The Preparation of 3,6-Bis(3-hexylthien-2-yl)-*s*-tetrazine and Its Conjugated Polymers

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Received 1 April 2011; accepted 11 May 2011 DOI: 10.1002/pola.24774 Published online 31 May 2011 in Wiley Online Library (wileyonlinelibrary.com).

ABSTRACT: We demonstrated, for the first time, that 3,6-bis(3-hexylthien-2-yl)-s-tetrazine (TTz) with hexyl group at the 3-position of thiophene rings can be prepared using a modified sulfur-assisted Pinner synthesis. Although the hexyl group creates large steric hindrance to the tetrazine ring formation reaction, and the reaction under a traditional condition only produces trace amount of the target product, the yield of this reaction under a modified reaction condition using anhydrous hydrazine at 68 °C can reach 65%. Two new copolymers of the resulting TTz and hexyl- or 2-ethylhexyl-substituted cyclepenta-dithiophene have been prepared. The polymers show a broader light absorption in film than in solution attributing to the large distribution of effective conjugation length of poly-

mer chain due to the existence of both cis- and trans-orientations of the 3-hexylthiophene units in the planar polymer chain in solid state. Although the polymers show a narrow band gap and a deep HOMO level, which are desirable for generating an efficient light absorption and a larger open circuit voltage (V_{oc}) of the resulting solar cell devices, the device performance is not as good as expected. It is attributed to the random distribution of the cis- and trans-conformations along the polymer chain. © 2011 Wiley Periodicals, Inc.[§] J Polym Sci Part A: Polym Chem 49: 3374–3386, 2011

KEYWORDS: bulk heterojunction; conjugated polymer; narrow band gap; *s*-tetrazine; steric hindrance; solar cell

INTRODUCTION s-Tetrazine (Tz) in conjugated molecules is one of the most electron-deficient moiety with the electronpulling ability equivalent to tetranitrophenyl unit.¹ Owing to the successful work on developing sulfur-assisted Pinner synthesis of Tz unit in conjugated molecules by Abdel-Rahman,^{2,3} and the recent extensive study on the synthesis of a wide range of tetrazines by Audebert,⁴ the development of new conjugated Tz structures in conjugated small molecules¹⁻⁴ and polymers has achieved significant progresses.^{4(a),5} These materials showed a great potential for the use in optical and electronic devices such as nonlinear optical devices,⁶ sensors,⁷ and smart windows.⁸ The highly electron-deficient property of Tz unit is extremely attractive for constructing push-pull structures in pendent groups for nonlinear optical applications^{1(a),6} and inside polymer main chains for solar cell applications.⁹ Because of the extremely strong electron pulling effect of Tz, the resulting polymers with this push-pull structure have a narrow band gap and deep HOMO level,⁹ which enhance sun light absorption and promote open circuit voltage $(V_{\rm oc})$ of solar cell devices. Although a few different approaches can be used to prepare Tz, which are summarized in a recent review article by Audebert,^{1(a)} the sulfur-assisted Pinner synthesis appears the most practicable way to produce Tz unit in conjugated aromatic molecules such as dithienyl-*s*-tetrazine.¹⁻⁴ Furthermore, to further adjust the properties of the final product, such as solubility and processability, it is desired to introduce an alkyl group to the 3- or 4-position of the thiophene ring as shown in Scheme 1.

Recently, we have successfully prepared a TTz compound with the hexyl group at the 4-position, 3,6-bis(4-hexylthien-2-yl)-stetrazine) (TTz-6_{out}) using the sulfur-assisted Pinner synthesis.⁹ After bromination, this molecule was copolymerized with 2,6-bis(trimethylstannane) monomer of 4,4-dihexyl-4H-cyclepenta[2,1-b:3,4-b']dithiophene) (CPDT) by Stille coupling reaction to yield PCPDTTTz-6:6_{out} (Scheme 1), where the first 6 in the suffix represents hexyl group on CPDT, and the second 6 with a subscript "out" represents hexyl group at the 4-position of thiophen ring, which faces away from the Tz ring. It is used to distinguish the hexyl group at the 3-position, which faces toward Tz ring in poly[2,6-(4,4-dihexyl-4H-cyclepenta[2,1b:3,4-b']dithiophene)-alt-5,5'-(3,6-bis(3-hexylthien-2-yl)-s-tetrazine)] (PCPDTTTz- $6:6_{in}$), which will be reported in this article. This out-polymer (PCPDTTTz-6:6_{out}) was tested for polymer solar cell applications and devices with power conversion efficiency (PCE) up to 5.4% have been achieved,^{9(a)} indicating a high potential of the Tz polymers for solar cell applications.

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Journal of Polymer Science Part A: Polymer Chemistry, Vol. 49, 3374–3386 (2011) © 2011 Government of Canada. [§]Exclusive worldwide publication rights in the article have been transferred to Wiley Periodicals, Inc.



SCHEME 1 Structures of TTz monomers and polymers, the suffix 6 with a subscript "out" or "in" in the sample name represents hexyl group on the thiophene ring which faces away from or toward the Tz ring.

An advantage of the in-polymers (PCPDTTTz-6:6_{in}) over the out-counterpart is that the alkyl group will provide a protection to the Tz ring from undesired side reactions. It is well known that Tz is a reactive aromatic unit and many high nitrogen-containing tetrazines are widely used as energetic materials.¹⁰ The Tz unit in conjugated molecules can take part in Diels-Adler cycloaddition with a double bond to lose a N₂ molecule.¹¹ This reaction even occurs with fullerene derivatives at elevated temperatures.¹² Although this reaction is desired for the preparation of many special chemicals,¹¹ it becomes a concern when a Tz containing polymer is used together with a fullerene derivative such as [6,6]phenyl-C₆₁-butyric acid methyl ester (PCBM) for solar cell applications. The solution of the mixture of a polymer with PCBM is usually prepared and coated at a high temperature to form a high quality film with a controlled morphological structure.9 Our preliminary test showed this process could induce cycloaddition of Tz ring with C_{60} when the temperature reached 110 °C. The conversion of this reaction in

ortho-dichlorobenzene (o-DCB) can reach ~20% in 1 h at this temperature for the out-polymer. This reaction will degrade the structure and property of the polymer and must be prevented or controlled in the device fabrication. Obviously, we can expect to reduce this undesired reaction for the in-polymer (PCPDTTTz-6:6_{in}), where the Tz ring is surrounded by the hexyl groups to obtain a steric protection to prevent this side reaction (Scheme 1). Our test indeed showed that the reaction rate of PCPDTTTz-6:6_{in} with C₆₀ is about 28-fold lower than the "out" analog under the same condition.

Unfortunately, this steric effect also makes the preparation of the corresponding monomer, 3,6-bis[3-hexylthien-2-yl]-s-tetrazine (TTz- 6_{in}) extremely difficult. This synthesis has to go through dihydrotetrazine for any possible approaches, with two examples shown in Scheme 2 for the Pinner and Stolle syntheses.^{2,13} In these reactions, a hydrazine molecule has to approach the carbon atom of the cyano group or oxadiazole group, respectively. The alkyl substituent at the 3-position of



SCHEME 2 Pinner and Stollé synthesis for the preparation of tetrazines.



SCHEME 3 Synthetic approach for the preparation of the TTz- Br_2-6_{in} monomer using the sulfur-assisted Pinner synthesis.

the thiophene ring will obviously make this process more difficult than at the 4-position. Although the one with a methyl substitution at the 3-position appeared possible for Stollé synthesis,¹⁴ we do not find in the literature any synthesis of similar structure with the substituent at this position larger than a methyl group.^{1(a)} Furthermore, a methyl group attached to this position will make the nitrile inert in the sulfur-assisted Pinner synthesis.³ Interestingly, we found that TTz-6_{in} with a hexyl group at 3-position can be prepared in a reasonable yield by the sulfur-assisted Pinner synthesis under a modified reaction condition. Therefore, in this article, we will report our approach to optimize the synthesis of TTz-6_{in}, the preparation of the corresponding polymers and their characterizations for solar cell applications.

RESULTS AND DISCUSSION

The Preparation of TTz-6_{in} Monomer

Based on the reasons mentioned above, the sulfur-assisted Pinner synthesis was chosen for the preparation of TTz-6_{in}. Therefore, a synthesis approach as shown in Scheme 3 was designed. The synthesis started from 2-bromo-3-hexylthiophene, which was converted to 3-hexylthiophene-2-carboxaldehyde through a lithiation reaction.¹⁵ This product was further converted to 2-cyano-3-hexylthiophene by a two-step reaction with hydroxylamine and then acetic anhydride. Although this process gave a high yield, the obtained product always contained \sim 7% of 2-cyano-4-hexylthiophene isomer, which was produced during the lithiation reaction. This isomer was hard to remove in the aldehyde form, but most of this impurity can be removed in the nitrile form by a column chromatographic purification with the content reduced to less than 3%. It is important to remove this isomer as much as possible, because the existence of this isomer will reduce the regioregularity of the final conjugated polymer and hamper its chain stacking capability.

The obtained 2-cyano-3-hexylthiophene was then converted to TTz-6_{in} using the sulfur-assisted Pinner synthesis followed by an aromatization. The sulfur-assisted Pinner synthesis has been successfully used to produce TTz-6_{out} in a high yield in our previous work.^{9(a)} However, the reaction to prepare TTz-6_{in} is much more difficult. Under a similar reaction condition by using hydrazine monohydrate in anhydrous ethanol at 78 °C in our initial tests, we only observed a trace amount of the desired product in the reaction. We attributed it to the high steric hindrance created by the adjacent hexyl group to the reaction on the cyano group. It is interesting to find that a reaction at 70 °C by using anhydrous hydrazine gave a much higher yield, and therefore, this reaction for the formation of dihydro-s-tetrazine was monitored by ¹H NMR. In this case, 2-cyano-3-hexylthiophene, sulfur, and anhydrous hydrazine at molar ratios of 1.0:0.6:4.0 were added into 0.6 mL of methanol- d_4 in a capped NMR tube. The reaction solution was placed in a water bath with temperature controlled subsequently at 22 °C (for 1 h), 50 °C (for 1 h) and then 70 °C with occasional shaking. NMR spectra of the reaction solution were collected at different times and compared with the predicted spectrum of the two possible dihydrotetrazine products in Figure 1.

The ¹H NMR spectra showed that the molecular structure of 2-cyano-3-hexylthiophene did not have obvious change when the reaction solution was kept at room temperature and then at 50 °C for 1 h. But the sulfur powder in the solution was completely disappeared after 1 h reaction at 50 °C, indicating that most of the sulfur had reacted with hydrazine to form the sulfur-hydrazine adduct as indicated in the reaction mechanism proposed by Audebert (Scheme 4).^{4(b)} Although the formed adduct did not react with the nitrile at 50 $^\circ$ C, it readily reacted at 70 °C as indicated by the appearance of a pair of new peaks at 7.29 (5') and 6.91 (4') ppm. Their intensities steadily increased with time over the next 17 h. Meanwhile, another pair of new peaks appeared in 7 h at 7.40 (5") and 6.93 ppm (4") and slowly increased in intensity. These two pairs of the peaks might be attributed to 1,4and 1,2-isomers of the dihydrotetrazine. However, to accurately assign them is difficult. One possible way is to use ¹⁵N NMR, where the peak of two tetrazine N in the 1,4-isomer will be a doublet with a coupling constant of \sim 6.5 Hz due to the two-bond ¹⁵N—N—¹H coupling,¹⁶ while this coupling does not exist in 1,2-isomer. But this measurement is impossible in solution due to the extremely low abundance of ¹⁵N. Therefore, we used the Advanced Chemistry Development C+H NMR prediction software to predict the spectra of 1,2and 1,4-isomers.¹⁷ The predicted spectrum of a 1:1 mixture of 1,2- and 1,4-isomers was shown in Figure 1(a). It indicates that the chemical shifts of the thiophene protons in 1,2-isomer is slightly higher than 1,4-isomer, probably due to the higher conjugation of 1,2-dihydro-s-tetrazine. As there is very good concordance between the predicted and the experimental spectra, we believe that we can reasonably assign the first pair of peaks (5' and 4') to 1,4-dihydro-s-tetrazine and second pair (5" and 4") to 1,2-dihydro-s-tetrazine. Furthermore, with the appearance of the second pair, a new



FIGURE 1 (a) Predicted ¹H NMR spectrum of 1:1 mixture of bis(3hexylthiophen-2yl)-1,2-dihydro-*s*tetrazine and bis(3-hexylthiophen-2yl)-1,4-dihydro-*s*-tetrazine by ACD software.¹⁷ (b) NMR spectra of the reaction solution taken at deferent reaction times at indicated temperatures.

peak of the α -protons in the hexyl group also emerged at a slightly higher frequency (2.85 ppm). This also suggests a higher conjugation of the molecule, consistent with the 1,2-dihydro-structure [see Fig. 1(a)].

The conversion rate to these two dihydrotetrazines was estimated by comparing the integral intensities of these two pairs of the peaks (5', 4' and 5", 4") with that of the methyl group at 0.89 ppm in the ¹H NMR spectra (Fig. 1). The result is plotted in Figure 2 along with the conversion rate of the starting material calculated from peak 5 and 4. It shows that conversion rate of the starting material steadily increases in 17 h and then levels off. The conversion to 1,4-dihydro-*s*-tetrazine shows the same trend but with lower values and reaches the maximum of 47% at 17 h. The difference between these two curves is obviously due to the formation of 1,2-isomer, as well as small amount of byproducts as indicated by the small peaks in Figure 1(b). After 17 h, the decrease of the 1,4-isomer peak intensities was more or less

equal to the increase of the 1,2-isomer, indicating 1,4-isomer was being slowly converted to 1,2-isomer in this period. It should be noted that peaks 5" and 4" completely disappeared when additional 3 equiv of anhydrous hydrazine was added at 42 h. Meanwhile the conversion rate to 1,4-dihydro-*s*-tetrazine dramatically increased from 40 to 66%. This result indicates that the 1,2-isomer is completely reverted to the 1,4-isomer under the assistance of excess hydrazine. It also means the presence of high concentrated hydrazine in the solution will depress the conversion of 1,4-isomer to 1,2-isomer.

Figure 2 also shows that the conversion of the starting material was leveled off after 17 h, but it resumed when extra hydrazine was added into the reaction. This result indicates that the cease of the reaction is due to the exhaustion of hydrazine. It should be noted that a large amount of gas released from the reaction in the initial 7 h. The gas turned wet pH paper blue, indicating the gas is mostly composed of



SCHEME 4 Reaction mechanism of the sulfur-assisted Pinner synthesis proposed by Audebert.^{4(b)}

ammonia. It means that the decomposition of hydrazine to ammonia competed with the Tz ring formation in this process. With the decrease of the hydrazine concentration, the ring formation reaction reduced its speed and almost stopped after 17 h. In this case, the addition of extra hydrazine into the reaction pushed the ring formation reaction forward again.

¹H NMR study of this reaction under different reaction conditions, for example, at 78 °C in methanol- d_4 , resulted in complex NMR spectra, indicating side reactions predominated. Reactions using hydrazine monohydrate at 70 °C only yielded a conversion to the desired product lower than 10% in 2 days. These results explain why our initial attempt for making TTz-6_{in} failed by reacting with hydrazine monohydrate at 78 $^\circ$ C, which was successfully used to prepare TTz-6_{out} isomer.^{9(a)} However, the reason behind this low conversion by the use of hydrazine monohydrate is not fully understood. NMR study showed the starting 2-cyano-3-hexylthiopene mostly remained in the reaction solution after 1 day at 70 °C, while the sulfur powder was consumed at the early stage of the reaction. This might indicate the presence of water in the reaction reduces the reactivity of the sulfurhydrazine adduct based on the reaction mechanism shown in Scheme 4.

Based on these observations, a new reaction was designed. Therefore, anhydrous hydrazine was added into the ethanol reaction solution in three portions (2, 1, and 1 equiv) at 0, 6, and then 12 h at 68 $^{\circ}$ C. The reaction was stopped at 20 h.

After cooling to room temperature, the solution turned to slurry, which was diluted with MeOH, filtered, and rinsed with MeOH to obtain a white powder. The ¹H NMR spectrum of the crude product shows a rather pure product (Fig. 3), indicating the selectivity of this reaction to the 1,4-isomer is high under this reaction condition. This result confirms our observation in the ¹H NMR study that the conversion of 1,4-



FIGURE 2 Conversion with the reaction time of the starting materials, and to the formation of 1,4- and 1,2-isomers calculated from NMR spectra shown in Figure 1.



FIGURE 3 NMR spectrum in C_6D_6 of the crude product from 2-cyano-3-hexylthiophene by the modified sulfur-assisted Pinner reaction.

isomer to 1,2-isomer is depressed by the presence of hydrazine. Similar phenomenon was also reported for another ring closure reaction leading to dihydro-*s*-tetrazine.¹²

The obtained white powder was then dissolved in 20 mL of $CHCl_3$ and was aromatized by isoamyl nitrite at 40 °C. The reaction was completed in 8 h. Recrystallization of the crude product in 2-propanol gave red shinning needle-like crystal in a yield of 65%. TTz-6_{in} was then brominated using *N*-bromosuccinimide (NBS) in the presence of a small amount of

silica gel in CH_2Cl_2 at room temperature to form the dibromo monomer, 3,6-bis{5-bromo-3-hexylthien-2-yl]-*s*-tetrazine (TTz-Br₂-6_{in}). It is worth to note that the aromatic proton of TTz-Br₂-6_{in} has a much smaller chemical shift (7.05 ppm) than its TTz-Br₂-6_{out} analogs (7.95 ppm).^{9(a)} The 3-H of the thiophene ring in TTz-Br₂-6_{out} is strongly deshielded by the Tz ring, hence, its peak shifted toward a higher frequency, while this effect does not apply to the 4-H in TTz-Br₂-6_{in}.



SCHEME 5 Reaction scheme for the preparation of the copolymers of TTz and CPDT by Stille coupling reaction.



FIGURE 4 DSC and TGA curves of PCDPTTTz-6: 6_{in} and PCDPTTTz-2,6: 6_{in} .

The Preparation and Characterization of the Polymers

TTz-Br₂-6_{in} was copolymerized with 2,6-bis(trimethylstan-nyl)-4,4-dihexyl-4*H*-cyclopenta[2,1-*b*:3,4-*b*']dithiophene and 2,6bis(trimethylstannyl)-4,4-bis(2-ethylhexyl)-4*H*-cyclopenta[2,1*b*:3,4-*b*']dithiophene by Stille coupling reaction to yield two polymers,⁹ PCPDTTz-6:6_{in} and PCPDTTz-2,6:6_{in}, respectively, as shown in Scheme 5. The structure of the polymers was confirmed by ¹H NMR. However, the NMR spectra of both the polymers had one aromatic proton peak missing when the spectrum was collected in o-DCB- d_4 . This is due to that the missing peak is overlapped with one of the solvent peaks. Both the proton peaks were observed in the spectrum collected in toluene- d_8 (see Supporting Information). Gel permeation chromatography (GPC) study showed that both polymers had a high-molecular weight with number-average molecular weights of 15.7 and 48.0 kDa for PCPDTTTz-6:6_{in} and poly[2,6-(4,4-bis(2-ethylhexyl-4H-cyclepenta[2,1-b:3,4b']dithiophene)-alt-5,5'-(3,6-bis(3-hexylthienyl-2-yl)-1,2,4,5tetrazine)] (PCPDTTTz-2,6: 6_{in}), respectively. The differential scanning calorimetry (DSC) analysis and thermal gravimetric analysis (TGA) under nitrogen [Fig. 4(a) and (b)] showed both polymers started to decompose at \sim 190 °C. It resulted in a broad exothermal peak at ${\sim}260$ °C in DSC curves and a stage with ${\sim}5\%$ weight loss from 200 to 300 $^\circ\text{C}$ in TGA curves. As discussed in our previous publications,⁹ this decomposition is due to the breaking of the Tz ring. We can see that the decomposition temperature of the in-polymer is similar to its out-counterpart,⁹ indicating the hexyl substituent at the 4-position will not create additional protection to the Tz ring in the polymers for thermal decomposition.

The Steric Effect on the Chain Conformation of the Polymers

The hexyl group at the 4- or 3-position of the thiophene ring in PCPDTTTz- $6:6_{out}$ or PCPDTTTz- $6:6_{in}$ might have a significant impact on the conformation of the polymer chains. As indicated in Scheme 6, the methylene unit of the hexyl group on the thiopene ring will overlap in the space with the hydrogen atom on the adjacent CPDT unit to create a high steric energy for the cis-orientation of the 4-hexylthiophene unit in PCPDTTTz- $6:6_{out}$. Therefore, only trans-conformation



SCHEME 6 Illustration of the cis- and trans-conformations of a repeat unit of PCPDTTTz-6:6_{out} and PCPDTTTz-6:6_{in}. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]



FIGURE 5 Models of the trans- and cis-conformations for the "out" and "in" isomers with minimized steric energy calculated by MM2 simulation.¹⁸

will be predominately taken in this polymer chain, resulting in a regioregular chain conformation. This feature is the same as that of regioregular poly(3-hexylthiophene). Relocation of the hexyl group to the 3-position of the thiophene ring in PCPDTTTz-6:6_{in} will eliminate this overlap as indicated in Scheme 6. Although the methylene unit might create some interaction with the lone pair on the nitrogen atom in Tz ring, the energy might be much smaller than overlapping with a hydrogen atom due to the smaller size of the lone pair. Therefore, this feature will offer the polymer a low steric energy for both the cis- and trans-orientations, and a random distribution of cis- and trans-conformations along the polymer chain will be taken for PCPDTTTz-6:6_{in}.

To verify this effect, the molecular mechanical MM2 method has been used to calculate the steric energy of the cis- and trans-conformations of a chain segment which includes the interaction of the methylene unit with the hydrogen atom in the out-polymer and with the lone pair in the in-polymer.¹⁸ Therefore, a simplified molecular model in Figure 5 was used for this calculation, where the hexyl group was represented by a methyl group to avoid unnecessary interference of the additional carbons in the side group. The trans- and cis-conformations of the out- and in-isomer models (out-trans, out-cis, in-trans, and in-cis) were simulated to obtain minimized steric energies, which are also listed in Figure 5.18 The calculation showed that the cis-conformation of the out-isomer possesses an extra high steric energy of 66.1 kcal/mol, while the three others have a similar low energy around 64.2 kcal/mol. This calculation confirmed that the low-energy trans-conformation will be predominated in the polymer chain of PCPDTTTz-6:6_{out}, while both the trans- and cis-conformations will be taken in PCPDTTTz-6:6_{in}.

Photovolatic Properties of the Polymers

The UV-vis spectra of the polymer solutions in chlorobenzene, toluene, and the polymer films are displayed in Figure 6. The spectra of PCPDTTz- $6:6_{in}$ show a maximum at 585 nm in chlorobenzene and 576 nm in toluene with a shoulder around 640 nm. The peak of the film becomes much broader with an increased intensity of the shoulder, indicating chain stacking occurred both in solution and solid state for this polymer. PCPDTTz- $2,6:6_{in}$ displays similar UVvis spectra, but the shoulder peak disappears for the



FIGURE 6 UV-vis Spectra of the Tz copolymers in chlorobenzene, in toluene and as a film. The spectra for PCPDTTz-6: 6_{in} were shifted up by 0.7. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]



FIGURE 7 Cyclic voltammograms of the polymer films on a Pt electrode referred to an Ag quasi-reference electrode in 0.1 M Bu_4NPF_6 /anhydrous CH₃CN solution at a scan rate of 50 mV/min.

solution samples, indicating much less chain stacking of this polymer in solution. We believe this is attributed to the increased solubility of the polymer due to the branched side group. Both the polymer films show much broader absorption covering 400–700 nm with an onset at 730 and 715

TABLE 1 Characterization	Data of	the Po	lymers
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nm, corresponding to an optical band gap of 1.70 and 1.73 eV, respectively. It is interesting that the film spectra of both samples do not show red shift as usually observed for solar cell polymers such as the PCPDTTz-6:6_{out} conterpart.⁹ We believe that this is due to the low steric energy for both the cis- and trans-orientations of the thiophene ring in the main chain. It leads to a highly random conformation and a broader distribution of effective conjugation length of the polymer chain in the solid state. This feature results in a broad light absorption and could be beneficial for improving the performance of solar cell devices. The shorter maximum absorption wavelength of these two polymers than PCPDTTz-6:6_{out} also indicates that the polymer chains are less coplanar in solid state due to the random chain conformation.

The electrochemical properties of the polymers were studied using cyclic voltammetry by coating a polymer thin film on the platinum working electrode from its toluene solution. The results are shown in Figure 7(a) and (b). Calculated from the onset potential of the first oxidation and reduction waves,¹⁹ the HOMO and LUMO energy levels are -5.45 and -3.90 eV for PCPDTTz-6:6_{in} and -5.50 and -3.87 eV for PCPDTTz-2,6:6_{in}. The HOMO energy levels are $0.05\sim0.1$ eV higher than its out-counterpart (see Table 1), indicating the hexyl group at the 3- or 4-positions has very small effect on the energy level. These values are also about 0.15 eV deeper than the benzothiadiazole analogs (PCPDTBT).^{9a,20} Benzothiadiazole is a widely used electron-deficient unit in solar cell polymers. This property means a higher V_{oc} can be expected from these polymers.

Polymer solar cell devices were then fabricated from these two polymers with a general structure of ITO/PEDOT:PSS/ polymer:PC₇₁BM/LiF/Al. The weight ratio of polymer/ PC₇₁BM was 1:2. Typical current density-voltage (*J*-*V*) curves in dark and under illumination of AM 1.5G (100 mW/cm²) are shown in Figure 8. Device based on PCPDTTTz-2,6:6_{in} gives an open-circuit voltage (V_{oc}) of 0.69 V, a short-circuit current density (J_{sc}) of 3.36 mA/cm², and a modest fill factor (FF) of 29.4%, leading to a PCE of 0.68%. The device from PCPDTTTz-6:6_{in} has a lower V_{oc} of 0.57 V, an improved J_{sc} of 6.23 mA/cm² and a FF of 34%. The PCE thus reaches 1.21%. The improvement of PCE arose mostly from the increased J_{sc} . This can be explained by the structure

Polymer	<i>M</i> n ^a (kDa)	PDI ^a	<i>T</i> d ^{1%b} (°C)	λ ^S max ^c (nm)	λ ^F max ^c (nm)	E′ _{re} d (V)	<i>E</i> ″ _{ox} ^d (V)	E _{LUMO} ^e (eV)	Е _{номо} е (eV)	E ^f (eV)
PCPDTTTz-6:6 _{in}	15.7	2.24	236	583	575	-0.83	0.72	-3.90	-5.45	1.55 (1.70)
PCPDTTTz -2,6:6 _{in}	48.0	1.82	231	592	571	-0.86	0.77	-3.87	-5.50	1.63 (1.73)
PCPDTTTz-6:6 _{out}	20.0	1.41	234	587	600	-0.82	0.76	-3.91	-5.49	1.58 (1.68)
PCPDTTTz-2,6:6 _{out}	29.4	1.51	242	562	564	-0.82	0.87	-3.91	-5.60	1.69 (1.66)

^a Average number molecular weight and polydispersity index (GPC vs. polystyrene standards in chlorobenzene).

^b Decomposition temperature of 1% weight loss.

^c Solution (in chlorobenz ene) and film absorption.

^d Onset potentials from CV measurements of thin films in a 0.1M Bu4NPF6/CH3CN solution versus Ag.

 $^{\rm e}$ Estimated from LUMO $= -({\it E'}_{\rm re}$ + 4.73) eV and HOMO $= -({\it E'}_{\rm ox}$ + 4.73) eV. 19

^f Energy gap: value in the bracket was calculated from the onset of the thin film UV absorption.



FIGURE 8 J-V curve of PCPDTTTz-6:6_{in}:PC₇₁BM and PCPDTTTz-2,6:6_{in}:PC₇₁BM (weight ratio 1:2) solar cell devices under illumination of AM 1.5G, 100 mW/cm².

difference between two polymers. PCPDTTTz- $6:6_{in}$ has a small and linear alkyl side chain, which means better chain packing and higher charge carrier mobility, and hence, the J_{sc} increased from 3.36 to 6.23 mA/cm². Comparatively, PCPDTTTz- $2,6:6_{in}$ has relatively weak electronic coupling with PCBM acceptor in the device due to the slightly bulky ethylhexyl side groups. It will lead to less recombination of dissociated charges.²¹ In addition with the slightly deeper HOMO level (0.05 eV), this effect leads to a device with a V_{oc} about 0.12 eV higher than that from PCPDTTTz- $6:6_{in}$.

It is a big surprise to us that this type of polymers have much poor photovoltaic performance then their out-counterpart.⁹ This poor performance is partially attributed to the lower V_{oc} of the in-polymers related with their higher HOMO level (See Tables 1 and 2). However, we believe the major reason is related to the random distribution of the cis- and trans-orientations of the thiophene rings along the polymer chain as discussed above. This random conformation results in a loose π - π stacking of the polymer in film, leading to a poor device performance. This was confirmed by X-ray diffraction study of the polymer films. As reported in Ref. 9c, the out-polymers showed the [100] peak at 2θ of 6.6° . A [010] peak at 2θ of 27° was also observed for PCPDTTTz- $6:6_{in}$. However, we do not observed any well-developed dif-

fraction peak for the in-polymers, indicating a much loose π – π stacking of these two in-polymers in the solid state.

EXPERIMENTAL

Materials

2-Bromo-3-hexylthiophene (97%), anhydrous hydrazine (95%), anhydrous dimethylformamide (DMF), hydroxylamine hydrochloride, isoamyl nitrite, NBS, and all the solvents were purchased from Sigma-Aldrich and used as received. Anhydrous tetrahydrofuran (THF) was purified by running through a Pure Solv-400-4-MD solvent purification system. Tetrakis(triphenylphosphine)palladium(0) [(PPh₃)₄Pd(0)] was prepared based on a reported method and stored in a glove box.²²

Characterization

GPC, Waters Breeze HPLC system with 1525 Binary HPLC Pump, and 2414 Differential Refractometer were used for measuring the molecular weight and polydispersity index (PDI). Chlorobenzene was used as eluent, and commercial polystyrenes were used as standard. ¹H and ¹³C NMR spectra were recorded in CDCl3 for organic molecules and in o-DCB- d_4 at 140 °C or in toluene- d_8 at 100 °C for polymers using a 400-MHz Varian Unity Inova spectrometer. The NMR solvent peaks were used as references (CDCl₃, 7.25 ppm; o-DCB-d₄, 6.92, 7.20 ppm; toluene-d₈, 2.09, 7.09 ppm). The DSC analysis and TGA were performed at a heating rate of 10 °C/min under a nitrogen atmosphere (50 mL/min) using a TA Instruments DSC 2920 and TGA 2950, respectively. DSC was 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 (5.10 eV below the vacuum level) as an external standard.¹⁹ The half wave potential of the Fc/ Fc^+ redox couple was found to be 0.42 V versus the Ag quasi-reference electrode. Therefore, the HOMO and LUMO energy levels of the copolymers can be estimated using the empirical equation $E_{\rm HOMO} = - (E'_{\rm ox} + 4.68)$ eV and $E_{\rm LUMO} =$ $-(E'_{\rm re} + 4.68)$ eV, where $E'_{\rm ox}$ and $E'_{\rm re}$ stand for the onset potentials for the first oxidation and reduction pair relative to the Ag quasi-reference electrode, respectively.

TABLE 2 Summary of the Device Fabrication Conditions and Photovoltaic Performance

Polymer ^a	Temperture ^b (°C)	J _{sc} (mA/cm²)	V _{oc} (V)	FF (%)	PCE (%)
PCPDTTTz-6:6 _{in}	80	6.23	0.57	34.0	1.21
PCPDTTTz-2,6:6 _{in}	80	3.36	0.69	29.4	0.68
PCPDTTTz-6:6 _{out}	85	12.5	0.75	59.0	5.53
PCPDTTTz-2,6:6 _{out}	21	10.2	0.81	38.7	3.20

^a Devices were fabricated from a solution of polymer/PCBM₇₁ (1/2, w/w) in 1,2-dichlorobenzene containing 3% of 1,8-diiodooctane.

^b Device fabrication temperature.

3-Hexylthiophene-2-carboxaldehyde¹⁵

2-Bromo-3-hexylthiophene (19.8 g, 80.0 mmol) was added into a 500-mL round-bottomed flask with a stir bar, which was then purged with argon under vacuum, and was added with 300 mL of anhydrous THF. The solution was cooled to -78 °C using an acetone/dry ice bath. *n*-Butyl lithium (2.5 M) in hexane (32.0 mL, 80.0 mmol) was added dropwise into the stirring solution over a period of 30 min and then warmed to -40 °C and stayed for 30 min. The solution was cooled down to -78 °C again, and anhydrous DMF (7.02 g, 96.0 mmol) was added in one shot. The solution was allowed to warm up to room temperature and stirred overnight. A total of 150 mL of water was added into the solution. The organic layer was separated, and the aqueous layer was extracted with 200 mL of hexanes. The organic phases were combined and washed with distilled water (100 mL) twice, dried over anhydrous magnesium sulfate, and rotary evaporated to remove the solvent. The liquid residue was subjected to a silica-gel column chromatography (CHCl₃/hexanes = 3/7, $R_f = 0.2$) to yield a light brown liquid (14.7 g, yield 93.6%).

¹H NMR (400 MHz, CDCl3): δ 10.03 (s, 1H); 7.62 (d, J = 5.0 Hz, 1H); 6.99 (d, J = 5.0 Hz, 1H); 2.66 (t, J = 7.8 Hz, 2H); 1.66 (m, 2H); 1.22–1.40 (m, 6H); 0.88 (m, 3H)).¹³C NMR (100 MHz, CDCl₃): δ 182.2, 152.9, 137.6, 134.4, 130.6, 31.5, 31.3, 28.9, 28.4, 22.5, 14.0.

2-Cyano-3-hexylthiophene

A mixture of 3-hexylthiophene-2-carboxaldehyde (9.82 g, 50.0 mmol) and hydroxylamine hydrochloride (5.2 g, 75 mmol) in pyridine/ethanol (60 mL, 1/1, v/v) was stirred and refluxed overnight. The solution was rotary evaporated to remove the solvent. The residue was extracted with chloroform (100 mL), and the resulting solution was washed with distilled water (2 \times 50 mL) and then dried over anhydrous magnesium sulfate. After the solvent was removed using a rotary evaporator. The viscous liquid residue was then dissolved in acetic anhydride (30 mL) containing 0.3 g of potassium acetate and was refluxed at 140 °C for 3 h. Then the solution was added with 50 mL of water and was extracted with hexanes (50 mL) twice. The combined organic extracts were washed subsequently with 50 mL of 5% aqueous sodium hydroxide solution and 50 mL of water twice, dried over anhydrous magnesium sulfate, and rotary evaporated to remove the solvent. The yellow liquid residue was subjected to a silica-gel column chromatography (8% EtOAc/ hexanes, v/v, $R_f = 0.4$) to yield a light green liquid (8.3 g, 86% yield).

¹H NMR (400 MHz, CDCl₃): δ 7.46 (d, J = 5.0 Hz, 1H); 6.95 (d, J = 5.0 Hz, 1H); 2.78 (t, J = 7.8 Hz, 2H); 1.64 (m, 2H); 1.24–1.36 (m, 6H); 0.88 (m, 3H).¹³C NMR (100 MHz, CDCl₃): δ 154.8, 131.6, 128.5, 114.3, 105.4, 31.4, 30.1, 29.8, 28.7, 22.5, 14.0.

TTz-6_{in}

2-Cyano-3-hexylthiophene (3.95 g, 20.4 mmol), sulfur (0.39 g, 12.3 mmol), and ethanol (15 mL) were added into a 50 mL round-bottomed flask, which was equipped with a mag-

netic stir bar and was then sealed with a rubber septum. The reaction system was connected to a thick-wall rubber balloon for regulating the pressure inside the flask during the reaction. Anhydrous hydrazine (95%, 2.0 g, 40.8 mmol) was added into the solution using a syringe at room temperature. The temperature was then raised to 50 °C. The solution turned to brown with gas evolved. The sulfur in the solution was completely dissolved within 5 min, and then the temperature was increased to 68 °C. The solution was stirred at 68 °C with the pressure regulated by the thickwall rubber balloon. Second and third portions of anhydrous hydrazine (95%, 1.0 g, 20.4 mmol each) were added in 6 h interval. The reaction was stopped in 20 h by cooling to room temperature, where the solution turned to slurry. It was mixed with 15 mL of MeOH and then filtered to collect the solid, which was rinsed with MeOH and dried in air for 30 min to give a pale white powder.

¹H NMR (400 MHz, C₆D₆): δ 6.84 (s, 2H), 6.64 (d, J = 5.0 Hz, 2H); 6.55 (d, J = 5.0 Hz, 2H); 2.71 (t, J = 7.8 Hz, 4H); 1.51 (m, 4H); 1.14–1.26 (m, 12H) 0.85 (t, J = 7.2 Hz, 6H).

The resulting powder was then dissolved in 20 mL of $CHCl_3$ and isoamyl nitrite (5.5 g, 47 mmol) was added. The resulting solution was stirred at 40 °C for 8 h. The solvent was removed by a rotary evaporation, and the resulting red solid was washed with methanol twice, and then subjected to recrystallization in 2-propanol to yield red needle-like crystal (2.7 g, 65% yield).

¹H NMR (400 MHz, CDCl3): δ 7.54 (d, J = 5.0 Hz, 2H); 7.09 (d, J = 5.0 Hz, 2H); 3.23 (t, J = 7.6 Hz, 4H); 1.69 (m, 4H); 1.41 (m, 4H); 1.26–1.34 (m, 8H) 0.87 (t, J = 7.2 Hz, 6H). ¹³C NMR (100 MHz, CDCl₃): δ 161.8, 149.3, 132.0, 130.7, 129.3, 31.7, 30.5, 30.3, 29.1, 22.6, 14.1.

TTz-Br₂-6_{in}

To a mixture of 3,6-bis[2-hexylthien-2-yl]-s-tetrazine (0.525 g, 1.266 mmol) and SiO₂ (0.2 g) in CH₂Cl₂ (10 mL) was added NBS (0.50 g, 2.80 mmol) and was stirred at room temperature for 2 days in dark. The solution was filtered to remove SiO₂ and was then mixed with 20 mL of distilled water and then extracted with 30 mL of CH₂Cl₂. The water phase was separated and extracted with 30 mL of CH₂Cl₂ again. The combined organic phases were washed with 20 mL of distilled water twice, dried over anhydrous magnesium sulfate, and rotary evaporated to remove the solvent. The resulting red solid residue was run through a silica-gel column (20% CHCl₃/hexanes, v/v, $R_{\rm f} = 0.5$) to yield a red powder (0.48 g, 66% yield).

¹H NMR (400 MHz, CDCl₃): δ 7.05 (s 2H); 3.16 (t, J = 7.8 Hz, 4H); 1.65 (m, 4H); 1.39 (m, 4H); 1.26–1.33 (m, 8H) 0.88 (t, J = 7.2 Hz, 6H). ¹³C NMR (100 MHz, CDCl₃): δ 161.0, 150.0, 134.8, 130.7, 119.5, 31.6, 30.5, 30.1, 29.0, 22.5, 14.1.

PCPDTTTz-6:6_{in}

TTz-Br₂-6_{in} (0.2019 g, 0.353 mmol) and 4,4-dihexyl-2,6-bis (trimethylstannanyl)-4H-cyclopenta[2,1-b:3,4-b']dithiophene (0.2414 g, 0.359 mmol) were added to a mixture of 8 mL of anhydrous toluene and 0.8 mL of DMF in a 25-mL flask. The

system was purged with argon under vacuum and was moved to a glove box to add $(PPh_3)_4Pd(0)$ (8 mg, 0.07 mmol). The solution was stirred and refluxed under argon for 5 h. A total of 5 mL of degassed anhydrous toluene was added, and the solution was refluxed overnight. One drop of trimethylstannanylbenzene followed by two drops of bromobenzene was added in 3 h intervals under refluxing. The solution was cooled to room temperature in 5 h and poured into methanol to precipitate the polymer. The resulting polymer was further purified by Soxhlet extraction with acetone and then hexanes. The polymer was recovered with CHCl₃ and dried under vacuum for 16 h to get PCPDTTTz-6,6_{in} as a shining dark solid (190 mg, yield: 72%), $M_n = 15,700$ Da, PDI, 2.24).

¹H NMR (400 MHz, *o*-DCB-*d*₄): δ 7.36 (2H); {7.29 (2H); 7.14 (2H) in toluene-*d*₈} 3.26 (4H); 2.03 (4H); 1.79 (4H); 1.48 (4H); 1.28–1.42 (8H); 1.11–1.27 (16H); 0.89 (6H); 0.80 (6H).

PCPDTTTz-2,6:6in

TTz-Br₂-6_{in} (0.1145 g, 0.200 mmol) and 4,4-bis(ethylhexyl)-2,6bis(trimethylstannanyl)-4H-cyclopenta[2,1-b:3,4-b']dithiophene (0.1493g, 0.205 mmol) were added into 5 mL of anhydrous toluene in a 25-mL flask. The system was purged with argon under vacuum and was moved to a glove box to add (PPh₃)₄Pd(0) (6 mg, 0.005 mmol). The solution was refluxed overnight under argon. One drop of trimethylstannanylbenzene followed by two drops of bromobenzene was added in 3 h intervals under refluxing. The solution was cooled to room temperature in 5 h and poured into methanol to precipitate the polymer, which was further purified by Soxhlet extraction with acetone and then hexanes. The polymer was recovered by o-DCB at 120 °C, and the solvent was removed under vacuum to give PCPDTTTz-2,6:6_{in} as shining dark solid (115 mg, yield: 66%), $M_n = 48,000$ Da, PDI, 1.82.

¹H NMR (400 MHz, *o*-DCB- d_4): δ 7.37 (2H); {7.33 (2H), 7.17 (2H) in toluene- d_8 } 3.26 (4H); 2.06 (4H); 1.78 (4H); 1.47 (4H); 1.26–1.40 (8H); 1.05-1.21 (16H); 0.99 (2H). 0.88 (6H); 0.79 (6H); 0.74 (6H).

Device Fabrication and Testing

Patterned ITO glass substrates were cleaned with detergent before sonicated in acetone and isopropanol for 15 min. The organic residue was further removed by treating with UVozone for 10 min. A thin layer of PEDOT:PSS (Clevios P, H. C. Starck, 45 nm) was then spin coated and dried for 1 h at 120 °C. The polymer and PC71BM (ADS; 1:2 weight ratio) were dissolved in o-DCB-containing 3.0% (v/v) diiodooctane at 80 °C. The solution was filtered and spin-coated on the PEDOT:PSS layer before 1.0 nm of LiF and 100 nm Al layer were thermally evaporated through a shadow mask at a pressure of 5 \times 10⁻⁷ mbar in a Boc Edwards Auto 500 System. The active area was 50 mm². The current-voltage (*J*-*V*) characteristics were measured with a Keithley 2400 digital source meter under simulated air mass (AM) 1.5 solar irradiation of 100 mW/cm² (Sciencetech, SF150). The light intensity was calibrated with a power meter (Gentec Solo PE Laser Power & Energy Meter).

CONCLUSIONS

Dithienyl-s-tetrazine with a hexyl group at the 3-position of the thiophene ring (TTz-6_{in}) is interesting for polymer solar cell applications. However, the preparation of this type of molecules is challenging. Using the sulfur-assisted Pinner synthesis under a traditional condition only gives trace of this product. Monitoring the reaction by ¹H NMR shows that reaction using anhydrous hydrazine at a low temperature (68 °C) can efficiently promote the conversion and depress side reactions. We find that the decomposition of hydrazine competes with this reaction; using excess hydrazine by adding successively in several portions will improve the yield and reduce side reactions. The yield of this reaction reached 65% by adding anhydrous hydrazine (4 equiv) in three potions over 12 h at 68 °C. From the TTz-6_{in} monomer, two new copolymers of TTz-6in with two cyclepentadithiophene units (CPDT-6, and CPDT-2,6) have been prepared. The polymers show broad light absorption, attributing to the wider distribution of effective conjugating length of polymer chain in the film due to the low steric energy of both the cis- and trans-orientations of the thiophene unit in the chain. The polymers also show a narrow band gap with a deep HOMO level. Polymer solar cell devices are fabricated and tested based on the blends of these polymers with PC₇₁BM.

The authors acknowledge the financial support from NRC-CSIC, NRC-NSERC-BDC, and NRC-NANO programs.

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