Thieno[3,4-b]pyrazine-Based Low Bandgap Photovoltaic Copolymers: Turning the Properties by Different Aza-heteroaromatic Donors

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ABSTRACT: A new series of low-bandgap copolymers based on electron-accepting thieno[3,4-b]pyrazine (TPZ) and different electron-donating aza-heteroaromatic units, such as carbazole (CZ), dithieno[3,2-b:2',3'-d]pyrrole (TPR) and dithieno[3,2-b:2',3'e]pyridine (TPY), have been synthesized by Suzuki or Stille coupling polymerization. The resulting copolymers were characterized by NMR, elemental analysis, gel permeation chromatography, thermogravimetric analysis, and differential scanning calorimetry. UV-vis absorption and cyclic voltammetry measurements show that TPZ-based copolymer with TPR has the best absorption due to the strongest intramolecular charge transfer effect and smallest bandgap. The basic electronic structure of D-A model compounds of these copolymers were also studied by density functional theory (DFT) calculations. The conclusion of calculation agreed also well with the experimental results.

INTRODUCTION Polymer solar cells (PSCs) have attracted more and more attention recently as a promising renewable clean energy source because of their unique advantages of low cost, light weight, and flexibility in fabricating large-area devices.¹ In earlier times, poly(3-hexylthiophene) (P3HT) and poly(phenylene vinylene) (PPV) have been widely investigated in PSCs to understand the photovoltaic processes.² Based on the bulk-heterojunction (BHJ) solar cells, power conversion efficiencies (PCEs) of 4-5% were achieved by blending P3HT as donor and [6,6]-phenyl-C61-butyric acid methyl ester (PC₆₀BM) as acceptor.³ However, the PCEs of P3HT and PPVbased solar cells were limited by their narrow absorption spectra ranging from 300 to 650 nm due to their large band gaps (>1.9 eV).⁴ To achieve enhanced absorption, it is necessary to design and prepare low-bandgap (LBG) conjugated polymers by incorporating electron-rich donor (D) and electron-deficient acceptor (A) segments in the polymer backbones.⁵ Because of the push-pull interaction, efficient photoinduced intramolecular charge transfer (ICT) occurs from the donor to the acceptor units on photoexcitation, giving rise to a lower energy absorption band.⁶ In addition, the interesting ICT structures in D-A copolymers can also lead to higher hole

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mobility.⁷ Actually, power conversion efficiency (PCE) values up to 8% were obtained by using LBG conjugated copolymers in BHJ solar cells as electron donors.⁸

Among the wide variety of LBG copolymers, benzothiadiazole (BT),⁹ quinoxaline (QX),¹⁰ pyrazinoquinoxaline,¹¹ pyran-4-yli-denemalononitrile,¹² diketopyrrolopyrrole,¹³ and thienopyrroledione (TP)¹⁴ have been investigated in detail as electronacceptor segments. When these polymeric materials have been applied to fabricate PSCs, high PCEs have been achieved. Thieno[3,4-b]pyrazine (TPZ) is an isomer of BT and QX which contain an imine nitrogen (C=N), and has proven to be an attractive acceptor for the development of LBG conjugated polymers in PSCs.¹⁵ TPZ moiety has the resonance structure of quinoid form throughout the polymer backbone with a six-membered aromatic sextet, which is helpful to reduce the bandgap of the corresponding conjugated polymers.¹⁶ On the other hand, the TPZ moiety can make a more planar polymer backbone between repeating units due to the lower steric hindrance of the thiophene ring compared to the benzene ring in BT-based polymers.¹⁶ Up to now, most of TPZ-based LBG polymers were prepared using thiophene,¹⁷ fluorene,^{15(a),15(b),16,18} and carbazole (CZ)¹⁹ as

The polymer solar cells (PSCs) based on these copolymers were fabricated with a typical structure of ITO/PEDOT:PSS/copolymer:PC₇₁BM/Ca/Al under the illumination of AM 1.5G, 100 mW cm⁻². The performance results showed that TPZ-based copolymer with TPR donor segments showed highest efficiency of 1.55% due to enhanced short-circuit current density. The present results indicate that good electronic, optical, and photovoltaic properties of TPZ-based copolymers can be achieved by just fine-tuning the structures of aza-heteroaromatic donor segments for their application in PSCs. © 2011 Wiley Periodicals, Inc. J Polym Sci Part A: Polym Chem 49: 4458–4467, 2011

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FIGURE 1 Structures of the LBG copolymers, **PCZTPZ**, **PTPRTPZ**, and **PTPYTPZ**. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

donor. For example, a polymer containing a TPZ and 9,9-dialkylfluorenes exhibits a PCE of about 2%.^{15(b)} However, their solar cell efficiency is relatively poor. Previous work verified that the highest occupied molecular orbital (HOMO) level of these D-A copolymers is predominantly determined by the donor moiety, and the lowest unoccupied molecular orbital (LUMO) almost exclusively resides on the acceptor moiety.²⁰ As TPZ's growing significance as an *n*-type building blocks receives broad interest, it is a challenge to investigate the energy levels, optical, and photovoltaic properties of TPZbased LBG copolymers consisting different donor units.

To further turn and optimize the electronic, optical, and other properties, exploration of different aza-heteroaromatic donors incorporated into TPZ-based polymeric backbone is highly desirable. In this article, we report the synthesis, properties, and device applications of three novel TPZ-based D-A alternating conjugated copolymers using CZ, dithieno[3,2b:2',3'-d]pyrrole (TPR) and dithieno[3,2-b:2',3'-e]pyridine (TPY) as donor segments (Fig. 1), which contain nitrogen atoms leading to strong electron-donating ability. These copolymers were synthesized by palladium(0)-catalyzed Suzuki or Stille coupling reaction, as shown in Scheme 1. The effects of the different donor segments, donor-acceptor strength, and backbone planarity on the absorption spectra, electronic and optoelectronic properties of the resulting copolymers were investigated. This study indicated that these polymers had promising applications for PSCs.

RESULTS AND DISCUSSION

Synthesis and Characterization

The synthetic route toward the monomers and copolymers is depicted in Scheme 1. 2,5-Dibromothiophene was nitrated in the three and four positions using the forcing conditions to



SCHEME 1 Synthetic route of monomers and conjugated copolymers.

Materials



FIGURE 2 Optical absorption spectra of **PCZTPZ**, **PTPRTPZ**, and **PTPYTPZ** in CHCl₃ solution and thin film on quartz plates. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

give 2,5-dibromo-3,4-dinitro-thiophene **1**.²¹ A Stille-type coupling of **1** with tributyl(4-hexylthiophen-2-yl)stannane afforded the compound 2. Reduction to the diamino derivative 3 was accomplished using tin(II) chloride in reasonable yield. Subsequently, the compound 3 was condensed with a series of 3,4-hexanedione to produce the dithienylthienopyrazine 4. Finally, the bromination has been successfully carried out using n-bromosuccinimide (NBS) in anhydrous tetrahydrofuran (THF) to afford the monomer TPZ. The monomer CZ was obtained by further alkylation and borylation of 2,7-dibromocarbazole, which was synthesized using starting material of 4,4'-dibromobiphenyl.²² For synthesis of monomer TPR, the precursor of 8 was prepared by reacting 3,3'-dibromo-2,2'-bithiophene with 1-dodecyl amine in the presence of Pd₂dba₃ catalyst. After that, compound 8 was treated with *n*-butyllithium and then quenched with tributyltin chloride to give monomer TPR.²³ Another monomer TPY was prepared by reaction of 3-aminothiophene with tridecanal under acidic conditions leading to the formation of 4dedocylbithieno[3,2-b:2'3'-e]pyridine, which was further treated with *n*-butyllithium and then quenched with tributyltin chloride, as first described by Müllen and coworkers.²⁴

Copolymers were synthesized by a Pd(0)-mediated Suzuki or Stille coupling polymerization in toluene. The structures of the copolymers were confirmed with NMR spectroscopy and elemental analysis. All the polymers are soluble in common organic solutions, such as toluene, dichloromethane, chloroform, chlorobenzene, dichlorobenzene, and THF. The number-average molecular weights (M_n) and polydispersity index (M_w/M_n) of **PCZTPZ**, **PTPRTPZ**, and **PTPYTPZ** were determined by gel permeation chromatography (GPC) against polystyrene standards in THF as the eluent. The results showed that these copolymers have a M_n of 15400–21800 with polydispersity indices of 1.91–2.65. The resulting copolymers also exhibited a good thermal stability with decomposition onset temperatures (T_d) (about 5% weight loss) of 348–395 °C as measured by thermogravimetric analysis (TGA). The glass transition temperatures (T_g) of these copolymers were investigated by differential scanning calorimetry (DSC) to be 89–110 °C, respectively. The thermal properties are good enough for fabricating and testing the PSCs and other optoelectronic devices.

Optical Properties

All electronic absorption properties of the obtained copolymers were measured both in CHCl₃ solutions and as thin films on quartz slides. The spectroscopic data are listed in Table 2. As shown in Figure 2, all three copolymers present two absorption bands. The band at shorter wavelength in the range of 350–500 nm originates from π - π * electronic transitions of the conjugated polymer backbones with different selected donor segments. The band at the longer wavelength in the range of 500-1000 nm can be attributed to ICT transitions between the donors and the TPZ acceptor moieties. PCZTPZ, PTPRTPZ, and PTPYTPZ show absorption spectra with absorption maxima at 415, 586 nm; 451, 678 nm; and 443, 590 nm, respectively. The slight red shift for PTPRTPZ, compared to PCZTPZ and PTPRTPZ, is likely due to its stronger electron-donating properties, giving rise to higher formed ICT. The results also indicate that changing donating segment of a TPZ-based copolymer would easily tune its absorption behavior, which is very useful for the design of the photovoltaic materials with enhanced absorption.

The optical absorption spectra of thin films of the resulting TPZ-based copolymers were also shown in Figure 2. The thin-film absorption spectra with two characteristic bands centered at 350-500 and 500-1000 nm are generally similar in shape to those in dilute solutions. The absorption maximum of PCZTPZ, PTPRTPZ, and PTPYTPZ at 422, 453, and 448 nm are only 7, 2, and 5 nm red-shifts compared to their counterparts in the solution state. The broad peaks in the wavelength range of 500-1,000 nm showed larger red-shifts of about 20 nm. The reason can be explained by the formation of π -stacked structures in the solid state^{12(a)} which could facilitate charge transportation for photovoltaic applications. The energy bandgaps calculated from the absorption band edges of the optical absorption spectra were about 1.63, 1.38, and 1.53 eV for PCZTPZ, PTPRTPZ, and PTPYTPZ, respectively. The results indicate that the TPR-TPZ show stronger ICT effect than CZ-TPZ and TPY-TPZ

TABLE 1 Molecular Weights and Thermal Properties of the Copolymers

Copolymers	Yield (%)	<i>M</i> n ^a (×10 ³)	PD ^a (<i>M</i> _w / <i>M</i> _n)	<i>T</i> _d ^b (°C)	7 _g ^c (°C)
PCZTPZ	72	15.4	1.91	363	89
PTPRTPZ	82	20.3	2.30	348	102
PTPYTPZ	76	21.8	2.65	395	110

^a Molecular weights and polydispersity indices were determined by GPC in THF using polystyrene as standards.

 $^{\rm b}$ Onset decomposition temperature measured by TGA under $N_{\rm 2}.$

^c Glass transition temperature measured by DSC under N₂.



FIGURE 3 Cyclic voltammograms of PCZTPZ, PTPRTPZ, and PTPYTPZ.

systems, leading to smaller bandgap, which is useful to increase the short circuit current ($J_{\rm sc}$) in PSCs.^{3(a),25} As expected, **PTPRTPZ** has a smallest bandgap because of the best electron-donating property of TPR moiety compared to CZ and TPR. The tunable optical bandgaps and broad absorption bands across the entire visible wavelength region of TPZ-based copolymers were achieved by tailoring different aza-heteroaromatic donor structures, suggesting their useful application in PSCs.

Electrochemical Properties

The electrochemical properties of the copolymers were investigated by cyclic voltammetry (CV). The CV curves were carried out referenced to a Ag/AgCl electrode. The energy level of the Ag/AgCl reference electrode was calibrated against FC/FC⁺ system to be 4.32 eV below the vacuum level.26 The cell was 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 oxidation and reduction of the copolymer thin films are shown in Figure 3, and all the electrochemical redox data are summarized in Table 2. These three copolymers have reversible oxidation process. However, PCZTPZ and PTPYTPZ do not show reversible reduction waves. On anodic sweep, the onset potentials of the *p*-doping process for PCZTPZ, PTPRTPZ, and PTPYTPZ are determined to be 0.94, 0.72, and 0.70 V, which correspond to a HOMO energy level of 5.26, 5.04, and 5.17 eV, respectively. On sweeping the polymers cathodically, the onset potentials of the *n*-doping process for PCZTPZ, PTPRTPZ, and PTPYTPZ occur at

about -0.71, -0.70, and -0.70 V. The LUMO energy levels of the corresponding copolymers are estimated to be -3.61, -3.62, and -3.62 eV, respectively. The results indicated that the HOMO values of TPZ-based copolymers could be affected much by incorporation of different aza-heteroaromatic donors. But the LUMO values would be affected a little. As calculated from the HOMO and LUMO values, the bandgaps (E_g) of the **PCZTPZ**, **PTPRTPZ**, and **PTPYTPZ** were found to be about 1.65, 1.42, and 1.56 eV. These values are close to those obtained by the optical method described above. The electrochemical data of the copolymers are summarized

Theoretical Calculations

in Table 2.

To gain deeper insight into the effect of aza-heteroaromatic donors and nature of the excited states of these TPZ-based copolymers, we performed density functional theory (DFT) calculations at the B3LYP/6-31G* level on D-A model compounds (CZ-TPZ, TPR-TPZ, and TPY-TPZ) and optimized their geometrical structures followed by calculation of the lowest vertical excitations using the Gaussian 09 program suite.²⁷ DFT/B3LYP/6-31G* method was used here, 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 compounds are shown in Figure 4. Ab initio calculations on the model compounds for the resulting copolymers show that they are almost planar molecules, which enable the electrons to be delocalized within the molecule systems by conjugation to get higher carrier mobility.²⁸ As shown in Figure 4, the results indicate that the electron density of LUMO is mainly localized on the TPZ unit. However, the electron density of HOMO of CZ-TPZ and TPY-TPZ are partially distributed over the entire conjugated molecule, which implys the weaker ICT formed in these D-A system. The HOMO values were calculated to be -4.65, -4.47, and -4.79 eV, and the LUMO values to be -2.33, -2.40, and -2.54 eV for CZ-TPZ, TPR-TPZ, and TPY-TPZ, respectively. Thus, the bandgaps are determined to be about 2.32, 2.07, and -2.25 eV. Obviously, the HOMO energy levels and bandgaps were affected largely by different aza-heteroaromatic donors, however, the LUMO energy levels were affected a little. The results are in

TABLE 2 Optical and Electrochemical Data of the Copolymers

Copolymers	Abs. (nm) λ_{\max}^{CHCI3}	Abs. (nm) $\lambda_{\max}^{\text{film}}$	E_{g}^{a} (eV)	$E_{\text{onset}}^{\text{ox}}(V)$ /HOMO (eV)	E ^{ox} _{onset} (V)/LUMO (eV)	E_{g}^{b} (eV)
PCZTPZ	415, 586	422, 606	1.63	0.94/-5.26	-0.71/-3.61	1.65
PTPRTPZ	451, 678	453, 696	1.38	0.72/-5.04	-0.70/-3.62	1.42
PTPYTPZ	443, 590	448, 610	1.53	0.85/-5.17	-0.70/-3.62	1.56

^a Optical band gap was estimated from the wavelength of the optical absorption edge of the copolymer film.

 $^{\rm b}$ Electrochemical band gap was calculated from the LUMO and HOMO energy levels.



FIGURE 4 Optimized geometry, molecular orbital surfaces of the HOMO and LUMO of the model compounds, obtained at the DFT/ B3LYP/6-31G*. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

good agreement with those obtained by CV and UV-vis measurements.

Photovoltaic Properties

To investigation of the photovoltaic properties of these TPZbased copolymers, PSCs were fabricated with the structure of indium tin oxide (ITO)/poly(3,4-ethylenedioxythiophene) (PEDOT):poly(styrenesulfonate) (PSS) (40 nm)/active layer (90 nm)/Ca (10 nm)/Al(140 nm) according to the method described in our previous work.^{10(d),11(c),12(a)} Here, ITO glass was used as an anode, Ca/Al as a cathode, and the blend film of the copolymer and [6,6]-phenyl-C71-butyric acidmethyl ester (PC₇₁BM) between them as an active layer. The ITO glass was precleaned and modified by a thin layer of PEDOT:PSS (Bayer), which was spin-cast from a PEDOT:PSS aqueous solution onto the ITO substrate. The active layer was prepared by the spin coating of a blend solution of the copolymer and $PC_{71}BM$ in chlorobenzene on the ITO/ PEDOT:PSS electrode. Then, a metal cathode, which was made of Ca (10 nm) and Al (140 nm), was deposited onto the polymer layer by vacuum evaporation under 9 \times 10⁻⁷ torr. The devices were illuminated through the transparent ITO anode. The devices were optimized by changing some conditions, such as the ratio of the copolymer and PC71BM from 1:1 to 1:4, the thickness of active layer, and the thermal annealing temperature. For this work, using Ca/Al as the cathode and no annealing the blend films afforded the best device performance. Better fabrication conditions were obtained by spin-coating from a 10 mg mL^{-1} chlorobenzene solution of copolymer/PC71BM ratio of 1:3 (w/w). Using lower weight ratios of PC71BM in blended copolymer:PC71BM (1:1 and 1:2, w/w) resulted in low J_{sc} values because of the

inefficient charge separation and electron transporting properties giving rise to lower PCEs.²⁹ However, the copolymer:PC₇₁BM (1:4, w/w) blends with higher PC₇₁BM contents showed reductions of lower PCE values due to the poor interfacial contacts between the copolymers and PC₇₁BM leading to the suppression of charge separation/transportation within the active layer.³⁰ In addition, hole-only devices with the structure of ITO/PEDOT:PSS/copolymer:PC₇₁BM/Au were fabricated to evaluate the hole mobility in the blended films (copolymer:PC₇₁BM = 1:3, w/w). The hole mobility was measured using the space charge limited current method reported previously.³¹ The dark current is given by J



FIGURE 5 Current–voltage curves of the polymer solar cells based on **PCZTPZ**, **PTPRTPZ**, and **PTPYTPZ** under the illumination of AM 1.5, 100 mW cm⁻². [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]



FIGURE 6 AFM topographic images of the blend films (copolymer:PC₇₁BM = 1:3, w/w). (a) **PCZTPZ**, (b) **PTPRTPZ**, and (c) **PTPYTPZ**. Image size: $5 \times 5 \mu m^2$.

= $9\varepsilon_0\varepsilon_r\mu V^2/8L^3$, where $\varepsilon_0\varepsilon_r$ is the permittivity of the copolymer, μ is the hole mobility, and *L* is the sample thickness. The measured hole mobility of **PCZTPZ**:PC₇₁BM, **PTPRTPZ**:PC₇₁BM, and **PTPYTPZ**:PC₇₁BM was 2.5 × 10⁻⁵ cm² V⁻¹ s⁻¹, 8.3 × 10⁻⁵ cm² V⁻¹ s⁻¹, and 5.9 × 10⁻⁵ cm² V⁻¹ s⁻¹, respectively. These mobilities are not so high which can be attributed to the almost amorphous morphology of the copolymer blends. The mobility exhibited by **PTPRTPZ** is higher than those measured in **PCZTPZ** and **PTPYTPZ**. The result suggests that **PTPRTPZ** would be obtained larger $J_{\rm sc}$ and improved device performance in PSCs.³²

Figure 5 shows current-voltage curves of the devices. The corresponding open-circuit voltages (Voc), short-circuit current densities (J_{sc}) , fill factors (FF), and PCE values of these devices under the illumination of AM1.5 (100 mW cm^{-2}) are measured to be 0.62 V, 3.85 mA cm $^{-2}$, 0.36, and 0.86% for copolymer **PCZTPZ**, 0.51 V, 7.16 mA cm⁻², 0.42, and 1.55% for copolymer PTPRTPZ, 0.54 V, 5.73 mA cm⁻², 0.38, and 1.18% for copolymer PTPYTPZ, respectively. Obviously, PTPRTPZ-based device has the highest J_{sc} due to its smallest bandgap of 1.38 eV compared to PCZTPZ and PTPYTPZ, allowing the highest PCE value. However, the device using **PCZTPZ** shows highest V_{oc} The reason can be attributed to the CZ donor with two phenyl group, which described in our previous work.^{12(a)} The surface morphology of the active layer in the PSCs plays an important role in determining the device performance.³³ Figure 6 shows the AFM topographies of copolymer blends (copolymers:PC₇₁BM = 1:3, w/w) where the images were obtained in a surface area of 5 \times 5 μ m² by the tapping mode. The studied surfaces were seemed quite smooth. The root mean squares (rms) roughness of the blend films of PCZTPZ, PTPRTPZ, and PTPYTPZ are 2.86, 1.92, and 2.13, respectively, which indicates no significant aggregation. Anyway, considering low FF of these devices, there is a big room for future improvement in performance of PSCs based on the resulting copolymer/PC71BM. The present results indicate that the TPZ-based copolymer with different aza-heteroaromatic donors is promising efficient photovoltaic materials. Furthermore, suitable electronic, optical, and photovoltaic properties can be easily achieved by just fine-tuning the structures of aza-heteroaromatic donors.

CONCLUSIONS

A novel series of LBG copolymers based on electron-accepting TPZ and different electron-donating aza-heteroaromatic

units, such as CZ, TPR, and TPY, have been synthesized by Suzuki or Stille coupling polymerization. Their optical and electrical properties can be facilely fine-modulated by adjusting the structures of aza-heteroaromatic donors. UV-vis absorption and cyclic voltammetry measurements show that **PTPRTPZ** has best light harvest and smallest bandgap among the three copolymers due to the strongest ICT effect. The basic electronic structure of D-A model compounds of these copolymers were also studied by DFT calculations at the B3LYP/6-31G* level. The PSCs based on these copolymers were fabricated with a typical structure of ITO/ PEDOT:PSS/copolymer:PC71BM/Ca/Al under the illumination of AM 1.5G, 100 mW cm⁻². The results showed that TPZbased copolymer with TPR donor segments had highest efficiency of 1.55% due to its smallest bandgap. The present results indicate that suitable electronic, optical, and photovoltaic properties of TPZ-based copolymers can be achieved by just fine-tuning the structures of aza-heteroaromatic donors for application in polymer solar cells.

EXPERIMENTAL

Materials and Instruments

NMR spectra were obtained on a Bruker Avance-400 spectrometer with *d*-chloroform as the solvent and tetramethylsilane as the internal standard. The average and weight molecular weight of the copolymers were determined using Waters1515 GPC analysis with THF as eluent and polystyrene as standard. Cyclic voltammetry measurements were made on a CHI660C potentiostat/galvanostat electrochemical workstation at a scan rate of 50 mV s^{-1} , with a platinum wire counter electrode and a Ag/AgCl reference electrode in an anhydrous and nitrogen-saturated 0.1 mol L^{-1} acetonitrile (CH₃CN) solution of tetrabutylammonium perchlorate (Bu₄NClO₄). The copolymers were coated on the platinum plate working electrodes from dilute chloroform solutions. UV-vis spectra were obtained on a Carry 300 spectrophotometer. TGA and DSC measurements were conducted on a TA Instrument Model SDT Q600 simultaneous TGA/DSC analyzer at a heating rate of 10 $^{\circ}$ C min⁻¹ and under a N₂ flow rate of 90 mL min⁻¹. Polymer photovoltaic cells were fabricated with ITO glass as an anode, Ca/Al as a cathode, and the blend film of the copolymer and [6,6]-phenyl-C₇₁-butyric acid methyl ester (PC71BM) as a photosensitive layer. The photosensitive layer was prepared by spin-coating a blend



solution of the copolymer and $PC_{71}BM$ in chlorobenzene on the ITO/PEDOT:PSS electrode. The current-voltage (I-V) characterization of the devices was carried out on a computer-controlled Keithley 236 Source Measurement system. A solar simulator was used as the light source, and the light intensity was monitored by a standard Si solar cell. The thickness of films was measured using a Dektak 6 M surface profilometer.

All reagents were purchased from Aladdin, Alfa Aesar, and Aldrich Chemical, unless stated otherwise. Commercial chemicals were used without further purification. 2,5-Dibromo-3,4-dinitrothiophene (1),²¹ 4,4'-dibromo-2-nitrobiphenyl (5),²² 2,7-dibromocarbazole (6),²² *N*-dodecyl dithieno[3,2-b:2',3'-d]pyrrole (8),²³ 2,6-di(tributyltin)-*N*-dodecyl dithieno[3,2-b:2',3'-d]pyrrole (**TPR**)²³ were prepared according to the previous literature reports.

2,5-Bis(3-hexylthiophene-5-yl)-3,4-dinitrothiophene (2)

To the solution of 2,5-dibromo-3,4-dinitrothiophene (2) (4.05 g, 15.0 mmol) and tributyl(4-hexylthiophen-2-yl)stannane (16.51 g, 36.1 mmol) in 100 mL of THF, Pd(PPh₃)₂Cl₂ (0.22 g, 0.32 mmol) was added. The mixture was refluxed overnight. After the reaction, THF was removed under reduced pressure, and the residue was extracted by CH₂Cl₂. The organic phase was separated and dried over MgSO₄. After purification by column chromatography using CHCl₃:hexane = 1:2 as the eluent, the compound **2** was afforded as an orange powder with a yield of 72%.

¹H NMR (400 MHz, CDCl₃, δ /ppm): 7.38 (s, 2H), 7.20 (s, 2H), 2.66–2.61 (t, 4H), 1.67–1.61 (m, 4H), 1.36–1.29 (m, 12H), 0.94–0.87 (t, 6H). ¹³C NMR (100 MHz, CDCl₃, δ /ppm): 144.97, 134.01, 132.29, 127.79, 126.05, 31.60, 30.32, 30.29, 28.89, 22.58, 14.08.

2,5-Bis(3-hexylthiophene-5-yl)-3,4-diminothiophene (3)

2,5-Bis(3-hexylthiophene-5-yl)-3,4-dinitrothiophene (2) (4.59 g, 9.05 mmol) and SnCl_2 (51.19 g, 270 mmol) were mixed in ethanol (90 mL), concentrated HCl (60 mL). The reaction mixture was stirred at 30 °C for 18 h. Then solvents were evaporated in vacuum, and the resultant mixture was transferred into a continuous extraction apparatus and basified with 25% KOH (100 mL) followed by pH adjustment to about 8 with solid NaHCO₃. The solution was extracted with toluene for three times and dried over MgSO₄. The compound **3** was obtained by evaporated off the solvent as a grey solid with a yield of 90%.

¹H NMR (400 MHz, CDCl₃, *δ*/ppm): 6.94 (s, 2H), 6.87 (s, 2H), 3.72 (s, 4H), 2.64–2.60 (t, 4H), 1.68–1.60 (m, 4H), 1.38–1.25 (m, 12H), 0.92–0.86 (t, 6H). ¹³C NMR (100 MHz, CDCl₃, *δ*/ ppm): 144.03, 135.61, 133.36, 125.15, 124.96, 118.47, 110.38, 31.69, 30.54, 30.37, 29.36, 29.03, 22.62, 14.11.

5,7-Bis(4-hexylthiophen-2-yl)-2,3-diethylthieno[3,4-b] pyrazine (4)

To a solution of 5,7-bis(4-hexylthiophen-2-yl)-2,3-diethylthieno[3,4-b]pyrazine (4) (2.09 g, 4.69 mmol) in ethanol (50 mL) and water (6 mL), 3,4-hexanedione (0.54 g, 4.69 mmol) was added. The mixture was refluxed for 40 h and then poured into water. The solution was extracted with CH_2Cl_2 . The organic phase was separated and dried over MgSO₄, and then purified by column chromatography using $CHCl_3$:hexane = 1:2 as the eluent to afford **4** as a purple powder with a yield of 65%.

¹H NMR (400 MHz, CDCl₃, δ /ppm): 7.44(s,2H), 6.93(s,2H), 2.97–2.90 (t, 4H), 2.67–2.61(t, 4H),1.69–1.63(m, 4H), 1.52– 1.27 (m,12H), 0.93–0.87(m,12H). ¹³C NMR (100 MHz, CDCl₃, δ /ppm): 156.63, 143.32, 137.60, 134.63, 125.30, 123.68, 121.01, 31.72, 30.44, 29.01, 28.17, 22.63, 14.13, 10.82.

5,7-Bis(4-hexyl-5-bromothiophen-2-yl)-2,3diethylthieno[3,4-b]pyrazine

To a solution of 5,7-bis(4-hexylthiophen-2-yl)-2,3-diethylthieno[3,4-b]pyrazine (4) (0.58 g, 1.1 mmol) in 20 mL THF, *N*bromosuccinimide (0.39 g, 2.17 mmol) was added in one portion. The mixture was stirred in absence of light at 0 °C for 5 h and was allowed to reach room temperature for 24 h. Then water (5 mL) was added followed by extraction with CH_2Cl_2 . The organic phase was washed with 0.5 M NaOH, water, respectively, and dried with Na_2SO_4 . The crude product was obtained after the solvent was removed under reduced pressure. The pure **TPZ** was afforded as a purple solid by column chromatography using $CHCl_3$:hexane = 1:2 as the eluent with a yield of 80 %.

¹H NMR (400 MHz, CDCl₃, δ /ppm): 7.17 (s, 2H), 2.94–2.87 (t, 4H), 2.61–2.55 (t, 4H), 1.64–1.55 (m, 4H), 1.50–1.27 (m, 12H), 0.94–0.86 (m, 12H). ¹³C NMR (100 MHz, CDCl₃, δ /ppm): 157.16, 141.75, 137.59, 134.28, 123.90, 123.07, 111.06, 31.66, 29.66, 29.47, 28.93, 28.19, 22.61, 14.12, 10.86.

2,7-Dibromo-N-dodecylcarbazole (7)

To a dried three-necked flask was charged with 2,7-dibromocarbazole (6) (10 g, 31 mmol), NaH (1.03 g, 43 mmol), 1-bromododecane (9.97 g, 40 mmol), and 100 mL anhydrous *N*,*N*-dimethylformamide. The resulting mixture was stirred at room temperature for 24 h under N₂ atmosphere. The reaction solution was quenched with 5 mL of distilled water and extracted with CHCl₃. The combined organic layers were washed with water and dried over anhydrous MgSO₄. After removal of solvent under reduced pressure, the residue was subjected to purification by column chromatography using ethyl acetate:hexane = 1:9 as the eluent to afford **7** as a colorless oil with a yield of 76%.

¹H NMR (400 MHz, CDCl₃, δ /ppm): 7.85 (d, 2H), 7.51 (d, 2H), 7.34–7.31 (dd, 2H), 4.15 (t, 2H), 1.82 (q, 2H), 1.34–1.22 (m, 18H), 0.91–0.84 (t, 3H). ¹³C NMR (100 MHz, CDCl₃, δ /ppm): 141.98, 123.21, 122.97, 121.98, 121.74, 120.51, 120.27, 112.73, 43.94, 43.70, 32.26, 31.99, 30.04, 29.80, 29.08, 28.84, 27.37, 23.22, 22.74, 14.43.

2,7-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-N-dodecylcarbazole (CZ)

To a dried three-necked flask, 2,7-dibromo-*N*-dodecylcarbazole (7) (6.03 g, 12.22 mmol) and freshly distilled THF (350 mL) were added. The resulting solution was cooled at -78 °C and 14.66 mL *n*-butyllithium (36.66 mmol, 2.5 M in hexane) was added over 15 min under nitrogen atmosphere. The mixture was stirred at -78 °C for 1.5 h, warmed to 0 °C for 15 min, and cooled again at -78 °C for 15 min. 2-Isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (23.20 g, 124.69 mmol) was added rapidly to the solution, and the resulting mixture was warmed to room temperature and stirred for 24 h. The mixture was poured into 1000 mL of water and extracted with CHCl₃. The combined organic layers were washed with brine and dried over anhydrous MgSO₄. The solvent was removed by rotary evaporation, and the residue was purification by column chromatography using CHCl₃:hexane = 2.5:1 as the eluent to afford **CZ** as a colorless oil with a yield of 72%.

¹H NMR (400 MHz, CDCl₃, δ /ppm): 8.10 (d, 2H), 7.86 (s, 2H), 7.67 (d, 2H), 4.37 (t, 2H), 1.90–1.83 (m, 2H), 1.42–1.35 (m, 24H), 1.29–1.21 (m, 20H), 0.89 (t, 3H). ¹³C NMR (100 MHz, CDCl₃, δ /ppm): 140.43, 125.05, 124.83, 120.02, 115.25, 83.79, 42.90, 31.92, 29.64, 29.56, 29.44, 29.35, 29.21, 27.15, 24.93, 22.69, 14.13.

4-Dodecylbithieno-[3,2-b:2',3'-e]pyridine (9)

A solution of tridecanal (1.02 g, 5.16 mmol) and trifluoroacetic acid (0.10 g, 0.88 mmol) in 50 mL anhydrous CH_2Cl_2 was added dropwise to a solution of 3-aminothiophene (0.93 g, 9.38 mmol) in 50 mL anhydrous CH_2Cl_2 at -5 °C. The reaction mixture was stirred at room temperature for 2 h. Trifluoroacetic acid (1.07 g, 9.38 mmol) was added, and the reaction mixture was refluxed for 8 h. The mixture was cooled and added 150 mL of diethyl ether and 30 mL of water. The aqueous layer was subsequently basified with 0.5 mol L⁻¹ aqueous sodium hydroxide solution. The mixture was extracted by diethyl ether and the combined organic extracts were dried over NaSO₄. The solvent was removed by rotary evaporation, and the residue was purification by column chromatography using CH_2Cl_2 as the eluent to afford **9** as yellow oil with a yield of 71%.

¹H NMR (400 MHz, CDCl₃, δ /ppm): 7.82 (d, 2H), 7.66 (d, 2H), 3.21(t, 2H), 1.95 (m, 2H), 1.51–1.37 (m, 6H), 0.95 (t, 3H). ¹³C NMR (100 MHz, CDCl₃, δ /ppm): 156.62, 140.84, 131.21, 129.93, 125.45, 34.66, 31.74, 29.52, 28.66, 27.34, 24.85, 22.82, 14.21.

2,6-di(tributyltin)-4-dodecylbithieno[3,2-b:2',3'e]pyridine(TPY)

A 2.5 M solution of butyllithium in hexanes (20 mL, 48.13 mmol) was added to a solution of 4-dodecylbithieno-[3,2b:2'3'-e]pyridine (9) (5.5 g, 20 mmol) in 140 mL of anhydrous THF at -78 °C. The solution was stirred at -78 °C for 1 h and then at 0 °C for 5 h. The solution was cooled back down to -78 °C again, and a solution of tributyltin chloride (20 g, 60 mmol) was added dropwise. The reaction was stirred for 24 h at room temperature. The reaction mixture was poured into 50 mL ice water and extracted with diethyl ether. The combined extracts were washed with 3% aqueous ammonia solution and water, respectively, and then dried over sodium sulfate. The solvent was removed by rotary evaporation, and the residue was purification by column chromatography using CH₂Cl₂:hexane = 1:4 (containing 1% triethylamine) as the eluent to afford TPY as pale yellow oil with a yield of 10%.

¹H NMR (400 MHz, CDCl₃, δ /ppm): 7.63(s, 2H), 3.17(t, 2H), 1.91(t, 2H), 1.65–1.59(m, 12H), 1.40–1.33(m, 20H), 1.23– 1.19(m, 10H), 0.93–0.88(m, 21H). ¹³C NMR (CDCl₃, 100 MHz, δ /ppm): 157.2, 144.9, 138.1, 133.5, 132.8, 34.6, 31.6, 29.5, 29.0, 28.0, 27.3, 22.5, 14.0, 13.6, 10.9.

Poly{[N-dodecylcarbazole-2,7-diyl]-alt-[5,7-Bis(4-hexylthiophen-2-yl)-2,3-diethyl thieno[3,4-b]pyrazine-5,5'-diyl]} (PCZTPZ)

To a three-necked flask, monomer **CZ** (0.5874 g, 1.00 mmol), monomer TPZ (0.6826 g, 1.00 mmol), and 10 mL of anhydrous toluene were added. Pd(PPh₃)₄ (2% mmol, 0.023 g) was added into the mixture under N₂ atmosphere. 2 M aqueous potassium carbonate (8 mL, 16 mmol) that has been degassed for 30 min was transferred to the mixture. The reaction mixture was stirred and heated under N2 at 90 °C for 72 h. At the end of polymerization, the terminal boronic ester and bromine groups were end-capped by sequentially adding excess 2-bromothiophene and 2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-thiophene and refluxing another 12 h, respectively. The reaction mixture was cooled to about 50 °C and slowly added to a vigorously stirred mixture of 500 mL methanol and 50 mL of 1 M aqueous HCl. The precipitate was collected by filtration from methanol. The polymers PCZTPZ were further purified as dark red solid with a yield of 72% by Soxhlet extraction in acetone for 2 days to remove oligomers and catalyst residues.

¹H NMR (400 MHz, CDCl₃, δ /ppm): 8.14–7.25(m, 8H), 4.34(br, 2H), 3.14(br, 4H), 2.85(br, 4H), 1.94–1.21(m, 42H), 0.98–0.88(m, 9H). Anal. Calcd for (C₅₄H₆₉N₃S₃)_n: C 75.74, H 8.12, N 4.91, S 11.23; found: C 74.98, H 8.05, N 4.97, S 11.29. $M_{\rm n} = 15.4$ kDa; $M_{\rm w} = 29.4$ kDa; PDI = 1.91.

Poly{[N-dodecyl-dithieno(3,2-b:2',3'-d)pyrrole-2,6-diyl]alt-[5,7-Bis(4-hexyl-thiophen-2-yl)-2,3-diethylthieno [3,4-b]pyrazine-5,5'-diyl]} (PTPRTPZ)

Monomer TPZ (0.3413 g, 0.5 mmol) and monomer TPR (0.4342 g, 0.5 mmol) were dissolved in 15 mL of toluene. The solution was flushed with argon for 10 min, and then Pd₂dba₃ (9.2 mg, 2 mol %) and P(o-tolyl)₃ (16.36 mg, 8%) 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 was stirred for 48 h under argon atmosphere. 2-Tributylstannyl thiophene (20 μ L) was added to the reaction, and then after 2 h, 2-bromothiophene (6.3 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 350 mL of methanol. The precipitate was filtered and washed with methanol and hexanes in a soxhlet apparatus to remove the oligomers and catalyst residue. Finally, the polymer was extracted with chloroform. The organic solution was condensed by evaporation and precipitated into methanol. The polymer was collected as a dark purple solid with a yield of 82%.



¹H NMR (400 MHz, CDCl₃, δ /ppm): 8.21–7.49(m, 4H), 4.12 (br, 2H), 3.18(br, 4H), 2.91(br, 4H), 2.01–1.22(m, 42H), 0.82– 0.79(m, 9H). Anal. Calcd for (C₅₀H₆₅N₃S₅)_n: C 69.16, H 7.54, N 4.84, S 18.46; found: C 68.59, H 7.42, N 4.92, S 18.51. $M_{\rm n}$ = 20.3 kDa; $M_{\rm w}$ = 46.7 kDa; PDI = 2.30.

Poly{[4-dodecylbithieno[3,2-b:2',3'-e]pyridine-2,6-diyl]alt-[5,7-Bis(4-hexylthiophen-2-yl)-2,3-diethyl thieno[3,4-b]pyrazine-5,5'-diyl]} (PTPYTPZ)

PTPYTPZ was synthesized as a dark purple solid with a yield of 76% according to the method of **PTPRTPZ** described above.

¹H NMR (400 MHz, CDCl₃, δ /ppm): 8.16–7.41(m, 4H), 3.18(br, 4H), 3.09 (br, 2H), 2.87(br, 4H), 1.98–1.19(m, 42H), 0.83–0.78(m, 9H). Anal. Calcd for $(C_{51}H_{65}N_3S_5)_n$: C 69.58, H 7.44, N 4.77, S 18.21; found: C 69.14, H 7.36, N 4.83, S 18.27. $M_n = 21.8$ kDa; $M_w = 57.8$ kDa; PDI = 2.65.

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