

Supporting information  
For Journal of Material Chemistry A

## Dopant free 3,3'-bithiophene Derivatives as Hole- transport Materials for Perovskite Solar Cells

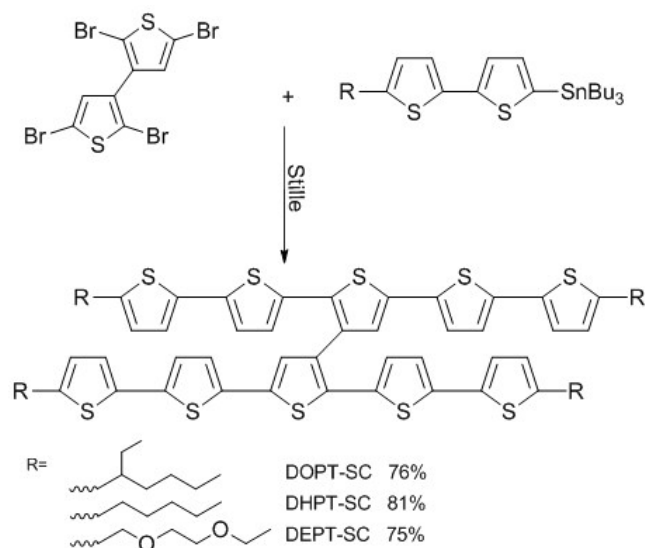
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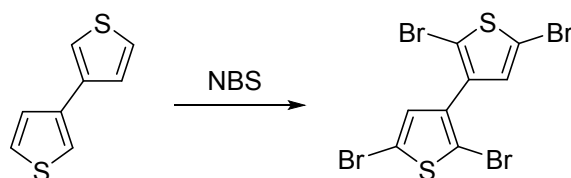
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### Experimental Section

All commercially available chemicals were used as received without further purification. Solvents were purified by standard methods and dried if necessary. Reactions were monitored by thin layer chromatography (TLC) that was conducted on plates precoated with silica gel Si 60-F254 (Merck, Germany). Column chromatography was carried out on silica gel SI 60 (Merck, Germany), mesh size 0.063-0.200 mm (normal) or 0.040-0.063 mm (flash). <sup>1</sup>H NMR was recorded on a Bruker Avance 600 spectrometer. Cyclic voltammetry measurements were carried out on a CHI600 electrochemical workstation, using a concentration of a few mM in dichloromethane containing tetrabutylammonium hexafluorophosphate, Bu<sub>4</sub>N<sup>+</sup>PF<sub>6</sub><sup>-</sup> (*ca.*, 0.01 M as a supporting electrolyte) in a three-electrode cell, where the Ag/AgCl electrode was used as the reference electrode and platinum wire as the working electrode. The scanning rate was set at 100 mV s<sup>-1</sup>. The absorption spectroscopy of various samples was measured using a UV/Vis spectrometer (SHIMADZU, UV-3600 UV/Vis/NIR Spectrophotometer). Phase transitions were studied by differential scanning calorimetry (DSC) with a PerkinElmer Instruments Diamond DSC at a scanning rate of 10 °C min<sup>-1</sup> for both heating and cooling cycles. Thermogravimetric Analysis (TGA) was tested on Pyris1 TGA. The crystal date was tested by the X-Ray Diffractometer (BRUKER, SMART APEX CCD).

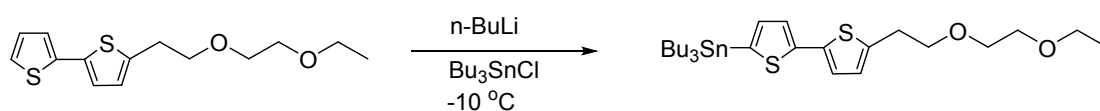


**Fig .1** Synthetic route of DHPT-SC, DOPT-SC, DEPT-SC



#### Synthesis of 2,2',5,5'-tetrabromo-3,3'-bithiophene.

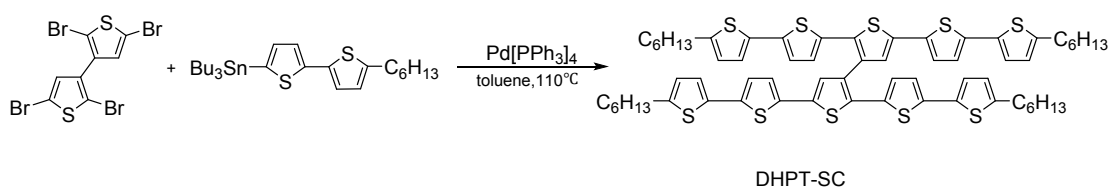
3,3'-Dithienyl (1.66g, 10mmol) and the NBS (14.24 g,80 mmol) were added to a pre-dried 250 ml two-neck flask and placed under a nitrogen atmosphere. Dry THF (200 mL) was added and the reaction mixture was stirred at room temperature for 2 days in the dark. The solvent was removed and the residue was chromatographed on silica with chloroform as eluent to get white needlelike solid, which recrystallized in alcohol in 67% yield. <sup>1</sup>HNMR (600 MHz, CDCl<sub>3</sub>, δ): 7.05 (s, 2H).



#### Synthesis of tributyl(5'-(2-(2-ethoxyethoxy)ethyl)-[2,2'-bithiophen]-5-yl)stannane.

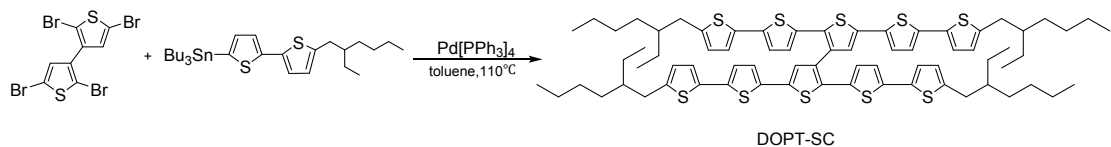
To a stirred solution of 5-(2-(2-ethoxyethoxy)ethyl)-2,2'-bithiophene (14.1g, 50mmol) in 100 mL of anhydrous THF at -10 °C was added dropwise a solution of n-BuLi (2.5 M, 21 mL). The resulting solution was stirred for 1 h at -10 °C and warmed to room temperature over 30 min. The mixture was cooled to -10 °C, and tributyltin chloride (16.3 g, 50 mmol) was added dropwise. The resulting mixture was stirred at -10 °C for 10 min, warmed to room temperature over 3h, poured into water, and extracted with ether. The combined organic extracts were washed with saturated NaCl, dried, and

filtered, and the filtrate was concentrated under reduced pressure to afford brown liquid. This crude product was reduced pressure distillation under the pressure  $1.6 \times 10^{-2}$  mbar to get light yellow liquid.  $^1\text{H NMR}$  (600 MHz,  $\text{CDCl}_3$ ,  $\delta$ ): 7.26 (d, 1H), 7.07(dd, 1H), 7.02(d, 1H), 6.77(d, 1H), 3.76(t, 2H), 3.68(m, 2H), 3.64(m, 2H), 3.58(dd, 2H), 3.11(t, 2H), 1.62(m, 6H), 1.38(m, 6H), 1.26(t, 3H), 1.15(m, 6H), 0.94(m, 9H).  $^{13}\text{C NMR}$ : 143.158, 140.257, 136.021, 135.970, 135.928, 125.872, 124.394, 123.079, 77.290, 77.080, 76.868, 71.850, 70.464, 69.836, 66.720, 30.688, 28.972, 27.283, 15.216, 13.698, 10.866.



#### Synthesis of $\alpha, \alpha'$ -dihexyloligothiophenes (DHPT-SC).

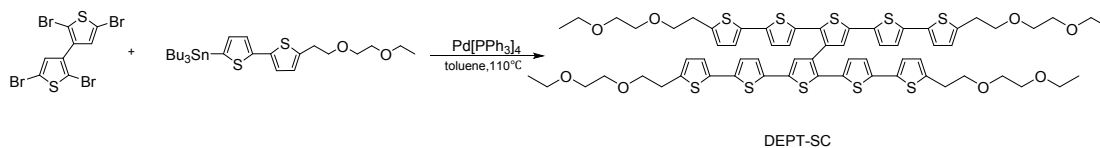
2,2',5,5'-tetrabromo-3,3'-bithiophene (482mg, 1mmol), tributyl(5'-hexyl- [2,2'- bithiophen]-5-yl)stannane (3234mg,6mmol),  $\text{Pd}[\text{PPh}_3]_4$  (115.6mg,0.1mmol), dry toluene were added to 100ml dry Schlenk flask. After three freeze-pump-thaw cycles the reaction mixture was immersed in a thermostated oil bath at 110 °C in the dark. After 48h, the solvent was removed and the crude product was purified by column chromatography (chloroform/hexane=1:10) to give the desired compound as a light yellow solid. (939.6 mg, 81%).  $^1\text{H NMR}$  (600 MHz,  $\text{CDCl}_3$ ,  $\delta$ ): 7.12(d, 2H), 7.04 (d, 2H), 7.03(s, 2H), 7.00(d, 2H), 6.95(d, 2H), 6.89 (d, 2H), 6.87(d, 2H), 6.70(d, 2H), 6.63(d, 2H), 2.81(t, 4H), 2.76(t, 4H), 1.70-1.69(m, 4H), 1.66-1.64(m, 4H), 1.35-1.30(m, 24H), 0.93-0.88(m, 12H).  $^{13}\text{C NMR}$ : 145.829, 145.655, 138.312, 137.268, 134.954, 134.851, 134.379, 133.951, 133.634, 131.956, 126.377, 125.815, 124.961, 124.820, 124.687, 124.438, 123.607, 123.569, 123.198, 123.111, 31.574, 30.221, 30.175, 28.749, 22.594, 14.102. mp:199 °C.



#### Synthesis of $\alpha, \alpha'$ -diisooctyloligo thiophenes (DOPT-SC).

Methods as DHPT-SC, purified by column chromatography (chloroform/hexane=1:10) to give the desired compound as a light yellow solid. (965.2 mg, 76%).  $^1\text{H NMR}$  (600 MHz,  $\text{CDCl}_3$ ,  $\delta$ ): 7.12(d, 2H), 7.04 (d, 2H), 7.03(s, 2H), 7.01(d, 2H), 6.96(d, 2H), 6.90 (d, 2H), 6.88(d, 2H), 6.69(d, 2H),

6.61(d, 2H), 2.77(d, 4H), 2.71(d, 4H), 1.62-1.55(m, 4H), 1.41-1.30(m, 32H), 0.95-0.88(m, 24H). <sup>13</sup>C NMR: 144.395, 144.206, 138.350, 137.309, 134.964, 134.831, 134.606, 133.974, 133.608, 131.976, 126.402, 126.000, 125.887, 124.441, 123.601, 123.490, 123.461, 123.150, 41.398, 34.186, 34.144, 32.395, 32.348, 28.894, 28.859, 25.546, 25.489, 23.012, 14.140, 10.854, 10.810. mp:140 °C.



### Synthesis of $\alpha, \alpha'$ -diethoxyethyl-oligothiophenes (DEPT-SC).

Methods as DHPT-SC, purified by column chromatography (DCM: EA=20:1) to give the desired compound as an earth yellow solid. (964.5 mg, 75%). <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>,  $\delta$ ): 7.12(d, 2H), 7.04 (d, 4H), 7.01(d, 2H), 6.95(d, 2H), 6.90 (d, 2H), 6.88(d, 2H), 6.78(d, 2H), 6.70(d, 2H), 2.77(d, 4H), 3.76(t, 4H), 3.70(t, 4H), 3.68-3.67(m, 4H), 3.65-3.63(m, 8H), 3.61-3.59(m, 4H), 3.59-3.56(m, 4H), 3.55-3.52(m, 4H), 3.12(t, 4H), 3.06(t, 4H), 1.25(t, 6H), 1.23(t, 4H). <sup>13</sup>C NMR: 141.199, 141.002, 138.130, 137.104, 135.219, 135.190, 134.972, 133.958, 133.777, 131.970, 126.393, 126.095, 125.982, 125.857, 124.474, 123.825, 123.553, 123.330, 71.710, 71.698, 70.476, 70.442, 69.824, 69.798, 66.733, 66.709, 30.715, 30.672, 15.218, 15.201. mp:153 °C.

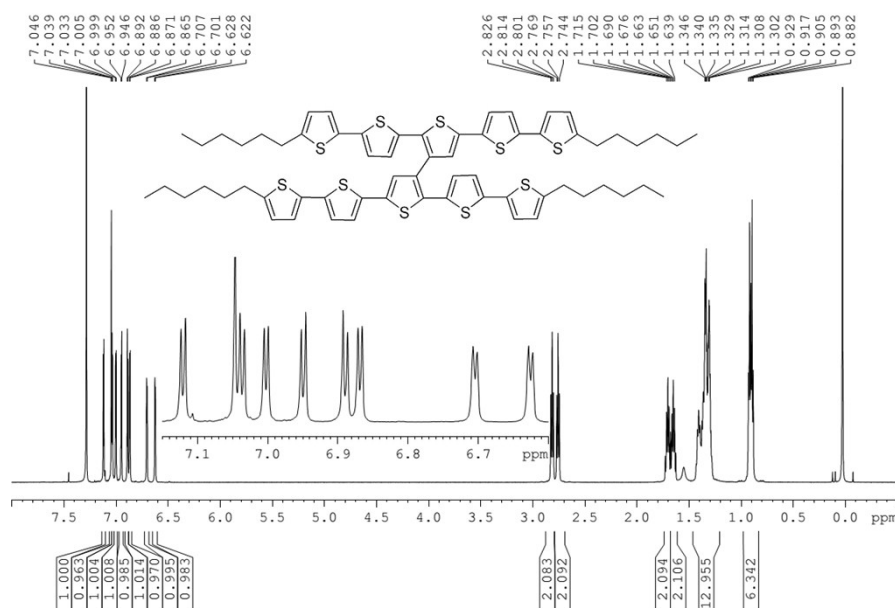


Fig.2 <sup>1</sup>H NMR spectrum of DHPT-SC in CD<sub>3</sub>Cl

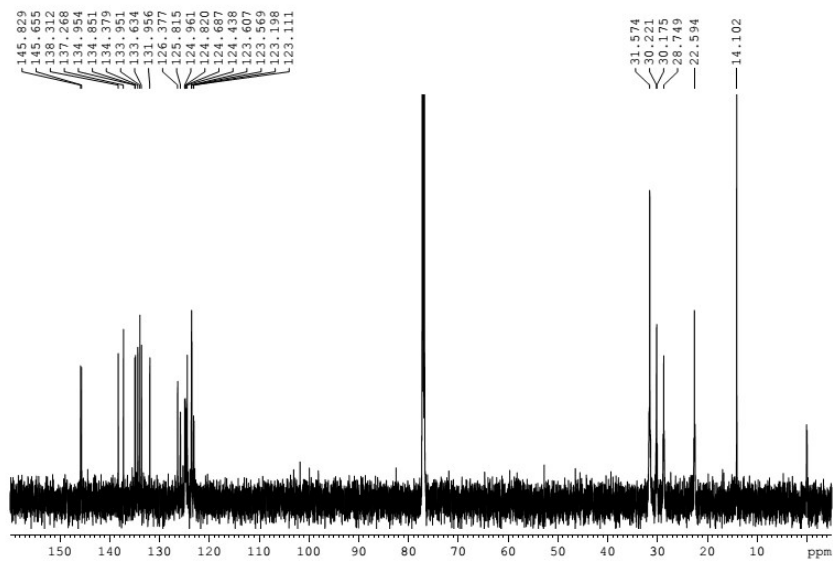


Fig.3  $^{13}\text{C}$ NMR spectrum of DHPT-SC in  $\text{CD}_3\text{Cl}$

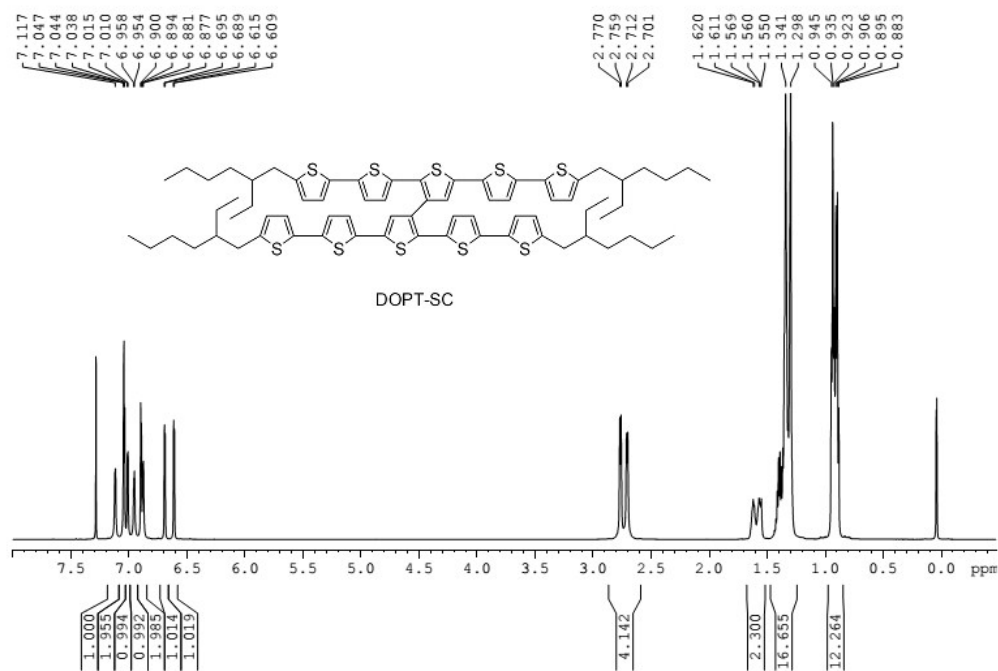


Fig.4  $^1\text{H}$  NMR spectrum of DOPT-SC in  $\text{CD}_3\text{Cl}$

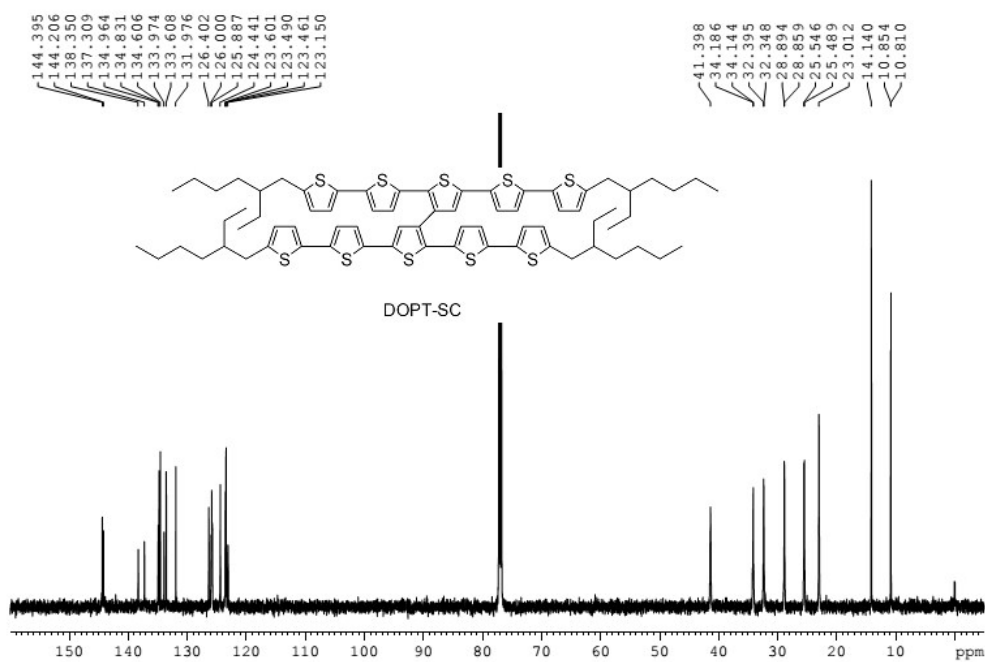


Fig.5  $^{13}\text{C}$  NMR spectrum of DOPT-SC in  $\text{CD}_3\text{Cl}$

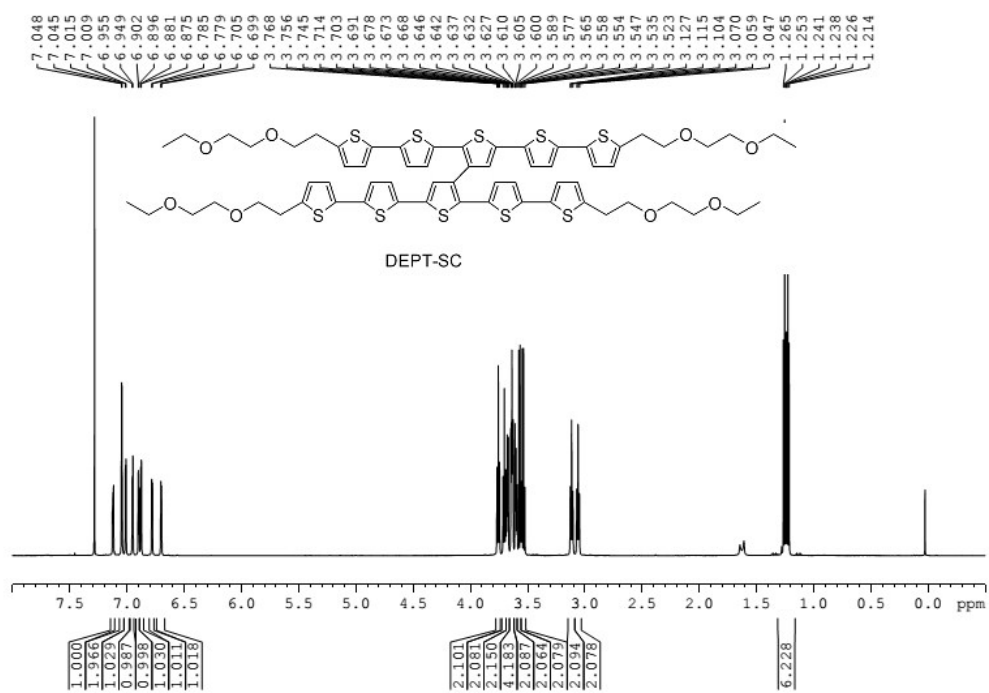
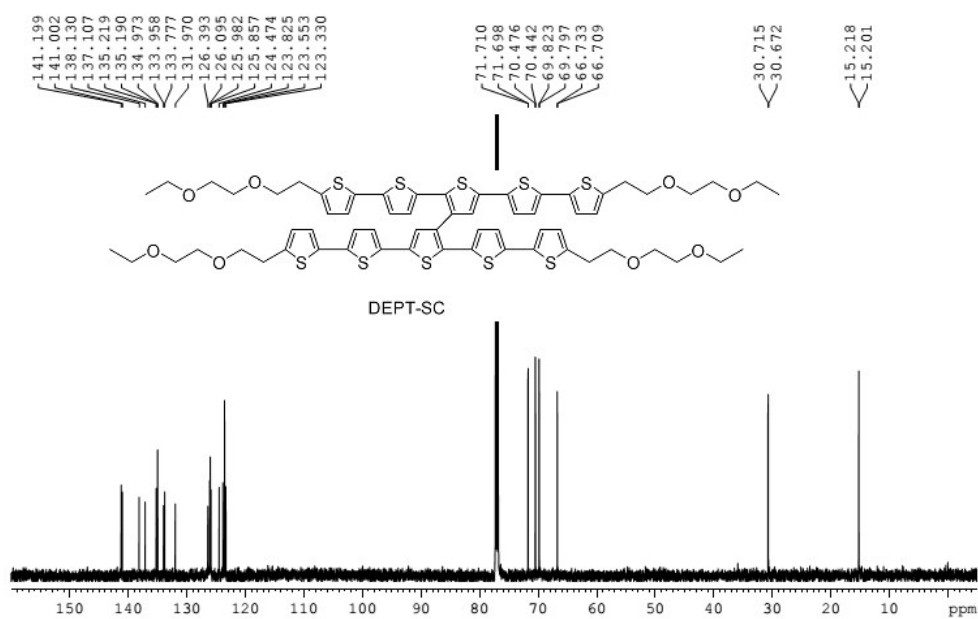
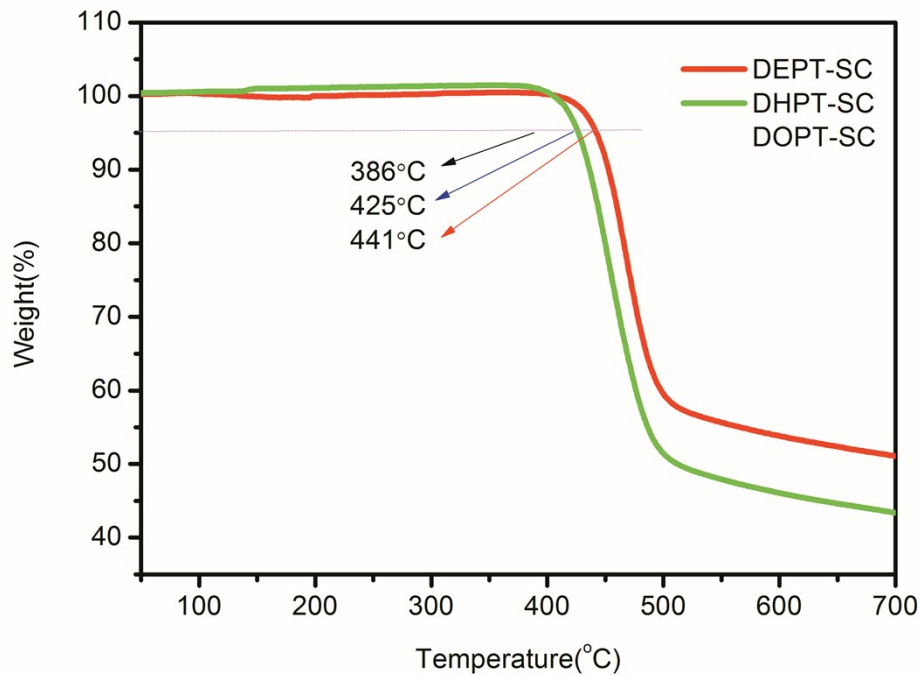


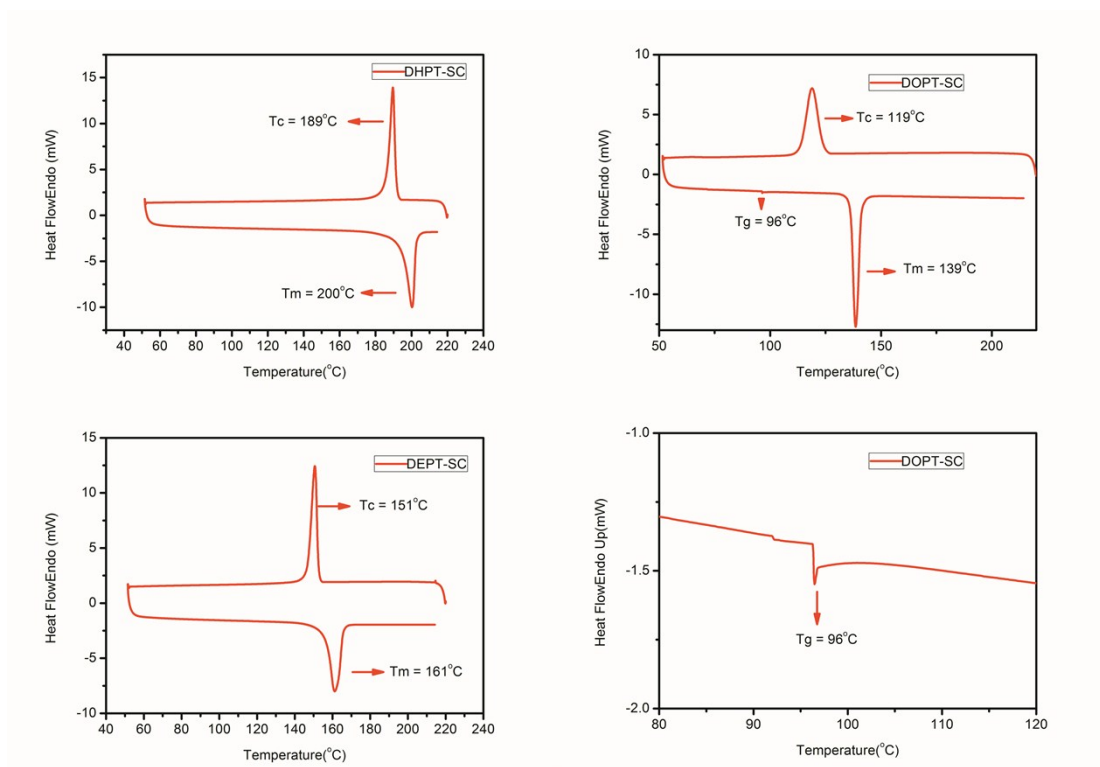
Fig.6  $^1\text{H}$  NMR spectrum of DEPT-SC in  $\text{CD}_3\text{Cl}$



**Fig.7**  $^{13}\text{C}$  NMR spectrum of DEPT-SC in  $\text{CD}_3\text{Cl}$



**Fig. 8** TGA curves of DHPT-SC, DOPT-SC, DEPT-SC with a heating rate of  $10\text{ }^{\circ}\text{C min}^{-1}$  under  $\text{N}_2$  atmosphere.



**Fig. 9** DSC curves of DHPT-SC, DOPT-SC, DEPT-SC with a heating rate of 20 °C min<sup>-1</sup> under N<sub>2</sub> atmosphere.