Investigation of Substitution Effect on Poly(bis-3,4-ethylenedioxythiophene methine)s through Solid State Polymerization†

Kai Peng, Tong Pei, Zhaoxiang Li, Lili Huang, Jiangbin Xia*

Receipt/Acceptance Data **[DO NOT ALTER/DELETE THIS TEXT]**

Publication data **[DO NOT ALTER/DELETE THIS TEXT]**

DOI: 10.1039/ c1cc000000x [DO NOT ALTER/DELETE THIS TEXT]

Thieno[3,4-b]-1,4-dioxin, 5,5'-methylenebis[2,3-dihydro] was chosen as a universal solid state polymerization (SSP) platform due to its readily synthesis procedure, further tunable substitution groups on CH_2 bridge and its excellent conjugated quinonoid structure of corresponding poly(bis-3,4-ethylenedioxythiophene methine). These monomers were designed by taking the steric effect and molecular flexibility into consideration and by carefully investigated under SSP. In addition, the aromatic moieties were firstly introduced in branch chain in this polymer matrix, which may offer amazing properties and further modification opportunities based on this unique platform. Our results reveal that the substitution groups on the CH_2 bridge play an important role in SSP. The bulkier the substitution group and the longer effective halogen distance the monomers have, the higher onset temperature (T_{onset}) the SSP will have. Furthermore, the primitive dependence of T_{onset} with effective halogen distance was established.

Keywords: Solid state polymerization, Molecular flexibility, Poly(bis-3,4-ethylenedioxythiophene methine), Quinonoid structure

Introduction

Conductive & conjugated polythiophene have been intensely investigated due to its numerous application such as light-emitting device, supercapacitors, electrochromic devices, including organic photovoltaic cells.[1-5] Through rational design, it can be easily tailored and synthesized with outstanding and multi-functional properties. It is known that eliminating the hydrogen atoms from a thiophene ring can construct corresponding conducting polymer, take this into consideration, the synthesis methods mainly cover chemical oxidation polymerization, electropolymerization and photo-polymerization. Meanwhile, the metal-catalyzed polycondenstion plays a key role in those neutral polymers synthesis. Recently, a new method of solid state polymerization (SSP)[6-7] attracted much attention due to its solvent free, oxidant free and/or external applied potential free special features, which are required by traditional methods as mentioned above.

Recently, different from the popular longitudinal direction design concept, we and others proposed a new design strategy which is along with 3,4-Ethylenedioxythiophene (EDOT) parallel direction through introducing a flexible linker between EDOT units and it made great SSP success.[8] Meanwhile, it is noticed that the substitution group has great influence on SSP excluding the linker atoms effect. For instance, introduction of rigid benzene ring would increase the onset temperature of SSP (T_{onset}).[8b] In addition, Perepichka group observed similar substitution steric effect that the fixed 5-member ring monomer was more stable than the molecule which is with free two methyl group attached on ethylene 2,3-dihydro-thieno[3,4-b][1,4]dioxine.[7c] These interesting observation reminded us that it would be possible to accurate control SSP process by simply fixing the flexible linker, changing the monomers flexibility as well as their basic platform structures.

Except for obtaining crystals structures information based on non-conjugated platform of EDOT-CH_2-N(R)-CH_2-EDOT,[8c] we stop further work on this system and switch our efforts to those one atom linker containing systems due to the generation of quinoidal structure of polymers. In addition, empirical rule for SSP for polythiophene synthesis can not be established due to lack of enough crystal data.

Here, thieno[3,4-b]-1,4-dioxin, 5,5'-methylenebis[2,3-dihydro] was chosen as a universal SSP platform due to its readily synthesis procedure, tunable substitution groups on CH_2 bridge and excellent photo physical & chemical properties in the corresponding poly(bis-3,4-ethylenedioxythiophene methine) matrix. All these monomers were designed mainly based on their steric effect, molecular flexibility and aromatic groups were introduced due to their abundance and versatility. Meanhile, due to the existence of conjugated quinonoid structure, poly(3,4-ethylenedioxythiophene methine) is a typical small band

*College of Chemistry and Molecular Science, Wuhan University, Wuhan 430072, China. E-mail: jbxia@whu.edu.cn (J. Xia)

Phone & Fax: 86-27-68756707

†Electronic supplementary information (ESI) available: CCDC 1410882-1410884, ^{1}HNMR and ^{13}C-NMR. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c5ra…

gap polymer and appeared in 1980s,[9] and it is poorly investigated for organic-electronic applications.[10]

This study would help us to establish the SSP database systematically and efficiently. Meanwhile, an equation has been primitively established to probe the relationship between effective halogen distances[8b] with their T_{onset}, which would be a powerful tool to design or explain much more interesting samples for SSP.

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-Iodo-2,3-dihydro-thieno[3,4-b][1,4]dioxine (I-EDOT)[11] was synthesized according to previous report.

Monomer synthesis and solid state polymerization

Linking the thiophene moieties: synthesis of I_2-CH(R)-EDOT

General method

Monomers of I_2-CH(R)-EDOT were synthesized in accordance with previous method[12] as shown in Scheme 1. To a stirred solution of zinc chloride in hydrochloric acid between -8˚C and -10˚C, 5-iodo-3,4-ethylenedioxythiophene (2.0 eq.) was added over several minutes. Different aldehydes (1.0 eq.) were added dropwise over 60 min while maintaining the temperature around -10˚C. The reaction mixture was stirred for 60 min while maintaining this temperature and then quenched with water and extracted with ether. The organic extract was washed with 5% sodium bicarbonate solution, and dried over magnesium sulfate, and then the solvent was evaporated. Purification by column chromatography (silica gel, light petroleum-CH_2Cl_2, 2 : 1) afforded white solid.

Monomer I_2-Ph-EDOT

White powder (24%), ^{1}H NMR: δ (300 MHz, DMSO-d_6) 7.24-7.31 (m, 3 H); 7.17-7.19 (m, 2 H); 5.76 (s, 1 H); 4.20 (m, 4 H); 4.16 (m, 4 H). ^{13}C NMR: δ (300 MHz, DMSO-d_6) 144.4, 141.4, 137.8, 128.9, 127.9, 127.6, 123.0, 65.3, 64.7, 49.9.

Monomer I_2-Naph-EDOT

White powder (25%), ^{1}H NMR: δ (300 MHz, DMSO-d_6) 7.80-7.98 (m, 3 H); 7.42-7.58 (m, 3 H); 7.21 (m, 1 H); 6.47 (s, 1 H); 4.23 (m, 4 H); 4.18 (m, 4 H). ^{13}C NMR: δ (300 MHz, DMSO-d_6) 144.4, 137.7, 137.2, 133.8, 130.7, 129.4, 128.3, 125.8, 124.8, 122.9, 65.3, 64.9, 50.1, 36.5.

Monomer I_2-Triph-EDOT

Yellowish powder (20%), ^{1}H NMR: δ (300 MHz, DMSO-d_6) 6.92-7.07 (m, 6 H); 6.70-6.85 (m, 6 H); 5.62 (s, 1 H); 4.15 (m, 4 H); 4.11 (m, 4 H); 2.18 (s, 6 H). ^{13}C NMR: δ (300 MHz, DMSO-d_6) 147.8, 145.9, 145.2, 138.6, 133.6, 131.3, 129.7, 125.6, 124.2, 122.7, 66.1, 65.6, 50.8, 21.7.

Monomer I_2-Pr-EDOT

White powder (13%), ^{1}H NMR: δ (300 MHz, DMSO-d_6) 4.33-4.44 (t, 1 H); 4.21 (m, 4 H); 4.19 (m, 4 H); 1.70-1.84 (m, 2 H); 1.18-1.29 (m, 2 H); 0.80-0.90 (t, 3 H). ^{13}C NMR: δ (300 MHz, DMSO-d_6) 144.2, 138.2, 137.6, 124.1, 65.3, 64.8, 48.3, 38.2, 34.9, 20.6, 13.8.

General Solid state polymerization

The SSP procedure was conducted according to previous method.[7,8] In a closed 5 mL vial, the iodinated compounds (100-300 mg) were incubated at 60-150^o C for 2-24 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. At last, the vacuum drying afforded the nearly fully dedoped respective polymers.

Crystal Structure Determination

Intensity data for the obtained three crystals were collected by 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 three monomers are given in Table S1 (see in the Supporting Information). Data sets reduction and integration were performed by using the software package SAINT PLUS.[13] The crystal structure is solved by direct methods and refined by using the SHELXTL 97 software package.[14]

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 were deposited by spin-coating or drop-casted with 0.5-3 wt% of $CHCl_3$ monomers solution on fluorine doped tin oxide (FTO) substrate or slide glasses. These monomer coated substrate were employed for SSP and then resulted polymers or polymer/FTO substrates. These products were used for XRD, UV-Vis or as working electrode for electrochemical measurements. For the three-electrode electrochemical measurements in 0.1 M $LiClO_4$ in acetonitrile, a 1 cm^2 area of FTO/Polymer substrate, platinum foil, and Ag/AgCl were 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 molecular weight and molecular weight distribution of the polymers were determined by gel permeation chromatography (GPC) which was 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 their solid state polymerization

All designed monomers were synthesized as shown in Scheme 1. Monomers of I_2-CH(R)-EDOT were obtained through the corresponding aldehydes reaction with I-EDOT in the existence of zinc chloride in hydrochloric acid. It is noted that the aromatic aldehydes show better yields compared with alkyl aldehyde. SSP results show that all monomers can successfully form corresponding polymers under heat treatment with different T_{onset} and also indicate that the substitution groups play a key role in their SSP behavior. It is interesting that after introducing of propyl group, I_2-Pr-EDOT requires the lowest T_{onset} of 70 ^{o}C while others need higher temperature in range of 80-130 ^{o}C. It appears that the bulkier aromatic group the monomer has, the higher T_{onset} it needs. Detailed analysis & discussion concerning of effective halogen distance and the relationship with T_{onset} will be done in the crystal structure section. These interesting results encourage us to the further explore much more acutely controllable and fine tunable thiophene monomers for SSP.

XRD Patterns of monomers and respective polymers

As shown in Fig. 1, except for I_2-Pr-EDOT, most monomers show typical sharp peaks in the rage of 5-50º, which are quite consist with their simulated results through their crystal structure data. Because of the wax-state at room temperature, I_2-Pr-EDOT's XRD shows wide peak around 23º. After SSP, polymers show broad peak around 24.0°, 22 and 26° for P(Nap-EDOT), P(Triph-EDOT) and P(Pr-EDOT) respectively, while in the case of P(Ph-EDOT), it shows poor resolution peak in its XRD pattern. All these results indicate that substituted groups on CH_2-bridge have big effect on chain packing[9e] in poly(bis-3,4-ethylenedioxythiophene methine) matrixes.

In order to further investigate what happened during SSP procedure, *in-situ* XRD measurement was carried out for those typical monomers of I_2-Ph-EDOT and I_2-Nap-EDOT, which their crystals were obtained for further analysis. In addition, their most crystal phases were labeled according to their crystal simulated results. As shown in Fig. 2, it is obvious that the drastic intensity decrease for (321) phase was observed at the initial one hour's polymerization for monomer of I_2-Ph-EDOT while (421) phase's intensity decrease was found along with the disappearance of (401) phase within two hours of SSP. In addition, (420) phase was decreased or even disappeared within three hours. Meanwhile, in the case of I_2-Nap-EDOT, the drastic intensity decrease of (1,0,-2), (0, 2, 2), (4,1,0) and (1,2,4) phases were observed at the initial 2 hours' polymerization. In addition, (222) phase was decreased within eight hours heat-treatment.

Solution UV-Vis spectra for those polymers

Compared with typical insoluble PEDOT polymer, these monomers show small solubility in THF or DMF solvents. Therefore, their solution absorption spectra and those of hydrazine treated samples were presented in Fig. 3. It is clear that all polymers show typical p-type featured character while their neutral type polymers were obtained after hadrazene treatment due to the observation of drastic intensity drop at near-IR region around 700-1400 nm.[15,16] Among those SSP generated polymer solutions' absorption spectra, most of them show peak at 760 nm except that P(Nap-EDOT) exhibits a peak at longer wave length of 1000 nm. It indicates that P(Nap-EDOT) has the highest polaron or charge carrier density.

As for those neutral polymers, it has big difference compared with poly(3,4-ethylenedioxythiophene methine) which has typical strong peak at longer wavelength of 1000 nm.[12b] We attribute this to the less quinonoid structure in these poly(bis-3,4-ethylenedioxythiophene methine)s chain because of their repeat unit of bis-EDOT other than EDOT. Briefly, the introduction of benzene and naphthalene generates wide absorption range with well resolved peaks at 470 and 493 nm respectively. However, triphenylamine group results in a red shifted curve with two peaks at 540 nm and a shoulder peak around 650 nm. However, no distinct peak was observed for P(Pr-EDOT) as shown in Fig. 3d. Their detailed parameters of optical properties were summarized in Table 1. These absorption spectra results indicate that the substitution groups on CH_2-bridge have drastic effect on polymers optical properties, which may offer much modification opportunity[17] for different functional usage.

FTIR Spectroscopy

A comparison of the FTIR spectra of these polymers is shown in Fig. 4. Except for P(Ph-EDOT), most polymers have peaks around 1471, 1434, and 1360 cm^{-1} originated from the stretching of C=C and C-C in the thiophene ring[18,19] Meanwhile, all polymers demonstrate the featured peaks around 696 cm^{-1} related to in-plane deformation of C-S-C of thiophene ring.[18] In the case of P(TriPh-EDOT), it shows distinct strong sharp peak at 2920 and 2870 cm^{-1}, which are assigned to CH_3 stretching modes.[20] In addition, due to the existence of C-N bond, C-N and C-N-C bend modes at 1321 and 924 cm^{-1} were observed.[21]

Cyclic voltammetry behavior of the polymers

The CV curves are shown in Fig. 5, with the corresponding data summarized in Table 1. It is obvious that except for P(Pr-EDOT), all polymer films show typical CV curves which were commonly observed based on PEDOT. It indicates that such kind of polymers may have great potential usage in capacitance charge storage devices such as lithium battery, fuel cell and catalytic electrode materials. Meanwhile, most polymers have similar initial oxidation potential around 0 V vs Ag/AgCl while P(Pr-EDOT) has higher initial oxidation potential of 0.32 V, revealing that the introduction of propyl on CH_2 bridge will cause more difficulty for oxidization. In addition, P(Triph-EDOT) shows initial oxidation potential around 0.18 V with an additional oxidation potential of 0.8 V vs Ag/AgCl, which is assigned to N oxidation[22,23] in the polymer matrix. Furthermore, the N involved peak shows typical reversible redox behavior, indicating that it is a good candidate for charge storage or other redox alternatives in some other electrochemical devices.

Furthermore, according to their CV curves, the primitive charge storage capability sequence of the polymer is P(Nap-EDOT) > P(Ph-EDOT) > P(Triph-EDOT) > P(Pr-EDOT). In addition, it is noticed that previous result indicates that the poly(CH_2-EDOT)[8a] with non-substitution on CH_2 bridge has good electrochemical behavior, revealing that alkyl chain may destroy quinonoid structure and lead to poor conjugation in the polymer matrix to some extent. Therefore, the aromatic ring in polymer matrix would enhance the quinonoid conjugation and the stabilization of charge carrier in polymer matrix.

Crystallographic X-ray Analysis

Three single crystals of the monomers were obtained and studied by X-ray analysis (shown in Figure 6-9) for further understanding of the structural requirements for SSP. Though all monomers are designed based on the same platform of EDOT-CH(R)-EDOT, their crystal structures are quite different and their parameters are listed in Table S1. In addition, the substitution of R has big effect on I/I distances in monomers as shown in Fig 6. Their I/I distances were derived from corresponding molecules structures and it is found that the bulkier substitution group generates longer intramolecular I/I distance.

The Fig. 6 shows the monomers structure and those intramolecular distance and angles information are derived from crystals and listed in Table 2. It is obvious that along with the introduction of the bulkier substitution groups, the I_1/I_2 and S_1/S_2 intramolecular distance increase gradually while the bridge length of (C-CH(R)-C) almost keep the original distance of 2.50 Å with an angle of 112.00˚ for∠C-CH(R)-C. Meanwhile, angles of ∠$S_1C_7S_2$ and ∠$I_1C_7I_2$ increase greatly along with the introduction of bulkier substitution group. All these facts reveal that the steric effect plays an important role in their monomers structures. In addition, the long flexible chain may not have big effect on it if further increase alkyl chain length.

As shown in Fig. 7, no dimmer exists in I_2-Pr-EDOT crystal, but it is with the first and the second closest Hal/Hal distance of 4.267 and 4.878 Å respectively, accompanying with C11-C11 and C11-C1 contact of 7.681 and 5.517 Å respectively. Meanwhile, it has the third closest Hal/Hal distance of 6.305 Å, accompanying with the second shortest C-C (C1-C1) contact of 4.820 Å. It is found that the first polymerization pathway (formation of a spring circle, shown in Fig. 7c,) involves sole I/I distance of 4.878 Å while the second polymerization pathway (shown in Fig. 7d) involves two I/I distances of 4.267 Å and 6.305 Å, indicating that the formal pathway is the preferred one with the effective halogen distance of 4.878 Å for SSP.

As shown in Fig. 8, it is with the first and the second closest Hal/Hal distance of 4.374 and 4.514 Å respectively, accompanying with C19-C1 and C19-C1 contact of 5.460 and 5.298 Å respectively. Meanwhile, it has the third closest Hal/Hal distance of 6.115 Å with the corresponding shortest C-C (C19-C19) contact of 4.957 Å. Similar like I_2-Pr-EDOT, it forms a spring circle with the first polymerization pathway along with *c*-axil direction as shown in Fig. 8c. In addition, the second possible polymerization pathways along with *b*-axil direction was demonstrated in Fig 8d. Interestingly, the sole I/I distances of 4.374 and 4.514 Å are involved for these two pathways respectively, so taking this into consideration, the first pathway is a preferred one.

As shown in Fig. 9, the first and the second closest Hal/Hal distance for I_2-Nap-EDOT are 5.242 and 5.375 Å respectively, accompanying with C1-C1 and C13-C13 contact of 5.941 and 4.839 Å respectively. Meanwhile, it has the third closest Hal/Hal distance of 6.522 Å with corresponding the C13-C1 contact of 7.306 Å. Compared with the above two monomers, its first Hal/Hal distance is very long and it is the largest one among all obtained monomers by other groups including ours.[9] After carefully analysis, a plausible polymerization pathway along with *b*-axis direction was presented in Fig. 9c. In this pathway, it involves two I/I distances of 5.242 Å and 5.375 Å with its effective halogen distance of 5.375 Å.

The dependence of effective I/I distances with their onset temperature of SSP

So far, T_{onset}, effective halogen distance[8b] have been defined T_{onset}, effective halogen distance[8b] for SSP and SSP model[8b] have been proposed a for rigid and flexible monomers. Here we try to establish an equation to probe its relationship between effective halogen/halogen distances and their T_{onset} according to these obtained crystals data. The dependence of effective I/I distance with their T_{onset} were shown in Fig. 10 (data derived from those samples was presented in Table S2). According to the fitted line, it gives an equation of y = 26.1x - 31.5, with R of 0.92, revealing that increasing 1 Å of effective I/I distance needs the elevated T_{onset} of around 26°C.

Meanwhile, it is noticed that I_2-Pr-EDOT's effective halogen distance is longer than that of I_2-Ph-EDOT while the former shows higher T_{onset} than that of the latter. Due to the existence of alkyl chain, it would weaken inter-molecule π-π stacking in the crystal and result in lower T_{onset}. A pridiction would be made that I_2-Triph-EDOT's effective I/I distance is over 5.5 Å because of its highest T_{onset} of 120 °C among all monomers. Taking SSP condition range from room tempeature to 300 °C into consideration, heat process would drastically control molecule movement and SSP should have bright future in getting great success for the synthesis of other polythiophene systems.

Molecule weight information and thermal stability TGA analysis

Though solution absorption spectra of P(Ph-EDOT), P(Nap-EDOT), P(Triph-EDOT) can be obtained, their molecule weight information cannot be measured due to their limited solubility. M_n of 2.15 kg mol^{-1} with PDI of 1.64 indicates that the P(Pr-EDOT) has a repeat units of 6, which is a litter bit shorter than that of P(3-alkyl-EDOT)[8c] with CH_2-N(R)-CH_2 linker. The thermal stability of the polymers was investigated with thermogravimetric analysis (TGA). The 5% weight-loss temperatures for P(Pr-EDOT), P(Ph-EDOT), P(Nap-EDOT), P(Triph-EDOT) were 238, 244, 229 and 273°C, respectively, indicating that the introduction of triphenylamine moiety would enhance thermal stability greatly.

Conclusions

In this work, several new thiophene derivatives were synthesized based on EDOT-CH(R)-EDOT platform and successfully employed in SSP. Due to their quinonoid structures, our results may allow us to drastically expand the SSP scope and to prepare new types of poly(bis-3,4-ethylenedioxythiophene methine)s. Our results show that these polymers have excellent optical and electrical properties, implying that their will be great application potential with promising future, though they were ignored at present. Moreover, the relationship between monomers' effective halogen distance and their T_{onset} was established, revealing of SSP's powerful molecule arrangement & interaction.

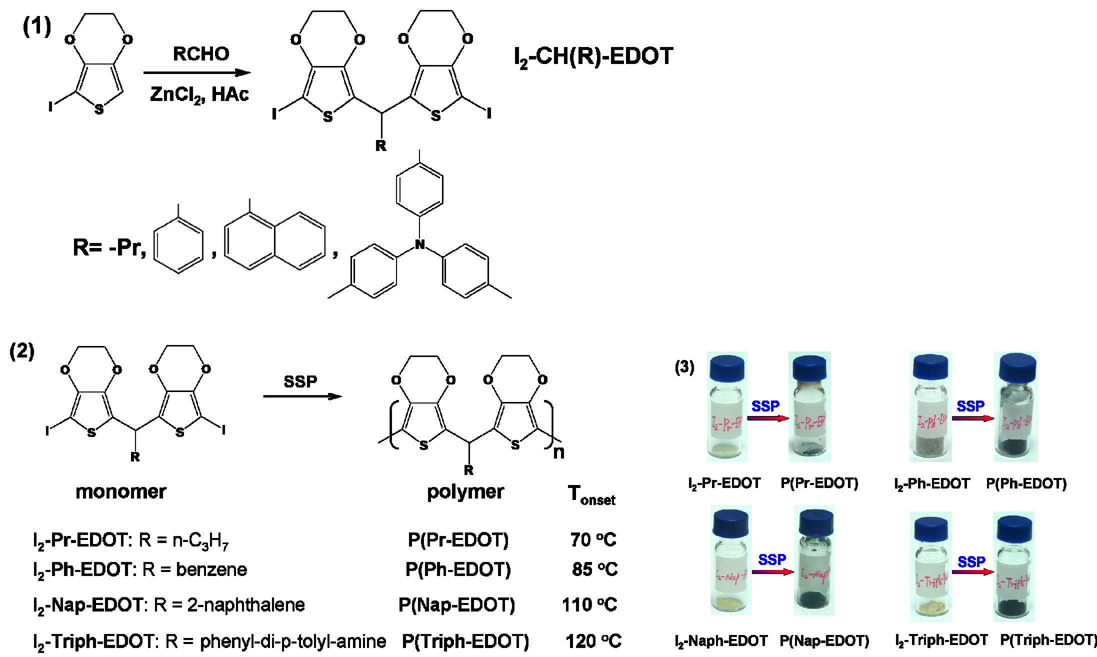
Acknowledgments

This work was supported by the Natural Science Foundation of China (21371138) the Funds for Creative Research Groups of Hubei Province (2014CFA007), the Fundamental Research Funds for the Central Universities (2042015kf0180) of China and Large-scale Instrument And Equipment Sharing Foundation of Wuhan University.

References

1. Q. Pei, Y. Yang, G. Yu, C. Zhang and A. J. Heeger, *J. Am. Chem. Soc.*, 1996, **118**, 3922.
2. H. L. Wang, F. Huang, A. G. MacDiarmid, Y. Z. Wang, D. D. Gebler and A. J. Epstein, *Synth. Met.*, 1996, **80**, 97.

3. A. Laforgue, P. Simon, C. Sarrazin and J.-F. Fauvarque, *J. Power Sources*, 1999, **80**, 142.
4. W. Lu, F. Andrei, B. Qi, S. Elisabeth, M. Benjamin R. J. Ding, S. Geoffrey, M. Jakub, D. Zhou, W. Gordon., M. Douglas, F. Stewart and F. Maria, *Science*, 2002, **297**, 983.
5. (a) L. S. Roman, M. R. Andersson, T. Yohannes and O. Inganaes, *Adv. Mater.*, 1997, **9**, 1164; (b) J. Xia, N. Masaki, K. Jiang and S. Yanagida, *J. Mater. Chem.*, 2007, **17**, 2845; (c) J. Xia, N. Masaki, M. Lira-Cantu, Y. Kim, K. Jiang and S. Yanagida, *J. Am. Chem. Soc.* 2008, **130**, 1258; (d) J. Xia, L. Chen and S. Yanagida, *J. Mater. Chem.*, 2011, **21**, 4644. (e) L. Chen, J. Jin, X. Shu and J. Xia, *J. Power. Souces*, 2014, **248**, 1234.
6. (a) H. Meng, D. F. Perepichka and F. Wudl, *Angew. Chem. Int. Ed.*, 2003, **42**, 658; (b) H. Meng, D. F. Perepichka, M. Bendikov, F. Wudl, G. Z. Pan, W. Yu, W. Dong and S. Brown, *J. Am. Chem. Soc.*, 2003, **125**, 15151.
7. (a) H. J. Spencer, R. Berridge, D. J. Crouch, S. P. Wright, M. Giles, I. McCulloch, S. J. Coles, M. B. Hursthouse and P. J. Skabara, *J. Mater. Chem.*, 2003, **13**, 2075; (b) A. Patra, Y. H. Wijsboom, S. S. Zade, M. Li, Y. Sheynin, G. Leitus and M. Bendikov, *J. Am. Chem. Soc.*, 2008, **130**, 6734; (c) M. Lepeltier, J. Hiltz, T. Lockwood, F. Bélanger-Gariépy and D. F. Perepichka, *J. Mater. Chem.*, 2009, **19**, 5167; (d) A. Patra, Y. H. Wijsboom, G. Leitus and M. Bendikov, *Chem. Mater.*, 2011, **23**, 896; (e) S. Chen, J. Xu, B. Lu, X. Duan and F. Kong, *Adv. Mater. Res.*, 2011, **239–242**, 924; (f) S. Chen, B. Lu, X. Duan and J. Xu, *J. Polym. Sci. Part A, Polym. Chem.,* 2012, **50**, 1967.
8. (a) C. Tusy, L. Huang, J. Jin and J. Xia, *RSC Adv.*, 2014, **4**, 8011; (b) C. Tusy, L. Huang, K. Peng and J. Xia, *RSC Adv.*, 2014, **4**, 29032; (c) C. Tusy, L. Huang, K. Peng and J. Xia, *RSC Adv.*, 2015, **5**, 16292; (d) A.-L. Barrès, M. Allain, P. Frère and P. Batail, *Isr. J. Chem.* 2014, **54**, 689.
9. (a) S. A. Jenekhe, *Nature*, 1986, **322**, 345; (b) W. -C. Chen, C. -L. Liu, C.-T. Yen, F.-C. Tsai, C. J. Tonzola, N. Olson and S. A. Jenekhe, *Macromolecules* 2004, **37***,* 5959; (c) M. B. Zaman and D. F. Perepichka, *Chem. Commun.*, 2005, 4187; (d) A. Abdolmaleki, Z. Mohamadi, B. Rezaei and N. Askarpour, *Polym. Bull.*, 2013, **70**, 665; (e) S. Ahn, K. Yabumoto, Y. Jeong and K. Akagi, *Polym. Chem.*, 2014, **5**, 6977.
10. (a) H. Neugebauer, C. Kvarnström, C. Brabec, N. S. Sariciftci, R. Kiebooms, F. Wudl and S. Luzzati, *J. Chem. Phys.*, 1999, **110**, 12108; (b) T. Umeyama, Y. Watanabe, M. Oodoi, D. Evgenia, T. Shishido and H. Imahori, *J. Mater. Chem.*, 2012, **22**, 24394.
11. V. Lemau de Talance, M. Hissler, L-Z. Zhang, T. Karpati, L. Nyulaszi, D. Caras-Quintero, P. Baeuerle and R. Reau, *Chem. Commun.*, 2008, **19**, 2200.
12. (a) K. J. Hoffmann, L. Knudsen, E. J. Samuelsen and P. H. J. Carlsen, *Synth. Metal.*, 2000. **114***,* 161; (b) T. Benincori, S. Rizzo, F. Sannicolo,G. Schiavon, S. Zecchin and G. Zotti, *Macromolecules*, 2003, **36**, 5114.
13. G. M. Sheldrick, SHELXTL, Version 6.14, Bruker Analytical X-ray Instruments, Inc, Madison, WI, USA, 2003.
14. G. M. Sheldrick, *Acta Crystallogr. Sect. A*, 2008, **A64**, 112.
15. Y. Xia, A. G. MacDiarmid and A. J. Epstein, *Macromolecules*, 1994, **27**, 7212.
16. D. Hohnholz, A. G. MacDiarmid, D. M. Sarno and Jr. W. E. Jones, *Chem. Commun*., 2001, 2444.
17. B. Bhushan, S. K. Kumar, S. S. Talwar, T. Kundu and B. P. Singh, *Appl. Phys. B*, 2012, **109**, 201.
18. C. Kvarnström, H. Neugebauer, S. Blomquist, H. J. Ahonen, J. Kankare and A. Ivaska, *Electrochim. Acta*, 1999, **44**, 2739.
19. G. Louarn, J. Kruszka, S. Lefrant, M. Zagorska, I. Kulszewicz-Bayer and A. Pron, *Synth. Met.*, 1993, **61**, 233.
20. M. S. Agashe and C. I. Jose, *J. Chem. Soc. Faraday Trans.* 2, 1977, **73**, 1232.
21. I. Reva, L. Lapinski, N. Chattopadhyay and R. Fausto, *Phys. Chem. Chem. Phys.*, 2003, **5**, 3844.
22. T. L. Macdonald, W. G. Gutheim, R. B. Martin and F. P. Guengerich, *Biochem.*, 1989, **28**, 2071.
23. J. W. Arbogast, C. S. Foote and M. Kao, *J. Am. Chem. Soc.*, 1992, **114**, 2277.



Scheme 1. Synthesis of the monomers, corresponding polymers and digital imagines of crystals of monomers and respective polymers.

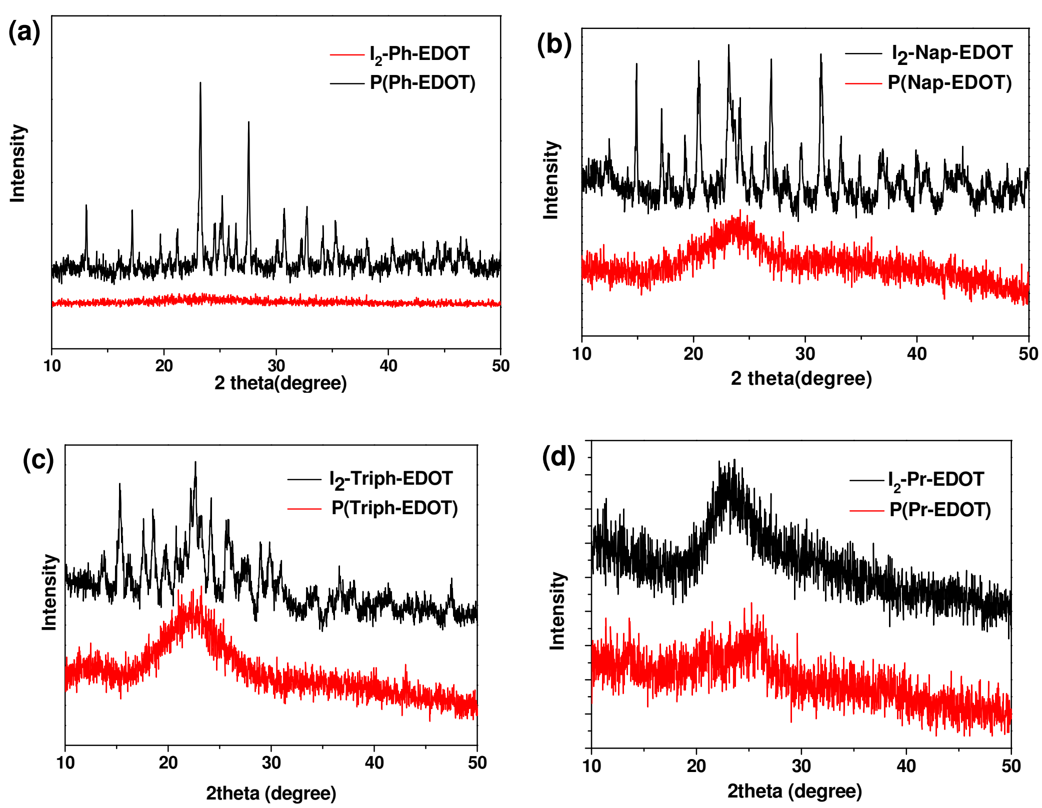


Fig. 1 XRD spectra of monomers and corresponding polymers.

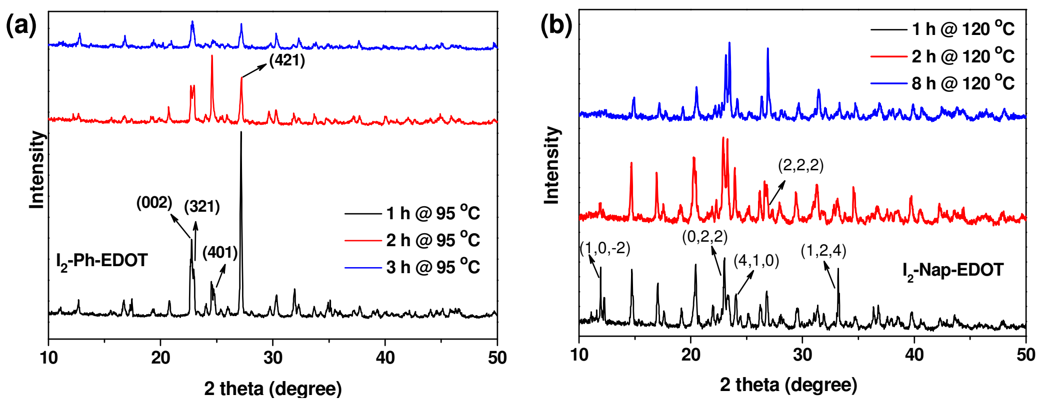


Fig. 2 In situ-XRD patterns for (a) I_2-Ph-EDOT and (b) I_2-Nap-EDOT.

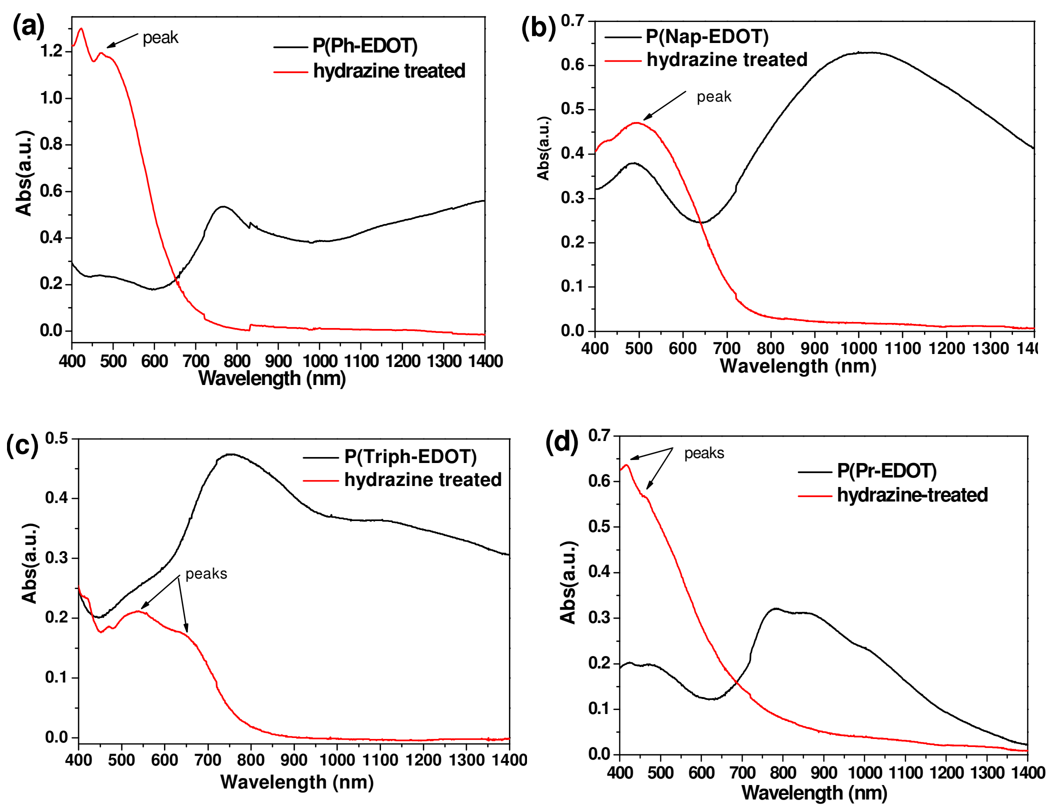


Fig. 3 Solutions absorption spectra of the polymer solutions obtained by SSP and dedoped polymers.

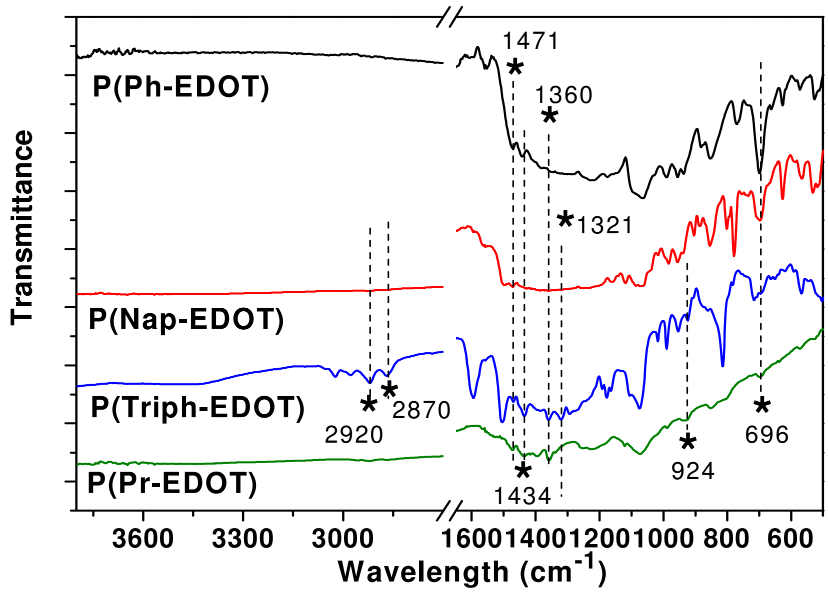


Fig. 4 FTIR spectra for these Poly(bis-3,4-ethylenedioxythiophene methine)s obtained through SSP.

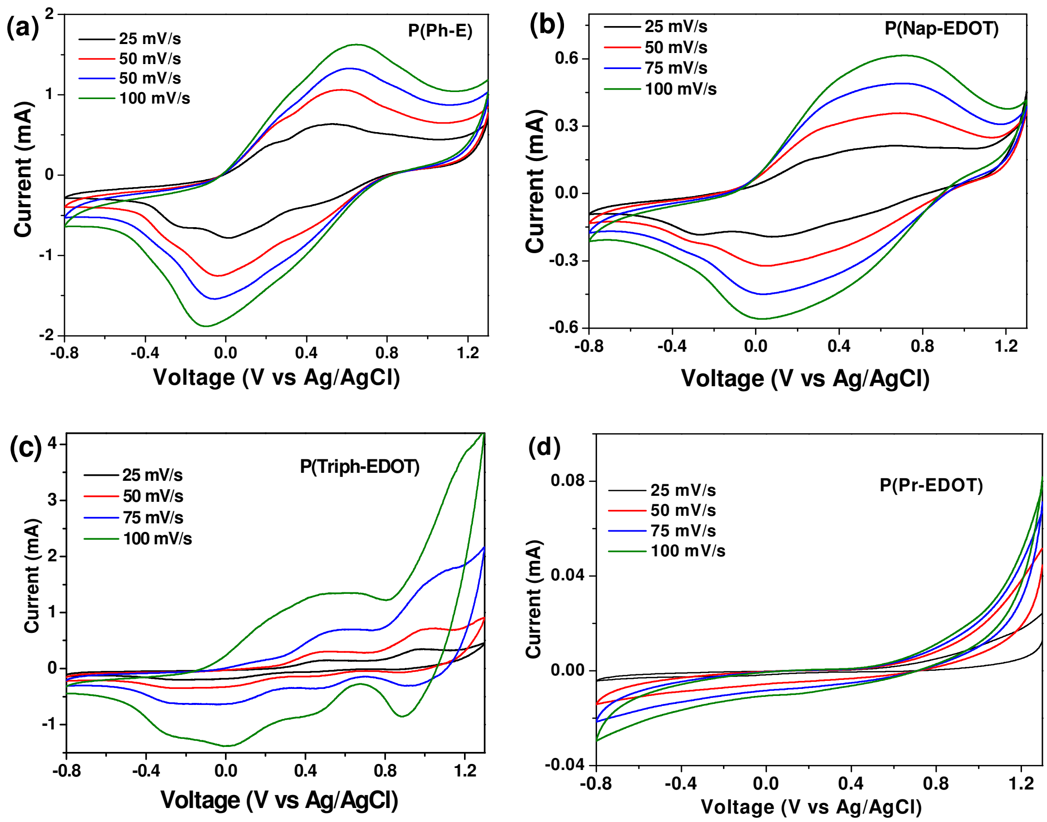


Fig. 5 The CVs of Polymers films in acetonitrile solution containing 0.1 M Bu_4NClO_4 taken at various scan rates.

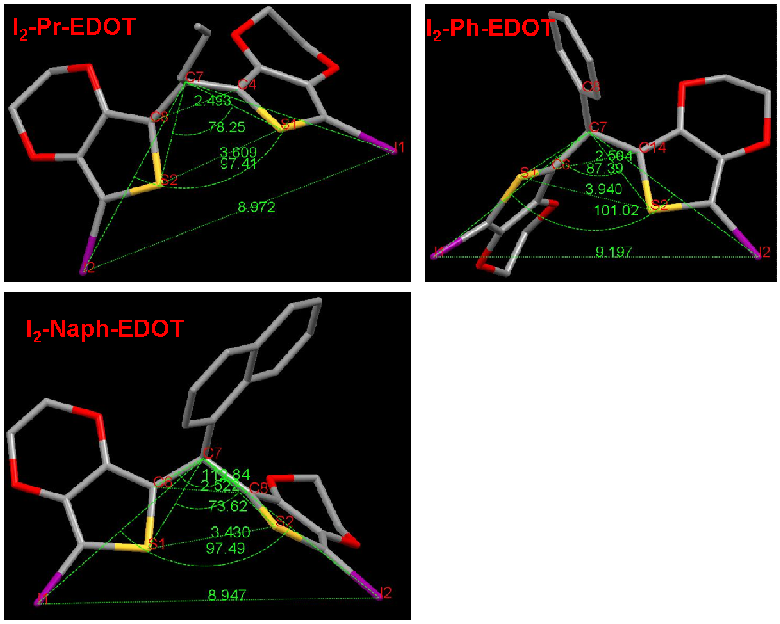


Fig. 6 Intermolecular I/I distance and different angles in these monomers.

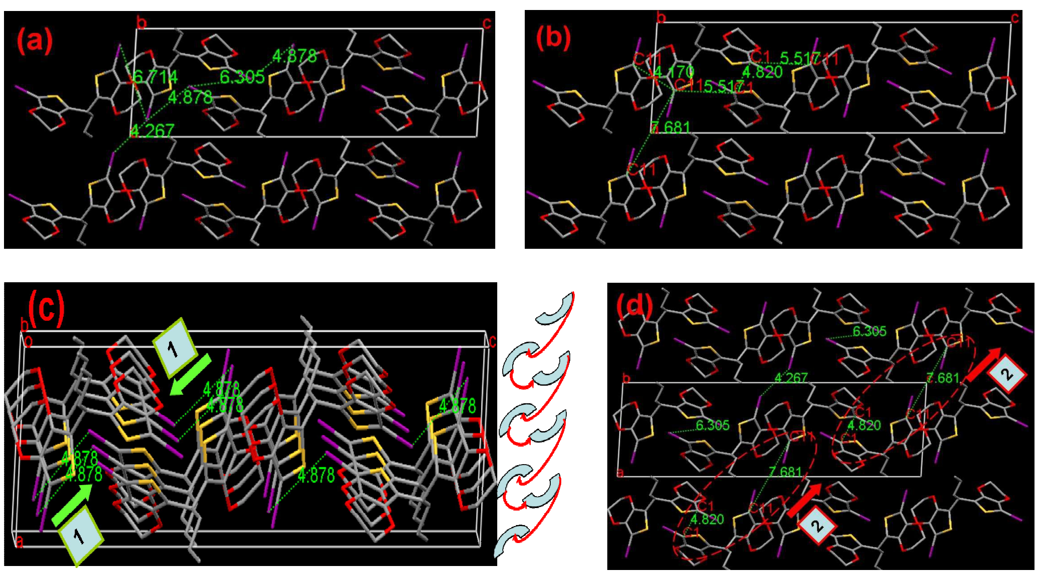


Fig. 7 Single-crystal X-ray structure of compound I_2-Pr-EDOT. (a) view of I/I distance, (b) view of corresponding C/C contact distance, (c) crystal packing viewed along the *b*-axis, proposed the first polymerization pathway and involved I/I and C/C contact distances, (d) proposed the second polymerization pathway. Hydrogen atoms are omitted for clarity: I, purple; S, yellow and C, gray.

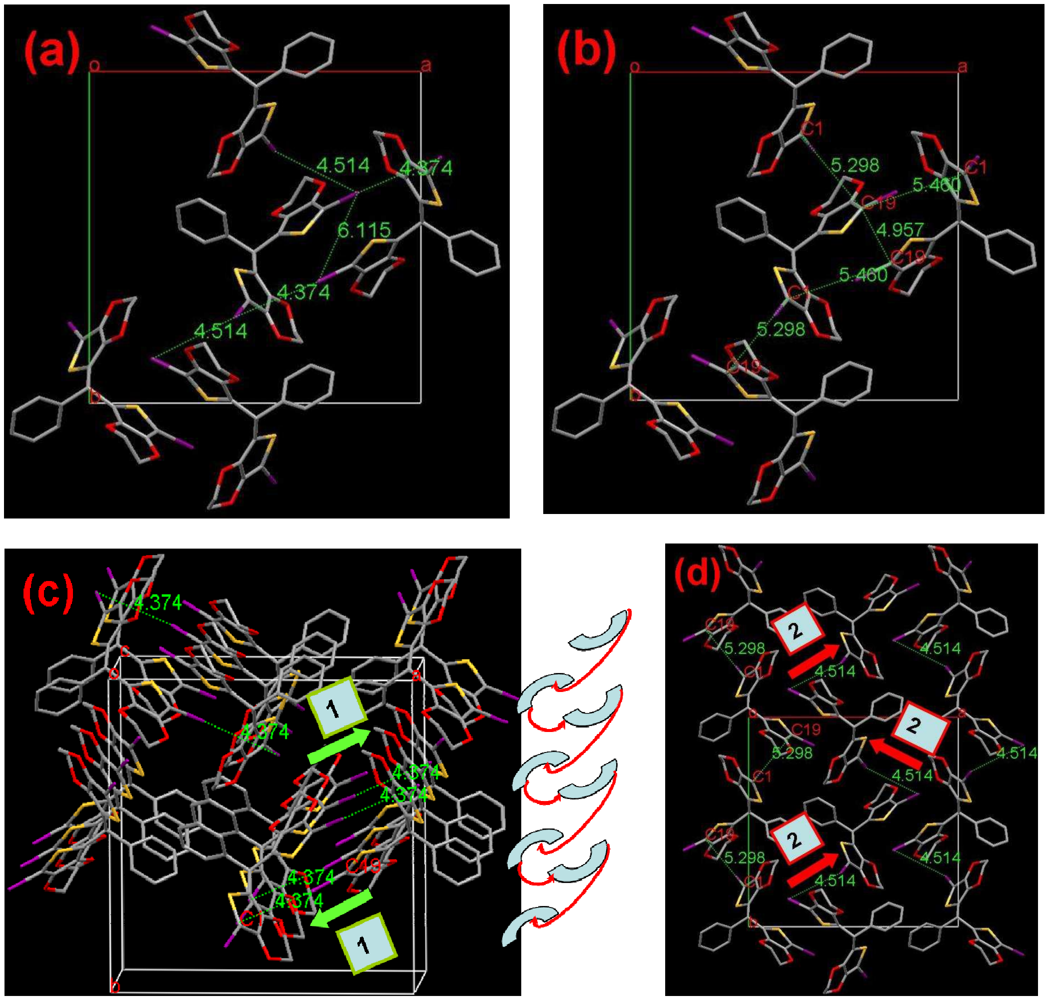


Fig. 8 Single-crystal X-ray structure of compound I_2-Ph-EDOT. (a) view of I/I distance, (b) view of corresponding C/C contact distance, (c-d) crystal packing viewed along the *c*-axis, proposed first polymerization pathway and involved I/I and C/C contact distance, (e) proposed the second polymerization pathway. Hydrogen atoms are omitted for clarity: I, purple; S, yellow and C, gray.

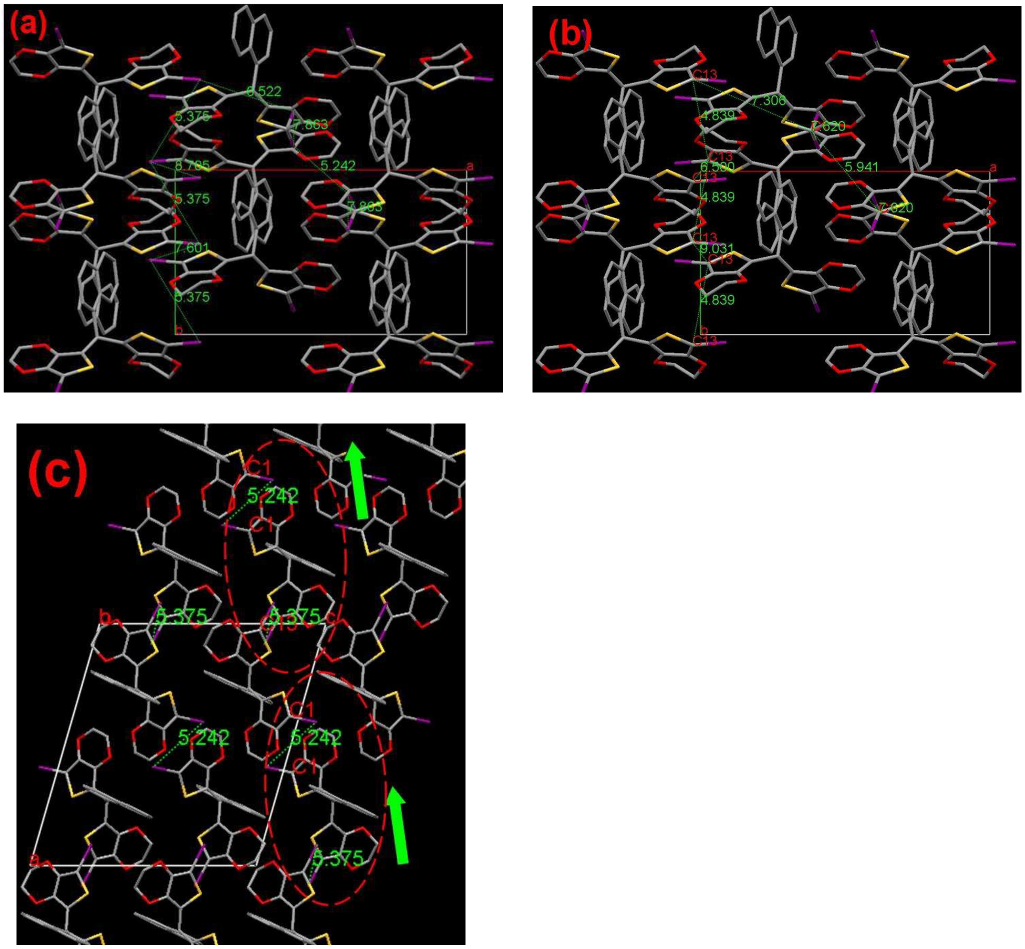


Fig. 9 Single-crystal X-ray structure of compound I_2-Nap-EDOT. (a) view of I/I distance, (b) view of corresponding C/C contact distance, (c) crystal packing viewed along the *b*-axis, proposed plausible polymerization pathway and involved I/I and C/C contact distances. Hydrogen atoms are omitted for clarity: I, purple; S, yellow and C, gray.

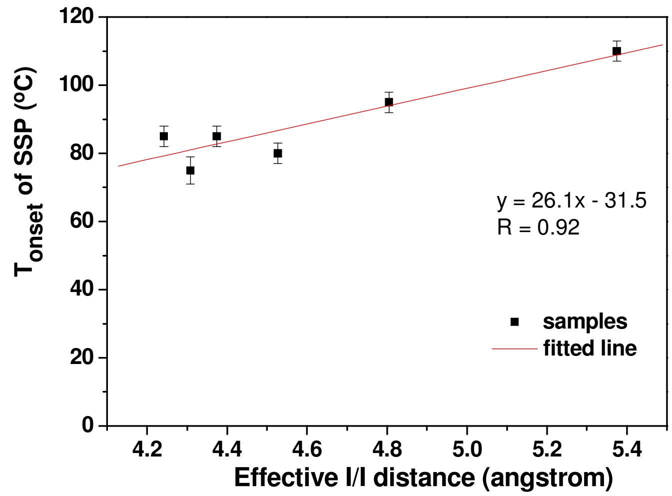


Fig. 10 Linear dependence of effective I/I distance with T_{onset} of SSP

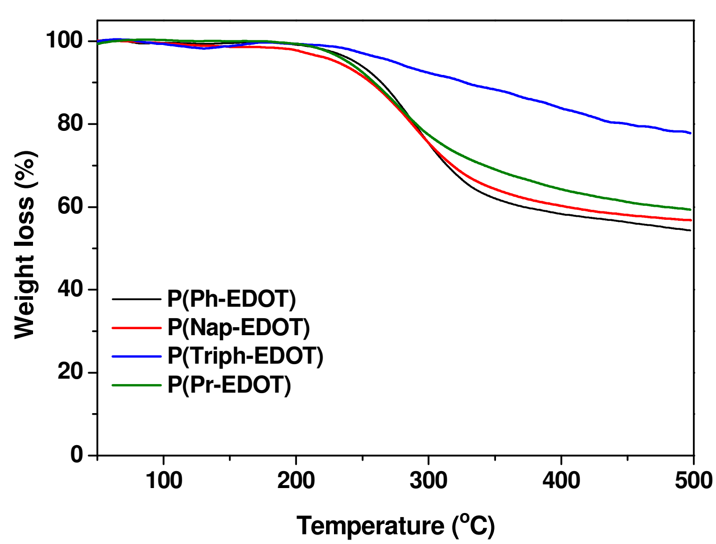


Fig. 11 TGA of the polymers under N_2 atmosphere with heating rate of 10°C/min

Table 1 Optical and electrochemical data for all neutral polymers

	Conversion for 24 h (temperature)	Abs. λ_{max}/nm film	Abs. λ_{edge}/nm film	E_{gap}[a] (eV)	HOMO (eV)	LUMO[b] (eV)
P(Ph-EDOT)	> 90 %, 110 °C	422, 470	695	1.78	-4.38	-2.60
P(Nap-EDOT)	> 90 %, 130 °C	493	724	1.71	-4.33	-2.62
P(Triph-EDOT)	> 90 %, 150 °C	540	785	1.58	-4.54	-2.96
P(Pr-EDOT)	> 90 %, 100 °C	420, 465	690	1.80	-4.68	-2.88

[a] Determined from the onset wavelength in the absorption spectra of film samples.[b] Determined from HOMO levels and optical bandgaps.

Table 2 Intramolecular halogen distance and angles

	Distance (Å)			**Angles (°)**		
	$\mathbf{I_1/I_2}$	$\mathbf{S_1/S_2}$	**bridge length (C-$\mathbf{C_{H(R)}}$-C)**	$\angle$**C-$\mathbf{C_{H(R)}}$-C**	$\angle\mathbf{S_1C_7S_2}$	$\angle\mathbf{I_1C_7I_2}$
I_2-Pr-EDOT	8.972	3.609	2.493 (C_4/C_8)	111.92 ($\angle C_8C_7C_4$)	78.25	97.41
I_2- Ph-EDOT	9.197	3.940	2.504 (C_6/C_{14})	112.00 ($\angle C_6C_7C_{14}$)	87.39	101.02
I_2-Nap-EDOT	8.947	3.430	2.522 (C_6/C_8)	112.84($\angle C_6C_7C_8$)	73.62	97.49

Table 3 Selected I/I and C-C contact distance (Å) for the reported crystals

Molecules parameters	**$\mathbf{I_2}$- Ph-EDOT**	**$\mathbf{I_2}$- Nap-EDOT**	**$\mathbf{I_2}$-Pr-EDOT**
shortest I/I distance	4.374[a]	5.242	4.267
2nd shortest I/I distance	4.514	5.375[a]	4.878 [a]
3rd shortest I/I distance	6.115	6.522	6.305
C-C contact shortest distance	4.957	4.839	4.170
C-C contact 2nd shortest distance	5.298	5.941	4.820
longer than $2r_w$ of iodine[b]	10.9%	34.4%	21.9%
T_{onset} of SSP (°C)	85	110	70

[a]Effective Hal/Hal distance

[b]$2r_w$ of iodine: double evan der Waals radius of iodine: 4.0 Å

GRAPHICAL ABSTRACT

Investigation of Substitution Effect on Poly(bis-3,4-ethylenedioxythiophene methine)s through Solid State Polymerization

Kai Peng, Tong Pei, Zhaoxiang Li, Lili Huang, Jiangbin Xia*

EDOT-*CH(R)*-EDOT was chosen as a prototype model monomer for solid state polymerization (SSP). The aromatic moieties were first introduced in branch chain in the polymer matrix, which may offer amazing properties and further modification opportunities based on this unique platform.