

Optimizing the Self-Assembly of Conjugated Polymers and Small Molecules Through Structurally Programmed Non-Covalent Control

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Abstract

Organic conjugated polymers and oligomers are key electronic materials for applications such as transistors, photovoltaics, and light emitting devices due to their potential for solution processability, mechanical flexibility, and precise structure-based tuning compared to inorganic materials. In dilute environments, the optoelectronic properties of conjugated polymers are largely governed by their constitutional structure and, to a lesser degree, their solution-state intramolecular configuration. In the solid state, intramolecular conformation, and intermolecular electronic coupling impact these properties substantially, especially in relation to device performance. Therefore, an increasingly important area of research concerning conjugated materials is the development of design strategies aimed at optimizing the solid-state packing for electronic applications. Programming solid-state packing arrangements through discrete non-covalent interactions is an emerging strategy within the context of conjugated polymers. This review focuses on the use of the two most prevalent discrete and directional interactions used to dictate the self-assembly of conjugated

polymers and oligomers—hydrogen bonds and chalcogen bonds. We also discuss how these design motifs can imbue conjugated materials with appealing physical properties while simultaneously retaining or improving electronic capabilities.

1. Introduction

Conjugated polymers and oligomers have received an immense amount of attention from the scientific community for the past several decades as next generation semiconducting materials for a variety of optoelectronic applications.¹ Conjugated materials are unique in that they combine the semiconducting characteristics of inorganic materials with physical characteristics of organic materials, such as flexibility, solubility, and the potential for comparatively low costs. These materials lie at the heart of groundbreaking achievements in organic electronics, as more sophisticated conjugated materials emerge to yield field-effect transistors^{2,3}, photovoltaics^{4,5}, and light emitting diodes with improved performance.^{6,7} The development of new conjugated systems begins at the design stage, where conjugated building blocks are connected, often in a donor-acceptor type fashion in order to imbue properties like charge-transport and luminescence. Solution processability is often enabled by side groups such as long alkyl chains grafted onto the conjugated, optoelectronically active backbones.⁸ Chemical structures of the pi-conjugated main chain of these materials dictate many of these optical and electrochemical properties when they are dissolved in a dilute solution, as there are few intermolecular interactions between them.⁹ Understanding and developing predictive power over these structure-property relationships in dilute solution is critical, but represents only a first step for impactful rational design, as the applications of conjugated materials—photovoltaics, field effect transistors, light emitting devices, and conjugated polymer nanoparticles in biological environments—require ensembles of conjugated materials. These ensembles, most often in the solid-state, however, present a much more complicated situation in which combinations of structure, conformation, and intermolecular coupling dictate electronic structure and optoelectronic properties.¹⁰ The

difficulty inherent in controlling these solid-state optoelectronic properties is one of the major barriers that currently inhibits the realization of rational design of materials for higher efficiency devices. Therefore, a significant area of research has emerged focused on correlating the solid-state packing of conjugated materials with their resultant electronic properties, as well as developing strategies aimed at optimizing this packing for high efficiency materials.

Among the many factors dictating the self-assembly of polymers and oligomers in the solid-state, the large collection of intramolecular and intermolecular non-covalent interactions can be fine-tuned through various types of structural modifications. In contrast to relying upon ubiquitous dispersion forces that are difficult to program and differentiate, identifying and harnessing specific, discrete non-covalent interactions through rational molecular design can enable a degree of control over the local packing arrangements of these materials. In addition, several secondary and tertiary properties aside from charge transport can also be engineered, such as self-healing and stimuli responsiveness.^{11,12} Deploying this strategy usually involves a reexamination of the chemical structure of the polymer or oligomer in question, followed by the installation of functional groups capable of facilitating the desired interactions. These groups can be as small as a few atoms, or much larger.

In the context of conjugated polymers, two classes of discrete, non-covalent interactions are the most prevalent in the literature: hydrogen bonding interactions and chalcogen bonding interactions. Although other types of interactions such as halogen bonding are frequently used in other contexts, including conjugated small molecules and non-conjugated polymers, hydrogen bonds and chalcogen bonds represent the majority of programmed discrete non-covalent interactions used to control the properties of conjugated polymers. Hydrogen bonds lie on the stronger end of the spectrum of non-covalent interactions and have been utilized in both main-chain and side-chain designs to increase molecular packing efficiency, as well as to increase the tensile strength and deformability of

conjugated materials. As such, they have become common in studies where the goal is to develop flexible electronic materials for applications such as electronic skins.¹³ Chalcogen bonds are generally weaker than hydrogen bonds, but offer their own set of advantages. Aside from being directional and reliable, the high population of chalcogen atoms (especially oxygen in side-chain groups and sulfur atoms in thiophene rings) within modern conjugated materials for transistors and photovoltaics provide a low barrier to entry, decreasing the amount of synthetic manipulation required. Chalcogen bonds form a cornerstone of several novel design motifs, most notably conformational locking of conjugated polymer planarity for transistor and photovoltaics applications.

In this review, we describe a number of recent studies within approximately the last five years in which hydrogen and chalcogen bonds control the ensemble properties of conjugated materials through molecular assembly. In addition, we introduce several instances of including hydrogen and chalcogen bonds in conjugated oligomers and other small conjugated molecules as these contributions are also relevant to conjugated polymers. The intended scope of this review encompasses recent and highly cited examples of conjugated systems imbued with sophisticated functionality that perturb and control solid-state assembly through non-covalent interactions, which are programmed through rational structural augmentation. Throughout this review, we emphasize chemical structure, describe how programmed non-covalent interactions manifest and impact material properties, and discuss relevant applications. This review concludes with several perspectives on advancing the use of hydrogen and chalcogen bonds to design and control the ensemble properties of conjugated polymers, as well as the use of discrete non-covalent interactions for conjugated materials more broadly.

2. Hydrogen Bonding

Among the diverse panoply of non-covalent interactions at the disposal of materials chemists, hydrogen bonding interactions are considered some of the strongest and most reliable. Hydrogen bonding interactions are attractive electrostatic interactions that occur between lone pairs of electrons, such as those on oxygen and nitrogen, and hydrogen atoms covalently bound to electronegative elements. From the secondary structure of complex proteins and DNA, to the self-assembly of commercial polymers and adhesives, hydrogen bonding interactions are responsible for the self-assembly and physical properties of many materials.^{14–16} The propensity for hydrogen bonding relies heavily on molecular structure, and the systematic and repeated incorporation of hydrogen bonding synthons has made rational design of these motifs commonplace in the literature.¹⁷ As described below, taking advantage of hydrogen bonding interactions from the perspective of materials has led to the development of sophisticated ensembles with a multitude of interesting properties, such as self-healing conjugated polymers and phosphorescent small-molecule crystals. We begin by showing how hydrogen bonding interactions can be programmed at the molecular level to engineer various characteristics in polymer and oligomer self-assembly, such as backbone planarity and tighter chain-packing. Subsequent examples will demonstrate how these engineered traits impact the mechanical, electronic, and optical properties of materials. While the bulk of examples discussed here are conjugated polymeric systems, we also present selected studies on hydrogen bond-driven self-assembly of conjugated small molecules. These selected studies represent materials with interesting physical properties as a direct consequence to their solid-state packing. However, we recognize that this area of supramolecular chemistry is vast, and direct readers to review articles on a broader array of hydrogen-bonded constructs such as organic frameworks, supramolecular polymers, and cages.^{18–20}

2.1 Supramolecular Assembly, Solid-State Morphology and Mechanical Properties

The power to control and dictate the supramolecular assembly and solid-state morphology of conjugated materials has made hydrogen bonding an indispensable tool for designing new materials. Several broad uses of hydrogen bonding in conjugated polymers, described here, impact functional properties as explored in subsequent sections. For conjugated polymers and oligomers, the intermolecular and intramolecular solid-state configurations contribute critically to their performance as semiconductors. Characteristics such as torsional angle, interchromophore distances, and solubility can all be tuned with precisely engineered hydrogen bonds. This section reviews selected examples in which hydrogen bonding has been used to dictate the solid-state assembly and morphology of conjugated polymers, oligomers, and small molecules.

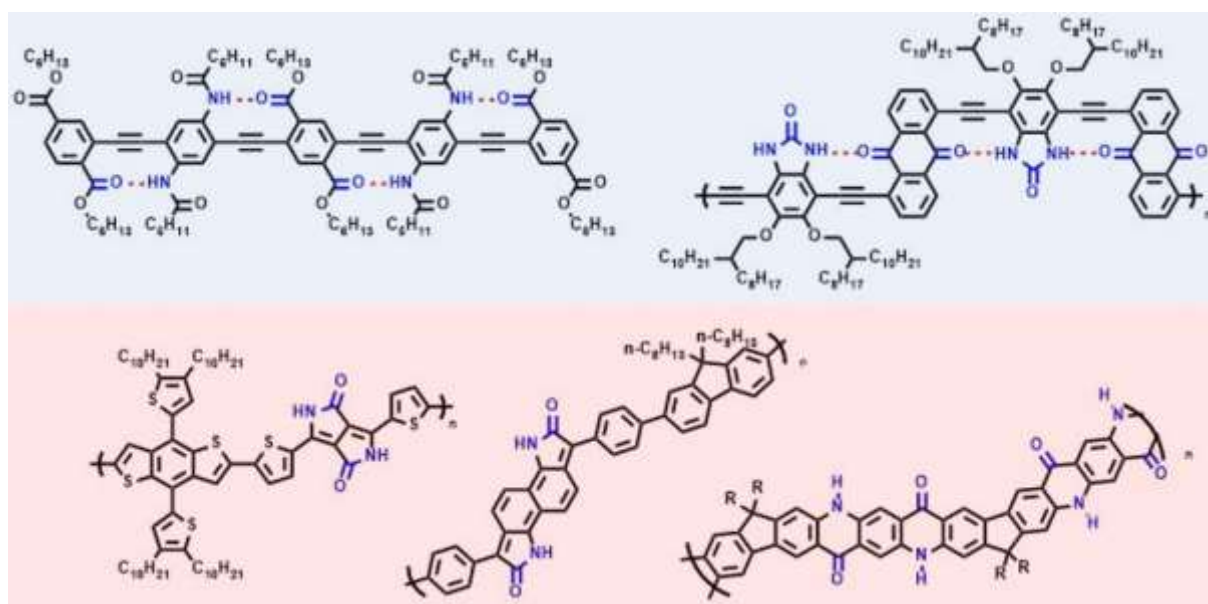


Figure 1. Selected chemical structures of some hydrogen bonding conjugated polymers and oligomers.^{23, 24, 30, 32, 36} Hydrogen bond donor and acceptor groups (blue) form hydrogen bonding interactions (red dashes) and can be intramolecular (top) or intermolecular (bottom) in nature, depending on structure.

A relatively common function of hydrogen bonding interactions within conjugated materials is to control both their intramolecular and intermolecular structural configurations in

the solid state.²¹ This can be achieved by including substituents that can participate in hydrogen bonding, and can yield more complex secondary structures such as nanofibers.^{22,23} Like conjugated polymers, conjugated oligomers can model hydrogen bonding self-assembly, as they can be rigorously purified, and their three-dimensional structure can be precisely elucidated through X-ray crystallography and other means. As with polymers, the intramolecular configuration, as well as the intermolecular assembly of oligomers can impact the semiconducting abilities of conjugated oligomers. Hydrogen bonding interactions can enforce coplanarity of conjugated oligomers such as oligo(phenylene-ethynylenes) and other linear conjugated networks with dynamic covalent linkages.^{24–27} For more rigid frameworks, intermolecular interactions between molecules are more prominent.^{28,29} Latent hydrogen bonding, in which hydrogen bond donors are suppressed through thermally cleavable substituents, can further tune the rigidity of already-cast materials.^{30–34} For example, the group of Lei Fang has championed rigid hydrogen bonding interactions between quinacridone oligomers and polymers to generate highly robust and solvent resistant thin films.^{35,36}

Further, the propensity for hydrogen bonds to outcompete weaker interactions allows access to otherwise inaccessible motifs that can yield desirable optoelectronic properties. Liu and coworkers modeled hydrogen bonding between oligothiophenes appended with amides and ureas to investigate how the local arrangements of oligomers could affect charge transport pathways.³⁷ Interactions between strong hydrogen bond aggregators yield packing motifs characterized by large chromophore displacements typically inaccessible due to strong Pauli repulsion, which could lead to enhanced charge-transport properties. Photovoltaics and transistors would be two possible applications, which are discussed later in this section.

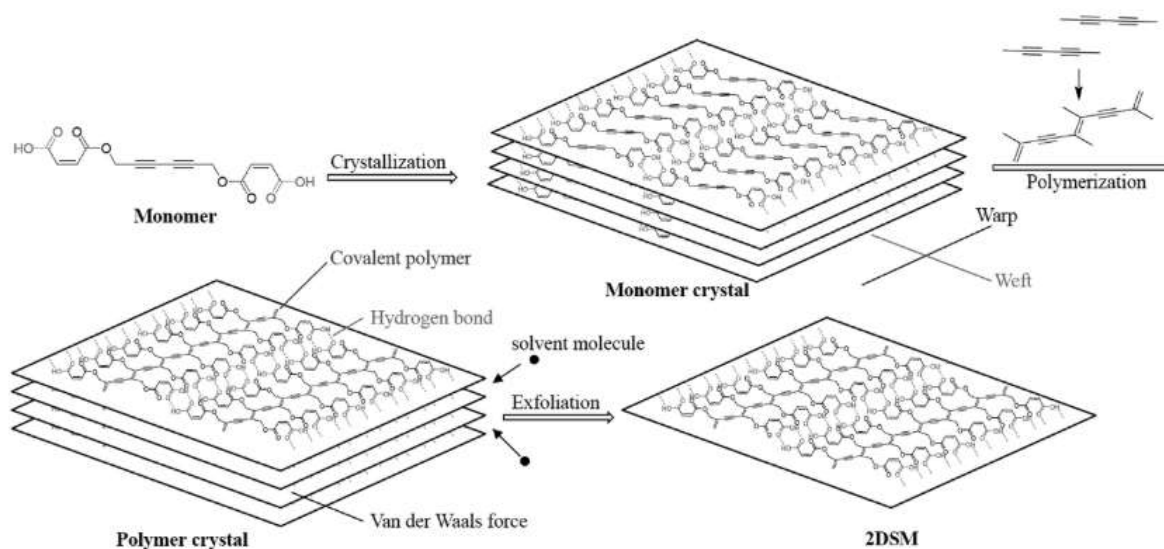


Figure 2. Schematic representation of two-dimensional supramolecular material developed by Li and coworkers. Reproduced with permission.⁴¹ Copyright 2017, Wiley-VCH.

Controlled assembly within conjugated polymers can rely critically on their spatial organization *prior* to their preparation. Polymerization reactions can depend strongly on the spatial relationship between reactive moieties on monomer units, making optimizing their self-assembly specifically for these processes a top priority to produce high-quality materials. For example, 1,3-butadiynes, can be polymerized using light to produce highly insoluble polydiacetylenes and have been used to produce conjugated polymers with complex structures, including nanorods.^{38–40} Recently, Li and coworkers used hydrogen bonding interactions between carboxylated butadiynes (**Figure 2**) to assemble nanosheets for topochemical polymerization.⁴¹ These nanosheets could be exfoliated in the form of two-dimensional supramolecular materials with nanometer level thickness and self-healing capability. Due to the spatial-selectivity of light-activated polymerization, photopatternable films are easily obtained through 1,3-butadiyne polymerization. This type of polymerization can be applied to other conjugated polymers as an effective cross-linking method, as demonstrated by Nyayachavadi and coworkers,⁴² in which isoindigo-based donor-acceptor polymers were appended with reactive 1,3-butadiyne groups that self-assembled due to

hydrogen bonding amides within the butadiyne chains. This approach represents an additive-free approach to producing conjugated polymers with well-defined structures and morphologies. Supramolecular polymers based on conjugated molecules have optical properties suited for multiple platforms without the need for complex covalent bond forming chemistries.^{43,44} The bis[alkynylplatinum(II)]terpyridine molecular tweezer developed by the Wang group has been used to develop multiple supramolecular systems, and uses hydrogen bonding as one of its modes of action.⁴⁵⁻⁴⁷ Its core contains a pyridine hydrogen bond acceptor, which can interact with a number of different hydrogen bond donors, such as amines and alcohols. The use of the transition metals, in tandem with the complexation of photoactive groups, imbue these supramolecular systems with photoresponsive capabilities, including the generation of singlet oxygen, a chemical species used in cancer treatments.⁴⁸

Moreover, within conjugated polymers generally, the presence of hydrogen bonding within common designs of chromophoric units can advantageously dictate their alignment. For example, the donor-acceptor design paradigm has become commonplace in organic semiconductors with specialized building blocks, joined together through covalent bonding, serving as electron rich donor and electron poor acceptors.⁴⁹ Hydrogen bonding can be responsible for the supramolecular assembly of popular electronic building blocks such as diketopyrrolopyrrole, perylene diimide, and naphthylene diimide.⁵⁰⁻⁵³ However, the group of Dmitrii Perepichka has demonstrated across multiple publications that hydrogen bonding can also promote energy transfer between complimentary pairs of electron donor and acceptor small molecules. In an initial 2014 communication, they described the three unique assemblies of diphenyldipyrrolopyridine and naphthalenetetracarboxydiimides.⁵⁴ NMR measurements of H-bonding donor/acceptor pairs showed shifting of amine proton signals that suggested hydrogen bonding, which was confirmed in single crystal structures of cocrystallized donor/acceptor pairs. The close contact between donor and acceptors brought about by hydrogen bonding allowed for electron transport between them. These observations

led to a series of recent publications which expanded the structural scope of both donor and acceptor moieties.^{55–57} As a result of complexation between donor and acceptor small molecules, the authors observed lower band gaps, intense absorption in the near infrared region, and short inter-chromophore separation, all of which make these molecules interesting candidates for organic transistors.

The biological hydrogen bonding motifs responsible for large biological constructs such as DNA and protein secondary/tertiary structures can also be adapted to control the self-assembly of conjugated polymers, oligomers, and small molecules. For example, the amide groups formed by joining individual amino acids together in short chains are excellent complimentary hydrogen bonding functional groups. Peptides installed onto conjugated units can direct their self-assembly into more complicated structures, such as helical nanofibers^{58,59} and spherical micelles,⁶⁰ and also can also improve their physical adhesion to cells.⁶¹ The choice of amino acid residues is critical, as larger groups such as phenylalanine can inhibit binding interactions.⁶² Analogously, nucleobases can form hydrogen bonded pairs through various carbonyl and amine acceptor/donor pairs. In 2020, Sabury and coworkers demonstrated how hydrogen bonding between nucleobases in side-chains of conjugated polymers direct the self-assembly of polymer chains.⁶³ Adenine- and thymine-functionalized conjugated polymers (**Figure 3**) exhibited large bathochromic shifts in solid state absorbance compared to polymers with simple alkoxy chains due to stronger polymer chain aggregation brought on by hydrogen bond facilitated phase separation and organization.

Similar designs have found application drug-delivery, as nucleobase side-chains can bind small molecule drugs such as functionalized doxorubicins,⁶⁴ and though small molecule drugs are seldom considered as organic semiconductors, a recent example has shown their potential for charge transport. In 2019, Zhang and coworkers investigated how the hydrogen bond mediated self-assembly of ellipticine, a failed anticancer medication, modulates the charge transport in ellipticine crystals.⁶⁵ Ellipticine (**Figure 3**) was chosen from a list of

DNA topoisomerase inhibitors due to its calculated HOMO being similar to typical p-type organic semiconductors. Crystal structures of two polymorphs of ellipticine reveal distinct packing patterns featuring both short inter-chromophore separation and hydrogen bonding. However, both polymorphs demonstrated distinct charge transport capabilities, particularly along the H-bonding direction. Calculations revealed that lack of a hydrogen bond decreased the charge transport integral, stressing the importance of hydrogen bonding between units and resultant supramolecular assembly in charge transport.

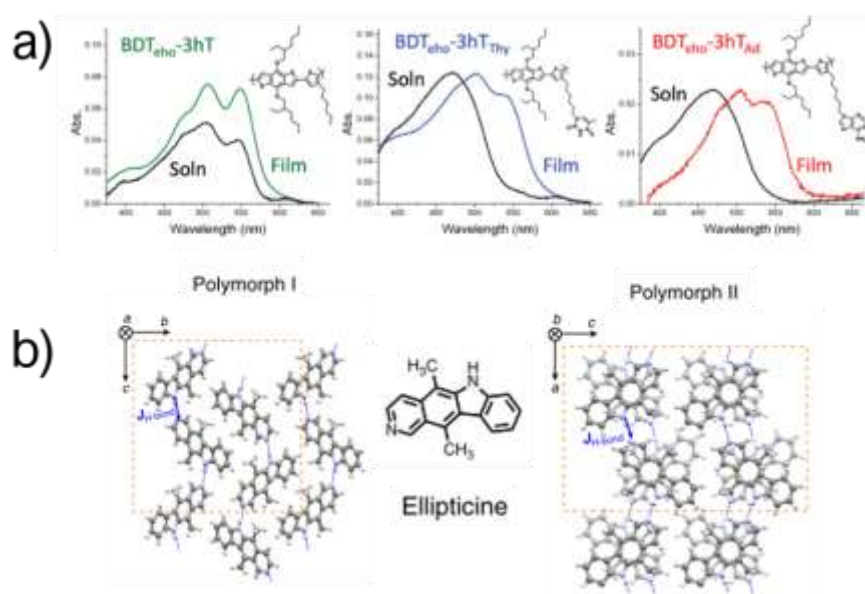


Figure 3: a) Chemical structures and absorbance profiles of polymers developed by Sabury and coworkers in solution and thin-film. Reproduced with permission.⁶³ Copyright 2020, RSC Publishing. b) Chemical structure and polymorphic crystal structures of ellipticine, showing unit cells (orange dash) and hydrogen bonding interactions (blue dash). Reproduced with permission.⁶⁵ Copyright 2019, Nature Publishing Group.

In addition to dictating optoelectronic properties, solid-state packing of conjugated polymers strongly influences their mechanical properties which are critical to their utility in applications such as flexible electronics. However, direct investigation of how assembly influences mechanical properties is not yet commonplace in this research area.⁶⁶ In some

circumstances, hydrogen bonding interactions can imbue conjugated materials with stretchability, flexibility, and self-healing properties, all distinct from their typically rigid and sometimes crystalline nature. For a material to be ductile, the force applied to the material must dissipate in a way that minimizes physical deformation as cuts or tears. These secondary dissipation pathways also should be reversible to facilitate repeated acts of deformation. Hydrogen bonding interactions can facilitate this process because: 1) hydrogen bonds are weaker than covalent bonds, so they break preferentially upon exposure to mechanical strain, forming a network of sacrificial linkages that can dissipate mechanical force and 2) hydrogen bonds can reform in the solid state, either through thermal or solvent treatment. These bonding motifs can be engineered through the use of hydrogen bonding crosslinkers^{67,68} and hydrogen bonding side-chains.^{69–71}

Synthetically, there are several approaches to fabricating conjugated polymers with hydrogen bonding side-chains. One such strategy is to graft hydrogen bonding side-chains onto already formed polymer chains, an example of which was recently reported by Baek and coworkers for the development of stretchable and self-healable conjugated polymers. In 2017, Baek and coworkers grafted self-complimentary hydrogen bonding amide-containing alkyl chains onto polythiophenes.⁷² The amide-containing side-chains formed intrachain hydrogen bonds, as confirmed by concentration-dependent NMR studies of both polymers and monomer solutions. During polymer synthesis, amide-containing side-chains were grafted onto the existing polymer through an ATRP reaction, allowing the side-chain content and extent of hydrogen bonding to be controlled through this synthesis step. This grafting of flexible side-chains yielded polymers with lower Young's moduli than that of a control polymer with no hydrogen bonding, indicating an increasingly deformable material; longer graft lengths of amide-containing side-chains, however, dramatically decreased electrical conductivity due to the insulating nature of the side-chains. Voorhaar and coworkers extended this approach to poly(thiophene-phenylenes) with similar results.⁷³

2.2 Optical Properties

The luminescent properties of conjugated materials also depend vitally on the arrangement of chromophores in the solid-state. Non-covalent control over assembly architecture can maximize the competitiveness of radiative decay in the form of fluorescence or phosphorescence.⁷⁴ Stimuli responsive behavior can be engineered as well, as the perturbation of hydrogen bonding interactions by external stimuli such as mechanical force or molecular analytes can lead to changes in luminescent intensity and wavelength for application in sensors and stimuli-responsiveness solid-state lighting. Such non-covalent control over molecular assembly can also yield photophysical properties that are unusual or difficult to realize, such as room temperature phosphorescence.

A tremendous amount of progress has been realized in the field of luminescent materials that can change their solid state luminescence upon exposure to external stimuli.^{75,76} The observed changes in luminescence can result from disturbing the solid-state assembly of chromophores. One example is mechanofluorochromism (MFC), in which a material changes luminescence upon exposure to mechanical force often through transitioning through one or more other accessible polymorphs.⁷⁷ By analyzing the intermolecular interactions in crystal structures of isolated polymorphs, researchers have determined that mechanical force can disrupt hydrogen bonding interactions, changing the luminescence of small molecular solids.^{78,79} For example, Sudhakar and coworkers recently described the mechanofluorochromic behavior of a series of donor-acceptor borylated aryl amines for use in OLEDs and sensors.⁸⁰ Each compound possessed the same general conjugated structure (**Figure 4**), but differed in the number, regiochemistry, and substitution of amine groups able to form hydrogen bonding interactions. While hydrogen bonding interactions were observed in crystal structures of each compound, slightly different packing patterns and luminescence were observed in polymorphs of a single compound. Different hydrogen bonding motifs led to the formation of either trimer or tetramer-based crystal lattices, altering the torsional angles

between donor and acceptor groups and shifting crystal emission. In another study, Jiang and coworkers developed an oligourethane gel based on aurintricarboxylic acid and tolylene-2,4-diisocyanate that demonstrated mechanofluorochromism under mild conditions.⁸¹ By introducing hydrogen bonding carboxyl groups into a soft urethane matrix, their material changed luminescence when ground or stretched, showing that soft materials could also exhibit MFC, with potential implications for soft and stretchable pressure sensors.

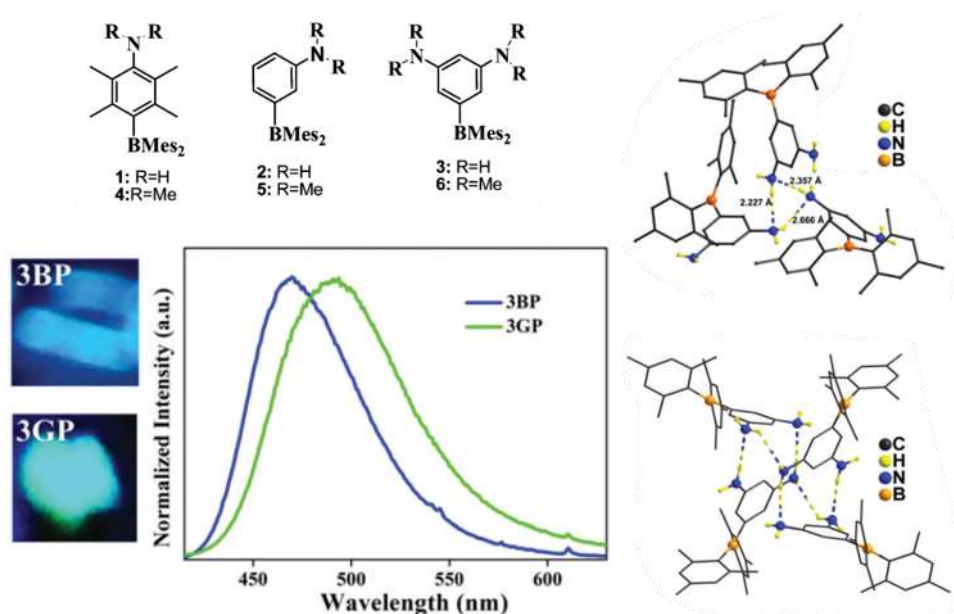


Figure 4. Top left: chemical structures hydrogen-bonded borylate amines developed by Sudhakar and coworkers. Bottom left: fluorescence images and spectra of polymorphs of compound **3**. Top right: crystal structure of polymorph 3BP showing hydrogen bonded trimer. Bottom right: crystal structure of polymorph 3GP showing hydrogen bonded tetramer. Reproduced with permission.⁸⁰ Copyright 2017, Royal Society of Chemistry.

Beyond mechanical force, the sensitivity of hydrogen bonds to interactions with guest molecules can yield conjugated polymers with sensing capabilities. Hydrogen bonding interactions are particularly sensitive to solvent effects, as polar protic solvents compete with or displace other participating moieties from bonding networks, changing luminescence behavior. Tao and coworkers recently reported luminescent supramolecular polymers

constructed by grafting chromophores onto a polyvinyl backbone via hydrogen bonding interactions.⁸² The non-conjugated PVA backbone served as a hydrogen bond donor capable of binding to pyridine-functionalized tetraphenyl ethylene chromophore, resulting in a supramolecular material with solid-state emission. This luminescence of the polymer changed upon fuming with acid due to protonation of the pyridine rings and disruption of the H-bonding interactions. Interestingly, the luminescence change resulting from fuming with weaker acids was easily reversible, while fuming with stronger acids such as trifluoroacetic acid (TFA) could only be reversed by fuming with a base such as triethylamine. Such reversibility is promising for applications such as rewriteable paper and optical memory systems. In a separate study, Majumdar and coworkers showed how inclusion of polar solvents like DMSO in crystals of benzimidazole-based chromophores both shifted the luminescence color from red to yellow and increased the luminescence quantum yield by 30%.⁸³ They postulated that hydrogen bonding between DMSO and chromophores was responsible for this change in luminescence. Moreover, such designs can yield colorimetric redox activity as well, as demonstrated by Yang and coworkers,⁸⁴ who employed latent hydrogen bonding to fabricate insoluble materials for free-standing redox active polymer films.

Luminescence changes upon exposure to specific small molecule analytes can underlie optical chemical sensors; numerous reports exist in which hydrogen bonding interactions participate in the output signal of conjugated materials. The fluoride ion is of particular interest for sensing applications, as the increase of fluoride usage in organic synthesis and medical fields has uncovered the need for reusable fluoride sensors in various media.⁸⁵ Various colorimetric sensors based on intermolecular proton transfer between hydrogen bond donors and fluoride ion have been developed.^{86,87} In 2019, Wu and coworkers reported a novel polyimide fluoride sensor and extractor based on hydrogen bonding interactions.⁸⁸ Their polymer (**Figure 5**) featured two hydroxyl groups capable of hydrogen bonding with

fluoride ions in solution to produce quantitative changes in absorbance in a linear fashion with respect to concentration of fluoride ion. Fluoride ions were the only anionic species out of 11 that produced this response. Their platform also displayed similar selectivity and precision in the solid state. Finally, fluoride bound to the polymer reversibly in both the solution and solid state, which was realized by washing their material with an acid such as TFA.

Hydrogen bonding sensors for other species have also been recently developed.⁸⁹ Sabury and coworkers recently showed that hydrogen bonding adenine moieties on polythiophene could control the assembly of polymer chains in the solid state, while simultaneously constituting a sensor for metal cations.⁹⁰ Hydrogen bonding interactions between adenine moieties improved the packing of polymer chains (**Figure 5**), as demonstrated in the 70° increase in glass transition temperature. In solution, the fluorescence quantum yield decreased upon exposure to metal cations, such as Cu²⁺, as chelation to paramagnetic ions enhanced intersystem crossing or other non-radiative decay pathways from the singlet excited state. Fluorescent emission recovered completely after washing with a solution of EDTA, demonstrating the reversibility of the chelation and sensing process.

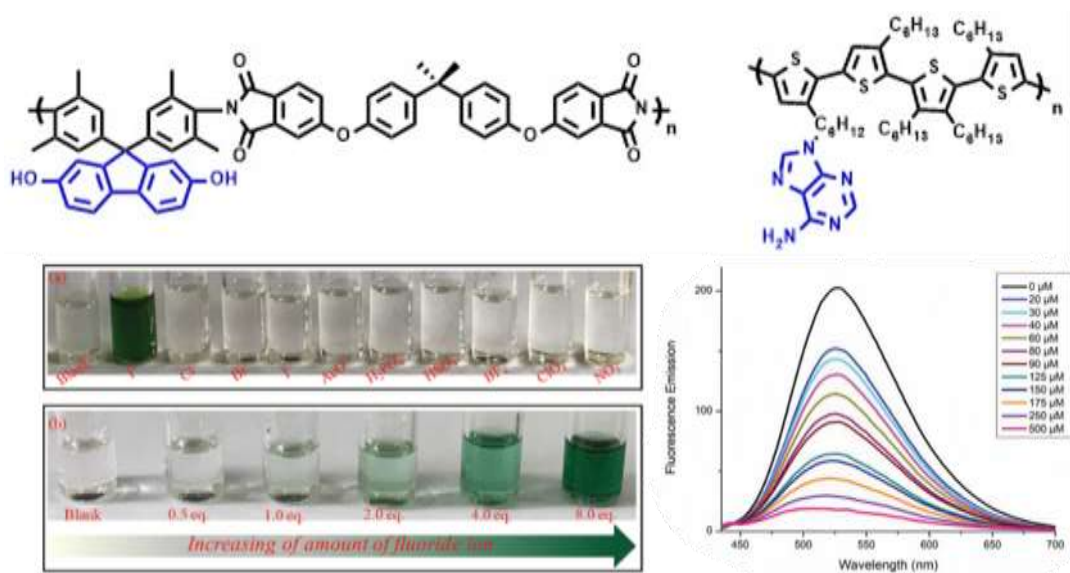


Figure 5. Left: Polyimide fluoride sensor developed by Wu and coworkers and its colorimetric response to fluoride ion. Reproduced with permission.⁸⁸ Copyright 2019, Wiley-VCH. Right: Polythiophene metal cation sensor developed by Sabury and coworkers and its

fluorescence quenching upon addition of copper (II). Reproduced with permission.⁹⁰

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While room temperature phosphorescence (RTP) has received an immense amount of attention due to its usefulness in optoelectronics and biological applications, transition metal-free RTP is relatively difficult to attain in conventional organic materials. A common requirement in all-organic phosphorescent materials is a strongly rigid environment that suppresses non-radiative decay of triplet excited states. Hydrogen bonding interactions can be useful in creating such environments, consequently contributing to RTP in carbon dots and small molecular crystals.^{91,92} In 2018, Bian and coworkers reported enhancing both the photoluminescence efficiency and ultralong lifetime of organic phosphorescent materials through hydrogen bond-driven molecular assembly.⁹³ Their new supramolecular crystalline framework of melamine and isophthalic acid (**Figure 6**) showed a lifetime of 1.91 seconds and a remarkably high PL efficiency up to 24%, a record in organic materials at that time. Crystal structures showed abundant hydrogen bonding interactions of multiple functional groups, as well as water molecules contributing to the rigid framework. Thermal removal of water molecules from the crystalline lattice caused the PL efficiency and lifetime to decrease by 20% and 0.7 s, respectively, due to loss of rigidity in the crystalline framework. Crystallization of melamine with other diacids, like terephthalic acid and phthalic acid, produced frameworks with similarly impressive PL behaviors, highlighting the broad scope of this approach. Finally, the authors fabricated a two-dimensional barcode painting that upon irradiation could be recognized by a popular multi-purpose messaging app in a cellular phone.

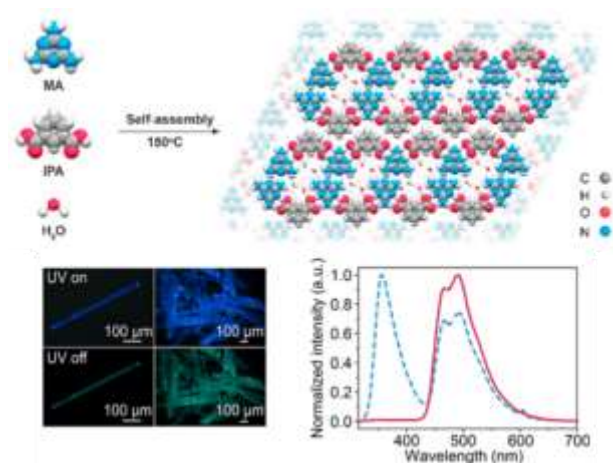


Figure 6. Top: Hydrogen bond driven self-assembly of organic phosphorescent MA-IPA crystals presented by Bian and coworkers. Bottom-left: fluorescent and phosphorescent images of MA-IPA crystals. Bottom right: steady-state fluorescent (blue dash) and phosphorescence spectra (red line) of MA-IPA crystals. Reproduced with permission.⁹³ Copyright 2018, American Chemical Society.

2.3 Organic Electronics

Due to the high levels of conjugation and ability to transport charge carriers, conjugated materials are important materials for electronic devices such as organic photovoltaics and transistors. These devices comprise varying levels of structural complexity and usually require the components to be in the solid state, which ensures close physical contact between active molecules and efficient charge transport. A key area of research is understanding how the solid-state assembly of conductive materials impacts their performance as devices, and how molecular design can favor beneficial morphologies.⁹⁴ Due to the influence that non-covalent interactions have over solid-state assemblies and electronic properties, it comes as no surprise that researchers often pay close attention to how these interactions direct assemblies in the context of charge transport efficiency. Therefore, we focus here on how hydrogen bonding interactions can direct solid-state assembly to improve

the performance of organic photovoltaics and transistors that comprise conjugated polymers and small molecules.

Earlier efforts to design organic solar cells have involved blending of conjugated polymer donors with fullerene-based acceptors.⁹⁵ One of the fundamental drawbacks to this methodology is the resultant dependence on phase separation between donor and acceptor moieties. The interface between donor and acceptor domains impacts device performance as charge is transferred between them. Hydrogen bonding was adapted in early efforts to facilitate more efficient blending of photovoltaic components.^{96,97} Programmed hydrogen bonding interactions between polymers and functionalized fullerenes could effectively disperse fullerene phases throughout bulk polymer, producing nanostructured, interpenetrated donor-acceptor networks.⁹⁸ Recently, blends with non-fullerene acceptors have received increasing amounts of attention, due to their higher absorption of visible light and tunable energy levels.⁹⁹ Although familiar problems have emerged with all-polymer solar cell architectures, hydrogen bonding can mitigate some problems that arise from the assembly of polymer chains in the solid-state.^{100,101} In 2015, Yao and coworkers reported hydrogen bonding side-chains for optimizing polymer blending and aggregation for organic photovoltaics with a series of diketopyrrolopyrrole quaterthiophene conjugated polymers functionalized with varying amounts of urea-containing alkyl side-chains.¹⁰² FTIR and temperature-dependent NMR studies revealed the presence of hydrogen bonding between urea groups in solution. They found that polymers containing urea side-chains showed higher hole mobilities than polymers with both branched and linear alkyl chains. After annealing, their polymers showed hole mobilities up to $13 \text{ cm}^2 \text{ s}^{-1} \text{ V}^{-1}$, which was among the highest hole-mobilities for conjugated polymers at that time. Power conversion efficiency (PCE) values for these polymers blended with the fullerene acceptor PC₇₁BM also improved upon incorporation of urea side-chains. AFM and GIXRD analyses showed micro-phase separation and enhanced lamellar packing encouraged by hydrogen bonding interactions that improve the

electrical performance of these polymers. Overall, the authors concluded that the installation of urea groups into the side-chains of conjugated polymers can be an effective design strategy for new photovoltaic materials, especially since it could be applied to the bulk of existing photovoltaic polymers already reported.

Given their ability to transport charge across relatively long distances, conjugated polymers have been employed in transistors for several decades.¹⁰³ A recent area of research focuses on developing stretchable conjugated polymer frameworks for flexible transistors in applications such as electronic skin.¹⁰⁴ In 2016, Oh and coworkers published a landmark study using hydrogen bonding “conjugation breakers” to produce stretchable and self-healing conjugated polymer transistors.^{12,105} Their study comprised a class of conjugated DPP polymers with 2,6-pyridine dicarboxamide (PDCA) non-conjugated segments designed to form intrachain hydrogen bonds. Adding more PDCA segments decreased the charge carrier mobility while simultaneously increasing polymer flexibility. The effects of stretching on the conductivity of their polymers was investigated by subjecting devices to various degrees of stretching in different directions. Repeatedly applying 100% strain along a direction perpendicular to the direction of charge mobility decreased charge mobility by 26%. Even after cutting, followed by treating with heat and solvent vapor, the polymer recovered conductivity, showing losses as little as 12%. Finally, these materials responded to bodily movements such as twisting and bending of joints that they were appended to. In a more recent study, Zheng and coworkers assessed the correlation between strength of hydrogen bonding through conjugation breakers and polymer physical properties.¹⁰⁶ Stronger hydrogen bonding through urea groups yielded materials with higher flexibility, modulus, and charge mobility.

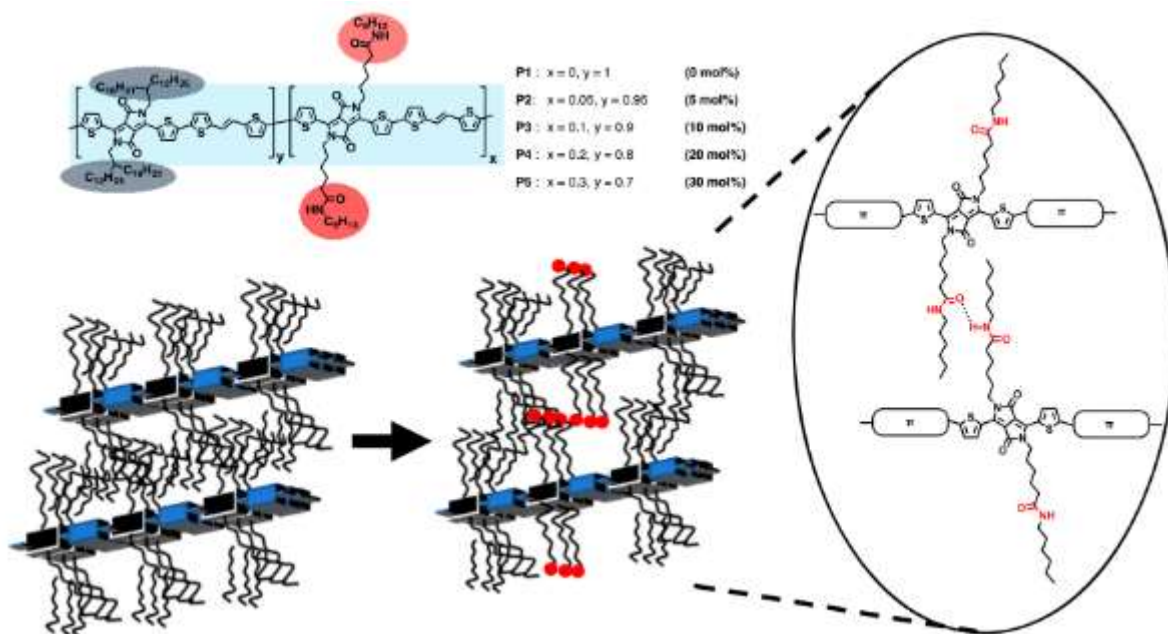


Figure 7. Conjugated polymers developed by Ocheje and coworkers functionalized with hydrogen bonding side-chains. Reproduced with permission.¹¹⁶ Copyright 2018, American Chemical Society.

Strategic incorporation of hydrogen bonding in polymer structure can further improve device performance as well as imbue organic electronics with novel functionality. Side-chains of conjugated polymers are usually thought of as components to provide solubility in the form of linear or branched alkyl, oligo(ethylene glycol),¹⁰⁷ and siloxy chains.¹⁰⁸ However, designer side-chains possessing hydrogen bonding functional groups, such as amides and ureas, can accomplish more than simply imparting solubility. Hydrogen bonding side-chains can improve interchain packing, solid-state microstructure, and charge transport of both n-type and p-type conjugated polymers,^{109–111} with amide groups especially useful given the strength of hydrogen bonding between them.^{112–115} An exemplar of this design came in 2018 from Ocheje and coworkers.¹¹⁶ Their family of diketopyrrolopyrrole (DPP) polymers (**Figure 7**) possessed amide-containing aliphatic chains that participated in interchain hydrogen bonding throughout the polymer network. A small percentage of amide containing side-chains (5 mol%) increased charge mobility by 32% in annealed devices, which the authors

attributed to stronger interchain interactions throughout the polymer network. In pristine devices with no annealing, a similar effect occurred, albeit with lower mobilities due to poor crystallinity. Yang and coworkers reported a similar example in 2019,¹¹⁷ using thymine hydrogen bond dimers to improve the crystallinity and charge carrier mobility of DPP-based polymers. Beyond dimerization, thymine also coordinates certain metallic cations, such as palladium (II) and mercury (II). Carbon monoxide can disrupt the resulting metal-thymine complexes, and the resultant changes in conductivity provide a OFET sensor. Both studies demonstrate how hydrogen bonding of side-chains can apply to transistor materials with improved charge carrier mobility and secondary function.

Aside from their polymeric counterparts, organic transistors based on small molecules offer their own advantages. While offering similar structural tuneability, processability, and environmental stability, crystalline solids of small molecules offer greater organization and can be structurally interrogated by single crystal X-ray crystallography.¹¹⁸ Several notable building blocks have emerged as candidates for efficient transistors, such as naphthylene diimide¹¹⁹ (NDI), perylene diimide¹²⁰ (PDI) and diketopyrrolopyrrole.^{121,122} Hydrogen bonds can dominate crystalline small molecule organic semiconductors and direct packing patterns that offer efficient charge transport.^{123–127} However, free hydrogen bond donors can decrease solubility and limit processability. Zhang and coworkers reported an innovative solution to this problem by fabricating semiconductors with latent hydrogen bonding motifs.¹²⁸ BOC protecting groups, which are thermally labile in the solid state, rendered soluble three otherwise insoluble pigment molecules. FT-IR spectra recorded during the annealing process show the formation of strong hydrogen bonds above 220°C. Single crystal structures of sparingly soluble, deprotected pigments confirm hydrogen bonding, and revealed more efficient interactions between chromophores compared to soluble analogs. Charge carrier mobility in devices increased up to 100-fold upon revealing hydrogen bonding interactions.

Zhang later extended this strategy to other small molecules, such as isoepindolidiones,¹²⁹ with similar results.

3. Chalcogen Bonding

While comparatively weaker than hydrogen bonds, chalcogen bonding interactions have become more popular in recent years for the rational design and engineering of materials with appealing electronic properties and solid-state assemblies, particularly with conjugated polymers and small molecules. Described by Rosenfield and coworkers in 1977,¹³⁰ these interactions stem from attraction between regions of electron density on a donor species, such as a lone pair of electrons, and the electron-poor σ^* orbital of an acceptor. We base our discussion of chalcogen bonding interactions on one of the most widely adopted design strategies in conjugated polymers, colloquially known as “conformational locking”, in which interactions of chalcogen atoms help to lock polymer backbones in near-coplanar arrangements. In addition, we will expand on the use of non-traditional chalcogen bonding interactions incorporating Se and Te in supramolecular synthons that are effective in crystal engineering applications. The prevalence of chalcogen bonding interactions in conjugated materials has led to substantial review literature—we direct readers to these sources in this section. Our discussion will present examples of chalcogen bonding that demonstrate the central nature of this class of interactions over time, and key recent developments.



Figure 8. Schematic representation of chalcogen bonding interactions (left) employed in conformational locking strategies and crystal engineering (right).

3.1 Conformational Locking of Conjugated Polymers and Small Molecules

High performance conjugated polymers in organic solar cells and thin film transistors often require extensive π -electron delocalization, which requires planar conjugated structures. Two existing strategies to achieve this are: i) covalent bonding between adjacent rings, and ii) specific non-covalent interactions of substituents on adjacent rings. The latter, often referred to as conformational locking in the context of chalcogen bonds, takes advantage of heteroatoms such as sulfur, oxygen, and nitrogen in conjugated polymers that can interact with chalcogen atoms, and offers greater structural flexibility and increased synthetic ease by avoiding the need to produce complicated, tethered structures. The resulting planar structure allows for long-range charge carrier transport and close interchain contact. Here we focus on examples where this approach improves the performance conjugated polymers and oligomers in electronic devices. Several review articles have appeared in the last five years on conformational locking^{131,132}, such as that of Hui Huang in 2017.¹³³

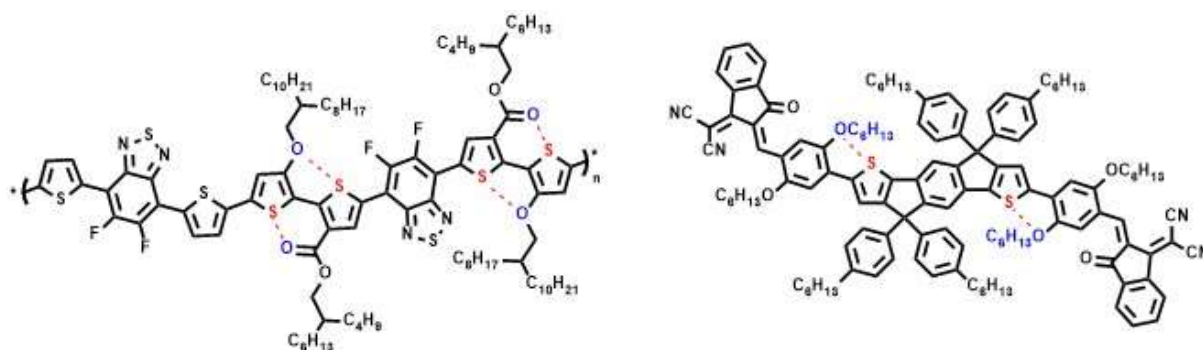


Figure 9. Chemical structures of Chen's conformationally locked polymer¹³⁶ (left) and Liu's conformationally locked oligomer (right).¹⁴⁹

Conformational locking through chalcogen bonding has improved the power conversion efficiency of some organic solar cells (OSCs).^{134,135} This strategy, however, usually requires installation of electron-donating alkoxy groups onto the polymer backbone, which may raise polymer HOMO levels, decrease OSC open-circuit voltages, and render the device more susceptible to oxidative degradation. In 2018, Chen and coworkers

circumvented this issue by using a combination of alkoxy and electron-withdrawing ester substituents installed onto polymers comprising thiophene donor units and benzothiadiazole acceptors (**Figure 9**).¹³⁶ Both substituents could form S...O chalcogen bonding interactions, which enforced backbone planarity as observed in crystal structures of model compounds. The lower energy HOMO of the ester-substituted polymer (-5.19 eV) than that of an all-alkoxy functionalized control polymer (-4.92 eV) increased resistance to unwanted oxidation and increased OSC open-circuit voltage while preserving highly planar conformations through inter-ring chalcogen bonding. Photovoltaic devices fabricated from their ester-substituted polymer showed PCE values as high as 10%, which were higher than those of alkoxy-substituted polymers (7%), which the authors attributed to increased backbone planarization, closer interchain interactions, and lower energy of the polymer HOMO. In a separate study, Chen and coworkers elaborated on their use of chalcogen interactions by studying the effects ester side-chains had on the backbone planarity of thienothiophene building blocks, and their resultant OSC performance.¹³⁷ Chalcogen interactions again improved the backbone planarity of conjugated polymers featuring this unit, allowing for higher PCE values.

Conformational locking can be achieved through a number of different chalcogen bonding interactions, such as S...O,^{100,138–141} S...N,^{142,143} S...S,¹⁴⁴ and S...F^{145,146} interactions. These interactions can also be engineered through rationally designed building blocks, such as the benzodifurandione-based oligo(phenylene-vinylene) (BDOPV) derivatives designed by the Pei group.^{147,148} In 2017, Yahui Liu et al published an important study on conformational locking of a non-fullerene acceptor molecule that had a profound impact on PCEs of devices compared to an unlocked analog.¹⁴⁹ Although fused-ring electron acceptors are effective building blocks for organic photovoltaics, they can involve demanding syntheses and poor solubility. Chalcogen bonding interactions between alkoxy side-chains and main-chain sulfur atoms on an indacenodithiophene-based (IDT) electron acceptor (**Figure 9**)

simulated a highly fused and planar structure in the solid state. Because these interactions do not persist in solution, the molecule was sufficiently soluble for solution-based synthesis and processing. The impact of this seemingly small structural perturbation on device performance was striking: devices comprising the chalcogen-bonding derivative showed PCE values up to 9.6%, while control devices bearing only alkyl chains showed PCE values up to 2.3%. Dongxue Liu and coworkers corroborated these findings with a series of low bandgap nonfullerene acceptors (NFAs) with stronger chalcogen interactions along their conjugated backbones using thiophene, selenophene and thienothiophene.¹⁵⁰ These NFA molecules possessed an A-D-A structure, with conjugated spacer units between donor and acceptor moieties that could participate in chalcogen bonding interactions and increase backbone planarity. As a result, bulk heterojunction photovoltaic devices containing these molecules as electronic acceptors demonstrated some of the highest PCE values with such long NFAs.

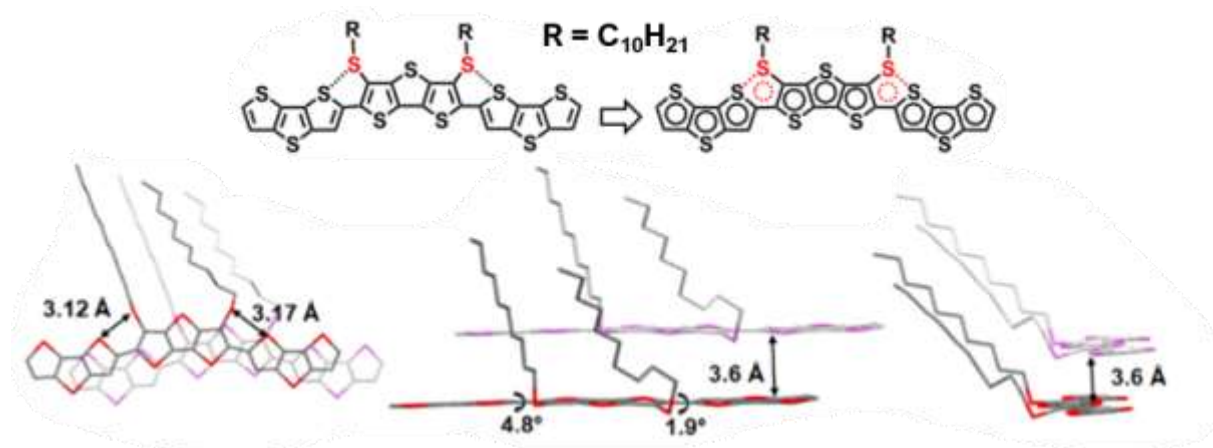


Figure 10. Chemical structure and crystal packing of pseudo n-thienoacenes developed by Vegiraju and coworkers. Reproduced with permission.¹⁵² Copyright 2020, American Chemical Society.

Several recent organic field effect transistors based on conjugated small molecules also take advantage of conformational locking through chalcogen bonding interactions to enforce chromophore planarity and encourage close packing arrangements.¹⁵¹ Molecules with

fused thiophene building blocks are leading candidates for organic electronics as they have highly planar structures and excellent electronic properties. However, systems possessing more than five fused rings are difficult to synthesize and have poor solubility. In response to this challenge, Vegiraju and coworkers recently implemented conformational locks in a series of fused thiophene oligomers (**Figure 10**) to achieve some of the highest hole mobilities reported for this class of compounds.¹⁵² Alkylthiol substituents rendered dithienothiophene oligomers planar, akin to completely fused undeca-thienoacenes, through chalcogen bonds between the substituents and main-chain sulfur atoms. Crystal structures showed interatomic distances between the sulfur atoms of 3.12 Å, less than the sum of their van der Waals radii. The torsional angles between individual thiophene units and interoligomer distances also decreased compared to alkyl substituted oligomers, indicating near planar oligomers and close cofacial interactions. Transistors fabricated with these oligomers had hole mobilities of up to 2.6 cm² V⁻¹ s⁻¹, which represents substantial improvement compared to other covalently fused three-ring thiophene systems.¹⁵³ Vegiraju and coworkers followed this work with a similar group of terthiophene oligomers bearing alkylthio chains.¹⁵⁴ Chalcogen bonding interactions impact these oligomers similarly, enforcing planarity and improving intermolecular interactions, yielding transistors with charge mobilities up to 0.77 cm² V⁻¹ s⁻¹. S...F interactions can also simulate highly fused structures¹⁵⁵ for solar cell applications as demonstrated by Feng and coworkers.¹⁵⁶

3.2 Supramolecular Assembly and Crystal Engineering Through Chalcogen Bonds

Many supramolecular synthons are being capable of programming materials to assemble via σ -hole bonding interactions such as halogen bonding and chalcogen bonding. Wire-like and macrocyclic self-assembly motifs have been demonstrated through various forms of single and double chalcogen bonding interactions. These systems often rely on interactions through selenium and tellurium, as the increased polarizability of these atoms

exacerbates the magnitude of the σ -hole and increases interaction strength. Electron withdrawing groups installed in close proximity to the chalcogen atom can further enhance this interaction. Here we elaborate on recent examples in which the strength and directionality of chalcogen bonding interactions enable assembly of smaller molecular fragments into novel crystalline assemblies, as well as supramolecular materials with secondary functionality available through chalcogen bonds. Although this area may be a slight departure from our previous discussions of conjugated polymers, the strategies described here possess applicability to future polymeric systems, and have garnered a place in this review. This section will be limited to some recent, select studies; for a more in-depth overview of additional examples, we recommend a recent review by Biot and Bonifazi on chalcogen-bond driven molecular recognition.¹⁵⁷

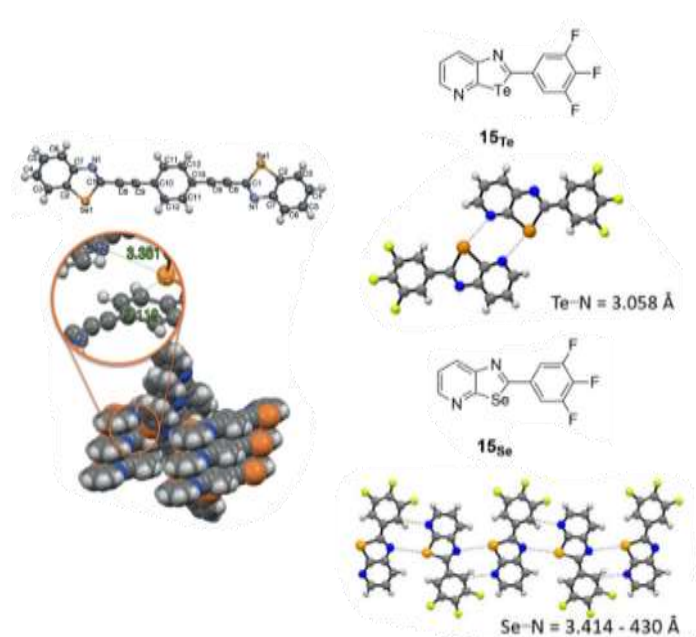


Figure 11. Designs and crystal structures of some oligomers developed by the Bonifazi group showing molecular frameworks constructed through Se and Te chalcogen bonds. Reproduced with permission.^{158, 160} Copyright 2015, 2018 Wiley-VCH.

With the goal constructing metal-free organic phosphorescent materials for optoelectronic applications, in 2015 the Bonifazi group first published work on

benzocalcogenazole moieties (**Figure 11**),¹⁵⁸ featuring a series of organic emitters containing different chalcogen atoms in the same positions along the conjugated backbone. Crystal structures of these oligomers showed an abundance of Y•••N interactions (Y = O, S, Se, Te) that assembled individual fragments in a wire-like fashion. These interactions strengthened noticeably going down Group 16, with closer Y•••N distances and lower offset distances between molecules. These units are candidates for the construction of elaborate recognition arrays based on predictable packing motifs, leading to increased structural diversity of these compounds through new synthetic protocols for the preparation of functionalized benzocalcogenazole units.¹⁵⁹ Moreover, pyridine-functionalized benzocalcogenazoles formed dimer-like assemblies, as the addition of a new chalcogen-interaction donor formed complimentary assemblies in dimer-like fashions.¹⁶⁰ This motif could serve as method for pairing of polycyclic aromatic hydrocarbons such as pyrene, as well as moieties popular in organic electronics like bithiophene.¹⁶¹ Most recently, these recognition motifs have been exploited for the construction of supramolecular polymers with the aid of additional halogen bonding crosslinkers.¹⁶²

The Vargas-Baca group publishes leading research on Te-based chalcogen bonding interactions.¹⁶³ Their recent contributions come in the form of novel macrocycles (**Figure 12**) constructed from iso-tellurazole *N*-oxides joined together through Te•••O interactions.¹⁶⁴ Remarkably, crystallization with different solvents and additives produces a wide variety of macrocyclic polymorphs, all featuring Te•••O interactions. Additive-free crystallization produces either neat macrocycles consisting of four or six units, or an arrangement of monomers that resembles an infinite helical structure. Crystallization from a mixture of THF and CH₂Cl₂/hexanes produced crystals in which THF molecules occupied the void space of six-membered macrocycles, indicating these macrocycles can encapsulate small molecule guests. NMR analysis of monomer solutions provided evidence for macrocyclic assembly in

solution. In addition, these macrocycles can coordinate metal cations and encapsulate larger molecules such as fullerenes.

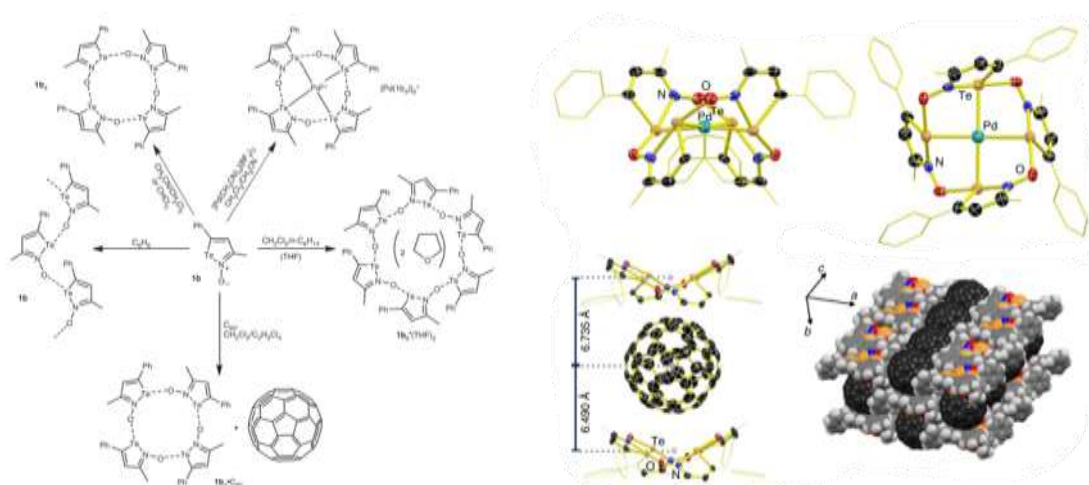


Figure 12. Left: Chalcogen-bond based macrocycles developed by Ho and coworkers by crystallizing monomeric units under different conditions. Right: Crystal structures of macrocycles complexed with metal cations (top) and fullerene (bottom). Reproduced with permission.¹⁶⁴ Copyright 2016, Nature Publishing Group.

Complex synthons based on chalcogen bonding can further produce complex supramolecular architectures for applications beyond optoelectronic devices described above. Liang Chen and coworkers reported a novel amphiphilic system (**Figure 13**) based on reversible chalcogen bonding interactions in 2018.¹⁶⁵ Their system comprised a macrocyclic donor capable of encapsulating the hydrophilic head of an anionic surfactant, 4-dodecylpyridine N-oxide (DPN), through chalcogen bonding interactions. Changing the chalcogen atom significantly changed the assembly patterns: Te atoms gave hollow spherical vesicles, while Se atoms produced nanofibers with radial diameters of 6.5 nm. The differences in assembly motifs can be attributed to the differing level of interaction strengths between the hydrophilic head and chalcogen atoms. Isothermal titration calorimetry (ITC) experiments revealed that the interaction strength between DPN and Te is stronger than that involving Se, shortening bond lengths and changing the overall architecture. Due to the dynamic nature of

these interactions, the Te-based vesicles ruptured upon introduction of halide anions (Cl^- or Br^-) or decreasing pH ($\text{pH} \leq 5.2$). Thus, a proof-of-concept drug delivery system was demonstrated by assembling and rupturing vesicles prepared in the presence of the anticancer drug doxorubicin.

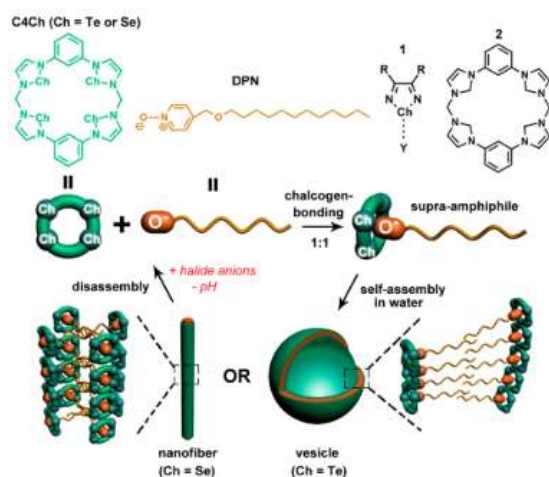


Figure 13. Chalcogen bonded nanofibers and vesicles developed by Chen and coworkers.

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In a 2020 follow-up publication, Zeng et al used the same amphiphilic design to engineer supramolecular polymers that further assembled into supramolecular hydrogel fibers.¹⁶⁶ By adapting the macrocyclic approach proposed by Chen et al into a bicyclic/bidonor motif, the same chalcogen bonding interactions enabled monomeric units to assemble into linear supramolecular polymer chains. NMR studies of solutions containing both monomers confirm the placement of the DBN anionic head into the chalcogen-based macrocycle in a concentration dependent fashion, while asymmetric flow field flow fractionation (AF4) analysis, which is a form a liquid chromatography designed to provide supramolecular polymerization parameters, provided insight into the chain-growth process by showing increasing molecular weights of supramolecular polymers in conjunction with increasing monomer concentration. Similarly to Chen and coworkers, ITC revealed that $\text{Te} \cdots \text{O}$ interactions were stronger than $\text{Se} \cdots \text{O}$ interactions, which impacted polymerization

parameters such as degree of polymerization. Both polymers formed fibrous hydrogels, with the Te-based polymer being 26-times stronger than the Se-based polymer. Competing anions such as chloride disrupt the polymer network and can dissolve the gel within one minute. Owing to the dynamic and reversible nature of this process, excess DBN monomer could restore the gel state.

Resorcin[4]arene cavitands (RC) are a class of molecules that, through non-covalent interactions, can form host-guest complexes with a variety of species for applications in molecular recognition.¹⁶⁷ Riwar and coworkers reported the first dimeric capsular assembly of RCs based on chalcogen bonding in 2018, taking advantage of the square-like dimeric interactions that chalcogenic diazole building blocks form.¹⁶⁸ By using 2,1,3-benzotelluradiazole and 2,1,3-benzothiadiazole, they assessed the impact of the relative chalcogen bonding strengths on the solid-state assembly of these cavitands, as tellurium interacts more strongly with nitrogen than does sulfur. These different interactions strengths yielded drastically different crystal packing patterns. Te-based cavitands crystallize in a head-to-head circular array bound by 16 Te•••N interactions, forming a cavity capable of encapsulating an aromatic solvent molecule through additional π -stacking interactions. In contrast, S-based cavitands either form shifted capsular assemblies with only 12 S•••N interactions or supramolecular polymeric arrangements based solely on π -stacking that feature no chalcogen bonds at all. Therefore, the disparity in interaction strength leads to varying levels of chalcogen bonding in crystals of these cavitands and the ability to tune the outcome of supramolecular assembly.

In 2020, Rahman et al built on the Riwar study¹⁶⁹ by including Se through three novel cavitands possessing Se atoms in the diazole components, and also by including water solubilizing groups. The observed crystal packing patterns of these Se-based cavitands resembled that of the Te-based molecule designed by Riwar, with a total of 16 interactions stabilizing dimeric assemblies. They also expanded the population of possible guest

molecules, including anhydrides, amides, long *n*-alkanes, and carboxylic acids. The size of the guest molecule dictated the style of encapsulation these Se-based cavitands adopted, in terms of the ratio between guest and cavitand. These findings were elaborated in a computational study by Tzeli and coworkers, also in 2020.¹⁷⁰ Calculations of the binding energies of dimeric complexes consisting of cavitands with four chalcogen atoms (O, S, Te, Se) revealed stronger binding energies in Se and Te cavitands than S and O, as well as more effective encapsulation of *n*-nonane.

The group of Paul Beer at Oxford has published multiple papers on the use of macrocycles for solution-phase ion sensing and recognition using chalcogen bonds. A 2017 study described the use of chalcogen-containing macrocycles for metal cation chelation, rotaxane generation, and anion binding.¹⁷¹ In 2019, Borissov and coworkers reported novel macrocycles for the recognition of anions in aqueous media featuring either iodo- or 5-methyltellanyl triazoles with numerous ethylene glycol chains to impart water solubility, taking advantage of chalcogen bonding interactions between Te and the iodide ion.¹⁷² Due to steric restrictions, these macrocycles folded and created a pocket for anions to bind. Functionalizing this pocket with Te atoms enabled efficient anion binding through chalcogen bonding interactions, yielding macrocycles with more efficient iodide binding than the Na⁺/I⁻ symporter protein NIS, which is involved in thyroid hormone biosynthesis. Computational modeling describes several different binding motifs involving dimeric and monomeric assemblies of varying strengths. The selectivity of binding to iodide over other anionic species such as Br⁻, Cl⁻ and ClO₄⁻ was also highlighted. Finally, other macrocycles appended with 4-aminonaphthaleneimide fluorophores produced a fluorescent output upon anion binding as a result of the imposed restriction of intramolecular motion upon complexation. For example, iodide ion doubled fluorescence intensity of one macrocycle, indicating potential application in aqueous anion sensing.

4. Outlook and Conclusions

Conjugated polymers and oligomers are critical semiconducting materials for applications in next generation organoelectronic devices. The electronic and physical properties of these materials as solids are all influenced by the self-assembly of individual molecular chains and the nature of intermolecular coupling, both of which are driven by non-covalent interactions. In this review, we have summarized how two classes of non-covalent interactions—hydrogen bonding and chalcogen bonding—can control the design and assembly of conjugated polymers and oligomers to yield materials with desirable properties such as increased charge transport and physical robustness. In particular, hydrogen bonding interactions has increased intermolecular coupling and provide mechanisms for self-healing and chemical sensing, while chalcogen bonding interactions have benefitted transistor and photovoltaic ensembles by effectively locking the intermolecular conformations of polymers in the solid state, yielding highly planar structures. In addition, employing non-covalent interactions in small molecule and oligomeric examples provide valuable insight into new strategies that may be applied to future polymer designs.

Despite the advances in the use of these design motifs in transistors and photovoltaics, we have noted fewer direct applications to light emitting technologies based on conjugated polymers. Organic light-emitting device (OLED) technology based on conjugated polymers remains a popular area of research due to possible applications such as printable and flexible lighting.¹⁷³ An ongoing challenge for these devices is achieving intra- and intermolecular solid-state assemblies optimal for the electrical production of excitons, as well as their radiative decay, particularly in the blue part of the spectrum.¹⁷⁴ Thermally activated delayed fluorescence (TADF) has the potential to improve OLED efficiency by harnessing the large number of triplet excitons generated by electron-hole recombination.^{175,176} Efficient TADF requires a low difference in energy between triplet and singlet excited states to enable thermal population of the S1 state. Low degrees of orbital overlap, usually achieved by twisting of

conjugated molecules through steric buttressing, promotes this small ΔE_{ST} . One could imagine programmed, discrete, directional non-covalent interactions enabling such conformations and broadening the applicable structural space for these materials and open new possibilities for discovery.

Finally, hydrogen bonding and chalcogen bonding are just some of the wider breadth of possibilities of non-covalent interactions. For example, halogen bonding interactions are strong and directional, and becoming increasingly popular in crystal engineering, but are seldom integrated into conjugated polymers themselves.¹⁷⁷ We surmise that this may be because aromatic halides are typically used as coupling partners during polymer synthesis, and attempting to retain or install halides after a polymerization reaction could pose synthetic challenges. Nevertheless, as the work reviewed here makes clear, having more types of discrete and programmable interactions at our disposal leads to the discovery of new materials, and helps to advance the applications that the unique combination of optoelectronic, chemical, and physical properties of conjugated polymers provide.

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Optimizing the Self-Assembly of Conjugated Polymers and Small Molecules Through Structurally Programmed Non-Covalent Control

