## **Supplementary Information**

The cyclic voltammetry measurement



Fig. S1 (a) Cyclic voltammogram of copolymers and (b) illustration of the  $E_{\text{HOMOS}}$  and  $E_{\text{LUMOS}}$  of copolymers.

## The TGA measurement



Fig. S2 Thermogravimetric analysis of (a) PTh<sub>4</sub>FBSe (b) P1 (c) P2.



Fig. S3 Differential scanning calorimetry thermograms of (a) PTh<sub>4</sub>FBSe (b) P1 (c) P2.



**Fig. S4** Illustration of dipole moment of DTFBSe and DTFBT. The arrow indicates

the direction of the dipole moment. The length of the arrow is decided by the strength of the dipole moment. The unit of the dipole moment is given in Debye and the direction is denoted by the arithmetic sign.



**Fig. S5** 2D fiber XRD pattern of the sheared (a)  $PTh_4FBSe$  (b) P1 (c) P2 (d)  $PTh_4FBT$ . The solid arrow indicates the direction of mechanical shearing force applied on the sample.

**Table S1.** The shunt and series resistances of the FBSe/FBT copolymer: PC<sub>71</sub>BM BHJ PSCs

Polymer/PC <sub>71</sub> BM	R <sub>sh</sub>	R <sub>s</sub>	FF
(w/w; 1 : 2)	$(\Omega cm^2)$	$(\Omega cm^2)$	(%)
PTh <sub>4</sub> FBSe	606	7.3	66.5
P1	537	5.4	60.5
P2	757	11.0	59.3
PTh <sub>4</sub> FBSe <sup>a</sup>	456	6.0	61.8
P1 <sup>a</sup>	531	3.3	64.1
<b>P2</b> <sup>a</sup>	481	7.0	60.6

 $^{a}$  With 3 v% of DIO as additive



Fig. S6 The equatorial integrations of the 2D fiber XRD patterns in Fig. S5.