

Electronic Supporting Information  
*For*

**Synthesis and Investigation of Novel Thiophene Derivatives  
Containing Heteroatom linkers for Solid State Polymerization**

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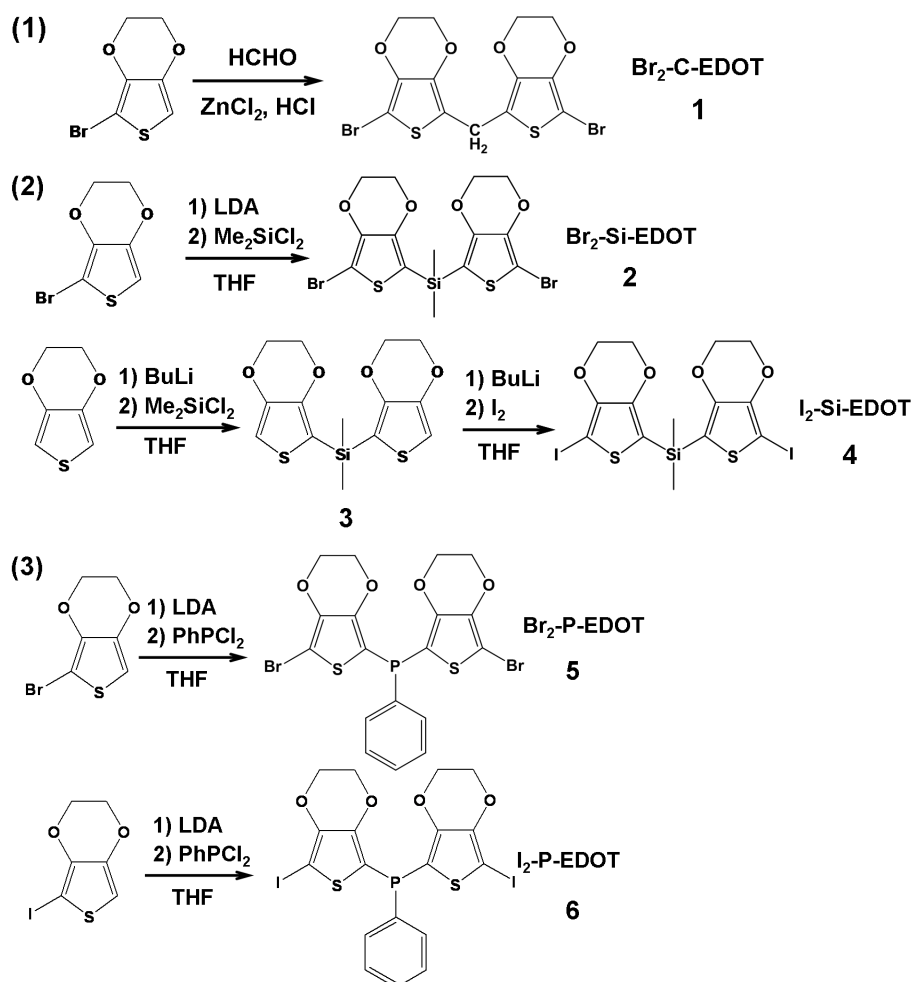
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## 1. Experimental details

**1.1 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. Diethyl ether anhydrous solvent was distilled from commercial diethyl ether with  $\text{CaH}_2$ . 2-Bromo-3,4-ethylenedioxythiophene<sup>1</sup> was synthesized according to our previous report. 5-Iodo-2,3-dihydro-thieno[3,4-b][1,4]dioxine<sup>2</sup> was synthesized similar to 2-bromo-3,4-ethylenedioxythiophene except that 2,5-diiodo-3,4-ethylenedioxythiophene was used during reduction by n-butyllithium.

### 1.2. Monomers synthesis and solid state polymerization.



**Scheme S1.** Synthesis of the monomers.

**Bis(7-bromo-2,3-dihydrothieno[3,4-b][1,4]dioxin-5-yl) methane (1, Br<sub>2</sub>-C-EDOT).**

Monomer **1 (Br<sub>2</sub>-C-EDOT)** was synthesized in accordance with previous method<sup>3</sup> shown in **Scheme S1**. To a stirred solution of zinc chloride in hydrochloric acid between -8°C and -10°C, 2-bromo-3,4-ethylenedioxythiophene was added over several minutes. Formaldehyde (37%) was 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, dried over magnesium sulfate, and the solvent was evaporated. Purification by column chromatography (silica gel, light petroleum-CH<sub>2</sub>Cl<sub>2</sub>, 2 : 1) afforded white solid **1** (60%). <sup>1</sup>H NMR: δ (CDCl<sub>3</sub>) 4.25 (m, 2 H); 4.22 (m, 2 H); 3.89 (s, 2 H). <sup>13</sup>C NMR: δ (CDCl<sub>3</sub>) 139.7, 137.7, 114.9, 84.4, 65.3, 64.7, 22.2. CI-MS: Calcd, 451.8; found (M + 2)<sup>+</sup>, 453.8.

**Bis-(7-bromo-2,3-dihydro-thieno[3,4-b][1,4]dioxin-5-yl)-dimethyl-silane (2, Br<sub>2</sub>-Si-EDOT)**

Monomer **2 (Br<sub>2</sub>-Si-EDOT)** was synthesized by modification of previous method<sup>4</sup> Anhydrous THF (30 ml) was slowly added dropwise to a solution of lithium diisopropylamide (prepared by addition of *n*-butyllithium to diisopropylamine, 10 mmol), the temperature being maintained around -15 °C. The reaction mixture was cooled to -60°C, and a solution of 2-bromo-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<sub>2</sub>SO<sub>4</sub>. Purification by column chromatography (silica gel, light petroleum-CH<sub>2</sub>Cl<sub>2</sub>, 2 : 1) afforded colorless crystal **2** (50%). <sup>1</sup>H NMR: δ (CDCl<sub>3</sub>)

4.24 (m, 2 H); 4.21 (m, 2 H); 0.55 (s, 6 H).  $^{13}\text{C}$  NMR:  $\delta$  (d-DMSO) 147.6, 140.9, 107.6, 91.9, 64.5, -1.55. Anal. Calcd For  $\text{C}_{14}\text{H}_{14}\text{Br}_2\text{O}_4\text{S}_2\text{Si}$ : C, 33.75%; H, 2.83%. Found: C, 32.95%; H, 2.96%.

**Bis-(2,3-dihydro-thieno[3,4-b][1,4]dioxin-5-yl)-dimethyl-silane (3, Si-EDOT)**

To a solution of EDOT (2.10 g, 14.8 mmol) dissolved in 50 ml of THF under argon was added 6.2 mL (14.8 mmol) of *n*-BuLi (2.4 M) dropwise. After stirring for 1 h at room temperature, the mixture was cooled to  $-78\text{ }^\circ\text{C}$ . Dichlorodimethylsilane (0.98 g, 7.6 mmol) was added dropwise and the mixture was stirred for a further 3 h at  $-78\text{ }^\circ\text{C}$  followed by 21 h at room temperature. The mixture was then poured into 100 ml of water and the product was extracted using  $2 \times 100$  ml portions of  $\text{CH}_2\text{Cl}_2$ . The organic layers were combined and dried over  $\text{MgSO}_4$ . After evaporation of the solvent, the product was purified by chromatography on silica gel using  $\text{CH}_2\text{Cl}_2$  as an eluent. The desired product was a colorless crystalline solid (1.90 g, yield 75%).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , ppm) : 6.58 (s, 2H), 4.19 (m, 8H), 0.58 (s, 6H), which is consisted with reported result.<sup>12</sup>

**Bis-(7-iodo-2,3-dihydro-thieno[3,4-b][1,4]dioxin-5-yl)-dimethyl-silane (4, I<sub>2</sub>-Si-EDOT)**

To a solution of **3** (0.67 g, 2 mmol) in anhydrous THF at  $-78\text{ }^\circ\text{C}$  was added *n*-BuLi (2.4 M in hexane; 1.8 mL, 4.3 mmol) in THF (10 mL). The reaction mixture was allowed to warm to  $0\text{ }^\circ\text{C}$  for 30 min and cooled to  $-78\text{ }^\circ\text{C}$ , and iodine crystals (1.1 g, 4.2 mmol) were added in one portion. The reaction mixture was allowed to warm to  $20\text{ }^\circ\text{C}$  overnight, the solvent was removed in vacuum, and the residue was taken up in  $\text{CHCl}_3$ . After washing with KI solution (to remove excess iodine) and water, the organic layer was concentrated in vacuum and purified by flash chromatography on silica eluting with petroleum / $\text{CH}_2\text{Cl}_2$  (2:1 v/v), followed by recrystallization from EtOH to give pure **4** as light-yellow crystals (0.71 g, 60%),  $^1\text{H}$  NMR:  $\delta$  ( $\text{CDCl}_3$ ) 4.24 (m, 2 H); 4.20 (m, 2 H); 0.54 (s, 6 H).  $^{13}\text{C}$  NMR:  $\delta$  ( $\text{CDCl}_3$ ) 147.1, 145.0, 114.8, 65.2, 64.7, 56.2, -1.37. Anal. Calcd For  $\text{C}_{14}\text{H}_{14}\text{I}_2\text{O}_4\text{S}_2\text{Si}$ : C, 28.39%; H, 2.38%. Found: C, 27.78%; H, 2.21%.

**Bis-(7-bromo-2,3-dihydro-thieno[3,4-b][1,4]dioxin-5-yl)-phenyl-phosphane ( 5, Br<sub>2</sub>-P-EDOT)**

The compound was synthesized by a similar procedure to **2**. Dichlorophenyl phosphine (0.89 g) was added in place of dichlorodimethylsilane. Yield: 2.57 g (40%); <sup>1</sup>H NMR: δ (CDCl<sub>3</sub>) 7.8-7.9 (m, 2H), 7.6 (d, 1H), 7.5(m, 2H), 4.24-4.26 (m, 4 H). <sup>13</sup>C NMR: δ (d-DMSO) 146.4, 146.2, 140.6, 134.8, 134.7, 131.8, 131.6, 129.4, 128.8, 128.7, 92.5, 64.7. Anal. Calcd For C<sub>18</sub>H<sub>13</sub>Br<sub>2</sub>O<sub>4</sub>PS<sub>2</sub>: C, 39.44%; H, 2.39%. Found: C, 39.38%; H, 2.31%.

**Bis-(7-iodo-2,3-dihydro-thieno[3,4-b][1,4]dioxin-5-yl)-phenyl-phosphane ( 6, I<sub>2</sub>-P-EDOT)**

The compound was synthesized by a similar procedure to **5**. 5-Iodo-2,3-dihydro-thieno[3,4-b][1,4]dioxine was added in place of 5-bromo-2,3-dihydro-thieno[3,4-b][1,4]dioxine. Yield: 40%. <sup>1</sup>H NMR: δ (CDCl<sub>3</sub>) 7.3-7.5 (m, 5H), 4.24-4.26 (m, 4 H). <sup>13</sup>C NMR: δ (d-DMSO) 146.1, 145.9, 144.5, 135.2, 131.7, 131.5, 129.2, 128.7, 111.9, 111.6, 64.6, 59.5. ESI-MS: Calcd, 642.2; found (M + 2)<sup>+</sup>, 644.6. Anal. Calcd For C<sub>18</sub>H<sub>13</sub>I<sub>2</sub>O<sub>4</sub>PS<sub>2</sub>: C, 33.66%; H, 2.04%. Found: C, 34.2%; H, 2.26%.

### 1.2. General solid state polymerization

In a closed vial, the brominated or iodinated compounds (300 mg) were incubated at 60° C or 80° C, respectively, for 2-96 h. The grounded polymers were additionally dried in vacuum at 80° C overnight, then stirred with hydrazine hydrate (50% aqueous solution, in CH<sub>3</sub>OH) overnight, filtered, and washed with CH<sub>3</sub>OH and vacuum drying afforded a nearly fully dedoped respective polymers.

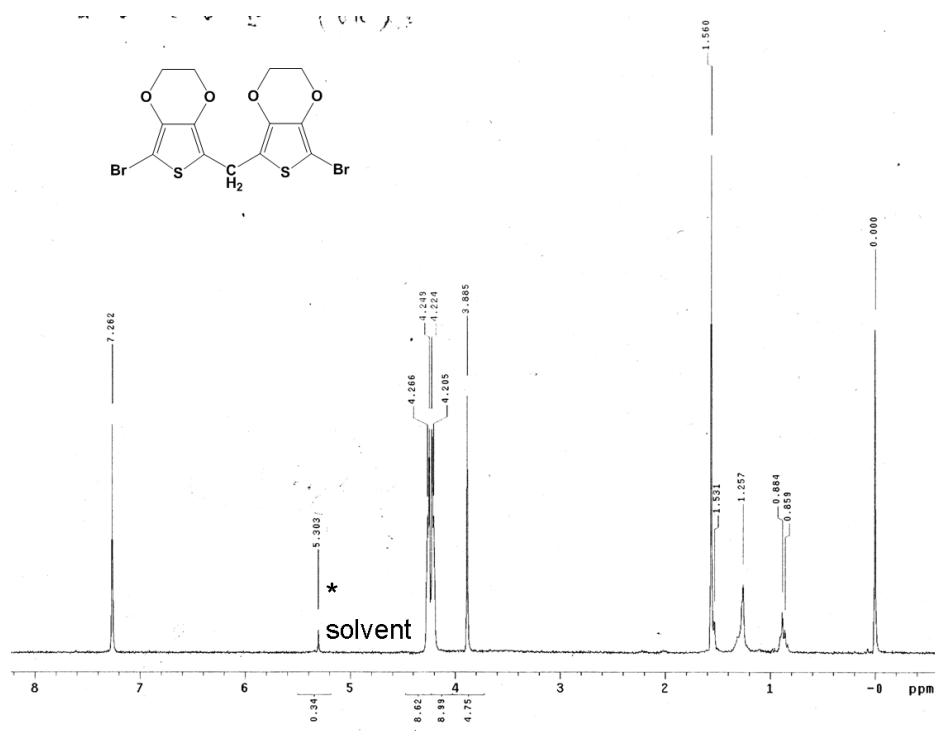
### 1.3. Other characterizations

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) substrates or slide glasses were prepared by spin-coating or drop-casting with 0.5-3 wt% of CHCl<sub>3</sub> monomers solution. These

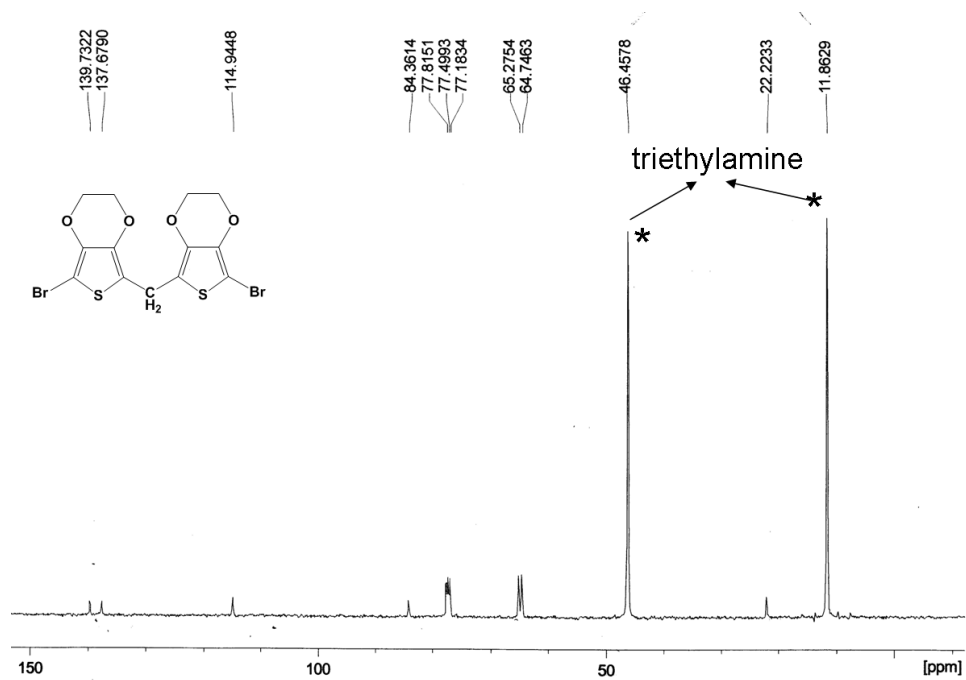
monomer coated substrate were employed for SSP (80° C for I<sub>2</sub>-P-EDOT while 60° C for others) and resulted polymers or polymer/FTO substrates were used for XRD, UV-Vis and as working electrode for electrochemical measurements. For the three-electrode electrochemical measurements in 0.1 M LiClO<sub>4</sub> in acetonitrile, a 1cm<sup>2</sup> area of 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-Kα radiation at rt. Thermogravimetric analysis (TGA) data were obtained from a SETSYS 16 with a heating rate of 10 °C/min in a nitrogen atmosphere. The surface morphologies of monomers and SSP polymers were analyzed by using field emission scanning electron microscopy (JEOL, JSM-6700F). Conductivity of the polymers in compressed pellets were measured by a TRS-9 (4-probe, Guangzhou) four-probe-type resistance meter and the results were summarized in Table S2 (see in the Supporting Information).

## 2. $^1\text{H}$ -NMR and $^{13}\text{C}$ -NMR spectra of the compounds

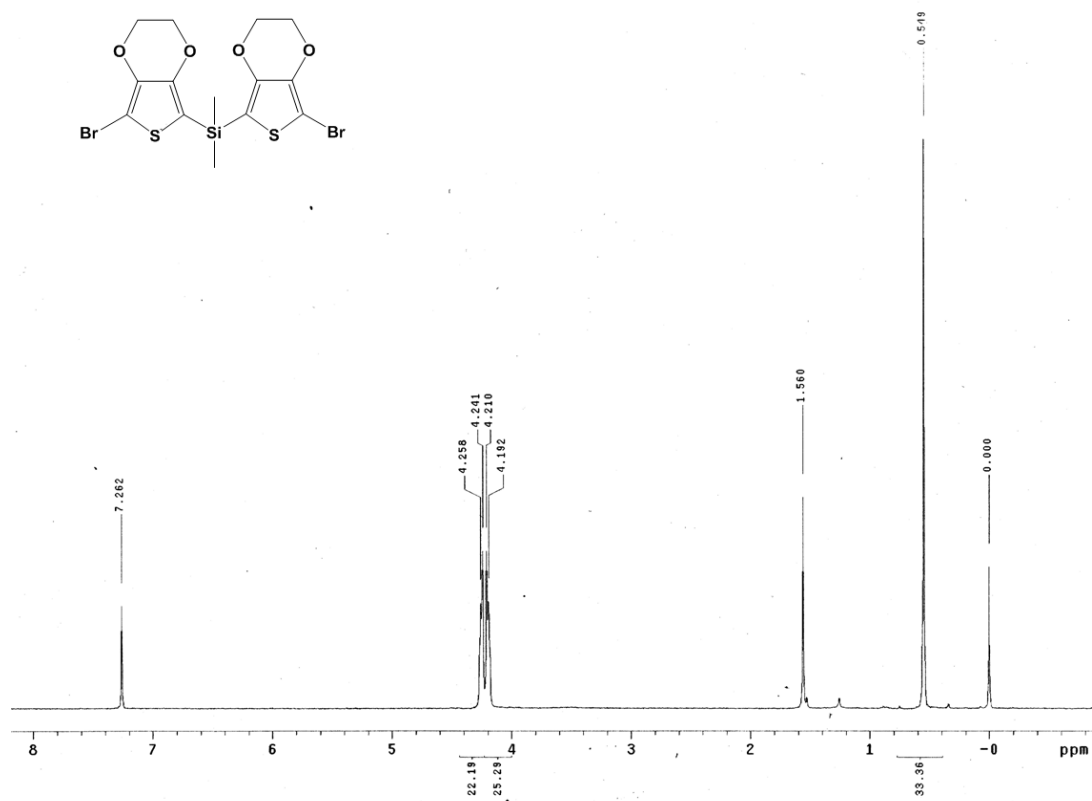
**Figure S1.**  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ) spectrum of Bis(7-bromo-2,3-dihydrothieno[3,4-b][1,4]dioxin-5-yl) methane (**1**).



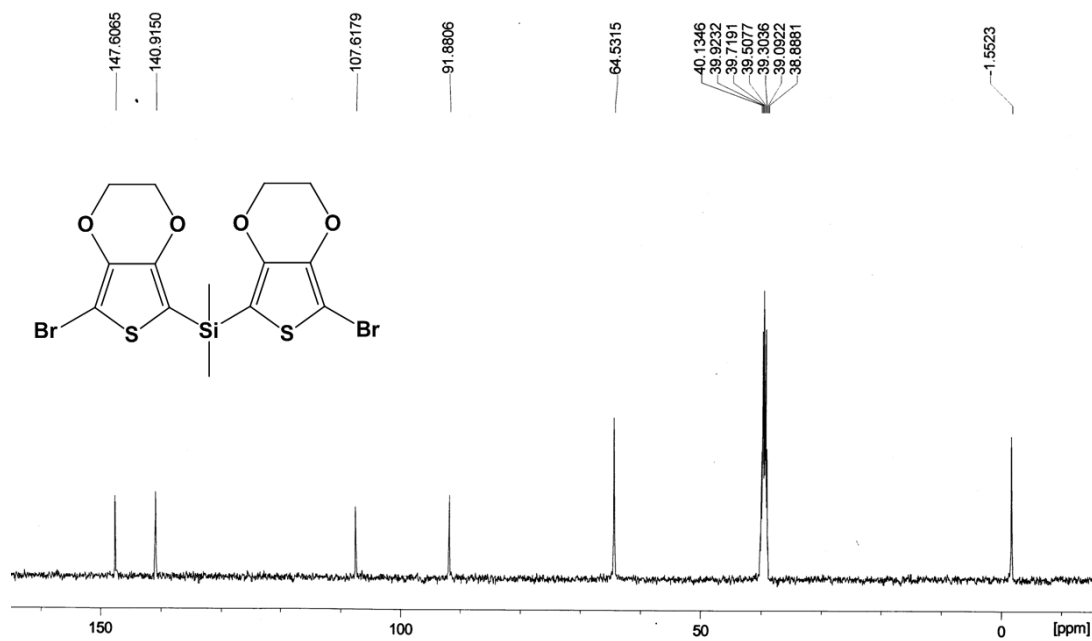
**Figure S2.**  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ) spectrum of Bis(7-bromo-2,3-dihydrothieno[3,4-b][1,4]dioxin-5-yl) methane (**1**).



**Figure S3.**  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ) spectrum of Bis(7-bromo-2,3-dihydro-thieno[3,4-b][1,4]dioxin-5-yl)-dimethyl-silane (**2**).

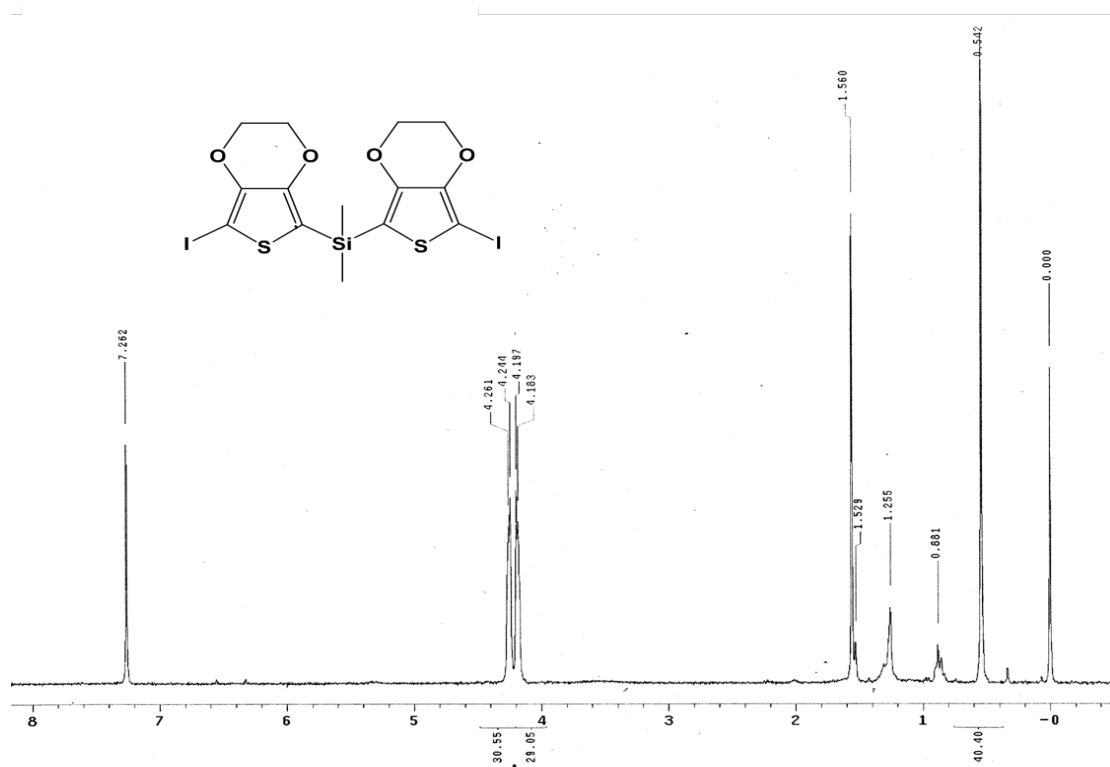


**Figure S4.** <sup>13</sup>C NMR (d-DMSO) spectrum of Bis-(7-bromo-2,3-dihydro-thieno[3,4-b][1,4]dioxin-5-yl)-dimethyl-silane (2)



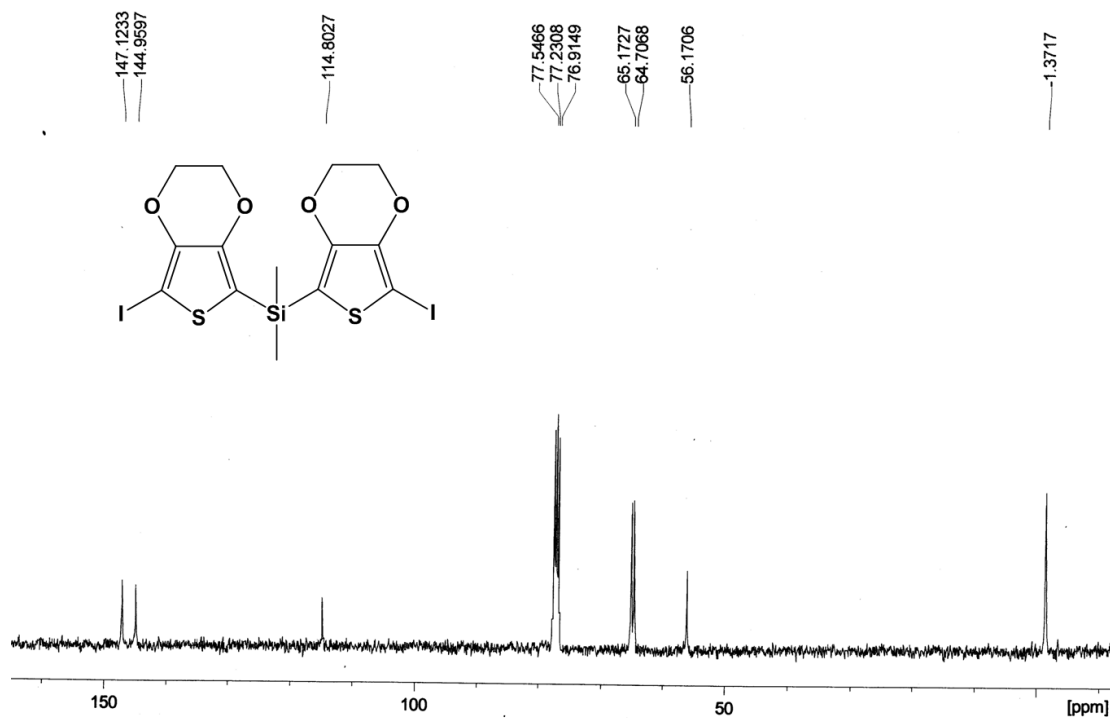
**Figure S5.** <sup>1</sup>H NMR (CDCl<sub>3</sub>) spectrum of Bis-(7-iodo-2,3-dihydro-thieno[3,4-b][1,4]dioxin-5-yl)-dimethyl-silane (4)





**Figure S6.**  $^{13}\text{C}$  NMR (CDCl<sub>3</sub>)

**Bis-(7-iodo-2,3-dihydro-thieno[3,4-b][1,4]dioxin-5-yl)-dimethyl-silane (4)**



**Figure S7.**  $^1\text{H}$  NMR (CDCl<sub>3</sub>) spectrum of

**Bis-(7-bromo-2,3-dihydro-thieno[3,4-b][1,4]dioxin-5-yl)-phenyl-phosphane (5)**

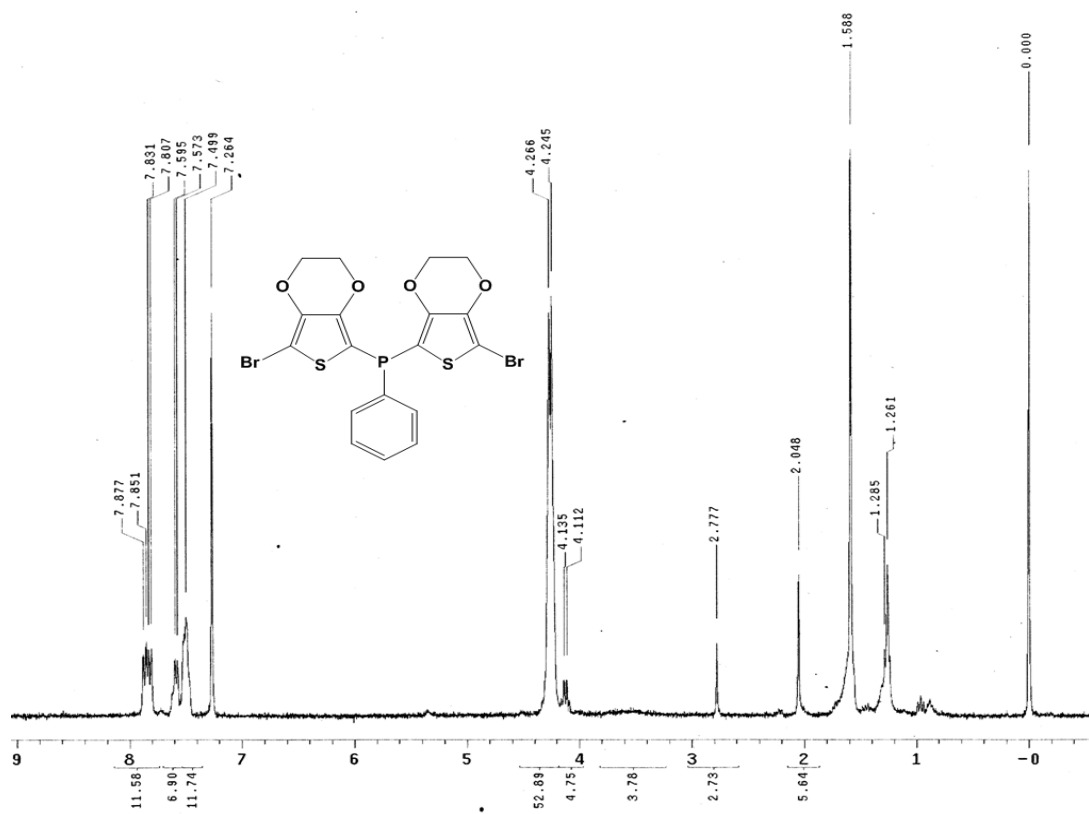
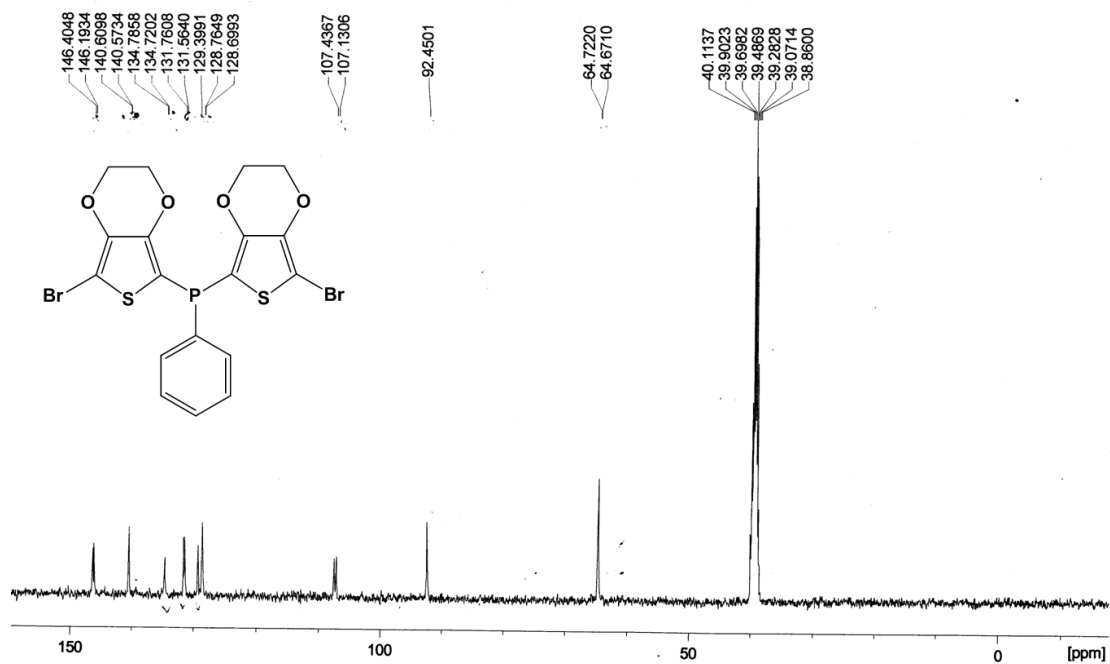
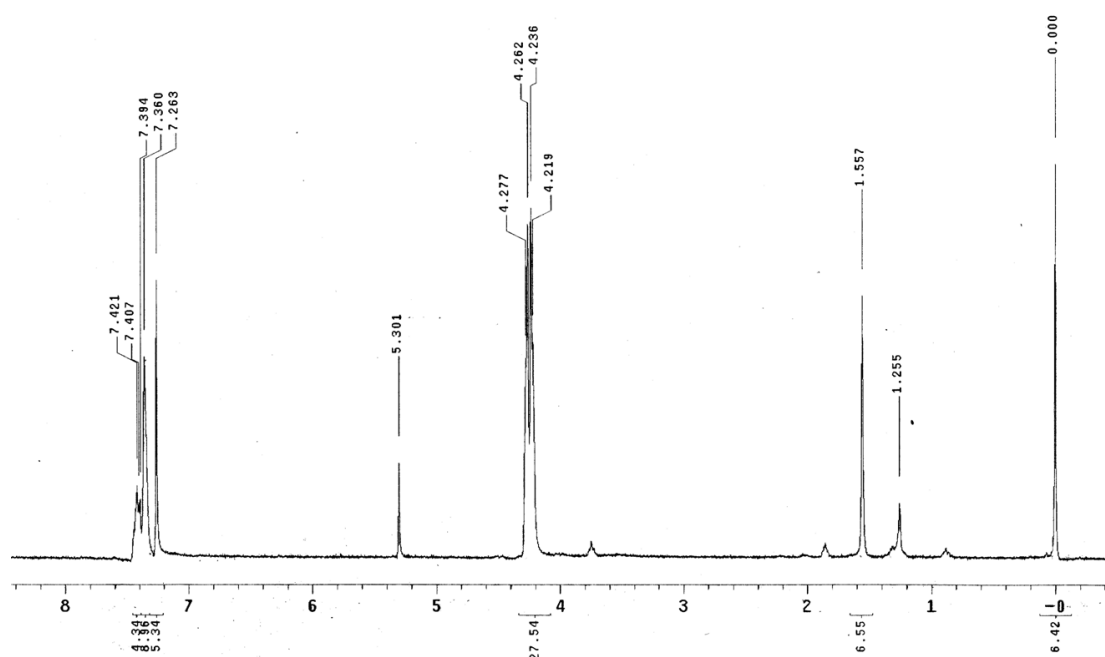


Figure S8.  $^{13}\text{C}$  NMR (d-DMSO)

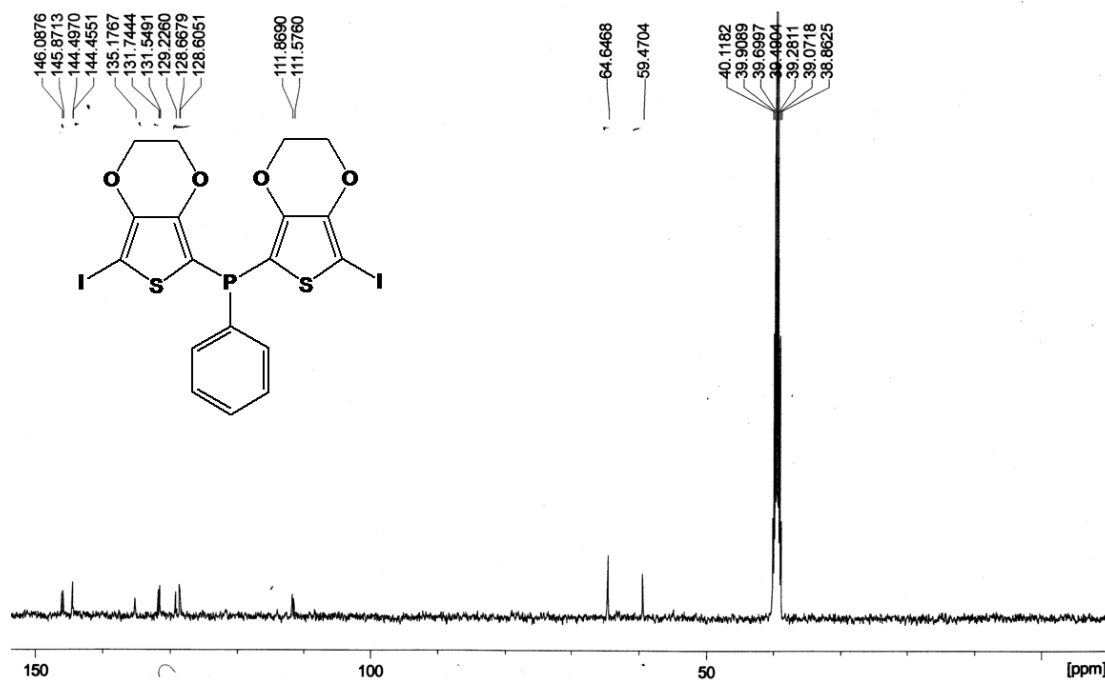
Bis-(7-bromo-2,3-dihydro-thieno[3,4-b][1,4]dioxin-5-yl)-phenyl-phosphane (5)



**Figure S9.**  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ) spectrum of **Bis-(7-iodo-2,3-dihydro-thieno[3,4-b][1,4]dioxin-5-yl)-phenyl-phosphane (6)**

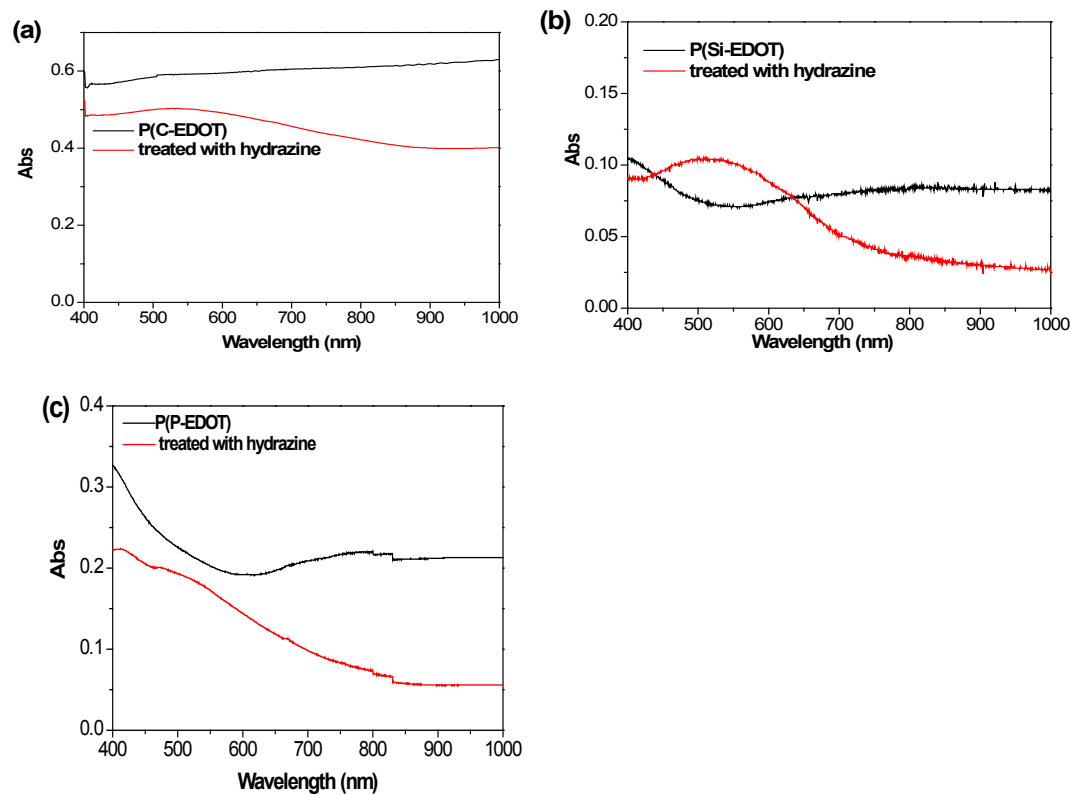


**Figure S10.**  $^{13}\text{C}$  NMR ( $\text{d-DMSO}$ ) spectrum of **Bis-(7-iodo-2,3-dihydro-thieno[3,4-b][1,4]dioxin-5-yl)-phenyl-phosphane (6)**



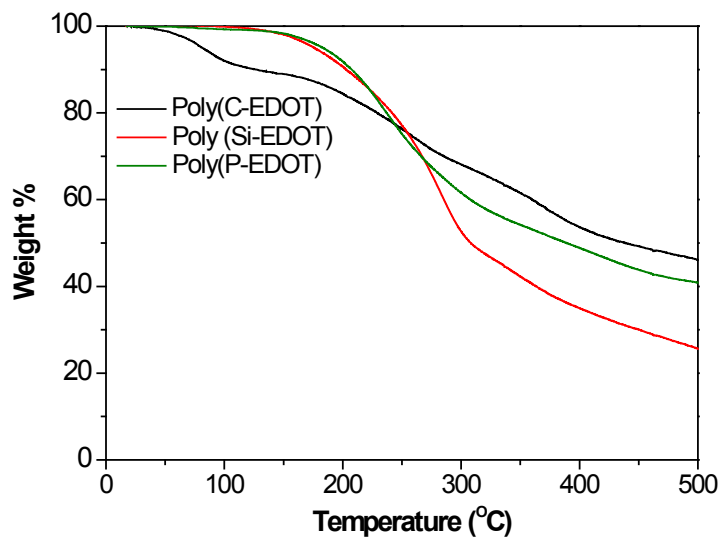
### 3. Absorbance spectra of the monomers, polymers by SSP and dedoped polymers

**Figure S11.** Absorbance spectra of the monomers, polymers by SSP and dedoped polymers by hydrazine treatment (fresh made).



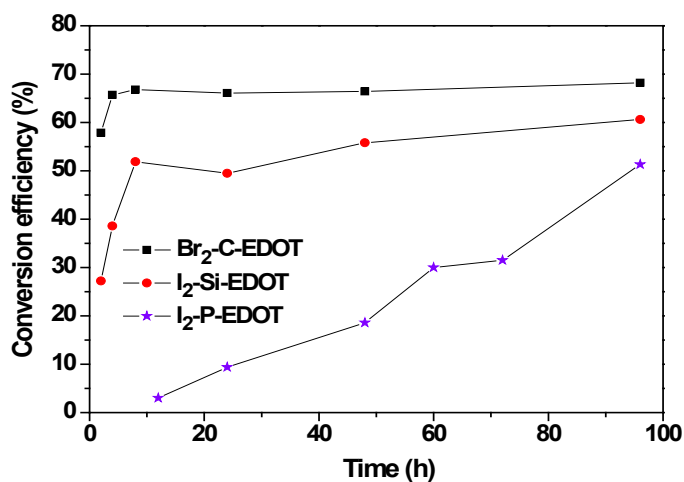
### 4. TGA curves

**Figure S12.** TGA curves for P(C-EDOT), P(Si-EDOT) and P(P-EDOT)

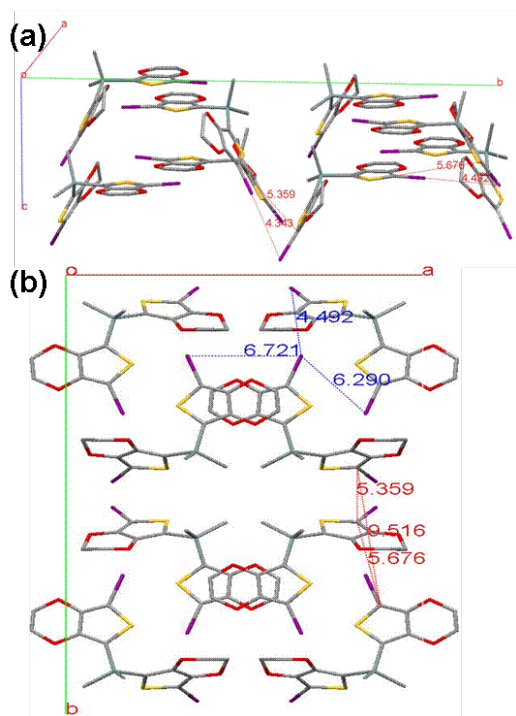


## 5. Conversion percentage vs. reaction time of SSP

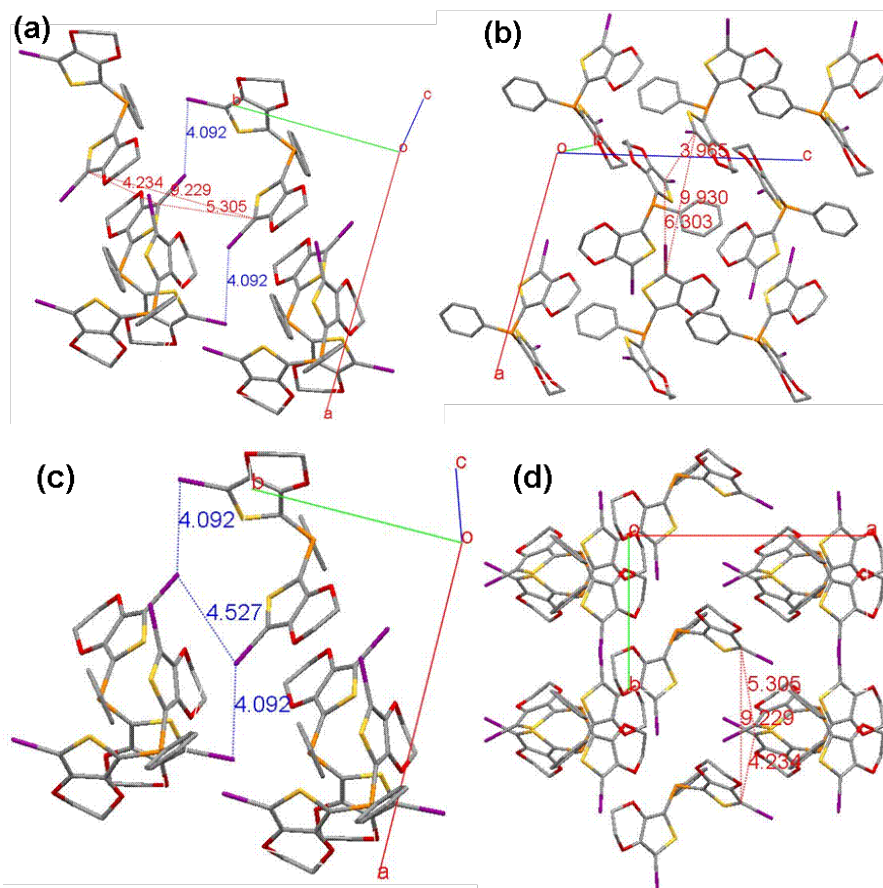
**Figure S13.** Conversion percentage vs. reaction time of SSP of examined monomers at 60 °C.



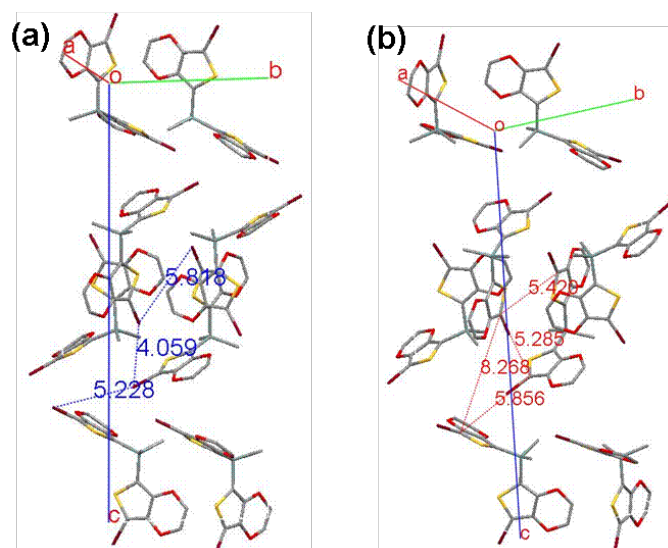
## 6. Crystal structures



**Figure S14.** Single-crystal X-ray structure of compound I<sub>2</sub>-Si-EDOT (4). Hydrogen atoms are omitted for clarity: I, purple; S, yellow and C, Si gray.



**Figure S15.** Single-crystal X-ray structure of compound I<sub>2</sub>-P-EDOT (**6**). Hydrogen atoms are omitted for clarity: I, purple; S, yellow; P, yellowish brown and C, gray.



**Figure S16.** Single-crystal X-ray structure of compound Br<sub>2</sub>-Si-EDOT (**2**). Hydrogen atoms are omitted for clarity: Br, red; S, yellow and C, gray.

## 7. Details of the Data Collection and Structure Refinements for All Complexes

**Table S1** Details of the Data Collection and Structure Refinements for All Complexes Reported in This Work

parameter	Br <sub>2</sub> -C-EDOT	I <sub>2</sub> -Si-EDOT	I <sub>2</sub> -P-EDOT	Br <sub>2</sub> -Si-EDOT
empirical formula	C <sub>13</sub> H <sub>10</sub> Br <sub>2</sub> O <sub>4</sub> S <sub>2</sub>	C <sub>14</sub> H <sub>14</sub> I <sub>2</sub> O <sub>4</sub> S <sub>2</sub> Si	C <sub>18</sub> H <sub>13</sub> I <sub>2</sub> O <sub>4</sub> S <sub>2</sub> P	C <sub>14</sub> H <sub>14</sub> Br <sub>2</sub> O <sub>4</sub> S <sub>2</sub> Si
fw	454.15	592.26	642.17	498.28
cryst syst	Monoclinic	Orthorhombic	Monoclinic	Orthorhombic
space group	P2(1)/c	Iba2	P2(1)/c	Pbca
a (Å)	12.665(3)	16.903(8)	14.6939(12)	13.2636(18)
b (Å)	8.8588(19)	28.697(13)	9.2288(7)	10.1957(13)
c (Å)	14.424(3)	8.005(4)	15.8097(12)	27.784(4)
α (deg)	90	90	90	90
β (deg)	110.803(3)	90	104.924(1)	90
γ (deg)	90	90	90	90
V (Å <sup>3</sup> )	1512.8(5)	3883(3)	2071.6(3)	3757.3(9)
Z	4	8	4	8
D <sub>calcd</sub> (g/cm <sup>3</sup> )	1.994	2.026	2.059	1.762
cryst size (mm <sup>3</sup> )	0.32×0.22×0.20	0.29×0.22×0.20	0.3×0.29×0.28	0.29×0.28×0.26
diffractometer	SMART CCD	SMART CCD	SMART CCD	SMART CCD
F(000)	888	2240.0	1224	1936.0
T (K)	296(2)	296(2)	296(2)	293(2)
θ <sub>max</sub>	26.5	26.00	26.50	26.50
reflns collected	9083	11749	13288	23315
indep reflns	3134	3775	4288	3895
param refined	191	210	245	210
R <sub>1</sub> , wR <sub>2</sub>	0.0643, 0.2005	0.0741, 0.2056	0.0253, 0.0532	0.0517, 0.1223
GOF (F2)	1.054	1.050	1.019	1.01

## 8. Polymers conductivities

**Table S2** Three polymers' conductivities

Polymers	Thickness ( $\mu\text{m}$ )	Resistivity ( $\Omega\cdot\text{cm}$ )	Conductivity (s/cm)
P(C-EDOT)	190	$10^6$	$10^{-6}$
P(Si-EDOT)	180	54	0.019
P(P-EDOT)	200	$10^7$	$10^{-7}$

## 9. Reference for supporting information

1. a) Y. Yin, Z. Li, J. Jin, C. Tusy and J. Xia, *Synth. Met.*, 2013, **175**, 97.; b) M. Belletête, S. Beaupre, J. Bouchard, P. Blondin, M. Leclere and G. Durocher, *J. Phys. Chem. B*, 2000, **104**, 9118.
2. 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.
3. a) Y. L. Gold'faarb and Y. L. Danyushevsky, *Bull. Acad. Sci. USSR*, 1956, 1395.  
b) K. J. Hoffmann, L. Knudsen, E. J. Samuelsen and P. H. J. Carlsen, *Synth. Met.*, 2000. **114**, 161.
4. S. Ponomarenko, A. Muzafarov, O. Borshchev, E. Vodopyanov, N. Demchenko and V. Myakushev, *Russ. Chem. Bull. Int. Ed.*, 2005, **54**, 684.