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Journal of Polymer Science Part A: Polymer Chemistry

The Preparation of a Sterically Hindered s-Tetrazine and Its Conjugated Polymers[†]

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

Abstract

We demonstrated, for the first time, that dithienyl-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 this ring formation reaction, and the reaction under a traditional reaction 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 TTz and cyclopentadithiophene (CPDT) with hexyl or 2-ethylhexyl groups attached to its 4-position have been prepared. The polymer films show a broad light absorption

attributing to the large distribution of effective conjugating length of polymer chain in the film due to the low steric hindrance for the rotation of the monomer units. The polymers also 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.

Introduction:

s-Tetrazine (Tz) in conjugated molecules is one of the most electron deficient moiety with the electron-withdrawing 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 small molecules¹⁻⁴ and in conjugated polymers has achieved significant progresses.^{4a,5} These materials showed a great potential for the use in optical and electronic devices such as non-linear 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 non-linear optical applications,^{1a,6} and inside polymer main chains for solar cell applications.⁹ Due to the extremely strong electron pulling effect of Tz, the resulting polymers with this push-pull structure have narrow band gaps, and low-lying HOMO levels,⁹ which enhances sun light absorption and promotes the open circuit voltage (V_{oc}) of solar cell devices. Although a few different approaches can be used to prepare s-tetrazines and summarized in a recent review paper by Audebert,^{1a} the sulfur-assisted Pinner synthesis appears the most practicable way to produce Tz unit in conjugated aromatic molecules such as dithienyl-s-tetrazine (TTz).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 4- or 3-position of the thiophene ring as shown in Scheme 1.

Scheme 1. Structure of TTz molecules, the suffix 6 with a subscript “out” or “in” in the sample name represents hexyl group on the thiophene ring which points out, or in.

Recently, we have successfully prepared TTz compound with a hexyl group at the 4-position, 3,6-bis(4-hexylthienyl-2-yl)-s-tetrazine) (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-4*H*-cyclopenta[2,1-*b*:3,4-*b'*]dithiophene) (CPDT) by Stille coupling reaction to yield PCPDTTTz-6:6_{out} (Scheme 2), where the first 6 in the suffix represents hexyl group on CPDT, and the second 6 with a subscript “out” represents hexyl group on the TTz unit which pointed away from the Tz ring. They are used in the purpose to distinguish with 2-ethylhexyl group (2,6), and with the hexyl group at the 3-position of the thiophene ring which points toward Tz ring (6_{in}). This polymer was tested for polymer solar cell applications and devices with power conversion efficiency up to 5.4% have been achieved,^{9a} indicating a high potential of the Tz polymers for this application.

In PCPDTTTz-6:6_{out}, the hexyl group on the thiophene ring will create a high energy barrier for the thiophene rotating along the chain axis, because the first carbon of the hexyl group on thiophene will overlap with the 2- or 5-proton of CPDT as indicated in Scheme 2 when the hexyl groups on thiophene and on CPDT approaches to the same side. Relocating the hexyl group to the 3-position of the thiophene ring will eliminate the overlap as indicated in Scheme 2, meanwhile will not create other major steric hindrance

due to the bare structure of Tz ring. Therefore, this structure will offer the polymer a low steric hindrance for the monomer units rotating along the chain axis.

Scheme 2. The difference of the steric hindrance to the monomer unit rotating in PCPDTTz-6:6_{out} and PCPDTTz-6:6_{in}.

Another advantage of this structure 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 many 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 the cycloaddition of Tz with C₆₀ when the temperature reached 110 °C. The conversion of this reaction in o-DCB can reach ~20% in 1 h at this temperature for the

polymer with “out” conformation. 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 by using the polymer with “in” conformation, PCPDTTTz-6:6_{in}, where the Tz ring is surrounded by the hexyl groups to obtain a sufficient steric protection to prevent this side reaction (Scheme 2). Our test indeed showed that the reaction rate of PCPDTTTz-6:6_{in} with C₆₀ is about 28 fold lower than the “out” analogue under the same condition.

PCPDTTTz-6:6_{in} must be prepared from the corresponding TTz-6_{in} monomer, 3,6-bis(3-hexylthienyl-2-yl)-s-tetrazine, which, unfortunately, is difficult to synthesize due to the large steric hindrance of the large 3-substituent to the Tz ring formation. The synthesis of Tz ring has to go through di-hydrotetrazine for all the possible approaches, with two examples shown in Scheme 3 for the Pinner synthesis and Stollé synthesis.^{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 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 a substituent at this position larger than a methyl group.^{1a} Furthermore, a methyl group attached to this position will make the nitrile inert in the sulfur-assisted Pinner synthesis.³ Interestingly, we found in our work that sterically hindered 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 paper, 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.

Scheme 3, Pinner and Stollé synthesis for the preparation of tetrazines.

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 4 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 ~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.

Scheme 4. Synthetic approach for the preparation of the TTz-Br₂-6_{in} monomer using the sulfur-assisted Pinner synthesis.

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 sterically non-hindered tetrazines,^{1a} such as TTz-6_{out} in a high yield in our previous work.^{9a} However, under a similar reaction condition by reacting with hydrazine monohydrate in anhydrous ethanol at 78 °C in our initial tests for the preparation of TTz-6_{in}, we only observed a trace amount of the desired product in the reaction. We interestingly found that a reaction conducted at a lower temperature (70 °C) by using anhydrous hydrazine gave a much higher yield, and therefore studied the reaction for the formation of dihydro-s-tetrazine 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 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 hr), 50 °C (for 1 hr) and then 70 °C with occasional shaking. NMR spectra of the reaction solution at different times were taken and compared with the predicted spectrum of the predicting products in Figure 1b.

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

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 $50\text{ }^\circ\text{C}$ for 1 hr. But the sulfur powder in the solution was completely disappeared after 1 hr reaction at $50\text{ }^\circ\text{C}$, 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 5).^{4b} Although the formed adduct did not react with the nitrile at $50\text{ }^\circ\text{C}$, it readily reacted at $70\text{ }^\circ\text{C}$ 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 hrs. Meanwhile, another pair of new peaks appeared in 7 hrs at 7.40 (5'') and 6.93 ppm (4'') and slowly increased in intensity. These two pairs of the peaks might be attributed to 1,4- and 1,2-isomer of dihydrotetrazine. However, to accurately assign them is difficult. One possible way is to use ^{15}N NMR, where the peak of two tetrazine N in the 1,4-isomer will be a doublet with a coupling constant of $\sim 6.5\text{ Hz}$ due to the two-bond $^{15}\text{N}\text{-N-}^1\text{H}$ 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 ^{15}N . Therefore, we used the Advanced Chemistry Development (ACD) C+H NMR prediction software to predict the spectrum difference of 1,2- and 1,4-isomers.¹⁷ The predicted spectrum of a 1:1 mixture of 1,2- and 1,4-isomer was shown in Figure 1a. 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 structure. Since 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 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 Figure 1a).

Scheme 5. Reaction mechanism of the sulfur-assisted Pinner synthesis proposed by Audebert.^{4b}

The conversion rate to these two dihydrotetrazines was monitored 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 (Figure 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 hrs 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 hrs. The difference between these two curves is obviously due to the formation of 1,2-isomer, as well as small amount of by-products as indicated by the small peaks in Figure 1b. After 17 hrs, 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 equivalents 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 with the assistance of excess of 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. 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 2 also shows that the conversion of the starting material was leveled off after 17 hrs, 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 hrs. The gas turned wet pH paper blue, indicating the gas is mostly composed of ammonia. It means that the decomposition of hydrazine to ammonia competed with the Tz ring formation reaction in this process. With the decrease of the hydrazine concentration, the ring formation reaction reduced its speed and almost stopped after 17 hrs. 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 °C, which was used to successfully prepare TTz-6_{out} isomer.^{9a}

Based on these observations, a new reaction was designed, where anhydrous hydrazine was added into the methanol reaction solution in three portions (2, 1 and 1 equivalent) at 0, 6 and then 12 hrs at 68 °C. The reaction was stopped at 20 hrs. 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 (Figure 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-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.¹¹

Figure 3. NMR spectrum in C_6D_6 of the product from the modified sulfur-assisted Pinner reaction.

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 hrs. Re-

crystallization of the crude product in 2-propanol gave red shining 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 CH₂Cl₂ at room temperature to form the dibromo-monomer, 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} analogues (7.95 ppm).^{9a} The 3-H of the thiophene ring in TTz-Br₂-6_{out} is strongly de-shielded by the Tz ring hence its peak shifted towards a higher frequency, while the 4-H in TTz-Br₂-6_{in} is shielded by the bromine atom and the alkyl group and thus its peak appeared at a lower frequency.

The preparation and characterization of polymer: TTz-Br₂-6_{in} was copolymerized with 2,6-bis(trimethylstannyl)-4,4-dihexyl-4*H*-cyclopenta[2,1-*b*:3,4-*b'*]dithiophene and 2,6-bis(trimethylstannyl)-4,4-bis(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 6.

Scheme 6, Reaction scheme for the preparation of the copolymers of TTz and CPDT by Stille coupling reaction.

The structure of the polymers was confirmed by ^1H NMR. However, the NMR spectra of both polymers had one aromatic proton peak missing when the spectrum was collected in ortho-dichlorobenzene- d_4 (o-DCB- d_4). This is due to that the missing peak is overlapped with one of the solvent peaks. Both proton peaks were observed in the spectrum collected in toluene- d_8 (see SI). Gel permeation chromatography study showed that both polymers had a high molecular weight with number average molecular weights of 15.7 and 48.0 kDa for PCPDTTz-6:6_{in} and PCPDTTz-2,6:6_{in} respectively. The differential scanning calorimetry (DSC) analysis and thermal gravimetric analysis (TGA) under nitrogen (Figure 4) showed both polymers started to decompose at ~ 190 °C. As discussed in our previous publications,⁹ this decomposition is due to the broken of the Tz ring. We can see that the decomposition temperature of the “in” polymer is slightly lower than its “out” counter-part.⁹ indicating the hexyl substituent at the steric hindered position will reduce the thermal stability of the Tz ring in the polymers.

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

Table 1. Characterization data of the polymers

polymer	Mn (kDa)	PDI	T _d ^{1%} (°C)	E ^{1/2} _{re} (V)	E ^{1/2} _{ox} (V)	E _{LUMO} (eV)	E _{HOMO} (eV)	E _g ¹⁾ (eV)
PCPDTTz-6:6 _{in}	15.7	2.24	236	-0.96	0.90	3.42	5.28	1.86 (1.70)
PCPDTTz-2,6:6 _{in}	48.0	1.82	226	-0.94	0.93	3.44	5.31	1.87 (1.73)

Note: ¹⁾Value in the bracket was calculated from the onset of the UV absorption.

The UV-vis spectra of the chloroform, toluene solutions and the films of both polymers are displayed in Figure 5. The spectra of PCPDTTz-6:6_{in} shows a maximum at 585 nm in chloroform 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 a similar behavior in the UV-vis spectra, but the shoulder peak disappears for the 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 polymer films show a much broader absorption covering 400 to 700 nm with an onset at 730 and 715 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 their PCPDTTz-6:6_{out} counterpart.⁹ We believe that this is due to its lower steric hindrance for monomer units rotating along the chain axis. It leads to a higher random orientation of the monomer units inside the chain plain, which results in a broader distribution of effective conjugated length of the polymer chain in the solid state. This feature results in a broad light absorption, and will be beneficial for improving the performance of solar cell devices.

Figure 5. UV-Vis Spectra of the Tz copolymers in chloroform, in toluene and as a film. The spectra for PCPDTTz-6:6_{in} were shifted up by 0.7.

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 result is shown in Figure 6. Calculated from the half wave potential of the first oxidation and reduction waves, the HOMO and LUMO energy levels are -5.28 eV and -3.42 eV for PCPDTTz-6:6_{in} and -5.31 eV and -3.44 eV for PCPDTTz-2,6:6_{in}.^{9a} These energy levels are similar to the PCPDTTz-6:6_{out} counterpart, indicating the hexyl group at the sterically hindered or non-hindered position has no apparent effect on the energy level. These HOMO energy levels are about 0.2 eV deeper than the benzothiadiazole analogues (PCPDTBT).^{9a,18} Benzothiadiazole is a widely used electron deficient unit in solar cell polymers. This property means a higher V_{oc} can be expected from Tz polymers.

Figure 6. 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 CH_3CN solution at a scan rate of 50 mV/min.

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 7. 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 power conversion efficiency (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 mostly comes from the increased J_{sc} . This can be

explained by the structure difference between two polymers. PCPDTTz-6:6_{in} has a small and linear alkyl side chain, which means better chain packing, shorter pi-pi stacking distance and higher charge carrier mobility, hence the J_{sc} increased from 3.36 to 6.23 mA/cm². It is a big surprise to us that this type of polymers have poor photovoltaic performance then their “out” counterpart,⁹ contrary to our expectation. The reason is under investigation.

Figure 7. J-V curve of PCPDTTz-6:6_{in}:PC₇₁BM and PCPDTTz-2,6:6_{in}:PC₇₁BM (weight ratio 1:2) solar cell devices under illumination of AM 1.5G, 100 mW/cm².

Experimental Section:

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.¹⁹

Characterization: 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. ^1H and ^{13}C NMR spectra were recorded in CDCl_3 for organic molecules and in $o\text{-DCB-}d_4$ 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 (CDCl_3 , 7.25 ppm; $o\text{-DCB-}d_4$, 6.92, 7.20 ppm; toluene- d_8 , 2.09, 7.09 ppm). The differential scanning calorimetry (DSC) analysis and thermal gravimetric analysis (TGA) were performed at a heating rate of $10^\circ\text{C}/\text{min}$ 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 Bu_4NPF_6 in anhydrous CH_3CN 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 (4.80 eV below the vacuum level) as an external standard. 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 $E_{\text{HOMO}} = -(E_{\text{ox}}^{1/2} + 4.38)$ eV and $E_{\text{LUMO}} = -(E_{\text{red}}^{1/2} + 4.38)$ eV, respectively, where $E_{\text{ox}}^{1/2}$ and $E_{\text{red}}^{1/2}$ stand for the half wave potentials for the first oxidation and reduction pair relative to the Ag quasi-reference electrode, respectively.

3-Hexylthiophene-2-carboxaldehyde:¹⁹ 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 with an acetone/dry ice bath. 2.5 M *n*-butyl lithium 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. 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 ($\text{CHCl}_3/\text{hexanes} = 3/7$, $R_f = 0.2$) to yield a light brown liquid (14.7 g, yield 93.6%). ^1H NMR (400 MHz, CDCl_3): 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). ^{13}C NMR (100 MHz, CDCl_3): 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 (2x50 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 hrs. Then the solution was added with 50 mL of water, and was extracted with hexanes (50 mL) twice. The combined organic extract 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, CDCl_3): 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). ^{13}C NMR (100 MHz, CDCl_3): 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}, 3,6-Bis[3-hexylthien-2-yl]-s-tetrazine: 2-cyano-3-hexylthiophene (3.95 g, 20.4 mmol), sulfur (0.39 g, 12.3 mmol) and methanol (15 mL) were added into a 50 mL

round-bottom flask, which was equipped with a magnetic 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 thick-wall rubber balloon. 2nd and 3rd portion of anhydrous hydrazine (95%, 1.0 g, 20.4 mmol each) were added in 6 hrs interval. The reaction was stopped in 20 hrs 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 CHCl₃ and isoamyl nitrite (5.5 g, 47 mmol) was added. The resulting solution was stirred at 40 °C for 8 hrs. The solvent was removed by a rotary evaporation and the resulting red solid was washed with methanol twice, and then subjected to re-crystallization 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}, 3,6-Bis[5-bromo-3-hexylthien-2-yl]-s-tetrazine: 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 overnight. 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_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}, poly[2,6-(4,4-dihexyl-4H-cyclopenta[2,1-b:3,4-b']dithiophene)-alt-5,5'-(3,6-bis(3-hexylthienyl-2-yl)-s-tetrazine)]: 3,6-Bis[5-bromo-3-hexylthien-2-yl]-s-tetrazine (0.2019 g, 0.353 mmol) and 4,4-dihexyl-2,6-bis(trimethylstannanyl)-4H-cyclopenta[2,1-b:3,4-b']dithiophene (0.2414g, 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 (PPh₃)₄Pd(0) (8 mg, 0.07 mmol). The solution was stirred and refluxed under argon for 5 hrs. 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 hrs intervals under refluxing. The solution was cooled to room temperature in 5 hrs 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 hrs 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-d₄): δ 7.36 (2H); {7.29 (2H); 7.14 (2H) in toluene-d₈} 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-2,6:6_{in}: poly[2,6-(4,4-bis(2-ethylhexyl-4H-cyclopenta[2,1-b:3,4-b']dithiophene)-alt-5,5'-(3,6-bis(3-hexylthienyl-2-yl)-1,2,4,5-tetrazine)]; 3,6-Bis[5-bromo-3-hexylthien-2-yl]-s-tetrazine (0.1145 g, 0.200 mmol) and 4,4-bis(ethylhexyl)-2,6-bis(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 2 drops of bromobenzene was added in 3 hrs intervals under refluxing. The solution was cooled to room temperature in 5 hrs 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 DCB at 120 °C and the solvent was removed under vacuum to give PCPDTTz-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 UV-ozone for 10 min. A thin layer of PEDOT:PSS (Clevios P, H. C. Starck, 45 nm) was then spin coated and dried for 1 hr at 120 °C. The polymer and PC₇₁BM (ADS) (1:2 weight ratio) was dissolved in o-DCB containing 2.5% (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 5×10^{-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 Inc., SF150). The light intensity was calibrated with a power meter (Gentec Solo PE Laser Power & Energy Meter).

Conclusion:

Sterically hindered conjugated tetrazine molecules such as dithienyl-s-tetrazine with hexyl group at the 3-position of the thiophene ring (TTz-6_{in}) is interesting for polymer solar cell application. 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 ($68\text{ }^\circ\text{C}$) 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 equivalents) in three portions over 12 hrs at $68\text{ }^\circ\text{C}$. From the TTz- 6_{in} monomer, two new sterically hindered copolymers of TTz- 6_{in} with two cyclopentadithiophene 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 hindrance for the free rotating of the monomer unit. 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 PC $_{71}$ BM.

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Graphical Abstract

Bis(3-hexylthien-2-yl)-s-tetrazine was prepared using a modified sulfur-assisted Pinner synthesis at a yield of 65%. Two new copolymers of this unit with cyclopentadithiophene such as PCPDTTz-6,6_{in} have been prepared and characterized for polymer solar cell applications. The advantage of this polymer over its “out” counterpart (PCPDTTz-6,6_{out}) includes lower steric hindrance for monomer unit rotating along the main chain and higher steric protection of tetrazine ring from side reactions.

Supporting Information

Additional Supporting Information may be found in the online version of this article.

Supporting Information:

The Preparation of a Sterically Hindered s-Tetrazine and Its Conjugated Polymers

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Figure S6. ^1H NMR spectrum of TTz-6_{in} in CDCl_3 .

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