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## New Aspect of Cyclopentadithiophene Based Polymers: Narrow Band Gap Polymer upon Protonation

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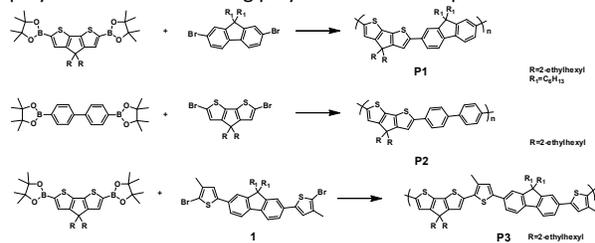
**A new aspect of cyclopentadithiophene (CPDT) based conjugated polymers was reported. CPDT units in conjugated polymers can be facily protonated with a significant optical and electronic properties change. The protonation was confirmed by NMR spectra studies and the remarkable decrease of energy band-gap was attributed to charge separation upon protonation.**

Electroactive cyclopentadithiophene (CPDT) derivatives have attracted tremendous interests recently due to their semiconducting and unique electronic characteristics, which were used for constructing high performance organic electronic and optical materials.<sup>1-3</sup> The fused rings, rigid and planar structures of CPDT lead to a more extended conjugation length in the ground state, a lower HOMO-LUMO energy separation and easy  $\pi$ - $\pi^*$  intermolecular charge transport.<sup>4,5</sup> The rigid fused rings structure of CPDT also lower the reorganization energy, a parameter that strongly affects the rate of intermolecular hopping and hence the charge carrier mobility in organic semiconductors.<sup>6</sup> As a result, CPDT and its derivatives have been extensively employed as building blocks in preparation of electroactive conjugated polymers, especially the narrow band-gap  $\pi$ -conjugated polymers, as electronic donor or  $\pi$ -conjugated spacer. Most of these CPDTs based conjugated polymers showed excellent electronic and optical properties, which have been exploited for application in organic semiconducting devices such as organic field effect transistors (OFETs),<sup>7-12</sup> photovoltaic devices (PVDs),<sup>13-17</sup> light emitting diodes (LEDs)<sup>18,19</sup> and electrochromic devices (ECDs).<sup>20,21</sup>

Because CPDTs based materials display a wide range of interesting physical properties such as low band gaps and high

conductivities, many new CPDTs based conjugated polymers have been reported recently.<sup>22-27</sup> The most common used methods are to design and synthesize of new polymer by modifying the side chains of existing polymer or by building a totally new polymer structures.<sup>28</sup> For instance, CPDT can be functionalized at the  $\alpha$ -positions of thiophenes and/or at the bridgehead position.<sup>27,28</sup> However, in most cases, tedious synthetic steps are required, and the complicated new structures are limited by their low yields and high cost. Furthermore, enormous synthetic effort often leads to minor tuning of their physical properties.<sup>31,32</sup> Thus, new and simple approaches to significantly modulate the optical and electronic properties of CPDT based polymers are greatly desired.

Here we report a new and interesting aspect of the CPDT based conjugated polymers. We show that CPDT units in the polymers can be protonated by organic acid with significant optical and electronic properties changes. A significant decrease of the energy bandgap ( $> 1.5$  eV) can be achieved simply by protonation. The CPDT based conjugated polymers showed ultrasensitive response to acid with a remarkable optical and electronic properties change. With the help of DFT calculation, the remarkable decrease of HOMO-LUMO band-gap was attributed to charge separation upon protonation. To the best of our knowledge, for the first time, it is demonstrated that CPDTs based polymers can be protonated with significant tunable optical and electronic properties, and thus a new series of polyaniline-like conducting polymers was developed.



**Scheme 1** Synthesis of polymers P1-P3.

To demonstrate the new interesting properties of CPDTs based conjugated polymers, three CPDT-containing conjugated polymers were prepared in high yields by coupling of CPDT derivatives with other aromatic units such as fluorene and biphenyl through Suzuki

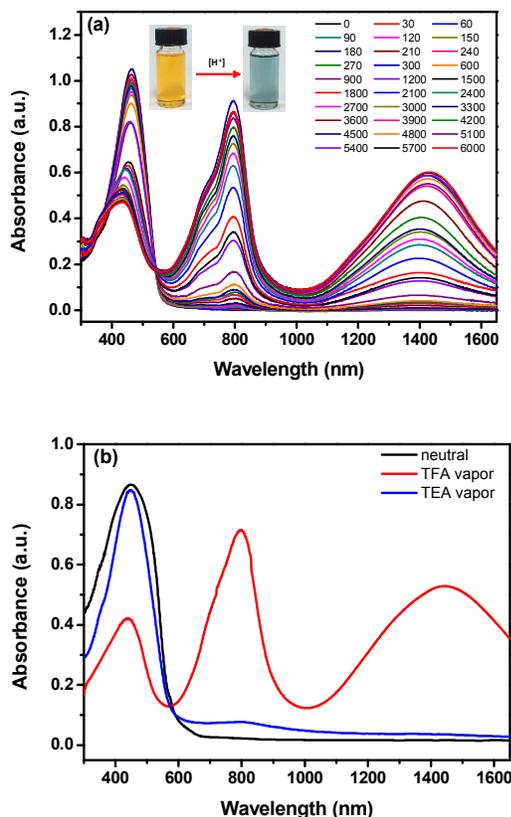
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coupling (Scheme 1). The obtained polymers could be readily dissolved in common solvents such as THF, chloroform, toluene and dichloromethane. In addition, these polymers showed good thermal stability with decomposition temperatures ( $T_d$ ) between 291–390 °C (Fig. S1, ESI†).

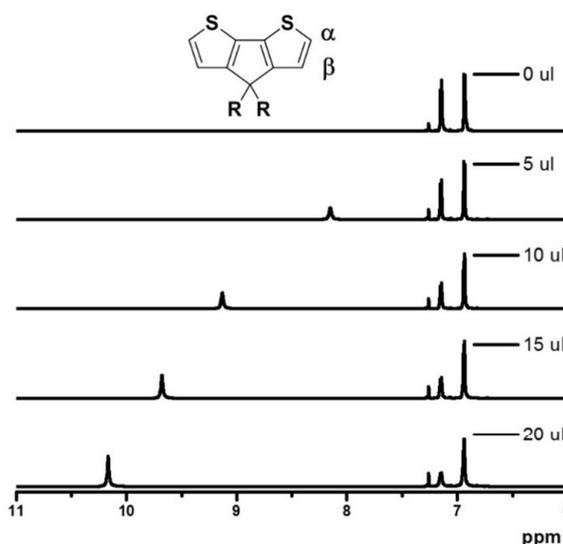


**Fig. 1** UV-vis-NIR spectra of the polymer **P3** (a) in chloroform solution as a function of TFA concentration (ppm) (insets show the color change of **P3** solution after protonation); (b) as-cast film on quartz substrates upon different treatments (the pristine neutral polymer film, film exposed to TFA vapor, and neutralization of the protonated film by TEA vapor).

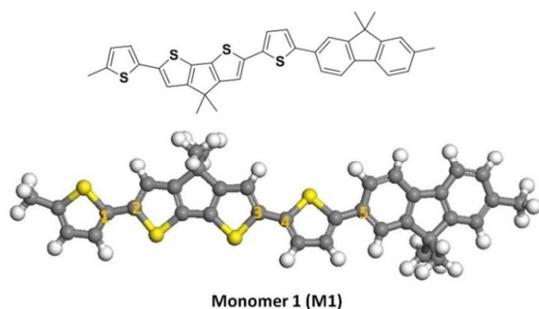
Their optical properties were studied by using UV-vis-NIR spectrometer. All three CPDT-containing polymers in chloroform exhibit absorption maxima in the range of 463 and 472 nm, similar to the reported CPDTs based polymers (Fig. S2, ESI†).<sup>13</sup> However, significant optical behavior was observed when these polymers were treated with trifluoroacetic acid (TFA), and **P3** is here used as an example to show the optical properties change upon protonation (Fig. 1). At very low concentration of TFA (0.0067 % (V), ~ 60 ppm), two new absorption bands at 800 and 1401 nm were emerged. Further addition of TFA leads to the continuing increase of the newly appeared broad absorption bands with the bleaching of  $\pi$ - $\pi^*$  transition at 463 nm. An isosbestic point observed at 542 nm is consistent with two inter-converting optically different

phases being present in the solution. Finally, the spectra exhibits little change when the TFA concentration was beyond 0.6% (V), suggesting an acidic saturation is reached at this TFA concentration. Other CPDT based polymers such as **P1** and **P2** showed similar response to the acid protonation (Fig. S3, ESI†). It is interesting to note that, the acid-mediated optical changes of CPDT based polymers are reversible in solution, with the original spectral characteristics being recovered after neutralization of the protonated species. For instance, treatment of **P3** dissolved in chloroform containing 1% TFA with equivalent triethylamine (TEA) results in the recurrence of identical absorption profiles to the neutral **P3** prior to protonation. Most interestingly, this protonation-deprotonation process in solution could be cycled for many times (Fig. S3, ESI†).

The TFA induced near IR absorption and reversible optical properties upon protonation and deprotonation were also observed in the solid state of CPDT based polymers. As shown in Fig. 1b, polymer **P3** film casted from solution showed the same maximum absorption as in solution (chloroform), except the  $\lambda_{\text{onset}}$  value was red-shifted (~36 nm). Upon exposure to TFA vapor, the yellow polymer film was changed to grey in seconds. From the corresponding UV-vis-NIR spectra, we can see the emergence of absorbance bands at 793 and 1443 nm with the decreased intensity of  $\pi$ - $\pi^*$  transition after the TFA vapor treatment, which is quite close to the spectra change as in solution. Similarly, the protonated film can be neutralized with TEA vapor, to nearly recover the original neutral polymer film spectra, indicating the majority of **P3** are deprotonated. Therefore, the protonation-deprotonation process for the CPDT based polymers is reversible and can be repeated for many times, both in solution and at solid states,<sup>33-36</sup> indicating their highly potential applications in chemical sensors.

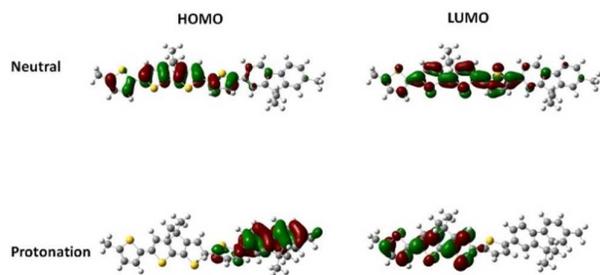


**Fig. 2** Aromatic regions of the  $^1\text{H}$  NMR spectra of CPDT as a function of trifluoroacetic acid-d concentration from 0 to 20  $\mu\text{l}$  at 300 K. All spectra were recorded in  $\text{CDCl}_3$ .



Monomer 1 (M1)

Scheme 2 Simplified Monomer 1 (M1) for DFT calculation.

Fig. 3 Optimized structures of frontier molecular orbitals for model compounds **M1** in their neutral and protonated states.Table 1 The corrected Zero Point Vibrational Energies (ZPE) and Proton Affinities (PA) calculated by G09 and DMOL calculated Proton Affinities (PA) at different sites of **M1**.

Entry	G09: scaled ZPE (au)	G09: PA (kcal/mol)	DMOL: PA (kcal/mol)
Site 1	0.5487	211.8	220.7
Site 2	0.5504	236.8	240.3
Site 3	0.5503	233.6	235.9
Site 4	0.5498	222.4	227.4
Site 5	0.5491	205.4	214.0

Further insight into the reaction between TFA and **CPDT** was examined via  $^1\text{H}$  NMR spectroscopic studies. The  $^1\text{H}$  NMR spectrum of **CPDT** in  $\text{CDCl}_3$  shows two doublet peaks at  $\delta$  6.94 ( $\beta$  position) and 7.15 ( $\alpha$  position). Upon the addition of trifluoroacetic acid-d (TFA-d), a new singlet peak appeared at low field with the decreased intensity of peak at  $\delta$  7.15 and unchanged peak intensity at  $\delta$  6.94. In addition, doublet peak at  $\alpha$  position changed to multiplet peak due to the extra deuterated proton at  $\alpha$  position. With the increase of TFA-d concentration, the intensity of doublet peak at  $\alpha$  position continued decreasing, accompanied by the rising intensity of the newly formed singlet peak at low field. Moreover, the overall integration ratio of protons at  $\beta$  position (6.94 ppm) to the protons at both  $\alpha$  position (7.15 ppm) and newly occurred singlet peak (8-11 ppm) was remained at 1:1. The NMR behavior validates the protonation occurs at the  $\alpha$  position of **CPDT** by TFA. The NMR spectra of **P3** upon protonation was also investigated and similar chemical shifts change was observed (Fig. S4, ESI $^\dagger$ ). Upon addition of TFA-d into **P3** solution, a large deshielding of  $\alpha$ -H ( $\delta$ , 8-10.5) indicates that the positive charge was brought into the thiophene ring by the captured proton. All these results suggest that **CPDT**

and **CPDT** based polymers can be protonated by TFA at their  $\alpha$  positions.

Density functional theory (DFT) is used to calculate the optimal protonation site via proton affinity (PA). The geometry optimisation and energy calculations were performed with Gaussian 09 software suite using B3LYP/6-31+G(d,p) (Table 1, Scheme 2, Fig. 3).<sup>37</sup> **M1** is used the representative monomer for **P3**. For simplification, the long alkyl chains were replaced with methyl groups in **M1**. DFT calculated from the optimized structure shows that protonation at site 2/3 ( $\alpha$  position of **CPDT**) is more preferable by the highest relative zero-point vibrational energies (ZPE) and PA. DMol optimized by PW91-dspp/dnp was also calculated to find protonation site. Results obtained by DMol exhibits the same trend as that of G09. These results are consistent with our NMR results that the pronounced affinity of proton to  $\alpha$  position of **CPDT** is caused by the electron-rich property of  $\alpha$  position and high basicity of **CPDT**.<sup>36</sup> Meanwhile, molecular orbital (MO) calculations for **M1** in the neutral and protonated states were carried out using B3LYP functional with 6-31+G(d,p) basis set. For the neutral monomer, both HOMO and LUMO are nearly delocalized on the whole backbone of **M1**. However, protonation of **CPDT** leads to significant changes in the distribution of HOMO/LUMO orbitals (Scheme S1, Table S1, ESI $^\dagger$ ). HOMO now is mainly located on fluorene unit, while LUMO is delocalized on **CPDT** unit. The dipole moment of protonated **M1** (17.14 D) is almost 40 times higher than that of neutral **M1** (0.43 D), which should be responsible for imposing charge separation of protonated **M1**. Therefore, the protonation induced NIR absorption can be attributed to the effective charge separation and related significant intramolecular charge transfer (ICT) upon protonation.<sup>39-41</sup> When the **CPDT** based polymers were protonated, protonated **CPDT** units were changed from electronic donors or  $\pi$ -spacer to strong electron acceptor, which lead strong ICT effect in the polymer backbone and finally extends the absorption into the NIR region. This conclusion was further confirmed by comparing the acid response of **P1** and **P2** with **P3**. Compared with **P1** and **P2**, **P3** shows much higher intensity of NIR absorption under the same TFA concentration, which is due to a more efficient intramolecular charge transfer by the presence of  $\pi$  spacer.

In this study, a simple and effective approach to modulate optical and electronic properties of **CPDT** based polymers is reported for the first time. The synthesis, optical properties and structural characterizations demonstrate an easy and sensitive protonation process of polymers upon the exposure to TFA. The proton NMR spectroscopy and DFT calculation validate that the most preferable protonation site is the  $\alpha$  position of **CPDT** due to its high ZPE and PA. This study provides a new approach to remarkably tune optical and electronic properties of existing **CPDTs** based conjugated polymers, to greatly broaden their applications in chemical sensors and optical devices.

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