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induced by using copolymer was demonstrated

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Small Bandgap Naphthalene diimide Copolymers for Efficient Inorganic/Organic Hybrid Solar Cells

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Two low band-gap naphthalene diimides (NDI)-based conjugated polymers have been designed and grafted with benzo[1,2-b:4,5-b']dithiophene (BDT), Dithieno [3,2-b:2',3'-d]pyrrole (DTP) by Stille cross-coupling reaction, respectively. The inorganic/organic hybrid solar cells (HSCs) based on the copolymers deliver high performances by suitable molecular design and careful selection of chemical structures with different electronic nature. The well designed copolymers exhibit broader solar light absorption, which is attributed to their smaller band gaps. The density functional theory calculations and cyclic voltammetry characteristics reveal that the copolymers have small band gaps and deep HOMO and LUMO energy levels. Moreover, after introducing the copolymers, the energy level formation of bulk-heterojunction become more matchable, thus giving rise to excellent photovoltaic performances of HSCs. The results showed that NDI-based copolymer with DTP donor segments exhibits a higher power conversion efficiency of 2.36%. This work highlights developed bipolar host materials with the focus on molecular design strategies, which benefits the light harvest and enhances the efficiency by well aligned energy level formation.

1. Introduction

Recently, organic/inorganic bulk-heterojunction (BHJ) hybrid solar cells (HSCs) based on composites of p-type conjugated polymers and n-type inorganic nanomaterials have attracted much attention.¹⁻³ HSCs can take advantages of the beneficial properties of both types of materials, such as low-cost solutionprocessing of organic semiconductors at low temperatures and high electron mobility of inorganic semiconductors.⁴⁻⁶ Despite the advantages of organic/inorganic HSCs, further improvement of power conversion efficiency (PCE) is still required towards commercialization.⁷ Although the polymeric solar cells that are made with regioregular poly(3hexylthiophene) (P3HT) as donor material have exhibited excellent performances, nonetheless because of poor light harvest of the solar spectrum and the mismatching of the energy levels between the donor and acceptor, further efficiency enhancement is hindered. In particular, most of the reported PCE of organic/inorganic HSCs based on the conjugated polymer P3HT is around 2%, ranging from 1.7~3.0%, depending on the type of inorganic nanocrystals (except quantum dots, which are more related to colloidal quantum dot solar cells⁸), their morphologies and others.⁹⁻¹¹ In order to enhance efficiencies even further, this work is focusing on

research activities for developing new small band gap materials with better aligned energy levels.

In general, the influencing factors of PCE include the opencircuit voltage (V_{oc}), short-circuit current ensity (J_{sc}), and fill factor (FF).¹² In HSCs, the degree of the matchment between the absorption of the conjugated polymers and the solar spectrum has an obvious effect on J_{sc} .¹³ The V_{oc} is determined by the difference between the energy levels of lowest unoccupied molecular orbital (LUMO) of the inorganic semiconductor acceptors and the highest occupied molecular orbital (HOMO) of the conjugated polymer donors.¹⁴ Therefore, further improvement in the PCE needs the development of novel conjugated polymers with an appropriate energy level as well as broader absorption of the solar spectrum. The energy level band edges are as important as the band gap of the material, both of which critically determine the photovoltaic performance of HSCs. Narrowing the band gap of copolymers will eventually result in a decreased PCE due to the decrease in $V_{\rm oc}$.¹⁵ In practice, the optimal band gap will not only depend on the suitable energy level formation between donor and acceptor that enables efficient charge separation, but also the absorption properties of the donor. An effective route to boost PCE is to adjust energy level band edge positions of the donor by modifying/designing the molecular structure of conjugated polymers by copolymerizing with different segment units.

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As a structural analogue to pervlene diimides, naphthalene diimides (NDI) demonstrate comparable LUMOs and outstanding organic thin-film transistor (OTFT) performance, which make NDI small molecules as one of the best n-channel semiconductors.¹⁶ Therefore, NDI molecules has been extensively employed and successfully incorporated into diverse polymers.¹⁷⁻²⁰ The small band-gap, low-lying LUMO, and good electron mobility of NDI polymers herald their potential as acceptor semiconductors in HSCs.²¹ It is accepted that the energy levels can be tuned effectively by the strong electron-withdrawing imide groups, such as p- or n-type behaviors. However, imide-functionalized conjugated polymers as p-systems are rarely reported thus far. On one hand, copolymers containing naphthalene-1,4,5,8-tetracarboxylic bisimide (PFTBTN) have exhibited promising small band gap characteristics with large absorption coefficient;²²⁻²⁴ on the other hand, the LUMO energy level can be elevated after introducing imide groups, by which the partial charge transfer can be enhanced. Yet, the HSCs based on these materials such as PFTBTN suffer from poor device performances. Inspired by these incentives, we introduced NDI into conjugated polymer as an electron acceptor. With further construction in structural modification and device optimization, we anticipate that the small band gap NDI polymers with better energy level alignment can be achieved, thus leading to a notable increase in PCE. For benzo[1,2-b:4,5-b']dithiophene (BDT), however, steric hindrance between adjacent units is very small, as 4, 9bis-alkoxy-BDT has no substituent on 1, 3, 5, and 7 positions.²⁵ Dithieno[3,2-b:2',3'-d]pyrrole (DTP) has good planarity and strong electron-donating ability of nitrogen atoms, which might lead to the development of a low band gap polymer.²⁶ So, BDT and DTP are ideal conjugated units for designing new photovoltaic materials. Herein, copolymers containing the combination of BDT and DTP as electron-donating units, NDI strong electron-accepting units were designed and as synthesized. We note that the suitable energy offset between the donor/acceptor can be achieved by utilizing novel either BDT or DTP-grafted NDI-based alternating conjugated copolymers (namely P1 and P2, as seen in Chart 1), which enhances solar spectrum harvest as well as heightens V_{oc} in HSCs.



P2.

2. Experimental

2.1 Materials and instruments.

All chemical reagents were purchased from Acros, TCI and Aldrich Chemical Co. and were used as received except stated otherwise. All solvents were distilled over appropriate drying agent(s) prior to use and were purged with nitrogen. All manipulations involving air-sensitive reagents were performed in a dry argon.

The nuclear magnetic resonance (NMR) spectra were collected on a Bruker ARX 400 NMR spectrometer. The cyclic voltammetry (CV) results were obtained using a BAS 100B instrument at room temperature at a scan rate of 50mV/s, Tetrabutylammonium hexafluorophosphate (Bu₄NClO₄) in an anhydrous and nitrogen-saturated acetonitrile (CH₃CN) solution $(0.1 \text{ mol } L^{-1})$ was used as the supporting electrolyte, a platinized platinum (0.5 cm^2) as the counter electrodes and Ag/Ag+ electrode as the reference electrode, the values are expressed in potentials versus Fc/Fc⁺. Polymer to be measured was coated on the platinum plate working electrodes from dilute chloroform solutions. UV-vis spectra were recorded on a Lambda 900 UV-vis/NIR PerkinElmer spectrometer. Thermogravimetric analyses (TGA) were conducted on a TA Instruments Model TGA Q500 thermogravimetric analyzer at a heating rate of 10 °C min⁻¹ under N₂ flow (100 mL min⁻¹). The photocurrent-voltage (J-V) curves of the assembled HSCs were recorded on an Electrochemical Workstation (Xe Lamp Oriel Sol3A[™] Class AAA Solar Simulators 94023A, USA) under irradiation of a simulated solar light from a 100 W xenon arc lamp in ambient atmosphere.

2.2 Synthesis of the Monomer.

The synthesis and structure of the monomer are outlined in Scheme 1.



2, 6-dibromonaphthalene-1, 4, 5, 8tetracarboxydianhydride, 1¹⁸ **RSC Advances Accepted Manuscri**

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A mixture of 1, 4, 5, 8-naphthalenetetracarboxylic dianhydride (2.83 g) and oleum (20% SO₃, 100 mL) was stirred at 55 °C for 2 hours. A solution of dibromoisocyanuric (3.12 g) in oleum (50 mL) was then added over a course of 40 mins. The resulting mixture was then heated to 85 °C and maintained at this temperature for 43 hours. Upon cooling to room temperature, the reaction mixture was poured onto crushed ices. This mixture was diluted with water and then stirred at room temperature for 1 hour. The precipitates were collected by centrifuge, washed with distilled water and methanol, and dried under vacuum, finally leading to a greenish yellow solid (3.87g, yield 81.1%).

N, N,- didodecyl-2, 6-dibromonaphthalene-1, 4, 5, 8tetracarboxylic acid bisimide, 2²⁷

The mixture of compound **1** (1 g), dodecylamine (2.2 mL), and acetic acid (70 mL) was filtered and then refluxed for 4 h under argon. After having been cooled to room temperature, the precipitate was filtered and washed with distilled water (300 mL), the residue was purified by column chromatography (eluant: hexane:methylene chloride = 1:2) to give **2** as an orange crystal (1.2, 52.8%). ¹H NMR (CDCl₃, 400Hz, δ /ppm): 8.85 (s, 2H, Ph-H), 4.22-4.18 (m, 4H, N-CH₂), 1.76-1.73 (m, 12H, CH₂), 1.41-1.35 (m, 28H, CH₂), 0.92-0.86 (m, 6H, CH₃). ¹³C NMR (CDCl₃, 100MHz, δ /ppm): 162.5, 162.3, 161.7, 161.6, 135.9, 131.4, 128.0, 127.0, 126.0, 125.4, 124.0, 121.8, 41.9, 31.9, 31.2, 29.6, 29.3, 27.9, 27.1, 22.6, 14.1.

Bis-(2, 2'-didodecylthienyl)-2, 6-naphthalene-N, N'didodecyl-1, 4, 5, 8-tetracarboxylicdiimide, 3

A solution of 2 (0.57g, 0.75 mmol), and 3-dodecyl-5-(tribytylstannyl) thiophene (1.01 g, 1.8 mmol) in freshly distilled THF (15 mL) was degassed. The mixture was heated reflux under a nitrogen atmosphere and then to dichlorobis(triphenylphosphine)palladium (II) [PdCl₂(PPh₃)₂] (14 mg, 0.02 mmol) was added. After 12 h, the THF was removed off by vacuum distillation. The residues were purified by column chromatography (eluant: hexane:methylene chloride = 1 : 1) to give pure compound **3** as a red solid (0.5g, 67.5%). ¹H NMR (CDCl₃, 400Hz, δ/ppm): 8.70 (t, 2H, Ph-H), 7.14 (s, 2H, thiophene-H), 7.11 (s, 2H, thiophene-H), 4.19-4.08 (m, 4H, N-CH₂), 2.68 (t, 4H, α-CH₂), 1.72-1.65 (m, 6H, CH₂), 1.42-1.24 (m, 74H, CH₂), 0.86 (t, 12H, CH₃). ¹³C NMR (CDCl3, 100MHz, δ/ppm): 162.6, 143.7, 141.1, 140.4, 136.4, 136.3, 131.3, 130.5, 129.6, 127.9, 126.8, 126.5, 126.1, 125.0, 123.3, 122.8, 41.1, 41.0, 31.9, 30.5, 30.4, 29.6, 29.5, 29.3, 28.0, 27.1, 25.6, 23.0, 22.7, 22.2, 14.1.

Bis-{2, 2'-(5, 5'-dibromo)-didodecylthienyl}-2, 6naphthalene-1, 4, 5, 8-tetracarboxylic-N, N'didodecyldiimide (M1)

To a solution of **3** (0.5 g, 0.45 mmol) in chloroform (25 mL), Nbromosuccimide (NBS) (0.16 g, 0.9 mmol) was added. This mixture was then stirred for 4 h at room temperature in darkness. The solvent was removed off by vacuum distillation. The residues were purified by column chromatography (hexane:methylene chloride = 2 : 1) to give pure compound **M1** (0.48 g. 85%) as a purple solid. ¹H NMR (CDCl₃, 400Hz, δ /ppm): 8.70 (s, 2H, Ph-H), 7.03 (s, 2H, thiophene-H), 4.11 (t, 4H, N-CH₂), 2.64 (t, 4H, α -CH₂), 1.67-1.58 (m, 8H, CH₂), 1.26-1.24 (m, 72H, CH₂), 0.87 (t, 12H, CH₃). ¹³C NMR (CDCl₃, 100MHz, δ /ppm): 162.0, 142.5, 140.1, 139.4, 136.4, 129.6, 127.4, 125.5, 122.9, 112.4, 41.2, 31.9, 29.7, 29.6, 29.5, 29.4, 29.3, 28.0, 27.1, 22.7, 14.1.

2, 6-Bis(tributyltin)-4, 8-didodecyloxybenzo[1, 2-b; 3, 4b]dithiophene (M2)

M2 was synthesized following methods described in the literature.²⁵ ¹H NMR (CDCl₃, 400Hz, δ/ppm): 7.48 (s, 2H, thiophene-H), 4.30 (t, 4H, O-CH₂), 1.90-1.84(m, 4H, CH₂), 1.66-1.58 (m, 12H, CH₂), 1.41-1.27 (m, 48H, CH₂), 1.20-1.12 (t, 12H, CH₂), 0.93-0.88 (m, 24H, CH₃). ¹³C NMR (CDCl₃, 100MHz, δ/ppm): 142.9, 139.9, 134.2, 132.9, 128.2, 73.6, 31.9, 30.6, 29.7, 29.7, 29.6, 29.4, 29.1, 29.0, 28.9, 27.3, 26.2, 22.7, 14.1, 13.7, 10.9.

2,6-Di(tributyltin)-N-[1-(2'-ethylhexyl)-3-ethylheptanyl]dithieno[3,2-b:2',3'-d]pyrrole (M3)

M3 was synthesized following methods described in the literature.²⁶ ¹H NMR (CDCl₃, 400Hz, δ /ppm): 6.92(t, 2H, thiophene-H), 4.04(s, 2H, N-CH₂), 1.99(s, 1H, CH), 1.49-1.68(m, 10H, CH₂), 1.31-1.39(m, 24H, CH₂), 1.23-1.27(m, 16H, CH₂), 1.08-1.17(m, 10H, CH₂), 0.84-0.92(m, 24H, CH₃). ¹³C NMR (CDCl₃, 100MHz, δ /ppm): 148.3, 134.56, 120.10, 118.23, 51.57,39.19, 31.97, 31.90, 31.66, 30.00, 29.66, 29.38, 29.15, 29.04, 28.94, 27.60, 27.31, 27.03, 26.53, 26.47, 22.73, 22.70, 14.16, 13.74, 10.92.

2.3 Polymerization.

The synthesis and structures of the copolymers are outlined in Scheme 2. A typical experimental procedure for the polymerization of monomer **M1** and monomer **M2** was as follows:



Scheme 2 Synthetic route for copolymers.

P1: Under argon atmosphere, monomer **M1** (0.3 mmol, 0.3784 g) and monomer **M2** (0.3 mmol, 0.3411 g) were dissolved in 15 mL of toluene. The solution was flushed with argon for 10 min, and then Pd_2dba_3 (5.40 mg) and $P(o-tolyl_3)$ (7.20 mg) were added into the flask. The flask was purged three times with successive vacuum and argon filling cycles. The polymerization reaction was heated to 110 °C, and the mixture

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was stirred for 72 h under argon atmosphere. 2-Tributylstannyl thiophene (23.50 μ L) was added to the reaction. After two hours, 2-bromothiophene (7.90 μ L) was added. The mixture was stirred overnight to complete the end-capping reaction. The mixture was cooled to room temperature and poured slowly in 400 mL of methanol. The precipitate was filtered and washed with methanol and hexane in a soxhlet apparatus to remove the oligomers and catalyst residue. Finally, the polymer was extracted with chloroform. The solution was condensed by evaporation and precipitated into methanol. The polymer was collected as a dark purple solid with a yield of 76.8% (389 mg). ¹H NMR (CDCl₃, 400Hz, δ /ppm): 8.28 (d, 2H, Ph-H), 7.49-7.33 (m, 4H, thiophene-H), 4.22-4.08 (m, 8H, O-CH₂, N-CH₂), 1.96-1.50 (m, 124H, CH₂, CH₃), 0.80 (s, 18H, CH₃).

P2: **P2** was synthesized from monomers **M1**(0.3 mmol, 0.3784 g) and **M3** (0.3 mmol, 0.2729 g) as a dark purple solid with a yield of 89% according to the method of polymer P1 described above. ¹H NMR(CDCl₃, 400Hz, δ /ppm): 8.75(br, 4H, thiophene-H), 8.39(br, 1H, thiophene-H), 7.26(br, 11H, Ph-H), 6.97(br, 11H, Ph-H), 5.12(br, 2H, N-CH₂), 4.12(br, 28H, N-CH₂), 2.04(br, 16H, CH₂),1.24(br,673H,CH₂),0.86(br, 138H, CH₃).

2.4 Device fabrication.

 TiO_2 colloid was prepared by the procedures in a similar way as done in the previous works.^{28,29} A layer of n-type TiO_2 film with a thickness of ~300 nm was prepared by coating the TiO_2 colloid on Fluorine-doped tin oxide (FTO) glass using a spincoated technique, followed by sintering in air at 450 °C for 30 min. Then, the acceptor film was soaked in a 5 mg mL⁻¹ copolymer in CHCl₃ solution for 12 hr to uptake p-type polymer and dried under nitrogen flow. Next, PEDOT: PSS layer was spin-coated onto the BHJ. Finally, Pt electrodes were deposited on the top of the PEDOT: PSS layer by thermal evaporation under vacuum.

3. Results and discussion

3.1 Synthesis and characterization

Copolymers show good solubility at room temperature in organic solvents such as chloroform, tetrahydrofuran and toluene. The incorporation of alkyl side chains on NDI, BDT and DTP segments enables them to have a good solubility. The weight-average molecular weight (M_w) and polydispersity index (PDI= M_w/M_n) were measured by gel permeation chromatography (GPC) technique using THF as the eluent and polystyrenes as the internal standards. As shown in Table 1, P1 gives a $M_{\rm p}$ of 15000 and a PDI of 1.2. **P2** has a $M_{\rm p}$ of 9465 and a PDI of 1.2. Stille coupling usually results in a broad molecular weight distribution.^{30,31} However, it is worth mentioning that the polymerization reaction was performed at 110 °C for 72 h under vigorous stirring. Such long time reaction at relative high temperature may induce a uniform weight distribution, which agrees well with the related systems.^{32,33} Moreover, the resulting copolymers exhibit good thermal stability with the decomposition onset temperatures (T_d) (about

Table 1 Molecular weights and thermal properties of different copolymers.

Copolymers	$M_{\rm n}^{\ \rm a}$	$M_{ m w}{}^{ m a}$	PDI	<i>T</i> _d (℃)
P1	15000	18000	1.2	343
P2	9465	11519	1.2	340

 ${}^{a}M_{n}$, M_{w} and PDI of the different copolymers were obtained by GPC technique using polystyrene in THF as standards.



Fig. 1. TGA thermograms of **P1** and **P2** polymers.

3.2 Absorption spectra of copolymers.

The absorption spectra of copolymers in CHCl₃ solution and copolymer films are shown in Fig. 2. The spectroscopic data are listed in Table 2. As shown in Fig. 2, both P1 and P2 present two absorption bands. For solution, the absorption peaks of the P1 are located at about 394 and 644 nm, while those of P2 are at about 388 and 673 nm. For the thin-film, the absorption band edge is located at about 438 and 699 nm for P1, 433 and 759 nm for P2. In general, the thin-film absorption spectra are similar in shape to those in dilute solutions. All absorption spectra exhibit two characteristic bands centered at 350-500 and 500-1000 nm, respectively. As compared to their counterparts in the solution, the broad peaks of the thin-film absorption spectra show obvious red-shifts. This can be explained by the formation of π -stacked structures in the solid state,³⁴ which could facilitate charge transport for photovoltaic applications. The results also indicate that the absorption characteristics of copolymer P1 and P2 could be readily tuned, which are very useful for the design of the photovoltaic materials with enhanced absorption. The energy band gap E_g calculated from the absorption band edges of the optical absorption spectra

were about 1.62 and 1.57 eV for **P1** and **P2**, respectively, as per $E_g=1240/\lambda$ eV, where λ is the absorption band edge. The tunable optical bandgap and broad absorption bands across the entire visible wavelength region of NDI-based copolymer was achieved by tailoring the donor structures, suggesting their potentially useful applications in HSCs.



Fig. 2. Optical absorption spectra of copolymers in $CHCl_3$ solution and thin film on quartz plates.

	Absorption peaks in CHCl ₃ (nm)	Absorptio n peaks of thin film (nm)	E_g^{opt} (eV)	E ^{ox} _{peak} /HOMO	E ^{red} /LUMO	E_g
P1	394, 644	438, 699	1.62	0.43/ -5.14	-1.39/ -3.32	1.82
P2	388, 673	433, 759	1.57	0.51/ -5.22	-1.28/ -3.43	1.79

3.3 Electrochemical Properties.

The electrochemical properties of the copolymers are investigated by CV technique. The CV characteristics are carried out with Ag/Ag^+ as reference electrode. The energy level of the Ag/Ag^+ reference electrode was calibrated against F_C/F_C^+ system and determined to be 4.71 eV below the vacuum level.³⁵ The cells are purged with pure argon prior to each scan. The scans toward the anodic and cathodic directions were performed at a scan rate of 50 mV s⁻¹ at room temperature. The voltammetric measurements of the copolymer thin films are shown in Fig. 3, and all the electrochemical redox data are summarized in Table 2. Both oxidation and reduction waves are clearly revealed in the CVs, which indicates the capability of copolymers to transport both electrons and holes. Based on the HOMO and LUMO values, the bandgap (E_g) of the P1 and P2 were found to be about 1.82 and 1.79 eV, respectively. These values are comparable to those obtained from the optical





Fig. 3. Cyclic voltammogram measurements of different copolymers.

3.4 Theoretical Calculations.







Fig. 4. Optimized geometry, molecular orbital surfaces of the HOMO and LUMO of the model compounds, obtained at the DFT/B3LYP/6-31G*.

To gain deeper insight into the effect of BDT, DTP and the nature of the excited states of these NDI-based copolymers, we performed density functional theory (DFT) calculations at the B3LYP/6-31G* level for NDI-BDT and NDI-DTP compounds and optimized the geometrical structure, followed by calculating the lowest vertical excitations using the Gaussian 09 program suite. DFT/B3LYP/6-31G* method was used here,

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because it has been found to be an accurate method for calculating the optimal geometry and electronic structures in many molecular systems. The alkyl groups were replaced by methyl groups to simplify the calculations because the length of alkyl chains does not significantly affect the equilibrium geometry and the electronic properties.

The optimized geometry molecular structures and frontier energy levels (HOMO and LUMO) of the model compound are shown in Fig. 4. As shown in Fig. 4, the results indicate that the electron density of LUMO is mainly localized on the NDI unit. The HOMO values were calculated to be -5.26 and -4.99 eV, and the LUMO values to be -3.36 and -3.24 eV for NDI-BDT and NDI-DTP, respectively. Thus, the bandgaps are determined to be about 1.90 and 1.75 eV. The results are in good agreement with those obtained by CV characteristics and UV-vis absorption spectra.

3.5. Photovoltaic Properties

It is generally accepted that the photogeneration in present HSC can be boosted by simple consideration of the energetics at the donor/acceptor interface (Fig. 5). First, copolymers act as a donor by absorbing photons, after which delocalized charges are created. Then the electrons diffuse towards an electron acceptor (TiO₂) interface while the holes are transferred to the opposite phases by utilizing the hole extraction material (PEDOT:PSS). However, not all of the holes and electrons can reach the interface, owing to the fact that the electron-hole pairs are strongly bound by Coulomb interaction. Note that, the energy offset between the LUMO of copolymers and the CB of TiO_2 is 0.48 and 0.43 eV, respectively, which is close to the Coulomb attraction (typically 0.1~0.5 eV), thus enabling the initial electron transfer step to be energetically downhill.³⁷ After the electrons and holes are dissociated into free electron or hole charge carriers, they are transported through the two respective phases and can be collected at the electrodes.



Fig. 5. Schematic of an HSC incorporating an active layer TiO_2 /copolymers and the energy band diagram of the materials used in HSC. The VB (-7.40 eV) and CB (-4.20 eV) of TiO_2 is obtained from the literature.³⁶

To reveal the electron transport properties at the interface of acceptor/donor BHJs, the steady state photoluminescence (PL) spectra were measured and the steady state PL results of copolymer donor neat films, TiO₂/copolymer BHJ blend films,

respectively, following excitation at 510 nm, are shown in Fig. 6. The emission of TiO_2 /copolymer BHJ was quenched by more than 80% as compared to copolymer emission, indicating that lots of the charges transport from donor to acceptor in BHJs has occurred.³⁸ However, the PL for the BHJ has not yet been completely quenched, which may be ascribed to the large pores of acceptor films and hence copolymer is not in ideally direct but still intimate contact with the TiO₂ acceptor.



Fig. 6. Steady state PL of copolymer neat films and TiO_2 /copolymers blend films.

The porous acceptor film was soaked in co-polymer solution to form BHJs. The cross-sectional SEM image in Fig. 7 shows that the polymers were permeated well into the porous structure of TiO₂ film. The intimate contact between donor and acceptor benefits the efficient charge transfer at the interface because of the short diffusion length of the phtotoexcited carrier in polymer, typically ~ 12 nm.³⁹ The photocurrent-voltage (J-V) characteristics of the TiO₂/P1 BHJ and TiO₂/P2 BHJ HSCs under a simulated solar light irradiation of 100 mW cm⁻² are shown in Fig. 8. Each type of the HSCs was tested for 5 times under the identical experimental conditions, and the statistics of the device parameters with standard derivations were listed in Table 3. The corresponding V_{oc} , J_{sc} , FF, and PCE parameters of these devices under the illumination of AM1.5 (100 mW cm⁻²) are measured to be 0.64 V, 5.45 mA cm⁻², 0.53, and 1.94% for copolymer P1, and 0.67 V, 6.19 mA cm⁻², 0.57, and 2.36% for copolymer **P2**, respectively. The current density J_{sc} is governed by the device quantum efficiency, which depends on the light harvest capacity of the polymer.⁴⁰ P2 exhibits better light harvest ability than its counterpart P1 due to the smaller band gap, thus delivering a notable current density. Additionally, HOMO level of P2 is below than P1, while the energy levels of acceptor (i.e. TiO_2) remains unchanged, which is prone to give rise to a higher V_{oc} according to the following relationship:^{41,42}

$$V_{OC} = \left| \text{HOMO}_{D} \right| - \left| \text{CB}_{A} \right| - \frac{kT}{q} \ln \left(\frac{N_{eff}^{2}}{np} \right)$$
(1)

where HOMO_D is the highest occupied molecular orbital (HOMO) of the donor, CB_A is the conduction band of the acceptor, *k* is the Boltzmann constant, *q* is the elementary charge, T is temperature, N_{eff} is the effective density of state, and *n*, *p* are the concentrations of electrons and holes, respectively. This relationship demonstrates that the V_{oc} is

determined by the energy offset between HOMO_D and CB_A.⁴³ Note that the CB-HOMO offset of TiO₂/**P2** is 1.02 eV, which is greater than TiO₂/**P1** (0.94 eV) system. The enhanced J_{sc} and V_{oc} finally result in a higher PCE for TiO₂/**P2** HSC than TiO₂/**P1** HSC. The present results indicate that the NDI-based copolymers grafted with different donors are one of the promising efficient photovoltaic materials. Furthermore, suitable electronic, optical, and photovoltaic properties can be easily achieved by simply tuning the molecular structures of donors.



Fig. 7. Cross-sectional SEM image of TiO₂/co-polymer BHJ.



Fig. 8. J-V characteristics curves of HSCs made from different TiO₂/copolymers BHJs.

Table 3. Photovoltaic parameters of the HSCs based on different BHJs.

BHJs	$V_{OC}\left(\mathbf{V}\right)$	$J_{sc} (\mathrm{mA} \cdot \mathrm{cm}^{-2})$	FF	PCE (%)
TiO ₂ /P1	0.64±0.01	5.53±0.12	0.55±0.03	1.94±0.10
$TiO_2/P2$	0.67±0.01	6.19±0.16	0.57±0.01	2.36±0.08

Conclusions

In summary, two NDI-based conjugated copolymers P1 and P2, as new polymeric donors in BHJ HSCs, were successfully synthesized via the Stille coupling reaction. All the welldesigned copolymers showed good thermal stability as well as broader solar light absorption owing to the small band gap. Especially, HSCs based on polymer P2 deliver a higher PCE of 2.36% than its counterpart (1.94%), i.e., enhanced by 21%, owing to its smaller band gap as well as more suitable energy levels formation. This study indicates that both the band gap and HOMO level of the donor can be efficiently lowered by grafting carefully chosen monomers. This work opens up a new route to achieve small band gap polymers with well-matched energy level alignment for robust HSC applications.

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Notes

The authors declare no competing financial interest.

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