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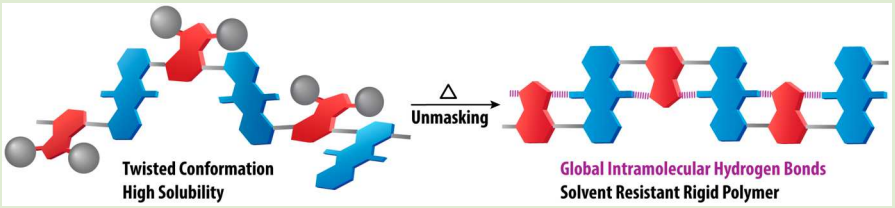
Synthesis and Solution Processing of a Rigid Polymer Enabled by Active Manipulation of Intramolecular Hydrogen Bonds

Congzhi Zhu,[†] Anthony U. Mu,[†] Chenxu Wang,[‡] Xiaozhou Ji,[†] and Lei Fang*[,†,‡]

[†]Department of Chemistry and [‡]Department of Materials Science and Engineering, Texas A&M University, 3255 TAMU, College Station, Texas 77843, United States

Supporting Information



ABSTRACT: Global intramolecular hydrogen bonds were installed and manipulated in a rigid artificial synthetic polymer in order to actively control its conformation for synthesis and processing. The polymer solubility was switched on and off by chemically inhibiting and regenerating these preorganized intramolecular hydrogen bonds. Such active manipulation made it possible to synthesize this highly rigid polymer with elevated molecular weights. A well-solubilized, noncoplanar polymer precursor with thermally cleavable Boc groups was synthesized (M_n = 32.4 kg/mol). After processing this precursor into thin films, *in situ* thermal treatment regenerated the latent intramolecular hydrogen bonds and led to a rigid ladder-type conformation. Such manipulation of the intramolecular hydrogen bonds allowed for multilayer deposition of this polymer, laying the foundation for potential additive manufacturing using this strategy.

Intramolecular hydrogen bonds are ubiquitous in biomacromolecules and synthetic polymers, playing a pivotal role in shaping macromolecular conformations and governing macroscopic properties of these polymers. For example, they induce and stabilize the secondary structures of polypeptides (Figure 1a) and proteins.[1−3] They are also important in determining the properties and functions of polysaccharides,[4] poly(vinyl alcohol),[5] polyacrylamide,[6,7] polyhydroxyalkanoates,[8,9] poly(*p*-sulfophenylene terephthalamide),[10] a variety of copolymers,[11] etc. Inspired by these natural and synthetic examples, chemists designed and incorporated intramolecular hydrogen bonds into artificial polymers to tailor their conformations and functions. These noncovalent interactions were employed to lock molecular conformations of a variety of synthetic polymers, to construct helical architectures,[12−15] to access desired optical behaviors,[16−18] and to achieve favorable charge transport properties.[19,20] However, after locking the global conformation, specifically to a coplanar geometry, decreased solubilities of the polymers were often encountered,[16,18,21,22] leading to low molecular weights and poor solution processability that prohibit the urgently demanded wide application of this promising strategy for desired properties.

We envisioned that the critical challenges associated with the poor solubility and processability of these rigid polymers can be addressed by manipulating the intramolecular noncovalent interactions. In fact, the modulation of intramolecular hydrogen bonds represents one of the fundamental mechanisms for biomacromolecules to adopt different conformations to perform diverse functions in many essential life processes.[23]

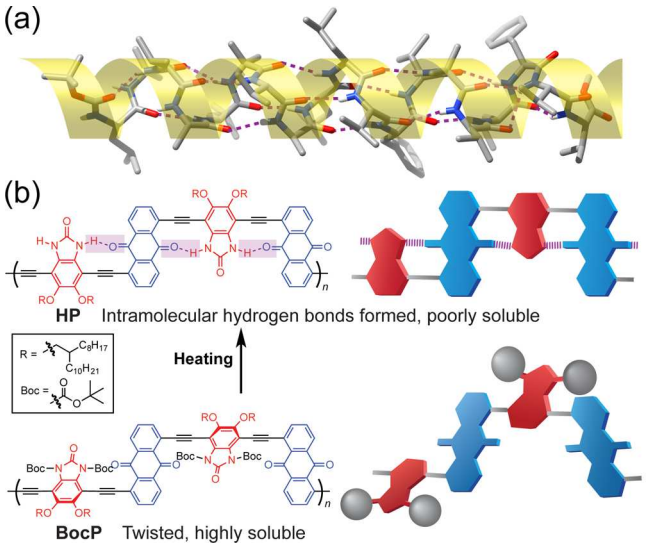


Figure 1. (a) Example of intramolecular hydrogen bonds: crystal structure of a polypeptide with helical conformation induced by intramolecular hydrogen bonds[25] and (b) chemical structures and graphical representations of **HP** and **BocP**.

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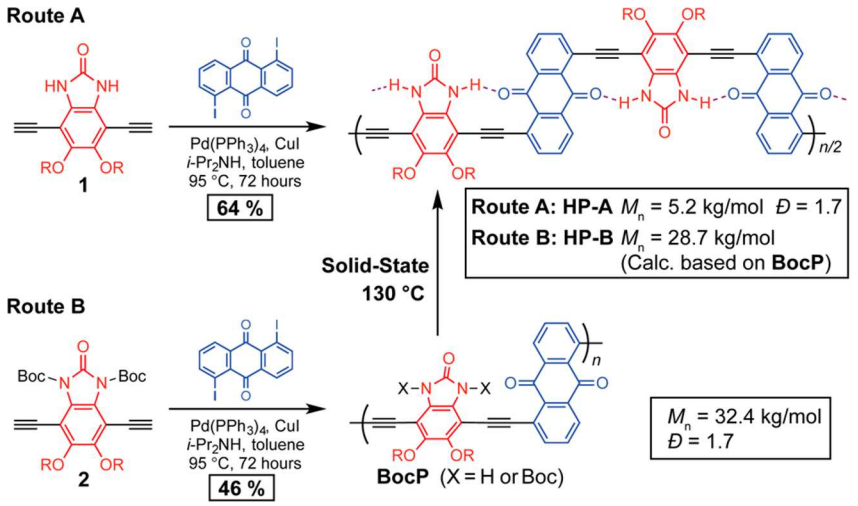
Scheme 1. Two Synthetic Routes to HP[a]



[a]Route A: direct polymerization of monomer **1** without masking the hydrogen bonds. Route B: polymerization of Boc-protected monomer **2** followed by solid-state unmasking of the hydrogen bonds.

For artificial polymers, it is still formidably challenging to actively control these intramolecular hydrogen bonds to achieve tunable properties, specifically those relating to synthesis and processing. In this context, global intramolecular hydrogen bonds (ubiquitously formed between each two adjacent building units throughout the backbone) need to be accurately arranged and efficiently manipulated in macromolecular backbones. Meanwhile, the typical high degrees of freedom of these hydrogen bonding moieties and the flexible macromolecular chains increase the complexity in controlling the conformations.[24] Herein, we report a molecular engineering strategy to address this long-standing issue by chemically inhibiting and regenerating global intramolecular hydrogen bonds that are preorganized in a model polymer (**HP**). By inhibiting hydrogen bonds, a well-soluble precursor **BocP** was synthesized with a high molecular weight (Figure 1b) and good solution processability. Regenerating these global hydrogen bonds in the solid state afforded the polymer **HP** with a rigidified backbone, leading to excellent solvent resistance while enabling multilayer processing.

The hydrogen-bonded polymer model system (**HP**, Figure 1b) was designed upon a poly(phenylene acetylene) backbone and composed of alternating hydrogen bond donating 2*H*-benzimidazol-2-one units and hydrogen bond accepting anthracene-9,10-dione units. These hydrogen bond donors and acceptors were fused to the polymer backbone so that the degree of freedom of these functional groups was significantly reduced compared to single bonded moieties,[26] leading to a much smaller entropy penalty for the formation of intramolecular hydrogen bonds.[27] Therefore, the hydrogen bond strength was expected to be enhanced, and the rigid backbone conformation can be precisely predicted. Meanwhile, the length of the ethynylene spacer allowed for the formation of a strong hydrogen bond with a favorable distance.[28] These design principles were validated by a single-crystal structure of a small molecular model system.[27] Furthermore, density functional theory (DFT) calculations on a representative structural segment of the **HP** backbone demonstrated torsional angles of 0.2° and 3.2° in the ground state (Figure S1). In this context, the conformation of **HP** was expected to be constrained by these intramolecular hydrogen bonds, giving torsional angles smaller than 5° between the alternating units. Such a constrained and rigidified molecular conformation, however, could lead to poor solubility as a result of strong intermolecular $\pi-\pi$ interactions,[27] bringing difficulties in characterization and processing. More importantly, this rigid polymer is likely to precipitate during the solution-phase synthesis, terminating the polymerization prematurely and resulting in a low molecular weight of the product. In this context, **HP** could serve as a model system to test the hydrogen bond manipulation strategy to address the aforementioned challenges.

It was envisioned that a hydrogen bond "masking" strategy can be implemented in the synthesis and processing of **HP** (Figure 1b). The 2*H*-benzimidazol-2-one units were functionalized with *t*-butyloxycarbonyl (Boc) groups so that the hydrogen bond donating ability was "masked". Once the corresponding polymer **BocP** was formed, the lack of intramolecular hydrogen bonds and the presence of bulky Boc groups twisted the molecule into a conformation with a torsional angle over 40°, as revealed by DFT calculation (Figure S2). Such a highly twisted backbone was expected to prevent the interchain aggregation and consequently increase the solubility and processability. It would also allow for the achievement of high molecular weight polymers without precipitation during the solution-phase synthesis. More importantly, because Boc groups are thermally cleavable in a quantitative manner without leaving behind nonvolatile residues,[29−31] the intramolecular hydrogen bonds can be regenerated in the solid state by simple heating, converting **BocP** into **HP**. In other words, the processing and solid-phase synthesis of **HP** can be achieved on the basis of highly soluble precursor **BocP**, followed by unmasking intramolecular hydrogen bonds through thermal treatment.

To test the aforementioned hypothesis, we first attempted the synthesis of the target polymer **HP** *without* Boc protection. The monomer, compound **1**, was prepared according to a literature report (Scheme S1).[27] The polymerization was conducted through a Sonogashira coupling reaction between **1** and 1,5-diiodoanthracene-9,10-dione in a mixed solvent of toluene and diisopropylamine (Route A, Scheme 1). During this solution-phase step-growth polymerization, a large amount

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of precipitates were observed. These precipitates, labeled as "batch A" (**HP-A**), were only partially soluble in organic solvents (8% dissolved in 2-methyltetrahydrofuran, 17% dissolved in chlorobenzene). After extracting with hot tetrahydrofuran, analytical size exclusion chromatography (SEC) of the soluble fraction revealed (Figure 2a) a low

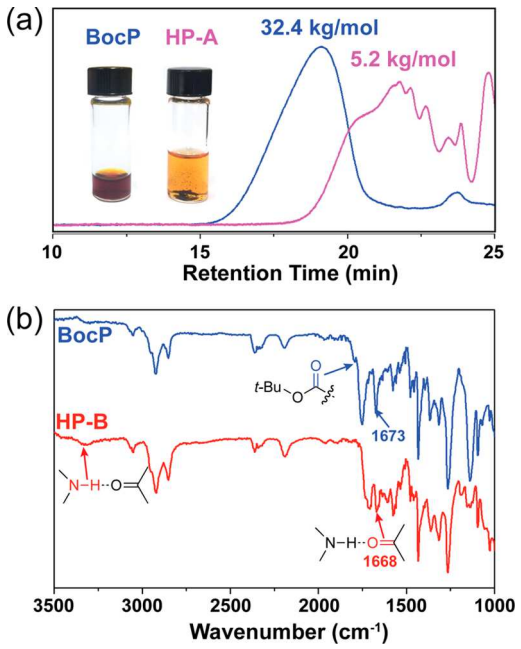

Figure 2. (a) Size exclusion chromatogram of **BocP** and the soluble fraction of **HP-A**. Inset is a photograph of **HP-A** and **BocP** (5 mg/mL) in 2-methyltetrahydrofuran at room temperature. (b) FT-IR spectra of **BocP** and **HP-B**.

number-average molecular weight (M_n) of 5.2 kg/mol, which is similar to an intramolecular hydrogen bond rigidified model study reported in the literature.[16] Most of the polymer sample, however, remained insoluble likely due to the high rigidity and strong interchain aggregations. Therefore, extensive characterization and solution processing of **HP-A** were not feasible.

To implement the hydrogen-bond masking strategy, the synthesis of precursor **BocP** was performed, followed by solid-state conversion of **BocP** into a higher molecular weight batch **HP-B** (Route B in Scheme 1). The synthesis started from the polymerization of 1,5-diiodoanthracene-9,10-dione and monomer **2**, in which the hydrogen bond donating urea groups were protected by Boc groups. The polymerization did not result in any precipitate. After workup and purification by preparative SEC to remove oligomers, **BocP** was isolated as a readily soluble material not only in conventional organic solvents like dichloromethane, chloroform, and toluene but also in environmentally friendly solvents such as 2-methyltetrahydrofuran (>10 mg/mL) (Figure 2a).[32]

BocP was first characterized by analytical SEC, showing a much higher molecular weight (32.4 kg/mol) than the soluble fraction of **HP-A** and a polydispersity index of 1.7. In the ^{1}H NMR spectrum of **BocP** (Figure S9), all resonance signals were assigned based on the spectra of the monomers. An unexpected small resonance peak at 10.55 ppm[27,28] indicated that some of the Boc groups were cleaved during the polymerization. Apparently, this partial Boc group cleavage did not lower the solubility of the polymer significantly to impact the solution-phase synthesis. It was also noticed that the resonance peak of the Boc groups was upfield shifted for 0.21 ppm after the polymerization, a result of the shielding effect of the ring current coming from the neighboring aromatic units. This observation also corroborated the twisted molecular geometry calculated by DFT, in which the Boc groups were in close proximity with the π-face of anthracene–dione units (Figure S2).

In thermal gravimetric analysis, an expected weight loss of 9.1% from 130 to 160 °C was observed (Figure S11), corresponding to the thermal cleavage of Boc groups.[29−31] This weight loss was smaller than the theoretical calculated value (16.8%), further confirming the preceding partial cleavage of Boc groups during the solution-phase polymerization. This well-soluble polymer **BocP** was converted into **HP-B**, by heating at 130 °C for 1 h. Intramolecular hydrogen bonds were unmasked, and consequently, **HP-B** became insoluble in organic solvents (Figure S17) due to its rigid backbone, strong intermolecular interactions, and higher molecular weight (compared to **HP-A**). This process represents an example of switching the macromolecular properties of this rigid model polymer through the manipulation of intramolecular hydrogen bonds.

Fourier transform infrared (FT-IR) spectroscopy was employed to further investigate the Boc cleavage process. The IR spectrum (Figure 2b) of **BocP** showed three peaks at 1796, 1751, and 1673 cm^{-1}, corresponding to C═O stretching in the Boc groups,[29−31] benzimidazol-2-one, and anthracene-9,10-dione units, respectively. In addition, a weak peak at 3318 cm^{-1} was observed, which was attributed to stretching of the partially deprotected N−H groups, consistent with that of a reported small molecular analogue.[27] After the sample was treated by heating, the C═O stretching peak of Boc groups at 1796 cm^{-1} disappeared. Meanwhile, the intensity of the N−H stretching peak increased (Figure 2b), suggesting the increased amount of hydrogen bonded N−H groups after the cleavage of Boc groups. It was also noticed that the C═O stretching energy in anthracene-9,10-dione units decreased to 1668 cm^{-1} as a result of accepting intramolecular hydrogen bonds.[27] Moreover, the characteristic IR peaks of **HP-B** were identical to those of directly synthesized **HP-A** (Figure S12), further corroborating the successful regeneration of functional groups in **HP-B** after the thermal treatment of **BocP**.

Thin-film processability of polymeric materials is essential for many important applications and is often a prerequisite for their solid-state characterization.[33−35] The directly synthesized batch, **HP-A**, was difficult to solution process due to the low solubility. Melt processing was not feasible due to either its rigid nature or lack of glass transition. Therefore, its solid-state properties, such as photophysics, energy levels, morphology, and packing, cannot be comprehensively characterized. In contrast, the switched-on solubility of **BocP** and feasible regeneration of intramolecular hydrogen bonds allowed for solution processing of **HP-B** into thin films despite its insoluble nature. This strategy of manipulating intramolecular hydrogen bonds enabled characterization of **HP-B** in the thin film state. UV−vis absorption and cyclic voltammetry measurements of **HP-B** and **BocP** thin films were conducted. Both polymers possessed two major absorption bands at around 500 and 370 nm (Figure S13). Compared to **BocP**, **HP-B** showed a slightly red-shifted absorption, indicating a narrowed optical band gap due to its constrained conformation and enhanced intermolecular electronic coupling. The cyclic

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voltammetry trace (Figure S14) of the film of **BocP** on indium tin oxide showed a reduction potential of −1.26 V and an oxidation potential of 0.83 V [vs ferrocene/ferrocenium (Figure S14)]. After the *in situ* formation of **HP-B** by heating, the oxidation potential decreased to 0.75 V. Meanwhile, the reduction potential shifted positively to −1.22 V, which can be attributed to the more electron-deficient anthracene-9,10-dione units induced by the intramolecular hydrogen bonds in **HP-B**.[27] Overall, due to the formation of intramolecular hydrogen bonds and its coplanar conformation, **HP-B** possessed a narrowed frontier orbital band gap compared to the twisted polymer **BocP**.

The atomic force microscopy (AFM) image of the **BocP** thin film [spin-casted from a solution of chlorobenzene (2 mg/mL)] showed an amorphous morphology and a smooth surface with root-mean-square (RMS) roughness of 0.28 nm (Figure 3a), suggesting an excellent film-forming ability. Grazing incidence wide-angle X-ray scattering (GIWAXS) of this sample showed no significant features (Figure S15), further confirming the amorphous nature of the film. After the thermal treatment at 130 °C, the AFM image of the **HP-B** film demonstrated a similar morphology with only a slightly increased RMS roughness (0.30 nm). Meanwhile, the GIWAXS pattern remained featureless, indicating that the Boc cleavage process did not alter the morphology of the film significantly. This retained morphology was likely a result of the low chain mobility of **HP-B** due to the strong $\pi-\pi$ interactions between the rigid and coplanar polymer backbones.

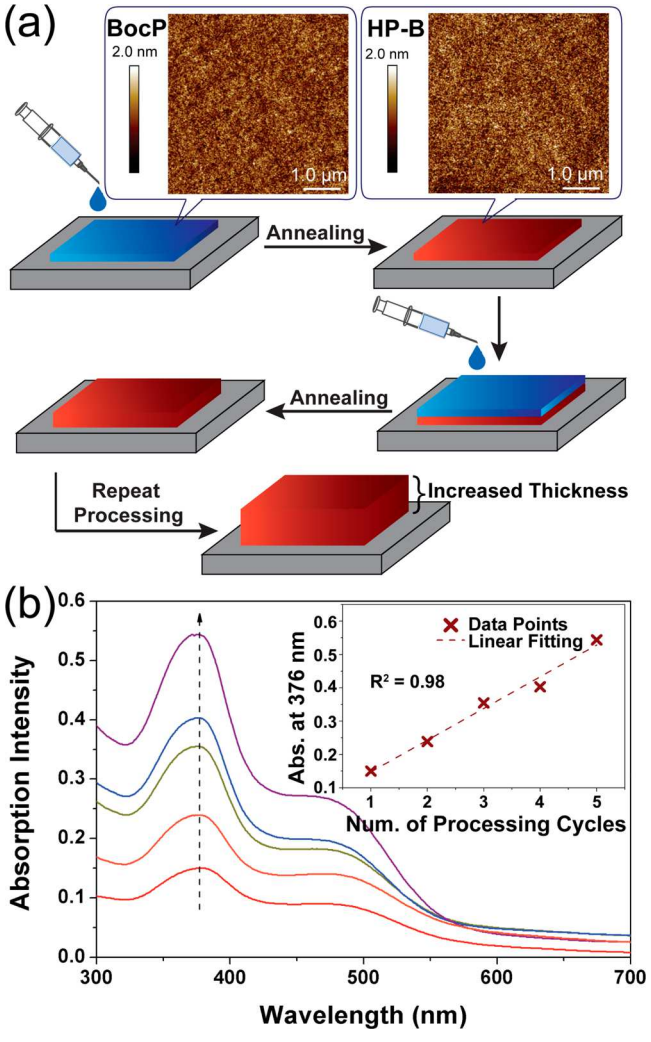

Figure 3. (a) AFM images of thin films of **BocP** and **HP-B**; graphic representation of multilayer-film processing of solvent-resistant film of **HP-B**. (b) UV−vis spectra of the **HP-B** films after different numbers of processing cycles. Inset is the plot between the processing cycle numbers and absorption intensities at 376 nm.

After thermal cleavage of Boc groups, the resulting film of **HP-B** became resistant to common organic solvents (Figure S16). For most reported solution-processed thin films of polymers, if not further cross-linked, additional contact with organic solvents would often lead to redissolution or solvent damages of the original films. This problem represents a major challenge for multilayer film fabrication using solution-processing techniques.[29,36] The demonstrated *in situ* formation of intramolecular hydrogen bonds in **HP-B** offered an ideal strategy to address this issue. In our model test, several cycles of the solution casting and thermal cleavage were performed (Figure 3a) to deposit multiple layers of **HP-B** in a cumulative manner. In these cycles, solution casting an additional **BocP** layer did not impact the **HP-B** layer on the substrate, due to the switched off solubility of **HP-B** after the regeneration of intramolecular hydrogen bonds. This well-controlled multilayering process led to a linear correlation between the absorption intensities and the number of processing cycles (Figure 3b).[29,36] This method sets the foundation for future developments of polymeric materials suitable for multilayer solution processing and 3D printing by manipulating intramolecular noncovalent bonds and the backbone conformation.[37−39]

In conclusion, we present here a molecular engineering strategy to manipulate intramolecular hydrogen bonds of rigid macromolecules, offering an innovative fundamental method to accomplish the challenging synthesis and processing of this important class of polymeric materials. After masking intramolecular hydrogen bonds with Boc groups, the synthesis of a high molecular weight batch of **BocP** with an excellent solubility was accomplished. Thermal cleavage of these Boc groups unmasked the preorganized intramolecular hydrogen bonds in **HP-B** in the solid state. As a result, the rigidified backbones of **HP-B** amplified the interchain interactions, leading to good resistance toward organic solvents. This approach was employed to demonstrate the multilayer solution casting of **HP-B**, providing a practical method for multilayer processing and 3D printing of such materials without the concern of solvent orthogonality. This strategy can be feasibly applied to other monomers containing amide, amino, or urea groups as hydrogen bond donors to access diverse structures and properties of this class of rigid polymers.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsmacrolett.8b00388.

General methods, synthesis, characterization data, and computational data (PDF)

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: fang@chem.tamu.edu.

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ORCID

Lei Fang: 0000-0003-4757-5664

Notes

The authors declare no competing financial interest.

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■ REFERENCES

(1) Voet, D.; Voet, J. G. *Biochemistry*; Wiley, 2010.

(2) Pauling, L.; Corey, R. B.; Branson, H. R. The Structure of Proteins: Two Hydrogen-Bonded Helical Configurations of the Polypeptide Chain. *Proc. Natl. Acad. Sci. U. S. A.* **1951**, *37*, 205−211.

(3) Dado, G. P.; Gellman, S. H. Intramolecular Hydrogen Bonding in Derivatives of β-Alanine and -Amino Butyric Acid; Model Studies for the Folding of Unnatural Polypeptide Backbones. *J. Am. Chem. Soc.* **1994**, *116*, 1054−1062.

(4) Kondo, T. The Relationship Between Intramolecular Hydrogen Bonds and Certain Physical Properties of Regioselectively Substituted Cellulose Derivatives. *J. Polym. Sci., Part B: Polym. Phys.* **1997**, *35*, 717−723.

(5) Terao, T.; Maeda, S.; Saika, A. High-Resolution Solid-State Carbon-13 NMR of Poly(vinyl alcohol): Enhancement of Tacticity Splitting by Intramolecular Hydrogen Bonds. *Macromolecules* **1983**, *16*, 1535−1538.

(6) Nakahira, T.; Lin, F.; Boon, C. T.; Karato, T.; Annaka, M.; Yoshikuni, M.; Iwabuchi, S. Intramolecular Hydrogen Bonding in Isotactic Poly(methacrylamide)s and Its Implications for Control of Side-Chain Orientation. *Polym. J.* **1997**, *29*, 701.

(7) Hulvat, J. F.; Sofos, M.; Tajima, K.; Stupp, S. I. Self-Assembly and Luminescence of Oligo(p-phenylene vinylene) Amphiphiles. *J. Am. Chem. Soc.* **2005**, *127*, 366−372.

(8) Sato, H.; Murakami, R.; Padermshoke, A.; Hirose, F.; Senda, K.; Noda, I.; Ozaki, Y. Infrared Spectroscopy Studies of CH···O Hydrogen Bondings and Thermal Behavior of Biodegradable Poly(hydroxyalkanoate). *Macromolecules* **2004**, *37*, 7203−7213.

(9) Sato, H.; Ando, Y.; Dybal, J.; Iwata, T.; Noda, I.; Ozaki, Y. Crystal Structures, Thermal Behaviors, and C−H···O═C Hydrogen Bondings of Poly(3-hydroxyvalerate) and Poly(3-hydroxybutyrate) Studied by Infrared Spectroscopy and X-ray Diffraction. *Macromolecules* **2008**, *41*, 4305−4312.

(10) Peng, M.; Xiao, G.; Tang, X.; Zhou, Y. Hydrogen-Bonding Assembly of Rigid-Rod Poly(p-sulfophenylene terephthalamide) and Flexible-Chain Poly(vinyl alcohol) for Transparent, Strong, and Tough Molecular Composites. *Macromolecules* **2014**, *47*, 8411−8419.

(11) Stals, P. J. M.; Gillissen, M. A. J.; Nicolay, R.; Palmans, A. R. A.; Meijer, E. W. The Balance Between Intramolecular Hydrogen Bonding, Polymer Solubility and Rigidity in Single-Chain Polymeric Nanoparticles. *Polym. Chem.* **2013**, *4*, 2584−2597.

(12) Cheuk, K. K. L.; Lam, J. W. Y.; Chen, J.; Lai, L. M.; Tang, B. Z. Amino Acid-Containing Polyacetylenes: Synthesis, Hydrogen Bonding, Chirality Transcription, and Chain Helicity of Amphiphilic Poly(phenylacetylene)s Carrying l-Leucine Pendants. *Macromolecules* **2003**, *36*, 5947−5959.

(13) Nomura, R.; Nishiura, S.; Tabei, J.; Sanda, F.; Masuda, T. Stereoregular Poly(N-propargylcarbamates) Having Helical Conformation Stabilized by the Intramolecular Hydrogen Bonds. *Macromolecules* **2003**, *36*, 5076−5080.

(14) Okoshi, K.; Sakurai, S.-i.; Ohsawa, S.; Kumaki, J.; Yashima, E. Control of Main-Chain Stiffness of a Helical Poly(phenylacetylene) by Switching On and Off the Intramolecular Hydrogen Bonding through Macromolecular Helicity Inversion. *Angew. Chem., Int. Ed.* **2006**, *45*, 8173−8176.

(15) Ferrand, Y.; Huc, I. Designing Helical Molecular Capsules Based on Folded Aromatic Amide Oligomers. *Acc. Chem. Res.* **2018**, *51*, 970−977.

(16) Delnoye, D. A. P.; Sijbesma, R. P.; Vekemans, J. A. J. M.; Meijer, E. W. π-Conjugated Oligomers and Polymers with a Self-Assembled Ladder-like Structure. *J. Am. Chem. Soc.* **1996**, *118*, 8717−8718.

(17) Monkman, A. P.; Pålsson, L.-O.; Higgins, R. W. T.; Wang, C.; Bryce, M. R.; Batsanov, A. S.; Howard, J. A. K. Protonation and Subsequent Intramolecular Hydrogen Bonding as a Method to Control Chain Structure and Tune Luminescence in Heteroatomic Conjugated Polymers. *J. Am. Chem. Soc.* **2002**, *124*, 6049−6055.

(18) Vetrichelvan, M.; Valiyaveettil, S. Intramolecular Hydrogen-Bond-Assisted Planarization of Asymmetrically Functionalized Alternating Phenylene−Pyridinylene Copolymers. *Chem. - Eur. J.* **2005**, *11*, 5889−5898.

(19) Lei, T.; Xia, X.; Wang, J.-Y.; Liu, C.-J.; Pei, J. Conformation Locked" Strong Electron-Deficient Poly(p-Phenylene Vinylene) Derivatives for Ambient-Stable n-Type Field-Effect Transistors: Synthesis, Properties, and Effects of Fluorine Substitution Position. *J. Am. Chem. Soc.* **2014**, *136*, 2135−2141.

(20) Huang, H.; Yang, L.; Facchetti, A.; Marks, T. J. Organic and Polymeric Semiconductors Enhanced by Noncovalent Conformational Locks. *Chem. Rev.* **2017**, *117*, 10291−10318.

(21) Moroni, M.; Le Moigne, J.; Pham, T. A.; Bigot, J. Y. Rigid Rod Conjugated Polymers for Nonlinear Optics. 3. Intramolecular H Bond Effects on Poly(phenyleneethynylene) Chains. *Macromolecules* **1997**, *30*, 1964−1972.

(22) Zhu, C.; Fang, L. Locking the Coplanar Conformation of π-Conjugated Molecules and Macromolecules Using Dynamic Noncovalent Bonds. *Macromol. Rapid Commun.* **2018**, *39*, 1700241.

(23) Kooijman, E. E.; Tieleman, D. P.; Testerink, C.; Munnik, T.; Rijkers, D. T. S.; Burger, K. N. J.; de Kruijff, B. An Electrostatic/Hydrogen Bond Switch as the Basis for the Specific Interaction of Phosphatidic Acid with Proteins. *J. Biol. Chem.* **2007**, *282*, 11356−11364.

(24) Nomura, R.; Tabei, J.; Masuda, T. Biomimetic Stabilization of Helical Structure in a Synthetic Polymer by Means of Intramolecular Hydrogen Bonds. *J. Am. Chem. Soc.* **2001**, *123*, 8430−8431.

(25) Karle, I. L.; Gopi, H. N.; Balaram, P. Crystal Structure of a Hydrophobic 19-Residue Peptide Helix Containing Three Centrally Located D Amino Acids. *Proc. Natl. Acad. Sci. U. S. A.* **2003**, *100*, 13946−13951.

(26) Hu, W.; Yan, Q.; Zhao, D. Oligo(p-phenylene-ethynylene)s with Backbone Conformation Controlled by Competitive Intramolecular Hydrogen Bonds. *Chem. - Eur. J.* **2011**, *17*, 7087−7094.

(27) Zhu, C.; Mu, A. U.; Lin, Y.-H.; Guo, Z.-H.; Yuan, T.; Wheeler, S. E.; Fang, L. Molecular Coplanarity and Self-Assembly Promoted by Intramolecular Hydrogen Bonds. *Org. Lett.* **2016**, *18*, 6332−6335.

(28) Gilli, P.; Pretto, L.; Bertolasi, V.; Gilli, G. Predicting Hydrogen-Bond Strengths from Acid−Base Molecular Properties. The pKa Slide Rule: Toward the Solution of a Long-Lasting Problem. *Acc. Chem. Res.* **2009**, *42*, 33−44.

(29) Guo, Z.-H.; Ai, N.; McBroom, C. R.; Yuan, T.; Lin, Y.-H.; Roders, M.; Zhu, C.; Ayzner, A. L.; Pei, J.; Fang, L. A Side-Chain Engineering Approach to Solvent-Resistant Semiconducting Polymer Thin Films. *Polym. Chem.* **2016**, *7*, 648−655.

DOI: 10.1021/acsmacrolett.8b00388
ACS Macro Lett. 2018, 7, 801−806

(30) Yang, K.; He, T.; Chen, X.; Cheng, S. Z. D.; Zhu, Y. Patternable Conjugated Polymers with Latent Hydrogen-Bonding on the Main Chain. *Macromolecules* **2014**, *47*, 8479−8486.
(31) Zou, Y.; Ji, X.; Cai, J.; Yuan, T.; Stanton, D. J.; Lin, Y.-H.; Naraghi, M.; Fang, L. Synthesis and Solution Processing of a Hydrogen-Bonded Ladder Polymer. *Chem.* **2017**, *2*, 139−152.
(32) McDowell, C.; Bazan, G. C. Organic Solar Cells Processed from Green Solvents. *Curr. Opin. Green Sustainable Chem.* **2017**, *5*, 49−54.
(33) Fang, L.; Zhou, Y.; Yao, Y.-X.; Diao, Y.; Lee, W.-Y.; Appleton, A. L.; Allen, R.; Reinspach, J.; Mannsfeld, S. C. B.; Bao, Z. Side-Chain Engineering of Isoindigo-Containing Conjugated Polymers Using Polystyrene for High-Performance Bulk Heterojunction Solar Cells. *Chem. Mater.* **2013**, *25*, 4874−4880.
(34) Iwashita, K.; Katoh, H.; Ohta, Y.; Yokozawa, T. Photodeprotectable N-Alkoxybenzyl Aromatic Polyamides. *Polymers* **2017**, *9*, 246.
(35) Badoux, M.; Drechsler, S.; Pal, S.; Kilbinger, A. F. M. Facile Synthesis of a High Molecular Weight Amphiphilic Aramid−ROMP Block Copolymer. *Macromolecules* **2017**, *50*, 9307−9314.
(36) Smith, Z. C.; Meyer, D. M.; Simon, M. G.; Staii, C.; Shukla, D.; Thomas, S. W. Thiophene-Based Conjugated Polymers with Photolabile Solubilizing Side Chains. *Macromolecules* **2015**, *48*, 959−966.
(37) Stansbury, J. W.; Idacavage, M. J. 3D Printing with Polymers: Challenges Among Expanding Options and Opportunities. *Dent. Mater.* **2016**, *32*, 54−64.
(38) Aizawa, N.; Pu, Y.-J.; Chiba, T.; Kawata, S.; Sasabe, H.; Kido, J. Instant Low-Temperature Cross-Linking of Poly(N-vinylcarbazole) for Solution-Processed Multilayer Blue Phosphorescent Organic Light-Emitting Devices. *Adv. Mater.* **2014**, *26*, 7543−7546.
(39) Cheng, C.-C.; Chu, Y.-L.; Chang, F.-C.; Lee, D.-J.; Yen, Y.-C.; Chen, J.-K.; Chu, C.-W.; Xin, Z. New Bioinspired Hole Injection/Transport Materials for Highly Efficient Solution-Processed Phosphorescent Organic Light-Emitting Diodes. *Nano Energy* **2015**, *13*, 1−8.

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