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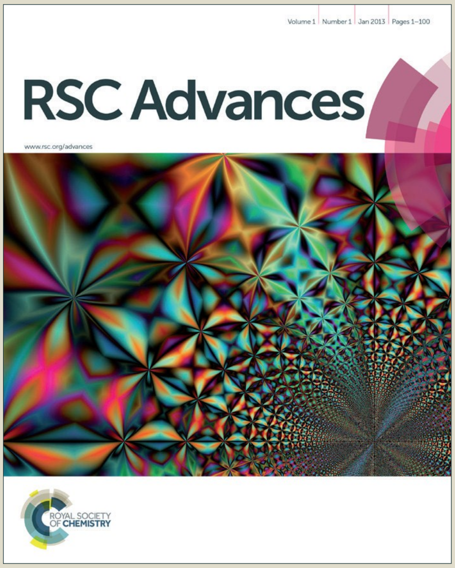

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Effect of Flexible Linker Length in 3,4-Ethylenedioxythiophene Derivatives for Solid State Polymerization †

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Previously, we made great breakthrough in solid state polymerization (SSP) for polythiophene by the new parallel design strategy of introduction of one-atom linker between 3,4-ethylenedioxythiophene (EDOT) unit. Following this strategy, several EDOT derivatives with different length by simply tuning linker atoms number were rationally designed, synthesized and studied as potential candidates for SSP. Now the question is raised here: Does the flexible linker has limited length for a successful SSP? Here, we chose EDOT-linker-EDOT as a prototype monomer model due to its facile synthesis procedure and tunable flexible linker length. We examined up to four-atom length and also investigated different halogen substituted effect. Detailed characterizations of their corresponding polymers were carried out and all monomers' crystals were obtained for structures analysis. Our results reveal that those successful monomers' linker length can be up to three atoms at least while four-atom linker monomer failed to pass SSP due to its low melt point though having preferred polymerization pathway according to the theoretical prediction based on its crystal structure. Meanwhile, iodo-substituted monomer is inclined to form corresponding polymer when compared with bromo-substituted one. Furthermore, it is the first time to get the polymer's molecule weight information and the observation of its dependence with temperature concerning of SSP. Our results are very important for fully understanding SSP process, the exploring monomer structures, further rational designing new monomers and the tuning of the corresponding polymers properties as well

Keywords: Solid state polymerization (SSP), 3,4-Ethylenedioxythiophene, Flexible linker length

Introduction

Conductive polymer is a kind of attractive material since it was invented in 1977.[1] It is an amazing functional material because of its wide application in light-emitting device[2-3], supercapacitors, electrochromic devices and organic photovoltaic cells.[4] In addition, it can be easily tailored by rationally designed and synthesized. As far as its synthesis methods are concerned, it mainly includes chemical oxidation polymerization, electropolymerization and photo-polymerization. Recently, new method of solid state polymerization (SSP) attracts much attention due to its special features such as solvent free and oxidant or external applied potential free, which are necessary required through traditional methods. The first polythiophene by SSP was successfully realized one decade ago,[5] subsequently, several groups focused on finding novel suitable monomers and analyzing their crystal structures.[6]

Generally, among all these monomers developed so far, symmetrical dihalogen-substituted monomers[6] and 3,4-ethylenedioxythiophene (EDOT) framework are necessary. Meanwhile, it is noted that all successful dihalogen-substituted monomers are modified through EDOT molecule's longditudinal direction. For instance, oxygen atoms of EDOT were replaced by sulfur or selenium[6a]; or sulfur atom in the thiophen ring was replaced by selenium.[6d] In addition, the modification on EDOT whether based on EDOT framework or its derivative, is a kind of burdensome work involving multi-step synthesis. Due to such restriction based on present monomer design strategy, recently, we successfully designed a monomer along with EDOT parallel direction through introducing a flexible linker between EDOT units and obtained corresponding conductive polymers by SSP.[7]

Meanwhile, the widely investigated and million-ton scale of non-conjugated polyester, amides were obtained by SSP. Generally, these polymers were formed from polyfunctional monomers through various organic chemistry reactions, resulting in the repeating units of ester, amide, ether and so on. Previous study reveal that sometimes crystal structures especially crystals size have a strong effect on their SSP process and collision and steric factors may contribute to polymerization reaction as well.[8a-b] Scientiests have paid much attention on SSP through exploring new reactions and applications. [8c-e]

It should be pointed out that though the introduction of non-conjugated linker results in the generation of non-conjugated polymers, it demonstrates the possible limitation of the monomer size for SSP whether it is conjugated or non-conjugated one. In addition, compared with well-investigated polyester and others[8f],

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few study concerning of thiophene containing non-conjugated polymer through SSP was reported.

Here, we further examined the flexible linker length effect among these EDOT derivatives and checked their SSP behavior. This study not only revealed fundamental information in SSP, but also broadened the monomer design concept and obtained novel polymers as well.

Experimental

Materials. Chemicals were purchased from Wuhan Shenshi Chemicals Co., Ltd. and were used without further purification unless otherwise noted. EDOT was purchased from J & K. 5-Bromo-3,4-ethylenedioxythiophene[9] was synthesized according to our previous report. 5-Iodo-2,3-dihydro-thieno[3,4-b][1,4]dioxine[10] was synthesized similar to 5-bromo-3,4-ethylenedioxythiophene except that 5,7-diiodo-3,4-ethylenedioxythiophene was used during reduction by n-butyllithium.

Monomer synthesis and solid state polymerization.

Linking the EDOT moieties: synthesis of bis(thien-2-ylmethyl) Mannich bases. General method

Monomer **1-3** was synthesized in accordance to previous method[10] shown in **Scheme 1**. The bromo or iodo mono substituted EDOT (2.0 eq.) was dissolved in glacial acetic acid (1.25 cm^3 mmol). To an equal volume of glacial acetic acid was added the primary amine (40% aqueous solution for methylamine) (1.0 eq.) and aqueous formaldehyde (37%, 2.0 eq.) with ice cooling. After addition was complete, the solution was stirred for a further 12 hours. The solvent was removed in vacuo to give a dark oily residue. Purification by column chromatography gave the required Mannich base.

Bis-(7-iodo-2,3-dihydro-thieno[3,4-b][1,4]dioxin-5-ylmethyl)-methyl-amine (Br_2-3-EDOT, 1)

Yellow-brown (35%), 37%, ^{1}H NMR: δ ($CDCl_3$) 4.25 (m, 4 H); 4.20 (m, 4 H); 3.59 (s, 4 H), 2.28 (s, 3 H). ^{13}C NMR: δ ($CDCl_3$) 139.7, 138.7, 115.3, 85.8, 65.4, 64.8, 51.2, 42.0. Calcd For $C_{15}H_{15}I_2NO_4S_2$: C, 36.23%; H, 3.04%; N, 2.82%. Found: C, 30.50%; H, 2.56%; N, 2.56%.

Bis-(7-iodo-2,3-dihydro-thieno[3,4-b][1,4]dioxin-5-ylmethyl)-methyl-amine (I_2-3-EDOT, 2)

Yellow-brown (35%), ^{1}H NMR: δ ($CDCl_3$) 4.25 (m, 4 H); 4.17 (m, 4 H); 3.62 (s, 4 H); 2.28 (s, 3 H). ^{13}C NMR: δ ($CDCl_3$) 143.8, 138.6, 120.2, 65.4, 64.7, 51.4, 47.7, 41.9. ESI-MS: Calcd, 590.8; found $(M + 1)^+$, 591.6. Calcd For $C_{15}H_{15}I_2NO_4S_2$: C, 30.47%; H, 2.56%; N, 2.37%. Found: C, 30.50%; H, 2.56%; N, 2.56%.

Butyl-bis-(7-iodo-2,3-dihydro-thieno[3,4-b][1,4]dioxin-5-ylmethyl)-amine (I_2-3-butyl-EDOT, 3)

Yellow solid (40%), ^{1}H NMR: δ ($CDCl_3$) 4.23-4.37 (m, 4 H); 4.13-4.18 (m, 4 H); 3.67 (s, 4 H); 2.42-2.49 (t, 2 H); 1.44-1.51 (m, 2 H); 1.25-1.36 (m, 2 H); 0.85-0.92 (t, 3 H). ^{13}C NMR: δ ($CDCl_3$) 143.9, 138.4, 121.5, 65.6, 64.8, 52.9, 48.8, 47.6, 29.6, 20.7, 14.4. Calcd For $C_{18}H_{21}I_2NO_4S_2$: C, 34.14%; H, 3.34%, N, 2.21%.Found: C, 35.72%; H, 3.31%; N, 2.66%.

1,2-Bis-(7-iodo-2,3-dihydro-thieno[3,4-b][1,4]dioxin-5-yl)-bis-dimethylsilanyl-methane (I_2-4-EDOT, 4)

Monomer **4 (I_2-4-EDOT)** was synthesized by modification of previous method.[7,12] Anhydrous THF (30 ml) was slowly added dropwise to a solution of lithium diisopropylamide (10 mmol), the temperature being maintained around -15 ˚C. The reaction mixture was cooled to -60˚C, and a solution of 5-iodo-3,4-ethylenedioxythiophene (2.21 g, 10 mmol) in anhydrous THF (10 ml) was slowly added dropwise, the temperature being maintained around -50 ˚C. Then the reaction mixture was warmed up to -20 ˚C and stirred at this temperature for 15 min. After that, the reaction mixture was cooled to -78 ˚C and dichlorodimethylsilane (0.65 g, 5 mmol) was added, then the cooling bath was removed and the temperature was raised to room temperature. After completion of the reaction, the mixture was poured into a mixture of ice water (50 ml) containing 2 ml 1 M HCl and freshly distilled ether (100 ml). The organic layer was washed with water and dried with Na_2SO_4. Purification by column chromatography (silica gel, light petroleum-CH_2Cl_2, 2 : 1) afforded colorless crystal **4** (50%). ^{1}H NMR: δ ($CDCl_3$) 4.20-4.30 (m, 4 H); 0.67 (s, 4 H); 0.24 (s, 12 H). ^{13}C NMR: δ ($CDCl_3$) 146.5, 145.0, 117.0, 65.2, 64.6, 61.8, 54.4, 8.1, -2.9. Calcd For $C_{14}H_{14}Br_2O_4S_2Si$: C, 33.75%; H, 2.83%. Found: C, 32.95%; H, 2.96%.

General solid state polymerization

The SSP procedure was according to previous method.[5,7] In a closed 5 ml vial, the brominated or iodinated compounds (300 mg) were incubated at 60^o C to 130^o C, respectively, for 2-72 h. The grounded polymers were additionally dried in vacuum at 80^o C overnight, then stirred with hydrazine hydrate (50% aqueous solution, in CH_3OH) overnight, filtered, and washed with CH_3OH and vacuum drying afforded a hydrazine-treated polymers.

Crystal Structure Determination Intensity data for all four crystals were collected using Mo Kα radiation (λ = 0.7107 Å) on a Bruker SMART APEX diffractometer equipped with a CCD area detector at rt. The crystallographic data and details of data collection for four monomers were given in Table S1 (see in the Supporting Information). Data sets reduction and integration were performed using the software package SAINT PLUS.[13] The crystal structure was solved by direct methods and refined using the SHELXTL 97 software package.[14] Simulated XRD pattern of monomers were extracted using a Mercury 1.4.1. software. (The Cambridge Crystallographic Data Centre)

Other Characterizations IR spectra for the characterization of the resulted polymers were recorded on a Perkin-Elmer FTIR spectrometer. Absorption spectra were measured on a Unicam UV 300 spectrophotometer at wavelengths from 300 to 1000 nm. Monomers deposited on fluorine doped tin oxide (FTO) substrate or slide glasses were prepared by spin-coating or drop-casted with 0.5-3 wt% of $CHCl_3$ monomers solution. These monomer coated substrate were employed for SSP and resulted polymers or polymer/FTO substrates were used for XRD, UV-Vis and as working electrodes for electrochemical measurements. For the three-electrode electrochemical measurements in 0.1 M Bu_4NClO_4 in acetonitrile, a FTO/Polymer substrate, platinum foil, and Ag/AgCl served as the working, counter, and reference electrodes, respectively (CH Instruments 604D electrochemical system). X-ray diffraction (XRD) patterns were obtained by Bruker D8 advanced X-ray diffractometer by using Cu-Ka radiation at rt. Thermogravimetric analysis (TGA) data were obtained from a SETSYS 16 with a heating rate of 10 ^{o}C/min in a nitrogen atmosphere. The surface morphologies of monomer and polymers were analyzed using field emission scanning electron microscopy (JEOL, JSM-6700F). The molecular weight and molecular weight distribution of the polymers were determined by gel permeation chromatography (GPC) equipped with a Waters 2690 separation module and a Waters 2410 refractive index detector (Waters Co., Milford, MA). N,N-Dimethylformamide (DMF) was used as eluent at a flow rate of 0.5 ml min^{-1} with the temperature maintained at 30 °C, and the results were calibrated against polystyrene standards.

Results and Discussion

Synthesis of monomers and solid state polymerization

All designed monomers were synthesized as shown in Scheme 1. Due to the difficulty of the final bromination step, monobromo substituted EDOT was synthesized as starting material directly. Monomer **1-3** was obtained through Mannich reaction to link the thiophene moiety of 5-bromo or iodo substituted 3,4-ethylenedioxythiophene. Compound **4** was obtained by the reaction of mono-iodo substituted EDOT with 1,2-bis-dimethylsilanyl-ethane with the help of Li-reagent of LDA.

Finally, these resulting dihalogen-substituted monomers were polymerized through self-polycondensation process with formation of halogen vapor under SSP. According to SSP results, except for monomer **4**, other monomers can be successfully formed corresponding polymers, indicating linker distance plays a key role in their SSP behavior. Previously, we introduced one-atom of C, Si or P linker between EDOT units and got great SSP success.[7] Therefore, we can draw a conclusion that flexible linker of single bond with up to three atom is appropriate length for a successful SSP. Though we failed to obtain EDOT monomers with two-atom-length spacer, it can be expected that such structure could be a successful candidate for SSP. Therefore, flexible linker along parallel direction proves to be an excellent design strategy and the maximum length would be up to three atoms according to our results. Detailed discussion will be done in the following crystal analysis section. In order to establish the relationship between structure and SSP behavior, we define onset temperature of SSP (T_{onset}) as the temperature results in 10% of conversion efficiency in 24 hour. And all these T_{onset} are listed in Scheme 1.

It is interesting that after introducing long alkyl chain of butyl, monomer **3** requires lower about 15 ^{o}C to complete SSP when compared with monomer **2,** which needs 95 ^{o}C and monomer **1** needs the highest temperature of 125 ^{o}C. In addition, previous Perepichka group observed that the fixed 5-member ring monomer were stable than the molecule of free two methyl group attached on ethylene 2,3-dihydro-thieno[3,4-b][1,4]dioxine.[6c] All these facts reveal that the substitution groups, whether flexible or rigid, have great effect on their SSP behavior especially on their T_{onset}, which encourage us to further explore much more acutely controllable and fine tunable monomers for SSP.

XRD patterns of monomers and respective polymers

As shown in Figure 1, monomer of I_2-3-EDOT shows typical sharp peaks (2θ = 12.2, 22.0, 23.2, 24.8, 26.0 and 32.5°) in the rage of 5-60º while Br_2-3-EDOT has sharp peaks (2θ = 12.4, 13.7, 17.8,18.3, 22.3, 23.2, 23.7, 25.3 and so on) as well, which are featured characteristic for crystal compound. After butyl was attached on nitrogen, I_2-3-alkyl-EDOT changes its original structure with peaks at 13.8, 15.8, 19.5, 22.0, 26.7 and 29.3°, as indicated in its XRD pattern. And all these peak values are quite consisted with their simulated results based on crystal structure data. After polymerization, all polymers are in amorphous phase due to the halogen release, which resulting collapse of the crystals.

Absorption of polymers by SSP and hydrazine treated polymers

Figure 2 shows absorbance spectra of P(3-EDOT)-Br, P(3-EDOT)-I, P(3-alkyl-EDOT) and corresponding hydrazine treated polymers. It is obvious that these polymers obtained through SSP do not shown typical broad peak at near-IR region, indicating that these polymer were in low doped (oxidized) state.[14-16] In addition, after treated with hydrazine, there are no distinct peaks in the region 540-650 nm, which frequently observed in polythiophene and ascribed to the π–π* electronic transition of dedoped (reduced) polymer.[15,16] Previously[7], we observed such typical peak in those polymers obtained through SSP based one-atom linker EDOT monomers. Therefore, we attribute such special phenomena to the poor conjugation of the polymer due to the long three-atom linker existing in the polymer matrix. That is, due to the introduction of non-conjugated linker, the obtained polymers are non-conjugated without typical p-type feature peaks in absorbtion spectra under SSP. That is why the hydrazine treatment has little effect on their films' absorbtion spectra as well.

FTIR spectroscopy

The structural information was obtained using Fourier transform infrared (FTIR) spectrometer as shown in Figure 3. All polymers have peaks around 1480, 1439, 1340, and 1200 cm^{-1} originated from the stretching of C=C and C-C in the thiophene ring.[17,18] As we noted that all polymers shows distinct strong sharp peak at 2920, 2850 cm^{-1}, which are assigned to CH_3 stretching modes.[19] Due to the existence of C-N vibration, peak of 1080 cm^{-1} was observed.[20]

Photo-picture and SEM images

After SSP under desire temperature overnight, yellow-brown or yellow crystals of these monomers change to be sky-blue or black power as shown in Figure 4a. Figure 4b-g shows the SEM surface morphologies of the drop-casted monomers films and respective polymers on FTO substrate. It is obvious that the morphology has a great change after SSP. Except for Br_2-3-EDOT, most monomers show typical aggregation of micrometer-sized irregular-shape sheet while most polymers show similar shape with typical layered structure. It is noticed that in the case of P(3-alkyl-EDOT), it shows different morphology with sphere or ellipsoid with size range from 0.3-2 μm, even up to 10 μm sized sphere was observed. Such featured characteristic should be attributed to the its lower T_g because of the observation of large volume shrinkage under higher SSP temperature.

Crystallographic X-ray Analysis

Single crystals of the three successful monomers (**1, 2** and **3**) and a failure sample **4** were obtained and investigated by X-ray analysis (shown in Figure 5-9) for further understanding of the structural requirements and SSP polymerization pathway. All the parameters of these crystals were summarized in Table S1 in supporting information. As we can see that **1** and **2** share the same space group and almost have the same parameters of *a*, *b*, *c* values of the crystals. After methyl on nitrogen of **2** was replaced by butyl of **3**, it makes great changes from space group of P-1 (triclinic) to space group of P-42(1)c (tetragonal) in crystal, showing quite different structure information as summarized in Table S1 (see Supporting Information). In addition, the unit cell containing molecule number increases from two to eight. In the case of I_2-4-EDOT (**4**), it belongs to monoclinic with space group of P21/c. The monomer structure of 1-4 were shown in Figure 5. The distance between S-S is 5.112 and 5.136 Å for Br_2-3-EDOTand I_2-3-EDOT respectively while the introduction of alkyl chain results in the shortest distance of 3.781 Å. However, in the case of I_2-4-EDOT, the -Si- $(CH_2)_2$-Si- linker enhance the S-S distance greatly with up to 7.295 Å. Here we discuss in the following on their crystal structure and try to establish the relationship between structure information and their SSP behavior.

As shown in Figure 6a and b, **1** has the nearest halogen distance of 4.067Å with C1-C15 contact of 6.278 Å, followed by the second shortest distance of 4.678 Å with C1-C15 contact of 5.126 Å and then having the third shortest distance of 5.369 Å with the shortest C1-C1 contact of 3.568 Å. Previous study[6,7a] showed that SSP pathways usually involve C/C triangle unit composed of three monomer molecules in the chain. Here, the new polymerization mode composing of four monomer molecules is appeared, shown in Fig 6c. In such case, the polymerization process should be demonstrated in this way: first it forms trimer with the construction of triangle through C/C contact in a regular mode, then the trimer attacks the forth monomer to complete the repeatable four sub-units for the further construction of its polymer matrix, as demonstrated with C15-C1-C1-C15 pathway. In addition, we noticed that the C1/C15 contact with quite long Br/Br distance of 6.148 Å is involved in this pathway, which may not the real case due to the deformation of thiophene ring. In this case, the fact that the initial trigger of C15/C1 has a short halogen distance, et. effective halogen distance of 4.762 Å with 28.7% longer than double van der Waals radius of Halogen ($2r_w$) can well explain that **1** has SSP success with its SSP onset temperature (T_{onset}) of 125 ^{o}C.

Therefore, there are two possible modes of C15-C1-C1-C15 (Fig 6c) and a reverse one and all of their Hal/Hal and C/C distances are suitable for SSP. It is obvious that the former mode is the preferred polymerization pathway because the initial trigger of C1/C15 has a shorter halogen distance of 4.762 Å while the latter has that of 5.350 Å .

After bromo was replaced by iodo in monomer of **2**, its crystal structure basic parameters are almost the same as monomer **1**. However, there still has some change in detail. As shown in Figure 7a and b, **2** has nearest halogen distance of 4.131Å with C1-C13 contact of 6.652 Å, followed by the second shortest distance of 5.502 Å with C1-C1 the shortest contact of 3.689 Å. It is obvious that though the former mode has the nearest halogen distance, its C1/C13 distance (6.652 Å) is too long to form corresponding polymer. As shown in Figure 7c in a view along the a-axis, there are two possible pathway for the polymerization. The one way, as denoted by blue arrow, C1-C13 contact distance is 5.381 Å with the Hal/Hal distance of 4.805 Å while neighbor C1-C1 contact of 3.689 Å and Hal/Hal of 5.502 Å are found in the crystal. And C1/C13 distance between each third molecule is in the chain (7.826 Å), is almost the same as the corresponding distance in regular polythiophene (7.85 Å),[21] which is shorter than those have one atom-spacer derivatives as previously reported by us.[7]

Another possible polymerization direction (purple arrow denoted) is as follows. C1-C13 contact distance is 5.381 Å, with the Hal/Hal distance of 4.805 Å while neighbor C1-C1 contact of 5.595 Å and very long Hal/Hal of 6.159 Å are found in the crystal. And C1/C13 distance between each third molecule is in the chain (9.101 Å). That is, both modes share the first initial dimer formation procedure with effective Hal/Hal distance of 4.805 Å. Therefore, we think the former pathway might be a more favorable choice because of its shorter Hal/Hal distance involved. In addition, we noted that the effective Hal/Hal distance (4.805 Å) is much longer (20.1 %) than the $2r_w$ of iodine (4.0 Å). This result matches our expectation that the existence of flexible three-atom-spacer may have long halogen distance to guarantee SSP success.

As shown in Figure 8a and b, **3** has nearest halogen distance of 4.134Å with C12-C12 contact of 5.453 Å, followed by the second shortest distance of 5.497 Å with C6-C12 the shortest contact of 5.991 Å and the third shortest distance of 6.616 Å with C6-C6 the shortest contact of 6.594 Å is found in the crystal. Meanwhile, the shortest C12/C12 contacts of 5.453 Å, observed between the EDOT units with a dihedral angle of 83.35°, is shorter than a corresponding distance in **2**. These contacts form four one-dimensional chains in one crystal unit cell, which is quite different to that observed for **2**, but running along the crystallographic *c*-axis In this case, the C12/C12 distance (8.117 Å) between each third molecule in the chain is only 3% longer than the corresponding distance in traditional polythiophene chain (7.85Å[22]), which is the favorable for a SSP along this direction. Due to the fact that the other pathway has too long distance to construct polythiohene, therefore, the sole and reasonable polymerization pathway is along *c*-axis, clearly shown in Fig 8c. According to our previous study of those one-atom linker with V-shape monomers, including monomer **1** and **2** as discussed above, **3** demonstrates quite different polymerization pathway of involving of the same distance of 4.134 Å, which is frequently observed in those investigated small EDOT derivatives in SSP field.[6]

In addition, taking **3** is less stable than **2** as mentioned in the SSP behavior section into consideration, one may deduce that though the bulkier butyl chain would occupy bigger room in crystal packing and would be unfavorable for SSP, the butyl is much more flexible which help the V shape molecule rotate more freely than the methyl containing monomer. This is the simple qualitative explantation. In fact, **3** has shorter effective halogen distance of 4.134 Å while **2** gets up to 4.805Å, which are longer than $2r_d$ 3.4 and 20.1% respectively. This is the solid evidence to explain why **3** is more easily to undergo SSP compared with **2**. According to these facts, we can get conclusion that though the replacement from methyl to butyl group, it greatly changes crystal structure as well as the SSP behavior. Therefore, this finding may offer much opportunity to further rationally and accurately control the monomers' SSP behavior through a simple modification of the linker's steric structure.

After long flexible four-atom-chain was introduced,

I_2-4-EDOT demonstrates folded molecule with torsion angle of 50.31° and the two EDOT subunits are almost parallel with each other with their angles of C(EDOT)-Si-CH_2 with 107.65° and 105.65° respectively. As shown in Figure 9a and b, **4** has the shortest, second and third halogen distance of 4.388, 4.615, and 4.629 Å respectively with the corresponding all C1-C18 contact of 6.760, 4.598 and 5.624 Å respectively. Similar to I_2-3-EDOT (**2**), there are two possible polymerization pathways (shown in Figure 9c), demonstrated by two triangles of C/C distance and corresponding of triangles of Hal/Hal distance. In these two cases, it is noted that C/C distance between each third molecule in the chain (8.728 Å for C1/C1, 7.228 Å for C18/C18) are suitable and the Hal/Hal distance (4.388, 4.615; 4.615, 4.629 Å) are short enough too, which may construct corresponding polymers freely. However, taking the shortest Hal/Hal distance of 4.386 Å with the extraordinary long C1/C18 contact of 6.760Å into consideration, this is the unfavorable polymerization pathway as denoted purple arrow and the preferred one was presented as well (blue arrow sign) in Fig 9c. However, I_2-4-EDOT's SSP failure contradicts to the theoretical prediction. Compared with T_{onset} of I_2-3-EDOT (95°C), we can not expect lower T_{onset} of I_2-4-EDOT, because they donot share the same frame structure due to different linker length. We attribute such interesting observation to its relative low melt point of 115-116°C. In this case, its crystal structure collapses before it reaches T_{onset}. Such especial result reveals that crystal structure analysis is a powerful technique to guide monomers design and predict their SSP behavior and sometimes the prediction would be invalid in the case of low melt point of the monomers.

Through the above careful discussion, Table 1 summarizes all important distances derived from the crystal structures. As we can see that the effective Hal/Hal distances for Br_2-3-EDOT, I_2-3-EDOT, I_2-3-alkyl-EDOT show longer than 28.7, 20.1 and 3.4 % of their $2r_w$ respectively and all of them succeed in SSP. Though I_2-4-EDOT shows 15.4% longer than $2r_w$ of iodine, it fails to pass SSP test due to its lower melt point. We are trying to establish the relationship between effective Hal/Hal distances with onset SSP temperature through collecting numerous crystal data. However, it needs up to hundred samples because the variation of main structure, substitution groups have big effect on T_{onset}.

Molecule weight and thermal stability TGA analysis

Because of the insolubility of the other two polymers, the soluble P(3-alkyl-EDOT) was chosen as a typical model compound to further characterize especially concerning of molecular weight and its GPC profiles were presented in Fig.S10 (supporting information). Previous MALDI-TOF mass spectrometry reveals that poly(2,3-Dihydro-thieno[3,4-b][1,4]dithiine) obtained through SSP contains up to 5-14 monomer units and elemental analysis of dedoped one indicates an average of six repeat units per chain.[6a] Here we get a typical polymer molecular weights information of P(3-alkyl-EDOT) through GPC. Mn of 4.40 kg mol^{-1} with PDI of 2.19 indicates that the P(3-alkyl-EDOT) has a repeat units of 10, which is consistent with the above result as described above. And the temperature dependence with M_n and PDI was summarized in Table 2. As we can see that, higher temperature results in a litter bit lower molecule weight and extension of SSP time dose not have great influence on M_n. The thermal stability of the polymers was investigated with thermogravimetric analysis (TGA) (Fig. S11). The 5% weight-loss temperatures for P(3-EDOT)-Br, P(3-EDOT)-I and P(3-alkyl-EDOT) were 193, 185 and 248°C respectively, indicating that the introduction of alkyl chain would enhance thermal stability greatly. In addition, it seems that P(3-EDOT)-I shows less stability compared with P(3-EDOT)-Br. We attribute this to its lower stability with high halogen content in the polymer matrix, resulting quick halogen release under thermal treatment.

Conclusion

In this work, several kinds of new EDOT derivatives containing flexible linkers of different lengths were synthesized and investigated under SSP. Among these rational designed monomers, iodo substituted with flexible three-atom linkers has similar crystal structure and easily undergoes SSP when compared with bromo substituted one. Meanwhile, in the case of four-atom linker length, though it would get theoretical SSP success according to its crystal structure analysis, it cannot be polymerized because of its low melt point, indicating that at present we do not find length limit for the flexible chain linker. Combing with their crystals structure data, these observation and evidence not only may help to gain a deeper understanding of SSP but also enlarge thiophene-based SSP database. Furthermore, the substitution on the flexible linker moiety also plays an important role in the fine-tuning of their monomers' SSP behavior and corresponding polymers' functional properties. And such investigation are underway in our lab. Anyway, both of the linker length, linker structure and sometime the monomer's melt point are key factors to determine their SSP behavior.

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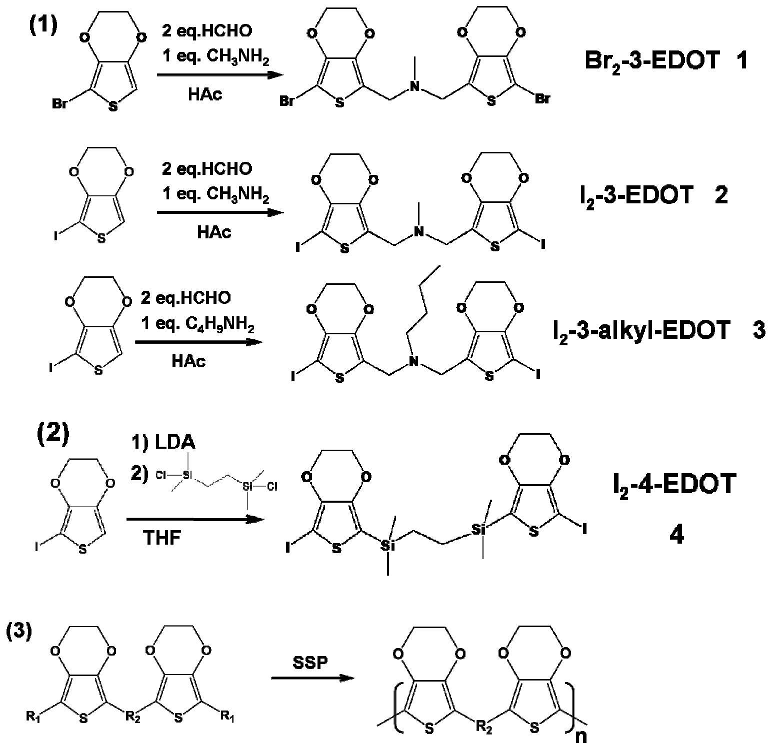


monomer	polymer	Onset T
Br_2-1-EDOT : R_1 = Br; R_2 = CH_2	P(1-EDOT) ref 7	< 60 °C
Br_2-3-EDOT (1): R_1 = Br; R_2 = CH_2-N(CH_3)-CH_2	P(3-EDOT)-Br	125 °C
I_2-3-EDOT (2): R_1 = I; R_2 = CH_2-N(CH_3)-CH_2	P(3-EDOT)-I	95 °C
I_2-3-alkyl-EDOT (3): R_1 = I; R_2 = -CH_2N(C_4H_9)CH_2-	P(3-alkyl-EDOT)	80 °C
I_2-4-EDOT (4): R_1 = I; R_2 = -Si(CH_3)$_2$$C_2H_4$Si($CH_3$)$_2$-	No reaction	

Scheme 1. Synthesis of the monomers and corresponding polymers.

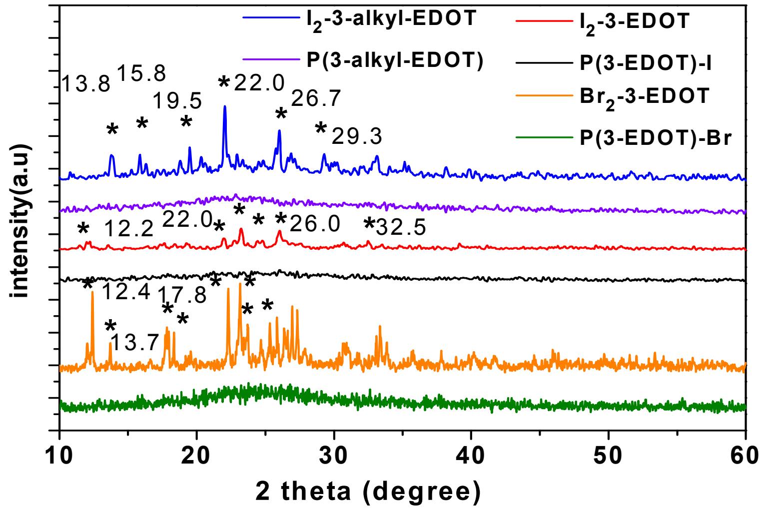


Figure 1. XRD spectra of monomers and corresponding polymers

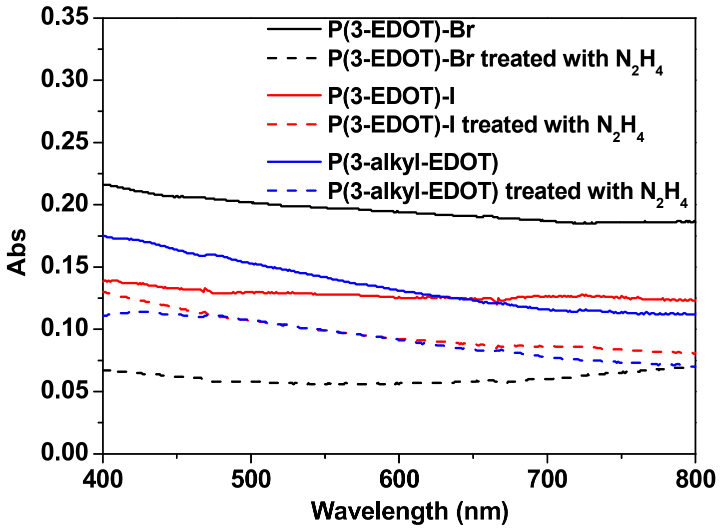


Figure 2. Absorbance spectra of the polymers and those hydrazine treated polymers (fresh made).

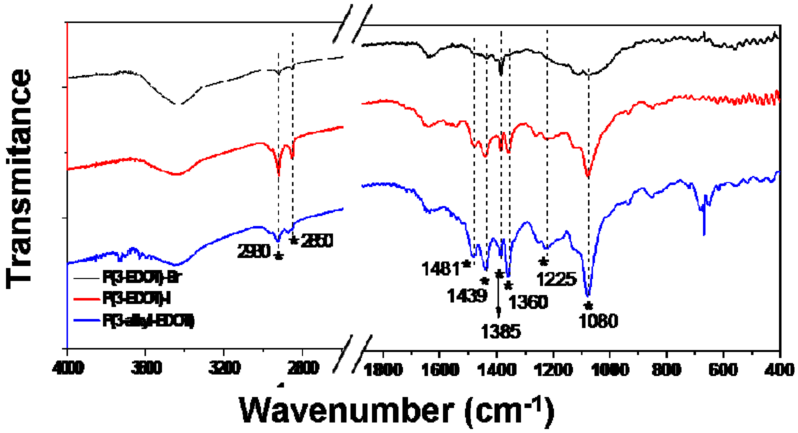


Figure 3. FTIR spectra for these polymers.

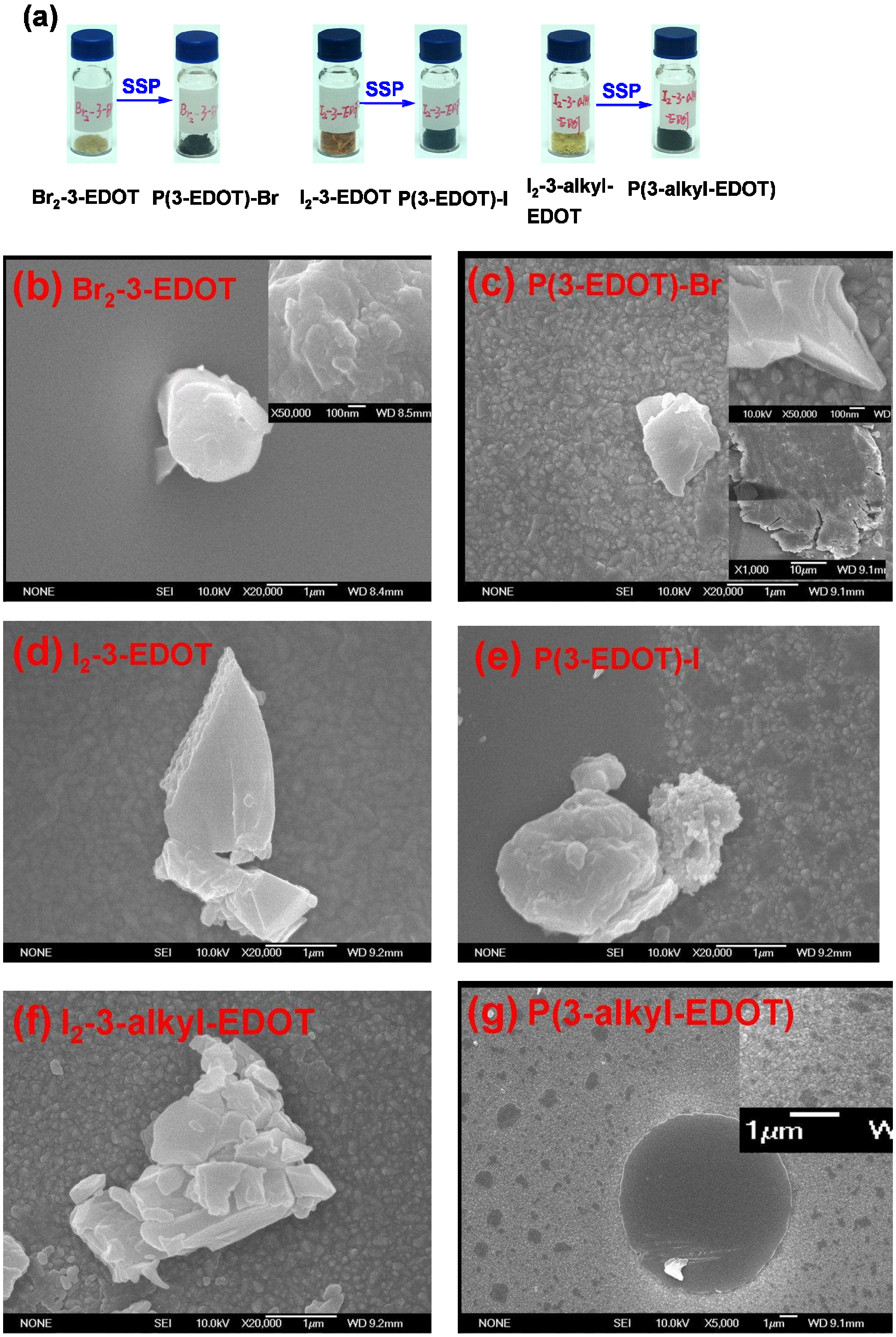


Figure 4. (a) Photographs of crystals of monomers and respective polymers. (b) Br_2-3-EDOT, (c) P(3-EDOT)-Br (d) I_2-3-EDOT, (e) P(3-EDOT)-I, (f) I_2-3-alkyl-EDOT and (g) P(3-alkyl-EDOT).

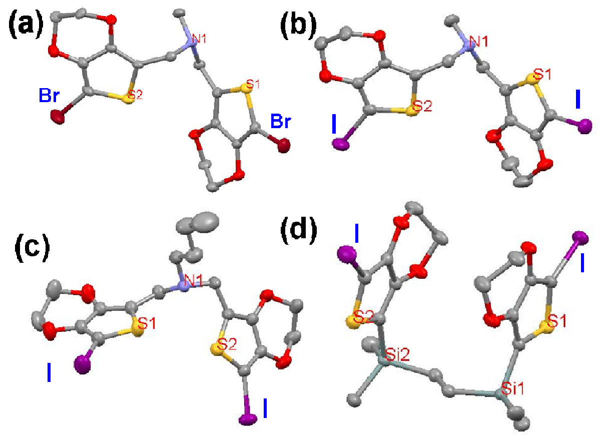


Figure 5. Crystal structure of (a) Br_2-3-EDOT (b) I_2-3-EDOT (c) I_2-3-alkyl-EDOT and (d) I_2-4-EDOT.

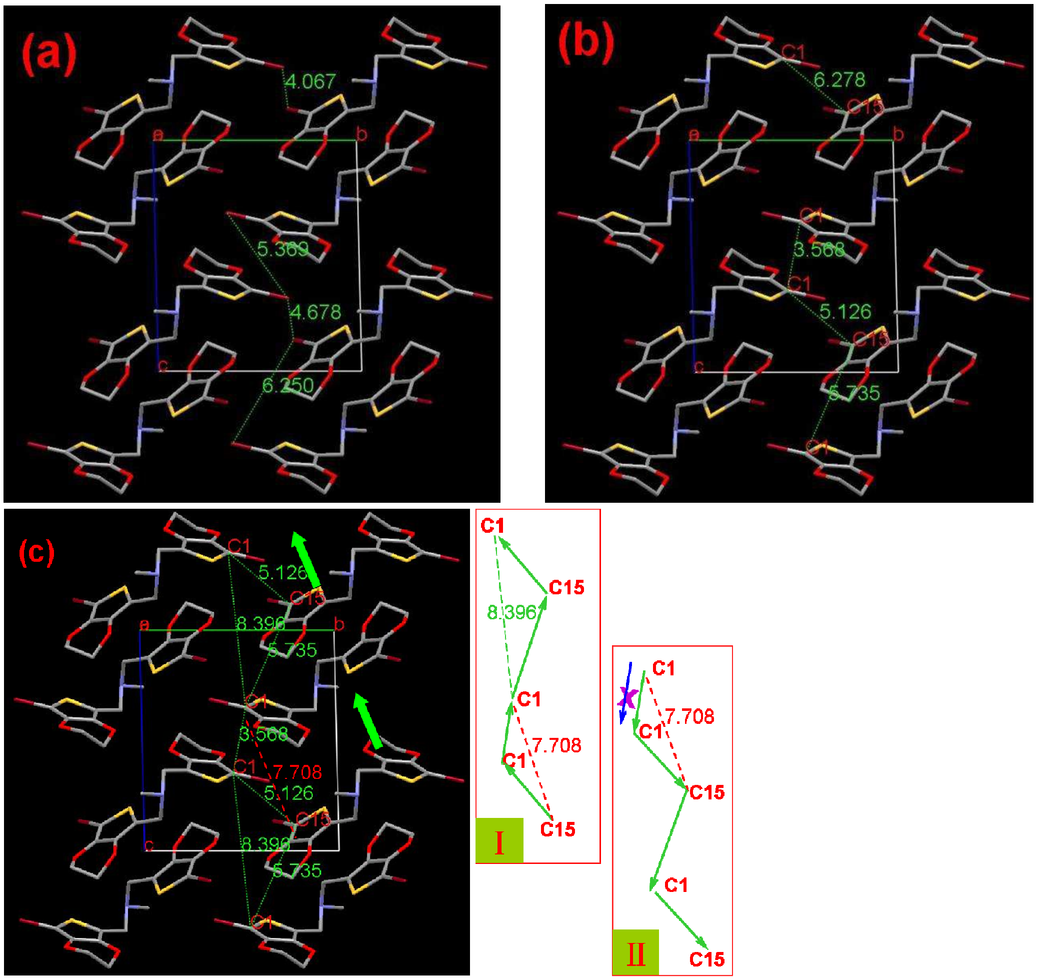


Figure 6. Single-crystal X-ray structure of compound Br_2-3-EDOT (**1**). (a) view of the halogen distances (b) view of C/C contact distances (c) crystal packing viewed along the a-axis, C1/C1 and C1/C15 distance between each third molecule and proposed polymerization pathways. The numbers indicate corresponding distances in Å. Hydrogen atoms are omitted for clarity: Br, red; S, yellow; N, light blue and C, gray.

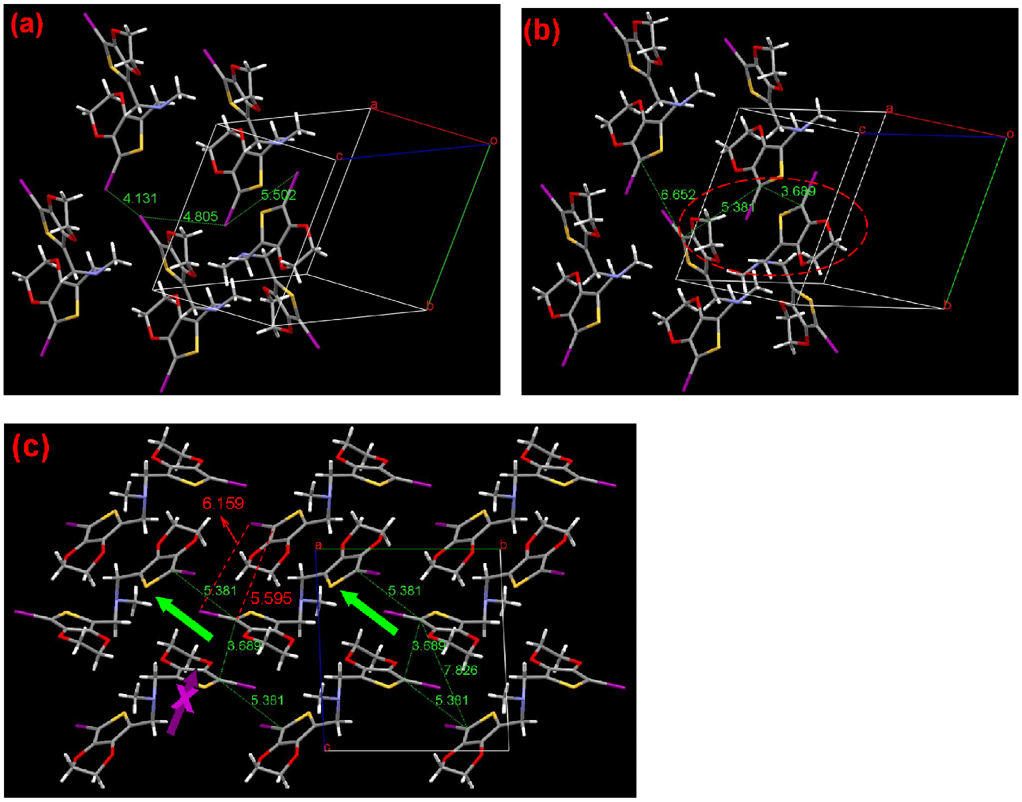


Figure 7. Single-crystal X-ray structure of compound I$_2$-3-EDOT (**2**). (a) view of the halogen distances (b) view of C/C distances (c) crystal packing viewed along the a-axis, C1/C13 distance between each third molecule and proposed polymerization pathways. the numbers indicate corresponding distances in Å. I, purple; S, yellow; N, light blue and C, gray.

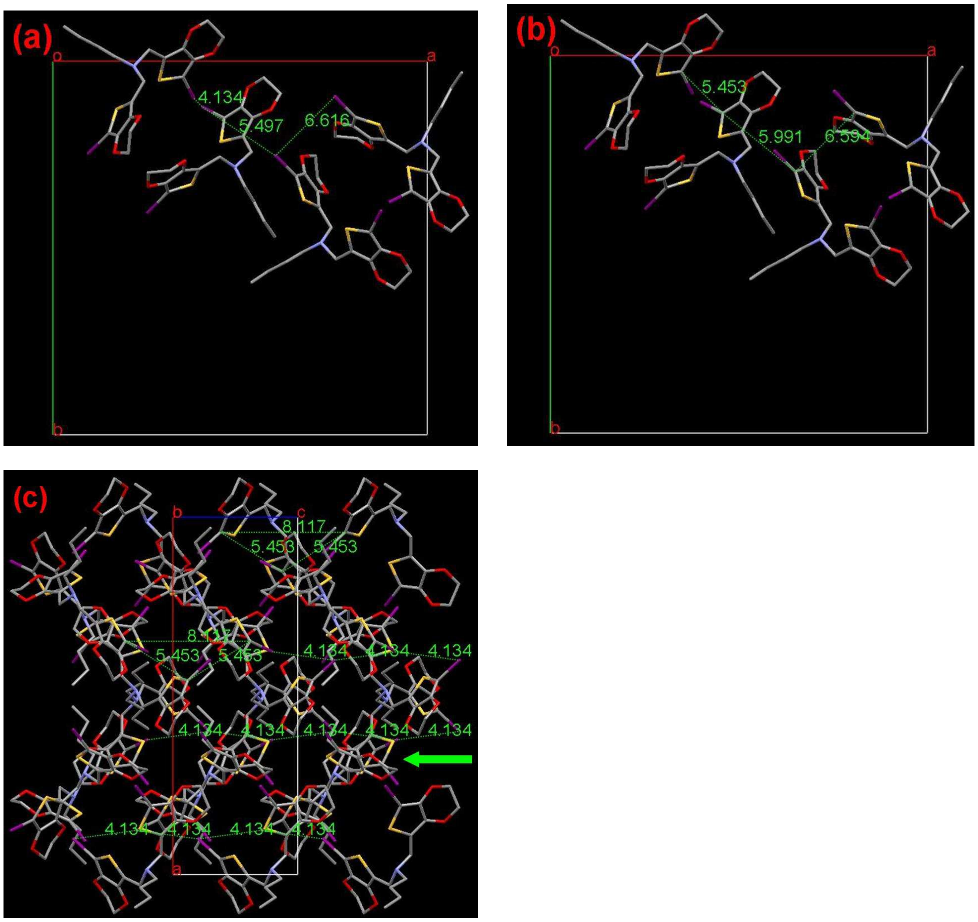


Figure 8. Single-crystal X-ray structure of compound I$_2$-3-alkyl-EDOT (**3**). (a) view of the halogen distances (b) view of C/C distances (c) crystal packing viewed along the a-axis, C1/C13 distance between each third molecule and proposed polymerization pathways. the numbers indicate corresponding distances in Å. Hydrogen atoms are omitted for clarity: I, purple; S, yellow; N, light blue and C, gray.

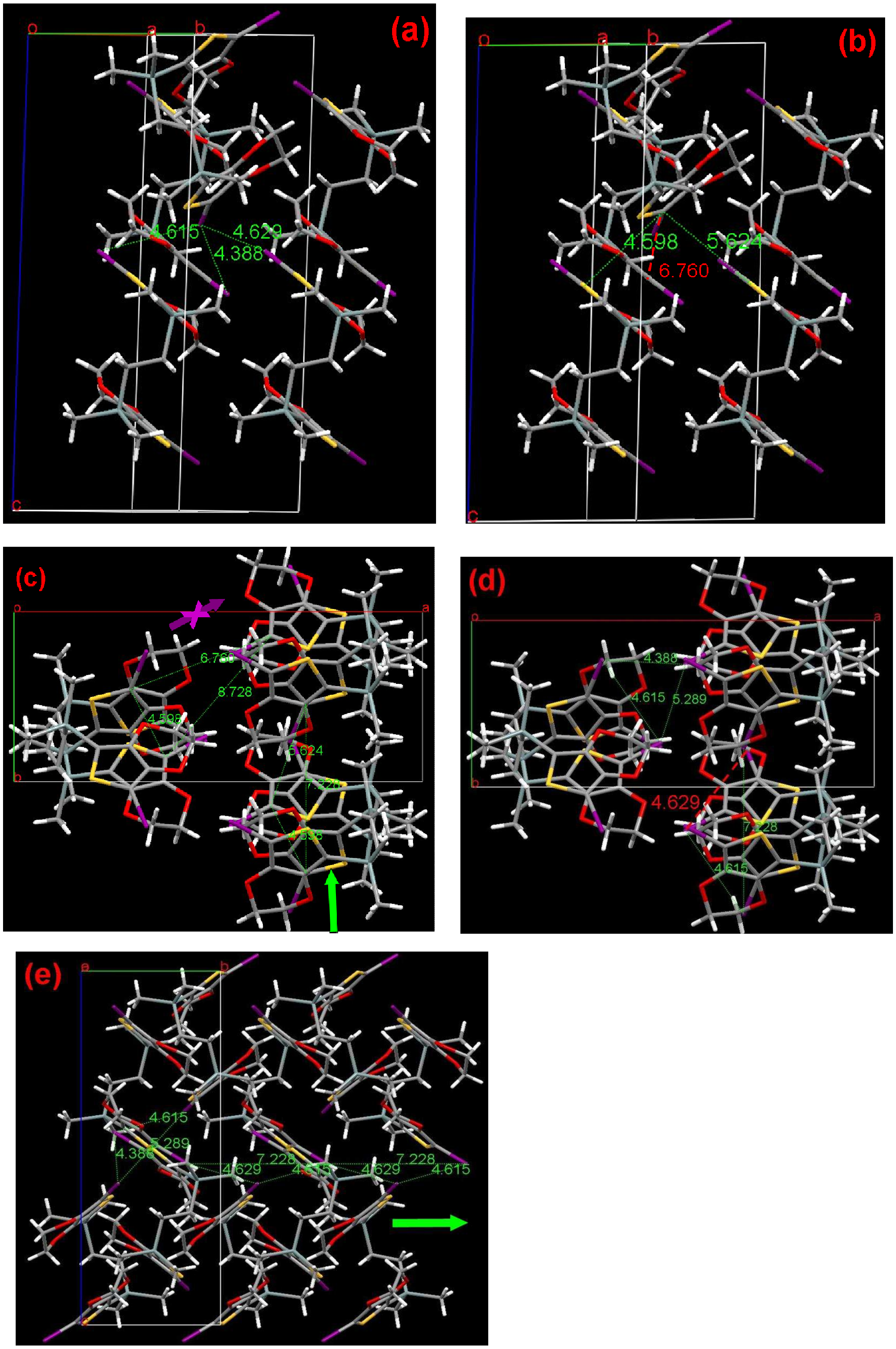


Figure 9. Single-crystal X-ray structure of compound I$_2$-4-EDOT (**3**). (a) view of the halogen distances (b) view of C/C distances (c) crystal packing viewed along the c-axis, C1/C1, C18/18 distance between each third molecule and proposed polymerization pathways. (d) corresponding of Hal/Hal distance based on C/C contact of Fig 9(c). the numbers indicate corresponding distances in Å. Hydrogen atoms are omitted for clarity: I, purple; S, yellow; Si and C, gray.

Table 1. Selected Hal/Hal and C-C contact distance (Å) for those crystals reported

molecules **parameters**	**Br_2-3-EDOT**	**I_2-3-EDOT**	**I_2-3-alkyl-EDOT**	**I_2-4-EDOT**
shortest Hal/Hal distance	4.056	4.131	4.134 [a]	4.388
2nd shortest Hal/Hal distance	4.762 [a]	4.805 [a]	5.497	4.615 [a]
3rd shortest Hal/Hal distance	5.350	5.502	6.616	4.629
C-C contact shortest distance	3.582	3.689	5.453	4.589
C-C contact 2nd shortest distance	5.167	5.381	5.991	5.624
C/C distance between each third molecule	8.303	7.826	8.117	7.228
$2r_w$	3.7	4.0	4.0	4.0
longer than $2r_w$ [a]	26.4	20.1%	3.4 %	15.4%
onset of Temperature	125 °C	95 °C	80 °C	-

[a]Effective Hal/Hal distance; $2r_w$: double van der Waals radius of halogen

Table 2. Effect of SSP temperature (24 h) on the Molecular Weight and PDI.

Temperature	Yield (%)	Retention time	M_n(kg mol^{-1})[a]	DP[b]	PDI[a]
80°C	> 90	23.55	4.40	11	2.19
90°C	>90	24.4	3.83	10	2.16
100°C	> 90	24.7	3.64	9	1.94
80°C (3 d)	> 90	24.1	4.11	10	2.20

[a] Molecular weights and PDI were determined by GPC with respect to polystyrene standards.

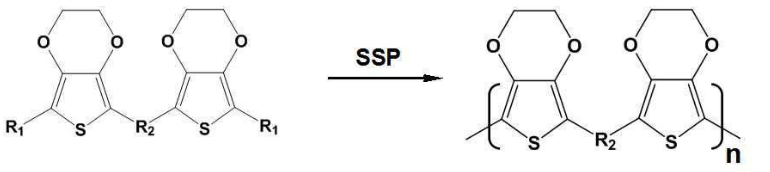
[b] Degree of polymerization (DP) was calculated based on the M_n values determined by GPC.

GRAPHICAL ABSTRACT

Effect of Flexible Linker Length in 3,4-Ethylenedioxythiophene Derivatives for Solid State Polymerization

Chuong Tusy, Kai Peng, Lili Huang, Jiangbin Xia

EDOT-*linker*-EDOT was chosen as a prototype model monomer for solid state polymerization (SSP) due to its readily synthesis procedure and tunable flexible linker length. Our results reveal that those successful monomers' linker length can be up to three atoms at least while four-atom linker monomer failed under SSP due to its lower melt point though having preferred polymerization pathway according to the theoretical prediction.



monomer	polymer	Onset T
Br_2-1-EDOT : R_1 = Br; R_2 = CH_2	**P(1-EDOT)** ref 7	**< 60 °C**
Br_2-3-EDOT (1): R_1 = Br; R_2 = CH_2-$N(CH_3)$-CH_2	**P(3-EDOT)-Br**	**125 °C**
I_2-3-EDOT (2): R_1 = I; R_2 = CH_2-$N(CH_3)$-CH_2	**P(3-EDOT)-I**	**95 °C**
I_2-3-alkyl-EDOT (3): R_1 = I; R_2 = -$CH_2N(C_4H_9)CH_2$-	**P(3-alkyl-EDOT)**	**80 °C**
I_2-4-EDOT (5): R_1 = I; R_2 = -$Si(CH_3)_2C_2H_4Si(CH_3)_2$-	No reaction