Conjugated Polymers with Sequential Fluorination for Enhanced Photocatalytic H₂ Evolution via Proton-Coupled Electron Transfer

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Supporting Information

ABSTRACT: The performance of donor–acceptor (D–A) conjugated polymer-based photocatalysts for solar hydrogen production is severely limited by poor charge mobility and weak reactive sites. Here, a series of D–A conjugated polymers with electronegative fluorine atoms on the backbone is presented and the influence of fluorination on charge transfer and catalytic site activity is investigated. Theoretical calculation reveals that sequential fluorination on the A unit benzothiadiazole will activate the catalytic site, and the photocatalytic H₂ generation process could be illustrated by a proton-coupled electron-transfer mechanism. Two series of fluorinated polymers were synthesized, and accelerated charge transfer was also verified. Among them, linear B-FOBT-1,4-E and porous B-FOBT-1,3,5-E with simultaneous electron-donating CH₃O⁻ and electron-withdrawing F⁻ substitution show a H₂ evolution rate that is 3.1 and 28.8 times higher than that of nonfluorinated counterparts, respectively, and the apparent quantum yield of 5.7% at 420 nm is obtained for B-FOBT-1,4-E. The results provide reciprocal understanding of the activation nature of substituent-regulating polymers.

Conjugated polymers, consisting of alternating electron-donating (D) and electron-accepting (A) units, are one class of unique polymers which have been applied widely in the construction of polymer solar cells (PSCs), and they are expected to exhibit strong visible light absorption ability and high photostability due to the push–pull intramolecular charge transfer. Very recently, D–A conjugated microporous polymers developed by Cooper’s group were also found to exhibit modest H₂ evolution rate (HER) under visible light irradiation (λ > 420 nm). In comparison to the most studied polymeric g-C₃N₄ with relatively fixed structures, the abundance of donors and acceptors contribute to tunable energy levels; as a result, more novel polymers by facile D or A unit choice were prepared with superior HER and overall water-splitting ability. However, D–A conjugated polymeric semiconductors still face drawbacks of low solar-to-H₂ conversion efficiency, and their structures may be further optimized with regard to the three dominating steps in the process of photocatalytic water splitting: (i) absorption of photons to form electron–hole pairs, (ii) charge separation and migration, and (iii) surface proton reduction.

Among various strategies for optimizing structures of D–A conjugated polymers with high photovoltaic efficiency, a combination of “weak donors” and “strong acceptors” proves to benefit charge transport. To obtain stronger acceptors, it has been widely reported that introduction of electronegative fluorine atoms on polymer backbone represents one effective method without changing the light-harvesting ability significantly. We have recently synthesized two D–A conjugated polymers: linear B-BT-1,4-E and porous B-BT-1,3,5-E in which benzothiadiazole (BT) acted as A unit, and both of them exhibited moderate HER. In this regard, it is expected that further fluorination on BT of the above two...
polymers will accelerate photogenerated carrier separation in the second step of the photocatalytic process. On the other hand, regulation of catalytic reaction sites is another crucial factor to afford desired photocatalysts. Tian’s group prepared several types of BT-based polymer nanoparticles (PDots), and they reported that heteroatom nitrogen in the BT units was the reactive site in the process of photocatalytic H2 evolution. Accordingly, surface proton reduction in the final step may also be assessed by theoretical prediction in terms of the catalytic site activity for fluorinated B-BT-1,4-E and B-BT-1,3,5-E.

To demonstrate the influence of F substitution on the photogenerated carrier mobility and catalytic active site. Theoretical density functional theory (DFT) calculations are performed to predict the activation energy of H2 formation from interacting hydrogen atoms in two different polymer chains with heteroatom N on BT units as active site, because it is the most difficult step of the HER reaction. Previously, similar theoretical investigation was successfully used to reveal the hydrogen evolution mechanism in nitrogenase-catalyzed N2 reduction. A series of linear fluorinated B-BT-1,4-E were designed with different number of fluorine atoms (0F, 1F, 2F, F/OCH3), and theoretical modeling indicates that the photocatalytic H2 release process for the polymer follows a proton-coupled electron transfer (PCET) facilitated route (Figure 1) which plays a vital role in a wide range of chemical and biological processes. As a result, it is predicted that B-FOBT-1,4-E in which BT is simultaneously substituted by an electron-donating methoxyl group (OCH3) and an electron-withdrawing F has the strongest catalytic site. In the experimental part, and HER change of as-prepared polymers obeys the theoretical prediction. Moreover, the same strategy could also be applicable to the microporous polymer B-BT-1,3,5-E system.

The simulated reaction begins with two hydrogenated oligomers on nitrogen, and then one H2 molecule leaves the dimer through a transition state. For nonfluorinated B-BT-1,4-E, the two N atoms are identical, and the activation energy barrier is calculated to be 1.75 eV between the energy of the transition state and the two hydrogenated monomers. However, the two N atoms in the BT unit are different in the monofluorinated B-FBT-1,4-E chain, and two model systems are evaluated. As shown in Figure 2b, positions of F substituents are regarded as para and meta relative to the position of the hydrogenated N atom, and the models are named as m-B-FBT-1,4-E and p-B-FBT-1,4-E, respectively. A lower activation energy barrier is found for p-B-FBT-1,4-E (1.65 eV) in comparison to m-B-FBT-1,4-E (1.79 eV); thus, the p-B-FBT-1,4-E model is more kinetically favorable than m-B-FBT-1,4-E for H2 generation.

The transition-state structures and corresponding highest occupied molecular orbital (HOMO) are further investigated, and the interaction between the two different hydrogenated polymers is far more interesting. In the transition state of B-BT-1,4-E, the p orbital of the meta carbon in one polymer chain tends to approach the p orbital of the N atom in the other polymer chain, and then the resulting H\textsuperscript{+} attacks H\textsuperscript{−} to form one H2 molecule. Similar to coupling between the proton motion and electron transfer that plays a key role in the proton-pumping mechanism of photosynthetic reaction centers, the photocatalytic H2 release process here may follow a typical PCET-facilitated route due to different transfer methods of the proton and electron. However, there still exists a gap between the two approaching p orbitals for B-BT-1,4-E, which limits the PCET effect. As shown in Figure 2c, the induction effect of the F atom at the para position enlarges the p orbital of meta carbon, which will form a bridge with the p orbital of the N atom in the other polymer chain, and then the PCET process is more favorable, revealing relatively lower activation energy of p-B-FBT-1,4-E. In contrast, for m-B-FBT-1,4-E, the induction effect of the F atom at the meta position has a negative impact on the PCET effect (Figure 2d). Therefore, it is reasonable that both meta and para fluorination result in a weaker PCET effect in comparison to a sole para
fluorination; as a result, the activation energy of B-DFBT-1,4-E is higher than that of p-B-FBT-1,4-E (Figure 2e). The above discussion sheds light on a way to improve the HER. Because we know the electron-withdrawing F group at the para site is beneficial to H₂ evolution while it is bad at the meta site, we hypothesize that the electron-donating OCH₃ group the at meta site along with the electron-withdrawing F atom at the para site may favor the charge transfer between two interacting polymer chains. To our delight, B-FOBT-1,4-E with 4-OCH₃-5-F-BT as A unit shows the lowest hydrogen release energy barrier at 1.54 eV among all the cases; thus, it should be the most promising candidate for photocatalytic H₂ evolution.

Inspired by theoretical predictions, nonfluorinated linear B-BT-1,4-E and three F-substituted B-FBT-1,4-E, B-DFBT-1,4-E and B-FOBT-1,4-E were synthesized according to the palladium catalyzed Sonogashira–Hagihara cross-coupling polycondensation (Figure 1a). In general, the mixture of two monomers, Pd(PPh₃)₂Cl₂ and CuI in DMF/TEA was first degassed with Ar for 20 min and then stirred at 80 °C for 24 h. The cooled mixture was filtered and washed thoroughly with methanol and CH₂Cl₂ in the Soxhlet for 48 h, and the final product was dried at 60 °C overnight. More synthetic details are described in the Supporting Information, and it should be noted that all the as-prepared polymers are completely insoluble in all solvents investigated. As shown in Figure 3a, the structures are first characterized by solid-stated ¹³C cross-polarization magic angle spinning (CP/MAS) nuclear magnetic resonance spectra (NMR). The main peaks at ≈96 and 87 ppm are identified to be C4 and C5 of the −C≡C− group, respectively. Specifically, peaks at ≈153 ppm are assigned to C1, and the peaks for other aromatic carbons could be found ranging from 116 to 132 ppm. In addition, the Fourier transform infrared (FT-IR) spectra for all the polymers reveal the characteristic signals of the C≡C group at around 2205 cm⁻¹ (Figure S1). In comparison to B-BT-1,4-E, new signals at around 1380 cm⁻¹ in B-FBT-1,4-E, B-DFBT-1,4-E, and B-FOBT-1,4-E can be assigned to C−F bonds, and C−O stretching bands of B-FOBT-1,4-E appear at 1200 cm⁻¹. The Brunauer–Emmett–Teller (BET) surface area of B-BT-1,4-E, B-FBT-1,4-E, and B-DFBT-1,4-E are determined to be 66, 207, and 233 m² g⁻¹, respectively, and it indicates that sequential fluorination results in remarkable increase of surface areas (Figure S2). However, introduction of OCH₃ reduces the surface area of B-FOBT-1,4-E to 58 m² g⁻¹, and pore volumes vary from 0.102 to 0.360 cm³ g⁻¹ (Figure S3). Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) images illustrate the change of the morphology (Figures S4 and S5), and all the conjugated polymers show amorphous properties by powder X-ray diffraction (PXRD, Figure S6). In addition, thermal gravimetric analysis (TGA) reveals their excellent stability up to 350 °C in air conditions (Figure S7).

The impact of fluorination on optical absorption properties is investigated by UV−vis diffuse reflectance spectroscopy (DRS), and all of the polymers show broad light absorption
spectra (Figure 3b). There exists only slight changes among B-BT-1,4-E, B-FBT-1,4-E, and B-DFBT-1,4-E, but B-FOBT-1,4-E has lower visible light absorption ability. The optical band gaps ($E_g$) of B-BT-1,4-E, B-FBT-1,4-E, B-DFBT-1,4-E, and B-FOBT-1,4-E are determined to be 2.14, 2.12, 2.12, and 2.18 eV (Table 1) according to the Kubelka–Munk function, respectively. The HOMO levels are estimated by cyclic voltammetry (CV) curves (Figures S8 and S9), and then lowest unoccupied molecular orbital (LUMO) levels are further calculated by CV and $E_g$. It can be seen that sequential fluorination gradually downshifts the HOMO and LUMO levels simultaneously because of the strong inductive electron-withdrawing property of F substituents, while B-FOBT-1,4-E exhibits a higher-lying HOMO level than B-DFBT-1,4-E because of less electron-deficiency of F- and CH$_3$O-substituted BT. The changing trends of HOMO and LUMO levels by sequential fluorination are also confirmed by DFT calculation (Figure S10). Therefore, the fluorination of D–A conjugated polymers definitely provides an effective strategy for optimizing the photoredox potentials.

Following the successful preparation of conjugated polymers, the photocatalytic hydrogen evolution activity is measured in a Pyrex top-irradiation reaction vessel connected to a closed gas system. In detail, 30 mg of the polymer was dispersed in 30 mL of aqueous solution containing 3 mL of TEOA as the sacrificial electron donor, and air was thoroughly removed by a repeated degassing procedure. The 300 W Xe lamp (PLS SXE300, Beijing Perfectlight Inc., China) equipped with a 420 nm cutoff filter is used as light source, and HER was determined by a gas chromatograph. As a result, the HER of mono-fluorinated B-FBT-1,4-E is determined to be 327 μmol h$^{-1}$, which is 2.6 times higher than that of non-fluorinated B-BT-1,4-E (Figure 4a). The second introduction of F atom decreases the HER of B-FBT-1,4-E to 214 μmol h$^{-1}$, and then it is not surprising that B-FOBT-1,4-E exhibits the highest HER of 399 μmol h$^{-1}$ (Table 1). Therefore, it is reasonable that the photocatalytic H$_2$ evolution process here follows the PCET mechanism based on the good correlation between experimental results and theoretical prediction. Subsequently, apparent quantum yield (AQY) measurement against light wavelength reveals that B-FOBT-1,4-E shows a broad light response region (Figure 4b). It renders an AQY of 5.7% at 420 nm, which is among the highest values for polymer photocatalysts, and an unprecedented AQY of 1.3% at 500 nm has also been achieved (Table S2).

### Table 1. Basic Optical, Energy Band Levels, and H$_2$ Production Properties of Polymers

<table>
<thead>
<tr>
<th>polymer</th>
<th>HOMO (eV)</th>
<th>LUMO (eV)</th>
<th>$E_g$ (eV)</th>
<th>HER (μmol h$^{-1}$)</th>
<th>AQY (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>B-BT-1,4-E</td>
<td>−5.87</td>
<td>−3.73</td>
<td>2.14</td>
<td>128</td>
<td>0.85</td>
</tr>
<tr>
<td>B-FBT-1,4-E</td>
<td>−6.03</td>
<td>−3.91</td>
<td>2.12</td>
<td>313</td>
<td>2.3</td>
</tr>
<tr>
<td>B-DFBT-1,4-E</td>
<td>−6.07</td>
<td>−3.95</td>
<td>2.12</td>
<td>207</td>
<td>1.3</td>
</tr>
<tr>
<td>B-FOBT-1,4-E</td>
<td>−5.83</td>
<td>−3.65</td>
<td>2.18</td>
<td>399</td>
<td>5.7</td>
</tr>
<tr>
<td>B-BT-1,3,5-E</td>
<td>−6.24</td>
<td>−3.78</td>
<td>2.46</td>
<td>10</td>
<td>0.07</td>
</tr>
<tr>
<td>B-FBT-1,3,5-E</td>
<td>−6.31</td>
<td>−3.84</td>
<td>2.47</td>
<td>165</td>
<td>0.8</td>
</tr>
<tr>
<td>B-DFBT-1,3,5-E</td>
<td>−6.40</td>
<td>−4.00</td>
<td>2.40</td>
<td>120</td>
<td>0.5</td>
</tr>
<tr>
<td>B-FOBT-1,3,5-E</td>
<td>−6.29</td>
<td>−3.88</td>
<td>2.41</td>
<td>288</td>
<td>1.8</td>
</tr>
</tbody>
</table>

$^a$Determined from cyclic voltammetry (CV). $^b$HOMO = LUMO − $E_g$. $^c$Determined by the absorption onset from DRS spectra. $^d$Conditions: 30 mg of polymer, 30 mL of 10% vol TEOA/H$_2$O, $\lambda > 420$ nm or =420 nm.

Figure 4. (a) Photocatalytic H$_2$ evolution of linear polymers; (b) AQY values light wavelength of B-FOBT-1,4-E; (c) long-term test of B-FOBT-1,4-E over 20 h; and (d) transient photocurrent response of linear polymers.

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The light-driven H₂ evolution process of conjugated polymers follows the order that fluorination reduces the second fluorination results in dramatic HER from 10 to 165 μmol h⁻¹; meanwhile, B-FOBT-1,3,5-E exhibits the highest HER at 288 μmol h⁻¹, which is 28.8 times higher than that of B-BT-1,3,5-E. Therefore, a similar PCET mechanism may also be utilized to explain the light-driven H₂ evolution process due to some alternating D and A units.

In order to gain insight into the influence of F substitution on the photogenerated transfer efficiency in the PCET process, the transient photocurrent response under visible light irradiation is compared. As shown in Figures 4d and S25, the trend of generated photocurrent intensity for linear and microporous D–A conjugated polymers follows the order that is consistent with the photocatalytic HER. It is noteworthy that all the conjugated polymers exhibited photocatalytic H₂ evolution ability without additional Pt as cocatalyst, but residual Pd may also act as a cocatalyst at low threshold. In our designed conjugated polymers, the residual Pd contents vary between 0.3% and 0.5% via inductively coupled plasma mass spectrometry (ICP-MS), and linear B-FOBT-1,4-E with the highest HER contained the lowest Pd content at 0.3%. As discussed, F incorporation has no obvious impact on the light-harvesting ability, and B-FOBT-1,4-E with the highest HER has a smaller surface area than B-FBT-1,4-E and B-DFBT-1,4-E. With regard to the photocatalytic process, the stronger active site N and accelerated charge transfer by incorporation of F in the polymers are the dominating factors enhancing the photocatalytic activity.

In conclusion, sequential fluorination of a linear D–A conjugated polymer led to regular change of barrier activation energy of H₂ formation by DFT calculation, and theoretical models indicate that the light-driven H₂ release process follows the typical PCET-facilitated route. Photocatalytic H₂ evolution activity of the as-prepared linear and microporous polymers follows the same trend of predicted activation energy change. The novel B-FOBT-1,4-E exhibits 3.1 times higher HER (399 μmol h⁻¹) than nonfluorinated B-BT-1,4-E with a record AQY of 5.7% at 420 nm, and HER of B-FOBT-1,3,5-E is also increased by 28.8 times. Moreover, a strong relationship between degree of fluorination and charge mobility was verified by photocurrent measurement. Therefore, F substitution proves to be an effective method to enhance the photocatalytic activity of D–A conjugated polymers in terms of enhanced active sites and accelerated charge transfer, and the PCET mechanism is first utilized to explain the photocatalytic H₂ evolution process of conjugated polymers. This study provides a simple but very attractive manner to rationally modulate the structure of D–A conjugated polymers based on DFT calculations.


