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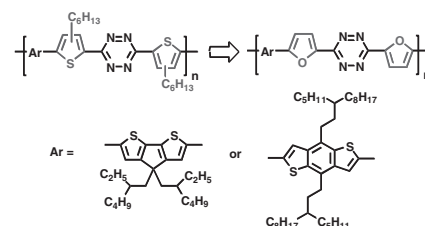
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Bisfuran-s-Tetrazine-Based Conjugated Polymers: Synthesis, Characterization, and Photovoltaic Properties

Zhao Li,* Jianfu Ding*

Bisfuran-s-tetrazine (FTz) and its copolymers with cyclopenta[2,1-b:3,4-b']dithiophene (CPDT) and benzo[1,2-b:4,5-b']dithiophene (BDT) (PCPDFTTz and PBDFTTz) are prepared with the alternating s-tetrazine and CPDT or BDT units bridged by a furan ring. Their optical and electrochemical properties are studied and compared with their thiophene analogs (PCPDTTTz-out and PCPDTTTz-in), in which the bridging unit is 4-hexylthiophene or 3-hexylthiophene, respectively. Bulk heterojunction (BHJ) solar cells fabricated from these polymers with PC₇₁BM have a power conversion efficiency (PCE) of 0.8%, which is much lower than that from the PCPDTTTz-out analog (3.2%), due to the low steric hindrance of the furan polymers in the absence of alkyl substitution on the furan ring.



1. Introduction

Recently, low-bandgap copolymers of alternating electron-donating and electron-accepting units have drawn much research attention for organic solar cell applications.^[1] Compared with well studied regioregular poly(3-hexylthiophene) (rr-P3HT), this type of copolymers has a broader absorption range due to the formation of intrachain donor/acceptor charge transfer and quinoidal structures. More importantly, the solubility, energy levels, and chain stacking of these copolymers can be easily fine-tuned by choosing different combination of the donor/acceptor building blocks or adjusting the position and bulkiness of alkyl side chains.^[1] A large number of electron-donating units based on benzene, pyrrole, or thiophene, such as fluorene, carbazole, benzodithiophene (BDT), cyclopentadithiophene (CPDT), dithienothiophene,

dithienopyrrole have been developed,^[1] while the number of electron-accepting units are relatively limited. Up to now, only benzothiadiazole, diketopyrrolopyrrole, thienothiophene, and recently emerged thieno[3,4-c]pyrrole-4,6-dione units showed a good potential for this application.^[1]

Our group introduced s-tetrazine to the family of electron-accepting building blocks and reported the first solution processable s-tetrazine-based conjugated polymers.^[2] Compared with other electron-accepting units, s-tetrazine is very attractive due to its simple synthetic approach, symmetric structure, and high electron affinity.^[3] Our previous work are mainly based on alkyl chain substituted bisthiophene-s-tetrazine (TTz) units and it was found that polymers from this thiophene based s-tetrazine have relatively poor solubility,^[4] and thus large side groups are required to achieve solution processability.

Very recently, furan-based materials attracted our attention, as they usually displayed improved solubility.^[5–7] In addition, compared with thiophene-based materials, they prefer more planar main chain conformation, are more electron-rich and have a slightly larger energy gap.^[6] Furan moiety was successfully introduced into conjugated polymers for field-effect transistor or photovoltaic

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applications.^[7] In this paper, we combined furan with s-tetrazine units to synthesize a new bisfuran-s-tetrazine (FTz) monomer, which was then converted to conjugated polymers. The photophysical, electrochemical, thermal stability, and photovoltaic performance of these polymers were investigated and compared with their thiophene analogs.

2. Experimental Section

2.1. Characterization

NMR spectra were recorded in CDCl₃ or 1,2-dichlorobenzene-d₄ using a Varian Unity Inova spectrometer at a resonance frequency of 399.96 MHz for ¹H and 100.58 MHz for ¹³C. UV-Vis spectra were measured using a Varian Cary 5000 Spectrometer. Gel permeation chromatography (GPC) (Waters Breeze HPLC system with 1525 Binary HPLC Pump and 2414 Differential Refractometer) was used for measuring the molecular weight and polydispersity index (PDI). Chlorobenzene was used as eluent and commercial polystyrenes were used as standard. The differential scanning calorimetry (DSC) analysis was performed under a nitrogen atmosphere (50 mL min⁻¹) using a TA Instruments DSC 2920 at a heating rate of 10 °C min⁻¹, calibrated with the melting transition of indium. Cyclic voltammetry (CV) measurements were carried out under argon in a three-electrode cell using 0.1 M Bu₄NPF₆ in anhydrous CH₃CN as the supporting electrolyte. The polymer was coated on the platinum-working electrode. The CV curves were recorded with reference to an Ag quasi-reference electrode, which was calibrated using a ferrocene/ferrocenium (Fc/Fc⁺) redox couple (5.1 eV below the vacuum level) as an external standard. The E_{1/2} of the Fc/Fc⁺ redox couple was found to be 0.37 V versus the Ag quasi-reference electrode. Therefore, the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) energy levels of the copolymers can be estimated using the empirical equation $E_{\text{HOMO}} = -(E_{\text{ox}}^{\text{ox}} + 4.73)$ eV and $E_{\text{LUMO}} = -(E_{\text{red}}^{\text{red}} + 4.73)$ eV, respectively, where $E_{\text{ox}}^{\text{ox}}$ and $E_{\text{red}}^{\text{red}}$ stand for the onset potentials for oxidation and reduction relative to the Ag quasi-reference electrode, respectively.

2.2. Synthesis

2.2.1. Synthesis of 3,6-Di(furan-2-yl)-s-tetrazine (2)

Fresh hydrazine monohydrate (10 g, 200 mmol) was slowly added at room temperature to a mixture solution of 2-cyanofuran (9.3 g, 100 mmol) and sulfur (1.93 g, 60 mmol) in anhydrous ethanol (50 mL). Then the solution was refluxed for 2 h before cooled in ice-bath. The light yellow powder (1) was collected by filtration and dissolved in a mixture of ethanol/chloroform (30/50 mL). Isoamyl nitrite (25 mL) was added and the solution was stirred overnight. Then, the solution was refluxed for 30 min and solvent was removed by rotary evaporator. The red solid was washed with methanol, purified by column chromatography with THF/toluene (1/2) and then further purified by recrystallization from isopropyl alcohol to yield a red crystal (5.5 g, 51% yield). ¹H NMR

(CDCl₃): δ(ppm) = 7.80 (d, 2H), 7.66 (d, 2H), 6.70 (dd, 2H). ¹³C NMR (CDCl₃): δ(ppm) = 157.58, 147.38, 147.20, 116.66, 113.03.

2.2.2. Synthesis of 3,6-Bis(5-bromofuran-2-yl)-s-tetrazine (3)

N-Bromosuccinimide (7.48 g, 42.0 mmol) was added into 2 (4.28 g, 20.0 mmol) in dichloromethane (100 mL) containing 1.0 g silica gel. The mixture was stirred at RT for 16 h and 40 °C for 6 h, and then the solvent was removed and the resulting red powder was dissolved in toluene to filter off silica gel at hot. The solution was concentrated and cold down for recrystallization to get red crystal (1.8 g, 24% yield). ¹H NMR (CDCl₃): δ(ppm) = 7.60 (d, 2H), 6.64 (d, 2H). ¹³C NMR (CDCl₃): δ(ppm) = 156.79, 148.73, 129.04, 118.85, 115.16.

2.2.3. General Procedure for Stille Reaction

Compound 3 (0.500 mmol), the trimethyltin monomer of BDT or CPDT (0.500 mmol), dimethylformamide (DMF; 1.0 mL), and toluene (15 mL) were added to a 25 mL flask. The system was purged with argon under vacuum, and then tetrakis(triphenylphosphine)-palladium (0) (0.06 g, 0.006 mmol) was added in a glovebox. The solution was stirred and refluxed for 24 h under Ar. After cooling down to room temperature, the solution was precipitated into acetone and the polymer was Soxhlet extracted with methanol, hexanes, and finally collected with chloroform. For poly[2,6-(4,8-bis(3-pentylundecyl) benzo[1,2-b:4,5-b']dithiophene-alt-5,5'-(3,6-bis(furan-2-yl)-s-tetrazine)] (PBDTFTz) (yield: 90%), ¹H NMR (1,2-dichlorobenzene-d₄, 150 °C): δ(ppm) = 7.97 (s, 2H), 7.81 (br, 2H), 7.63 (br, 2H), 3.30 (br, 4H), 1.20–2.08 (m, 50H), 0.90–1.12 (m, 12H). GPC analysis: $\bar{M}_n = 52\,200$ g mol⁻¹, $\bar{M}_w = 146\,840$ g mol⁻¹, PDI = 2.81. For poly[2,6-(4,4-bis(2-ethylhexyl-4H-cyclopenta[2,1-b:3,4-b']dithiophene-alt-5,5'-(3,6-bis(furan-2-yl)-s-tetrazine)] (PCPDFTz) (yield: 75%), ¹H NMR (1,2-dichlorobenzene-d₄, 150 °C): δ(ppm) = 7.54 (s, 2H), 7.49 (s, 2H), 6.67 (s, 2H), 2.06 (br, 4H), 0.95–1.20 (br, 16H), 0.61–0.80 (br, 12H). GPC analysis: $\bar{M}_n = 10\,679$ g mol⁻¹, $\bar{M}_w = 18\,621$ g mol⁻¹, PDI = 1.74.

2.2.4. Thermal Decomposition

Polymer was added into a 25 mL flask which was then purged with argon. The flask was then heated in an oil bath at 280–300 °C for 20 min. After cooling, the crude product was analyzed with NMR. The dinitrile product from PBDTFTz: ¹H NMR (CHCl₃): δ(ppm) = 7.71 (s, 2H), 7.19 (d, 2H), 6.71 (d, 2H), 3.08 (m, 4H), 1.71 (m, 4H), 1.52 (m, 2H), 1.42–1.20 (br, 44H), 0.80–0.97 (m, 12H). The dinitrile product from PCPDFTz: ¹H NMR (CHCl₃): δ(ppm) = 7.27 (s, 2H), 7.14 (d, 2H), 6.53 (d, 2H), 1.92 (m, 4H), 1.85–2.08 (m, 16H), 0.58–0.80 (m, 6H).

2.2.5. Device Fabrication and Characterization

Patterned indium tin oxide (ITO) glass substrates were cleaned with detergent before sonicated in electronic (CMOS) grade acetone and isopropyl alcohol for 15 min. The organic residue was further removed by treating with UV-ozone for 10 min. Then, a thin layer of poly(3,4-ethylenedioxythiophene)/poly(styrenesulfonate) (PEDOT:PSS) (Clevios P, H. C. Starck, 45 nm) was spincoated and dried for 1 h at 120 °C. A blend of polymer and [6,6]-phenyl C71 butyric acid methyl ester (PC₇₁BM) (ADS

was dissolved in solution containing different amount of diiodooctane. The solution was filtered and spin-coated on the top of PEDOT:PSS layer. 1.0 nm of LiF and 100 nm Al layer were thermally evaporated through a shadow mask at a pressure of 5×10^{-7} mbar in a Boc Edwards Auto 500 System. The active area of the devices is 50 mm². The current–voltage (*I*–*V*) characteristics were measured with a Keithley 2400 digital source meter under simulated air mass (AM) 1.5 solar irradiation of 100 mW cm^{−2} (Sciencetech Inc., SF150). The light intensity was calibrated with a power meter (Gentec Solo PE Laser Power & Energy Meter).

3. Results

3.1. Monomer and Polymer Synthesis

As shown in Scheme 1, a modified sulfur-assisted Pinner approach was employed to prepare bisfuran-*s*-tetrazine (FTz).^[8] First, 2-cyanofuran was treated with hydrazine monohydrate in the presence of sulfur to form 3,6-di(furan-2-yl)-1,4-dihydro-*s*-tetrazine (**1**) as light yellow powder, which was directly aromatized to 3,6-di(furan-2-yl)-*s*-tetrazine (**2**) without further purification, and was then brominated to 3,6-bis(5-bromofuran-2-yl)-*s*-tetrazine (**3**) with *N*-bromosuccinimide in chloroform using silica gel as a catalyst. This reaction is completed in 1 d at room temperature and we noticed that side reactions occurred when the reaction was conducted at 40 °C. This monomer was copolymerized by Stille coupling reaction with the bis(trimethyltin) monomers of the two electron-donating building blocks, cyclopenta[2,1-*b*:3,4-*b'*]dithiophene (CPDT) and benzo[1,2-*b*:4,5-*b'*]dithiophene (BDT) to offer two polymers (PCPDFTz and PBDFTz). These two building blocks have showed a strong electron donating property and the resulting polymers with an electron accepting block possess a narrow bandgap and displayed a high performance as solar cell materials.^[9] GPC reveals that the number average molecular weights (\bar{M}_n) of the polymers are 10.7 kDz for PCPDFTz and 52.2 kDa PBDFTz (Table 1). As expected, these

two polymers show good solubility in common organic solvents, such as toluene, chloroform, and chlorobenzene. For comparison, the structure of two bithiophene-*s*-tetrazine based polymers was also shown in Scheme 1. Depending on the location of hexyl side chain at 3- or 4-position of the thiophene linkage, these polymers are named as PCPDTTz-in and PCPDTTz-out.^[4] Although PCPDFTz has the “naked” bridging unit, while the thiophene analogs have a hexyl group attached to the bridging unit, they showed similar solubility in organic solvents, confirming the furan unit promoted solubility of the polymers.

3.2. Thermal Decomposition

The thermal stability of these two polymers was investigated by DSC and the curves are shown in Figure 1. Both PCPDFTz and PBDFTz are stable up to 220 °C, and start to decompose at 236 and 263 °C, respectively, associated with the breaking of *s*-tetrazine linkage.^[4] It is interesting that PBDFTz shows better thermal stability than PCPDFTz although their decompositions are based on the same mechanism, i.e., the breaking of *s*-tetrazine linkage. Upon cooling from 300 to 30 °C, a sharp exothermal peak appeared at 109.8 °C in the DSC curve of PBDFTz, which was attributed to the crystallization of the decomposition product of PBDFTz. NMR analysis (see Supporting Information, Figure S5,S6) showed that the decomposition product is highly pure (>90%) dinitrile compound as that of the thiophene polymers.^[4] In this process, the *s*-tetrazine ring was broken with the cleavage of the N=N unit to form a N₂ molecule. The decomposition product from PCPDFTz is a brown oil at room temperature so it will not crystallize in the testing temperature range.^[4]

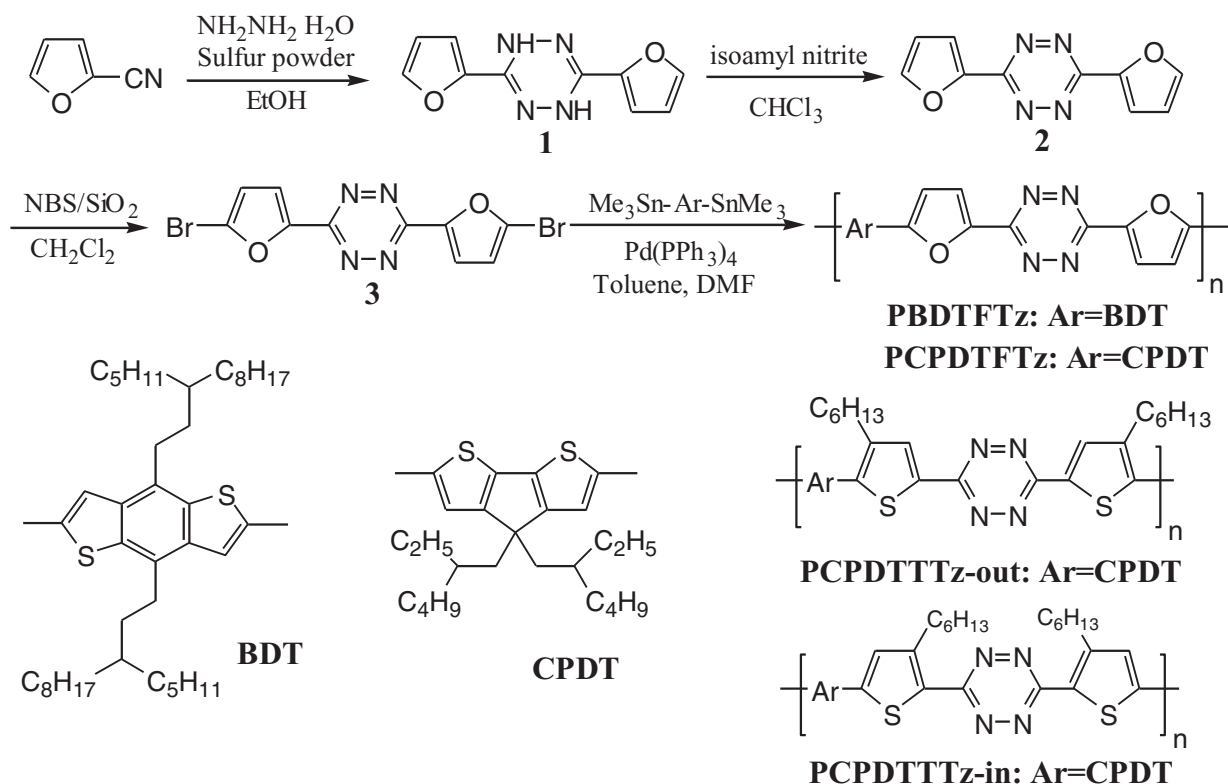
3.3. Optical Properties

The solution UV–Vis absorption spectra of these two polymers in chlorobenzene were compared with their film spectra

Table 1. Polymer characterization.

Polymers	\bar{M}_n ^{a)} [kDa]	PDI ^{a)}	Solution λ_{\max} ^{b)} [nm]	Film λ_{\max} [nm]	$E_g^{\text{opt c)}$ [eV]	$E_{\text{os}}^{\text{red d)}$ [V]	$E_{\text{os}}^{\text{ox d)}$ [V]	LUMO ^{e)} [eV]	HOMO ^{e)} [eV]
PBDFTz	52.2	2.81	518, 560	509, 557	1.94	−0.98	0.91	−3.75	−5.64
PCPDFTz	10.7	1.74	551, 592	538	1.86	−0.89	0.87	−3.84	−5.60
PCPDTTz-out	29.4	1.51	562	560	1.66	−0.82	0.87	−3.91	−5.60
PCPDTTz-in	48.0	1.82	592	571	1.73	−0.87	0.77	−3.86	−5.50

^{a)}Number average molecular weight and polydispersity index (GPC versus polystyrene standards in chlorobenzene); ^{b)}solution absorption in chlorobenzene; ^{c)}optical energy gap estimated from the onset of the UV curve measured in thin film; ^{d)}onset potentials from CV measurements of thin films in a 0.1 M Bu₄NPF₆/CH₃CN solution versus Ag; ^{e)}estimated from LUMO = $-(E_{\text{os}}^{\text{red}} + 4.73)$ eV and HOMO = $-(E_{\text{os}}^{\text{ox}} + 4.73)$ eV.



Scheme 1. Synthesis of FTz monomer, polymer, and the structure of the two TTz-based polymers.

in Figure 2a,b. Both polymer solutions have two close laying maxima. The solution of PBDTFTz shows maximum absorption at 518 and 560 nm, while that of PCPDFTz shifted to

longer wavelength at 551 and 592 nm due to stronger electron donating capability of CPDT units. Compared with solution, thin films of both polymers show a band with an

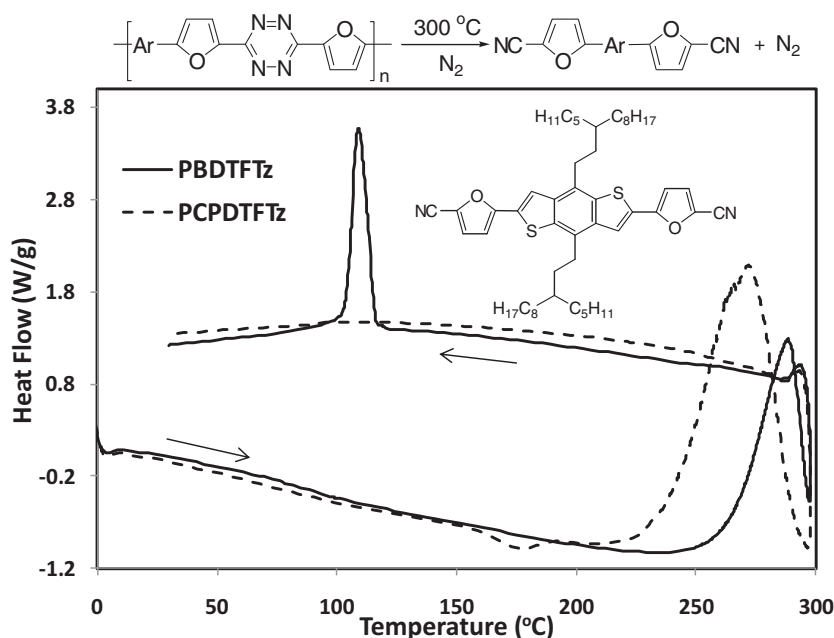


Figure 1. Thermal decomposition reaction and DSC curves (0–300–30 °C scan) of polymers at a heating rate of 10 °C min^{−1} in nitrogen. Inset shows the structure of decomposition product from PBDTFTz.

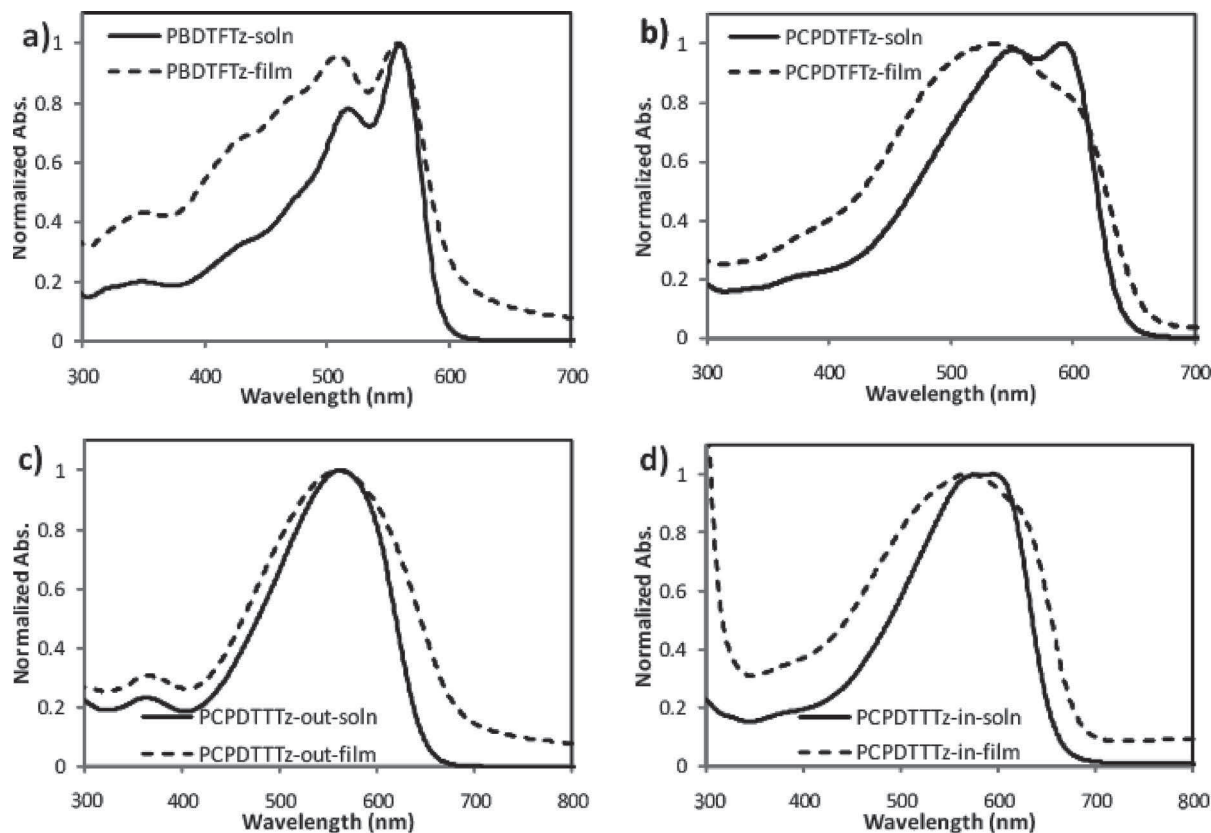


Figure 2. UV absorption spectra of (a) PBDTFTz, (b) PCPDFTTz, (c) PCPDTTTz-out, and (d) PCPDTTTz-in in dilute chlorobenzene solution or in thin film form.

enhanced absorption at short wavelengths. This phenomenon is unique, and contrary to that commonly observed for conjugated polymers, which usually show a red-shifted UV spectrum from solution to film due to the close packing of main chain in solid state. We believe this is related to the unique chain conformation of these two polymers and it will be further discussed in the following section.

3.4. Electrochemical Study

The frontier molecular orbital energy levels of these polymers were studied by CV as shown in Figure 3. The HOMO and the LUMO energy levels are summarized in Table 1 and compared with these of TTz analogs in Figure 4.^[4] PBDTFTz shows a broader electrochemical bandgap than PCPDFTTz (1.89 eV vs. 1.76 eV), agreeing well with their optical bandgaps at 1.94 and 1.85 eV, respectively. The bigger bandgap of PBDTFTz mainly comes from its higher LUMO energy level associated with the lower electron donating ability of BDT unit. On the other hand, the three copolymers of CPDT with FTz, TTz-in, and TTz-out show similar energy levels. It means that both thiophene and furan bridges have a similar effect on energy levels of the polymers.^[7]

3.5. Photovoltaic Performance

Polymer solar cell devices are fabricated based on the blends of these polymers with PC₇₁BM. Different fabrication conditions are tested and the best photovoltaic performance for each polymer is shown by the *J*-*V* curve in Figure 5. Detailed device processing and characterization data are provided in Table 2. Devices D1, D2, and D4 from PBDTFTz, PCPDFTTz, and PCPDTTTz-in give similar modest power conversion efficiency (PCE) of $\approx 0.7\%$, while the PCE of D3 from PCPDTTTz-out reaches 3.2%. This difference mainly comes from the short-circuit current density (J_{sc}). The device D1, D2, and D4 has a $J_{sc} \approx 4 \text{ mA cm}^{-2}$ while D3 shows a J_{sc} up to 10.2 mA cm^{-2} . Polymer PCPDTTTz-out and PCPDTTTz-in have similar structures, but the obtained open circuit voltage (V_{oc}) from their solar cell devices (D3 and D4) is 0.81 and 0.69 V. They agree well with the offset of their HOMO energy levels (-5.60 and -5.50 eV, respectively) and the LUMO of PC₇₁BM. The energy level difference between these two polymers is attributed to their special chain conformation due to the different steric hindrance created by the alkyl substituted group at the 4- or 3-position of the thiophene unit.^[4b] However, the lower V_{oc} of the two furan based polymers cannot be

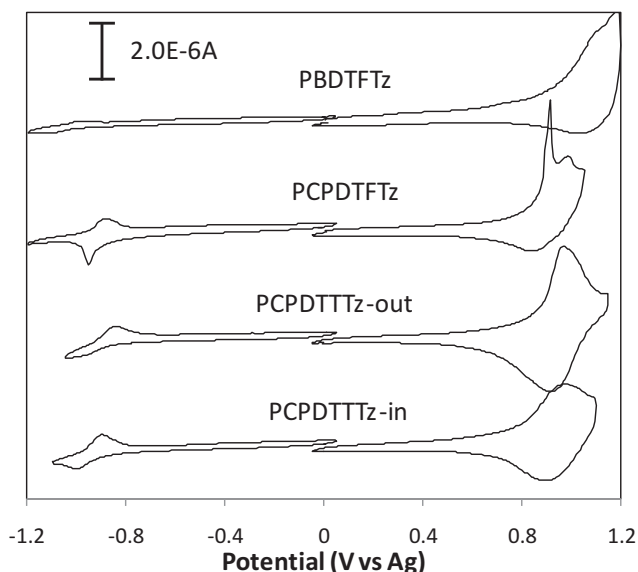


Figure 3. Cyclic voltammograms of polymer films on platinum electrode in $\text{Bu}_4\text{NPF}_6/\text{CH}_3\text{CN}$ solution.

explained by the chain conformation alone. In addition to the difference between the HOMO of polymer and LUMO of PCBM, V_{oc} is also closely related to the interface interaction between their domains, which will influence the charge photogeneration efficiency and recombination. We believe the loose packed structure of furan based polymers will lead to inefficient charge transport and increase charge recombination as will be discussed in the following section.^[10] And this may lower the V_{oc} of the corresponding devices.

4. Discussion

4.1. Influence of Steric Hindrance on Chain Stacking

The motivation of our design in this work to use furan instead of thiophene to bridge the electron donating and accepting units is the higher solubility of furan based

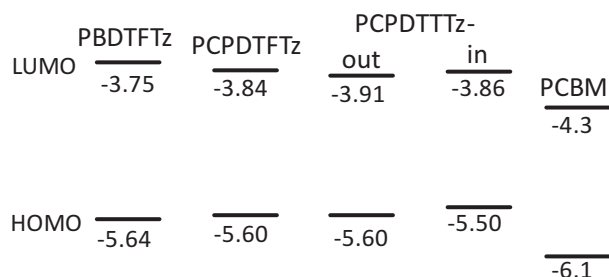


Figure 4. Energy levels of PBDTFTz, PCPDFTTz, PCPDTTz-out, and PCPDTTz-in.

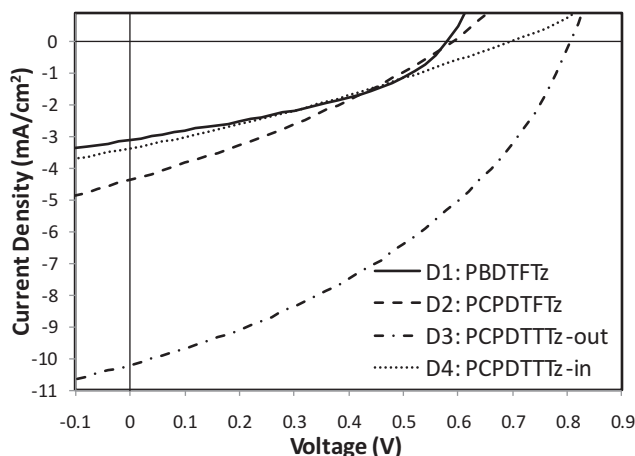


Figure 5. J - V curve of polymer:PC $_{71}$ BM (weight ratio 1:2) bulk heterojunction solar cells under a simulated AM 1.5 G irradiation of 100 mW cm^{-2} . See Table 2 for device fabrication conditions.

polymers. So less alkyl side chains are needed to retain a similar solubility and solution processibility. This will also result in polymers with higher content of functional main chain, which usually means higher optical absorption and better photovoltaic performance. However, the two furan polymers (PBDTFTz and PCPDFTTz) showed much poorer PCE than PCPDTTz-out. We believe this is attributed to the difference in chain conformations of these two types of polymers as illustrated in Scheme 2. The furan or thiophene bridging unit is possible to take both *cis*- and *trans*-conformations regarding its orientation related to the adjacent CPDT unit. Obviously the most stable orientation of these bridging units is the *trans*-conformation as shown in the left side of Scheme 2 due to the lower steric hindrance, where no any substitution on the bridge units will overlap with the hydrogen atom on CPDT unit. However, there is significant difference in *cis*-conformation between the furan and thiophene polymers. In PCPDFTTz, the protons on the almost “bare” furan ring will create very low steric hindrance for the *cis*-conformation. So the furan ring will take both *cis*- and *trans*-conformations along the main chain, leading to a poor stacking of the polymer chain in the solid state. This is also the case for PCPDTTz-in, where the hexyl group is at the 3-position and faces to the tetrazine ring, does not overlap with any substitute group due to the “bare” structure of tetrazine ring. However, in PCPDTTz-out, the hexyl group is at the 4-position and the first methylene unit of the hexyl group will overlap with the proton on the CPDT unit in the *cis*-conformation, creating a substantial steric effect.^[4b] So the main chain of PCPDTTz-out will predominately take *trans*-conformation to form a regioregular chain structure. It will result in a close chain stacking in solid state. Therefore, we believe the poor photovoltaic performance of the furan polymers as

Table 2. Summary of the device fabrication conditions and photovoltaic performance.

Devices	Polymer ^{a)}	Solvent ^{b)}	Temp ^{c)} [°C]	J_{sc} [mA cm ⁻²]	V_{oc} [V]	Fill Factor (FF) [%]	PCE [%]
D1	PBDTFTz	CHCl ₃ (1.5)	21	3.10	0.58	39.2	0.71
D2	PCPDFTTz	TCB (0.0)	21	4.37	0.59	30.7	0.79
D3	PCPDTTTz-out	DCB (0.0)	21	10.2	0.81	38.7	3.20
D4	PCPDTTTz-in	DCB (3.0)	80	3.36	0.69	29.4	0.68

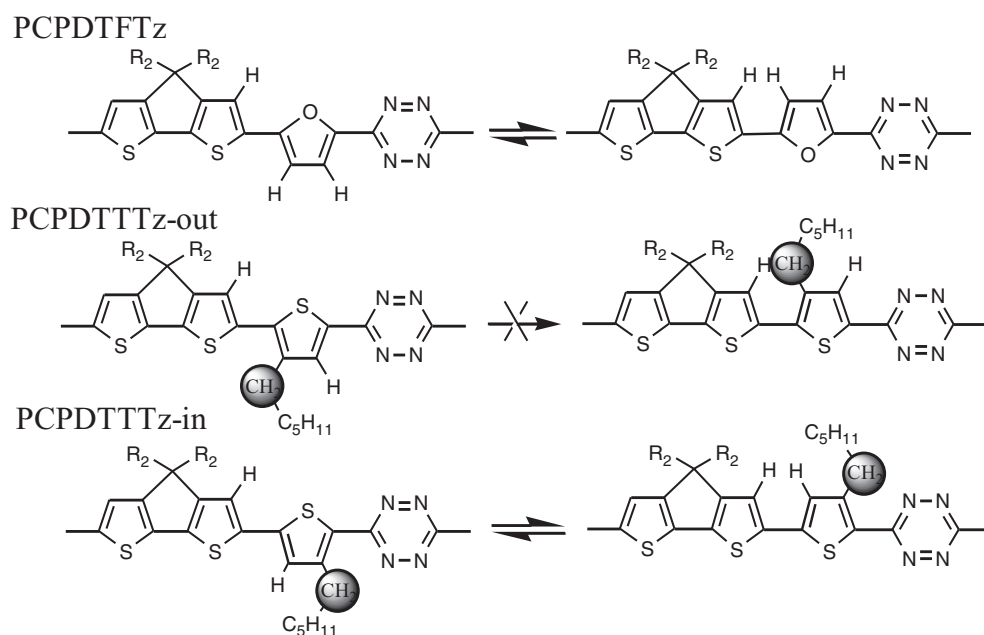
^{a)}Polymer to PC₇₁BM weight ratio = 1/2; ^{b)}volume ratio of 1,8-diiodooctane is shown in parentheses, DCB = 1,2-dichlorobenzene, TCB = 1,2,4-trichlorobenzene; ^{c)}device fabrication temperature.

well as PCPDTTTz-in is attributed to their random *cis*- and *trans*-orientation of the furan and thiophene linkages along the main chain. The presence of this random orientation might disturb chain conjugation and disrupt efficient π - π stacking. This loose chain stacking will lead to an inefficient charge transport in the polymer phase, which will result in decreased V_{oc} , J_{sc} , and modest PCE.^[11]

4.2. Evidence from UV Spectra

This feature can be verified by comparing their solution and film UV spectra as shown in Figure 2. It is interesting to find that only the polymer with the best photovoltaic performance, PCPDTTTz-out shows a slightly broadened peak in film with the absorption at the long wavelengths enhanced more than the short wavelengths, while all the others show a more significantly enhanced absorption at short wavelengths, indicating a shorter effective conjugation

length of these three polymers in solid states than in solution.^[11] This phenomenon appears contradictory to the behavior of the most high performance polymer solar cell materials. They usually show red-shifted absorption band from solution to thin film.^[12] We believe this is related to the random distribution of *cis*- and *trans*-conformation of these three polymers due to the low steric hindrance. It retarded the close chain packing in solid state and resulted in a lower effective conjugation length. However, this explanation seems not agree with the general understanding about the steric hindrance effect of conjugated polymers for organic electronics, where less steric hindrance is usually preferred to prevent chain twist.^[6] We believe this is due to the unique structure of s-tetrazine whose bare aromatic ring does not create any steric effect with adjacent groups. This may imply that, for organic semiconductor materials, certain degree of steric effect is needed to get optimized regioregular conformation as rr-P3HT, while too much steric hindrance

Scheme 2. Illustration of the steric effect on the *cis*- and *trans*-conversion of the polymers.

may create undesired chain twist to reduce the planarity of the conjugated main chain.^[6]

5. Conclusion

A new FTz monomer was designed and synthesized, which was then copolymerized with CPDT or BDT comonomers to afford two low bandgap polymers. These two polymers showed different optical absorption, bandgap, and energy levels associating with the different electron donating capability of the electron rich units. DSC studies revealed that they decomposed to dinitrile compounds in a high yield (>90%) at $\approx 260^\circ\text{C}$ with the break of s-tetrazine linkage. Photovoltaic devices based on these polymers gave modest PCEs of $\approx 0.7\%$, which was dramatically lower than the PCE of 3.2% for PCPDTTz-out, a thiophene analog. This was explained by inefficient chain conjugation and stacking in the solid state due to the existence of both *cis*- and *trans*-orientations of the furan units in the main chain.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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