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Covalent and Noncovalent Approaches to Rigid Coplanar π-Conjugated Molecules and Macromolecules

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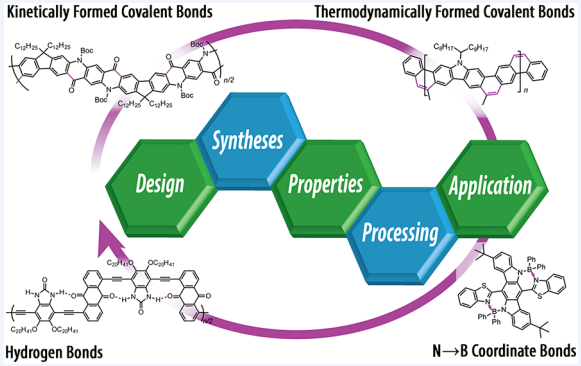
CONSPECTUS: Molecular conformation and rigidity are essential factors in determining the properties of individual molecules, the associated supramolecular assemblies, and bulk materials. This correlation is particularly important for π-conjugated molecular and macromolecular systems. Within such an individual molecule, a coplanar conformation facilitates the delocalization of not only molecular orbitals but also charges, excitons, and spins, leading to synergistically ensembled properties of the entire conjugated system. A rigid backbone, meanwhile, imposes a high energy cost to disrupt such a favorable conformation, ensuring the robustness and persistence of coplanarity. From a supramolecular and material point of view, coplanarity and rigidity often promote strong intermolecular electronic coupling and reduce the energy barrier for the intermolecular transport of charges, excitons, and phonons, affording advanced materials properties in bulk. In this context, pursuing a rigid and coplanar molecular conformation often represents one of the primary objectives when designing and synthesizing conjugated molecules for electronic and optical applications.



Two general bottom-up strategies—covalent annulation and noncovalent conformational control—are often employed to construct rigid coplanar π systems. These strategies have afforded various classes of such molecules and macromolecules, including so-called conjugated ladder polymers, graphene nanoribbons, polyacenes, and conformationally locked organic semiconductors. While pursuing these targets, however, one often confronts challenges associated with precise synthesis and limited solubility of the rigid coplanar systems, which could further impede their large-scale preparation, characterization, processing, and application. To address these issues, we developed and utilized a number of synthetic methods and molecular engineering approaches to construct and to process rigid coplanar conjugated molecules and macromolecules. Structure−property correlations of this unique class of organic materials were established, providing important chemical principles for molecular design and materials applications.

In this Account, we first describe our efforts to synthesize rigid coplanar π systems fused by various types of bonds, including kinetically formed covalent bonds, thermodynamically formed covalent bonds, N→B coordinate bonds, and hydrogen bonds, in order of increasing dynamic character. The subsequent section discusses the characteristic properties of selected examples of these rigid coplanar π systems in comparison with control compounds that are not rigid and coplanar, particularly focusing on the optical, electronic, and electrochemical properties. For systems bridged with noncovalent interactions, active manipulation of the dynamic bonds can tune variable properties at the molecular or collective level. Intermolecular interactions, solid-state packing, and processing of several cases are then discussed to lay the foundation for future materials applications of rigid coplanar π conjugated compounds.

1. INTRODUCTION

Imparting rigidity and coplanarity into large π-conjugated systems has been a long-pursued research topic for organic, polymer, and materials chemists.[1−10] Compared with more flexible and noncoplanar counterparts, rigid coplanar π systems often possess improved delocalization of molecular orbitals, charges, excitons, and spins.[3,5−7] Meanwhile, their typically strong intermolecular interactions and electronic coupling can facilitate faster transport of charges, phonons, and excitons in bulk, leading to advantageous materials properties.[2,3,5−7] Many well-known rigid coplanar conjugated small molecules, such as porphyrins, phthalocyanines, perylene diimides, oligoacenes, pyrene derivatives, quinacridones, indigos, etc.,[7,8,11−14] demonstrated remarkable molecular and materials properties long before attention was turned to their macromolecular analogues. To promote rigidity and coplanarity in a single-stranded, nonrigid conjugated backbone, an additional strand of either covalent bonds[2,3,15−19] or dynamic noncovalent interactions[5,6,20−23] can be installed to lock the molecular conformation into a flat geometry, affording so-called "ladder-type" structures, which consist of an uninterrupted sequence of rings with adjacent rings sharing two or more atoms.[24] Between these two types of bonds, covalent bonds can

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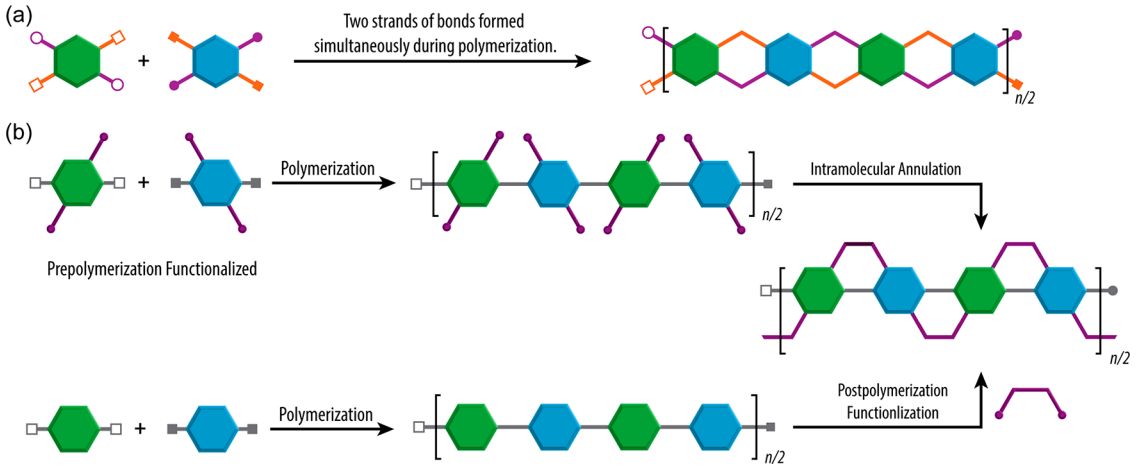

Figure 1. Graphical representation of general synthetic strategies for rigid coplanar conjugated structures: (a) single-step approach and (b) stepwise approaches through pre- or postpolymerization functionalization. Purple lines/bonds in the figures and schemes in this Account denote key bonds formed to rigidify the conjugated backbone and to lock the conformation.

drastically boost molecular rigidity by eliminating torsional motions in the conjugated backbone, leading to a robust and permanently fixed coplanar conformation; conversely, the reversible and dynamic noncovalent bonds permit active manipulation of the conformation, which results in highly tunable properties of such organic materials.

Early efforts on the synthesis of conjugated ladder polymers were in fact motivated by the expectation of high mechanical strength of such materials.[25,26] Afterward, the synthesis of these rigid macromolecules was explored using different synthetic methodologies, such as Friedel–Crafts alkylation,[27,28] imine condensation,[29] Diels–Alder reactions,[30] and electrophilic annulation.[31] The optical and mechanical properties were also investigated to a certain extent.[32−34] A few comprehensive reviews and perspectives regarding ladder polymers were published in the 1990s and recently.[1−4] As the field of organic electronics thrived, many new conjugated ladder polymers were synthesized and investigated in attempts to achieve the anticipated high conductivity originating from the fused conjugated backbone.[35,36] In the 1990s, the groups of Swager[31] and Scherf[37] reported the synthesis of all-sp^2-carbon ladder polymers, which could be considered as subunits of graphene. Later on, the discovery of the unique properties of carbon nanotubes and graphene further stimulated research on bottom-up-synthesized graphene nanoribbons,[7−9,38,39] which could be considered as analogues of rigid coplanar π-conjugated macromolecules. Meanwhile, noncovalent intramolecular interactions have also been incorporated, deliberately or unintentionally, into conjugated π systems to lock the coplanar conformation for the desired optical and electronic performances.[5,6] Overall, both covalent and noncovalent bonds can be employed to improve the molecular rigidity and to coplanarize the backbone conformation of conjugated π systems. Despite these numerous chemical approaches, the desired large-scale applications of rigid coplanar macromolecular materials are still very rare, likely on account of the challenges in achieving highly efficient, precise syntheses of these compounds and in processing of these often highly insoluble and unmeltable materials.[25,40] This Account summarizes our research efforts through a number of case studies on rigid coplanar conjugated π systems from the perspectives of synthesis, structure–property correlation, intermolecular interactions, and processing. Each case is deconstructed and systematically discussed in these separate sections.

2. SYNTHESIS

Synthetic strategies to construct rigid coplanar π-conjugated systems can be broadly divided into two categories, differentiated by the timing of the fusing bond formation. One is a single-step process during which two strands of bonds are formed simultaneously to fuse the conjugated building blocks (Figure 1a).[30,41−44] The other strategy, which we have employed primarily, is a stepwise approach in which the second strand of covalent or noncovalent bonds are formed subsequent to the formation of the first strand of covalent bonds (Figure 1b).[16,18,19,27,45−47] Compared with the single-step approach, the stepwise strategy enjoys a wider scope of applicable annulation reactions and improved synthetic feasibility.[3] In such a process, the reactive functional groups for the second strand of bonds can be preinstalled on the building units before coupling or incorporated after coupling (Figure 1b). This process shares a similar general principle with the production of carbon fibers from poly(acrylonitrile),[48] in which fused-ring substructures are generated from the non-ladder polymer precursor en route to the formation of graphitic carbon. When conducting *covalent* ring fusion, a highly efficient annulation reaction is required to achieve well-defined rigid coplanar backbones with minimum levels of structural defects. If *noncovalent* bonds are used to lock the conformation, they are expected to form spontaneously once the preorganized geometry for the intramolecular interactions is achieved.

2.1. Kinetically Controlled Covalent Bond Formation

The covalent approach was implemented by constructing rigid ladder-type backbones through intramolecular annulation of prefunctionalized precursors, including conjugated polymers, oligomers, or small molecules.[16,17,27,29,46,47,49−54] The ring-closing step can be either kinetically or thermodynamically controlled. Regardless, the conversion must be close to quantitative to minimize defects along the conjugated backbone. For example, a quinacridone-derived ladder polymer was synthesized via a highly efficient, kinetically controlled Friedel–Crafts acylation.[18] The synthetic strategy was first developed on a small molecule, namely, indenoquinacridone

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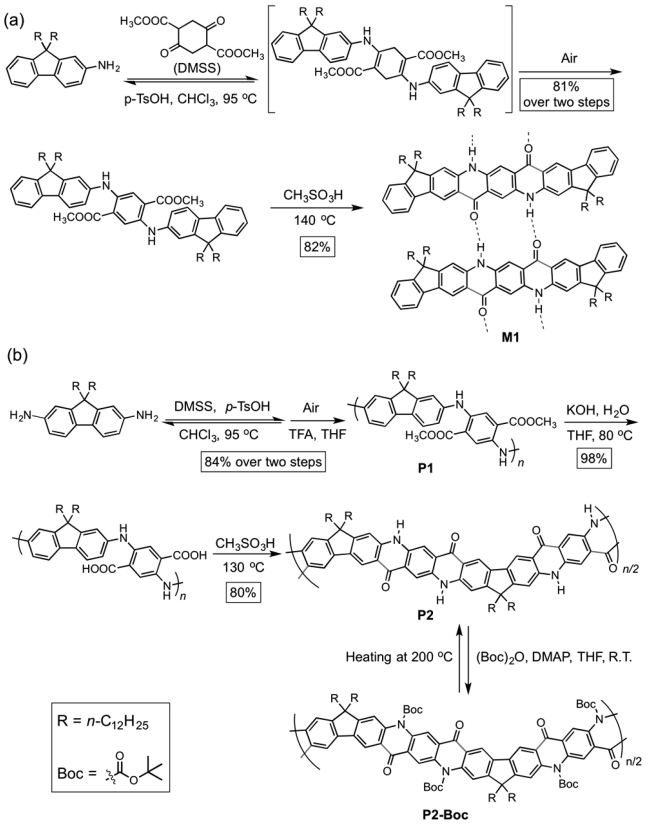
derivative **M1**.[15] To begin, imine condensation between dialkylaminofluorene and dimethyl succinylsuccinate (DMSS) afforded a cyclohexadienyl intermediate (Scheme 1a), which

Scheme 1. Synthesis of the Quinacridone-Derived (a) Rigid Molecule M1 and (b) Ladder Polymer P2 via Kinetically Controlled Ring Annulation



was spontaneously oxidized and aromatized in air. The kinetic annulation was accomplished in methanesulfonic acid to give **M1** in an isolated yield of 82%. It is noteworthy that the alkyl chains on the bridging sp^3 carbon of the fluorene component ensured excellent solubility and processability of **M1** without sacrificing the ability to form complementary intermolecular hydrogen bonds.[15]

This synthetic strategy was extended successfully to the construction of an analogous ladder polymer.[18] By driving the imine polycondensation of a diaminofluorene monomer and DMSS, the polymer intermediate **P1** was synthesized with a number-average molecular weight (M_n) of 24.0 kg/mol. Hydrolysis and kinetic annulation in methanesulfonic acid afforded the quinacridone-derived ladder polymer **P2**, which was insoluble in most common solvents because of strong interchain interactions. To address the solubility issue, a heterogeneous postfunctionalization was employed to mask the N−H groups with *tert*-butyl carbamate (Boc) groups. The introduction of the Boc groups inhibited the hydrogen bonds and weakened the $\pi-\pi$ stacking interactions between polymer chains.[55] The resulting product **P2-Boc** was therefore highly soluble in common organic solvents, allowing for a detailed characterization using ^{13}C NMR spectroscopy to confirm its structural constitution, regioregularity, and low level of defects along the backbone.[18]

2.2. Thermodynamically Controlled Covalent Bond Formation

The employment of thermodynamically controlled covalent annulation provides unique advantages compared with kinetically controlled reactions. If designed appropriately, such reactions could lead to quantitative conversion by pushing toward the thermodynamically favored product.[16,17,29,53,56−58] The "dynamic covalent" nature of such reactions can also self-correct during intramolecular annulation to prevent undesirable intermolecular cross-linking.[58] In our studies, ring-closing olefin metathesis (RCM) was selected for its synthetic versatility and the possibility to construct aromatic benzene rings. The formation of additional aromatic rings through RCM provides the desired thermodynamic driving force to the fused-ring polymer backbone.[16,17,54] By means of this strategy, we achieved the synthesis of rigid ladder polymers with ultralow levels of structural defects.[16] In this case, carbazole- and benzene-derived monomers with prepositioned vinyl groups were first polymerized through Suzuki coupling to afford precursor **P3** with molecular weights of up to 20 kg/mol. Subsequently, RCM gave the ladder polymer product **P4** with high conversion (Figure 2a). The α-branched 1-

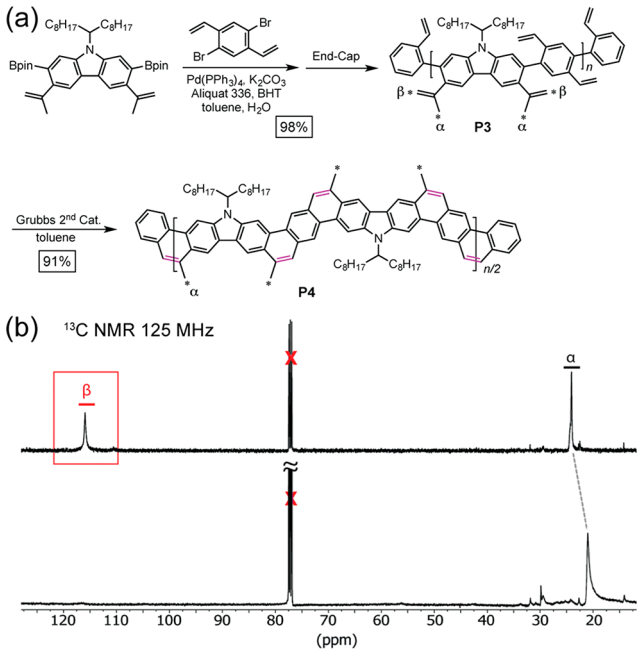


Figure 2. (a) Synthesis of ladder polymer **P4** by thermodynamically controlled ring-closing olefin metathesis. (b) ^{13}C NMR spectra of **P3** and **P4** with the "*" positions labeled with 99% ^{13}C isotope. Reproduced with permission from ref 16. Copyright 2016 Royal Society of Chemistry.

octylnonyl groups on the carbazole units imparted **P4** with good solubility and solution processability. To probe the defect level of **P4**, a batch of **P3** with 99% ^{13}C isotope-labeled isopropenyl groups was synthesized and converted to **P4**. After RCM, the sharp and strong ^{13}C resonance signal β corresponding to the terminal olefinic carbon was diminished in the ^{13}C NMR spectrum with a high signal/noise ratio (Figure 2b), indicating close-to-quantitative conversion of the RCM annulation and an extremely low level of unreacted defects.[16]

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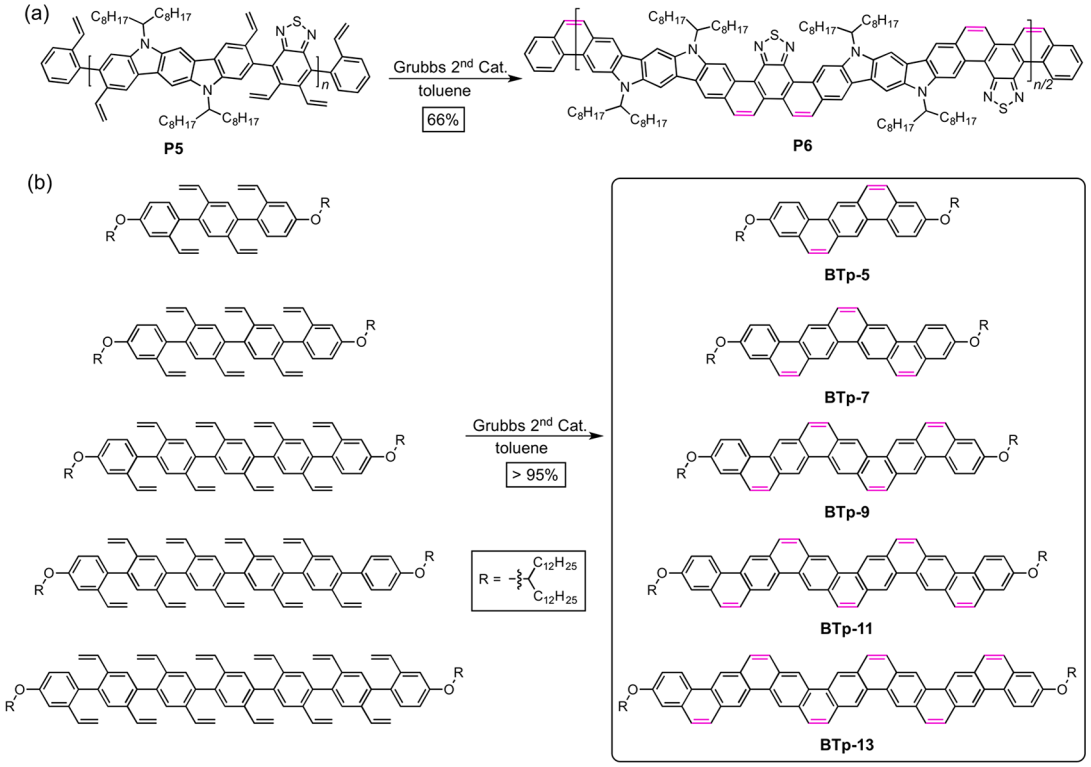
Scheme 2. Synthesis of (a) an Alternating Electron Donor–Acceptor Ladder Polymer and (b) BTp Oligomers Using Ring-Closing Olefin Metathesis Methods

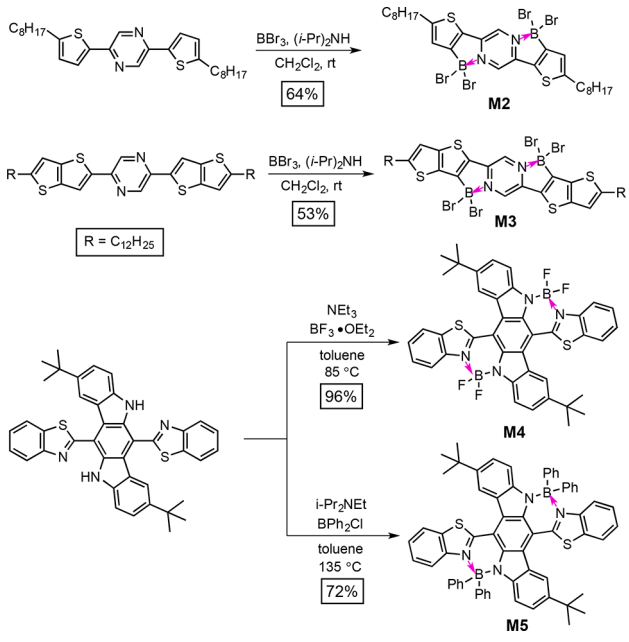


The highly efficient RCM reaction enabled access to new ladder polymers constituted of alternating electron-rich and -poor units (donor–acceptor ladder polymers), which were challenging to synthesize previously.[45,54,56] The electron deficiency of the acceptor units in these synthetic targets often impedes the commonly used Friedel–Crafts cyclization or oxidative coupling reactions in the key annulation step. Through RCM, however, the ring annulation of precursor **P5** could proceed without any significant negative impact from the electron-deficient benzothiadiazole units (Scheme 2a). Successful preparation of the desired rigid ladder polymer **P6** suggested that this RCM annulation strategy may be feasible for a broad range of substrates.[54] We also achieved the synthesis of a series of oligomeric benzo[*k*]tetraphene (BTp) derivatives using a similar strategy (Scheme 2b).[17] Precursor oligomers with well-defined lengths ranging from three to seven phenylene units were synthesized through sequential Suzuki–Miyaura couplings. The subsequent RCM reaction afforded the corresponding oligomeric derivatives (**BTp-5**, **BTp-7**, **BTp-9**, **BTp-11**, and **BTp-13**, with the numeric label indicating the number of fused aromatic rings in the backbone) in yields consistently over 95%. The close-to-quantitative conversions of these transformations, regardless of the lengths of the substrates, reinforced the significant synthetic advantages of this thermodynamically controlled annulation strategy.

2.3. N→B Coordinate Bonds

The use of dynamic noncovalent bonding, such as N→B coordination, represents another promising strategy to lock torsional conformations of conjugated molecules to achieve rigidity and coplanarity.[21,22,59,60] The relatively strong N→B coordinate bonds, which are isoelectronic and isosteric to C–C covalent single bonds, are ideal for this purpose.[60] We adopted highly efficient N-directed borylation reactions to incorporate intramolecular N→B coordinate bonds into conjugated molecules. For example, on pyrazine-derived donor–acceptor–donor precursors (Scheme 3), one-pot formation of two B–C covalent bonds and two N→B coordinate bonds was accomplished using highly Lewis acidic

Scheme 3. Synthesis of Rigid Coplanar Molecules M2–M5 with Conformations Locked by Intramolecular N→B Coordinate Bonds



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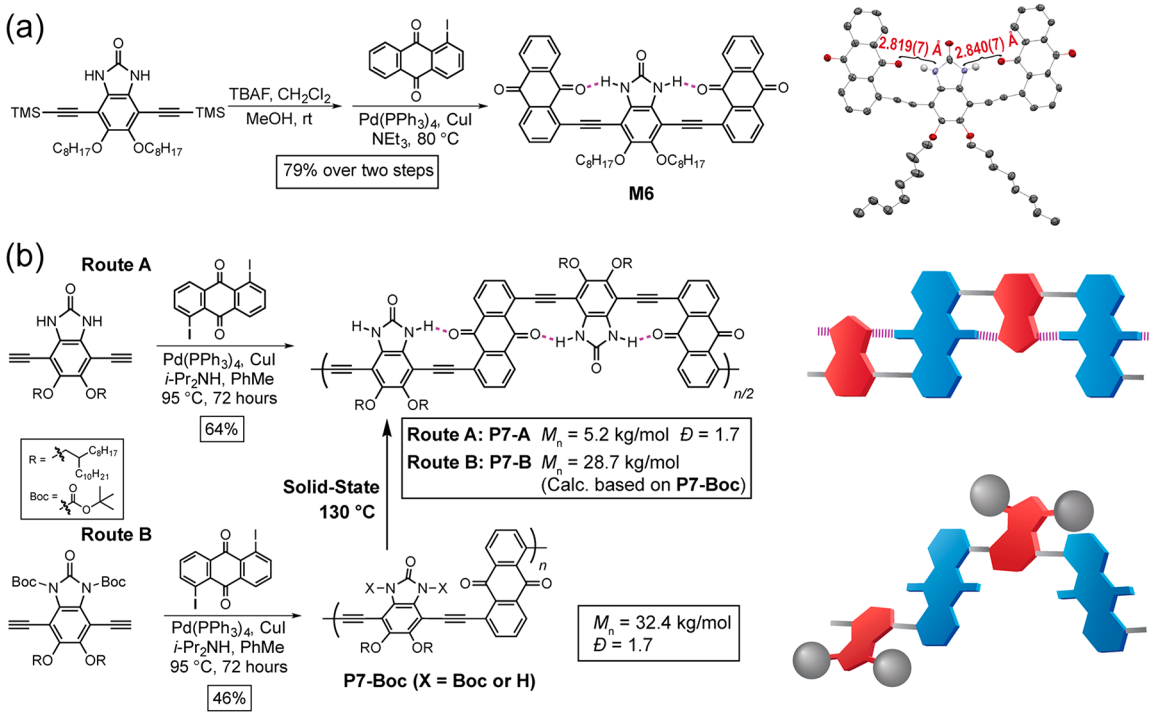

Figure 3. (a) Synthesis and single-crystal structure of **M6** locked by intramolecular hydrogen bonds. Reproduced from ref 21. Copyright 2016 American Chemical Society. (b) Two synthetic routes to coplanar polymer **P7** alongside graphical representations of **P7** and **P7-Boc**: route A, direct polymerization, route B, polymerization of Boc-protected monomers followed by solid-state cleavage of the Boc groups. Reproduced from ref 23. Copyright 2018 American Chemical Society.

BBr_3 in the presence of a sterically hindered base to afford the rigid coplanar molecules **M2** and **M3**.[20] In these reactions, the central Lewis basic pyrazine unit donated two electron lone pairs in a centrosymmeric manner to direct the formation of the B−C bonds while forming the conformation-locking N→B bonds. In another example, we installed N→B coordination onto an indolo[3,2-*b*]carbazole-derived acceptor−donor−acceptor precursor[61] to afford highly stable products **M4** and **M5**.[22] The strong acidity of N−H groups in the precursor allowed for a high-yield borylation using less corrosive boron reagents, such as $BF_3{\cdot}Et_2O$ or BPh_2Cl. In **M4** and **M5**, the nitrogen atoms on the indolo[3,2-*b*]carbazole unit provided the covalent attachment points for the boron centers, while the Lewis basic nitrogen atoms on the electron-deficient benzo[*d*]thiazole units donated the electron lone pairs to form the N→B coordinate bonds, affording a stable six-membered-ring architecture (Scheme 3). Single-crystal X-ray diffraction of **M5** unambiguously confirmed its rigid backbone and strong N→B coordination with a bond length of 1.643 Å.

2.4. Hydrogen Bonds

Although hydrogen bonds are even weaker and more dynamic than the Lewis acid−base coordinate bonds, their highly directional nature and synthetic versatility enable promising applications in enhancing molecular rigidity and inducing coplanar conformations.[62,63] We designed a model molecule **M6** in which intramolecular hydrogen bonds were constructed parallel to the π-conjugated backbone (Figure 3a).[21] To circumvent the relatively weaker strength of hydrogen bonds, the hydrogen-bond-donating urea moiety and -accepting ketone groups were fused with the backbone to reduce the entropy penalty during coplanarization[64] and to further increase the overall molecular rigidity. DFT computations revealed a 14 kcal/mol stabilization energy of the coplanar conformation. The intramolecular hydrogen bonds in **M6** and desired coplanar conformation were confirmed by single-crystal X-ray diffraction. The dihedral angles between the aromatic units were measured to be around 4°.

This successful molecular design strategy allowed us to extend the structure of **M6** to access its polymeric analogue **P7** (Figure 3b).[23] The direct Sonogashira polymerization (Figure 3b, route A), however, afforded **P7-A** as a poorly soluble material. The M_n of the soluble fraction of **P7-A** was only 5.2 kg/mol. To address this solubility issue, the hydrogen-bond-masking strategy was implemented by functionalizing the hydrogen-bond-donating monomer with Boc groups before polymerization (Figure 3b, route B). Consequently, after polymerization, the solubility of the resulting **P7-Boc** was greatly enhanced as a result of the lack of intramolecular hydrogen bonds and the twisted conformation.[23] **P7-Boc** was isolated with an M_n of 32.4 kg/mol. Further thermal cleavage of the Boc groups in the solid state unmasked the intramolecular hydrogen bonds, affording the desired rigid coplanar polymer **P7-B** with a much higher molecular weight.

Overall, a broad range of synthetic approaches involving the formation of covalent or noncovalent bonds with variable dynamic characters were developed to access rigid conjugated molecules and macromolecules. These synthetic approaches give different outcomes, face different challenges, and require different general strategies when designing the synthesis. For example, the covalent ladder structure synthesis requires a highly efficient annulation reaction to minimize the unreacted defects, while this concern does not apply to the systems bridged by spontaneously formed, dynamic noncovalent bonds. Among the covalent approaches, the thermodynamically controlled synthesis is superior in minimizing the levels of defects. However, suitable reactions and functional groups for

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thermodynamic annulation are relatively limited compared with the much wider scope of kinetically controlled annulations. Among the noncovalent bonding strategies, most synthetic challenges come from the installation and stability of the noncovalent bonding moieties. The boron bridging group was typically installed after the construction of the π-conjugated backbone because of the high probability of boron-involved side reactions such as cross-coupling or acid-base reactions. In contrast, the hydrogen-bond-donating and -accepting units can typically be prefunctionalized before the cross-coupling reactions, although a protecting group for the hydrogen-bond donor is often needed.

3. STRUCTURE–PROPERTY CORRELATION

It is well-known that torsional conformation twisting on the σ bonds in conjugated polymer backbones decreases the effective conjugation length and limits delocalization of molecular orbitals.[5,65] In contrast, rigidity and coplanarity in conjugated molecules are expected to impact their excited-state dynamics, optical band gaps, exciton delocalization, intermolecular electronic couplings, and electron transfer processes. In this context, we investigated the optical properties and radiative emission dynamics of ladder polymer **P4** and its nonladder counterpart **P8** as a control (Figure 4a).[16,66] Both the absorption and emission spectra of **P4** in solution were significantly red-shifted compared with those of **P8** as a result of its more extended conjugation and hence narrowed optical band gap.[16] Meanwhile, **P4** possessed an extremely small Stokes shift of 0.01 eV and a much higher quantum yield of 15%, attributed to its backbone rigidity that prevented conformational changes during the photoexcitation and the related decay. The average fluorescence lifetimes of **P4** in solution were also significantly longer than those of **P8** (Figure 4b), likely as a result of extended exciton delocalization over the rigid conjugated backbone and fewer trap states.

In thin films, the fluorescence of **P4** was almost completely quenched, while such a quenching effect was much less significant in **P8**, indicating stronger interchain electronic coupling and enhanced exciton−exciton annihilation among the rigid and coplanar backbones.[66] For this reason, the rigid coplanar ladder polymers **P4** and **P6** were also expected to form charge transfer complexes (CTCs) with a highly electron-deficient dopant such as 2,3,5,6-tetrafluoro-7,7,8,8-tetracyanoquinodimethane (F_4TCNQ). Indeed, both **P4** and **P6** underwent charge transfer with F_4TCNQ, showing the characteristic polaron absorption peaks in the near-infrared region (Figure 4c).[54] In drastic contrast, no CTCs were observed when the nonladder-type control polymers were treated with F_4TCNQ, even though they are composed of similar aromatic building blocks. This observation suggested that the extended coplanar π faces of the ladder polymers were essential in promoting CTCs with a π dopant.

Synthetic access to the BTp oligomer series with precise lengths allowed us to investigate systematically how the length of the conjugated ladder-type backbone impacts the optical properties. As expected, a bathochromic shift of the absorption spectra was observed with linear elongation of the BTp oligomers on account of the increased backbone conjugation (Figure 5a, b). From plots of the absorbance and emission wavelength maxima against the number of fused aromatic rings in the BTp derivatives (n), the effective conjugation length of

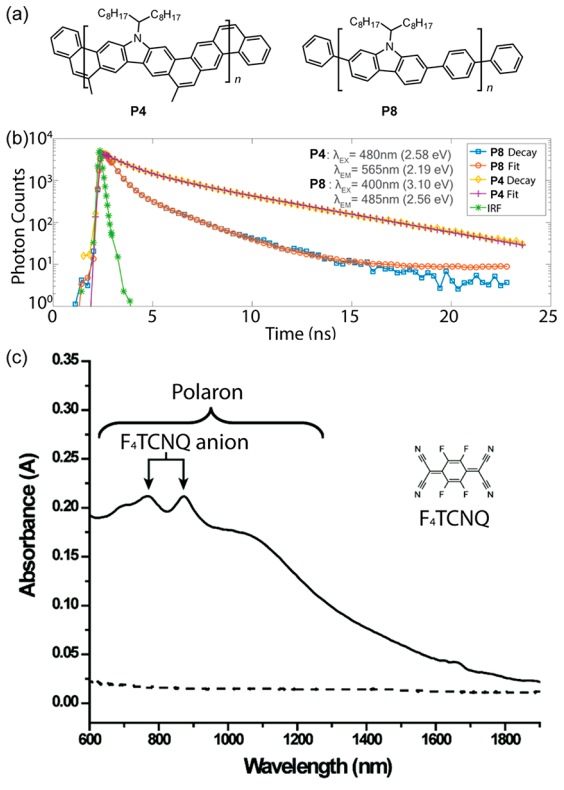

Figure 4. (a) Chemical structures of ladder polymer **P4** and its nonladder-type analogue **P8**. (b) Time-resolved photoluminescence decay traces of diluted solutions of **P4** and **P8**. Reproduced from ref 66. Copyright 2017 American Chemical Society. (c) Photoabsorption spectra of undoped **P4** (dashed line) and **P4** doped with F_4TCNQ (solid line). Reproduced with permission from ref 54. Copyright 2018 Royal Society of Chemistry.

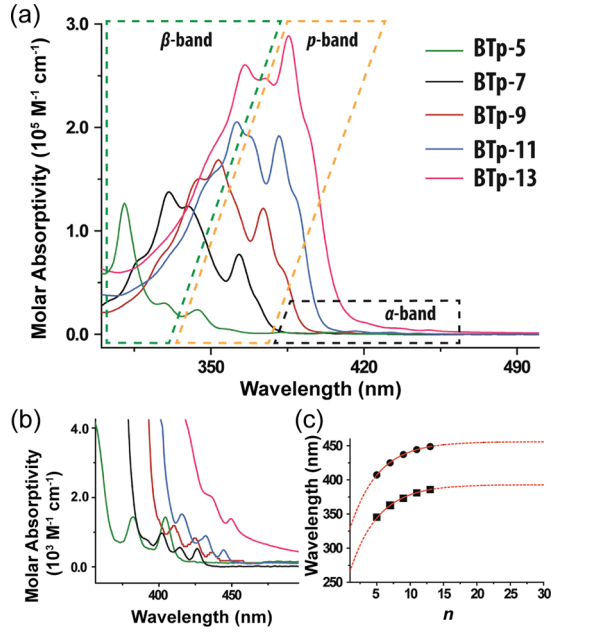

Figure 5. (a, b) Absorption spectra of BTp oligomers. (c) Correlation plots and exponential fits of the absorption maxima (squares) and fluorescence emission maxima (circles) vs the number of fused aromatic rings of BTp derivatives. Reproduced with permission from ref 17. Copyright 2017 John Wiley and Sons.

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this type of macromolecules was extrapolated to be approximately 21 rings (Figure 5c).[17] Interestingly, this length was similar to that of a non-ladder oligophenylene derivative, despite the fact that the rings in the BTp oligomers are fully fused. These data indicated that the molecular orbital delocalization and band properties of polycyclic aromatic hydrocarbon systems were dependent more significantly on parameters such as the edge constitution and the width of the backbones, instead of just the length and rigidity.[7,8,49,67−69]

The incorporation of heteroatoms into conjugated ladder-type π systems provides another valuable approach to impact the electronic structures and properties of these compounds. As demonstrated in our study, intramolecular N→B coordinate bonds not only locked the torsional conformation of the conjugated backbone but also significantly lowered the molecular orbital energy levels. The N→B coordination-bridged molecules **M2**−**M5** exhibited low HOMO and LUMO levels as well as near-infrared optical activities (Table 1), in contrast to their precursors without N→B bonds.[20,22]

Table 1. Optical and Electrochemical Properties of N→B Coordination-Bridged Compounds M2−M5

compound	$\lambda_{abs,max}$ (nm)	optical band gap (eV)	HOMO (eV)	LUMO (eV)
M2	648	1.60	−5.72	−4.40
M3	772	1.34	−5.40	−4.21
M4	695	1.78	−5.47	−3.66
M5	768	1.60	−5.15	−3.47

For example, compound **M3** with seven fused rings demonstrated absorption over 900 nm. Cyclic voltammetry studies revealed that the narrow band gaps of these molecules were a result of the low-lying LUMO energy levels (Table 1), which was attributed to the significant electron-withdrawing effect of the boron centers.

Electrochemical investigation of N→B coordination-bridged compound **M5** revealed four reversible and well-separated reductive and oxidative electron transfer processes, suggesting five distinct stable redox states.[22] The corresponding radical cation and anion states during these redox processes were highly stable, in sharp contrast to the precursor without N→B coordinate bonds, which showed irreversible reductions. Further study of **M5** demonstrated recyclable multicolor electrochromism (Figure 6a).[22] Moreover, single-crystal structures of the neutral state, radical cation, and dianion of **M5** revealed two distinct yet orthogonal pathways of structural transformations from benzenoid into quinonoid constitutions during the oxidation and reduction processes (Figure 6b, c). We also noticed significant hyperconjugative interactions between the σ^* orbital of the axial boron−ligand bond and the orbitals on the π-conjugated backbone in different redox states (Figure 6d). These hyperconjugative interactions and the enhanced molecular rigidity assisted the desired charge/spin delocalization to stabilize the different redox states.[22] In this case, N→B coordination played an important role in rendering robust and reversible multistage electrochemical processes by rigidifying the molecular conformation, by extending the charge and spin delocalization, by modulating the π-electron density, and by a hyperconjugation mechanism.[22]

These results showed that dynamic noncovalent bonds can effectively introduce unusual properties and materials functions in coplanar conjugated molecules.[5,6] Furthermore, compared with covalently fused ladder-type backbones, whose rigid conformations are not adjustable, those coplanarized by noncovalent bonds possess the unique intrinsic capability of undergoing dynamic control of molecular rigidity and conformation. Such control represents a facile pathway to switch and tailor their molecular, supramolecular, and solid-state properties. For example, in **M2**, the dynamic and reversible nature of N→B coordinate bonds allowed for

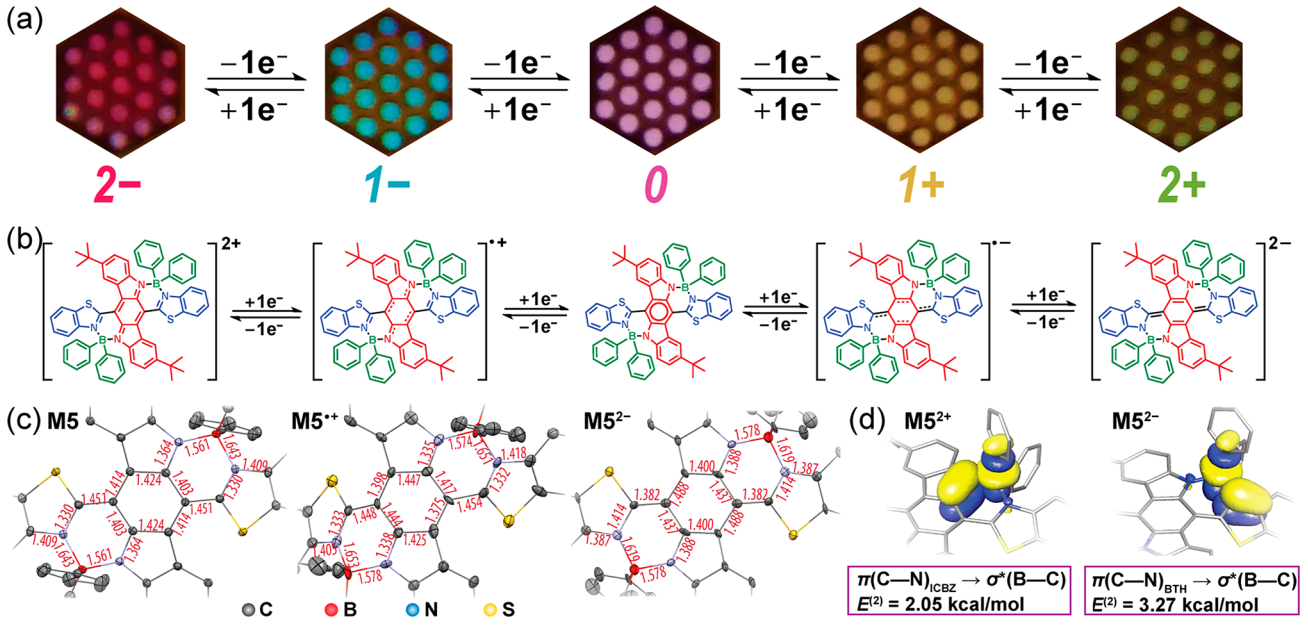

Figure 6. (a) Photographs of **M5** solutions in different redox states in the presence of a honeycomb working electrode in a spectroelectrochemical cell. (b) Chemical structures of the five different redox states of **M5**. (c) Single-crystal X-ray structures of the neutral state, radical cation, and dianion of **M5** with selected bond lengths. (d) Natural bond orbital plots of representative hyperconjugative interactions in $\mathbf{M5}^{2+}$ and $\mathbf{M5}^{2-}$. Reproduced from ref 22. Copyright 2018 American Chemical Society.

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manipulation of the bond strength and backbone conformation, leading to tunable electronic properties of the conjugated π system.[20] A Lewis basic solvent, for instance, could competitively form a coordinative interaction with the boron center to weaken the intramolecular N→B bonds, so that the boron-induced electronic effect was less profound and the coplanar conformation was disrupted (Figure 7a). Experimental results showed that the optical band gap of **M2** increased as the Lewis basicity of the solvent increased, corroborating the aforementioned hypothesis (Figure 7b). Meanwhile, as the Lewis basicity increased, the vibrational progressions in the absorption spectrum gradually disappeared as evidence of decreasing molecular rigidity.[20]

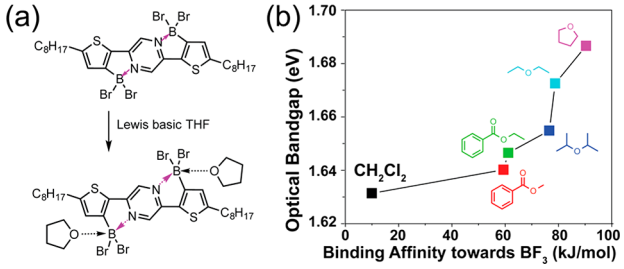

Figure 7. (a) Illustration of the boron binding competition against **M2** from a Lewis basic solvent. (b) Correlation between the optical band gap of **M2** and the Lewis basicity of the solvent, measured as the binding enthalpy between the solvent and BF_3. Reproduced from ref 20. Copyright 2016 American Chemical Society.

4. INTERMOLECULAR INTERACTIONS AND PROCESSING

Intermolecular interactions, solid-state packing, and processability of π-conjugated compounds are essential for their applications as functional materials.[6,12,55,70] The synthesis of BTp oligomers with well-defined molecular lengths provided an opportunity to investigate size-dependent solid-state properties such as packing, molecular mobility, and crystallinity of these rigid molecules.[10,17] The crystalline nature of spin-cast thin films of these oligomers was characterized by grazing-incidence wide-angle X-ray scattering (GIWAXS) (Figure 8a).[17] By comparing diffraction patterns from these BTp derivatives, we identified two competing factors governing the solid-state crystallization process: intermolecular interactions and molecular mobility (Figure 8b). The balance between these two factors was crucial in obtaining highly crystalline solid-state packing for ladder-type BTp-derived materials. For smaller molecules, such as **BTp-5**, the size of the coplanar aromatic backbone was comparatively too small to facilitate strong enough intermolecular forces to guide crystalline packing in the solid state. **BTp-7** and **BTp-9** showed higher crystallinity on account of their stronger $\pi-\pi$ stacking interactions. With further increases in size, however, molecular mobility decreased during the crystallization process. Consequently, larger molecules such as **BTp-11** were kinetically trapped in an amorphous state after spin-casting at room temperature, requiring thermal annealing for solid-state rearrangement into a crystalline state. For the larger **BTp-13**, the solid-state morphology was amorphous even with high-temperature annealing, indicating the dominating kinetic trapping effect during the casting process.[17]

Solution processability is vital for many of the practical applications of conjugated organic materials.[70,71] Achieving good solution processability of coplanar conjugated ladder polymers has been a particular challenge on account of the typically strong intermolecular interactions and backbone rigidity.[26,72] Introducing large flexible side chains can improve the processability and solubility.[70,71] However, these side chains often add nonactive components, create disordered

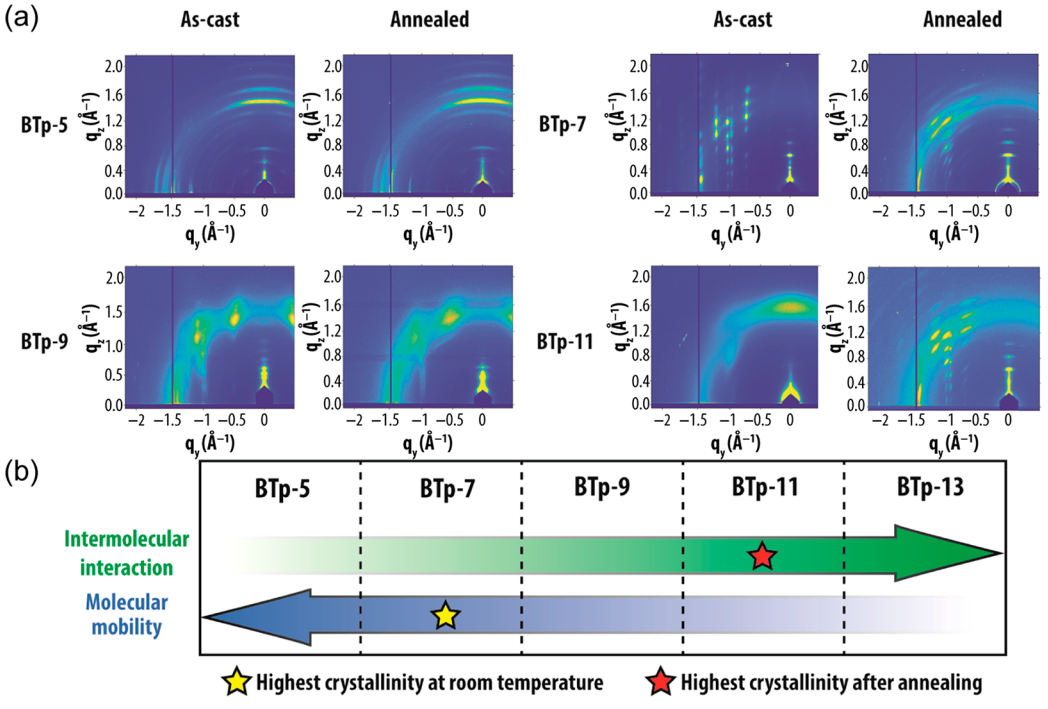

Figure 8. (a) GIWAXS images of thin films of BTp oligomers. (b) Chart showning the correlation between intermolecular interactions and molecular mobilities for the crystallization of BTp oligomers. Reproduced with permission from ref 17. Copyright 2017 John Wiley and Sons.

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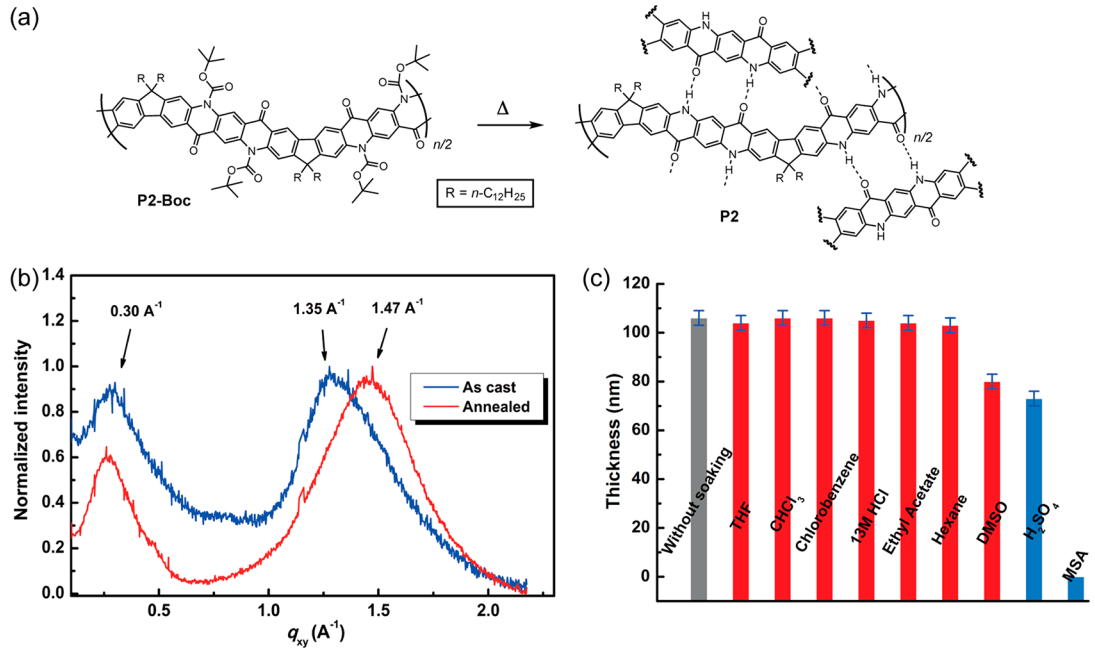

Figure 9. (a) Chemical transformation of **P2-Boc** to **P2** through the Boc cleavage reaction. (b) Out-of-plane GIWAXS profile of the as-cast thin film (blue) in comparison with that of the annealed thin film (red) showing the shortened $\pi-\pi$ stacking distance after Boc cleavage. (c) Thickness of **P2** films after soaking in different solvents for 30 min. The red bars represent boiling solvents or solutions, and the blue bars represent treatment at room temperature. Reproduced with permission from ref 18. Copyright 2017 Elsevier.

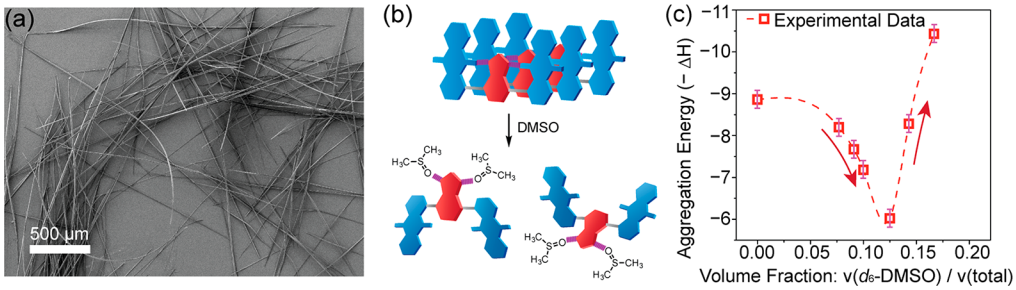

Figure 10. (a) Scanning electron microscopy image of self-assembled fibers of **M6**. (b) Graphical representation of changes in the aggregation behavior of **M6** before and after the addition of DMSO. (c) Aggregation energy of **M6** in $CDCl_3/d_6$-DMSO mixed solvents with increasing volume fraction of d_6-DMSO. Reproduced from ref 21. Copyright 2016 American Chemical Society.

phases in the bulk, and interrupt intermolecular electronic couplings, impacting the desired solid-state properties of these materials negatively.[73] In this context, it is essential to resolve such issues for synthesis, processing, and practical applications of rigid conjugated molecules. The quinacridone-derived ladder polymer **P2**, for instance, was completely insoluble in organic solvents because of the strong interchain interactions, including complementary intermolecular hydrogen bonds and $\pi-\pi$ stacking, preventing structural characterization and solution processing.[18] To address this problem, we converted **P2** into **P2-Boc** through postpolymerization modification to diminish these intermolecular interactions. Consequently, **P2-Boc** showed high solubility in common organic solvents, allowing for extensive solution-phase characterization and solution processing into thin films. Furthermore, the Boc groups can be thermally cleaved quantitatively to regenerate **P2** in the solid state (Figure 9a). Therefore, the insoluble ladder polymer **P2** can be processed into films by solution-casting of **P2-Boc** followed by thermal cleavage. GIWAXS analysis revealed a decreased $\pi-\pi$ stacking distance as a result of the cleavage of the bulky Boc groups (Figure 9b). The restored interchain interactions lent the films of **P2** excellent resistance to hot organic solvents and corrosive acid solutions (Figure 9c).[18] In addition to the chemical stability, **P2** demonstrated a high carbonization yield of 50% at 800 °C, agreeing well with the theoretical backbone weight. The low weight loss of the sp^2 component of **P2** indicated the importance of ladder-type constitution for a high carbonization yield, in accordance with the process of carbon fiber formation from poly(acrylonitrile).

The intermolecular interactions and self-assembly of coplanar π-conjugated molecules can also be controlled by actively manipulating the dynamic noncovalent bonds. The hydrogen-bond-bridged molecule **M6**, for example, showed strong intermolecular interactions due to the coplanar conformation and rigid backbone promoted by the intramolecular hydrogen bonds. These anisotropic interactions prompted the self-assembly of **M6** into one-dimensional organic fibers with a high aspect ratio (Figure 10a). In the solid state, the $\pi-\pi$ stacking distances were as short as 3.30 Å.[21] In the solution phase, the aggregation enthalpy was measured to be 8.86 kcal/mol in $CDCl_3$. The dynamic nature

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of the hydrogen bonds enabled tuning of the aggregation strength of **M6**. The addition of DMSO, a hydrogen-bond-competing reagent, disrupted intramolecular hydrogen bonds and afforded a less coplanar backbone conformation (Figure 10b). As a result, the intermolecular aggregation energy of **M6** decreased to less than 6 kcal/mol (Figure 10c).[21]

Active manipulation of intramolecular hydrogen bonds through the masking and unmasking method also enabled solution processability of rigid, hydrogen bonded polymer **P7**.[23] As described in the previous section, the switched-on solubility of **P7-Boc** allowed it to be solution-processed into a smooth thin film. Thermal cleavage of the Boc groups unmasked the intramolecular hydrogen bonds to feasibly regenerate **P7-B** without significant morphological changes, generating a smooth thin film of **P7-B** despite its insoluble nature (Figure 11).[23] This active manipulation approach

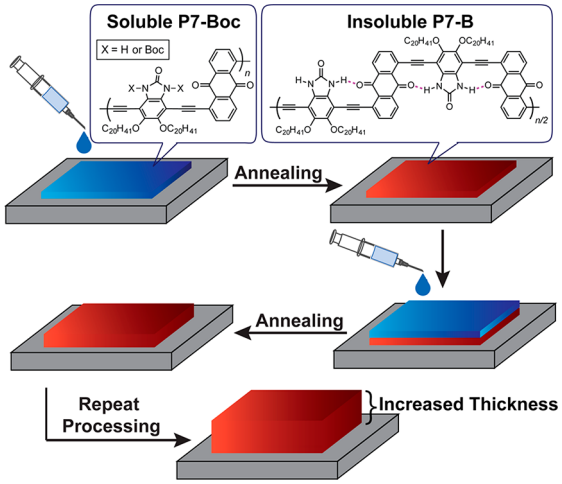

Figure 11. Graphic scheme of multilayer film processing of solvent-resistant films of **P7-Boc**. Reproduced from ref 23. Copyright 2018 American Chemical Society.

enabled multilayer processing of **P7-B** through several cycles of solution-casting and thermal cleavage in a cumulative manner (Figure 11). In these cycles, solution-casting of an additional **P7-Boc** layer did not impact the **P7-B** layer on the substrate, thanks to the switched off solubility of **P7-B** after unmasking of the intramolecular hydrogen bonds. This method sets a foundation for future developments of polymeric materials suitable for multilayer solution processing and 3D printing by manipulation of solubility through intramolecular noncovalent bonds and backbone conformation.

5. CONCLUSION AND OUTLOOK

We have established a series of synthetic strategies—employing kinetically formed covalent bonds, thermodynamically formed covalent bonds, or dynamic noncovalent bonds—to impart backbone rigidity and coplanarity into π-conjugated systems. These strategies differ from each other in terms of bond reversibility and strength, leading to variable synthetic outcomes, electronic properties, and property tunability of the resulting conjugated molecules and macromolecules. Throughout the synthesis and processing, we circumvented the low solubility and poor processability of these rigid coplanar molecules by attaching branched long flexible side chains and/or masking the key noncovalent bonding moieties using thermally cleavable groups. These rigid and coplanar compounds demonstrated intriguing properties that are not present in their noncoplanar counterparts, an encouraging indication of their future as novel organic functional materials.

The synthetic strategies and processing techniques discussed here pave the way for future exploration of unconventional applications of rigid coplanar organic molecules and macromolecules, expanding upon their well-documented applications in organic electronics and photovoltaics. For example, sp^2 carbon-based materials featuring unique backbone rigidity can be viewed as functionalized and heteroatom-doped molecular substructures of carbon nanotubes and graphene.[74,75] Now integrated with good processability, they are promising candidates to enhance the thermoconductivity and mechanical performance of plastic-like hybrid materials. In addition, the access to ladder polymers with ultralow defect levels sets the stage for urgently desired understanding of fundamental polymer physics parameters of rigid macromolecules, such as an accurate measurement of their persistence lengths.[34] The rigid coplanar structural feature can be translated further into structures beyond conventional small molecules and linear polymers, such as molecular macrocycles, water-soluble polymers, hyperbranched polymer nanoparticles, porous polymer networks, and more. New and superior molecular and materials properties stemming from these new chemistries will foster an exciting field of research opportunities for the near future.

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The manuscript was written through contributions of all authors.

Notes

The authors declare no competing financial interest.

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professor, where he leads a multidisciplinary research group studying functional organic materials.

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