Incorporation of hydrogen-bonding units into polymeric semiconductors toward boosting charge mobility, intrinsic stretchability, and self-healing ability

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Abstract
The soft nature has endowed conjugated polymers with promising applications in a wide range of field-effect transistor (FET) based flexible electronics. With unremitting efforts on revealing the molecular structure–property relationships, numerous novel conjugated polymers with high mobility and excellent mechanical property have been developed in the past decades. Incorporating hydrogen-bonding (H-bonding) units into semiconducting polymers is one of the most successful strategies for designing high-performance semiconducting materials. In this review, we aim to highlight the roles of H-bonding units in the performances of polymeric FETs from three aspects. These include (i) charge mobility enhancement for semiconducting polymers after incorporation of H-bonding units into the side chains, (ii) the effects of H-bonding units on the stretchability of conjugated polymers, and (iii) the improvement of self-healing properties of conjugated polymers containing dynamic hydrogen bonds due to the H-bonding units in the side chains or conjugated backbones.

KEYWORDS
conjugated polymers, field-effect transistors, flexible and stretchable electronics, hydrogen-bonding, self-healable and wearable electronics

1 | INTRODUCTION

Conjugated polymers are regarded as the most promising candidates for thin film field-effect transistors (FETs), due to the excellent film-forming properties suitable for large-area solution processing over a wide range of substrates.1–6 For one thing, the delocalization of π electrons and the ordered interchain packing ensure efficient charge transport along both π-stacking and π-conjugation directions.7 Through molecular design and aggregate structural engineering, the family of conjugated polymers with charge mobility over 10 cm2/(V·s) gets an exciting expansion in the past decades.8–10 For another, unlike inorganic semiconductors and conjugated small molecules, the chain entanglement and multiple weak interactions in thin films of conjugated
polymers cooperatively offer conjugated polymers unique superiority of mechanical flexibility with relatively low tensile modulus, which may meet the requirement of emerging flexible electronics such as health monitoring, electronic skin and flexible displaying. Currently, further improving charge mobility and promoting conjugated polymers to flexible device are running in the fast lane.

Structurally, a conjugated polymer consists of two parts, conjugated main chain and flexible side chains, which synergistically determine the interchain packing, and thus the charge transport properties. Design strategies for performance improvement usually start from these two aspects: design of conjugated units for main chain and side chain engineering. As for main chain engineering, exceptionally successful building blocks such as diketopyrrolopyrrole (DPP), isoindigo, and naphthalenediimide have been studied extensively. As for side chain engineering, the structures of side alkyl chains with regard to the branching site and the lengths of side chains have been usually finely tailored. Meanwhile, incorporation of H-bonding units into conjugated polymers is an effective means to regulate the crystalline behaviors and mechanical properties.

H-bonds play an important role in material sciences. Inspired by nature, many new materials based on H-bonds have been developed, such as biomaterials and self-healing elastomers. Beyond these, H-bonded organic framework (HOF), formed by the self-assembly of two dimensional H-bonding network, has become one of the most important crystalline porous materials. Meanwhile, the combination of H-bonds into organic semiconductors has brought out many new properties and functions. H-bonds are also found useful in organic solar cells (OSCs) and organic light emitting diodes.

In this review, we will not limit our discussions only to the effect of H-bonding units on the interchain packing and semiconducting performance. The key challenge faced in this cutting edge field is how to realize high semiconducting performance and good mechanical property simultaneously. Generally, achieving high mobility requires highly crystalline morphology. In contrast, high crystallinity can make material brittle and stiff. It seems that improving mechanical property of conjugated polymer is inevitable at the sacrifice of mobility. However, many excellent works show that the trade-off between semiconducting performance and mechanical property can be well balanced by taking the advantage of H-bonding (Figure 1). In this regard, we will discuss the molecular design of stretchable and self-healable conjugated polymers with high charge mobilities.
Kim et al.\textsuperscript{58} reported a series of DPP based conjugated polymers with side chains containing ester groups (Figure 3). They found that H-bond between the O atom of ester carbonyl and the H atom of alkyl could not only promote the π-π stacking of polymer backbone but also expand the domain size in thin films. They also investigated the influences of branching point and the length of side chain. As a result, \( \text{P3} \) displays the shortest π-π stacking distance of 3.61 Å, and \( \text{P5} \) shows the champion mobility of 2.30 cm\(^2\)/(V·s) when annealed at 150°C. The increase of charge mobilities in the ester substituted polymers comes down to the more ordered arrangement as confirmed by grazing-incidence wide-angle X-ray scattering (GIWAXS, Figure 3B).

Rondeau-Gagné et al.\textsuperscript{38} developed a series of new conjugated polymers combining DPP backbone and amide-containing side-chains. As shown in Figure 4, the amounts of amide groups in polymers were controlled by adjusting the feed ratios of monomers. Fourier transform infrared (FTIR) spectra and temperature dependent 1H NMR spectra were used to characterize the intermolecular H-bonds between the adjacent amide groups. The broad band between 3375 and 3275 cm\(^{-1}\) in FTIR spectra is attributed to the NH stretching, which progressively increases with the increase of the content of amide groups. The \(^1\)H NMR spectra of \( \text{M1} \) (containing 100 mol\% of amides), due to the protons of amide groups, shifts from 5.50 to 5.27 ppm in the temperature dependent 1H NMR spectra with the rising of temperature, which clearly proves the existence of H-bonds. The crosslinked network of H-bonds induced the self-assembly of the conjugated main chains. \( \text{P8} \) with 5 mol\% amide-containing side-chains showed the highest charge mobility of 2.46 cm\(^2\)/(V·s) when annealed at 170°C.

Some of us reported three DPP-quaterthiophene co-polymers with branching alkyl chains containing different molar ratios of the urea groups (Figure 5A–D).\textsuperscript{41} The presence of H-bonds among urea groups was investigated with FTIR and \(^1\)H NMR spectra. We found that H-bonds from the urea groups could not only significantly tune the charge transport property by altering the interchain interactions, but also improve the power conversion efficiencies (PCEs) of OSCs by tailoring the donor-acceptor phase separation scales in the blended thin films with PC\(_{71}\)BM as electron acceptor. As a result, a remarkably high hole mobility of 13.1 cm\(^2\)/(V·s) was reported for \( \text{P14} \) after thermal annealing at just 100°C. The optimal PCE of \( \text{P12:PC}_{71}\)BM based solar cell is more than twice that of \( \text{P15:PC}_{71}\)BM based solar cell fabricated under the same conditions. We further applied this strategy in thiazole-flanked DPP polymers (Figure 5E–H).\textsuperscript{40} Both hole and electron mobilities of \( \text{P17} \) were greatly improved compared with these of \( \text{P18} \). In addition, it is worth mentioning that the average \( I_{on}/I_{off} \) ratios for hole and electron were noticeably higher than those of the polymer without urea groups. Charron et al. extended this strategy to isoindigo-based conjugated polymers (Figure 5I,J).\textsuperscript{59} The improved nanoscale morphology and the enhancement of average charge mobility observed for \( \text{P22} \) confirm that grafting urea moieties in the side chains is an efficient strategy to elevate the performance of polymeric FETs.

Besides enhancing the charge mobility, incorporating H-bonding units into conjugated polymers can also bring out other new properties and functions. For instance, some of us reported a DPP-based conjugated polymer with thymine groups in the side chains (Figure 6).\textsuperscript{42} \( \text{P23} \) exhibits improved crystallinity and higher hole mobility of 9.1 cm\(^2\)/(V·s), while the mobility of its analogous polymers with alkyl chains is only 5.1 cm\(^2\)/(V·s). More importantly, the thymine group can efficiently coordinate with metal ions such as Pd(II) and Hg(II) by a simple approach of solvent evaporation induced self-assembly on water.\textsuperscript{60} The coordination of ions on air-water interfacial was confirmed by X-ray photoelectron spectroscopy analysis. Although the hole mobilities were reduced compared with that of the neat thin film, the \( \text{P23:Pd(II)} \) and \( \text{P23:Hg(II)} \) thin films show good sensitive
and selective responses toward CO (down to 10 ppm) and H₂S (down to 1 ppm), respectively. It is noted that the P23:Pd(II) based device is the first FET-based gas sensor for CO. But, these FET based gas sensors cannot be reused because the sensing is based on the reactions of Pd(II)/Hg(II) ions with CO and H₂S.

### Incorporating H-bonds in the main chains

Introduction of H-bonds in the main chains was also successfully used to improve the carrier mobility of conjugated polymers. The basic mechanism of this

| M_n/ PDI [kDa] | HOMO [eV] | LUMO [eV] | μ_\text{h}^{\text{avg.}}/μ_\text{h}^{\text{max.}} [cm^2/(V·s)] | μ_e^{\text{avg.}}/μ_e^{\text{max.}} [cm^2/(V·s)] | Ref. b |
|----------------|----------|----------|---------------------------------|---------------------------------|--------|
| P1 77.4/1.8    | −5.31    | −4.02    | 0.62^a                          | /                               | BGTC, 58 |
| P2 196.0/2.7   | −5.09    | −3.72    | 0.84^a                          | /                               |        |
| P3 192.8/3.4   | −5.05    | −3.75    | 1.56^a                          | /                               |        |
| P4 162.6/2.4   | −5.29    | −3.92    | 1.52^a                          | /                               |        |
| P5 173.2/2.7   | −5.11    | −3.74    | 1.55^a                          | /                               |        |
| P6 177.7/2.4   | −5.04    | −3.69    | 2.00^a                          | /                               |        |
| P7 46.9/2.1    | −5.29    | −3.91    | 1.52/1.91                       | /                               | BGTC, in glove box, 38 |
| P8 36.5/2.7    | −5.20    | −3.79    | 2.02/2.46                       | /                               |        |
| P9 37.6/2.3    | −5.17    | −3.77    | 0.46/0.67                       | /                               |        |
| P10 9.9/2.4    | −5.18    | −3.77    | 0.74/1.06                       | /                               |        |
| P11 5.7/2.8    | −5.40    | −3.95    | 0.45/0.59                       | /                               |        |
| P12 28.4/2.7   | −5.31    | −3.55    | 5.10/5.50                       | /                               | BGBC, in glove box, 43 |
| P13 19.8/2.3   | −5.29    | −3.58    | 7.10/8.40                       | /                               |        |
| P14 16.6/2.5   | −5.24    | −3.60    | 11.40/13.10                     | /                               |        |
| P15 18.8/2.1   | −5.32    | −3.54    | 3.00/3.40                       | /                               |        |
| P16 18/2.2     | −5.35    | −3.78    | 0.75/0.86                       | 0.010/0.014                     | BGBC, in glove box, 40 |
| P17 25/2.0     | −5.33    | −3.79    | 1.02/1.10                       | 0.018/0.020                     |        |
| P18 20/2.8     | −5.36    | −3.70    | 0.040/0.060                     | 0.0060/0.0070                   |        |
| P19 13.0/4.6   | −5.40    | −3.75    | 0.016/0.037                     | /                               | BGBC, in glove box, 59 |
| P20 12.2/6.1   | −5.35    | −3.71    | 0.022/0.042                     | /                               |        |
| P21 8.7/3.9    | −5.33    | −3.69    | 0.022/0.028                     | /                               |        |
| P22 9.6/1.9    | −5.38    | −3.76    | 0.032/0.051                     | /                               |        |
| P23 30.5/3.3   | /        | /        | 7.80/9.10                       | /                               | BGBC, ambient condition, 42 |

Abbreviations: BGBC, bottom gate-bottom contact; BGTC, bottom gate-top contact; FET, field-effect transistor.

^aAverage values.

^bFET device configuration (BGBC, BGTC), the testing environment and the reference number.

and selective responses toward CO (down to 10 ppm) and H₂S (down to 1 ppm), respectively. It is noted that the P23:Pd(II) based device is the first FET-based gas sensor for CO. But, these FET based gas sensors cannot be reused because the sensing is based on the reactions of Pd(II)/Hg(II) ions with CO and H₂S.
strategy is that H-bonds can reduce the torsional angle between the adjacent aromatic groups and minimize the \(\pi-\pi\) stacking distance of conjugated backbones. Highly planar structure is beneficial for the efficient delocalization of \(\pi\)-electrons, and the close packing can accelerate the charge transport between chains. C–H∙∙∙F and N–H∙∙∙N are two common types of H-bonds to ameliorate the planarity between the electron deficient moieties (isoindigo, thiazolothiazole, and DPP) and the neighboring thiophene units. In fact, the six-membered ring intramolecular H-bonds are also known as resonance assisted H-bonds (RAHBs). Different from the traditional H-bonds solely based on electrostatic interactions, RAHB is more stronger due to the partial covalent characters derived from the \(\pi\)-electron delocalization. In the following, four examples are enumerated to illustrate the role of H-bonds in the main chains for achieving high performance organic semiconductors (see Table 2).

Zheng et al. reported two conjugated polymers based on benzodifuran-dione-based oligo(\(p\)-phenylene vinylene) (BDOPV, Figure 7). Due to the four strong electron-deficient fluorine atoms, the lowest unoccupied orbital potential (LUMO) energy levels of P25 and P26 are both below \(-4.3\) eV. The films absorption edges of P25 and P26 all exceed 1000 nm. As shown in Figure 7C, F4BDOPV-2T unit of P25 showed smaller torsional angle (9.6°) than that of BDOPV-2T (21.9°) due to the intermolecular H-bonds. Benefiting from these features, a record electron mobility of 14.9 cm\(^2\)/(V·s) was reported for P25. The selenophene containing polymer P26 also shows excellent electronic transport property with an optimal electron mobility of 6.14 cm\(^2\)/(V·s). It is worth noting that all mobility tests were carried out in air, and the mobility of P25 shows excellent stability with only 40% decrease after stored in air for 30 days. The authors attributed the ordered polymer packing and small \(\pi-\pi\) stacking distance to the intermolecular H-bonds, and as a result the oxygen penetration barrier was enhanced. A voltage inverter based on a high-mobility isoindigo polymer (IIDDT-C3) as \(p\)-channel and P25 as \(n\)-channel was further constructed. The high gain values and clearly on and off feature indicate that P25 can be used in logic circuits to realize low power dissipation.

Isoindigo-based conjugated polymers P27 and P28 (Figure 8) with the electron-deficient building blocks possess deep-lying LUMO levels of \(-3.99\) and \(-4.17\) eV, respectively. In comparison to P27, the introduction of F atoms makes P28 exhibit red-shifted absorption. Being similar to P25, the optimal geometry of the repeat units of P28 shows better planarity with smaller phenyl-thienyl dihedral angle of 17.5°. In addition, P28 displays smaller \(\pi-\pi\) stacking distances of 3.53 Å and the thin film entails more ordered fibril networks (Figure 8D,E), indicating the strong interchain interaction driven by the planar conjugated backbone caused by H-bonds of...
C–H⋯F. Furthermore, P28 shows ambipolar transport property with hole mobility of 1.03 cm²/(V·s) and electron mobility of 1.82 cm²/(V·s), while P27 only shows a p-type transport behavior with a significantly lower hole mobility of 0.32 cm²/(V·s). These results demonstrate that introduction of H-bonds into main chains of conjugated polymers is also a promising strategy to construct high-performance polymeric materials.

Ni et al.66 reported two quinoline-flanked DPP copolymers (Figure 9, P31 and P32). Notably, P32, featuring F atoms in the thiophene units, exhibits a record electron mobility of 6.04 cm²/(V·s) for the device fabricated on flexible substrates. Due to the improved electron deficiency of quinoline-flanked DPP skeleton, P32 shows a suppressed hole mobility of 0.21 cm²/(V·s). The greatly enhanced electron mobility of P32 compared to P29, P30, and P31 was attributed to the shorter π–π stacking distance, the more pronounced (010) diffraction intensity and the higher crystalline order on the basis of the GI-WAXS patterns (Figure 9D,E).

Besides C–H⋯F interaction, RAHB of N–H⋯N interaction was also used to enhance the charge mobility of a thiazolothiazole-containing conjugated polymer.68 As shown in Figure 10, carbamate groups are attached to the thiophene units of P34, in which the hydrogens of carbamate groups and nitrogens of the adjacent thiazolothiazole units can form six-membered ring RAHBs. As revealed in the single-crystal structure of the thiophene-thiazolothiazole-thiophene compound (Figure 10B,C), thiophene and thiazolothiazole-thiophene are almost in
the same plane. Such planar conjugated backbone is favorable for the interchain packing with close $\pi-\pi$ contacts. As a result, thin film of $P34$ showed an optimal mobility of 2.3 cm$^2$/(V·s), being one order of magnitude higher than that of $P33$.

These results reveal that conjugated polymers with H-bonding units in the side chains show higher charge carrier mobilities than the corresponding polymers with the same conjugated backbones, but without H-bonding in the side chains. The studies indicate that the presence of H-bonding units in the side chains can improve the interchain packing order and thus boost the charge mobilities. Moreover, the presence of F$\cdots$H or N$\cdots$H interactions within the conjugated backbones are beneficial for improving the backbone planarity and thus interchain interactions, leading to the enhancement of charge mobilities of conjugated polymers. To conclude, incorporation of H-bonding units in either side chains or...
backbones become a useful strategy for designing semiconducting polymers with high charge mobilities.

### 3. THE EFFECTS OF H-BONDS ON THE STRETCHABILITY OF CONJUGATED POLYMERS

Likewise traditional polymers, the long chains in conjugated polymer films exhibit complex conformational and condensed state structures. Because of the entanglement of chains and various weak interactions among chains, conjugated polymer thin films usually exhibit a certain degree of intrinsic extensibility. But, unlike the traditional polymers that contain non-conjugate flexible main chains, conjugated polymers are composed of rigid aromatic groups which provide efficient charge transport channel, resulting in high crystallinity and relatively poor chain mobility. As a consequence, the tensile modulus of common deformable conjugated polymer films are usually on the order of several hundred MPa or higher, which badly mismatch with those of the flexible substrates. Therefore, it is still a great challenge for devices based on conjugated polymers to maintain stable semiconducting performance under high mechanical deformation.

Thin films of conjugated polymers with stretchable properties were prepared by embedding conjugated polymers in elastomer matrix. The elastic modulus of the blended thin films are significantly reduced by virtue of the excellent mechanical properties of elastomers. Alternatively, the intrinsic stretchability of conjugated polymers was explored by varying the structures of main chains and side chains, as well as the molecular weights. Herein, we focus on the discussions of the influence of H-bonds on the tear resistance of conjugated polymers. As illustrated in Figure 11, the resistance of thin films of conjugated polymers to mechanical cracking in the practical flexible devices can be improved by taking the advantage of H-bonds. Specifically, when external...
stress is applied, the intermolecular H-bonds in the amorphous region break as the molecules move away from each other. In this process, the stress energy can be successfully dissipated as the breakage of the noncovalent crosslinking network due to H-bonds instead of the breakage of the crystalline domains and thus forming irreversible cracks. As a result, the polymers can maintain good charge transport properties at high

| M<sub>n</sub>/PDI [kDa] | HOMO [eV] | LUMO [eV] | µ<sub>h</sub><sup>avg.</sup>/µ<sub>h</sub><sup>max.</sup> [cm²/(V·s)] | µ<sub>e</sub><sup>avg.</sup>/µ<sub>e</sub><sup>max.</sup> [cm²/(V·s)] | Ref.<sup>b</sup> |
|----------------------|------------|------------|--------------------------|--------------------------|----------------|
| P24 77.2/3.0         | −5.72      | −4.15      | 0.20/0.47                | 1.74/1.42                | TGBC, ambient condition, P24:64 |
| P25 38.0/2.7         | −5.96      | −4.32      | /                        | 9.00/14.90               | P25, P26:44               |
| P26 23.8/2.9         | −5.91      | −4.34      | /                        | 3.20/6.14                |                                |
| P27 46.3/4.6         | −5.60      | −3.99      | 0.26/0.32                | /                        | TGBBC, ambient condition,65  |
| P28 32.8/2.3         | −5.74      | −4.17      | 0.96/1.03                | 1.31/1.82                |                                |
| P29 27.2/2.9         | −5.33      | −3.62      | 5.00 × 10⁻⁴              | 2.00 × 10⁻³              | TGBBC, ambient condition,66  |
| P30 20.2/1.9         | −5.72      | −3.94      | 1.00 × 10⁻⁴<sup>a</sup>  | −8.00 × 10⁻⁴<sup>a</sup> |                                |
| P31 119.9/1.8        | −5.42      | −3.68      | 0.28–0.50<sup>a</sup>    | 0.015–0.021<sup>a</sup>  |                                |
| P32 67.4/2.0         | −5.64      | −3.84      | 0.13–0.21<sup>a</sup>    | 4.25–6.04<sup>a</sup>    |                                |
| P33 7.7/1.4          | −5.20      | −3.30      | 0.076/0.12               | /                        | P33: BGBC, ambient condition,67 |
| P34 50.3/1.7         | −5.33      | −3.58      | 1.98/2.30               | /                        | P34: BGTC, in glove box,68    |

Abbreviations: BGBC, bottom gate-bottom contact; FET, field-effect transistor; TGBC, top gate-bottom contact.

<sup>a</sup>The range of charge mobility.

<sup>b</sup>FET device configuration (TGBC), the testing environment and the reference number.

**Table 2** Molecular weights, HOMO/LUMO energies, charge mobilities of the conjugated polymers with main chains containing H-bonding units

**Figure 7** (A) Chemical structures of P24<sup>64</sup>, P25, and P26. (B) Absorption spectra of P25 and P26. (C) Optimized configurations of the repeat units of P25 and P26. (D) Stability of FETs with P25 and P26 in air. (E) Device configuration and characteristics of an inverter containing p-type channel of an isoindigo polymer and n-type channel of P26. Reprinted with permission. Copyright 2016, Wiley-VCH Verlag GmbH. FET, field-effect transistor.
Figure 8  (A) Chemical structures of P27 and P28. (B) Absorption spectra of P27 and P28. (C,D) The optimized configurations of repeat units of P27 and P28. (E–J) GIWAXS patterns and AFM images of P27 and P28. Reprinted with permission.© Copyright 2017, American Chemical Society. AFM, atomic force microscope; GIWAXS, grazing-incidence small-angle X-ray scattering
FIGURE 9  (A) Chemical structures of P29–P32. (B,C) Absorption spectra of conjugated polymers P29–P32. (D–G) GIWAXS patterns for thin films of P29–P32. Reprinted with permission. \(^{66}\) Copyright 2018, Wiley-VCH Verlag GmbH. GIWAXS, grazing-incidence small-angle X-ray scattering
Scheme 1 shows chemical structures of representative stretchable conjugated polymers (P35–P69), which contain H-bonding units such as ester, amide and urea. For instance, Bao and coworkers designed and investigated stretchable conjugated polymer P37 by introducing 2,6-pyridine dicarboxamide (PDCA) moieties into the conjugated main chain. Remarkably, the hole mobility of
SCHEME 1 Chemical structures of conjugated polymers containing H-bonds with improved stretchability
thin film of **P37** can maintain more than 1 cm²/(V·s) even with 100% strain after a hundred cycles. The design rationale for this stretchable polymer include: (i) the H-bonds between the nonconjugated PDCA moieties are moderate, which are sufficient to dissipate stress energy; (ii) the PDCA moieties containing two amide groups cannot noticeably increase the tensile modulus of the resulting polymers; (iii) the charge transport mobility cannot be drastically degraded due to the small loading fraction of PDCA moieties. As shown in Figure 12, a 5 × 5 device array of the fully stretchable transistors with thin films of **P37** was fabricated by using carbon nanotube and poly(3,4-ethylenedioxythiophene) polystyrene sulfonate as gate, source and drain electrodes, polydimethylsiloxane as the dielectric material on rubber substrate. The statistical distribution of those 25 devices were relatively uniform with average mobility of 0.286 ± 0.162 cm²/(V·s). Although the charge mobilities decreased linearly with 100% deformation, they could recover to their initial values after the strain is releasing. Importantly, both mobility and on/off current ratio were well maintained at 25% strain even after 500 cycles in the stretching durability tests. Moreover, the device performance showed no noticeable decrease on human skin after folding, twisting and stretching with the movement of human body. This strategy was also successfully applied to other

![Figure 12](image-url)
semiconducting polymers to enhance the flexibility and stretchability of the semiconducting thin films.\textsuperscript{39,41,78,79}

In this section, we summarized representative examples (P35–P69) of conjugated polymers containing H-bonds with improved stretchability. The mechanism of dissipation of stress energy in the H-bonding network was discussed. With P37 as an example, the effects of PDCA moieties in the backbone on both semiconducting properties and mechanical properties were highlighted. The results reveal that incorporation of H-bonding units in either conjugated main chains or side chains has become a useful strategy for the development of stretchable semiconducting polymers.

4 | IMPROVEMENT OF SELF-HEALING PROPERTIES OF CONJUGATED POLYMERS VIA DYNAMIC H-BONDS

As mentioned above, the tensile modulus of common conjugated polymers are far larger than the elastomers used in daily life.\textsuperscript{69} Therefore, although the deformation of films in practical use is not very large, mechanical crack is still one of the most remarkable damages for flexible devices based on conjugated polymers caused by the forces of stretching, extrusion, and twisting during cumulative uses. The performance degradation caused by such mechanical damage is a critical factor limiting the long-term stability of devices. For this reason, intensive efforts have been focused on improving the self-healing ability of thin films of semiconducting polymers in recent years. Development of self-healing conjugated polymers by using dynamic H-bonds has been proved to be a successful strategy.\textsuperscript{39,45}

H-bonds, as dynamic bonds, can reversibly break and reform under dynamic equilibria or exposure to external conditions such as heating or solvent annealing. In fact, elastomers based on dynamic H-bonds with healing feature have attracted intensive interests in the past decades.\textsuperscript{51,80,81} The multiple dynamic H-bonds provide elastomers driving force to maintain basic mechanical property and healing ability. Conceptually, combining H-bonds with conjugated polymers may provide an elegant molecular engineering toward high-performance semiconducting materials with excellent self-healing ability. As illustrated in Figure 13, cracks are formed due to the dissociation of the H-bonding crosslinking network of conjugated polymers when the polymeric thin films are under cumulative uses. The formation of cracks in the semiconducting thin films will induce the semiconducting properties to be significantly reduced. But, after exposure to external conditions such as heating or solvent annealing, the damaged thin films can be repaired by the regeneration of H-bonding network.

Generally, the self-healing ability of conjugated polymers is related with the intrinsic stretchability. For example, the intrinsically stretchable polymers P37 and P55 also featured self-healing properties with the repair of cracks caused by tensile deformation and the recovery of semiconducting performance after proper post-treatments.\textsuperscript{39,45} Specifically, as shown in Figure 14A–C, the cracks within the mechanically damaged film of P37 could be almost completely repaired as confirmed by AFM phase images before and after successive solvent annealing and heating. The average hole mobility could be significantly recovered to 1.13 cm\(^2\)/(V·s). Similarly, Figure 14D displays the AFM height and phase images of the thin films of P55 after 10 cycles of stretching with 130% external strain. The repair degree of thin films varies with the post treatment methods. These results show that solvent annealing is a critical step in the healing processes. The studies with P37 and P55 demonstrate that incorporating dynamic H-bonds into conjugated polymers is a viable approach to enhance the self-healing properties.

In this section, we introduced examples of healable semiconducting polymers by utilization of the dynamic H-bonds. The healing mechanism of the damaged thin

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{self_healing.png}
\caption{Illustration of the self-healing mechanism of conjugated polymers with dynamic H-bonds}
\end{figure}
films by the regeneration of dynamic H-bond after proper post treatments was also discussed. It is noted that the highly stretchable and healable features of these semiconducting polymers hold great potentials for the future applications in flexible circuits and wearable electronics.

5 | SUMMARY AND OUTLOOK

In this review, we discussed conjugated polymers with H-bonding units either in the main chains or side chains. First, we show that incorporation of H-bonding units in the side chains of semiconducting polymers can improve the interchain orderly packing and thin film morphology. As a consequence, charge mobilities of conjugated polymers with H-bonding units in the side chains are significantly boosted by comparing with those bearing the same conjugated backbones and having similar molecular weights. Alternatively, the presence of H-bonding units in the conjugated backbones can improve the backbone planarity, thus enhance the interchain π-π stacking and thus charge transport properties. Second, we demonstrate the effects of H-bonds on the stretchability of thin films of conjugated polymers. Specifically, we present the design rationales of stretchable semiconducting polymers by introducing PDCA moieties into...
the conjugated main chain. This stretchable semiconducting polymer can maintain more than 1 cm²/(V·s) even with 100% strain after a hundred cycles. Thirdly, we further show that the incorporation of H-bonds, which can be broken and repaired under certain conditions, into conjugated polymers is a viable approach to enhance the self-healing properties.

Semiconducting polymers of high charge mobilities with good stretchable and self-healable properties are highly demanding for future flexible and wearable electronics. The exploration of stretchable and self-healable conjugated polymers has received increasing attentions, and this study area will be the focus of future organic optoelectronics. Further studies include (i) further optimization of molecular design with the end to maintaining high charge mobility while having intrinsically stretchable and self-healable properties, (ii) integration of other dynamic bonding units with conjugated polymers besides H-bonding units, aiming to balance the charge transport and mechanical properties of conjugated polymers, (iii) combination of blending strategy with elastosmers to further improve stretchable properties of conjugated polymers, and (iv) development of self-healable semiconducting polymers without post-treatments such as solvent and thermal annealing, which will complicate the process of future large-scale device fabrication.

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CONFLICT OF INTERESTS
The authors declare no conflict of interest.

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REFERENCES
1. Fratini S, Nikolka M, Salleo A, Schweicher G, Sirringhaus H. Charge transport in high-mobility conjugated polymers and molecular semiconductors. Nat Mater. 2020;19:491-502.
2. Zaumseil J, Sirringhaus H. Electron and ambipolar transport in organic field-effect transistors. Chem Rev. 2007;107:1296-1323.
3. Wen Y, Liu Y, Guo Y, Yu G, Hu W. Experimental techniques for the fabrication and characterization of organic thin films for field-effect transistors. Chem Rev. 2011;111:3358-3406.
4. Wang C, Dong H, Hu W, Liu Y, Zhu D. Semiconducting π-conjugated systems in field-effect transistors: a material odyssey of organic electronics. Chem Rev. 2012;112:2208-2267.
5. Chen J, Das S, Shao M, et al. Phase segregation mechanisms of small molecule-polymer blends unraveled by varying polymer chain architecture. SmartMat. https://doi.org/10.1002/smmt.1036
6. Luo L, Huang W, Yang C, Zhang J, Zhang Q. Recent advances on π-conjugated polymers as active elements in high performance organic field-effect transistors. Front Phys. 2021;16:33500.
7. Rivnay J, Mannsfeld SCB, Miller CE, Salleo A, Toney MF. Quantitative determination of organic semiconductor microstructure from the molecular to device scale. Chem Rev. 2012;112:5488-5519.
8. Sirringhaus H. 25th Anniversary article: organic field-effect transistors: The path beyond amorphous silicon. Adv Mater. 2014;26:1319-1335.
9. Liu Z, Zhang G, Zhang D. Modification of side chains of conjugated molecules and polymers for charge mobility enhancement and sensing functionality. Acc Chem Res. 2018;51:1422-1432.
10. Luo H, Yu C, Liu Z, et al. Remarkable enhancement of charge carrier mobility of conjugated polymer field-effect transistors upon incorporating an ionic additive. Sci Adv. 2016;2:e1600076.
11. Root SE, Savagatrup S, Printz AD, Rodriguez D, Lipomi DJ. Mechanical properties of organic semiconductors for stretchable, highly flexible, and mechanically robust electronics. Chem Rev. 2017;117:6467-6499.
12. Gumyusenge A, Luo X, Zhang H, Pitch GM, Ayzner AL, Mei J. Isoindigo-based binary polymer blends for solution-processing of semiconducting nanofiber networks. ACS Appl Polym Mater. 2019;1:1778-1786.
13. Lu C, Lee W-Y, Gu X, et al. Effects of molecular structure and packing order on the stretchability of semicrystalline conjugated poly(tetrathienoacene-diketopyrrolopyrrole) polymers. Adv Electron Mater. 2017;3:1600311.
14. Zhao Y, Liu L, Zhang F, Di C, Zhu D. Advances in organic thermoelectric materials and devices for smart applications. SmartMat. https://doi.org/10.1002/smmt.1034
15. Yao Y, Chen Y, Wang H, Samori P. Organic photodetectors based on supramolecular nanostructures. SmartMat. 2020;1:e1009.
16. Shi C-Y, Zhang Q, Tian H, Qu D-H. Supramolecular adhesive materials from small-molecule self-assembly. SmartMat. 2020;1:e1012.
17. Kong L, Tang C, Peng H-J, Huang J-Q, Zhang Q. Advanced energy materials for flexible batteries in energy storage: A review. SmartMat. 2020;1:e1007.
18. Yuvaraja S, Nawaz A, Liu Q, et al. Organic field-effect transistor-based flexible sensors. Chem Soc Rev. 2020;49:3423-3460.
19. Zhang Q. Shooting flexible electronics. Front Phys. 2020;16:13602.
20. Wang S, Oh JY, Xu J, Tran H, Bao Z. Skin-inspired electronics: an emerging paradigm. Acc Chem Res. 2018;51:1033-1045.
21. Tien H-C, Huang Y-W, Chiu Y-C, Cheng Y-H, Chueh C-C, Lee W-Y. Intrinsically stretchable polymer semiconductors: molecular design, processing and device applications. J Mater Chem C. 2021;9:2660-2684.
22. Ma R, Chou SY, Xie Y, Pei Q. Morphological/nanostructural control toward intrinsically stretchable organic electronics. Chem Soc Rev. 2019;48:1741-1786.
23. Gao X, Di CA, Hu Y, et al. Core-expanded naphthalene diimides fused with 2-(1,3-dithiol-2-ylidene)malonitrile groups for high-performance, ambient-stable, solution-processed n-channel organic thin film transistors. J Am Chem Soc. 2010;132:3697-3699.
24. Takimiya K, Osaka I, Mori T, Nakano M. Organic semiconductors based on [1]benzothieno[3,2-b][1]benzothiophene substructure. Acc Chem Res. 2014;47:1493-1502.
25. Wu Z-H, Huang Z-T, Guo R-X, et al. 4,5,9,10-Pyrene diimides: a family of aromatic diimides exhibiting high electron mobility and two-photon excited emission. Angew Chem Int Ed. 2017;56:13031-13035.
26. Li Y, Sonar P, Singh SP, Soh MS, van Meurs M, Tan J. Annealing-free high-mobility diketopyrrolopyrrole–quaterthiophene copolymer for solution-processed organic thin film transistors. J Am Chem Soc. 2011;133:2198-2204.
27. Carsten B, He F, Son HJ, Xu T, Yu L. Stille polycondensation for synthesis of functional materials. Chem Rev. 2011;111:1493-1528.
28. Ruiz-Carretero A, Ávila Rovelo NR, Militzer S, Mésini PJ. Hydrogen-bonded diketopyrrolopyrrole derivatives for energy-related applications. J Mater Chem A. 2019;7:23451-23475.
29. Skonieczny K, Papadopoulos I, Thiel D, et al. How to make nitroaromatics glow: next generation large, x-shaped, centrosymmetric diketopyrrolopyroles. Angew Chem Int Ed. 2020;59:16104-16113.
30. Liu Q, Bottle SE, Sonar P. Developments of diketopyrrolopyrrole-dye-based organic semiconductors for a wide range of applications in electronics. Adv Mater. 2020;32:1903882.
31. Yan H, Chen Z, Zheng Y, et al. A high-mobility electron-transporting polymer for printed transistors. Nature. 2009;457:679-686.
32. Xin H, Ge C, Jiao X, et al. Incorporation of 2,6-connected azulene units into the backbone of conjugated polymers: towards high-performance organic optoelectronic materials. Angew Chem Int Ed. 2018;57:1322-1326.
33. Zhang C, Wang Z, Li H, Lu J, Zhang Q. Recent progress in the usage of tetrazhrom-substituted naphthalenitetetracarboxylic diimide as a building block to construct organic semiconductors and their applications. Org Chem Front. 2020;7:3001-3026.
34. Mei J, Bao Z. Side chain engineering in solution-processable conjugated polymers. Chem Mater. 2013;26:604-615.
35. Xue G, Zhao X, Qu G, et al. Symmetry breaking in side chains leading to mixed orientations and improved charge transport in isoindigo-alt-bithiophene based polyamide thin films. ACS Appl Mater Interfaces. 2017;9:25426-25433.
36. Liu Y, Yang Y, Shi D, et al. Photo-/thermal-responsive field-effect transistor upon blending polymeric semiconductor with hexaarylbimidazole toward photonically programmable and thermally erasable memory device. Adv Mater. 2019;31:1902576.
37. Yang Y, Liu Z, Zhang G, Zhang X, Zhang D. The effects of side chains on the charge mobilities and functionalities of semiconducting conjugated polymers beyond solubilities. Adv Mater. 2019;31:1903104.
38. Ocheje MU, Charron BP, Cheng Y-H, et al. Amide-containing alky1 chains in conjugated polymers: effect on self-assembly and electronic properties. Macromolecules. 2018;51:1336-1344.
39. Lee MY, Dharmapurikar S, Lee SJ, Cho Y, Yang C, Oh JH. Regular H-bonding-containing polymers with stretchability up to 100% external strain for self-healable plastic transistors. Chem Mater. 2020;32:1914-1924.
40. Ma J, Liu Z, Yao J, et al. Improving ambipolar semiconducting properties of thiazole-flanked diketopyrrolopyrrole-based ter-polymers by incorporating urea groups in the side-chains. Macromolecules. 2018;51:6003-6010.
41. Lin YC, Chen CK, Chiang YC, et al. Study on intrinsic stretchability of diketopyrrolopyrrole-based pi-conjugated co-polymers with poly(acryl amide) side chains for organic field-effect transistors. ACS Appl Mater Interfaces. 2020;12:33014-33027.
54. Mayoral MJ, Serrano-Molina D, Camacho-Garcia J, et al. Understanding complex supramolecular landscapes: non-covalent macrocyclization equilibria examined by fluorescence resonance energy transfer. *Chem Sci*. 2018;9:7809-7821.

55. Enengl C, Enengl S, Havlicek M, et al. The role of heteroatoms leading to hydrogen bonds in view of extended chemical stability of organic semiconductors. *Adv Funct Mater*. 2015;25:6679-6688.

56. Xiao Z, Duan T, Chen H, Sun K, Lu S. The role of hydrogen bonding in bulk-heterojunction (BHJ) solar cells: a review. *Sol Energy Mater Sol Cells*. 2018;182:1-13.

57. Zhang M, Zheng CJ, Wang K, et al. Hydrogen-bond-assisted exciplex emitters realizing improved efficiencies and stabilities in organic light emitting diodes. *Adv Funct Mater*. 2021;31:2010100.

58. Kim HJ, Pei M, Ko JS, et al. Influence of branched alkyl ester-labeled side chains on specific chain arrangement and charge transport properties of diketopyrrolopyrrole-based conjugated polymers. *ACS Appl Interfaces*. 2018;10:40681-40691.

59. Charron BP, Ocheje MU, Selivanova M, Hendsbee AD, Li Y, Rondeau-Gagné S. Electronic properties of isoindigo-based conjugated polymers bearing urea-containing and linear alkyl side chains. *J Mater Chem C*. 2018;6:12070-12078.

60. Yang Y, Liu Z, Chen J, et al. A facile approach to improve interchain packing order and charge mobilities by self-assembly of conjugated polymers on water. *Adv Sci*. 2018;5:1801497.

61. Góra RW, Maj M, Grabowski SJ. Resonance-assisted hydrogen bonds revisited. Resonance stabilization vs charge delocalization. *Phys Chem Chem Phys*. 2013;15:2514-2522.

62. Gilli P, Bertolasi V, Ferretti V, Gilli G. Evidence for resonance-assisted hydrogen bonding. 4. Covalent nature of the strong homonuclear hydrogen bond. Study of the O-H–O system by crystal structure correlation methods. *J Am Chem Soc*. 1994;116:909-915.

63. Mirzaei M, Eshtiaq-Hosseini H, Shamsipur M, et al. Importance of polarization assisted/resonance assisted hydrogen bonding interactions and unconventional interactions in crystal formations of five new complexes bearing chelidamic acid through a proton transfer mechanism. *RSC Adv*. 2015;5:72923-72936.

64. Lei T, Dou J-H, Cao X-Y, Wang J-Y, Pei J. A BDOPV-based donor–acceptor polymer for high-performance n-type and oxygen-doped ambipolar field-effect transistors. *Adv Mater*. 2013;25:6589-6593.

65. Xu L, Zhao Z, Xiao M, et al. pi-extended isoindigo-based derivative: a promising electron-deficient building block for polymer semiconductors. *ACS Appl Mater Interfaces*. 2017;9:40549-40555.

66. Ni Z, Dong H, Wang H, et al. Quinoline-flanked diketopyrrolopyrrole copolymers breaking through electron mobility over 6 cm²/(V·s) in flexible thin film devices. *Adv Mater*. 2018;30:1704843.

67. Osaka I, Zhang R, Liu J, Smilgies D-M, Kowalewski T, McCullough RD. Highly stable semiconducting polymers based on thiazolothiazole. *Chem Mater*. 2010;22:4191-4196.

68. Liu B, Li J, Zeng W, et al. High-performance organic semiconductor polymers by a resonance-assisted hydrogen bonding approach. *Chem Mater*. 2021;33:580-588.

69. Roth B, Savagatrup S, V. de los Santos N, et al. Mechanical properties of a library of low-band-gap polymers. *Chem Mater*. 2016;28:2363-2373.

70. Zhang S, Ocheje MU, Luo S, et al. Probing the viscoelastic property of pseudo free-standing conjugated polymeric thin films. *Macromol Rapid Commun*. 2018;39:1800092.

71. Song E, Kang B, Choi HH, et al. Stretchable and transparent organic semiconducting thin film with conjugated polymer nanowires embedded in an elastomeric matrix. *Adv Electron Mater*. 2016;2:1500250.

72. Ditte K, Perez J, Chae S, et al. Ultrasoft and high-mobility block copolymers for skin-compatible electronics. *Adv Mater*. 2021;33:e2005416.

73. Galuska LA, McNutt WW, Qian Z, et al. Impact of backbone rigidity on the thermomechanical properties of semiconducting polymers with conjugation break spacers. *Macromolecules*. 2020;53:6032-6042.

74. Melenbrink EL, Hilby KM, Choudhary K, et al. Influence of acceptor side-chain length and conjugation-break spacer content on the mechanical and electronic properties of semi-random polymers. *ACS Appl Polym Mater*. 2019;1:1107-1117.

75. Zheng Y, Wang GJN, Kang J, et al. An intrinsically stretchable high-performance polymer semiconductor with low crystallinity. *Adv Funct Mater*. 2019;29:1905340.

76. Chiang CY, Wu HC, Wen HF, et al. Tailoring carbosilane side chains toward intrinsically stretchable semiconducting polymers. *Macromolecules*. 2019;52:4396-4404.

77. Pei D, Wang Z, Peng Z, et al. Impact of molecular weight on the mechanical and electrical properties of a high-mobility diketopyrrolopyrrole-based conjugated polymer. *Macromolecules*. 2020;53:4490-4500.

78. Ocheje MU, Selivanova M, Zhang S, et al. Influence of amide-containing side chains on the mechanical properties of diketopyrrolopyrrole-based polymers. *Polym Chem*. 2018;9:5531-5542.

79. Lin Y-C, Shih C-C, Chiang Y-C, Chen C-K, Chen W-C. Intrinsically stretchable isoindigo–bithiophene conjugated copolymers using poly(acrylate amide) side chains for organic field-effect transistors. *Polym Chem*. 2019;10:5172-5183.

80. Wang Z, Lu X, Sun S, Yu C, Xia H. Preparation, characterization and properties of intrinsic self-healing elastomers. *J Mater Chem B*. 2019;7:4876-4926.

81. Fu D, Pu W, Escorihuela J, et al. Acylsemicarbazide moieties with dynamic reversibility and multiple hydrogen bonding for transparent, high modulus, and malleable polymers. *Macromolecules*. 2020;53:7914-7924.

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