

Electronic Supplementary Information

Self-assembly Nanopillar Arrays by Simple Spin Coating from Blending Systems Comprising PC₆₁BM and Conjugated Polymers with Special Structure

Jian Hu, Qian Luo, Zhanyuan Zhang, Yan Huang, Daobin Yang, Xuemei Pu*, Zhiyun Lu**

Key Laboratory of Green Chemistry and Technology (Ministry of Education), College of
Chemistry, Sichuan University, Chengdu 610064, P. R. China.

*E-mail: huangyan@scu.edu.cn (Y. Huang); luzhiyun@scu.edu.cn (Z. Lu);

xmpuscu@scu.edu.cn (X. Pu)

Contents

1. Experimental details	S2
2. Synthesis of the polymers	S3
3. Molecular weight of the polymers (Table S1)	S8
4. The molecular structure of PC ₆₁ BM (FigureS1)	S8
5. PT-BOAQ/PC ₆₁ BM blending films with different Mw of PT-BOAQ (Figure S2)	S9
6. The monomer BOAQ crystallizes in ethyl alcohol solution (Figure S3)	S10
7. Density functional theory (DFT) calculations (Figure S4)	S11

1. Experimental details

Materials and instruments All the chemicals were purchased from commercial suppliers and used without further purification. Tetrahydrofuran (THF), toluene and chlorobenzene were freshly distilled over sodium/benzophenone ketyl or phosphorus decaoxide under nitrogen before use. All polymers were synthesized by ourselves and their structures were characterized by ¹H NMR and ¹³C NMR. PC₆₁BM used in blend films were purchased from commercial suppliers and used without further purification. Number-average (M_n) and weight-average (M_w) molecular weights and polydispersity indices (PDI) of the polymers were determined on a PL-GPC model 210 chromatograph at 25°C with THF as solvent at a flow rate of 1 mL min⁻¹, and the calibration was based on polystyrene standards. The morphologies of the active layers were investigated

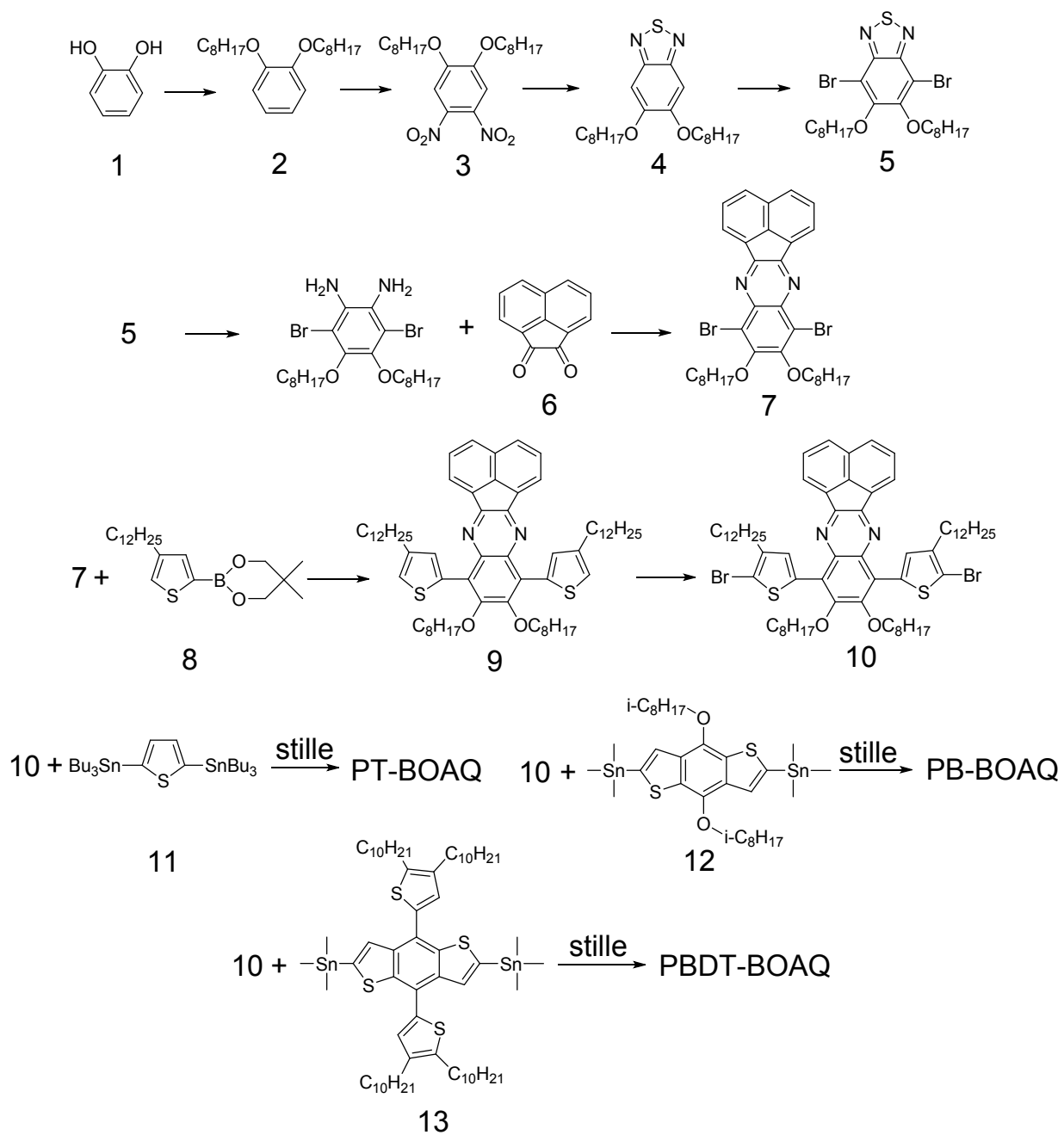
through atomic force microscopy (AFM) in tapping mode under ambient conditions using a MFP 3D Asylum Research instrument. The contact angles of pure water on different polymer films were measured by a DSA30 Contact Angle measurement instrument. The surface energies of the materials were calculated according to their contact angle data using Equation-of-State (Neumann) equation.

Fabrication of polymer nanopillar arrays. Both the polymers and PC₆₁BM were dissolved in chlorobenzene at concentrations of 25 mg·mL⁻¹. The two solutions were blended with volume ratio of polymer : PC₆₁BM = 1:3. After filtered through a 0.45µm poly(tetrafluoroethylene) filter, the composite solution was spin-coated onto the quartz substrates at 3000 rpm for 30 s (active area: 1×1 mm²). The thickness of the spin-casted films was measured by a profilometer (Alpha-step 200; Tencor Instruments).

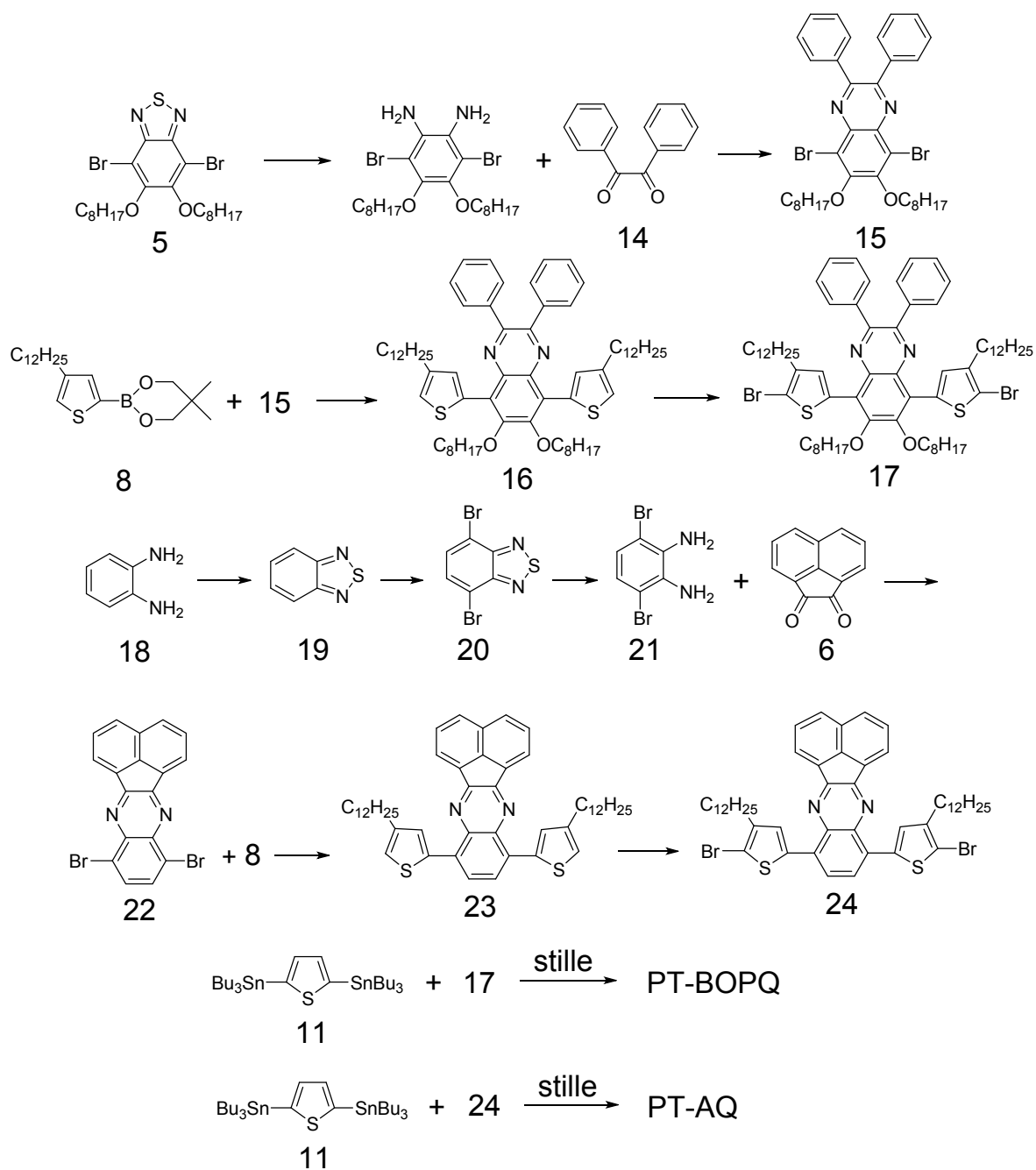
Fabrication of pure polymer films for surface energy measurement. The polymer was dissolved in chlorobenzene (15 mg mL⁻¹). After complete dissolution, the solution of pure polymer was filtered through a 0.45µm poly(tetrafluoroethylene) filter, then spin-coated at 3000 rpm for 30s onto the quartz substrates.

2. Synthesis of the polymers

The synthetic routes to the polymers are shown in Scheme 1 and Scheme 2. The compounds **1**, **6**, **11**, **12**, **13**, **14** and **18** were purchased from commercial suppliers and used without further purification. The intermediates **2-5**, **7-10**, **15-17** and **19-24** were synthesized according to the literature procedures.¹⁻³ The detailed synthetic processes of polymers are as follows.



Scheme S1. Synthetic route to the polymer **PT-BOAQ**, **PB-BOAQ** and **PBDT-BOAQ**.



Scheme S2. Synthetic route to the polymer **PT-BOPQ** and **PT-AQ**.

General procedure for Stille cross coupling polymerization^{1,2}

1.00 mmol distannyl-modified monomer **11**, 1.00 mmol dibromosubstituted monomer **10**, 20 mL of degassed toluene, catalytic amount (2% mmol) of Pd₂(dba)₃ and P(o-tol)₃ (16% mmol) were added into a flask under argon, then the reactant was brought to reflux under stirring for 48 h. The mixture was cooled down to room temperature and dropped into 200 mL of mixture of methanol and concentrated hydrochloric acid (10:1), and the precipitate was filtered and washed with methanol and acetone in a soxhlet apparatus to remove the oligomers and catalyst residue. Finally, the polymer was recovered as solid from the chloroform solution by precipitation from methanol, then dried under vacuum.

PT-BOAQ: black solid, yield: 67%. ¹H NMR (400 MHz, CDCl₃): δ (ppm) 8.49–8.37 (br, 2H), 8.15–8.03 (br, 4H), 7.88–7.77 (br, 2H), 7.41–7.32 (br, 2H), 4.26–4.08 (br, 4H), 3.11–2.87 (br, 4H), 2.01–1.10 (br, 64H), 0.94–0.78 (br, 12H). ¹³C NMR (100 MHz, CDCl₃): δ (ppm) 152.4, 151.7, 138.6, 137.0, 136.7, 134.8, 133.8, 132.4, 132.0, 130.0, 129.3, 128.7, 127.6, 125.9, 124.9, 122.6, 74.3, 32.1, 31.2, 30.9, 30.0, 29.6, 26.5, 22.9, 14.3.

PB-BOAQ: purple black solid, yield: 73%. ¹H NMR (400 MHz, CDCl₃): δ (ppm) 8.46–8.33 (br, 2H), 8.17–8.08 (br, 4H), 7.94–7.70 (br, 2H), 7.68–7.58 (br, 2H), 4.40–4.11 (br, 8H), 3.16–2.93 (br, 4H), 2.07–1.15 (br, 82H), 1.10–0.78 (br, 24H). ¹³C NMR (100 MHz, CDCl₃): δ (ppm) 152.5, 151.9, 144.6, 144.3, 144.1, 140.0, 136.9, 136.7, 136.6, 136.4, 135.0, 133.8, 133.7, 133.3, 132.4, 132.3, 131.7, 130.4, 130.1, 130.0, 129.8, 129.5, 128.8, 125.1, 77.4, 76.2, 74.4, 40.9, 32.1, 31.3, 30.9, 30.7, 30.6, 30.2, 30.0, 29.9, 26.4, 24.1, 23.3, 22.9, 14.3, 11.5.

PBDT-BOAQ: purple black solid, yield: 57%. ¹H NMR (400 MHz, CDCl₃): δ (ppm) 8.46–8.37 (br, 2H), 8.12–8.02 (br, 4H), 7.97–7.87 (br, 2H), 7.86–7.77 (br, 2H), 7.42–7.38 (br, 1H), 7.34–7.28 (br, 1H), 4.18–4.07 (br, 4H), 3.08–2.56 (br, 12H), 1.94–1.05 (br, 128H), 0.93–0.78 (br,

24H). ^{13}C NMR (100 MHz, CDCl_3): δ (ppm) 151.4, 150.7, 139.1, 138.7, 138.2, 137.9, 137.1, 136.5, 135.7, 134.3, 133.7, 133.9, 132.8, 132.2, , 131.3, 128.9, 128.2, 127.6, 124.0, 122.3, 121.5, 120.6, 73.2, 31.9, 31.0, 30.9, 30.0, 29.9, 29.6, 28.8, 28.5, 28.4, 27.4, 27.2, 25.3, 21.7, 13.1.

PT-BOPQ: black solid, yield: 69%. ^1H NMR (400 MHz, CDCl_3): δ (ppm) 8.10–8.20 (br, 2H), 7.85–7.75 (br, 5H), 7.45–7.30 (br, 7H), 4.25–4.10 (br, 4H), 3.05–2.90 (br, 4H), 2.00–1.18 (br, 64H), 0.95–0.80 (br, 12H). ^{13}C NMR (100 MHz, CDCl_3): δ (ppm) 151.66, 148.95, 137.75, 137.41, 135.45, 135.17, 133.58, 132.47, 130.46, 129.44, 127.79, 127.16, 124.60, 122.34, 76.30, 76.19, 75.98, 75.67, 73.15, 30.91, 28.97, 28.78, 28.74, 28.68, 28.37, 25.25, 21.70, 21.67, 13.11, 13.10.

PT-AQ: black solid, yield: 62 %. ^1H NMR(400 MHz, CDCl_3): δ (ppm) 8.46 (br, 2H), 8.11 (br, 4H), 7.86–7.66 (br, 4H), 7.57–7.52 (br, 2H), 2.87–2.73 (br, 4H), 1.56–1.25 (br, 40H), 0.87 (br, 6H). Anal. Calcd for $(\text{C}_{54}\text{H}_{62}\text{N}_2\text{S}_3)_n$: C, 77.65; H, 7.48; N, 3.35; S, 11.52. Found: C, 76.20; H, 6.88; N, 3.19; S, 10.83.

3. Molecular weight of polymers

Table S1. Molecular weight of polymers used in blend films

	Polymer	M _n (GPC)	M _w (GPC)	PDI(GPC)	M _n (¹ H-NMR)
1	PT-BOAQ _a	15000	21150	1.41	12140
2	PT-BOAQ _b	4820	6900	1.43	3650
3	PT-BOAQ _c	8850	14080	1.59	6080
4	PT-BOAQ _d	20700	27900	1.35	15610
5	PT-BOPQ	15030	26100	1.74	10190
6	PT-AQ	1470	1780	1.21	1140
7	PB-BOAQ	13300	19600	1.47	10250
8	PBDT-BOAQ	9900	13500	1.36	8020

PT-BOAQ_a is used in Figure 2. **PT-BOAQ_b**, **PT-BOAQ_c** and **PT-BOAQ_d** are used in Figure S2. Both M_n (GPC) and M_w (GPC) are the molecular weights of polymers measured by GPC, M_n (¹H-NMR) is the molecular weights of polymers measured by ¹H NMR integration.

4. The molecular structure of PC₆₁BM

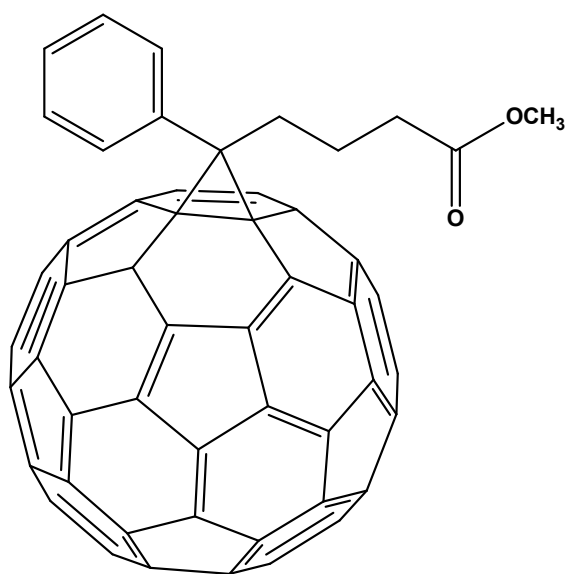


Figure S1 The molecular structure of PC₆₁BM

5. PT-BOAQ/PC61BM blending films with different Mw of PT-BOAQ.

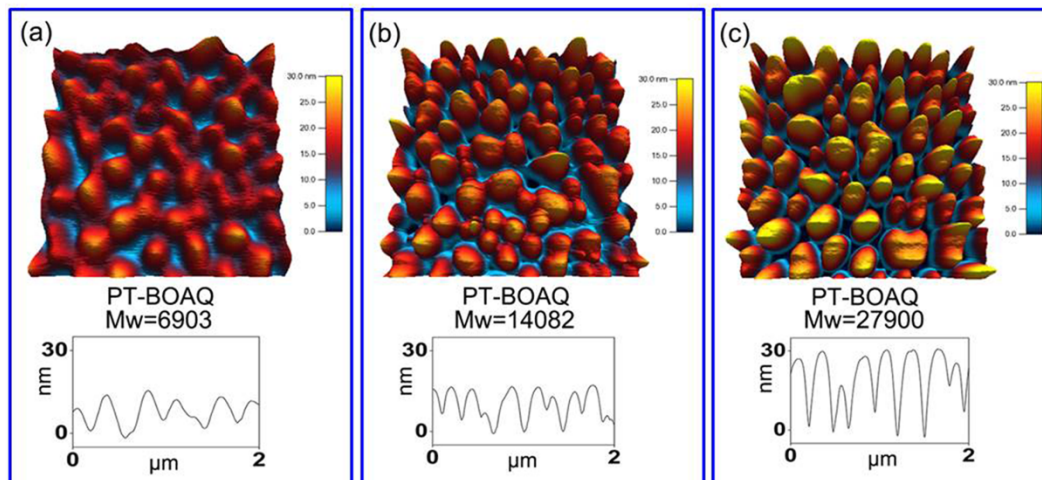


Figure S2. 3D-visualized AFM images and cross section view in height mode of PT-BOAQ/PC61BM blending films with different Mw of PT-BOAQ: (a) PT-BOAQ with Mw of 6900; (b) PT-BOAQ with Mw of 14080; (c) PT-BOAQ with Mw of 27900. All images are in $2.00 \times 2.00 \mu\text{m}$ size.

6. The monomer BOAQ crystallizes in ethyl alcohol solution.

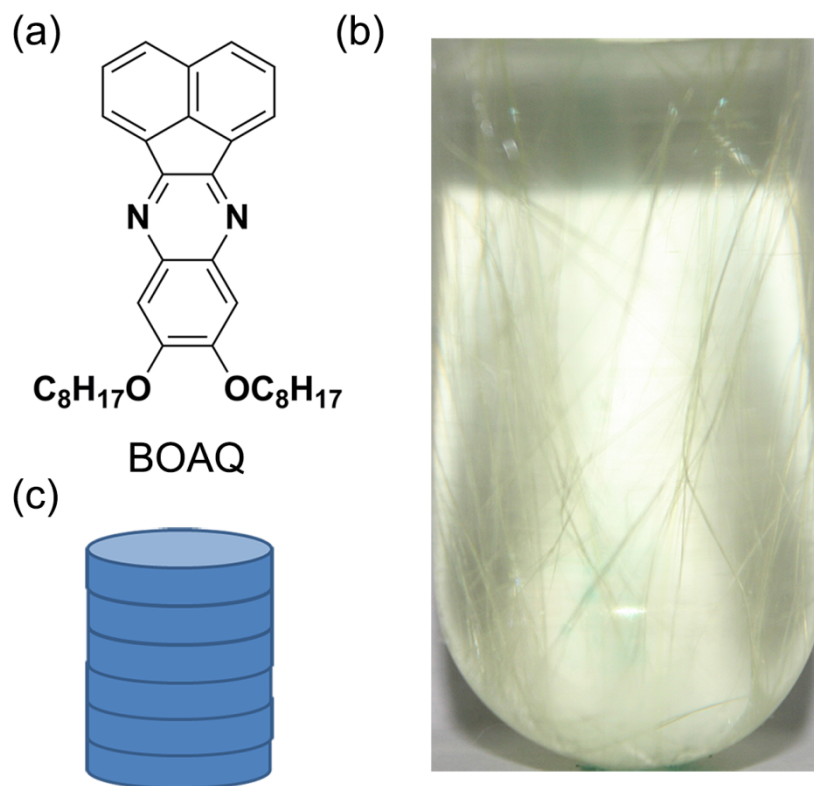


Figure S3. (a) Chemical structure of the monomer 9,10-bis(octyloxy)acenaphtho[1,2-b]quinoxaline (BOAQ), AQ not been used because of it is insoluble in common organic solvents. (b) The monomer BOAQ crystallizes in ethyl alcohol solution. (c) schematic column of stacked BOAQ molecules.

7. Density functional theory (DFT) calculations

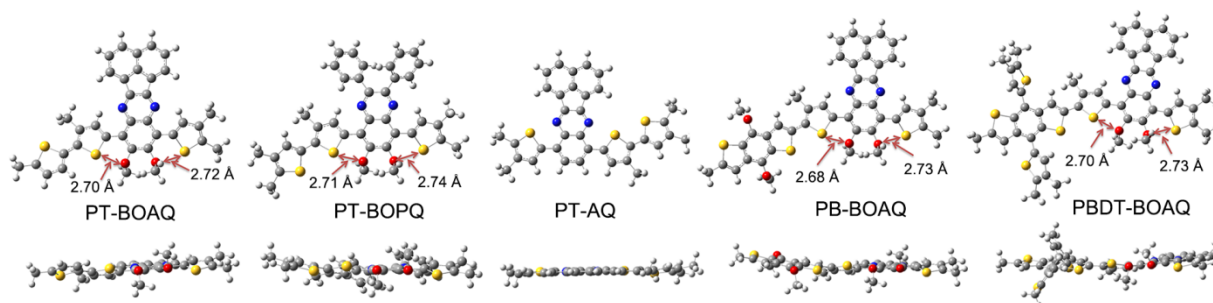


Figure S4 Optimized molecular geometries of repeating units of polymers investigated in this article. Upper row: vertical views; bottom row: horizontal views.

References

1. Z. Zhang, Q. Peng, D. Yang, Y. Chen, Y. Huang, X. Pu, Z. Lu, Q. Jiang, Y. Liu, *Synth. Met.* **2013**, 175, 21–29.
2. Y. Zou, Z. Guan, Z. Zhang, Y. Huang, N. Wang, Z. Lu, Q. Jiang, J. Yu, Y. Liu, X. Pu, *J. Mater. Sci.* **2012**, 47, 5535–5545.
3. H. J. Song, T. H. Lee, M. H. Han, J. Y. Lee, D. K. Moon, *Polymer* **2013**, 54, 1072-1079.