Synthesis, Optical and Electrochemical Properties of Two Series Electron-Donor Polymers with Diphenylpyranylidene Side Chain

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Abstract. Two series of novel conjugated polymers with diphenylpyranylidene as the side chain and thiophene as the main chain were designed, synthesized and characterized as electron donors of polymer solar cells for the first time. The absorption spectra showed that introduction of diphenylpyranylidene side chain can obviously complement the light absorption ability in the range from 300-500 nm. In addition, diphenylpyranylidene unit is also helpful to tune the HOMO energy level as low as -5.23 to -5.31 eV than P3HT polymers, for favoring higher open-circuit voltage in polymer solar cells.

1. Introduction
Nowadays, global energy shortage has been widely concerned and sustainable green solar energy becomes a focus of research in academic and industry. Polymer solar cells (PSCs) have attracted much attention due to their advantages of low cost, pliability, lightweight and easy preparation [1, 2], leading to a potential to produce large-scale flexible optoelectronic products [3]. Soluble polythiophene and its derivatives [4, 5] are commonly utilized as conjugated electron-donating materials in the active layer of PSCs devices. Poly(3-hexylthiophene), known as P3HT, is an extensively studied donor material with good photoresponse in visible light but poor one in ultraviolet and near infrared light. In order to enhance the cells photo-to-electron conversion efficiency, numerous soluble thiophene or benzothiophene (BDT) polymers based on alternating electron donors-acceptor (D-A) conjugated structure in main chain has been explored in the PSCs application [6].

These D-A polymers can effectively expand the light absorption range to near infrared region but still be lack of ultraviolet and some visible light absorption. In general, introduction of soluble alkyl or alkoxy chain as the side chain can effectively improve the solubility of the polymer, while the introduction of conjugated aromatic groups can regulate the light response capacity and electron orbital energy levels of the polymer. Therefore, some researchers applied triphenylamine group as the side chain of the thiophene or BDT donors to complement the light absorption ability [5]. Diphenylpyranylidene (DPP) group possessing a similar geometric structure to triphenylamines, not only has good light absorption in the range of ultraviolet light, but also shows good photovoltaic properties in the application of organic field-effect transistors (OFETs) and dye-sensitized solar cells (DSSC) [7, 8]. Geometric planar DPP group can provide good molecular arrangement, thus ensuring...
effective carrier transport and reducing charge recombination rate. As far as we know, the research and application of DPP in PSCs functional layer has not been reported yet. In this paper, we reported synthesis, photophysical and electrochemical properties of two series of new D-D conjugated polymers by using DPP as conjugate side chain, 2-phenyl-5-vinylthiophene group as bridge, thiophene as main chain (Figure 1a).

![Figure 1](image.png)

**Figure 1.** (a) Chemical structures of the series polymer of P1, P2; (b) Molecular orbitals and geometric configuration of the monomer T1 and T2.

2. Experimental

Synthesis of monomer T1 and T2 and all intermediates was obtained by following reference [9]. Synthesis of two series polymer was completed through Grignard metathesis [5, 10].

Nuclear magnetic resonance (NMR) spectra were recorded on a Bruker Advance III 600. Thermogravimetric analysis (TGA) was performed using a DTG-60H analyzer with a heating rate of 5°C/min under a nitrogen atmosphere. The molecular weight and polydispersity were determined by gel permeation chromatography (GPC) analysis using a waters 1515 HPLC system. Tetrahydrofuran (THF) was used as eluent (flow rate: 1 ml/min, 35°C) and polystyrene was used as the standard reference. The ultraviolet-visible (UV-vis) absorption spectra were recorded using a Lambda 35 UV-vis Spectrometer at room temperature. Photoluminescence (PL) spectra were measured by EDINBURGH-FS5 at room temperature. Cyclic voltammetry (CV) measurements were performed on a Zennium electrochemical workstation with a glassy carbon working electrode, a platinum wire counter electrode and an Ag/AgCl reference electrode, under an argon atmosphere in a THF solution of Bu4NPF6 (0.1 M) with a scan rate of 100 mV/s at ambient temperature.

3. Results and discussion

The structures of monomer T1 and T2 were optimized by density functional theory (DFT) using the B3LYP/6-31G(d) (Figure 1b). Both compounds showed quite geometrically planar structure, which is favorable for better carrier transport between molecules. Thermal properties of the polymers were investigated by TGA. The polymers exhibit high thermal stability and the decomposition temperature (T_d) at 5% weight loss are about 300°C, indicating that the changes on side chain have little influence on the thermal stability of the polymer, which meets the conditions for preparing polymer solar cells.
Figure 2. Absorption spectra of the monomers, polymers and P3HT in o-DCB solution and thin film. The light absorption of P1 and P3HT is complementary to a certain extent in the UV-visible region. Along with the enhancement of P3HT unit on the conjugated main chain, the conjugated DPP group in the side chain decreases, leading to the π-π* transition mainly occurs on the main chain and thus the extension of the light absorption range as well as redshift of the maximum absorption peak [4]. The thin film of P1 polymers formed larger absorption complementarity. The overall redshift of light absorption on the film compared to that in solution indicates a good π-π stacking. For the P2 series polymers, introduction of DPP group to the main chain through a 2-phenyl-5-vinylthiophene group reveals a less influence to the absorption spectra. After the self-polymerization of the monomer T2, the light absorption range of P2-1 changed little, while the relative light absorption intensity at 300-400 nm increased.

Figure 3 shows the PL spectra of the polymers in o-DCB solution excited by the maximum absorption peak in the UV-visible region. For P1-1 polymer, the peak value of PL spectrum is observed in ultraviolet region, mainly reflecting the DPP side chain. As the length of the conjugated main chain increases, the energy is transferred from the side chain to the main chain. As can be seen...
from the Figure 3(a), the secondary peaks at the long wavelength side gradually increase until they become dominant, indicating that excitons have transferred from the conjugate side chain to the main chain and energy transfer occurred in the molecule. At the same time, a certain degree of redshift occurred, indicating that the polymer formed a higher π-delocalization system with the increase of soluble side chains [4]. For P1-4, the proportion of T1 monomer in the polymer was too small, resulting in almost overlapping peak values with P3HT, except for an insignificant peak around 500 nm. P2-1 formed a good π system structure, leading to a wider the range of PL curve. For P2-2 and P2-3, the increase of soluble alkyl side chains reduced the conjugation of side chains and improved the conjugation of main chains, resulting in the red shift of the curve. For P2-4, the curve is further redshifted and similar to that of P3HT. The continuous red shift of the curve indicates a better transfer of carriers from the conjugate side chain to the main chain. It also explains the energy transfer from side chain to main chain and the formation of π-delocalization of higher extension [5].

Table 1. Photo-physical and electrochemical properties of the polymers.

| Molecular | \( \lambda_{\text{max}} \) / nm | \( E_{\text{ox}} \) / V (HOMO / eV) | \( E_{0-0} \) / eV | \( E_{\text{ox}} \) / V (LUMO / eV) |
|-----------|-----------------|-----------------|--------------|-----------------|
| P1-1      | 373             | 0.54(-5.25)     | 2.30         | -1.76(-2.95)    |
| P1-2      | 383             | 0.54(-5.25)     | 2.07         | -1.53(-3.18)    |
| P1-3      | 410             | 0.56(-5.27)     | 2.00         | -1.44(-3.27)    |
| P1-4      | 446             | 0.60(-5.31)     | 1.97         | -1.37(-3.34)    |
| P2-1      | 458             | 0.56(-5.27)     | 2.13         | -1.57(-3.14)    |
| P2-2      | 450             | 0.52(-5.23)     | 2.07         | -1.55(-3.16)    |
| P2-3      | 453             | 0.55(-5.26)     | 2.02         | -1.47(-3.24)    |
| P2-4      | 460             | 0.56(-5.27)     | 2.08         | -1.76(-2.95)    |

Figure 4. Cyclic Voltammograms of the polymers dissolved in THF solution of 0.1 mol L\(^{-1}\) Bu4 NPF6.

Cyclic voltammetry (CV) was performed to investigate the redox behavior of the polymers and also to determine the HOMO and LUMO energy levels of the polymers [4]. To obtain the oxidation and reduction potentials of the polymers, the reference electrode was calibrated using ferrocene/ferrocenium (Fc/Fc\(^+\)) as internal standard, which has an energy level of -4.71 eV at the vacuum level. Therefore, the HOMO level can be estimated through empirical equation, HOMO = - (\( E_{\text{onset}} \)ox + 4.71) eV. As shown in Figure 4, all the polymers showed similar redox behavior, revealing reversible oxidation potentials at positive direction and no reduction potential at negative direction. The LUMO energy levels can be calculated from HOMO energy levels and optical band-gaps (1.97-2.30 eV) estimated from absorption onset. Specific data were summarized in Table 1. As the electron-rich DPP participates less from P1-1 to P1-4, the HOMO level gradually decreases from -5.25 to -5.31 eV. For P2 series polymers, there is no obvious change of oxidation potentials observed from P2-1 to P2-4. Since the open circuit voltage of polymer solar cells is related to the LUMO of the acceptor and
the HOMO of the donor, the lower HOMO level of these conjugated donor polymers than P3HT is conducive to improve the open circuit voltage of polymer solar cells.

4. Conclusion
Taken together, to investigate the side-chain effect of DPP group in the thiophene donor polymers, herein two series polymers with DPP as side chain and thiophene as main chain were synthesized and characterized as the electron-donors of PSCs for the first time. Our results showed that introduction of DPP group into the thiophene core chain can obviously complement the light absorption ability in the range from 300-500 nm. Besides, DPP unit is also helpful to tune the HOMO energy level as low as -5.22 to -5.31 eV than P3HT polymers, for favoring higher open-circuit voltage in PCSs applications.

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