HT-7700 microscope operated at 120 kV. Au NC-K3 samples were prepared by first dropping 10 µL K3 solution (0.5 mM) on the carbon side of a TEM grid and allowed to settle for 1 minute before excess solution is wicked away with filter paper. The grid is let dry for 5 minutes and then 10 µL nanocrystal solution is dropped on the grid and allowed to settle for varying amounts of time, detailed in the results section. Excess solution is then wicked away and the grid is washed with 10 µL water, dried and then analyzed via TEM and XPS. Direct mineralization samples were prepared by pipetting 10 µL of the mineralization solution onto the carbon side of TEM grid. After letting sit for 5 minutes, excess solution was wicked away, the grid was washed 3 times with milli-Q water to remove excess salts from precipitating during drying, and then allowed to air dry. SEM was performed on a Hitachi SU8030 microscope. Mineralized thin film samples were washed with water and dried before imaging. Mineralized gel samples were prepared by solvent exchange from water to ethanol using a graded series. Following dehydration, samples were dried using critical point drying (CPD) and imaged without any conductive coating. XPS was performed using a Thermo Scientific ESCALAB 250Xi with a -8.0 V sample bias and a He I (hν = 21.2 eV) source, on samples dropcast on TEM grids or carbon tape.

Four-point probe measurements were collected using a Signatone S-302 stand with an SP4 model probe head (40 mil tip spacing and 10 mil tip radius). Two-point probe measurements were carried out on dried films prepared by dropcasting 100 µL of the mineralized or pure PA solutions. Au top contact electrodes were evaporated on to the thin films with 80 µm channel length and 50 nm thickness. Using voltage sweeps from -5 V to 5 V, the conductivity values were taken from the slope of the ohmic region of the I-V plots and were parameterized based on the electrode geometry (Signatone probe station, Agilent 4155C semiconductor parameter analyzer).
Chapter 5

Hydrogel 3D Printing with Liquid Crystalline Self-Assembling Building Blocks

5.1 Objectives and Significance

Supramolecular liquid crystalline hydrogels are an attractive class of materials for directing charge transport and cell migration using anisotropic nanoscale building blocks. By applying shear forces, these nanostructures can be aligned resulting in bulk anisotropic properties. However, reproducibly fabricating and patterning aligned domains in three dimensional hydrogels remains a challenge by conventional fabrication techniques. By leveraging recent advances in additive manufacturing, we report on a method for 3D printing ionic-crosslinked liquid crystalline hydrogels from low viscosity aqueous supramolecular inks composed of peptide amphiphile (PA) nanofibers. The supramolecular interactions play a critical role in determining the viscosity and printability of the PA inks, and the controlled printing parameters allow for precise positioning of hydrogel filaments in three dimensions with tunable shear-induced nanofiber alignment. In our printed supramolecular liquid crystalline hydrogels, we demonstrate anisotropic ionic and electronic charge transport as well as directed cell outgrowth due to the synergistic effects of molecular self-assembly and additive manufacturing.

5.2 Background

Biologically inspired hydrogels with nanoscale order have attracted widespread interest for applications in both energy and medicine. From electrolytes and electrodes for
energy conversion and storage\textsuperscript{121,122,235–237} to drug delivery vehicles and cell scaffolds for healthcare solutions,\textsuperscript{238–240} achieving the desired nanostructure morphology and orientation is critical for optimal performance of the hydrogel material. Supramolecular hydrogels, in particular, allow for intricate design and tunability of bulk material properties based on bottom-up assembly of molecular building blocks.\textsuperscript{52,218,241} Programming the attractive and repulsive interactions drives molecular assembly into defined nanoscale shapes with specific surface chemistry.

Our lab has demonstrated the use of peptide amphiphile (PA) and chromophore amphiphile (CA) building blocks to form chemically and mechanically tunable biomimetic hydrogels for various functions.\textsuperscript{83,86,90,242,243} The PA assemblies are of high interest because the anisotropic nanostructures form liquid crystalline domains in aqueous solutions which can be aligned in a monodomain gel via shear forces while pipetting into a salty media.\textsuperscript{244} The resulting gels exhibit bulk anisotropic properties due to the alignment of the nanoscale assemblies.\textsuperscript{243–247} In these examples, however, the gels were manually drawn by hand and therefore lack the control necessary to reproducibly build these materials into patterns and 3D objects with programmed nanoscale alignment.

Direct ink writing (DIW) is an extrusion-based 3D printing technique that has been demonstrated as a useful processing tool for patterning surfaces and building complex 3D structures.\textsuperscript{132,248–250} The shear forces present during extrusion have also been leveraged as a way to align anisotropic nanostructures along the printing direction.\textsuperscript{125,137,251} Here, we describe how to apply DIW technology to build macroscopic ionically crosslinked hydrogels with tunable nanoscale alignment from aqueous supramolecular inks. We investigate how the assembly state of the nanostructures affects the viscosity of the inks and printability, as well as the salt conditions necessary for rapid ionic crosslinking and high gel strength to maintain the extruded shape after printing and enable multilayer 3D parts. Using a combination of 2D X-ray scattering and polarized optical microscopy, we quantify the alignment
of the nanostructures within printed filaments and measure how the alignment effects bulk properties for energy gels, cell scaffolds and muscle-inspired actuators.

5.3 Results and Discussion

5.3.1 Direct Ink Writing Supramolecular Hydrogels

We synthesized an anionic and cationic version of a known PA molecule with a \( \beta \)-sheet forming domain that promotes elongation into nanofibers and either glutamic acid or lysine residues to impart solubility in water (Figure 5.1a). The anionic PA (E3) forms ionically crosslinked hydrogels when cationic ions or polyelectrolytes are present while the cationic PA (K3) ionically crosslinks with anionic species. To prepare the ink, we made aqueous PA solutions at 0.5-2 wt% that were thermally annealed and slow cooled to drive supramolecular assembly of high aspect ratio nanofibers. The anisotropy and surface charge of the nanofibers drives formation of liquid crystalline domains in the nanofiber suspension (Figure 5.2). Following the annealing step, the PA solutions were loaded into a syringe-based extrusion 3D printer without further additives. We printed square meander patterns onto salt coated substrates to ionically crosslink the shear-aligned PA solution upon contact with the surface (Figure 5.1b). We found that we could direct ink write supramolecular hydrogel filaments into arbitrary patterns with sharp corners (Figure 5.1c). Polarized Optical Microscopy (POM) images showed uniform colors when the filaments were oriented 45° to the polarizer, indicating monodomain alignment of the PA nanofibers within the hydrogels (Figure 5.1c). Scanning Electron Microscopy (SEM) imaging confirmed the massive alignment of the nanofibers along the direction of extrusion (Figure 5.1d). In comparison to gels printed on a substrate, filaments formed by extruding directly into a \( \text{CaCl}_2 \) solution had rougher edges and non-uniform birefringence patterns (Figure 5.3). This suggests that both shear forces in the nozzle and elongational forces from the substrate are responsible for nanofiber alignment.
Figure 5.1: Extrusion printing supramolecular liquid crystalline hydrogels. (a) Molecular structures of peptide amphiphiles used in anionic and cationic nanofiber inks. (b) Assembled nanofibers are extruded through a thin nozzle onto a salt coated substrate to gel the shear-aligned nanofibers in place. (c) Photo and POM images of printed E3 nanofiber gel on CaCl$_2$ coated substrate and (d) SEM image of printed E3 nanofiber gel filament (inset scale bar: 100 nm).

To optimize the printing conditions and alignment of ionically crosslinked PA gels, we studied the effects of the nanostructure assemblies on viscosity of the inks and how the salt valence and concentration determines the fidelity of the printed structures. The following sections outline the relationship how supramolecular chemistry can be used to modulate the printability of the inks and how the printing parameters can be used to enhance the properties of the anisotropic supramolecular nanostructures.
Figure 5.2: POM image of a droplet of annealed 1.5 wt% E3 PA solution. Different colors indicate liquid crystalline domains oriented in different directions. A small amount of methylene blue (∼0.2 mM) in the PA solution shifts the colors transmitted through the polarizers to emphasize the random orientation of the domains.

Figure 5.3: POM images of string hydrogels formed by manually-extruding PA solutions into CaCl₂ solution. (a) straight and (b) crossed string hydrogels show birefringence indicative of alignment. However, in the inverted images (c and d) it is clear that the birefringent signal (dark) is not uniformly dispersed through the whole width of the filaments.
5.3.2 Tuning Viscosity with Supramolecular Chemistry

For effective direct-write printing from aqueous solution, the ink must have viscosity above water to control the flow during extrusion. By increasing the PA loading in the ink above 1 wt%, we can achieve viscosity profiles that are suitable for 3D printing (Figure 5.4). For the rest of our studies, we chose PA inks at 1.5 wt% to achieve high enough viscosities for printing while maintaining a highly hydrated gel, on par with our previous biological studies. Both E3 and K3 inks exhibit strong shear thinning profiles in flow curve measurements at different pH values (Figure 5.5a, b). These curves can be fit to the Carreau model to measure the zero-shear viscosity and shear thinning exponent among other rheological properties for the PA inks (Table 5.1). There are three distinct regions in the flow curves: a slight plateau at low shear rates corresponding to the zero-shear viscosity, a shear thinning region where the PA assemblies align in the direction of shear, and a lower plateau near the water limit (∼1 mPa·s) at high shear rates. We attribute this lower plateau to fracturing of the PA assemblies at shear rates above 10,000 s⁻¹, based on TEM imaging of the inks directly after shearing (Figure 5.6).

Table 5.1: Carreau fit parameters from flow curves of PA inks in Figure 5.5a and b.

<table>
<thead>
<tr>
<th>Ink</th>
<th>η₀ (Pa·s)</th>
<th>η_∞ (Pa·s)</th>
<th>t (s)</th>
<th>a</th>
<th>n</th>
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<td>0.0019</td>
<td>158.4</td>
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</tr>
<tr>
<td>E3 pH 9</td>
<td>1.14</td>
<td>0.0015</td>
<td>11.9</td>
<td>0.98</td>
<td>0.396</td>
</tr>
<tr>
<td>E3 pH 11</td>
<td>0.002</td>
<td>0.0013</td>
<td>0.25</td>
<td>5.66</td>
<td>0.701</td>
</tr>
<tr>
<td>K3 pH 7</td>
<td>19.46</td>
<td>0.0026</td>
<td>37.57</td>
<td>0.81</td>
<td>0.165</td>
</tr>
<tr>
<td>K3 pH 5</td>
<td>2.656</td>
<td>0.0023</td>
<td>10.48</td>
<td>0.86</td>
<td>0.205</td>
</tr>
<tr>
<td>K3 pH 2</td>
<td>0.916</td>
<td>0.0022</td>
<td>10.14</td>
<td>1.53</td>
<td>0.125</td>
</tr>
</tbody>
</table>

Across the range of shear rates in the flow curve, we found that at pH values where we expect more of the ionizable groups to be charged (i.e. high pH for E3 and low pH for K3), that the bulk solution viscosity was lower compared to inks at pH values with lower
Figure 5.4: Rheological flow curves of E3 PA inks at different concentrations and pH values. A water flow curve is provided for comparison, showing Newtonian behavior. The shaded gray area marks the viscosity regime for inks that we were not able to effectively print due to the difficulty of flow control over these low viscosity fluids. We note that this regime is empirically derived and could potentially be decreased further with dispensing system improvements, provided that the ultra-low viscosity inks can form robust self-standing gels upon salt contact.

expected charge. To measure the charge state of the PA assemblies as a function of pH, we performed pH titrations for both E3 and K3 PAs (Figure 5.7). For E3, we observed clear transitions between charge states at pH 7, 9 and 11 corresponding to -1, -2 and -3 charge states respectively. Conversely, for K3, we do not see any clear pH transitions, but rather a steady increase in pH as base is titrated. This suggests that lysine residues can stabilize charge more effectively in mixed charged states, possibly due to the slightly longer carbon chain compared to glutamic acid.

We used cryogenic Transmission Electron Microscopy (cryo-TEM) to check the assembly state of the PA molecules at different pH values. For E3, we observe long nanofibers at pH 7 and 9 but only spherical micelles at pH 11, when the electrostatic repulsion between molecules overcomes the cohesive hydrogen bonding interactions (Figure 5.5c, d, e). This fiber to micelle transition corresponds to a sharp drop in viscosity, resulting in an
Figure 5.5: Viscosity and assembly structure in PA nanofiber inks at different pH values. Flow curves for (a) E3 and (b) K3 nanofiber inks at different pH values. Data is fit to the Carreau model for shear thinning fluids. (c-e) Cryo-TEM images of E3 ink at pH 7, 9 and 11, respectively. Inset in (e) is conventional TEM of E3 pH 11 ink. (f-h) Cryo-TEM images of K3 ink at pH 7, 5, and 2, respectively. SAXS patterns for (i) E3 inks and (k) K3 inks, and WAXS patterns for (j) E3 inks and (l) K3 inks. All scale bars are 500 nm, except inset in (e) where scale bar is 200 nm.

ink below the printability limit. In contrast, we see long nanofibers at all pH values for K3 (Figure 5.5f, g, h). Small-Angle X-ray Scattering (SAXS) measurements of the inks at each pH corroborated the TEM imaging, where a slope of -1 in the low q range corresponds to one-dimensional (fiber) nanostructures and a slope of 0 corresponds to zero-dimensional (micelle) nanostructures (Figure 5.5i, k). That K3 maintains the fiber nanostructure at all
Figure 5.6: TEM of (a) E3 pH 7 and (b) K3 pH 7 PA nanofibers after shearing in flow curve measurements. These samples were collected immediately following measurement with a final shear rate of 17000 s⁻¹ and diluted 10X before dropping on a TEM grid for imaging.

Figure 5.7: pH titration curves for (a) E3 PA and (b) K3 PA with the estimated charge states at different pH values. Each point is from an individual solution that was annealed with the added acid or base prior to measurement.

pH values agrees with the pH titration data, highlighting that K3 nanofibers can have all three amine side groups charged while still maintaining an elongated fiber structure.

While E3 and K3 PAs form nanofibers over a wide pH range, there are significant differences in the viscosity of nanofiber inks at each pH value. One explanation is that the fiber lengths are changing at different pH values due to varying electrostatic repulsion between adjacent charged head groups. From TEM imaging, however, there is no measurable difference in the fiber lengths because individual fibers are much longer than the TEM field of view. Another alternative is that the increased electrostatic repulsion at higher charge disrupts the internal attractive forces and lowers the nanostructure stiffness. To probe if the differences in viscosity for nanofiber inks at different charge states could be due to changes
in the internal structure of the fiber, we used Wide-angle X-ray Scattering (WAXS). We observe a WAXS peak at around 1.35 Å⁻¹ for E3 at pH 7 and 9, corresponding to a β-sheet d-spacing of 4.64 Å, while at pH 11 there is no WAXS peak when the nanostructures are in the micellar state (Figure 5.5j). We note that for E3 the intensity decreases by about half at pH 9 compared to pH 7, indicating that less molecules are participating in ordered β-sheet hydrogen bonding at higher charge states. In comparison, K3 has a WAXS peak at 1.34 Å⁻¹ for all pH values corresponding to a β-sheet d-spacing of 4.68 Å (Figure 5.5l). There is not a significant difference in the WAXS peak intensity for each pH value, implying that the charge state does not significantly affect the internal order of the K3 nanofibers. Previous studies from our group have shown that the β-sheet in K3 fibers at a single pH value can be ‘turned off’ in solutions below a critical ionic strength. In this work, all the inks were prepared at a constant ionic strength, well above the critical value that favors β-sheet formation, and thus the effect of fiber surface charge on the solution properties can be studied.

Since the nanofiber structures do not exhibit a clear trend in internal order by WAXS measurements at different charge states, we investigated the effect of fiber to fiber interactions to explain the decrease in ink viscosity at higher charge states. We measured the zeta potential of assembled fibers and found that as the pH of the solution is increased, the zeta potential also increases for E3 and decreases for K3 as expected (Figure 5.8). We hypothesize that the higher coulombic repulsion between the surface of fibers at higher charge states results in less fiber entanglement and decreases the bulk solution viscosity. Optical density measurements show an increase in turbidity for inks composed of nanofibers with lower surface charge, indicating larger scale aggregation and bundling due to less repulsive forces between nanofibers (Figure 5.9. In summary, our findings suggest that balancing the attractive and repulsive interactions in supramolecular assemblies not only determines the assembly morphology, but also highlights that higher order interactions between supramolecular as-
Assemblies govern the viscosity of PA nanofiber inks. Properly controlling these interactions can tune the viscosity from easily printable to completely unusable. Future work could explore using semi-atomistic coarse-grained modelling to determine optimal ink formulations a priori by leveraging the interactions outlined here.

**Figure 5.8:** (a) Zeta potential and (b) size measurements of PA assemblies at different pH values. Each sample started from an annealed solution and was then bath sonicated for 30 minutes directly before measurement. This led to a drastic decrease in solution viscosity and conventional TEM imaging after sonication showed broken up fibers for (c) E3 pH 7, (d) E3 pH 9, (f) K3 pH 7, (g) K3 pH 5, and (h) K3 pH 2. The micellar morphology was maintained for E3 pH 11 (e). We note that zeta and size measurements from DLS are a measure of the hydrodynamic radius for spherical particles, but since the apparent sizes are not significantly different we can use these values as a relative comparison of the PA surface charge in each ink.

### 5.3.3 Ionic Crosslinking Strength for Accurate Filament Size Control

For patterning surfaces accurately and building self-standing 3D hydrogels, the PA ink must rapidly gel upon leaving the extrusion nozzle. We coated glass substrates with varying valency and concentration of inorganic salts to study the conditions for maintaining the extruded filament width and thickness. We chose to use E3 pH 7 and K3 pH 7 inks
Figure 5.9: Optical density measurements for PA inks at different pH values. The absorbance at 600 nm was used to quantify the relative scattering from the suspended nanostuctures.

because they had the highest viscosity which allows for greater control during extrusion. Furthermore, we found that while the pH dictates the viscosity of the nanofiber inks, it does not significantly affect the hydrogel strength (Figure 5.10). When printing E3 with a 100 µm inner diameter nozzle on CaCl₂ coatings, we observe sharp features in square meander patterns and monodomain alignment of the nanofibers in the extruded filaments in POM images (Figure 5.11 a). In comparison, when printing on substrates without any salt coating, we see larger broad features and polydomain alignment of the nanofibers (Figure 5.11 b).

To quantify the amount of salt necessary for reproducible thin monodomain gels, we measured the printed filament width for different salt concentrations and salt valencies for E3 and K3 with a 100 µm nozzle (Figure 5.11 c, d, see Methods Section 5.5 and Figure 5.12 for details). We expect that for rapid gelation the hydrogel width will be close to the 100 µm nozzle, indicating that minimal bleeding of the printed features occurred. For both monovalent salts, Na⁺ and Cl⁻, we found that at all tested salt concentrations, thin filaments on the order of 100 µm were not achievable (Figure 5.13). However, for divalent and trivalent salts there was a threshold concentration above which thin gels were achieved. We note that a lower concentration of Al³⁺ and (PO₄)³⁻ are needed than Ca²⁺ and (SO₄)²⁻ for thin filaments.
Figure 5.10: Strength of ionically-crosslinked PA hydrogels at different pH values. (a) Storage and loss modulus of Ca$^{2+}$ crosslinked E3 gels from pH 7 and pH 9 inks. (b) Storage and loss modulus of (SO$_4$)$_{2-}$ crosslinked K3 gels from pH 7 and pH 5 inks.

Figure 5.11: Salt gelation properties for PA nanofiber inks. Photo and POM images of printed hydrogel filaments (100 µm nozzle diameter) in a square meander pattern for substrates (a) coated with CaCl$_2$ and (b) without a salt coating. The top and bottom POM images are with the samples oriented 0° and 45° to the polarizer, respectively. Printed filament width for varying salt concentrations and valency for (c) E3 inks and (d) K3 inks. Gel strength over time for gels crosslinked by different salt valencies with the same charge density for (e) E3 inks and (f) K3 inks.

This is in part due to a higher charge density per mol for the trivalent ions and when the divalent ionic species reach the same total charge density – rather than concentration – they
also form gels of similar width. To see if kinetics of gel formation or overall gel strength played a role in the differences between salt gelling agents, we measured the gel stiffness as a function of time (Figure 5.11e, f, and 5.14). We found that the gelation was nearly immediate for all salt valencies and therefore the rate of gelation is not the differentiating factor. Further, we observed that the strength of the gel increases with the valency even though the ionic strength of the gelling species and pH of the solutions were kept constant at 40 mM and pH 7. Thus, we conclude that differences in gel storage modulus are the reason why we see thinner filament widths for higher valency salts. This result suggests that a threshold storage modulus of at least $\sim 1$ kPa is necessary to form self-standing gels that can be effectively patterned and built into 3D architectures.

We note that the K3 gels are about 10 times less stiff than the E3 gels, which could be due to the charge equilibrium of sulfate and phosphate anions at pH 7 (so the effective charge is lower) or because the ionic radius is larger and more delocalized for these anions so ionic crosslinking is less robust. The weaker gel strength explains why K3 gels spread more and can only achieve filaments down to $\sim 170$ µm in width while E3 filaments can form gels with $\sim 130$ µm in width. We ruled out other possible explanations for this discrepancy, like the effect of ink viscosity or differences in surface wettability between salt coatings, by measuring filaments extruded from PA inks at different viscosities and calculating the contact angles of the salt coated surfaces (Figure 5.15).

From the contact angle measurements on glass, we found that the salt coatings have contact angles less than 20°, suggesting that these coatings could be used as surface treatments to print hydrogels on a variety of hydrophobic surfaces. We printed E3 filaments on CaCl$_2$-coated polyimide (PI) and polyethylene terephthalate (PET) films demonstrating the possibility to interface these nanostructured hydrogel materials with flexible polymer substrates (Figure 5.16). We also explored patterning the salt gelling agent on the surface via direct ink writing by adding a block copolymer (Pluronic F-127) to a CaCl$_2$ solution to
Figure 5.12: Representative optical micrographs of salt-coated substrates and printed filaments for different salts and salt concentrations on glass substrates. For each salt, one spray corresponds to 92 nmol/cm$^2$ of salt. For AlCl$_3$ and Na$_3$(PO$_4$), sprays less than one were achieved by diluting the spraying solution 10x or 2x such that 0.1 and 0.5 sprays correspond to 9.2 and 46 nmol/cm$^2$, respectively. The images of the printed filaments were extruded with a 100 µm nozzle at 5 mm/s and were used for measurement of the filament width for each condition. These images were taken after the gels had dried, however we only observed a decrease in the filament height and not the width. Drying also led to supersaturation of the gelling salt which resulted in salt crystallization for substrates with higher salt loadings.

increase the viscosity into the printable range. Then we printed the PA ink on top of the patterned salt trace resulting in similar hydrogel filaments but with salt deposition only where
Figure 5.13: (a) Filament width vs. salt concentration for K3 pH 7 ink with NaCl coated substrates out to 1.8 µmol/cm$^2$ (20 sprays). (b) Optical micrograph of 1.8 µmol/cm$^2$ NaCl coated substrate, and (c) K3 filament printed on 1.8 µmol/cm$^2$ NaCl coated substrate. Even though the salt concentration is more than double the multivalent salts we do not observe thin, straight-edged hydrogel filaments.

Figure 5.14: Full rheological characterization of E3 (a-c) and K3 (d-f) gels. (a, d) Damping factor at 10 rad/s and 0.1% strain as a function of time after initial salt contact, (b, e) frequency sweep at 0.1% strain and (c, f) strain amplitude sweep at 10 rad/s.
the hydrogel was extruded. Future work could explore using functional polymer additives to the gelling ink to enhance adhesion to specific substrates of interest.

5.3.4 Controlling Nanofiber Alignment through Printing Parameters

To optimize the alignment of PA nanofibers in extruded hydrogels, we measured the anisotropy from 2D SAXS patterns of printed gels. We printed E3 nanofiber gels on CaCl$_2$ coated substrates with different nozzle diameters and print speeds to test how the shear rate influenced nanofiber alignment. The shear rate during printing can be expressed as:

$$\dot{\gamma} = \frac{4\lambda Q}{\pi R^3}$$

(1)
where \( \lambda \) is an empirical shear thinning constant, \( Q \) is the flow rate and \( R \) is the nozzle radius. The flow rate is the product of the cross-sectional area \( \pi R^2 \) and the print speed \( (v) \), so by substituting we obtain:

\[
\dot{\gamma} = \frac{4\lambda v}{R}
\]

Equation 2 gives a simple relationship between the nozzle size and print speed to the shear rate at the walls of the nozzle. We note that the shear rate is non-uniform through the radius of the nozzle but this calculation gives a first order approximation to compare the shear forces experienced by the extruded fibers. At small nozzle sizes and fast speeds, we observe anisotropy in the x-ray scattering with a peak located 90° to the print direction in azimuthal line cuts (Figure 5.17a). By measuring the full width at half max (FWHM) of the azimuthal peak we can quantify the nanofiber alignment in the direction of the print (see Methods Section 5.5). Generally, we observed that at higher shear rates the FWHM decreases, indicating enhanced nanofiber alignment for smaller nozzle sizes and faster printing speeds. We found the same trend in both hydrated and dried gels, demonstrating that the alignment is locked upon initial gelation rather than evaporation induced alignment during drying (Figure 5.18). We also investigated the effect of nozzle geometry on nanofiber alignment.
There was not a significant difference in the FWHM for gels printed with longer (2 cm) versus shorter (1 cm) nozzles, but we did observe a clear enhancement of the anisotropy with straight nozzles compared to conical nozzles (Figure 5.19). This result is surprising since previous studies have shown that elongational flow in tapered nozzles is beneficial for anisotropic particle alignment.\textsuperscript{253,254} However, the PA nanostructures in our inks are at least an order of magnitude higher aspect ratio and our ink viscosity is also lower, which could favor aligned laminar flow in straight cylindrical nozzles as opposed to turbulent flow that could form in the higher angle conical nozzles tested here.

To corroborate the SAXS data and expedite data collection, we used POM images of printed filaments to calculate the ratio of the light intensity when the filament was oriented 0° and 45° to the polarizer (Figure 5.17b, see Methods Section 5.5 and Figure 5.20 for details). By background subtracting and normalizing for the thickness of the hydrogel filaments, we computed the birefringence ratio and used it as a rapid semi-quantitative method for measuring the relative alignment in printed samples. We observe that the birefringence ratio increases with shear rate and is inversely related to the FWHM from SAXS experiments, validating this method to rapidly compare the nanofiber alignment with different printing parameters (Figure 5.17c). Although this technique is only semi-quantitative, using POM rather than SAXS equipment provides a fast and easily accessible method for analyzing other aligned or anisotropic materials. Having established the SAXS-POM correlation for E3 pH 7 ink, we used the birefringence ratio to screen a range of printing speeds and nozzle sizes for various E3 and K3 nanofiber inks at different concentrations and pH values to explore which printing conditions effect alignment. We found that generally higher viscosity solutions were more aligned than lower viscosity solutions. For example, E3 pH 7 ink had a birefringence ratio of 27.4 while E3 pH 9 ink had a ratio of 12.4 with identical printing conditions, suggesting that viscosity is a major factor in achieving nanofiber alignment (Figure 5.21). To visualize which parameters affected nanofiber alignment, we produced heat maps of the birefringence
Figure 5.17: PA nanofiber alignment during extrusion printing. (a) SAXS diffraction patterns and azimuthal line cuts for different printing parameters. (b) POM images at 0° and 45° to the polarizer from different printing parameters with the birefringence ratio in the top left corner of each image. (c) Correlation between FWHM from x-ray scattering data and birefringence ratio as a function of shear rate for E3 pH 7 ink. (d, e) Heat plots of birefringence ratio of printed samples from various PA inks with different viscosities over a range of nozzle diameters and print speeds.

ratio plotted as a function of apparent viscosity, nozzle size and print speed (Figure 5.17d, e). The apparent viscosity for each ink was taken from the flow curves at a given shear rate calculated using the printing parameters in Equation 2. The birefringence data from each printing input was then concatenated and the surface was smoothed using Voronoi surface mapping.
Figure 5.18: Azimuthal line cuts from SAXS patterns of hydrated printed samples for different nozzle inner diameters. Line cuts were obtained from $0.65 < q < 0.85$ nm$^{-1}$. The average FWHM for the hydrated samples was 25.77° for 100 µm, 36.32° for 200 µm, and 68.76° for 410 µm.

Figure 5.19: Effect of nozzle length and geometry on alignment. (a) FWHM from azimuthal line cuts for 6.35 and 12.7 mm nozzle lengths at two different printing speeds. (b) FWHM from azimuthal line cuts for conical and straight nozzles at two different printing speeds. These prints were all extruded through a 150 µm ID nozzle.

From Figure 5.17d, we can observe clear trends in how the nozzle diameter affects nanofiber alignment. First, larger nozzle sizes have less alignment due to the lower shear rates as expected from the inverse relationship in Equation 2. Second, lower viscosity solutions
Figure 5.20: Example calculation of birefringence ratio for analyzing alignment from POM images. POM images of a printed filament oriented at (a) 0° and (b) 45° to the polarizer are collected and analyzed in ImageJ. The integrated density (i.e. intensity of transmitted light normalized per unit area) of light passing through the filament (yellow box) and in the background of the image (red box) are calculated at each angle. The intensity in the red box is subtracted from the yellow box and the background subtracted intensity at 45° is divided by the background subtracted intensity at 0°. To normalize for small variations in thickness, optical profilometry (c and d) was used to measure the average thickness of the printed filaments.

require smaller nozzles to obtain high degrees of alignment. This result can be attributed to higher and more uniform shear forces that promote laminar flow in the nozzle even for low kinematic viscosity aqueous inks. Third, for a desired feature size (defined by the nozzle diameter) the ink viscosity should be tuned accordingly. We note that we can still obtain modest alignment with nozzle sizes up to 1.5 mm diameter if the apparent ink viscosity is greater than 5 mPa·s. For higher viscosity solutions, we needed to use exceedingly slow print speeds (∼0.1 mm/s) to maintain high apparent viscosity at smaller nozzle sizes due to the shear thinning behavior of the PA inks. This explains the lower birefringence values in the bottom right corner of Figure 5.17d.
Figure 5.21: POM images of (a, c) E3 pH 7 and (b, d) E3 pH 9 prints on CaCl₂-coated substrates at 0° and 45° to the polarizer. Printing parameters: 100 µm ID nozzle, 10 mm/s.

From Figure 5.17e, we observe that generally faster speeds are required for alignment of low viscosity inks. This is a combination of higher flow rates in the nozzle and extensional shear as the filament is extruded on the surface. Ideal printing conditions for alignment are 5-10 mm/s with 10 mPa·s apparent viscosity solutions. For some applications, the difference between birefringence ratios of 30 and 10 is likely negligible but by laying out these maps we have outlined a general landscape for the printing parameters that can be tuned to enhance PA nanofiber alignment.

5.3.5 Applications of Printed Liquid Crystalline Supramolecular Hydrogels

Aligned liquid crystalline hydrogels can be programmed for anisotropic functions. To determine the effect of nanofiber alignment on ionic transport in the nanofiber gels, we printed a sheet of aligned PA filaments and encapsulated the gel in a PDMS microfluidic chip with defined Au electrode inserts (Figure 5.22a, b). We used Electrochemical Impedance Spectroscopy (EIS) to measure the ionic conductivity and we observed a lower impedance in the direction of shear alignment than perpendicular to it (Figure 5.22c). After normalization to conductivity, we found that the ionic conductivity was more than an order of magnitude
higher in the aligned direction than across the aligned fibers. This phenomenon has been measured in dried liquid crystalline films\textsuperscript{255,256} and in nanofluidic devices,\textsuperscript{257,258} but to our knowledge this is the first evidence in bulk supramolecular hydrogels. To demonstrate the biocompatibility of this printing technique we added C2C12 myoblasts to the E3 pH 7 ink to create a PA bioink (Figure 5.22d). After extruding onto a CaCl\textsubscript{2} coated coverslip and culturing for 7 days, we observed high cell viability and alignment of cells along the printing direction of the filament (Figure 5.22e, f, g). This lays the foundation for future bioprinting studies of more complex tissues with anisotropic hierarchical structures.

The DIW technique, and the information we obtained using peptide amphiphile molecules as a model material, can also be applied to other functional supramolecular inks. We chose to investigate the application of DIW to aqueous inks composed of chromophore amphiphile (CA) assemblies developed in our lab.\textsuperscript{90} Similar to PAs, balancing the repulsive electrostatic forces and the attractive interactions (\(\pi-\pi\) stacking rather than hydrogen bonding in this case) is critical for determining the self-assembly of specific nanostructures. In this CA ink, low charge screening conditions drive assembly of the nanostructures towards elongated helices rather than short scrolls (Figure 5.23). The helix nanostructures are longer and can entangle more, resulting in higher viscosity solutions that make them more amenable for printing applications. By extruding through a 100 \(\mu\)m nozzle at 10 mm/s onto a CaCl\textsubscript{2} coated substrate, we shear-aligned the CA assemblies as evidenced in POM and SEM imaging (Figure 5.22h, i). This structural anisotropy resulted in an enhancement of electronic conductivity in the dried gel along the direction of the print compared to randomly oriented dropcast gels (Figure 5.22j and 5.24). The successful extension of DIW to chromophore amphiphiles, that have very different covalent structures and intermolecular attractive forces than peptide systems, suggests that this technique can be applied to a wide range of supramolecular inks and possibly other aqueous inks with high aspect ratio assemblies or particles inside.
Figure 5.22: Applications of supramolecular liquid crystalline hydrogels. (a) Ionic conductivity chamber schematic, (b) optical micrograph of edge of printed E3 sheet gel using a 100 µm nozzle, and (c) Bode modulus and phase plot for conductivity parallel and perpendicular to the print direction. (d) PA bioink preparation, (e) patterned bioink on CaCl$_2$ coated glass coverslip (scale bar: 2 mm), (f) confocal image of myoblasts encapsulated in a filament after 7 days in culture, and (g) orientation analysis of the myoblasts in (f). (h) CA molecular structure and SEM image of a printed CA gel filament and (i) POM images at 45° (top) and 0° (bottom) to the polarizer of CA printed filament. (k) Electrical conductivity of CA nanostructures in aligned prints and randomly oriented dropcast films.
Figure 5.23: Characterization of CA inks. Confocal microscopy images of (a) short CA scrolls at high salt concentrations and (b) elongated helices at low charge screening conditions. (c) Rheological flow curves for inks composed of CA scrolls and CA helices.

Figure 5.24: CA films for conductivity measurements. (a) Optical micrograph of Au electrodes on dropcast CA helix film. (b) SEM image of CA helices with random orientation in dropcast film.

Finally, to demonstrate that direct ink writing of PA supramolecular gels can be extended to fabricate macroscopic 3D objects, we applied the salt crosslinking solution between layers via aerosol spray (Figure 5.25a). This step provided additional salt to crosslink the subsequent extruded layer and allowed us to build multilayer constructs in arbitrary shapes such as the Northwestern University logo and tubes of varying dimensions (Figure 5.25b, c). The tube walls are composed of circumferentially aligned nanofibers as observed by the Maltese cross pattern in POM imaging (Figure 5.25c, inset). We have previously demonstrated similar hydrogel tubes with circumferentially aligned PA fibers for use as artery repair scaffolds \(^{247}\) and as muscle-inspired actuators.\(^{259}\) The DIW technique opens possibilities for more
customizable and intricate patterning of nanoscale features within 3D PA hydrogels. Future work will focus on strengthening the printed hydrogel structures by using more robust crosslinking chemistry or polymeric additives to allow for more facile handling and use in mechanically demanding applications.

Figure 5.25: 3D printing multilayer hydrogel constructs from supramolecular inks. (a) Process for building multilayer hydrogel shapes with salt addition between subsequent layers. (b) Photos of printed NU logo from an angle, side view, and top-down. Scale bars are 5 mm. (c) Photos of printed tubes with heights of 3, 6 and 9 mm. Top inset shows top-down view (scale bar: 3 mm). Bottom inset is a polarized optical micrograph of a top-down view of a tube 3 layers tall (scale bar: 2 mm).
5.3.6 Muscle-Inspired PA Hydrogel Actuators

Using the DIW technique, we further studied PA hydrogels as aligned templates for the radial growth of thermoresponsive polymers from the PA fiber surface. This work was inspired by sarcomeres in muscle tissue where actin and myosin supramolecular polymers are linked to a macromolecular scaffold called titin. Here, PA molecules were chemically designed to initiate the polymerization of the thermoresponsive polymer using atom-transfer radical polymerization (ATRP). After printing sheets of ATRP functionalized PA fibers, the gels are transferred to a polymerization bath containing a methanol/water solution. This solution contains diethylene glycol methyl ether methacrylate (DEGMA) and oligo(ethylene glycol) methyl ether methacrylate (OEGMA) monomers (molar ratio 95:5 DEGMA:OEGMA), \(N,N'\)-methylenebisacrylamide (NBAA) crosslinker, catalyst, and reducing agent in order to carry out ATRP and generate covalent chains grafted from the supramolecular scaffold. Due to the controlled nature of ATRP, polymer chains can only grow from the initiator sites on the PA fibers. The chains had an expected degree of polymerization of 1500, and crosslinker was added at a concentration equivalent to 1 wt% of the monomers, resulting in approximately one crosslink per 75 monomer units. The random copolymer exhibits the expected lower critical solution temperature (LCST) of 32°C and by heating above the LCST, the hybrid material expels water and contracts.

To test the effect of global PA alignment, we printed sheets with various infill patterns (Figure 5.26). Interestingly, the aligned sheets bend unidirectionally, towards the printing substrate and perpendicular to the aligned fiber axis, upon increase in the surrounding temperature above the transition temperature of the covalent polymer. This bending is highly reversible and repeatable over multiple cycles. Similar bending and even rolling behavior of polymer sheets has been observed in the case of bilayers. However, these materials typically bend due to the mismatch in moduli or expansion coefficients between the two components of the bilayer. In contrast, the hybrid sheets presented here have a
homogeneous dispersion of supramolecular nanofibers within the polymer matrix, as shown in the cross-sectional confocal microscopy image (Figure 5.27). In polarized microscopy images, we find increased birefringence of the layers closest to the substrate, indicating stronger alignment, compared to the upper layers of the sheets (Figure 5.28). SEM imaging also suggests that there is better alignment on the bottom surface of the sheets than on the top surface (Figure 5.29). We hypothesize that the first layer may have a higher drag shear force during extrusion onto a hard glass substrate than the drag shear force experienced by the upper layers when extruded onto the soft hydrogel surface of the initial previous layer. The differences in alignment between layers may be responsible for the preferential direction of bending in the hybrid sheets, where the more aligned bottom layer contracts more along the direction perpendicular to fiber alignment than the top layers, resulting in a net bending motion towards the bottom of the gel. Interestingly, hybrid sheets that have a cross-hatch or square spiral pattern and do not feature net alignment, show a buckling behavior instead of a bending motion (Figure 5.26f, g, 5.30). This indicates that the stresses generated by the transition of the thermo-responsive polymer cannot be released in a directed motion as is the
case for sheets having a net alignment. We anticipate this feature to be useful in designing more complex macroscopic responses of our material by using pre-programmed patterns of the 3D printed material.

**Figure 5.27:** Confocal microscopy of the cross-section of a 3D printed three layer aligned sheet. L1 represents the first layer printed on the glass substrate and L2 and L3 are the subsequent printed layers. Scale bar corresponds to 100 µm.

**Figure 5.28:** Optical microscopy of (a) one layer and (b) three layer aligned 3D printed sheets. When the sample is aligned 45° to the polarizer, a more uniform and stronger birefringence is observed for one layer sheets than for three layer sheets. Scale bars correspond to 400 µm.
Figure 5.29: Representative SEM images from the bottom (a, b) and top (c, d) surfaces of a 3D printed three layer aligned sheet.

5.4 Conclusion

We demonstrated 3D printing as a processing technique for fabricating supramolecular liquid crystalline hydrogels in arbitrary patterns and shapes. The viscosity of the supramolecular inks, a key parameter during printing, can be tuned via molecular interactions and is critically influenced by supramolecular morphology. We describe the optimum salt type and concentration for ionic gelling of these supramolecular liquid crystals on both rigid and flexible substrates. Furthermore, we found that the alignment of the nanoscale assemblies was tunable by the shear forces set by the printing parameters. Finally, we demonstrate that anisotropic assemblies in these printed structures result in anisotropic ionic and electronic transport as well as in directed cell outgrowth for applications in regenerative medicine and organic electronics.
5.5 Materials and Methods

Peptide amphiphile synthesis and purification

PA synthesis was performed on a CEM Liberty or CEM Liberty Blue automated microwave peptide synthesizer using standard fluorenylmethyloxycarbonyl (Fmoc)-solid-phase peptide chemistry. Coupling reactions on the Liberty were performed using 4 molar equivalents (eq.) of Fmoc-protected amino acid or palmitic acid, 4 eq. of O-benzotriazole-N, N, N, N'-tetramethyluronium hexafluorophosphate (HBTU) and 8 eq. of N,N-diisopropylethylamine (DIEA) and removal of Fmoc groups on resin-attached amino acids was achieved with 30% 4-methylpiperidine and 0.1 M hydroxybenzotriazole (HOBt) in N,N-dimethylformamide (DMF). Coupling reactions on the Liberty Blue were performed using 4 eq. of Fmoc-protected amino acid or palmitic acid, 4 eq. of N, N'-diisopropylcarbodiimide (DIC)) and 8 eq. of ethyl(hydroxyimino)cyanoacetate (Oxyma pure) and removal of Fmoc groups on resin-attached amino acids was achieved with 20% 4-methylpiperidine in DMF.

PAs were cleaved from resin by shaking in a solution of 95% TFA, 2.5% triisopropylsilane, 2.5% water. After cleavage, the solvent was concentrated under reduced pressure and the remaining solution was precipitated into an excess of cold diethyl ether. The crude product was redissolved at 10 mg/mL in water with 0.1% NH₄OH or 0.1% TFA. This solution was purified using standard preparatory reverse-phase high-performance liquid chromatography techniques on a Shimadzu Prominence instrument equipped with a Phenomenex Gemini NX-C18, 50 x 250 mm column. A mixture of water/acetonitrile containing 0.1% NH₄OH or 0.1% TFA was used as eluent. Pure fractions were selected based on the corresponding product signals in electrospray ionization mass spectrometry (ESI-MS) using direct injection on an Agilent 6520 Q-TOF LC-MS. Organic solvent was removed from selected fractions under reduced pressure before being frozen, lyophilized, and stored at -20°C until further use.
Purity of the samples was determined to be 98% for C16V3A3E3 and 96% for C16V3A3K3 based on the absorption at 220 nm in analytical liquid chromatography-mass spectrometry (LC-MS).

The purity of the PAs after HPLC purification was determined by analytical LC-MS using an Agilent 1200 system equipped with a Phenomenex Gemini C18, 1 x 100 mm or Phenomenex Jupiter C12 column, and an Agilent 6520 Q-TOF LC-MS detector. Gradient: acetonitrile 5% for 5 min at 50 µL/min, 5 – 95% over 25 min at 50 µL/min followed by 95% for 5 min at µL/min. Peaks were detected by absorption at 220 nm wavelength.

All species up to 2% of the most intensive peak in the mass spectrum of C16V3A3E3 (Figure 5.31b and Table 5.2) could be identified as belonging to different ion clusters of the desired compound. In the case of the C16V3A3K3 sample some fragments of the peptide sequence as well as several unknown species were found in the mass spectrum (Figure 5.31d and Table 5.3), namely, species at the m/z values of 310.3204, 328.3172, 357.7657, 407.3019, and 576.2542. It is very likely that these species are an artifact of fragmentation occurring during the ionization in the mass spectrometer. When we decreased the fragmenter voltage from 140 to 80 kV, the relative intensities of these species decreased up to 4-fold, while all the relative signal intensities from C16V3A3K3 containing species did not change (Figure 5.31f and Table 5.4).

**Table 5.2:** Ion assignments, chemical formula, theoretical m/z values, and deviation between experimental and theoretical values of signals in the mass spectrum of HPLC purified C16V3A3E3 obtained from LC-MS (see Figure 5.31b). All signals with an intensity >2% of the most intense signal in the spectrum are listed.

<table>
<thead>
<tr>
<th>m/z_{exp}</th>
<th>Ion Assignment</th>
<th>Formula</th>
<th>m/z_{theor}</th>
<th>Δ m/z</th>
</tr>
</thead>
<tbody>
<tr>
<td>577.3631</td>
<td>[C16V3A3E3 + 2 H]^2+</td>
<td>[C_{55}H_{99}N_{19}O_{16}]^2+</td>
<td>577.3576</td>
<td>0.0055</td>
</tr>
<tr>
<td>1153.7215</td>
<td>[C16V3A3E3 + H]^+</td>
<td>[C_{55}H_{98}N_{19}O_{16}]^+</td>
<td>1153.7079</td>
<td>0.0136</td>
</tr>
<tr>
<td>1162.2273</td>
<td>[2 C16V3A3E3 + NH₄ + H]^2+</td>
<td>[C_{110}H_{197}N_{39}O_{32}]^2+</td>
<td>1162.2210</td>
<td>0.0063</td>
</tr>
<tr>
<td>1170.7437</td>
<td>[C16V3A3E3 + NH₄]^+</td>
<td>[C_{55}H_{100}N_{11}O_{16}]^+</td>
<td>1170.7344</td>
<td>0.0093</td>
</tr>
<tr>
<td>1175.6974</td>
<td>[C16V3A3E3 + Na]^+</td>
<td>[C_{55}H_{99}N_{10}O_{16}Na^{+}]</td>
<td>1175.6898</td>
<td>0.0076</td>
</tr>
<tr>
<td>1549.2962</td>
<td>[4 C16V3A3E3 + 2 NH₄ + H]^3+</td>
<td>[C_{220}H_{399}N_{42}O_{64}]^3+</td>
<td>1549.2924</td>
<td>0.0038</td>
</tr>
</tbody>
</table>
Table 5.3: Ion assignments, chemical formula, theoretical m/z values, and deviation between experimental and theoretical values of signals in the mass spectrum of HPLC purified C16V3A3K3 obtained from LC-MS (see Figure 5.31d) and measured at 140 kV. All signals with an intensity >2% of the most intense signal in the spectrum are listed.

<table>
<thead>
<tr>
<th>m/z_{expt}</th>
<th>Ion Assignment</th>
<th>Formula</th>
<th>m/z_{theor.}</th>
<th>\Delta m/z</th>
</tr>
</thead>
<tbody>
<tr>
<td>310.3213</td>
<td>unknown single charged</td>
<td>[C_{22}H_{40}N_{12}O_{12}]^{2+}</td>
<td>357.7529</td>
<td>0.0128</td>
</tr>
<tr>
<td>338.3185</td>
<td>unknown single charged</td>
<td>[C_{22}H_{40}N_{12}O_{12}]^{3+}</td>
<td>384.2932</td>
<td>0.0427</td>
</tr>
<tr>
<td>357.7657</td>
<td>[VA3K3 + 2 H]^{2+}</td>
<td>[C_{38}H_{12}N_{13}O_{13}]^{2+}</td>
<td>407.2871</td>
<td>0.0200</td>
</tr>
<tr>
<td>407.3071</td>
<td>[V2A3K3 + 2H]^{2+}</td>
<td>[C_{38}H_{12}N_{13}O_{13}]^{2+}</td>
<td>575.9361</td>
<td>0.0343</td>
</tr>
<tr>
<td>575.9704</td>
<td>[C16V3A3K3 + 2 H]^{2+}</td>
<td>[C_{38}H_{12}N_{13}O_{13}]^{2+}</td>
<td>575.9361</td>
<td>0.0343</td>
</tr>
<tr>
<td>576.2561</td>
<td>unknown double charged</td>
<td>[C_{38}H_{12}N_{13}O_{13}]^{2+}</td>
<td>1150.8650</td>
<td>0.0437</td>
</tr>
<tr>
<td>1150.9087</td>
<td>[C16V3A3K3 + H]^{+}</td>
<td>[C_{38}H_{12}N_{13}O_{13}]^{+}</td>
<td>1725.7923</td>
<td>0.0500</td>
</tr>
<tr>
<td>1725.8423</td>
<td>[3 C16V3A3K3 + 2 H]^{2+}</td>
<td>[C_{54}H_{38}N_{39}O_{39}]^{2+}</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 5.4: Ion assignments, chemical formula, theoretical m/z values, and deviation between experimental and theoretical values of signals in the mass spectrum of HPLC purified C16V3A3K3 obtained from LC-MS (see Figure 5.31d) and measured at 80 kV. All signals with an intensity >2% of the most intense signal in the spectrum are listed.

<table>
<thead>
<tr>
<th>m/z_{expt}</th>
<th>Ion Assignment</th>
<th>Formula</th>
<th>m/z_{theor.}</th>
<th>\Delta m/z</th>
</tr>
</thead>
<tbody>
<tr>
<td>310.3204</td>
<td>unknown single charged</td>
<td>[C_{22}H_{40}N_{12}O_{12}]^{2+}</td>
<td>384.2932</td>
<td>0.0362</td>
</tr>
<tr>
<td>338.3172</td>
<td>unknown single charged</td>
<td>[C_{22}H_{40}N_{12}O_{12}]^{3+}</td>
<td>407.2871</td>
<td>0.0148</td>
</tr>
<tr>
<td>384.3294</td>
<td>[C16V3A3K3 + 3 H]^{3+}</td>
<td>[C_{38}H_{12}N_{13}O_{13}]^{3+}</td>
<td>575.9361</td>
<td>0.0276</td>
</tr>
<tr>
<td>407.3019</td>
<td>[V2A3K3 + 2H]^{2+}</td>
<td>[C_{38}H_{12}N_{13}O_{13}]^{2+}</td>
<td>576.2542</td>
<td>0.0473</td>
</tr>
<tr>
<td>576.2542</td>
<td>unknown double charged</td>
<td>[C_{38}H_{12}N_{13}O_{13}]^{2+}</td>
<td>1150.8650</td>
<td>0.0396</td>
</tr>
<tr>
<td>1150.9046</td>
<td>[C16V3A3K3 + H]^{+}</td>
<td>[C_{38}H_{12}N_{13}O_{13}]^{+}</td>
<td>1725.7923</td>
<td>0.0500</td>
</tr>
<tr>
<td>1725.8396</td>
<td>[3 C16V3A3K3 + 2 H]^{2+}</td>
<td>[C_{54}H_{38}N_{39}O_{39}]^{2+}</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Material preparation

Peptide amphiphile (PA) molecules were synthesized by solid phase peptide chemistry and had a purity of more than 95% by liquid chromatography-mass spectrometry (LC-MS). PA solutions were prepared in Milli-Q water at different concentrations. Solutions were adjusted to the desired pH with addition of 1 M NaOH or 1 M HCl. Following pH adjustment, 1 M NaCl was added to maintain a constant ionic strength of 45 mM for all solutions used here. These solutions were then annealed in a water bath at 80°C for 30 min and allowed to
slow cool overnight. Following annealing, the pH was verified by a Mettler-Toledo pH meter before further experiments were performed. Dilute concentrations (∼0.2 mM) of methylene blue dye were added to the E3 printing inks to aid in visualization. All gelling solutions for substrate coating and rheology were prepared with 10 mM HEPES, to minimize effects due to pH differences with different salt types. CA molecules were synthesized as described previously. CA inks were prepared at 20 mM in DI water and annealed in a water bath at 80°C for 30 min with slow cooling overnight. Assembly of short scroll nanostructures was driven by the addition of 50 mM NaCl in the annealing solution, while for assembly of elongated helix nanostructures only 1 mM NaCl was added prior to annealing.

Direct ink writing

All prints (except cell studies) were carried out on a Hyrel System 30M printer (Hyrel LLC). Inks were poured into 10 mL syringes, inverted to remove the air bubble and loaded into the SDS-5 extruder print head. STL files were generated in OpenSCAD or AutoCAD and converted to G-code using Slic3r. Nozzle sizes ranged from 100 µm to 1.4 mm inner diameter (Nordson EFD), print speeds ranged from 0.1 to 20 mm/s and the tip-substrate height was kept between 50 and 800 µm depending on nozzle diameter. For this syringe-based printer, the flow rate is calculated by the product of the nozzle diameter, layer thickness, and print speed to dispense the proper volume. The scaling factor, Feed Rate %, was adjusted to further modify the flow rate for the range of shear rates tested. Salt coated substrates were prepared by spraying 0.1 M salt solutions with a fine mist spray bottle at a fixed distance from substrates heated on hot plate (see Methods Section 5.5 for calibration details). Substrates were cooled to room temperature before printing and could be stored for weeks prior to use. For patterning salt gelling agents on substrates, Pluronic F-127 (10 wt%) was added to 50 mM CaCl₂ or Na₂SO₄ solutions in a 1:1 ratio. These solutions were printed first on the substrate in a square meander pattern, with the PA solution immediately
following in the same pattern. For 3D printing of multilayer constructs, an aerosol spray gun (Master Airbrush SB80) was mounted on the print arm of the Hyrel printer in between printed layers. 0.1 M CaCl$_2$ solutions were sprayed manually at 10 kPa for 3 sec onto the previous printed layer at a height of 20 cm above the hydrogel construct, before printing the next layer. For these prints, an E3 pH 9 ink was used, with $\sim$20 µM methylene blue and $\sim$10 µM Congo red dyes added to aid in visualization.

**Material characterization**

Optical microscopy images were collected using a Leica DM750 P inverted light microscope in reflection mode with Leica Application Suite V4.2 software. POM was performed with the sample placed between two perpendicular light polarizers, and a stage that allowed for precise rotation of the samples. Images were collected with the sample oriented 0° and 45° to the polarizer using the same exposure time (see Methods Section 5.5 for birefringence ratio analysis). Optical profilometry was used to measure hydrogel filament and film thicknesses (Zygo 3D Optical Profiler and Bruker Contour GT-K). pH titration curves were collected at 1 mM PA concentration by first adding 5 mM NaOH (for E3 PA) or 5 mM HCl (for K3 PA) to fully charge the ionizable groups. Then different concentrations of either HCl for E3 or NaOH for K3 were added to individual Eppendorf tubes. Following annealing at 80°C for 30 minutes and slow cooling overnight, the pH of each sample was measured using a Mettler-Toledo pH meter. Optical density measurements on PA solutions were performed in a semi-micro 10 mm path length quartz spectrophotometer cell (Hellma) using a Shimadzu UV-1800 UV Spectrophotometer. Zeta potential measurements were recorded on a Malvern Zetasizer Nano ZSP spectrometer directly after bath sonication of each sample for 30 min to break up long fibers and decrease the effects of anisotropy and different viscosity solutions. Contact angle measurements were acquired using a Krüss DSA100 drop shape analyzer.
SEM imaging was performed on a Hitachi SU8030 SEM. Samples were prepared by solvent exchange from water to ethanol using a graded series. Following dehydration, samples were dried using critical point drying (CPD) and coated with 10 nm of osmium. TEM images were obtained using a Hitachi model HT-7700 electron microscope operating at 80 kV, equipped with an Orius SC 1000A camera. Plunge-freezing for cryogenic TEM samples was performed using a FEI model Vitrobot Mark IV. Samples were prepared from 1.5 wt% PA solutions that were diluted 10x (with the same pH and ionic strength as the sample) immediately before preparation and then placed on a lacey carbon grid (for cryo-TEM) or a carbon film grid (for conventional TEM). After blotting, uranyl acetate (1 wt%) was added on top of the grid to increase contrast of the nanostructures in conventional TEM.

All rheology experiments were measured on an Anton-Paar MCR 302 rheometer using cone-plate geometry. Viscosity flow curves were collected using a CP50-1 fixture. Careful consideration was taken to remove all bubbles and the samples were gently poured onto the bottom plate to minimize shear before measurement. Gel rheology was measured with a CP25-1 fixture, with 15 salt droplets (1 µL each) deposited uniformly on the top cone and 135 µL PA solution on the bottom plate. This mimics the gelation process during printing when PA solution contacts a salt-coated substrate. The ionic strength was kept constant for each salt species so that relative strength of crosslinking could be measured. The final salt concentrations for each gel were: 40 mM NaCl, 20 mM CaCl$_2$, 20 mM Na$_2$(SO$_4$), 13 mM AlCl$_3$, and 13 mM Na$_3$(PO$_4$).

X-ray scattering experiments were performed using beam line 5ID-D, in the DuPont-Northwestern-Dow Collaborative Access team (DND-CAT) Synchrotron Research Center at the Advanced Photon Source, Argonne National Laboratory. X-ray energy of 12 keV corresponding to a wavelength of 1.0332 Å$^{-1}$ was selected using a double-crystal monochromator. Data was collected simultaneously across three Rayonix detectors, model numbers SAXS – LX170HS, MAXS - LX170HS, WAXS – MX170HS. For studies of the nanostructures in solu-
tion, samples were oscillated with a syringe pump during exposure to prevent beam damage and obtain more uniform data. Samples containing 45 mM NaCl were also collected to perform background subtractions. For the SAXS alignment analysis, samples were prepared by printing 5 mm squares (1 layer thick) with an aligned filament fill pattern on salt-coated 7.5 µm thick Kapton films (Chemplex Spectromembrane) and allowed to air dry. Hydrated gel samples were also prepared by printing 2 layer thick, 5 mm squares onto 25 µm thick Kapton sheet (Dupont), isolated with an adhesive silicone spacer (Electron Microscopy Sciences) and a second Kapton sheet was placed on top to seal the chamber. Data was collected with the x-ray beam normal to the Kapton window (see Methods Section 5.5 for alignment analysis).

Electrical measurements

The ionic conductivity chamber was fabricated using photolithography on a Si wafer master chip. A 10 mm square test chamber with edge centered 1 mm square probe inlets was designed using AutoCAD. These dimensions were chosen to minimize edge effects and allow insertion of test probes without damaging the printed material’s structure. Piranha solution was prepared by mixing concentrated sulfuric acid (100 mL, Fischer Scientific) with 30% hydrogen peroxide (50 mL, Fisher Scientific). A 100 mm silicon wafer (University Wafers) was immersed in the piranha solution for 10 minutes and subsequently washed in DI water and dried with nitrogen. The cleaned and dried wafer was coated with S1813 (4 mL, Shipley) to a final thickness of 20 nm. Pre-exposure and post-exposure processing was performed according to the Data Sheet available from Shipley. The coated wafer was exposed using a maskless aligner (SF-100, Advanced Micro Patterning). The dimensions of features on the wafer were confirmed by optical profilometry (Zygo 3D Optical Profiler) prior to deep reactive ion etching (STS LpX Pegasus) to a depth of 80 µm. The wafer was placed in a vacuum chamber with trichloro(1H,1H,2H,2H-perfluorooctyl)silane (10 µL, Sigma-Aldrich) overnight to form a non-adhesive surface. Sylgard 184 elastomer base (20 g, Dow Corning)
was mixed with Sylgard 184 curing agent (2 g, Dow Corning) and the mixture was degassed under vacuum for 1.5 hours. The patterned master wafer was placed in an aluminum foil boat, and coated with the Sylgard mixture. The coated wafer was placed in an oven at 80°C for 2 hours. The cast was removed from the wafer and treated with an oxygen plasma (40 W for 5 min, SBT PC-2000) to render the surface hydrophilic. Then 0.1 M CaCl$_2$ was sprayed onto the base of the chamber with the remaining hydrophilic edges covered to allow for adhesion to a glass slide immediately after the peptide amphiphile materials were printed into the cast with 100 µm ID nozzle and 10 mm/s print speed. A 0.5 mm biopsy punch (World Precision Instruments) was used to make outlets on each side of the square, through which Au wire leads were inserted for connection to a Metrohm Autolab PGSTAT128N potentiostat equipped with a FRA32M module. Ionic conductivity was measured using EIS at 0 V vs. counter in a two-electrode set up with a 10 mV perturbation and frequencies ranging from 1 MHz to 10 Hz. The plateau on the Bode plot (where the phase is near 0°) was used as the impedance to calculate the conductivity after parameterizing for the geometry of the square channel.

Electronic conductivity of air dried CA films was measured after 1 mm x 1 mm x 50 nm Au pads were thermally evaporated through a shadow mask on top of printed and dropcast films on 300 nm thermal oxide Si wafers (University Wafer). For printed films, the shadow mask was aligned such that the electrodes were parallel to the direction of extrusion. A probe station was used to accurately place the contacts on the pads and voltage sweeps in the dark and with 0 V bias were performed (Signatone probe station, Agilent 4155C semiconductor parameter analyzer). The conductivity was calculated using the linear region of the I-V curve (voltage sweep from -1 to 1 V) and parameterized based on the channel length, electrode width and average film thickness in the channel. Optical profilometry was used to determine the thickness of each sample (Zygo 3D Optical Profiler).
Bioprinting studies and imaging

Murine myoblasts C2C12 were purchased from ATCC (ATCC CRL-1772). Cells were expanded in growth media consisting of Dulbecco’s Modified Eagle’s Medium with high glucose and L-glutamine (DMEM, ATCC 30-2002), 100 U/mL of penicillin and 100 µg/mL streptomycin (Gibco 15140-122) as well as 10% heat inactivated FBS (Gibco 10438-18). Media was changed every 2 days. When cell confluence reached 80%, C2C12 (passage 6) were sub-cultured using 0.25% Trypsin-EDTA (ThermoFisher, 25200056), and re-suspended in serum free medium at a density of $25 \times 10^6$/mL. To prepare the bio-ink for cell-laden constructs, annealed E3 PA solutions were prepared at 1.25 wt% with 150 mM NaCl, 4 mM KCl, and pH of 7.4. The PA solution was gently mixed with the cell suspension at 4:1 volume ratio to reach the final cell density at $5 \times 10^6$/mL. Cell laden constructs were printed using a Cellink BioX printer onto calcium chloride coated coverslips (18mm x 18mm) using a tapered 250 µm diameter nozzle (Nordson EFD) and printing speed of 20 mm/sec. The constructs were transferred into a sterile 12-well plate and cultured with 2 ml of growth media with refreshment every three days. After 7 days, the cell-laden constructs were gently washed with PBS (pH 7.4, Gibco 10010023), stained with 2 µM of Calcein AM (Invitrogen C3100MP) at 37°C for 15 minutes and visualized using a Nikon A1R confocal laser-scanning microscope. Images were captured with Large Image Acquisition of NIS-Elements, and further processed with OrientationJ, a plugin for ImageJ to analyze the local orientation of the cells within the construct. A minimum energy cutoff of 1% and minimum coherency cutoff of 0.1% was used to determine the orientation of every pixel based on the structure tensor.
Carreau fitting of PA ink flow curves

PA flow curves were fit using the Carreau model to quantify the rheological properties of each ink. In this model, the viscosity as a function of shear rate can be expressed as:

$$\eta(\dot{\gamma}) = \eta_\infty + (\eta_0 - \eta_\infty)(1 + (t\dot{\gamma})^a)^{(n-1)/a}$$ (3)

where $\eta_\infty$ is the infinite-shear viscosity, $\eta_0$ is the zero-shear viscosity, $t$ is the relaxation time, $a$ is a transition factor and $n$ is the shear thinning exponent. All fits started with initial guesses by manual fitting and then were allowed to converge between set limits for more accurate fits. Fit parameters for the flow curves in Figure 5.5 are included in Table 5.1.

Preparation of salt-coated substrates and calculation of salt concentration

To prepare reproducible salt coatings, we set up the salt spray bottle 30 cm from a hot plate covered with aluminum foil with clean substrates placed on top. For substrates used for printing, the hot plate was set to 70°C to rapidly dry the sprayed salt mist upon contact with the substrate and form small, uniformly-dispersed crystallites. We waited at least 10 seconds between sprays to allow for water evaporation and prevent salt water droplets from coalescing that would crystallize into large inhomogeneous salt chunks rather than a uniform coating. Upon cooling, the salt crystals would absorb moisture from the ambient air, but the distribution of salt on the surface remained uniform so long as the initial coating was prepared in small droplets as described above. All salt solutions were prepared at 0.1 M and between 1 and 10 sprays were used to coat substrates for evaluating the salt concentrations necessary for rapid gelation of printed filaments (see Figure 5.12).

To quantify the salt loading per area on coated substrates, we kept the hot plate at room temperature and weighed the amount of salt solution on substrates from 10 successive sprays immediately after spraying. This allowed us to achieve high enough weights to accurately
measure on a balance and back-calculate the salt concentration per spray. This setup was remarkably reproducible with an average salt solution loading of 359.4 ± 4.3 mg per 10 sprays (n = 5). Dividing by the substrate area and normalizing for the salt molarity in the solution, we found that the salt deposited per area per spray was 92.8 ± 1.1 nmol/cm². To achieve lower salt areal densities than this value for one spray, we lowered the salt concentration in the spray bottle to 10 mM or 50 mM. This allowed us to accurately calibrate the salt loading for different numbers of sprays and thereby analyze the optimal salt coatings for ionic-crosslinking of printed hydrogel filaments. From optical micrographs, the average width of printed filaments for each salt loading was calculated using ImageJ measurements from at least five regions on 3 different prints per condition.

**SAXS analysis of nanofiber alignment**

2D SAXS patterns were background subtracted and masked, and an azimuthal line cut was taken to measure the anisotropic alignment of the nanofibers. The azimuthal cut was taken from 0.65 < q < 0.85 nm⁻¹ to measure the Bragg peak at ~9 nm corresponding to the fiber-fiber distance in the dried state. The full-width at half maximum (FWHM) of the azimuthal cut was obtained by fitting a Gaussian curve after background subtraction for the range 0-120°. Printed samples were aligned with the extrusion direction along the 0° axis so intensity at 90° would be expected from scattering perpendicular to fiber axis.

**Birefringence ratio calculation**

Polarized Optical Microscopy (POM) was used to characterize the alignment of the printed filaments by comparing the intensity of the transmitted light when the sample was oriented 0° and 45° to the polarizer. Using ImageJ, the integrated density was measured where the filament was located at both angles (see Figure 5.20). The background integrated density was also measured for each and subtracted from the measured intensity in
the filament region. The birefringence ratio is given by the background subtracted intensity measured at 45° divided by the background subtracted intensity measured at 0°. This ratio was then normalized for filament thickness by multiplying by a thickness factor based on the average thickness for each condition measured in optical profilometry. Since all of the dried gels were between \( \sim 0.5-1.5 \) \( \mu m \) thick, we normalized to the thinnest gels that we measured such that taller samples would have a linearly scaled thickness factor less than one to account for the enhanced retardation with increasing thickness. Thus, the birefringence ratio can be expressed as:

\[
Birefringence \, Ratio = \frac{\text{Integrated density } 45^\circ - \text{background}}{\text{Integrated density } 0^\circ - \text{background}} \times \text{Thickness Factor}
\]  

(4)

We note that for materials with large thickness differences between samples that the thickness factor should include a cosine dependence term. This follows from the transmitted light intensity as a function of the rotation angle vs. the polarizer:

\[
I(\theta) = I_0 \left\{ a^2 \cos^4(\theta) + \sin^4(\theta) + \frac{a}{2} \left( \cos \left( \frac{2\pi t\Delta n}{\lambda} \right) \sin^2(2\theta) \right) \right\}
\]

(5)

where \( I_0 \) is the incident light, \( a \) is an experimental parameter, \( t \) is the thickness, \( \Delta n \) is the birefringence, and \( \lambda \) is the incident wavelength of the light. For relatively similar thin samples less than \( \sim 5 \) \( \mu m \), the transmitted light intensity varies roughly linearly.

**Preparation and printing of polymer-PA hybrids**

See publication for PA synthesis details.\(^{250}\) E3 PA and E3-ATRP PA were co-assembled in a 1:9 molar ratio as described above, but redissolved at a final concentration of 15 mg/mL before annealing. The annealed PA fibers were printed into 1 cm x 1 cm squares on CaCl\(_2\)-coated glass substrates using a Hyrel 3D System 30M printer. Substrates were prepared by first washing glass coverslips with milli\(\Omega\) water and drying on a hot plate at 70°C. The clean
and dry coverslips were then aerosol spray coated with 0.1 M CaCl$_2$ while still heated at 70°C, resulting in dispersed 10-50 µm CaCl$_2$ crystals at a surface density of $\sim$0.5 µmol/cm$^2$. The PA solution was extruded through a 0.41 mm inner diameter nozzle (Nordson EFD) and gelled immediately upon contact with CaCl$_2$, allowing for string hydrogels to be patterned into squares with varying print paths designed in Slic3r. The tip-to-substrate distance was approximately 200 µm, with a print speed of 10 mm/s and a flow rate of 0.42 µL/s. Typical gels were $\sim$1 mm thick and consisted of 3 or 4 printed layers, with salt introduced via aerosol spray between each subsequent layer. Following printing, the square gels were stored in a hydrated environment to prevent drying before polymerization. The printed PA hydrogels were polymerized using the molar ratios of DEGMA : OEGMA$_{500}$ : E3-ATRP : CuBr : Bpy : ascorbic acid of 14250:750:1:2:5:100. 1 monomer wt% of NBAA crosslinker and 0.5 monomer wt% fluorescein-O-methacrylate were also included in the polymerization solution.
Figure 5.30: 3D printed PA-polymer hydrogel sheets with varying print paths. (a) Print path for a uniaxially aligned three-layer sheet. (b) Optical microscopy of an aligned three-layer sheet, demonstrating strong birefringence when the sample is rotated 45° to the polarizer. (c) Print path for a square spiral three-layer sheet. (d) Optical microscopy on a corner of a square spiral three-layer sheet, showing bright birefringence at the point of the corner when the sample is at 0°, but a dark region at the corner point when the sample is rotated 45° to the polarizer. At the corner point, the fibers bend at ~45° to connect one edge of the square to the adjacent edge. (e) Print path for a cross-hatch four-layer square sheet. (f) Optical microscopy of a cross-hatch four-layer sheet, with birefringence extinguished at both 0° and 45° because the layers are oriented 90° to each other. Scale bars correspond to 400 μm.
Figure 5.31: LC-MS traces at 220 nm absorption of (a) C16V3A3E3 and (c, e) C16V3A3K3 for purity analysis. The mass spectra are obtained by integrating the ion counts from the full peak region in the LC-MS trace for (b) C16V3A3E3, (d) C16V3A3K3 at 140 kV, and (f) C16V3A3K3 at 80 kV.
Chapter 6

Biopolymer-Supramolecular Polymer Hybrids as Anisotropic Soft Semiconductors

6.1 Objectives and Significance

In the previous chapter we explored using 3D printing as a technique to build hierarchical structures from supramolecular building blocks in hydrogel materials. Here, we focus on the extension of 3D printing specifically towards chromophore amphiphile assemblies that have unique optoelectronic properties. By tuning the supramolecular interactions, we promote the assembly of nanofibrils with enhanced $\pi$-orbital overlap resulting in increased conductivity and hole mobility in thin films. While optoelectronically active, this material has very low viscosity and only forms weak gels upon ionic crosslinking, limiting the ability to achieve hierarchical structures from 3D printing. The addition of a biopolymer to the ink results in a higher solution viscosity and more robust gel formation, allowing for monodomain alignment of the nanofibrils during extrusion printing. Thin sheets of printed aligned filaments exhibit anisotropic electronic transport along the extrusion direction and show minimal degradation upon cyclic bending. This hybrid system combines the highly tunable electronic properties of supramolecular polymers with the robust mechanical properties of covalent biopolymers, resulting in soft semiconducting materials ideally suited for flexible and biologically compatible optoelectronic devices.
6.2 Background

The development of new bioelectronic materials, that can interface electronic signals with biological tissue, is of great interest for biomedical therapeutic and diagnostic devices. Aqueous based organic electronics offer an ideal bio-interface due to their reported biocompatibility and mechanical matching between the electronic component and biological environment. Supramolecular electro-active polymers are an attractive subset of organic electronics because they offer programmable structural and electronic properties, as well as long range order over multiple length scales. Supramolecular building blocks based on triarylamine and carbonyl-bridged triarylamine (CBT) aromatic cores, have demonstrated high conductivity and long-range energy transport in one-dimensional self-assembled nanofibers. To date, these studies have all focused on assembly in organic solvents for applications in electronic interconnects, nanophotonics and quantum information technology. A water-soluble CBT molecule with encoded interactions for aqueous self-assembly would open the possibility for use of these promising electro-active materials in biologically relevant environments. Our lab previously developed chromophore amphiphile (CA) molecules, with hydrophobic aromatic cores and peripheral hydrophilic charged groups, to drive assembly and crystallization of 1D and 2D nanostructures in water. These materials can form hydrogels upon ionic crosslinking and have demonstrated function as photosensitizers in light-driven catalysis. So far, however, CA materials have only been used in random hydrogel networks and it remains a challenge to achieve higher order structures that could enhance their function further.

Anisotropic hydrogels made with aligned bioelectronic materials could lower the detection limit in diagnostic devices by enhancing the conductivity or could direct cell outgrowth in combination with electrical stimulation in regenerative medicine. To generate anisotropy, previous studies on peptide based supramolecular materials, including some with electronic functional groups, have used shear forces during hand-drawn pipetting to align
anisotropic nanostructures in a hydrogel filament. However, this preparation method lacks the control necessary for precise positioning of the extruded filaments in three dimensions to fabricate functional architectures, and also suffers from heterogeneity along filaments and from filament to filament due to manual pipetting. Three-dimensional (3D) printing opens the possibility for fabricating programmed anisotropic hydrogels from asymmetric nanostructures by leveraging shear-induced alignment during extrusion and precise patterning of printed gel filaments with designed orientation and pore sizes.\textsuperscript{125,137,251} To achieve printable aqueous CA inks, solutions of the suspended nanostructures must have viscosities sufficiently above the aqueous solvent to control the flow accurately during extrusion and form robust self-standing hydrogels upon contact with a gelling agent. All of the CA molecules published to date have solution viscosities on par with water or form weak hydrogels with ionic crosslinkers hindering their use in 3D printing applications. In comparison, covalent biopolymers have found widespread use in 3D bioprinting applications due to the shear-thinning behavior during extrusion and high performance mechanical properties upon gelation.\textsuperscript{277–279}

Here, we describe the synthesis and self-assembly of new chromophore amphiphile molecules based on a CBT core for use as soft, conductive gels in flexible and biologically compatible electronic devices. First, we explore how tuning the supramolecular interactions effects the optoelectronic properties as well as hydrogel formation. Then we study the use of biopolymer additives in the CBT amphiphile solution to form hybrid biopolymer-supramolecular polymer inks for 3D printing robust soft electronic materials with hierarchical structures.

6.3 Results and Discussion

6.3.1 Aqueous CBT Amphiphile Self-assembly and Hydrogelation Properties

We first synthesized two CBT derivative molecules, one with an amide group in the carboxylate terminated arms (CBT-am, compound 1) and one with an alkyne group in the
same position (CBT-al, compound 2) (see Methods Section 6.5). Both compounds form ~5 nm diameter fibrils after dissolving in water and thermal annealing (80°C for 30 min in water bath, slow cool overnight), as observed in TEM imaging (Figure 6.1a, b). The assemblies have very different optoelectronic properties however. Compound 1 shows highly quenched fluorescence when assembled in water versus in the monomeric state in DMSO (Figure 6.1c). This behavior suggests co-facial \( \pi \) stacking in an H-aggregated state. In comparison, compound 2 shows only partial quenching and a distinct red shift in the emission spectrum for the assembled state in water versus the monomer in chloroform (Figure 6.1d). This is indicative of J-aggregates in a slipped stack arrangement. The hydrogen bonding motifs from the amide groups on compound 1 act as additional attractive forces and direct assembly of more aligned \( \pi \)-stacking interactions compared to compound 2. The different degrees of orbital overlap in these two systems also have a significant effect on the conductivity of the assemblies in thin film (Figure 6.1e). CBT-am shows over an order of magnitude higher conductivity than CBT-al both under illumination and in the dark. In a transistor geometry, both materials exhibited ambipolar transfer curves with slightly higher hole mobilities than electron mobilities (Figure 6.1f). Similar to the conductivity measurements, we observed roughly an order of magnitude higher hole mobility for the CBT-am films than the CBT-al films (0.194 cm\(^2\)/V·s vs. 0.0178 cm\(^2\)/V·s).

For fabrication of bioelectronic devices using 3D printing, the CBT assemblies must rapidly form robust hydrogels upon exposure to a gelling agent to lock the programmed spatial and orientational order. We chose CaCl\(_2\) as an ionic crosslinker due to its biocompatibility and robust gelling mechanism in other supramolecular hydrogels. Using oscillatory rheology, we measured the gelation properties of both CBT-am and CBT-al upon contact with CaCl\(_2\) (Figure 6.2a). Surprisingly, we found that the CBT-al nanofibrils formed robust gels immediately upon salt contact, while the CBT-am formed almost three orders of magnitude weaker gels. To investigate the difference, we imaged the crosslinked gels us-
**Figure 6.1:** Structure and optoelectronic properties of CBT amphiphile assemblies. (a, b) TEM images of molecular assemblies of 1 and 2, respectively. (c) Molecular structure and fluorescence emission spectra of 1 (10 µm) showing strong quenching due to formation of supramolecular assemblies ($\lambda_{\text{ext}}$ 440 nm). (d) Molecular structure and fluorescence emission spectra of 2 (10 µm) showing bathochromic shift in emission due to formation of supramolecular assemblies ($\lambda_{\text{ext}}$ 410 nm). (e) Electrical conductivity of thin films of 1 and 2 under light irradiation and in the dark. (f) Transfer curves of 1 and 2 with $V_{\text{sd}}$ = -1 V.

Scanning Electron Microscopy (SEM) and observed vast differences in gel morphology between the two CBT-derivatives (Figure 6.2b, c). CBT-al gels were composed of densely
intertwined thin fibrils while the CBT-am gels had thicker struts, composed of fibril bundles, with much more void space.

Figure 6.2: Hydrogel strength and microstructure for CBT amphiphile assemblies. (a) Storage and loss modulus as a function of time for CBT-am and CBT-al hydrogels ionically crosslinked with Ca\(^{2+}\). SEM images of hydrogels formed from (b) CBT-al and (c) CBT-am.

To test if the vast difference in mechanical strength was due to inherent material properties of each CBT assembly in the struts of the gels or due to the large difference gel microstructure, we performed nanoindentation measurements on CBT-am and CBT-al fibrils using Atomic Force Microscopy (AFM). We found that both materials had similar elastic moduli, indicating that the large difference in gel strength is governed by the large difference in crosslinking points between struts rather than any inherent mechanical property differences of the assemblies (Figure 6.3). The bundling of the CBT-am fibrils in the presence of Ca\(^{2+}\) led to thicker individual struts, but also much more void space and less crosslinking points between struts. In covalent polymer networks, it is well known that the network strength scales with the crosslinking density.

6.3.2 Extrusion Printing CBT Amphiphile Nanostructures

To build hierarchical structures of aligned CBT filaments, we extruded the aqueous CBT inks through thin nozzles onto CaCl\(_2\) coated substrates (Figure 6.4a). For effective 3D printing, the ink must have viscous flow characteristics to control extrusion of the printed
Figure 6.3: Nanomechanics of CBT amphiphile hydrogels. (a, b) AFM image and DMT modulus vs. height distribution of CBT-am fibrils. (c, d) AFM image and DMT modulus vs. height distribution of CBT-al fibrils.

material. We measured viscosity as a function of shear rate and found that both CBT-am and CBT-al inks exhibited Newtonian behavior with viscosities of \( \sim 1 \text{ mPa-s} \) across the range of shear rates applicable to 3D printing (Figure 6.4b). These values are not significantly different from the water solvent alone, and are too low for accurate extrusion printing.

Therefore, to increase the ink viscosity, we investigated the biopolymer alginate as an additive to our aqueous inks. By adding alginate in a 1:3 ratio with CBT, the ink viscosity increased by an order of magnitude and rendered the inks printable. We also found that alginate increased the gel strength of the hybrid inks upon contact with CaCl\(_2\) (Figure 6.5). While CBT-al fibrils already formed robust gels, the alginate additive was critical for forming robust gels with CBT-am. Since the hybrid gel strength was between the pure CBT-am and pure alginate, we expect that supramolecular fibrils and covalent polymer chains are interact-
Figure 6.4: 3D printing and flow curves of CBT inks. (a) 3D printing scheme for fabricating aligned gel filaments of CBT fibrils. (b) Viscosity flow curves for CBT-am and CBT-al with and without alginate.

With the addition of alginate to CBT-am, we observed string hydrogels with smooth edges and widths similar to the nozzle diameter from extrusion printing on CaCl₂ coated substrates. These gels also exhibited monodomain birefringence in polarized optical microscopy (POM), indicative of nanofibril alignment within the printed string gels (Figure 6.6). In comparison, CBT-amide inks alone formed smeared gels without global anisotropy, suggesting that the alginate is critical for aligning these materials. To test if only the alginate was causing the birefringence signal, we collected POM and SEM images of gels printed with 0.5 wt% alginate alone, the CBT/alginate ink and CBT alone. We found that only the combination of CBT with alginate led to reproducible thin filaments with monodomain alignment, suggesting a synergistic effect between the biopolymer and supramolecular polymer (vide infra).

We also explored extrusion printing the CBT-al inks with and without alginate. However, we found that in both cases the nozzle would frequently clog during extrusion (Figure 6.7a). This led to films that were heterogeneous (Figure 6.7b) and did not show any alignment in POM (Figure 6.7c). We observed that the clogging was due to gel formation at the nozzle tip that would drag and block the flow of more ink from the nozzle. Since these CBT inks have
very low viscosity, we were limited to very low flow rates to avoid over-extrusion. Therefore, if the gel that forms upon contact with the salt coated substrate is very strong, it will clog the nozzle because the flow rates are too low to push more material past it. From the rheology data in Figure 6.2, we see that the CBT-al gels are indeed quite strong even though solutions of CBT-al have very low viscosities. In contrast, the CBT-am/alginate gels form medium strength gels (Figure 6.5) and have medium viscosity, which allows for extrusion printing without clogging. Thus, we found that it is critical to match the ink viscosity with the gel strength in these ionically-crosslinked 3D printed systems.

Since the CBT-am assemblies had better electronic properties and printability when mixed with alginate, we focused on the development and characterization of the CBT-am/alginate hybrid ink. From the SEM images in Figure 6, we noticed a drastic difference in the gel morphology for the printed CBT-am/alginate ink compared to CBT-am alone. The thick bundles that we observe for Ca$^{2+}$-crosslinked CBT-am gels were not present when alginate was added to the ink. Instead, only single fibrils, indistinguishable from the alginate polymer chains, existed in the hybrid gels. Since TEM images without Ca$^{2+}$ show only single CBT-am fibrils, we hypothesize that Ca$^{2+}$ drives aggregation of fibril bundles. The amide

**Figure 6.5:** Storage modulus of hybrid alginate-CBT inks at 0.1% strain over a range of frequencies.
groups on CBT-am also likely play a role in lateral hydrogen bonding that could promote fibril-fibril bundling, while the CBT-al lacks this additional attractive interaction and does not bundle in the presence of Ca\(^{2+}\). To investigate how alginate inhibits bundling of CBT-am fibrils in the presence of Ca\(^{2+}\), we tested Mg\(^{2+}\) as a divalent ionic crosslinker that has less affinity for alginate binding (Figure 6.8). Interestingly, we found that in the presence of Mg\(^{2+}\), bundles were formed for the CBT-am/alginate hybrid and the pure CBT-am gels. Pure alginate did not form a solid gel, because the Mg\(^{2+}\) is too small to fit in the corru-
gated eggbox crosslinking structure necessary for rapid alginate chain crosslinking. This result suggests that divalent cations promote bundling of CBT-am fibrils, but that there is a competition for binding Ca\(^{2+}\) between supramolecular fibrils and covalent alginate chains. This competition leads to rapid Ca\(^{2+}\) crosslinking between the CBT-am fibrils and alginate chains instead of fibril-fibril bundling interactions. The resulting hybrid material is a solid solution mixture of the supramolecular and covalent polymers.

### 6.3.3 Anisotropic Soft Semiconducting Films

The synergistic effects that led to uniform mixing of the supramolecular and covalent components also promoted alignment of the nanostructures in the hybrid ink during extrusion printing. We measured the orientation of the \(\pi\) stacking peak using Wide Angle X-ray Scattering (WAXS) and compared the angular scattering intensity distribution for pure alginate, pure CBT-am and hybrid CBT-am/alginate printed gels (Figure 6.9). We observed no Bragg peaks or preferential scattering for alginate and only isotropic scattering of the \(\pi-\pi\) Bragg peak at 3.34 Å for pure CBT-am prints. In contrast, we saw a distinct orientation preference of the \(\pi-\pi\) peak along the direction of extrusion in the hybrid inks. This data
Figure 6.8: SEM images of Mg$^{2+}$ and Ca$^{2+}$ crosslinked gels composed of CBT-am alone, CBT/alginate hybrid and alginate alone.

corroborates the alignment observed in POM images in Figure 6.6 and further verifies that the $\pi$ orbitals are oriented in the same direction as the aligned columnar assemblies.

By programming anisotropic structure in the hybrid material via extrusion printing, we obtained anisotropic charge transport in printed xerogel films. We measured the conductivity parallel and perpendicular to the extrusion direction and found an anisotropy ratio of 76.2 (parallel: 9.5 mS/m, perpendicular: 0.13 mS/m), while spun-coat films had isotropic conductivity values of 1.6 mS/m (Figure 6.10a). Alginate films alone had conductivities $\sim$0.0048 mS/cm, indicating that the primary charge transport in the CBT xerogels is electronic rather than ionic. The enhanced conductivity under illumination due to increased charge carriers also suggests electronically dominant transport through $\pi$ stacks rather than ion hopping along the CBT fibrils and alginate chains. In transistor measurements, we also observed approximately an order of magnitude increase in the hole mobility for the aligned hybrid in the parallel vs. perpendicular direction (Figure 6.10b). This type of anisotropic
Figure 6.9: (a) 2D WAXS scattering profiles of alginate, CBT and CBT/alginate hybrid printed structures. In CBT samples the sharp peak at 3.34 Å corresponds to the $\pi$-stacking distance. (b) Azimuthal line cuts from 1.8-2.0 Å$^{-1}$ of the 2D patterns in (a).

transport could be beneficial for lowering the detection limit in biosensor devices or for more efficient and directed electrical signaling in bioelectronic therapeutic systems.

Finally, we investigated the mechanical durability of the printed films on flexible poly(ethylene terephthalate) (PET) substrates. We printed both the hybrid ink and CBT-am alone and measured the conductivity as a function of bending cycle over a radius of curvature of 1.6 mm. For the CBT-am films, we observed a sharp decrease in conductivity over 100 cycles while the hybrid ink showed no decrease in conductivity over 1000 cycles (Figure 6.11a). Optical micrographs after bending showed large crack formation in the CBT-am films while the hybrid films showed no signs of degradation, which is likely the cause of the drastic conductivity decrease in the CBT-am films (Figure 6.11b, c). We note that the water content in both xerogels is approximately 10 wt% by Thermogravimetric Analysis (TGA) (Figure 6.12) which does not explain the large difference in durability for
Figure 6.10: Anisotropic electronic transport properties in printed hybrid films. (a) Conductivity parallel and perpendicular to the printing direction of printed CBT-am/alginate hybrid films under illumination and in the dark. (b) Transfer curves of printed CBT-alginate films in the parallel and perpendicular direction of alignment in a transistor geometry.

The hybrid films. Instead, we hypothesize that the covalent alginate chains can extend to accommodate strain during bending. The intermolecular Ca\(^{2+}\) crosslinking points may allow for stress dissipation from the brittle supramolecular polymer to the more ductile covalent polymer in the hybrid system. We note that alginate xerogels alone also exhibit ductility during bending so this mechanical stability is largely driven by the covalent polymer.

6.4 Conclusion

We demonstrated that the combination of bottom-up self-assembly with additive manufacturing techniques is a powerful platform for fabricating hierarchical bioelectronic materials with unique functions. The presence of a hydrogen bonding motif to the electro-active CBT amphiphile building block promoted assembly of H-aggregated \(\pi\) stacks in nanofibril assemblies with enhanced electron transport properties. By adding the biopolymer alginate to suspensions of CBT nanofibrils, we increased the viscosity and gel strength which allowed for shear alignment of the nanostructures during extrusion printing. Films composed of
Figure 6.11: Conductivity during cyclic bending of CBT and CBT-hybrid films. (a) Normalized conductivity as a function of bending cycle for CBT and CBT/alginate xerogel films. Optical micrographs after 1000 bending cycles of (b) CBT/alginate hybrid films and (c) CBT-am film. The light squares are the evaporated Au electrodes. Cracks are visible in the channels between the electrodes, indicating that the cracks are generated in the CBT film rather than only in the thin Au pads.

Figure 6.12: TGA of CBT and CBT-hybrid xerogels with 5°C/min ramp rate. At 200°C, the water is loss is approximately 13% for CBT-am and 10% for CBT-am/alginate.

aligned hybrid gel filaments exhibited anisotropic electronic properties programmed by the printing direction, as well as strong mechanical durability during cyclic bending. This hybrid
system highlights the synergy between electro-active supramolecular polymers and robust covalent biopolymers that results in soft semiconducting materials for potential applications in bioelectronic devices and therapies.

**6.5 Materials and Methods**

**Synthesis of CBT Derivatives: CBT-amide**

![Figure 6.13: Synthesis of Compound (1) 2,6,10-Tris(6-carboxylhexylamide)benzo [1,9] quinolizinono[3,4,5,6,7-defg]acridin-4,8,12-tirone.](image)

*O,O’,O”-amino-tribenzoic aide-trimethylester:*

The Ullmann coupling which yields the starting point for scheme 1 was adapted from Venkataraman et al. Briefly, a 250 mL round bottom flask was charged with methyl antranilate (6.48 mL, 50 mmols), methyl 2-iodobenzoate (26.64 mL, 125 mmols), K$_2$CO$_3$ (20 g, 145 mmols), Cu powder -150 mesh (0.5 g), CuI (0.75 g) in diphenylether and the solution was purged with N$_2$ for 15 minutes. The mixture was then stirred and heated at 185°C for 48 hours after which the solvent was distilled away under reduced pressure at 120°C. The solid was dissolved in DCM filtered through Celite to remove the K$_2$CO$_3$ and copper species. Compound was rotovaped and resuspended in a mixture of 3:1 hexane/ethyl acetate. Note: sonication leads to a large amount of solid to precipitate. This solid was filtered and turned out to be the desired compound. The rest of the solution was passed through a silica column and the rest of the triphenyl-amine was collected. Note: there may
be a fair amount of diphenyl amine which can be collected on the column. Product Yield: 50%.

\[ \text{\^{1}H NMR (499 MHz, DMSO-}d_6\text{)} \delta 7.50 (dd, J = 7.7, 1.6 \text{ Hz, } 3\text{H}), 7.44 (td, J = 7.7, 1.7 \text{ Hz, } 3\text{H}), 7.15 (td, J = 7.6, 1.1 \text{ Hz, } 3\text{H}), 6.93 (d, J = 8.2 \text{ Hz, } 3\text{H}), 3.26 (s, 9\text{H}). \]

\[ \text{\^{13}C NMR (126 MHz, DMSO-}d_6\text{)} \delta 166.91, 146.13, 132.18, 130.50, 127.25, 126.04, 123.58, 51.32. \]

**Benzo[1,9]quinolizinoo[3,4,5,6,7-defg]acridin-4,8,12-tirone:**

Carbonyl bridged triarylamine (CBT) ring closure was also adapted from Venkataraman et.al. Deprotection of the trimethylester was carried out as follows. 1 gram of the trimethylester was added to a 250 RBF with 50 mL of ethanol, water and 1.2 grams of NaOH. The mixture was stirred and heated at 70°C for 5 hours followed by precipitation in 300 mL of 1 M HCl. The solid triacid was then filtered and dried in an oven overnight. The next day 750 mg (2 mmols) of the triacid was dissolved in 10 mL of DCM (dried on a solvent still with calcium hydride), with 10 drops of DMF (dried on a solvent still with calcium hydride), and 1.4 ml (19 mmols) of SOCl\textsubscript{2}. The solution was stirred and heated at 50°C for 2 hours at which point 18 mmols of SnCl\textsubscript{4} was added and the solution was held at temperature for another 18 hours. The next day the reaction mixture was poured into 100 mL of 1M HCl and stirred for 1 hour. The product was then filtered, and then stirred in 1M NaOH for another hour. Finally the solid was filtered and washed with 500 mL of water. Yield 75%.

\[ \text{\^{1}H NMR (499 MHz, 10% TFA-}d, \text{Chloroform-}d\text{)} \delta 9.19 (d, J = 7.7, 0.6 \text{ Hz, } 6\text{H}), 8.05 (t, J = 7.7, 0.6 \text{ Hz, } 3\text{H}). \]

\[ \text{\^{13}C NMR (126 MHz, 10% TFA-}d, \text{Chloroform-}d\text{)} \delta 178.65, 138.39, 137.02, 127.21, 123.12. \]

**2,6,10-triamino-benzo[1,9]quinolizinoo[3,4,5,6,7-defg]acridin-4,8,12-tirone:**

A new nitro reduction procedure was developed to improve isolated yields which can be difficult to achieve due to the work up in method by Schmidt et. al. Para nitration was
accomplished by adding the bare CBT (1.5 g, 4.64 mmol) to 40 mL of H₂SO₄, stirring until fully dissolved. KNO₃ (2.11 g, 20.8 mmol) was added and the solution was stirred at r.t. for 1 h followed by subsequent heating to 70°C for 15 hours. The reaction mixture was cooled to r.t. and poured into 250 mL cool water. The yellow precipitate was filtered off and washed excessively with water and EtOH. After drying in air the desired trinitro CBT intermediate was obtained as a yellow solid. To reduce the nitro groups 610 mg (1.33 mmols) of the nitro CBT was powdered and added to a 250 mL RBF with 60 mL of ethanol. Separately, 1.12 grams of HNaS H₂O (20 mmols) was dissolved in 5 mL of water and then added to nitro CBT suspension. A successful reaction should be immediately noticeable by a yellow to purple color change. The mixture was then stirred and heated at 65°C for 16 hours. The solution was cooled to room temperature and centrifuged to yield a deep purple pellet and a yellow supernatant. The pellet was then washed with 9:1 EtOH/2M HCl (5x) and then EtOH (5x) and finally with ether (2x). The compound was then placed in a drying oven at 100°C.

¹H NMR (499 MHz, DMSO-d₆) δ 8.096 (s, 6H), 6-4.5 (s, 6H).

¹³C NMR (126 MHz, DMSO-d₆) δ 175.70, 144.22, 128.95, 123.39, 118.41.

2,6,10-Tris(6-carboxylhexylamide)benzo [1,9] quinolizino[3,4,5,6,7-defg]acridin-4,8,12-tirone (1):

The triamino CBT (200 mg, 0.54 mmols) was dissolved in 20 mL NMP (dried with 3Å molecular sieves) with 650 µL of DIPEA (dried on a solvent still with calcium hydride) and purged with N₂ 10 minutes. Then methyl adipoyl chloride (425 µL, 2.72 mmols) was added under N₂ causing the solution to rapidly turn from a purple color to a brown yellow and the mixture was stirred and heated at 60°C for 36 hours. After, the solution was cooled to room temperature and poured into 0.2 M HCl (150 mL) where a rusty orange solid formed. This solid was filtered, washed with 500 mL of water and then dissolved in DCM/methanol and rotovapped. The compound was then loaded onto a silica column in 1% methanol/DCM.
The solvent was slowly increased to 5% methanol in DCM to remove the target compound. It can take a while to elute the target compound so be patient. 150 mg (0.19 mmols) of the column product (methylester protected) was added to a 250 RBF with 40 mL of THF and 20 mL of water. 150 mg (3.8 mmols) of NaOH was then added and the solution was stirred and heated at 60°C for 4 hours. After, the mixture was poured into 150 mL of 0.5 M HCl and the precipitate that formed was filtered, and washed with 500 mL water. The final compound can be collected by dissolving in DCM/methanol and used without further purification. Yield 45%.

$^1$H NMR (499 MHz, DMSO-$d_6$) $\delta$ 12.04 (s, 3H), 10.47 (s, 3H), 8.88 (t, 6H), 2.43 (t, $J = 7.1$ Hz, 6H), 2.29 (t, $J = 7.2$ Hz, 6H), 1.68 (p, $J = 7.7$ Hz, 6H), 1.60 (p, $J = 7.7$ Hz, 6H).

$^{13}$C NMR (126 MHz, DMSO-$d_6$) $\delta$ 175.00, 174.35, 171.55, 136.60, 132.07, 122.71, 122.61, 36.13, 33.45, 24.44, 24.17.

HRMS (ESI-TOF-MS): Expected $m/z$: (752.2349). Observed $m/z$: (753.2402) (M+H)$^+$, (751.2212) (M-H)$^-$.

**Synthesis of CBT Derivatives: CBT-alkyne**

![Synthesis of CBT Derivatives](image)

**Figure 6.14:** Synthesis of Compound (2) 2,6,10-Tris(7-carboxylhept-1-yne) [1,9] quinolizino[3,4,5,6,7-defg]acridin-4,8,12-tirone.

**P,P’,P”-trisiodo-O,O’,O”amino-tribenzoic aide-trimethylester:**

Iodination was carried out using a different method than prescribed in the literature. In our hands, the method given by Chen. et Al$^{282}$ yielded a mixture of the mono, di,
and tri-iodo species. Common yield of the tri-iodo ranged from 30-50%. Our method is as follows, a 250 mL RBF was filled with 1 g (2.36 mmols) of O,O',O''amino-tribenzoic aide-trimethylester, 2 g (8.85 mmols) of N-Iodosuccinimide, 56 µL (0.7 mmols) of TFA, and 60 mL of acetonitrile. The mixture was stirred and heated at 85°C (reflux) for 15 hours. After cooling to room temperature, the mixture was poured into 250 mL of water, filtered, and washed with an additional 500 mL of water. A silica column was run in 2:1 hexane/ ethyl acetate. Yield 85%.

\[ \text{H NMR (499 MHz, Chloroform-}d\text{)} \delta 7.91 \text{ (s, 3H), 7.65 (d, J = 8.6 Hz, 3H), 6.77 (d, J = 8.6 Hz, 3H), 3.44 (s, 9H).} \]

\[ \text{C NMR (126 MHz, Chloroform-}d\text{)} \delta 165.67, 145.86, 141.27, 139.65, 129.38, 127.76, 87.19, 52.24. \]

**2,6,10-trisiodo-benzo[1,9]quinolizino[3,4,5,6,7-defg]acridin-4,8,12-tirone:**

Trisiodo CBT ring closure was performed similar to above. Note the kinetics for each reaction step appear slower compared to the iodine free compound. Deprotection of the trisiodo-trimethylester was carried out as follows. 1 gram of the trisiodo-trimethylester was added to a 250 RBF with 50 mL of ethanol, water and 1 gram of NaOH. The mixture was stirred and heated at 70°C for 15 hours followed by precipitation in 300 mL of 1 M HCl. The solid trisiodo-triacid was then filtered and dried in an oven overnight. The next day 250 mg (0.33 mmols) of the trisiodo-triacid was dissolved in 10 mL of DCM (dried on a solvent still with calcium hydride), with 10 drops of DMF (dried on a solvent still with calcium hydride), and 225 µL (2.98 mmols) of SOCl₂. The solution was stirred and heated at 50°C for 4 hour at which point 5 mmols of SnCl₄ (from 1M SnCl₄ in DCM) was added and the solution was held at temperature for another 36 hours. The next day the reaction mixture was cooled to room temperature, filtered, and washed with DCM to yield a yellow solid. The product was then stirred in 1M NaOH for one hour. Finally, the solid was filtered and washed with 500 mL of water. Yield 50%.
2,6,10-Tris(7-carboxylhept-1-yne)benzo [1,9]quinolizino[3,4,5,6,7-defg]acridin-
4,8,12-tirone (2):

Coupling of the alkyne arms was adapted from work by Mullen et.al. Trisiodo-CBT (50 mg, 0.071 mmols), methyl-6-heptyneoate (100 µL, 0.355 mmols), CuI (5 mg), and [PdCl₂(pph₃)₂] (10 mg) were added to a 100 mL Schlenk flask with 3 mL of DIPEA and 9 mL of toluene (both dried on a solvent still with calcium hydride). The mixture was purged for 15 minutes with N₂, followed by stirring and heating to 70°C for 18 hours while covered with foil (desired compound can photobleach). The reaction was then cooled and 50 mL of DCM was added. The solution was then filtered through a silica plug. The excess solvent was then rotovaped to dryness and the remaining solid was dissolved in a minimum amount of DCM (~1 mL). 40 mL of hexane was then added and a yellow precipitate formed and was centrifuged. This procedure was repeated 3 times. The compound was then purified on a silica column using a 5% methanol/DCM mixture. If the compound remains impure by NMR recycle gel permeation chromatography (Japan analytical industry NEXT recycling preparative HPLC. JAIGEL 1H and 2.5H columns) was employed to further purify. The column product (methylester protected) (150 mg, 0.20 mmols) was added to a 250 RBF with 40 mL of THF and 20 mL of water. NaOH (150 mg, 3.8 mmols) was then added and the solution was stirred and heated at 55°C for 4 hours (covered in foil). After, the THF was stripped on a rotary evaporator and the mixture poured into 150 mL of 0.5 M HCl where a yellow precipitate formed. The solid was collected by centrifugation and washed with 30 mL water (4x). The pellet was then suspended in 4 mL of 1:1 DCM/methanol before being precipitated again in 36 mL of hexane followed by centrifugation (5x). Yield 65%.

¹H NMR (499 MHz, DMSO-d₆) δ 12.07 (s, 3H), 8.42 (s, 6H), 2.59 (t, J = 6.8 Hz, 6H), 2.35 (t, J = 7.1 Hz, 6H), 1.79 – 1.64 (m, 12H).

¹³C NMR (126 MHz, DMSO-d₆) δ 174.81, 174.32, 136.10, 135.80, 123.11, 121.50, 94.81, 78.31, 33.64, 27.90, 24.37, 19.04.
HRMS (ESI-TOF-MS): Expected $m/z$: (695.2156). Observed $m/z$: (694.2083) (M-H) $^-$. 

**Material Preparation**

CBT solutions were prepared at 1.5 wt% in Mili-Q water and solubilized with 1.5 mol equivalents of NaOH for CBT-amide and 3 mol equivalents for CBT-alkyne. Solutions were sonicated until all solid material was dissolved and then annealed at 80°C for 30 minutes and slow cooled overnight. Hybrid CBT inks were prepared in the same way as the pure inks except they were prepared at 2 wt% CBT and then mixed with 2 wt% sodium alginate in a 3:1 ratio for a final concentration of 1.5 wt% CBT and 0.5 wt% alginate.

**Material Characterization**

TEM imaging was performed on a JEOL 1230 microscope, operating at 100 kV. A 6.5 µL droplet of CBT solution was placed on the carbon side of a TEM grid (CF300-Cu, Electron Microscopy Science). The solution was allowed to rest for 1 minute before being wicked away and allowed to dry for another 3 minutes. The same method was then used for a wash step with water, a staining step with urinal acetate (1 wt%), and final wash step with water. Images were recorded using a CCD camera.

SEM images were collected on a Hitachi SU8030 SEM. After gelation, samples were prepared by direct solvent exchange from water to ethanol without using a graded series. This reduced leaching of the CBT molecules into the ethanol solution. Following dehydration, samples were dried using critical point drying (CPD) and then coated with 5 nm of osmium.

Absorbance spectroscopy on CBT solutions (20 mM) was performed in a 0.05 mm path length, closed demountable quartz spectrophotometer cell (Starna Cells) using a Shimadzu UV-1800 UV Spectrophotometer. Fluorescence emission and excitation spectra were collected on CBT solutions using an ISS PC1 spectrofluorimeter in a 1 cm quartz cuvette. Monomer fluorescence data was collected on the methylester protected species in good or-
ganic solvents (CHCl$_3$, DMSO). For the assembled states, samples were prepared at 20 mM in water and diluted to 10 µM directly before the fluorescence spectra were recorded. It is important to not allow samples to stand at low concentration for too long as the aggregation state is likely to change over time in such a dilute regime.

All rheology experiments were measured on an Anton-Paar MCR 302 rheometer using cone-plate geometry. Viscosity flow curves were collected using a CP50-1 fixture. Gel rheology was measured with a CP25-1 fixture, with 15 salt droplets (1 µL each) deposited uniformly on the top cone and 135 µL CBT solution on the bottom plate. This mimics the gelation process during printing when the ink contacts a salt-coated substrate.

Optical microscopy images were collected using a Leica DM750 P inverted light microscope in reflection mode with Leica Application Suite V4.2 software. POM was performed with the sample placed between two perpendicular light polarizers, and a stage that allowed for precise rotation of the samples. Images were collected with the sample oriented 0° and 45° to the polarizer using the same exposure time (see Supporting Methods for birefringence ratio analysis). Optical profilometry was used to measure hydrogel filament and film thicknesses (Zygo 3D Optical Profiler and Bruker Contour GT-K).

X-ray scattering experiments were performed using beam line 5ID-D, in the DuPont-Northwestern-Dow Collaborative Access team (DND-CAT) Synchrotron Research Center at the Advanced Photon Source, Argonne National Laboratory. X-ray energy of 12 keV corresponding to a wavelength of 1.0332 Å$^{-1}$ was selected using a double-crystal monochromator. Data was collected simultaneously across three Rayonix detectors, model numbers SAXS – LX170HS, MAXS - LX170HS, WAXS – MX170HS. For studies of the nanostructures in solution, samples were oscillated with a syringe pump during exposure to prevent beam damage and obtain more uniform data. For the WAXS $\pi$ stacking alignment analysis, samples were prepared by printing 5 mm squares (1 layer thick) with an aligned filament fill pattern on
salt-coated 7.5 µm thick Kapton films (Chemplex Spectromembrane) and allowed to air dry before measurement.

**Direct Ink Writing**

All prints were carried out on a Hyrel System 30M printer (Hyrel LLC). Inks were poured into 10 mL syringes, inverted to remove the air bubble and loaded into the SDS-5 extruder print head. STL files were generated in OpenSCAD or AutoCAD and converted to G-code using Slic3r. All prints used 100 µm inner diameter nozzles (Nordson EFD) except for the pure CBT-amide ink, which used a 210 µm ID nozzle. The print speed was set to 10 mm/s for all prints and the tip-substrate height was kept between 50 and 100 µm depending on nozzle diameter. For this syringe-based printer, the flow rate is calculated by the product of the nozzle diameter, layer thickness, and print speed to dispense the proper volume. The scaling factor, Feed Rate %, was adjusted to 0.275 to lower the flow rate for controlled extrusion and the pulses per nL were set to 0.58. All substrates were prepared by first washing with isopropanol, and then UV-ozone treated for 20 minutes. The substrates were then immediately sprayed with 0.1 M CaCl$_2$ solution using a fine mist spray bottle at a distance of 30 cm, while the substrates were heated at 80°C on a hot plate. The approximate salt concentration on the surface was 0.93 µg/cm$^2$. All substrates were freshly prepared before printing.

**Electrical Measurements**

Electronic conductivity of dried CBT films was measured after 50 nm thick Au pads were evaporated on printed and dropcast films on 300 nm thermal oxide Si wafers (University Wafer). For printed films, the shadow mask was aligned such that the electrodes were parallel to the direction of extrusion. A probe station was used to accurately place the contacts on the pads and voltage sweeps in the dark and light with 0 V bias were performed. The slope
of the IV-curve from -1 to 1 V was used as the resistance for the conductivity calculation, \( \sigma = \text{area}/(\text{resistance} \times \text{length}) \). To measure the mobility of the printed films, a series of source biases were applied, the gate voltage was swept from -50 to 50 V and the source-drain current was measured. The slope of this plot was taken in the linear region (far from the threshold voltage) on each side of the transfer curve to get the hole and electron mobilities. The following equation was used: 

\[
\mu_h = \frac{\text{slope} \times \text{length}}{\text{width} \times C_{ox} \times V_s},
\]

where \( C_{ox} \) is the gate capacitance and \( V_s \) is the source bias. For all measurements the width was 113 \( \mu \)m and the length of the channel was 20 \( \mu \)m.

Cyclic bending tests were performed on CBT-amide and hybrid inks printed into 1 layer thick, 1 cm squares on PET substrates. Samples were bent with a custom attachment to the 30M printer arm as the build platform moved laterally with the film under constant tension. The attachment housed a rod with a radius of curvature of 1.3 mm that applied a 7% bending strain during testing. The bending motor operations were manually written in GCode using the Python package, gcody (https://github.com/rtZamb/gcody).
Chapter 7
Summary and Future Outlook

The work in this thesis used a combination of molecular self-assembly and additive manufacturing to develop materials that mimic aspects of the structural hierarchy found in nature. Generating anisotropy in the soft and hybrid structures described here led to enhanced function for targets in energy and medicine. These studies lay the foundation for future work on rational design of small molecules for hybrid energy materials and 3D printing of supramolecular hydrogels.

7.1 Hybrid Nanostructures for Energy Conversion and Storage

7.1.1 Hierarchical Electrodes for Energy Storage Devices

The studies on hybrid supercapacitor electrodes in Chapter 2 highlighted the utility of hierarchical electrode structures with high surface area. In comparison to flat films made of the same material, films composed of nanotubes oriented perpendicular to the current collecting substrate exhibited three times higher energy storage capacity. The amphiphilic organic molecule that drove curling of the organic-cobalt hydroxide layers into nanotubes contained a pyrene hydrophobic component that could π-stack while also maintaining water solubility. Experimentally, organic molecules with small changes to the structure did not induce curved layers or formation of nanotubes. Therefore, it would be interesting to use computer simulations to model the conformations that occur at the electrode interface during electrodeposition to help elucidate the origin of nanotube formation.
From a device performance perspective, the charge storage capacity, rate capability and fade rate could all be improved with the addition of a supplemental electronically conductive phase. This would allow for more uniform charging and utilization of the electrodeposited material, while limiting overcharging and degradation in less conductive regions of the electrode. Possible conductive additives could include graphene sheets or conducting polymers, which could be added during or after electrodeposition.

In general, supercapacitors based on cobalt hydroxide electrodes with alkaline electrolytes are less promising for future energy storage devices than high-rate lithium-ion or solid-state batteries. This is primarily due to the inherent instability of cobalt hydroxide in the alkaline environments necessary for redox function, as outlined in Chapter 2. However, using organic molecules to template hierarchical structures could be applied to other more promising electrode materials like lithium iron phosphate or lithium titanate. These electrodes typically operate in organic solvents so the solubility of the organic template must also be considered.

7.1.2 Rational Design of Hybrid Perovskites for Solar Energy Conversion

In Chapter 3, a series of organic cations with aromatic cores were synthesized and incorporated into layered lead iodide perovskite crystals. Organic molecules with intramolecular hydrogen bonding minimized distortion of the inorganic lattice which decreased the band gap in these $n = 1$ perovskites. Further, edge-to-face interactions between the organic cations in the galleries led to enhanced out-of-plane conductivity which is critical since the semiconducting layers are typically isolated due to their orientation parallel to the substrate. The modifications to the organic constituents in the hybrid perovskite resulted in the highest power conversion efficiency reported for chemically stable layered perovskites to date. Future studies could investigate strategies to promote face-to-face $\pi$-stacking which would be expected to achieve higher out-of-plane conductivity than the edge-to-face interactions. The
use of bola-amphiphilic cations or molecules with kinked linkers may encourage the face-on stacking in the gallery. Other interesting experiments could target the crystallization process during spin coating for thin film devices. By designing organic cations that promote faster or slower crystallization, the perovskite crystal grain size could be controlled. Larger grains with fewer defects would be expected to result in higher efficiency devices.

### 7.1.3 Bio-inspired Mineralization for Soft Electronics

The pathway dependence for Au metallization on PA nanofiber templates was highlighted in Chapter 4. By using a direct metallization approach with Au salts compared to attachment of ligand-capped Au nanocrystals to PA fibers, the sheet resistance for thin films dropped by several orders of magnitude. The citrate ligand shell forms a resistive layer between crystals that restricts Au nanocrystal decorated PA fibers from applications where electronic conductivity is desired. This material may still be useful for plasmonic devices, particularly if the supramolecular template provides additional hierarchical order. Efforts to remove the ligand shell of the Au nanoparticles using plasma treatment were unsuccessful without ablating the PA fiber templates concurrently, which would result in isolated Au islands. Shorter plasma treatment times did work to successfully decrease the resistance for the mineralized Au nanofibers suggesting that lower plasma doses result in sintering of the nucleated Au particles.

While the sheet resistance was reduced enough to pass current in basic circuits, it is still about an order of magnitude higher than commercial transparent conducting electrodes. To reduce the sheet resistance further, a systematic study of the percolation threshold and fiber-fiber junction resistance would be useful. Other routes for ‘nano-welding’ the deposited particles and metallized fibers, such as pulsed laser annealing or moderate thermal annealing, could also work and allow for better conductivity. Another key area for development is enhancing the adhesion of the mineralized films to their substrates. By rubbing the surface
of the Au-PA films, a noticeable amount of material can be removed. For application in flexible electronics and touch screens, the conductive coating must be more robust. One way could be to test specific surface coatings that covalently bind the PA fibers to the substrate prior to metallization. Alternatively, a bifunctional linker could be designed to bind the post-metallized Au fibers with thiol chemistry and the substrate with a second specific functional group. One last area for improvement is optimizing the spray coating procedure to achieve uniform films over a large area. For this work, only the edges of the sprayed area were used since they had a thinner and more disperse coating, which wasted over half of the deposited material. An automated aerosol spray system with rastering may aid in limiting the wasted material.

7.2 3D Printing Hydrogels for Energy and Medicine

7.2.1 Programmed Electronic Transport, Pore Size and Additives for Energy Gels

In Chapters 5 and 6, 3D printing of supramolecular hydrogels was utilized to generate anisotropic ion and electron transport. The electronically conductive chromophore amphiphile (CA) assemblies showed increased conductivity and mobility in the direction of shear-alignment, and when alginate was added, mechanical durability during bending. This combination of properties offers promise for use of CA xerogels as semiconductors in flexible electronics and biosensor applications. For biosensors, the next step would be to combine the semiconducting CA component with a bio-recognition element (BRE). The BRE could be a peptide sequence, an aptamer or an antibody that specifically binds target analytes. Upon binding, the electronic properties of the semiconductor would be expected to change, and an electrical readout could be obtained by measuring changes in the transfer or output curve in transistor measurements. Encapsulating carbon nanotubes inside PA fibers could
be another way of producing conductive hydrogels, and these could also be shear aligned with 3D printing.

The 3D printing strategies outlined in this work could also be used for fabricating photocatalytic gels with programmed pore size and diffusion lengths. By using additives to make the CA inks self-standing, 3D shapes with defined filament thicknesses and space between filaments could be printed and optimized for light absorption and reactant diffusion in photocatalytic applications. Using ink additives that form thixotropic yield stress fluids would be an important step to move past the ionic crosslinking strategy studied in this work. This would allow for faster and more accurate 3D printing by obviating the need to deposit salt between layers. Possible additives could include laponite nanoclay particles, Pluronic-F127 block copolymer, or gelatin. These gels could be ionically-crosslinked post-printing to add strength as well.

7.2.2 3D Architectures for Regenerative Medicine and Therapeutics

The printed PA bioink in Chapter 5 demonstrates the feasibility of patterning hydrogels with aligned PA fibers to direct cell outgrowth. However, one critical area for improvement for PA gels is the mechanical and handling properties of the printed constructs. For most applications in the clinic, the patterned gels will need to be robust enough for handling by surgeons and for staying in the defect site. Adding biocompatible, elastic filler components like cross-linked collagen or hyaluronic acid particles could enhance the mechanical integrity. The development of more robust bioinks would allow for printing of more intricate structures with programmed vascularization for enhanced diffusion of nutrients. These types of bioinks would be useful in a number of regenerative medicine applications from printing multi-material osteochondral plugs to filling volumetric tissue loss. 3D printed constructs could also be useful for drug screening on organoids or other in vitro studies.

To generate more complex hierarchical structures the nozzle geometry could be adjusted. Core/shell structures or tubes could be fabricated by using a coaxial nozzle with tunable
inner and outer diameters. For further extruded shape control, the print head could be connected to a microfluidic chip as the nozzle that could combine multiple materials and extrude thin ribbons or multi-component cross-sections.

The CA inks described in Chapter 6 could also be directly interfaced with living tissues for regenerative medicine. By incorporating peptides with bioactive epitopes on the periphery of the CA molecules, conductive fibrous scaffolds could be prepared for combined electrical stimulation and cell signaling. For example, using 3D printing, aligned conductive scaffolds could direct neurite outgrowth along the direction of extrusion.

In the more distant future, the promise of 3D printing in vivo lies in fabricating complex tissues with multiple materials. This could eventually lead to full organ printing which would obviate the need for organ transplants. For this to become a reality, multiple bioinks with specific components for each tissue will need to be prepared, along with careful consideration of the interfaces between inks. Decreasing the nominal feature size of printed components to replicate natural structures will also be important. From a regulatory perspective, there is still a long path to get FDA approved bioinks, but in the future it’s not hard to imagine a 3D printer in every operating room for on-demand printing of patient-specific implants.
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Education

Northwestern University, Evanston, IL, September 2013-December 2018  
GPA: 3.9/4.0

Ph.D. candidate, Materials Science & Engineering, Samuel I. Stupp Laboratory 
Certificate: Management for Scientists and Engineers, Kellogg School of Management 
Thesis: “Encoding Electronic and Biological Function in Hierarchical Soft Materials”

Massachusetts Institute of Technology, Cambridge, MA, September 2009-June 2013  
GPA: 4.7/5.0

S.B. in Physics and Materials Science & Engineering 

GPA: 3.9/4.0

International Baccalaureate Scholar, National Honor Society, Male Student-Athlete of the Year, 
National Merit Commended Scholar, 7 Varsity Letters: Basketball, Baseball

Work Experience

Northwestern Ph.D. Research, Stupp Group, Evanston, IL, September 2013-Present  
Research Assistant, Samuel J. Stupp Lab

- Developed self-assembled hybrid organic-inorganic nanostructures via electrodeposition for use in supercapacitors and as catalysts for electro-oxidation of water
- Established bio-inspired strategies to mineralize organic nanostructures with functional energy materials
- Utilized 3D printing techniques to pattern hydrogels for energy (soft electronics and photocatalysis) and medicine (soft autonomous robots and scaffolds for human tissue regeneration)

Univ. of Colorado Anschutz Medical Campus, Aurora, CO, June 2013-August 2013  
Research Associate, Mark L. Dell’Acqua Lab

- Sub-cloned Ca^{2+} channel sub-units into cDNAs with appropriate drug resistance for stable cell line
- Performed whole-cell patch clamp recordings on transfected cells to test the current response of Ca^{2+} channels upon stimulation of the β2-adrenergic receptors in the presence of isoproterenol

MIT Undergraduate Research, Group Sadoway, Cambridge, MA, September 2012-June 2013  
UROP student, Donald R. Sadoway Lab

- Liquid Metal Battery Project for grid-scale energy storage
- Assembled small-scale versions of the device, exploring third generation battery chemistries
- Cross-sectioned and performed post-mortem analysis on tested battery cells

Colorado Fuel Cell Center at Colorado School of Mines, Golden, CO, May 2012-August 2012  
NSF REU Intern, Andrew M. Herring Group

- Characterized the electro-catalytic properties of bimetallic earth abundant catalysts for use in anion exchange membrane fuel cells (AEMFCs)
- Performed cyclic voltammetry, linear sweep voltammetry, and chronoamperometry to generate IV plots and Tafel plots for various fuels including hydrogen, methanol, ethanol, and methane
- Fabricated membrane electrode assemblies (MEAs) and tested fuel cells with each fuel listed above
MIT UNDERGRADUATE RESEARCH, MIT SUSTAINABILITY HUB, CAMBRIDGE, MA, February 2012-May 2012  
UROP student, Krystyn J. Van Vliet Lab
- Studied the cement hydration process in an effort to design a more environmentally friendly cement
- Grew tricalcium silicate (C$_3$S) crystals in high temperature furnace and dispersed them in epoxy for testing
- Used Atomic Force Microscopy (AFM) to generate images of the phases of clinker present in the C$_3$S samples

NATIONAL RENEWABLE ENERGY LAB (NREL), GOLDEN, CO, May 2011-August 2011  
Intern, Strategic Energy Analysis Center, Nate J. Blair Group
- Used System Advisor Model (SAM) to model photovoltaic systems across the country at residential, commercial and utility scales. Modeled Concentrating Solar Power (CSP) plants to validate the SAM model

TECHNICAL SKILLS

ELECTROCHEMISTRY & BATTERY/FUEL CELL TESTING
- Potentiostatic experiments such as Cyclic Voltammetry, Linear Sweep Voltammetry, Chronoamperometry
- Electrodeposition for thin-film growth. Fabrication of MEAs and CCMs
- Battery cycling (galvanostatic charge/discharge), fuel cell testing and polarization curves
- Electrochemical Impedance Spectroscopy (EIS) and Electrochemical Quartz Crystal Microbalance

MATERIALS ANALYSIS TECHNIQUES
- X-ray diffraction (XRD), crystallography, and Grazing Incidence X-ray Scattering (GIXS)
- Spectroscopy including Absorption, Fluorescence, and Dynamic Light Scattering (DLS) methods
- Surface techniques: Atomic Force Microscopy (AFM) and X-ray Photoelectron Spectroscopy (XPS)
- Differential Scanning Calorimetry (DSC) and Thermogravimetric Analysis (TGA)
- Electrical probe station, 4-point probe conductivity measurements
- Rheology measurements (rotational and oscillatory)

MODELING & COMPUTER SKILLS
- Experienced in Illustrator, Python, Mathematica, Matlab, Origin, Igor Pro and Cinema 4D
- Familiar with materials simulations using DFT (PWSCF) and Molecular Dynamics (LAMMPS)
- CAD modeling in AutoCAD, Fusion, and OpenSCAD

ADDITIVE MANUFACTURING
- Pneumatic and syringe based 3D printing (Hyrel3D System 30M, EnvisionTEC Bioplotter, Cellink BioX)
- Stereolithography based 3D printing (Formlabs Form2)
- Hydrogel ink development with various solidification mechanisms: thermal solidification, ionic crosslinking, physical crosslinking, UV covalent crosslinking, shear thinning pastes, embedded 3D printing

HONORS & AWARDS

FIRST PLACE, JOHN H. HILLIARD SYMPOSIUM: BEST PRESENTER AWARDS, Northwestern, May 2018
INTERNATIONAL INSTITUTE OF NANOTECHNOLOGY OUTSTANDING RESEARCH AWARD, Northwestern, 2017
NATIONAL DEFENSE SCIENCE & ENGINEERING GRADUATE (NDSEG) FELLOWSHIP, 2015-2018
NORTHWESTERN SCIENTIFIC IMAGES CONTEST WINNER, Science in Society at Northwestern, 2017
FIRST PLACE, SIMPSON QUERREY INSTITUTE (SQI) IMAGE CONTEST, Northwestern, 2017
BEST PRESENTATION, NORTHWESTERN INVO FORWARD INVESTOR PITCH, Medical Devices, Fall 2017
ENERGY MATERIALS SUBGROUP LEADER, Stupp Lab, 2014-2018
INSTITUTE FOR SUSTAINABILITY & ENERGY AT NU: POWERING THE FUTURE COHORT, Spring 2016
RYAN FELLOWSHIP, GRADUATE RESEARCH IN NANOTECHNOLOGY AT NORTHWESTERN UNIV., 2013-2015
MIT VARSITY BASKETBALL TEAM, Fall 2009-Spring 2012
NEWMAC ACADEMIC ALL-CONFERENCE TEAM, 2011-2012
DIRECTOR OF MARKETING, LAMBDA CHI ALPHA FRATERNITY, 2011-2012
GWHS MALE STUDENT ATHLETE OF THE YEAR, 2008-2009
JOHN LYNCH AWARD, Student athlete of the month in Colorado, January 2009
GWHS CHAUNCEY BILLUPS AWARD, For excellence in the community, classroom and on the court, 2008

TEACHING & EDUCATIONAL OUTREACH

GRADUATE STUDENT MENTORSHIP, Kristen Wek and Jacob Kupferberg (2017-present)
UNDERGRADUATE MENTORSHIP, Lisa Waring, Elad Deiss-Yehiely, Emily Beeman, Ryan Zambrotta (2016-18)
TECHNOLOGY AND BUSINESS OF ENERGY SEMINAR LEADER, Northwestern University, Jan. 2016-April 2018
NORTHERNWESTERN ENERGY TECHNOLOGY GROUP, COLLABORATION & MARKETING CHAIR, 2015-2018
TEACHING ASSISTANT, Northwestern University, M.E. Soft Materials, Winter 2018
TEACHING ASSISTANT, Northwestern University, M.E. Conducting Polymers, Fall 2015
LETTERS TO A PRE-SCIENTIST, Pen pal with 7th grade student in under-resourced school district, 2015-2016
ILLINOIS JUNIOR ACADEMY OF SCIENCE (IJAS) REGIONAL SCIENCE FAIR, JUDGE, March 2015
MORE PROGRAM AT NILES WEST HIGH SCHOOL, Mentored high school student’s science fair project, 2014-15
CHICAGO PUBLIC SCHOOLS’ ANNUAL SCIENCE & MATH FAIR, JUDGE, January 2014
JUNIOR SCIENCE CLUB MENTOR, BOYS & GIRLS CLUB OF AMERICA, Chicago, IL, 2013-2015
MIT ENERGY CLUB, 2011-2013

ACADEMIC PUBLICATIONS


In preparation:


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**POSTERS & INVITED TALKS**


