*Supporting Information*

# Synthesis of phenanthro[1,10,9,8-cdefg]carbazole-based conjugated polymers for green-selective organic photodiodes

*Min Jae Sung,*[‡] *Seongwon Yoon,*[§] *Soon-Ki Kwon,*[†] *Yun-Hi Kim,**[,‡] *and Dae Sung Chung**[,§]

[†]School of Materials Science & Engineering and ERI, Gyeongsang National University, Jinju 660-701, Korea

[‡]Department of Chemistry and Research Institute for Green Energy Convergence Technology (RIGET), Gyeongsang National University, Jinju 660-701, Korea

[§]School of Chemical Engineering and Material Science, Chung-Ang University, Seoul 156-756, Korea

*Y.-H. Kim, *e-mail*: ykim@gnu.ac.kr

*D. S. Chung, *e-mail*: dchung@cau.ac.kr

**Synthetic routes for PP-TPD**

**1. Synthesis of 1-Nitroperylene (1)**

In the 1 L flask, perylene (10.0 g, 39.9 mmol) was dissolved in 600 mL 1,4-dioxane. After the mixture was heated to 60°C , the mixture of 8.0 mL of water and 5 mL of nitric acid (d = 1.5) was added dropwisely into the solution. The reaction mixture was stirred at 60°C for 30 min., then the solution was cooled to room temperature and poured into 2 L water. The crude product was collected, washed with ethanol, dried and purified by chromatography on silica to get a brick-red crystal. (Yield: 2.5g, 21.8%) $^{1}$H.NMR (DMSO, 300MHz): 8.53-8.57 (d, 2H), 7.95-8.04 (m, 4H), 7.68-7.85 (m, 4H), 7.57-7.60(t, 1H). $^{13}$C NMR ($CDCl_3$, 500 MHz): d (ppm) 146.0, 134.4, 133.8, 131.9, 130.2, 129.0, 128.8, 128.0, 127.6, 127.2, 126.8, 125.6, 124.8, 122.8, 122.7, 122.1, 40.1, 39.9, 39.7, 39.5, 39.3, 38.9.

**2. Synthesis of 1H-phenanthro[1,10,9,8-cdefg]carbazole (2)**

After the solution of 1-nitroprerylene (10g, 34 mmol) and (70 mL, 0.4 mol) of triethylphosphite was refluxed at 160 °C for overnight, the reaction mixture was cooled down to room temperature and poured into hexane. The crude product was recrystallized using DMSO to get a yellow crystal. (Yield: 7.4g, 82.2%) $^{1}$H NMR (DMSO 300MHz): 12.21 (s, 1H), 8.74-8.77 (d, 2H), 8.17-8.19 (d, 2H), 7.92-7.99 (d, 4H), 7.79-7.85 (t, 2H). $^{13}$C NMR ($CDCl_3$, 500 MHz): d (ppm) 130.6, 129.7, 128.3, 125.0, 124.6, 123.5, 120.8, 116.9, 115.5, 40.12, 39.9, 39.7, 39.5, 39.2, 39.08, 38.87.

**3. Synthesis of 1-(2-decyltetradecyl)-1H-phenanthro[1,10,9,8-cdefg]carbazole (3)**

1H-phenanthro[1,10,9,8-cdefg]carbazole (4 g, 15.1 mmol), NaH (0.60 g, 25.2 mmol), and 11-(bromomethyl)tricosane (9.6 g, 22.6mmol) was dissolved into dry THF, then the solution was stirred at 66 °C for 12 h. After cooling to room temperature, the mixture was poured into water and extracted using dichloromethane. After the extracted organic solution was dried with anhydrous magnesium sulfate, the solvent was evaporated in low pressure. The crude product was purified by column chromatography on silica gel with n-hexane as eluent. (Yield: 6.5 g, 65.3%) $^{1}$H NMR ($CDCl_3$, 300 MHz): d (ppm) 8.60-8.63 (d, 2 H), 8.10-8.14 (d, 2 H), 7.91-7.93 (d, 2 H), 7.84-7.85 (d, 2 H), 7.85-7.91 (t, 2 H), 4.28-4.32 (d, 2 H), 2.16 (m, 1 H), 1.10-1.42 (m, 40 H), 0.85-0.91 (m, 6 H). $^{13}$C NMR ($CDCl_3$, 500 MHz): d (ppm) 132.08, 130.3, 128.7, 124.85, 124.79, 124.34, 123.44, 120.53, 117.24, 113.37, 77.25, 76.75, 49.94,

39.87, 31.94, 31.80, 29.84, 29.65, 29.51, 29.36, 29.3, 26.49, 22.7, 14.12.

**4. Synthesis of 3,10-dibromo-1-(2-decyltetradecyl)-1H-phenanthro[1,10,9,8-cdefg] carbazole (4)**

1-(2-Decyltetradecyl)-1H-phenanthro[1,10,9,8-cdefg]carbazole (4 g, 6.6 mmol) was dissolved into 150 mL dichloromethane. In the absent of light, N-bromosuccinimide (2.37 g, 13.3 mmol) was added into the solution and then the reaction mixture was stirred 6 hours at room temperature. After the reaction mixture was added into water, it was extracted with dichloromethane. After the extracted organic solution was dried with anhydrous magnesium sulfate, the solvent was evaporated in low pressure. The crude product was purified by column chromatography using petroleum ether as eluent to get a yellow product ( Yield: 3.67 g, 72.8%) $^{1}$H NMR ($CDCl_3$, 300 MHz): d (ppm) 8.71-8.69 (d, 2 H), 8.38-8.35 (d, 2 H), 8.06 (s, 2 H), 7.95-7.90 (t, 2 H), 4.45-4.43 (d, 2 H), 2.25-2.22 (m, 1 H), 1.10-1.42 (m, 40 H), 0.85-0.91 (m, 6 H). $^{13}$C NMR ($CDCl_3$, 500 MHz): d (ppm) 131.5, 129.5, 127.6, 125.3, 124.9, 123.7, 121.6, 117.9, 116.9, 115.9, 50.03, 39.66, 31.9, 31.8, 31.6, 29.8, 29.6,29.5, 29.52, 29.35, 29.30, 26.37, 22.7, 14.1, MS (EI) m/z: 759 (M+).

**5. Synthesis of 1-(2-decyltetradecyl)-3,10-bis(4,4,5,5-tetramethyl-1,3,2-dioxa-borolan-2-yl)-1H-phenanthro[1,10,9,8-cdefg]carbazole**

3,10-Dibromo-1-(2-decyltetradecyl)-1H-phenanthro[1,10,9,8-cdefg] carbazole (2.0 g, 2.6 mmol) was dissolved into 60 mL tetrahydrofuran. After the solution was cooled down to -78 °C, tn-BuLi ( 2.5M in hexane, 2.5 mL) was slowly dropped and the mixture was kept stirring 45 min under -78 °C. Isopropoxyboronic acid pinacol ester (1.22g, 6.6 mmol ) was slowly added into the mixture and was kept stirring 30 min. After the reaction was stirred 2 h at room temperature, the reaction mixture was poured into the ice water and extracted with ethyl ether. The organic phase was dried using anhydrous magnesium sulfate, and evaporated to remove the solvent. The crude product was purified by column chromatography on silica gel and then recrystallized in ethyl acetate and ethanol to get yellow solid product. (Yield: 0.6g, 27.3%) $^{1}$H NMR ($CDCl_3$, 300 MHz): d (ppm) 8.99-9.02 (d, 2 H), 8.70-8.73 (d, 2 H), 8.46 (s, 2 H), 7.86-7.92 (t, 2 H), 4.66-4.68 (d, 2 H), 2.37 (m, 1 H), 1.52 (m, 24 H), 1.10-1.42 (m, 40 H), 0.85-0.91 (m, 6 H). $^{13}$C NMR ($CDCl_3$, 500 MHz): d (ppm) 137.8, 130.9, 128, 127.8, 127.6, 127.1, 125.4, 125.3, 125, 120.2, 88.1, 62.5, 34.4, 32.9, 31.9, 29.2, 29.6, 29.3, 27.1, 24.7, 22.7, 14.1. MS (EI) m/z: 853.6 (M+)

**6. Synthesis of 5-octyl-1,3-di(thiophen-2-yl)-4H-thieno[3,4-c]pyrrole-4,6(5H)-dione**

1,3-Dibromo-5-octyl-4H-thieno[3,4-c]pyrrole-4,6(5H)-dione 7.50 g (17.73 mmol) and tributyl(thiophen-2-yl)stannane 16.53 g (44.31 mmol) were dissolved in toluene (300 mL). Under nitrogen condition, $Pd(PPh_3)_2Cl_2$ 0.40g (0.53 mmol) was added to the mixture at 100 $^oC$ for 12h. The mixture was extracted using chloroform, and then it was dried using $MgSO_4$ and the solvent was evaporated. The crude product was purified by chromatography using hexane/dichloromethane ( 4:1), and recrystallized in hexane.

Yield: 4.88 g (64%), $^1H$ NMR (300 MHz, $CDCl_3$): δ = 8.00 (d, 2H), 7.45 (d, 2H), 7.15 (t, 2H), 3.68(t, 2H), 1.72 (m, 2H), 1.32 (m, 10H), 0.88 (t, 3H). HRMS (EI): m/z for $C_{22}H_{23}NO_2S_3$ (M+) 429.0891.

**7. Synthesis of 1,3-bis(5-bromothiophen-2-yl)-5-octyl-4H-thieno[3,4-c]pyrrole-4,6(5H)-dione**

5-Octyl-1,3-di(thiophen-2-yl)-4H-thieno[3,4-c]pyrrole-4,6(5H)-dione 5.50 g (12.79 mmol)was dissolved in chloroform (200 mL), and NBS 3.0 g (17.0 mmol) was added to the mixture. After the solution was stirred in room temperature for 12 h, organic layer was extracted using chloroform and water and it was dried using $MgSO_4$. The crude product was purified by chromatography using hexane/dichloromethane (4:1), and recrystallized in hexane.

Yield: 4.88 g (64%), $^1H$ NMR (300 MHz, $CDCl_3$): δ =7.69 (d, 2H), 7.1 (d, 2H), 3.67 (t, 2H), 1.72 (m, 2H), 1.34 (m, 10H). 0.91 (t, 3H), HRMS (EI): m/z for $C_{22}H_{21}Br_2NO_2S_3$ (M+) 584.9101, $^{13}C$ NMR ($CDCl_3$, 500 MHz): d (ppm) 162.4, 135.2, 133.7, 131.1, 129.7, 128.7, 116.7, 38.7, 31.7, 29.1, 28.4, 26.9, 22.6, 14.0

**8. Polymerization of PP-TPD**

1-(2-decyltetradecyl)-3,10-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1H-phenanthro [1,10,9,8-cdefg]carbazole ( 0.4g, 0.468 mmol) and 1,3-bis(5-bromothiophen-2-yl)-5-octyl-4H-thieno[3,4-c]pyrrole-4,6(5H)-dione (0.275g, 0.468mmol) were dissolved in 12 mL toluene, then bubbling with nitrogen for 30 min. Pd $(PPh_3)_4$ (10.8 mg, 0.00936mmol) and $K_2CO_3$ (2 mL, 2M dissolved in water) were added to the mixture, and it was stirred for 36 h at 110 °C. 2-Bromothiophene and 2-thienylboronic acid were sequentially added into solution and reaction mixture was stirred for 3 h for end-capping. The reaction mixture was precipitated into methanol (300ml with 5 ml HCl aq) and the precipitated polymer was

filtered. The crude polymer was purified by soxhlet extraction with methanol, acetone, hexane, tetrahydrofuran, chloroform and chlorobenzene successively. The polymer was then precipitated into methanol. The filtered polymer was dried in the vacuum. (Yield: 0.36 g, 75%) $^{1}$H NMR (500 MHz, $CDCl_3$ ) d (ppm): δ 8.64-8.45 (br, 4H), 7.83-7.59 (br, 6H), 7.21-7.12 (br, 2H), 4.56 (br, 2H) 3.66 (br, 2H), 3.74 (s, 2H), 2.3 (s, 1H), 1.97 (s, 2H), 1.1 (br, 50), 0.77 (br, 9).

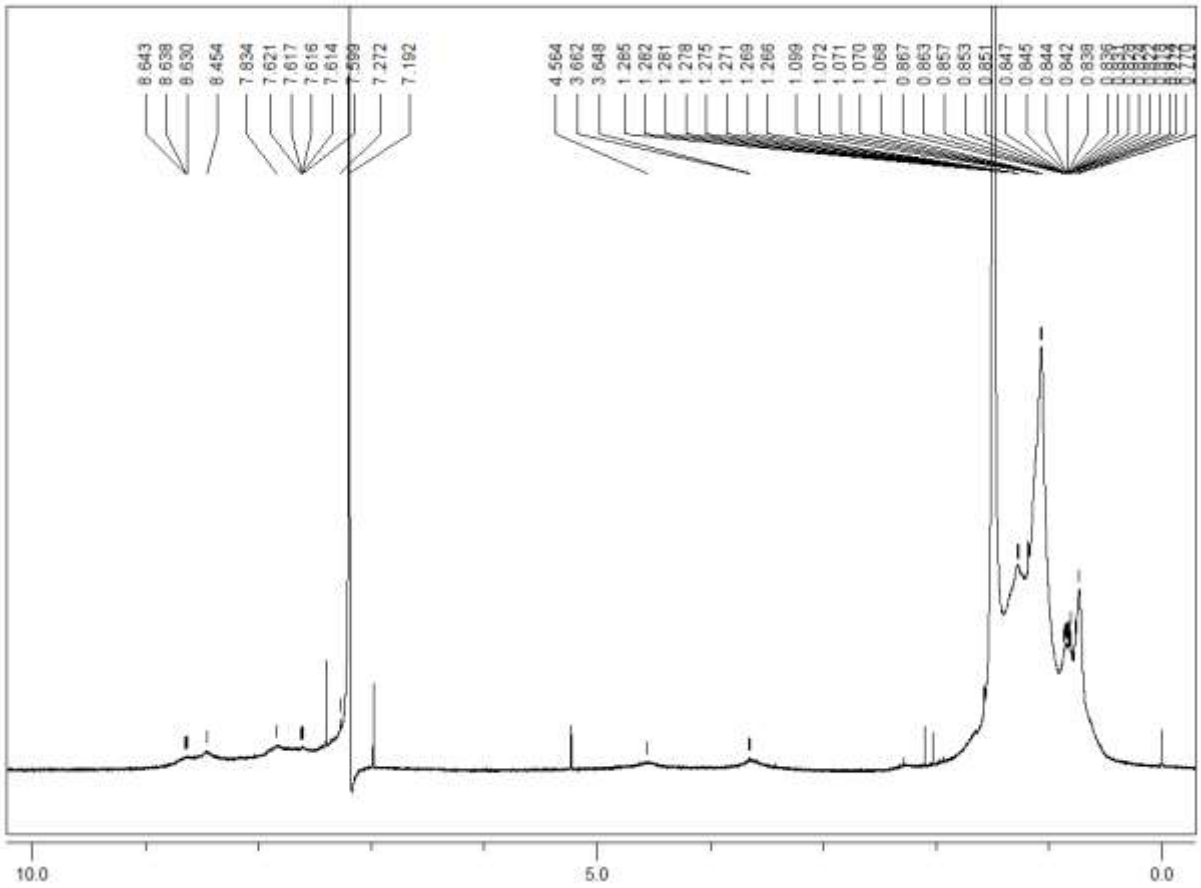


**Figure S1**. The $^{1}$H-nuclear magnetic resonance ($^{1}$H-NMR) spectrum of synthesized **PP-TPD**

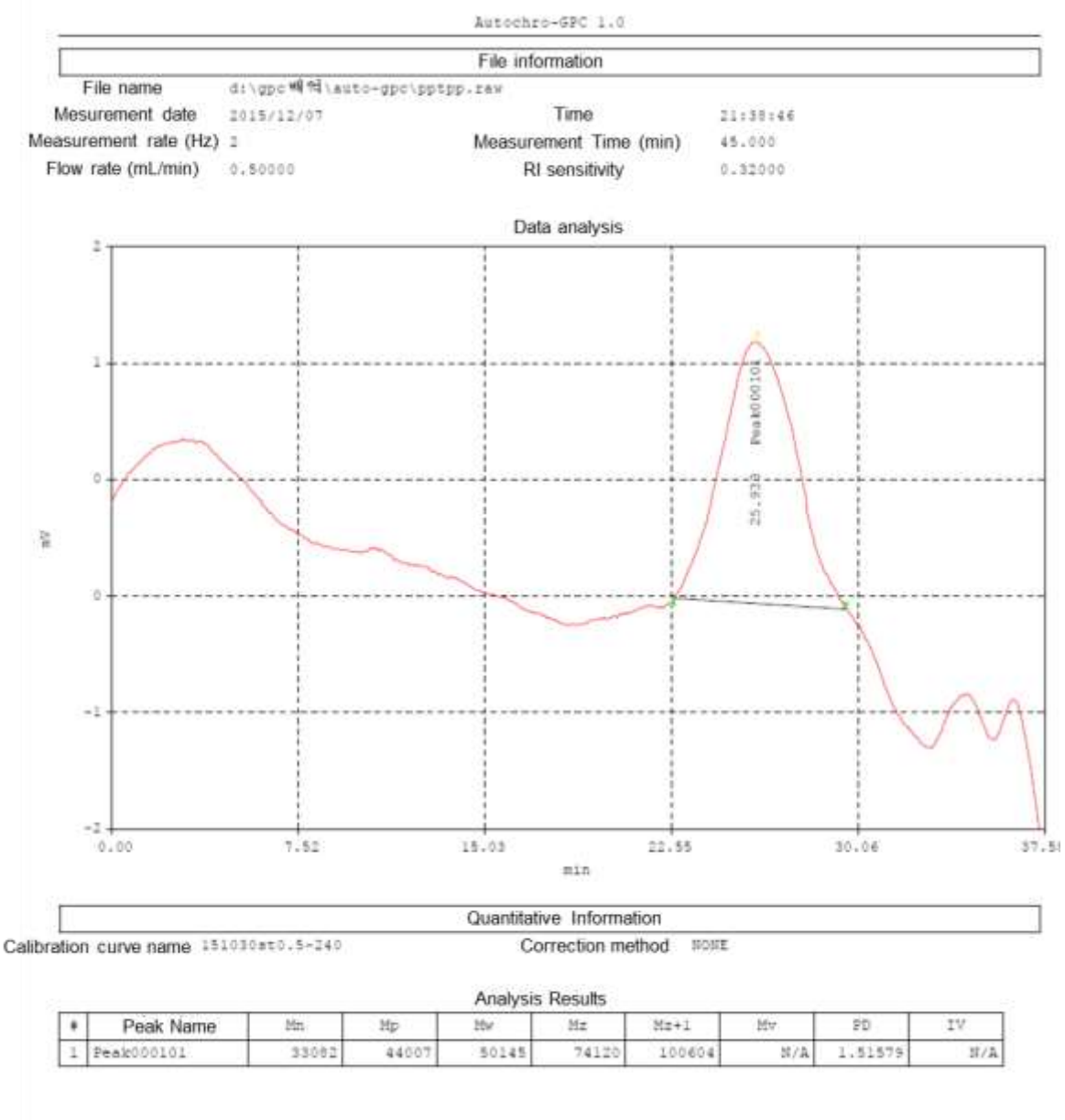


**Figure S2**. The gel permeation chromatography (GPC) data of synthesized **PP-TPD**

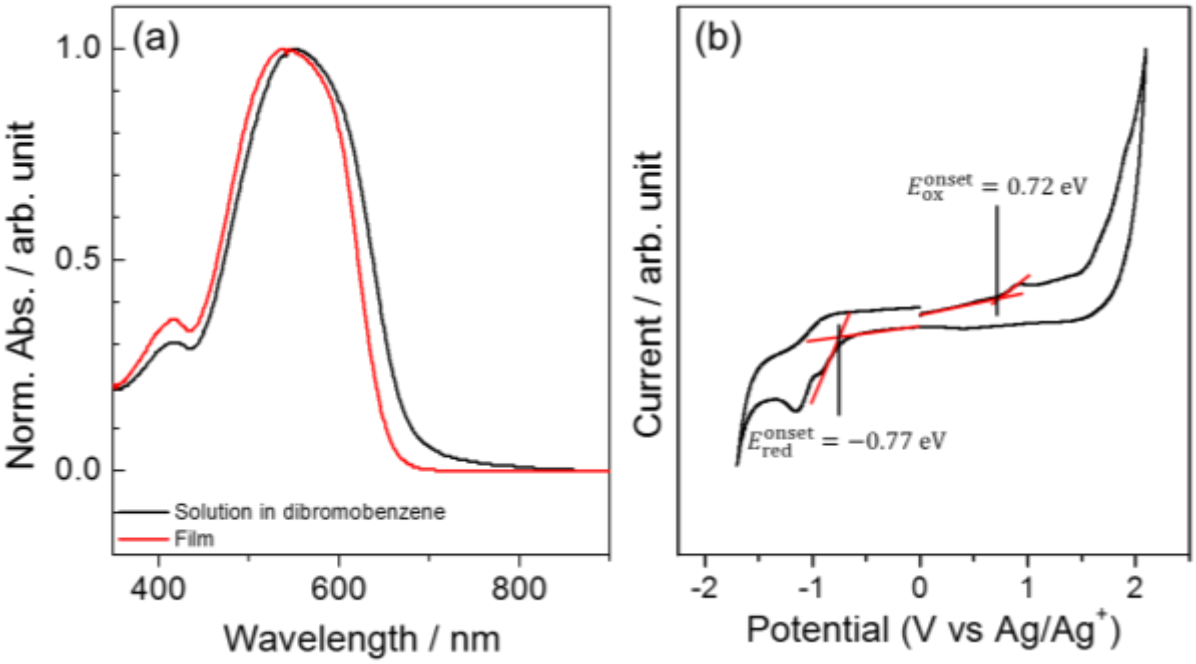


**Figure S3.** (a) Normalized UV-Vis. spectra and (b) cyclic voltammogram of **PP-TPD.**

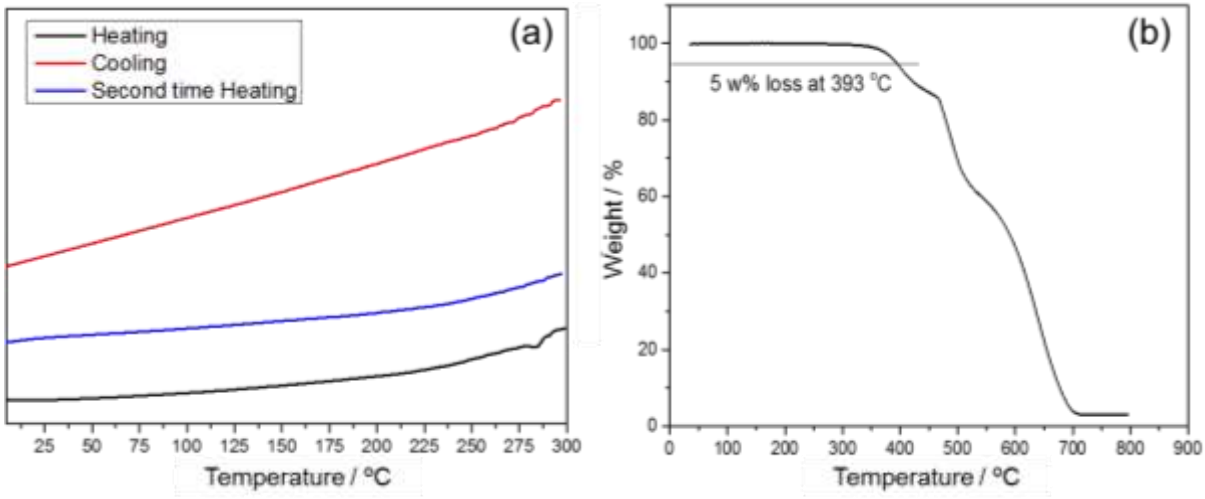


**Figure S4.** (a) The differential scanning calorimetry (DSC) and (b) thermogravimetric analysis (TGA) curves of synthesized **PP-TPD.**

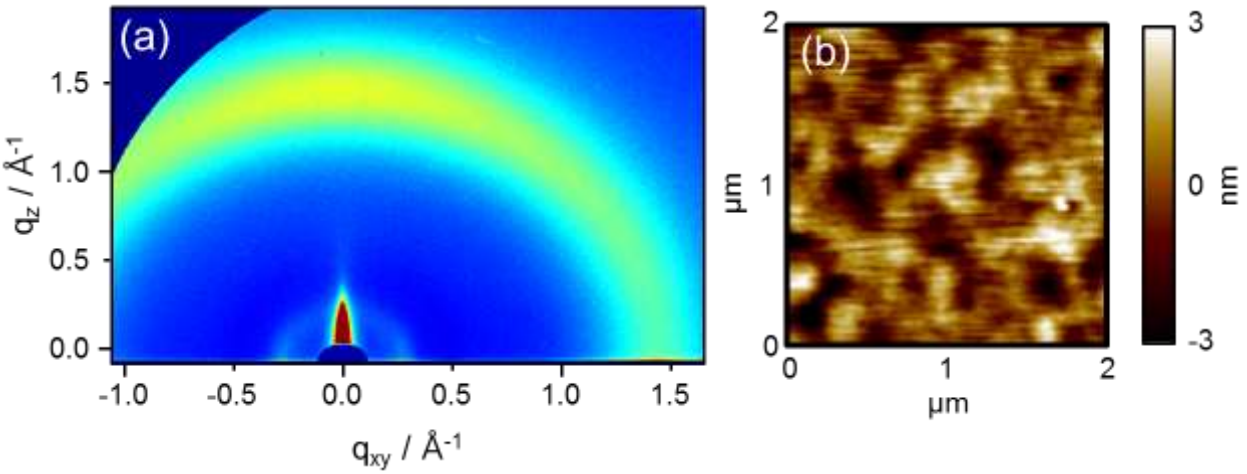


**Figure S5.** (a) The 2D-GIXD image and (b) the AFM topography image of **PP-TPD** film deposited on ZnO layer.