Beyond Conformational Control: Effects of Noncovalent Interactions on Molecular Electronic Properties of Conjugated Polymers

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ABSTRACT: Tuning the electronic properties of polymers is of great importance in designing highly efficient organic solar cells. Noncovalent intramolecular interactions have been often used for conformational control to enhance the planarity of polymers or molecules, which may reduce band gaps and promote charge transfer. However, it is not known if noncovalent interactions may alter the electronic properties of conjugated polymers through some mechanism other than the conformational control. Here, we studied the effects of various noncovalent interactions, including sulfur–nitrogen, sulfur–oxygen, sulfur–fluorine, oxygen–nitrogen, oxygen–fluorine, and nitrogen–fluorine, on the electronic properties of polymers with planar geometry using unconstrained and constrained density functional theory. We found that the sulfur–nitrogen intramolecular interaction may reduce the band gaps of polymers and enhance the charge transfer more obviously than other noncovalent interactions. Our findings are also consistent with the experimental data. For the first time, our study shows that the sulfur–nitrogen noncovalent interaction may further affect the electronic structure of coplanar conjugated polymers, which cannot be only explained by the enhancement of molecular planarity. Our work suggests a new mechanism to manipulate the electronic properties of polymers to design high-performance small-molecule-polymer and all-polymer solar cells.

KEYWORDS: noncovalent interactions, conjugated polymers, resonance effect, hole transfer, constrained density functional theory

INTRODUCTION

Organic solar cells (OSCs), which consist of heterojunctions of electron-donating and electron-accepting organic matter, have many promising properties; for example, they are inexpensive, environmentally friendly, lightweight, and flexible.1–5 Recently, substantial progress in designing and synthesizing small-molecule-polymer solar cells, in which the electron donors are conjugated polymers, and the acceptors are nonfullerene small molecules, has boosted the power conversion efficiency up to about 18%.4,6–11 All-polymer solar cells, where conjugated polymers work as both electron donors and acceptors, also show a promising efficiency of nearly 16%.12–13 In molecular engineering of small-molecule-polymer or all-polymer solar cells, polymers must be carefully designed so that electron donors and acceptors can match well.1 Tens of thousands of donor–acceptor combinations are available, but the scientific community still largely relies on the trial-and-error approach.5 Many fundamental electronic properties of polymers are not well understood.

Tuning the electronic properties of conjugated polymers plays an important role in optimizing the performance of OSCs. The widely used designing strategies include donor–acceptor copolymers,2,3,14 fluorination,15–18 and planar conformation locking.19–23 In particular, the high planarity of backbone chains of polymers facilitates electron delocalization and π–π intermolecular interactions, which result in narrower HOMO–LUMO band gaps and fast charge transfer.3,20 A promising approach for improving the planarity and rigidity of organic molecules is to introduce some noncovalent interactions such as sulfur–nitrogen, sulfur–oxygen, and sulfur–fluorine interactions.19,21–24 Yu et al. introduced the sulfur–nitrogen interaction as a noncovalent conformational lock in a small molecular acceptor to significantly enhance the photovoltaic performance.21 Xia et al. found that the sulfur–oxygen interaction has similar effects in the donor–acceptor conjugated polymers.22 Some theoretical studies also suggested that noncovalent interactions may enhance planarity of both conjugated polymers and small molecule acceptors.19,25 So far, most of previous studies focus on how noncovalent interactions control the conformation of polymers, which may further alter electronic properties; however, it is not yet known if noncovalent interactions may directly affect the electronic properties of planar polymers.

In this study, we considered six common noncovalent interactions: sulfur–nitrogen (S–N), sulfur–oxygen (S–O),...
sulfur–fluorine (S–F), oxygen–nitrogen (O–N), oxygen–fluorine (O–F), and nitrogen–fluorine (N–F), in 48 polymer structures with planar geometry. We found that after introducing the six noncovalent intramolecular interactions, the band gaps of most polymers decrease and the hole transfer rates increase; particularly, the sulfur–nitrogen interaction has the most obvious effect. Our findings are also consistent with the experimental data. This study paves the way for understanding and manipulating the electronic properties of polymers, which will facilitate the design of high-performance organic solar cells.

**RESULTS AND DISCUSSION**

Figure 1(a) shows the representative structures of conjugated polymers with the six noncovalent interactions. To compare the structures with and without the six noncovalent interactions, we rotated the corresponding moieties around the inter-ring carbon–carbon bonds by 180° or swapped the side chains (see Figure 1(a) and Figure S1). Before and after the modification, we relaxed both atomic positions and the inter-ring carbon bonds by 180° or swapping side chains. After the structure modification, the S, N, O, and F atoms form hydrogen bonds to keep the planar structures. (b) The change of band gaps after introducing the six noncovalent interactions, the sulfur, nitrogen, oxygen, and fluorine atoms form hydrogen bonds to keep the planar structures with the noncovalent interactions labeled by the red and black dashed lines: S–N, S–O, S–F, O–N, O–F, and N–F. X or X’ denotes the S or O atom, and Y is the F atom or the —OCH3 group. The arrows show that we break up the noncovalent interactions by rotating moieties by 180° or swapping side chains. After the structure modification, the S–N, O–N, and F–atoms form hydrogen bonds to keep the planar structures.

**Figure 1.** Polymer structures and band gap change. (a) The planar polymer structures with the noncovalent interactions labeled by the dashed lines: S–N, S–O, S–F, O–N, O–F, and N–F. X or X’ denotes the S or O atom, and Y is the F atom or the —OCH3 group. The arrows show that we break up the noncovalent interactions by rotating moieties by 180° or swapping side chains. After the structure modification, the S, N, O, and F atoms form hydrogen bonds to keep the planar structures. (b) The change of band gaps after introducing the six noncovalent interactions in panel a.

Figure 2(a) and (b) show that the HOMO is distributed closer to the polymer backbone than the LUMO, which means that the sulfur–nitrogen interaction may affect the electronic state of the polymer backbone. We plotted the projected density of states of conjugated carbon atoms in Figure 2(c) and (d), showing that the HOMO is the π bonding orbital, made by the px orbitals of the conjugated carbon atoms. The change of the π bonding orbital along the backbone carbon atoms may affect transport properties of polymers.

We calculated the change of hole transfer rates of the polymers after introducing the noncovalent interactions in Figure 3. Because polymers are often used as electron donors in the OSC devices, we mainly consider the hole transport in the hopping regime along the backbone chains. We applied the following adiabatic rate equation:

\[ \Delta E_g \text{ after introducing the six noncovalent interactions. We found that the } \Delta E_g \text{ values are largely negative, among which the sulfur–nitrogen interaction reduces band gaps most. The sulfur atom is in the thiophene moiety, and the nitrogen atom is from benzo[12]thiadiazole. We studied seven different polymer structures with the sulfur–nitrogen interaction (see Figures S2 and S3 in the Supporting Information), whose } \Delta E_g \text{ can be as low as } -0.15 \text{ eV. In our calculations, we used the vacuum energy level to align the HOMO and LUMO levels, and found that after introducing the sulfur–nitrogen interaction, the HOMO levels shift to higher energies, while the LUMO levels change little (see Figure S5 in the Supporting Information). Figure 2(a) and (b) show that the HOMO is distributed closer to the polymer backbone than the LUMO, which means that the sulfur–nitrogen interaction may affect the electronic state of the polymer backbone. We plotted the projected density of states of conjugated carbon atoms in Figure 2(c) and (d), showing that the HOMO is the π bonding orbital, made by the px orbitals of the conjugated carbon atoms. The change of the π bonding orbital along the backbone carbon atoms may affect transport properties of polymers. We calculated the change of hole transfer rates of the polymers after introducing the noncovalent interactions in Figure 3. Because polymers are often used as electron donors in the OSC devices, we mainly consider the hole transport in the hopping regime along the backbone chains. We applied the following adiabatic rate equation:} \]
We applied the constrained density functional theory (DFT) method to calculate the external reorganization energy \( E_{\text{in}} \), which is consistent with Breddas’ findings in polyaromatic molecules. The sulfur interacts with the pyridinic nitrogen, the sulfur atom loses electrons, while the nitrogen atom gains electrons; the charge redistribution is along the carbon backbone, as shown in Figure 4(a). The intramolecular charge redistribution affects the resonance effect in conjugated polymers, which may help to stabilize the quinoid structure and reduce the band gaps. For example, Figure 4(a) shows the aromatic and quinoid forms of the polymer NC\(_6\)S\(_5\)-N\(_1\) with the sulfur–nitrogen interaction. The single and double bonds of the thiophene ring in the aromatic structure become the double and single bonds in the quinoid structure, respectively, so the corresponding bond lengths may change if there is more quinoid character. Figure 4(b) shows the correlation between the bond length change (\( \Delta r \)) and the band gap change (\( \Delta E_g \)), suggesting that the more quinoid character helps to reduce the band gap, which is consistent with Breddas’ findings in polyaromatic molecules. Thus, the sulfur–nitrogen interaction reduces the intramolecular charge redistribution in polymers, which increases the quinoid character and reduces the band gaps.

The sulfur–nitrogen pair has the largest charge redistribution among all the noncovalent interactions studied here (see Table SII in the Supporting Information), so it affects band gaps and hole transfer rates more than other noncovalent atom pairs. When the thiophene sulfur interacts with the pyridinic nitrogen interaction not only reduces band gaps but also considerably improves transport properties.

In Figure 3, we compared the hole transfer rates between the two nearest repeating moieties participating in the noncovalent interactions. The sulfur–nitrogen interaction increases the hole transfer rate by \( \sim 10^3 \) to \( 10^7 \) times, which is overall the largest among all the noncovalent interactions studied here. The results suggest that the sulfur–nitrogen interaction not only reduces band gaps but also considerably improves transport properties.

To understand why the sulfur–nitrogen interaction changes band gaps and hole transfer rates most, we first examined the intramolecular charge redistribution using the Mulliken population analysis. We found that after the thiophene sulfur interacts with the pyridinic nitrogen, the sulfur atom loses electrons, while the nitrogen atom gains electrons; the charge redistribution is along the carbon backbone, as shown in Figure 4(a). The intramolecular charge redistribution affects the resonance effect in conjugated polymers, which may help to stabilize the quinoid structure and reduce the band gaps. For example, Figure 4(a) shows the aromatic and quinoid forms of the polymer NC\(_6\)S\(_5\)-N\(_1\) with the sulfur–nitrogen interaction. The single and double bonds of the thiophene ring in the aromatic structure become the double and single bonds in the quinoid structure, respectively, so the corresponding bond lengths may change if there is more quinoid character. Figure 4(b) shows the correlation between the bond length change (\( \Delta r \)) and the band gap change (\( \Delta E_g \)), suggesting that the more quinoid character helps to reduce the band gap, which is consistent with Breddas’ findings in polyaromatic molecules. Thus, the sulfur–nitrogen interaction reduces the intramolecular charge redistribution in polymers, which increases the quinoid character and reduces the band gaps.

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nitrogen, the sulfur atom loses about 0.062 ± 0.04 electrons and the nitrogen atom gains about 0.034 ± 0.007 electrons. If we replace the sulfur atom in the thiophene moiety by the oxygen atom, i.e., thiophene becoming furan (see Figure S4 in the Supporting Information), the oxygen atom loses about 0.039 ± 0.007 electrons, and the nitrogen atom may gain as little as 0.010 electrons or even lose 0.022 electrons. The oxygen atom is more electronegative than either the sulfur or nitrogen atoms, so it is difficult for the oxygen atom to donate electrons to the C–C bonds, which explains why the oxygen–nitrogen pair does not have the similar intramolecular charge redistribution as the sulfur–nitrogen pair. As a result, the quinoid character does not increase obviously with the oxygen–nitrogen interaction, and the band gaps and hole transfer rates do not change much.

For the sulfur–oxygen interaction, when the thiophene sulfur interacts with the benzodifuran oxygen, the quinoid character does not change much, so it does not greatly change the band gaps and hole transport rates. When the fluorine atom interacts with the sulfur, nitrogen, or oxygen atoms, as shown in Figure 1, the fluorine atom may increase the planarity of polymers and enhance the charge separation; however, it does not increase the quinoid character, so the noncovalent interactions with the fluorine atom do not greatly change the electronic properties.

The Mulliken population analysis largely depends on basis sets and so can only provide estimated partial atomic charges. We also performed the Löwdin population analysis and found that despite different charge values, both methods give a consistent charge transfer direction (see Table SII in the Supporting Information).

The effects of noncovalent interactions on the photovoltaic performance of polymers can also be found in experiment. Liu et al. reported that two planar polymers, P3TEA and P3TAE, differ only by the position of carboxyl side chains (see Figure 5(a) and (b)), but have different electronic properties and OSC performance.37 Our DFT calculations show that the band gap of P3TEA is smaller than that of P3TAE by 0.08 eV, which is consistent with the experimental optical gap change (∼0.05 eV).37 Additionally, when a hole hops between two nearest S,6-difluoro-2,1,3-benzothiadiazole (fBT) moieties, the calculated transfer rate of P3TEA is larger than that of P3TAE by 10⁶ times. When Liu et al. blended P3TEA with various molecular acceptors to make OSC devices, its narrower gap and faster charge transfer lead to the high photovoltaic performance.37–40 Both P3TEA and P3TAE have the sulfur–nitrogen interaction, except that the carboxyl side chain in P3TAE is next to the sulfur–nitrogen pair. The Mulliken population analysis in Figure 5(c) shows that the pyridinic nitrogen in P3TAE becomes less negatively charged than that in P3TEA, which explains why P3TAE has a larger band gap and worse OSC performance.

**CONCLUSION**

Here, we applied the unconstrained and constrained DFT method to study six noncovalent intramolecular interactions typically found in the polymers in organic solar cell applications. Besides conformational control, we found that most of the noncovalent interactions reduce the band gaps of polymers and increase the hole transfer rates, and the sulfur–nitrogen pair has the largest effect, which cannot be only explained by the enhancement of molecular planarity. The enhancement of electronic properties can be attributed to the intramolecular charge redistribution, which increases the quinoid character of conjugated polymers. Our findings are also consistent with the experimental data. Our study suggests that choosing suitable noncovalent intramolecular interactions may further manipulate the electronic properties of planar polymers. This work paves the way for understanding the electronic structure of polymers, and suggests a new mechanism to design high-performance polymers for small-molecule-polymer and all-polymer solar cells. This mechanism can also be used to improve the performance of organic field-effect transistors.

**METHODS**

We conducted first-principles calculations using the Quickstep module of the CP2K program package with a dual basis of Gaussian orbitals and plane waves.41 We used the Goedecker–Teter–Hutter norm-conserving pseudopotentials for the valence electrons.42,43 A plane-wave density cutoff of 600 Ry was adopted. We used three-dimensional periodic boundary conditions to simulate polymers, whose backbone chains are along the z direction. The length of repeating units was obtained by optimizing the structure of dimers and trimers with open boundary conditions.40 The vacuum along the x and y directions is at least 20 Å thick. We applied the molecularly optimized Gaussian basis sets of double–ζ plus polarization quality (DZVP-MOLOPT)44 and the Perdew–Burke–Ernzerhof (PBE)45 exchange-correlation (xc) functional with Grimme’s D3 dispersion correction46 in the structural relaxation, where the force tolerance is 0.01 eV/Å. In the band gap calculations, we used Gaussian basis sets of triple–ζ plus two sets of polarization functions (TZVP2) and the hybrid B3LYP xc functional.47–49 In the charge transfer calculations, we used the auxiliary density matrix method (ADMM)50 and the cFIT3 basis set to reduce computational costs of the B3LYP functional.

### Table SII. Mulliken atomic charges of the thiophene sulfur atom and the pyridinic nitrogen atom in P3TEA and P3TAE.

| Polymer | Thiophene-S | Pyridinic-N |
|---------|-------------|-------------|
| P3TEA   | 0.982       | -0.447      |
| P3TAE   | 1.144       | -0.425      |
The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/jacsau.1c00284.

Polymer structures, HOMO and LUMO levels, nonadiabatic electronic couplings, reorganization energies, hole hopping rates, and change of Mulliken atomic charges and Löwdin atomic charges (PDF)

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