

## NOTE

# Synthesis and photovoltaic properties of two-dimensional conjugated polymers with tunable pendant acceptor groups

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## INTRODUCTION

Polymer bulk heterojunction solar cells (PSCs), based on an electron-donating conjugated polymer and an electron-accepting fullerene derivative,<sup>1–2</sup> have attracted considerable attention over the past decade due to their unique advantages of low cost, light weight and feasible roll-to-roll fabrication for making flexible large-area devices.<sup>1–3</sup> Intensive research efforts have focused on improving the power conversion efficiency (PCE) of PSCs. There are several factors limiting the PCE of PSCs: first, limited light absorption of the photoactive layer leads to low short-circuit current; second, small energy level difference between HOMO of the polymer donors and LUMO of the acceptors limits the open-circuit voltage ( $V_{oc}$ ).<sup>4–7</sup> Therefore, development of conjugated polymers with low bandgaps for efficient solar energy absorption and deep HOMO levels for high  $V_{oc}$  are expected for highly efficient PSCs.<sup>8–9</sup> An efficient strategy is to synthesize two-dimensional conjugated polymers.<sup>10–12</sup> These polymers feature high hole mobility because of extended conjugation, and broad absorption contributed by both main chain and side chains, thus demonstrating remarkable photovoltaic properties.<sup>13–15</sup> In this work, we designed a series of two-dimensional conjugated polymers (**P1–P4**) based on a benzo [1,2-b:4,5-b']dithiophene (BDT) unit and a thiophene unit with a pendant acceptor group. BDT is a highly coplanar electron-donating moiety, which could improve the inter-chain  $\pi$ - $\pi$  stacking of conjugated polymers. Polymers based on BDT exhibit high performance in PSCs.<sup>16–18</sup> A thiophene unit with tunable pendant electron-deficient groups is used to efficiently tune the energy levels of the copolymers to achieve better optical properties for the polymers and high  $V_{oc}$  for the devices.

## RESULTS AND DISCUSSION

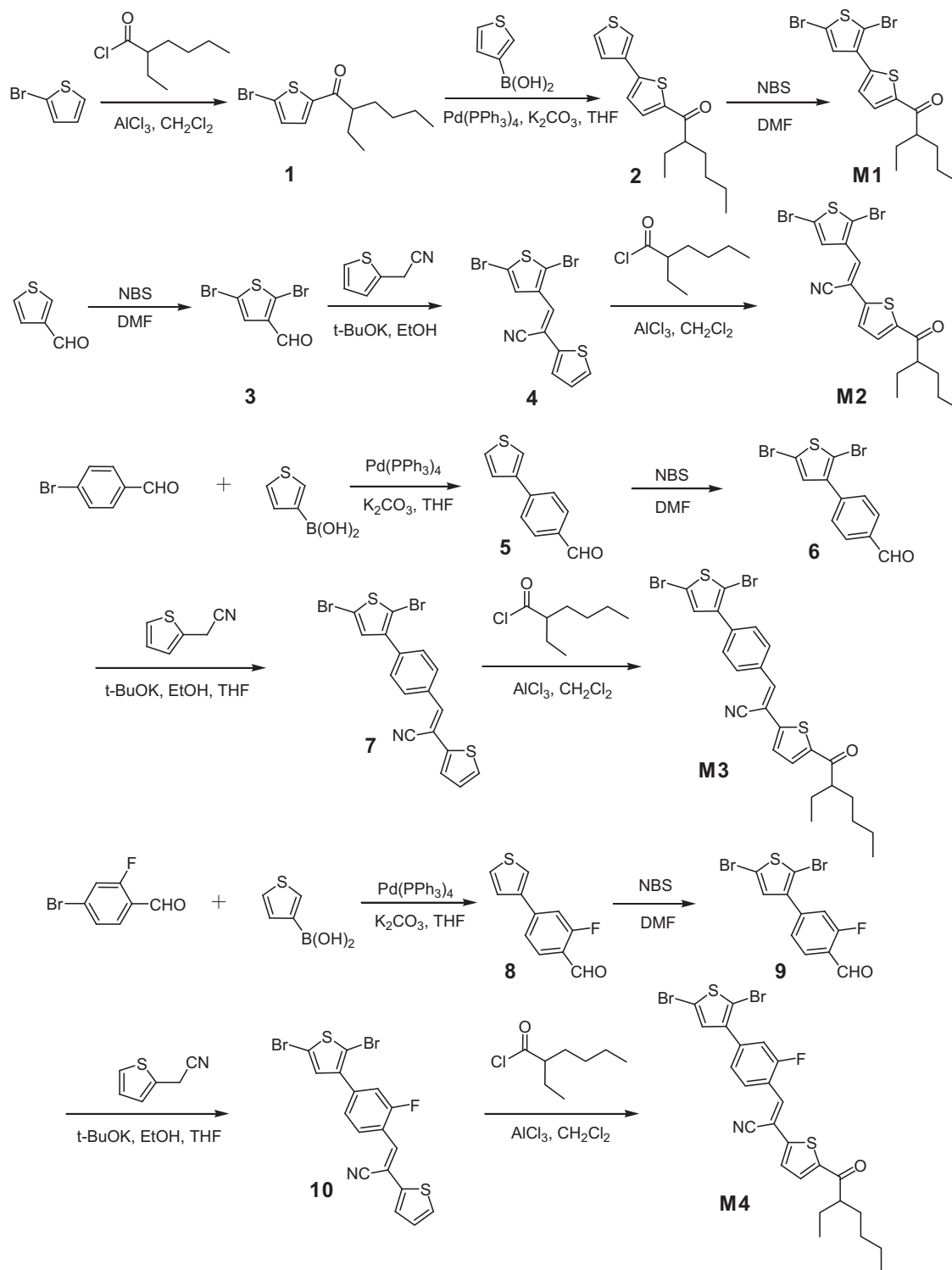
The synthetic routes for monomers (**M1–M4**) are shown in Figure 1. **M1–M4** were synthesized in moderate or good yields through reactions including Friedel–Crafts acylation, Suzuki coupling, Knoevenagel condensation and bromination. Detailed synthetic procedures and yields of the products are presented in the Supplementary Information. **M1** consists of a 2, 3'-bithiophene moiety. To enhance the solubility and electron-withdrawing property, we introduced a 2-ethylhexanoyl group at the C5 position of **M1**. We further designed monomers **M2–M4** by modifying **M1**. For **M2**, a cyanovinylene bridge is introduced between the two thiophenes of **M1**. This modification can effectively extend the conjugation and further enhance the electron-withdrawing property of the unit. For the same purpose, a phenylene and a 2-fluorophenylene group are introduced between the thiophene and cyanovinylene for **M3** and **M4**, respectively. The donor monomer **M5** was prepared according to the literature.<sup>18,19</sup> As shown in Figure 2, polymers (**P1–P4**) were prepared through a Stille coupling reaction between the donor monomer **M5** and the acceptor monomers (**M1–M4**). The crude products were precipitated in methanol, then purified by Soxhlet extraction using methanol, hexane and chloroform successively. The chloroform fraction was precipitated in methanol, filtered and dried under vacuum to obtain **P1–P4**. The chemical structures of **P1–P4** were verified by <sup>1</sup>H NMR. All polymers exhibited good solubility in common organic solvents, such as THF, CHCl<sub>3</sub> and chlorobenzene. The molecular weights of polymers (**P1–P4**) were determined by GPC and are listed in Supplementary Table S1.  $M_n$  of **P1–P4** are 20.8, 27.8, 19.6 and 17.0 kg mol<sup>-1</sup>, respectively.

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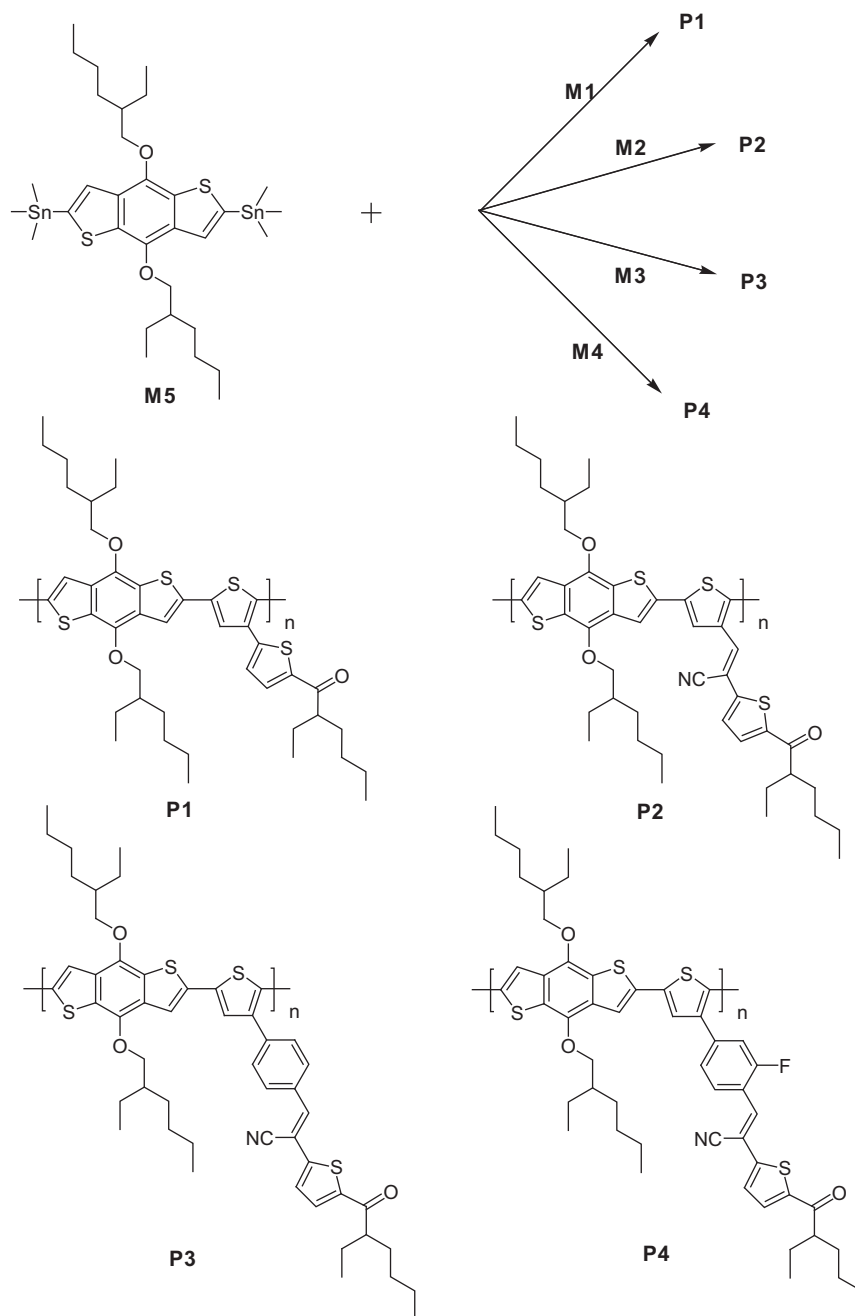


**Figure 1** Synthesis of monomers.

The thermal stabilities of the polymers were evaluated by TGA under  $N_2$ . As shown in Supplementary Figure S1, polymers **P1–P4** exhibit good thermal stability with decomposition temperatures at 325, 333, 283 and 325 °C, respectively, indicating that all polymers are thermally stable for solar cell applications.

Figure 3 shows the absorption spectra of the copolymers in solution and in films and the data are summarized in Table 1.

**P2**, **P3** and **P4** show similar absorption spectra. In solution, the absorption maxima are located at 389 nm for **P2**, 386 nm for **P3** and 385 nm for **P4** (Figure 3a), corresponding to the  $\pi$ - $\pi^*$  transition of the polymer backbone. Additionally, **P2**, **P3** and **P4** spectra all show a shoulder at longer wavelengths, which can be attributed to intramolecular charge transfer (ICT) between conjugated backbones and respective pendant acceptor groups.<sup>10</sup> **P1** shows an absorption



**Figure 2** Synthesis of polymers.

maximum at 474 nm, which might be due to the stronger ICT effect. In films, the intensity of the ICT bands for all polymers is significantly enhanced, indicating the improvement of interchain interactions in the solid state (Figure 3b). **P2** shows the broadest absorption (300~700 nm), suggesting the potential for high photocurrent. The optical bandgaps ( $E_g^{opt}$ ) of the polymers are 2.05, 1.86, 2.04 and 2.01 eV, respectively, which were calculated from the film absorption onsets.

Cyclic voltammograms of the polymers **P1–P4** are shown in Supplementary Figure S2. The onset oxidation and reduction potentials of the polymers are listed in Table 1. The HOMO and LUMO energy levels and electrochemical bandgaps ( $E_g^{ec}$ ) of polymers

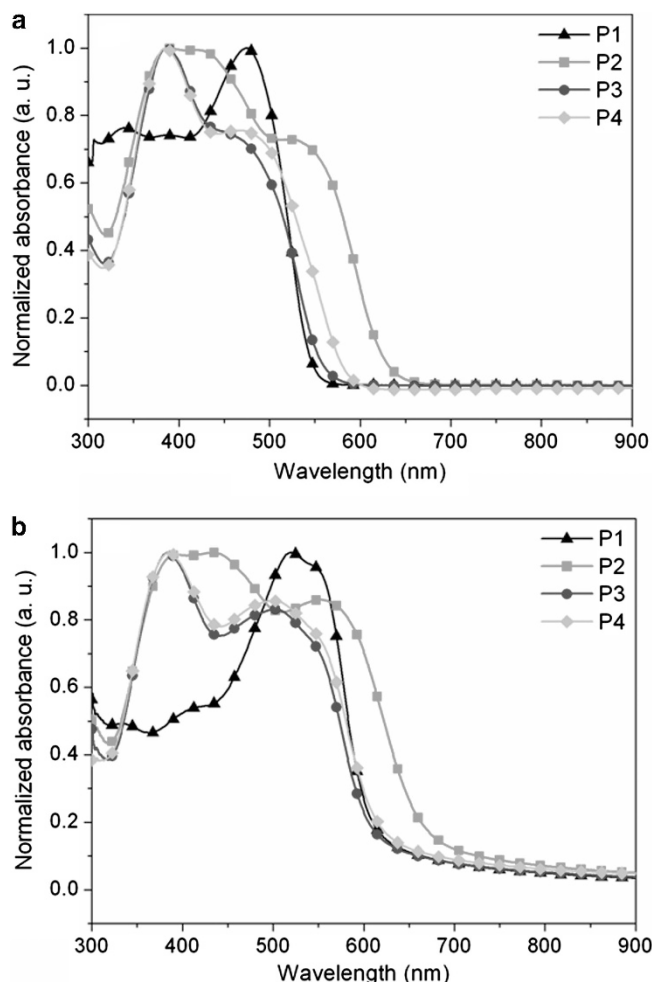
were calculated according to the following empirical equations:<sup>20</sup>

$$E_{HOMO} = -e(E_{ox}^{on} + 4.8)(eV)$$

$$E_{LUMO} = -e(E_{red}^{on} + 4.8)(eV)$$

$$E_g^{ec} = E_{LUMO} - E_{HOMO}(eV)$$

As shown in Table 1, **P1–P4** exhibit similar HOMO energy levels at  $-5.27$  to  $-5.38$  eV. The deep HOMO energy level could offer these polymers good chemical stability and high  $V_{oc}$ . The LUMO values for **P1–P4** are  $-2.97$ ,  $-3.39$ ,  $-2.91$  and  $-2.84$  eV, respectively. As expected, the introduction of electron-withdrawing cyanovinylene bridge into the pendant group of **P1** lowered the LUMO level from



**Figure 3** UV-vis absorption spectra of polymers **P1–P4**: (a)  $\text{CHCl}_3$  solution; (b) film. A full color version of this figure is available at *Polymer Journal* online.

**Table 1** Optical and electrochemical properties for polymers **P1–P4**

Polymers	$\lambda_{\text{max}}$ (nm)		$\lambda_{\text{onset}}$ (nm)	$E_{\text{g}}^{\text{opt}}$ (eV) <sup>a</sup>	$E_{\text{ox}}^{\text{on}}$ (V)	$E_{\text{red}}^{\text{on}}$ (V)	HOMO (eV) <sup>b</sup>	LUMO (eV) <sup>b</sup>	$E_{\text{g}}^{\text{c}}$ (eV) <sup>b</sup>
	Solution	Film							
<b>P1</b>	474	520	604	2.05	0.52	−1.83	−5.32	−2.97	2.35
<b>P2</b>	389	433	667	1.86	0.57	−1.41	−5.37	−3.39	1.98
<b>P3</b>	386	383	608	2.04	0.58	−1.89	−5.38	−2.91	2.47
<b>P4</b>	385	384	617	2.01	0.47	−1.96	−5.27	−2.84	2.43

<sup>a</sup>Calculated according to the onset wavelength of film absorption,  $E_{\text{g}}^{\text{opt}} = 1240/\lambda_{\text{onset}}$ .

<sup>b</sup>Calculated according to equations:  $E_{\text{HOMO}} = -e(E_{\text{ox}}^{\text{on}} + 4.8)$  (eV);  $E_{\text{LUMO}} = -e(E_{\text{red}}^{\text{on}} + 4.8)$  (eV);  $E_{\text{g}}^{\text{c}} = E_{\text{LUMO}} - E_{\text{HOMO}}$  (eV).

−2.97 eV of **P1** to −3.39 eV of **P2**. For **P3** and **P4**, with an additional phenylene bridge, there is almost no change in LUMO, suggesting that phenylene bridge might destroy the coplanarity of the conjugated side chain and block the electron-withdrawing effect of cyanovinylene moiety. **P2** has the smallest bandgap of 1.98 eV, which is favorable for absorbing more sunlight.

Solar cells with a configuration of ITO/PEDOT:PSS/Polymer:PC<sub>61</sub>BM/Ca/Al were fabricated. Polymer:PC<sub>61</sub>BM ratios (w/w) for **P1–P4** devices were optimized from 1:0.5 to 1:3. Performance

**Table 2** Performance for solar cells based on **P1–P4/PC<sub>61</sub>BM** blends

Polymers	Polymer/PC <sub>61</sub> BM (w/w)	$V_{\text{oc}}$ (V)	$J_{\text{sc}}$ ( $\text{mAcm}^{-2}$ )	FF (%)	PCE (%)
<b>P1</b>	1:1	0.92	1.71	49	0.90
<b>P2</b>	1:2.5	0.93	3.51	49	1.89
<b>P3</b>	1:1	0.93	1.98	44	0.95
<b>P4</b>	1:1.5	0.93	2.64	50	1.45

parameters for **P1–P4** solar cells are listed in Table 2 and *J–V* curves are shown in Supplementary Figure S3. As expected, all solar cells show high  $V_{\text{oc}}$  (0.92~0.93 V), resulting from the low HOMO levels of **P1–P4**. **P2** cells exhibit the highest PCE of 1.89% with a  $J_{\text{sc}}$  of 3.51  $\text{mAcm}^{-2}$  and a FF of 49%. The better photovoltaic performance of **P2** results from its higher  $J_{\text{sc}}$ , originating from better absorption of **P2** and the stronger ICT between the backbone donor and the pendant acceptor. The optimized thicknesses for **P1–P4/PC<sub>61</sub>BM** active layers are 103, 115, 98 and 105 nm, respectively. Solvent annealing did not help to improve solar cell performance in this work.

## SUMMARY

We have designed and synthesized a series of two-dimensional conjugated polymers (**P1–P4**) based on a backbone consisting of a BDT donor unit and a thiophene unit, which was grafted with different acceptor groups. These polymers show good solubility, thermal stability, and tunable optical and electrochemical properties. Bulk heterojunction polymer solar cells based on **P2** exhibit a PCE of 1.89% and an impressively high  $V_{\text{oc}}$  of 0.93 V. Further efforts to lower the bandgaps of these polymers with the aim to enhance photocurrent are currently ongoing.

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Supplementary Information accompanies the paper on Polymer Journal website (<http://www.nature.com/pj>)