

Supporting materials

I. Synthesis

I.1. Materials

$\text{Pd}(\text{PPh}_3)_4$ was purchased from Alfa Aesar Chemical Co, and used as received without further purification. Toluene was dried over molecular sieves and freshly distilled prior to use. The other chemical reagents and solvents were obtained commercially as analytical-grade quality and used without further purification. Column chromatography was carried out on silica gel (size: 200-300 mesh).

I.2. Synthesis and characterization of monomers

In order to obtain D-A copolymers, we have synthesized two dibromo-benzotrithiophene monomers **5** and **8**, in accordance with the reaction scheme shown in Fig. S1.

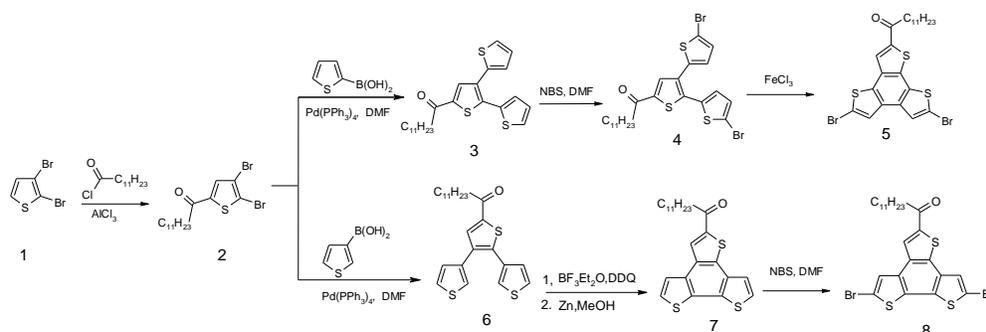


Fig. S1. The synthesis pathways of monomers **5** and **8**

The monomers play role of the acceptor units in the D-A copolymers. The target monomer **5** has been synthesized by a step-by-step transformation based on the reaction of lauroyl chloride with 2,3-dibromothiophene (**1**) to give the ketone **2** (yield 90%), which was then treated with a two-mole excess of thiophene-3-boronic acid under Suzuki–Miyaura conditions to form 5-dodecanoyl-2,3-bis(2-thienyl)thiophene (**3**, yield 63.43%). Afterwards, the chemical compound **3** was subjected to a bromination procedure (yield 88%) and then cyclization in the presence of FeCl_3 applied to form 2,5-dibromo-8-dodecanoylbenzo[1,2-*b*:3,4-*b'*:5,6-*d''*]trithiophene(**5**) with the product yield of 82%. The monomer **8** was synthesized according to the method described in detail in the reference [1] with product yield of 87%.

The structure and composition of the intermediate compounds **2-4**, **6**, **7** and the target products **5** and **8** have been characterized by elemental analysis, IR spectroscopy, ^1H and ^{13}C NMR. In particular, the ^1H NMR spectrum of compound **5** demonstrates three low-field singlets in the range of 7.4 – 7.9 ppm, attributed to three nonequivalent aromatic hydrogen atoms (Fig.S2a). In

the high-field region of 0.5 – 3.0 ppm, one can observe the multiplets assigned to 43 aliphatic hydrogen atoms. The aliphatic-to-aromatic ratio of integrated intensities confirms the structure suggested in Fig S2a. The ^{13}C NMR spectrum of monomer **5** reveals twelve signals in the aromatic range of 120 – 150 ppm, which corresponds to twelve different aromatic carbon atoms. A well pronounced ketonic signal might be observed at 194.18 ppm. The upfield region shows also eleven peaks related to eleven different aliphatic carbons (Fig S2b). The ^1H NMR and ^{13}C NMR spectra of compound **8** with the suggested structure are shown in Fig S2b.

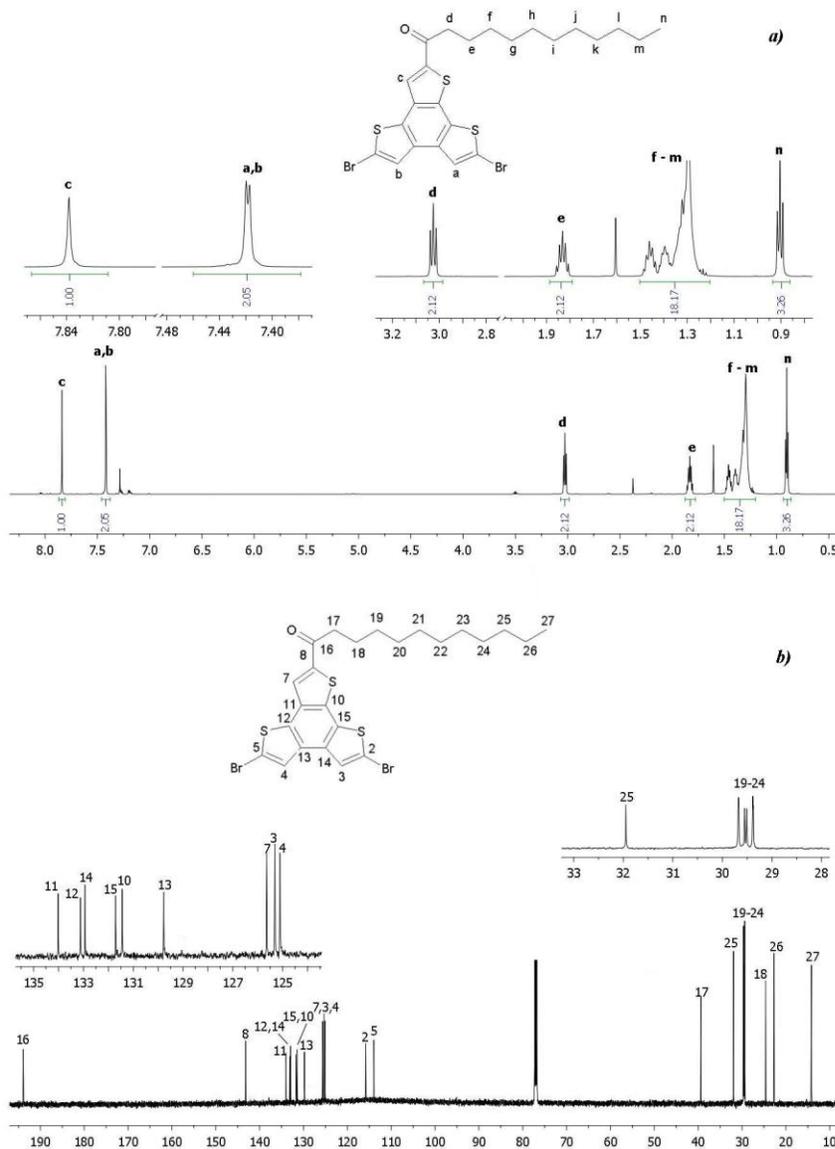


Fig S2. ^1H (a) and ^{13}C NMR (b) spectra of 2,5-dibromo-8-dodecanoylbenzo[1,2-b:3,4-b':5,6-d']trithiophene (**5**).

Synthesis polymers of polymer P1 and P2

In a 50 ml three-necked flask equipped with a reflux condenser and magnetic stirrer, 0.4423 g (0.5 mmol) 2,6-bis-trimethylstannyl-4,8-didodecyloxybenzo[1,2-b;4,5-b']dithiophene, 0.2932 g (0.5 mmol) 5,8-dibromo-2-dodecanoylbenzo[1,2-b:3,4-b':6,5-b'']trithiophene (**5**) and 0.033 g (0.028 mmol) Pd(Ph₃P)₄ were placed in a stream of argon and 16 ml dry toluene was added.

The reaction mixture was stirred at 110° C for 48 h under argon. The mixture was then cooled to room temperature and the product was poured into 200 ml methanol and filtered. The copolymer was dissolved in chloroform and reprecipitated in methanol, then purified by extraction with methanol, hexane, and acetone in a Soxhlet apparatus and dried in a vacuum. Yield 65%. M_n = 15500, PDI= 2.10 NMR ¹H (CDCl₃, 400 MHz, δ, ppm): 8.55–6.09 (m, 5H), 4.22–0.80 (m, 73H),. Anal. calculated (%) for (C₅₈H₇₈B₅O₃S₅)_n: C, 70.83; H, 7.99; S, 16.30. Found: C, 70.62; H, 7.74; S, 15.97.

A copolymer P2 has been synthesized similar to copolymer P1, using 2,6-bis-trimethylstannyl-4,8-didodecyloxybenzo[1,2-b;4,5-b']dithiophene and 2,8-dibromo-5-dodecanoylbenzo[1,2-b:3,4-b':5,6-d'']trithiophene (**8**). Yield 79 %. M_n = 13100, PDI= 2.12;. NMR ¹H (CDCl₃, 400 MHz, δ, ppm): 7.92–7.07 (m, 5H), 3.70–0.80 (m, 73H),. Anal. calculated (%) for (C₅₈H₇₈B₅O₃S₅)_n: C, 70.83; H, 7.99; S, 16.30. Found: C, 70.71; H, 7.78; S, 16.03.

The ¹H NMR spectra (Fig S2) of the P1 and P2 show multiplet signals in the ranges of δ_H = 8.00–7.00 and δ_H = 7.92–7.07 ppm, corresponding to aromatic protons of benzo[1,2-b; 3,4-b']dithiophene and the thiophene substituent of 5-dodecanoylbenzo[1,2-b:3,4-b':5,6-d'']trithiophene fragments, respectively. Moreover, there are broad signals observed in the range of δ_H = 4.50–3.50 ppm and δ_H = 3.50–2.90 ppm, corresponding to the protons of CH₂ groups directly bonded to the oxygen atoms of the 4,8-didodecyloxybenzo[1,2-b:3,4-b']dithiophene(O-CH₂-) fragment and (OC-CH₂) group of 5-dodecanoylbenzo[1,2-b:3,4-b':5,6-d'']trithiophene moiety. The signals obtained in the range of δ_H = 2.50–0.50 ppm and δ_H = 3.10–0.60 ppm can be related to the other protons of the alkyl substituent of the polymer unit. The aliphatic-to-aromatic ratio of integrated intensities for the copolymers P1 and P2 is compatible with the macromolecule structures supposed (Fig.S3).

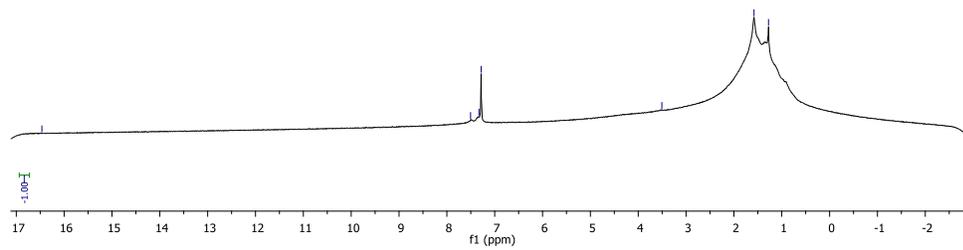
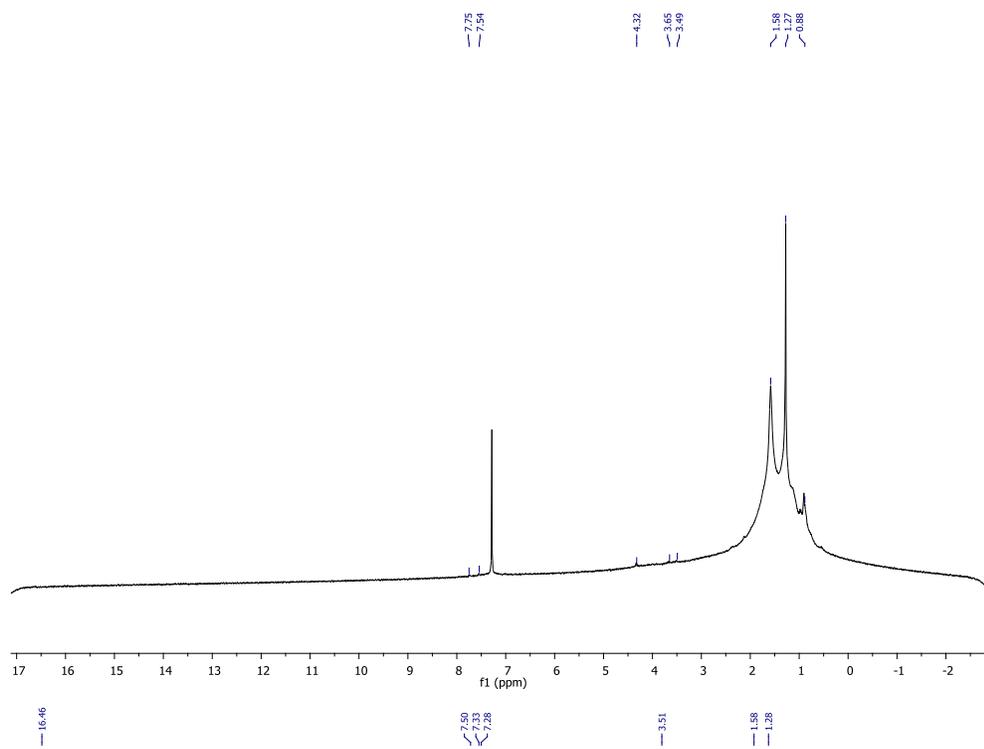


Figure S3. ^1H NMR of the polymers **P1** (a) and **P2** (b).

II. Additional photovoltaic characterization

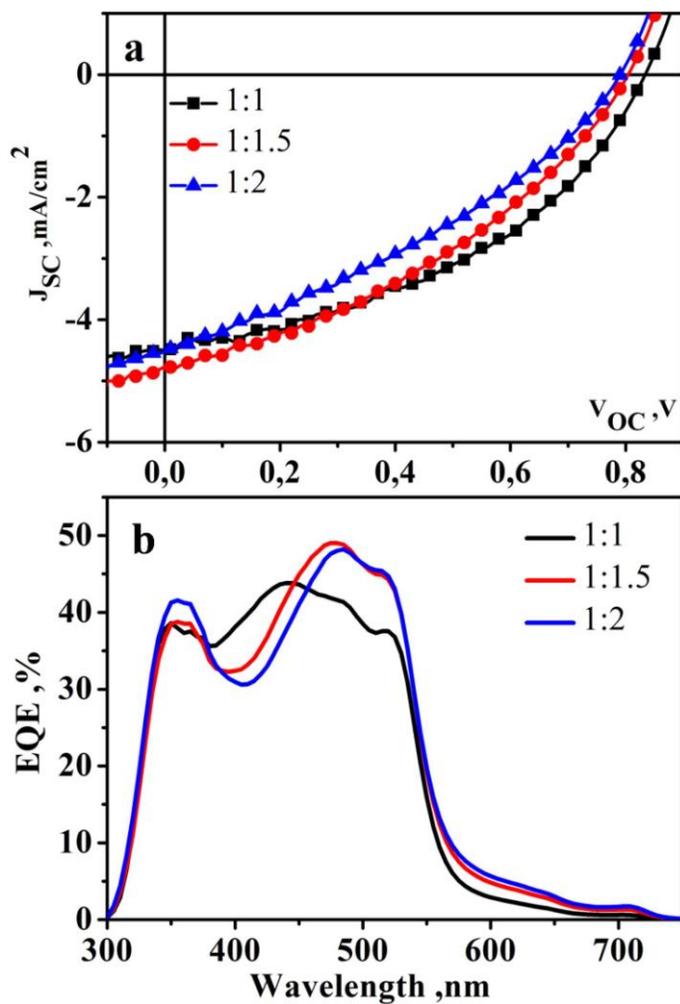


Fig. S4 J-V and EQE characteristics of P1/PC₆₁BM solar cells with different polymer-fullerene weight ratio.

Table S1. Photovoltaic characteristics of P1/PC₆₁BM devices with different polymer-fullerene weight ratio

Ratio	V _{oc} , V	J _{sc} , mA/cm ²	J _{sc} ^a , mA/cm ²	FF, %	PCE, %
1:1	0.83	4.5	4.1	42	1.6
1:1.5	0.80	4.8	4.6	37	1.4
1:2	0.79	4.6	4.5	34	1.2

^a Calculated from EQE

Table S2 Photovoltaic characteristics of P2/PC₆₁BM devices with different polymer-fullerene weight ratio

Ratio	V _{oc} , V	J _{sc} , mA/cm ²	J _{sc} ^a , mA/cm ²	FF, %	PCE, %
1:1	0.85	5.3	5.2	61	2.8
1:1.5	0.84	6.1	5.9	62	3.2
1:2	0.82	6.0	5.8	60	3.0

^a Calculated from EQE

Table S3. Photovoltaic characteristics of P2/PC₆₁BM devices with different thickness of the active layers.

Thickness (nm)	V _{oc} , V	J _{sc} , mA/cm ²	J _{sc} ^a mA/cm ²	FF, %	PCE, %
130	0.82	5.8	5.7	58	2.7
100	0.83	6.1	5.9	61	3.1
80	0.85	6.0	5.8	65	3.3

^a Calculated from EQE;

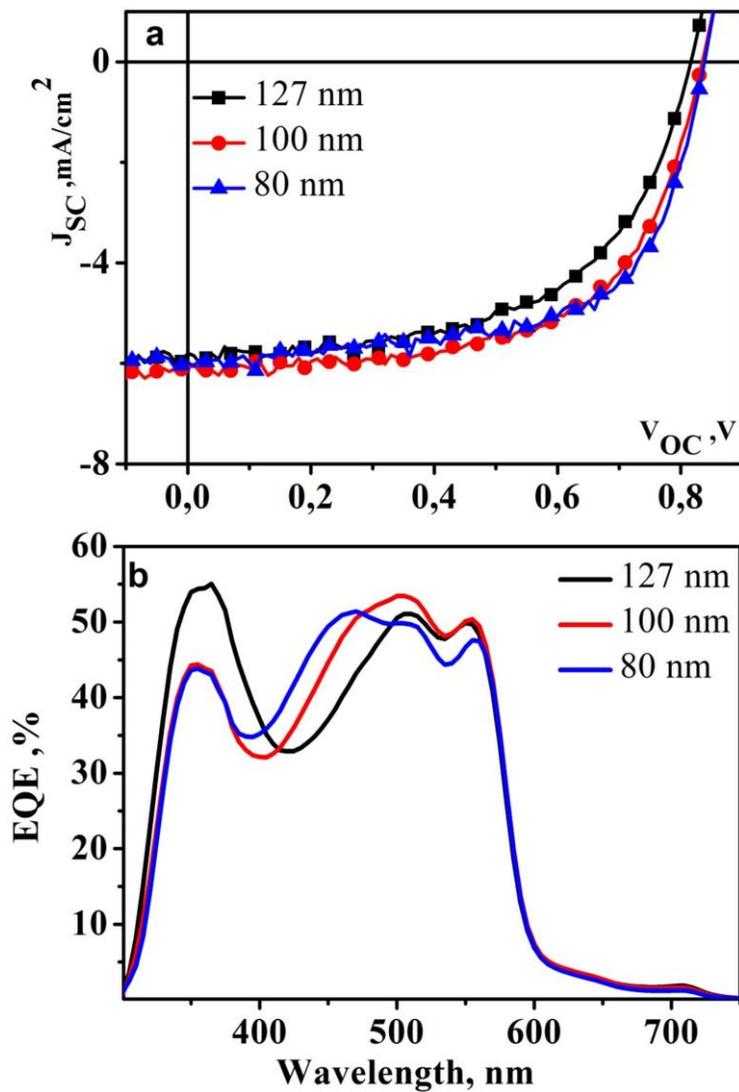


Fig. S5 J-V and EQE characteristics of P2/PC₆₁BM solar cells with different active layer thickness.

References

1. Goldberg, Y.; Alper, H. J. Org. Chem. 1993, 58, 3072.