Supporting Information

o-Quinodimethane-methano[60]fullerene and Thieno-*o*-quinodimethane-methano[60]fullerene as Efficient Acceptor Materials for Polymer Solar Cells

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1. Material characterization

NMR spectra were measured on a Bruker AVANCE-400 spectrometer. Mass spectra were measured on an Autoflex Ⅲ (MALDI-TOF) spectrometer. UV-Vis absorption spectra were recorded on a SHIMADZU UV-1800 spectrophotometer. IR spectra were measured by a Nicolet Magna 750 FTIR Spectrometer. Cyclic voltammetry (CV) was performed using a SHANGHAI CHENHUA CHI620D voltammetric analyzer. The CV measurements were carried out in a cell under Ar gas, equipped with a glassy-carbon working electrode, a platinum wire counter electrode, and a Ag/Ag^+ reference electrode. Measurements were performed in ODCB/CH_3CN (9:1) solution containing tetrabutylammonium hexafluorophosphate ($TBAPF_6$, 0.1 M) as a supporting electrolyte with a scanning rate of 0.1 V/s. All potentials were corrected against Fc/Fc^+. Thermogravimetric analysis (TG) was carried out by a PerkinElmer Diamond TG/DTA thermal analyzer. Differential scanning calorimetry (DSC) was measured by a TA Instruments DSC Q100 thermal analyzer.

2. Device fabrication and characterization

Conventional cells

Patterned ITO glass with a sheet resistance of 15 Ω/sq was ultrasonically cleaned using detergent, distilled water, acetone, isopropanol sequentially, and then given UV-ozone treatment. 30 nm thick poly(3, 4-ethylenedioxythiophene)-polystyrene sulfonic acid (PEDOT:PSS, Clevios™ P VP Al 4083) layer was formed on ITO

substrates by spin coating an aqueous dispersion onto ITO glass. PEDOT:PSS coated substrate were dried at 140 ℃ for 10 min. P3HT/fullerene blend in ODCB (24 mg/mL) was spin-coated (900 rpm for 60 s) onto PEDOT:PSS layer. Then the films were annealed at 170 □ for 10 min. The thickness of the active layer (100-110 nm) is measured by KLA Tencor D-120 profilometer. Finally, Ca (~10 nm) and Al (~100 nm) were thermally evaporated under a shadow mask (pressure ca. 10^{-4} Pa).

Inverted cells

ZnO precursor was prepared according to literature.[1] ZnO precursor solution was spin-coated (4000 rpm for 30 s) onto ITO glass. The films were annealed at 200 □ for 30 min in air. ZnO film thickness is about 30 nm. P3HT/fullerene blend in ODCB (24 mg/mL) was spin-coated (900 rpm for 60 s) onto ZnO layer. The films were annealed at 170 □ for 10 min. The thickness for the active layer is 100~110 nm. MoO_3 (~7 nm) and Ag (~100 nm) was successively evaporated onto the active layer under a shadow mask (pressure ca. 10^{-4} Pa). Effective device area is 7.57 mm^2. *J-V* curves were measured on a computerized Keithley 2420 SourceMeter. Device characterization was done in air using a Xenon-lamp-based solar simulator (Newport, AM1.5G, 100 mW/cm^2). The external quantum efficiency (EQE) was measured by a QE-R3011 measurement system (Enli Technology).

Electron-only devices

Al (~80 nm) was firstly evaporated onto a glass substrate. P3HT:fullerene blend solutions were spin-coated onto Al. The films were annealed at 170 ºC for 10 min. Finally Ca (~5 nm) and Al (~100 nm) were evaporated under a shadow mask (pressure ca. 10^{-4} Pa). *J-V* curves were measured using a computerized Keithley 2420 SourceMeter in dark.

3. Synthetic procedures and spectra data for OQMF and TOQMF

99.9% pure C_{60} was purchased from YongXin Co. (China). Reagents and chemicals were purchased from Alfa-Aesar Co., TCI Co., or other commercial suppliers and used as received. Methano[60]fullerene ($C_{60}CH_2$) and 2,3-bis(chloromethyl)thiophene were prepared according to literature.[2-3]

Synthesis of OQMF

To a solution of methano[60]fullerene ($C_{60}CH_2$) (100 mg, 0.136 mmol) in *o*-dichlorobenzene (10 mL) was added 1,2-bis(bromomethyl)benzene (72 mg, 0.272 mmol), potassium iodide (181 mg, 1.09 mmol) and 18-crown-6 (288 mg, 1.09 mmol). The mixture was degassed with Ar three times and was put into a 110 □ oil bath with stirring for 3 h. Then the reaction mixture was cooled to room temperature and poured into methanol. The solid was collected by filtration. Silica gel column chromatography (eluent: CS_2/petroleum ether = 1:1) afforded OQMF (33 mg, yield: 29%). ^{1}H NMR (400 MHz, $CDCl_3/CS_2$): δ (ppm) 2.75-5.00 (m, 6H, C*H*$_2$), 7.25-7.80

(m, 4H, Ar). ^{13}C NMR (400 MHz, $CDCl_3/CS_2$): δ (ppm) 25.08, 25.37, 27.29, 29.22, 45.79, 46.04, 46.35, 46.69, 63.04, 65.85, 66.03, 67.04, 70.49, 71.04, 71.39, 71.57, 71.66, 71.74, 128.72, 128.79, 128.83, 137.02, 138.92, 139.10, 141.72, 142.02, 142.27, 142.40, 142.56, 142.73, 143.20, 143.57, 143.69, 144.19, 144.29, 144.67, 144.72, 144.89, 144.97, 145.19, 145.49, 145.86, 145.92, 145.99, 146.12, 146.41, 146.53, 146.81, 147.25, 147.42, 147.80, 147.94, 148.03, 148.22, 148.34, 148.92, 149.07, 149.47, 149.85, 150.05, 151.38, 153.22, 154.35. IR (powder, cm^{-1}): 3069, 3043, 3023, 2970, 2938, 2870, 2840, 2328, 1946, 1907, 1572, 1539, 1488, 1458, 1427, 1196, 1117, 765, 748, 693. MALDI-TOF-MS for $C_{69}H_{10}$ [M^+]: 838.3.

Synthesis of TOQMF

To a solution of methano[60]fullerene ($C_{60}CH_2$) (140 mg, 0.190 mmol) in *o*-dichlorobenzene (14 mL) was added 2,3-bis(chloromethyl)thiophene (70 mg, 0.381mmol), potassium iodide (315 mg, 1.90 mmol) and 18-crown-6 (250 mg, 0.952 mmol). The mixture was degassed with Ar three times and was put into a 110 □ oil bath with stirring for 30 min. Then the reaction mixture was cooled to room temperature and poured into methanol. The solid was collected by filtration. Silica gel column chromatography (eluent: CS_2/petroleum ether = 1:1) afforded TOQMF (27 mg, yield: 17%). ^{1}H NMR (400 MHz, $CDCl_3/CS_2$): δ (ppm) 3.10-4.90 (m, 6H, C*H*$_2$), 7.2-7.43 (m, 2H, Ar). ^{13}C NMR (400 MHz, ODCB-d_4/CS_2): δ (ppm) 23.03, 23.33, 24.86, 25.23, 38.82, 39.39, 39.66, 39.81, 40.00, 40.76, 64.80, 65.64, 68.48, 69.35, 69.56, 122.05, 122.21, 122.30, 126.47, 129.38, 131.01, 131.67, 134.72, 136.53,

137.47, 139.51, 140.68, 140.81, 141.12, 141.36, 142.29, 142.76, 143.07, 143.32, 143.47, 143.75, 143.97, 144.10, 144.37, 145.79, 146.04, 146.73, 147.02, 147.29, 149.15, 147.60, 149.15, 150.54, 152.09, 163.45. IR (powder, cm^{-1}): 3103, 3064, 2969, 2941, 2864, 2837, 2328, 2194, 2128, 2082, 1814, 1730, 1571, 1538, 1456, 1428, 1191, 1117, 1071, 1034, 843, 765, 747, 699, 685. MALDI-TOF-MS [M^+]: 844.2.

4. NMR spectra of OQMF and TOQMF

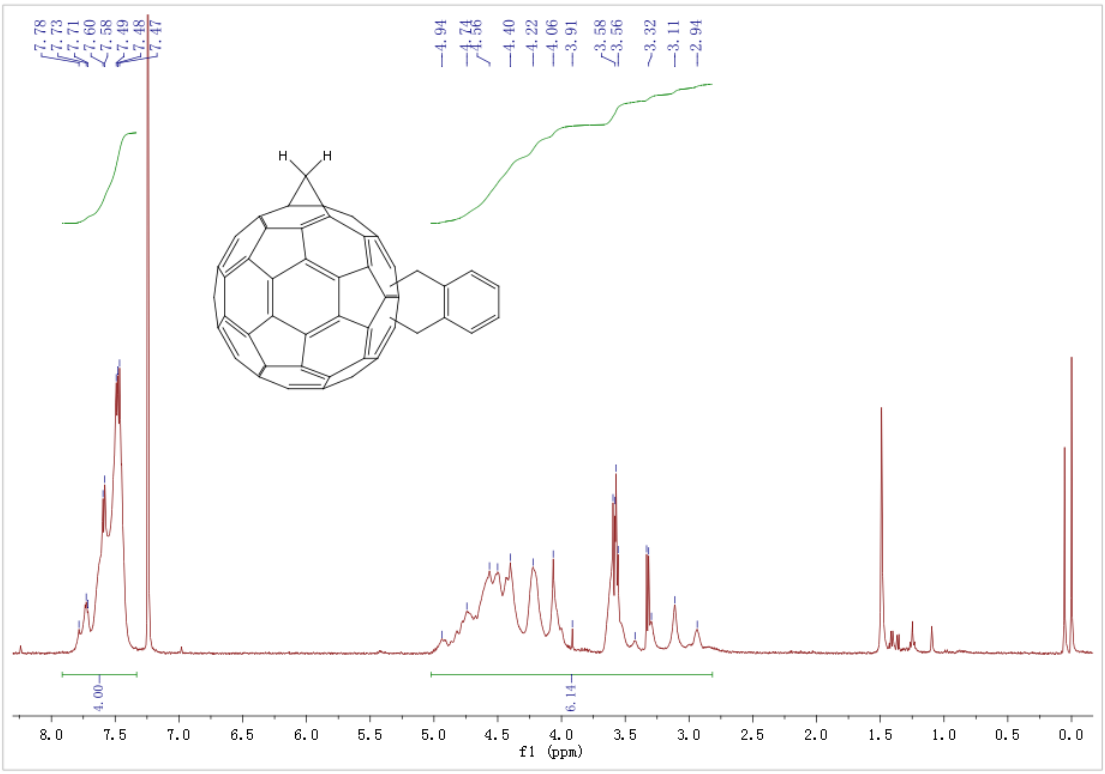

Figure S1. ^{1}H NMR of OQMF

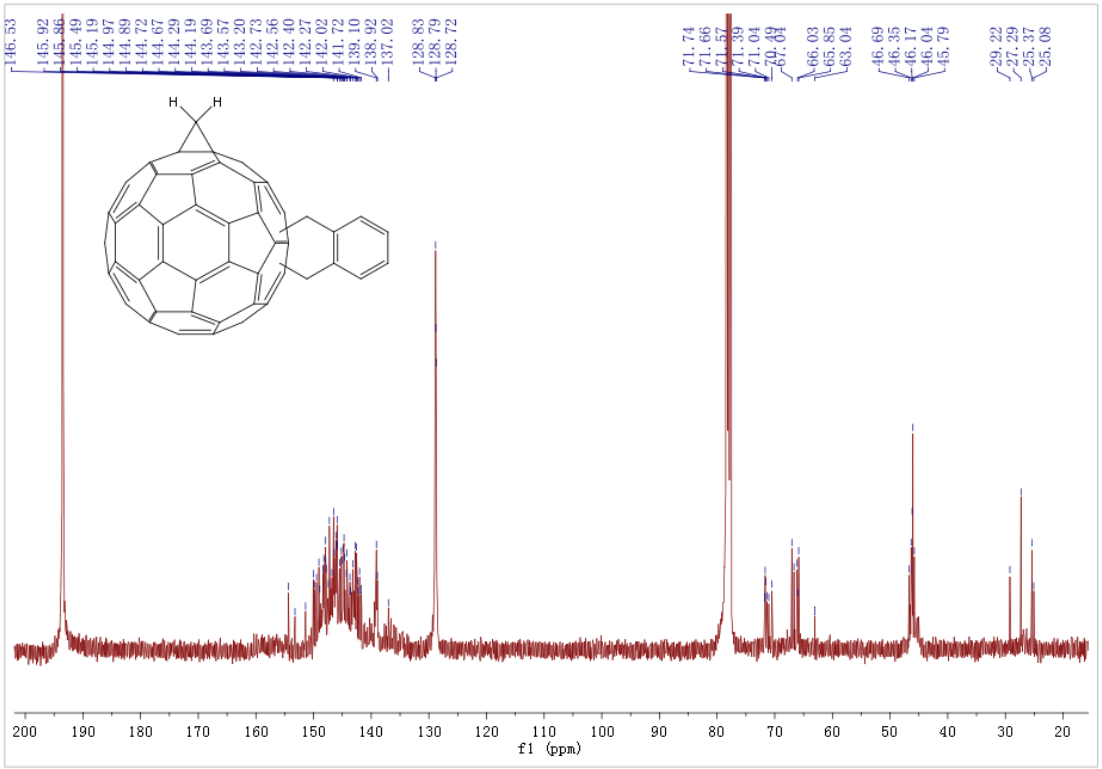

Figure S2. ^{13}C NMR of OQMF

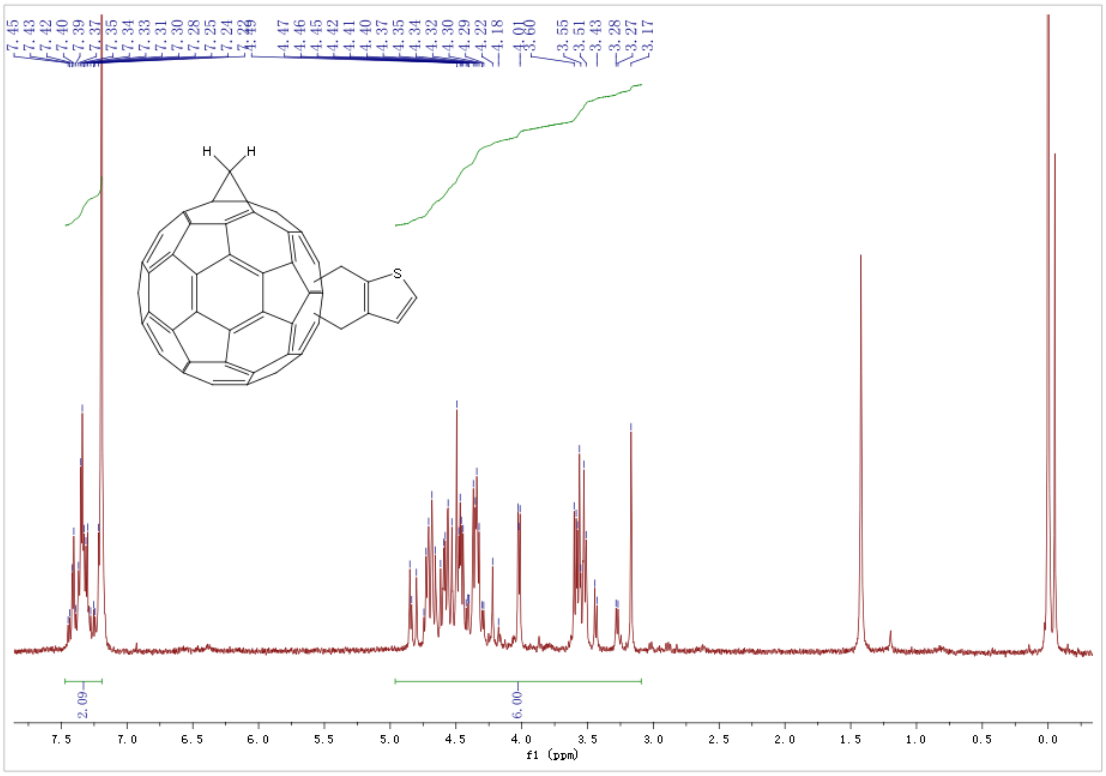

Figure S3. ^{1}H NMR of TOQMF

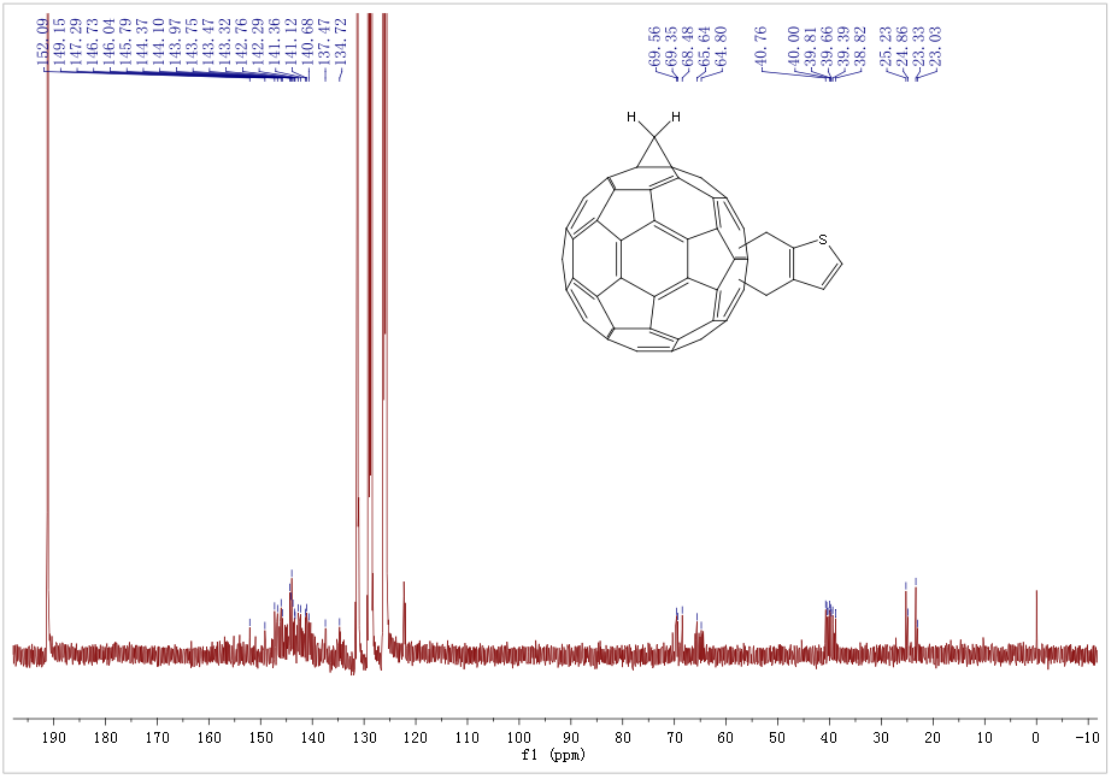

Figure S4. ^{13}C NMR of TOQMF

5. TGA measurements for OQMF and TOQMF

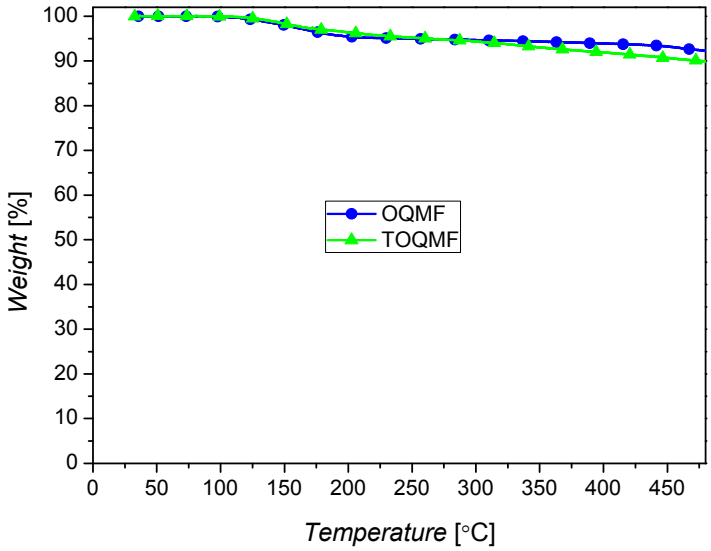

Figure S5. TGA curves of OQMF and TOQMF

6. DSC measurements for OQMF and TOQMF

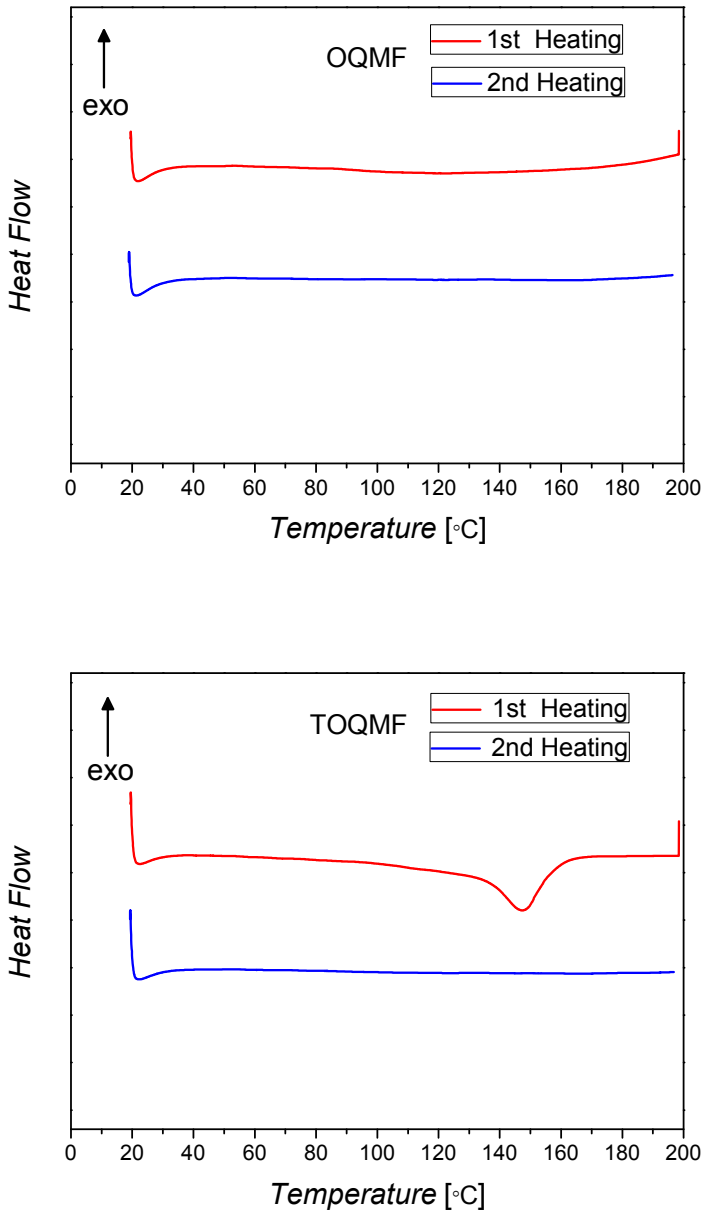

Figure S6. DSC curves of OQMF and TOQMF (scanning rate 10□/min).

7. Device optimization

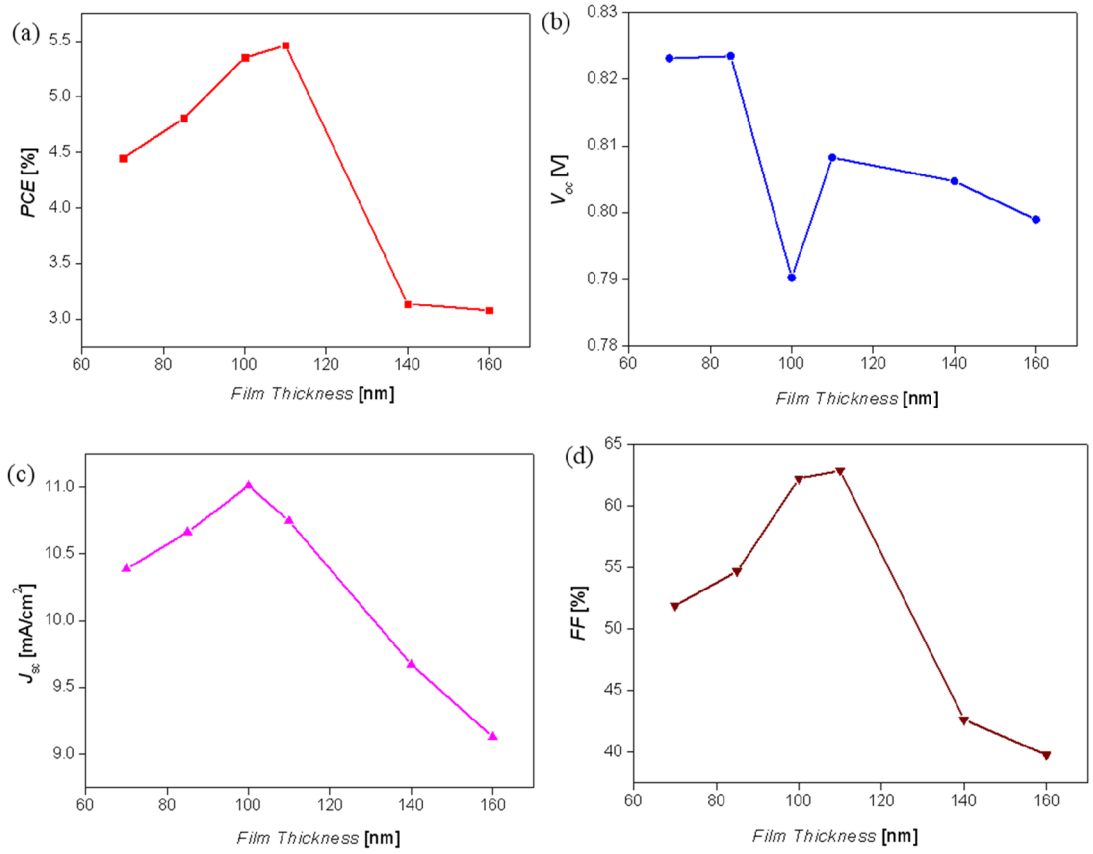

Figure S7. Effect of film thickness on performance of P3HT:OQMF solar cells: a) PCE; b) V_{oc}; c) J_{sc}; d) FF. Device fabrication parameters: annealing temperature: 170 □; D/A ratio: 1:0.6.

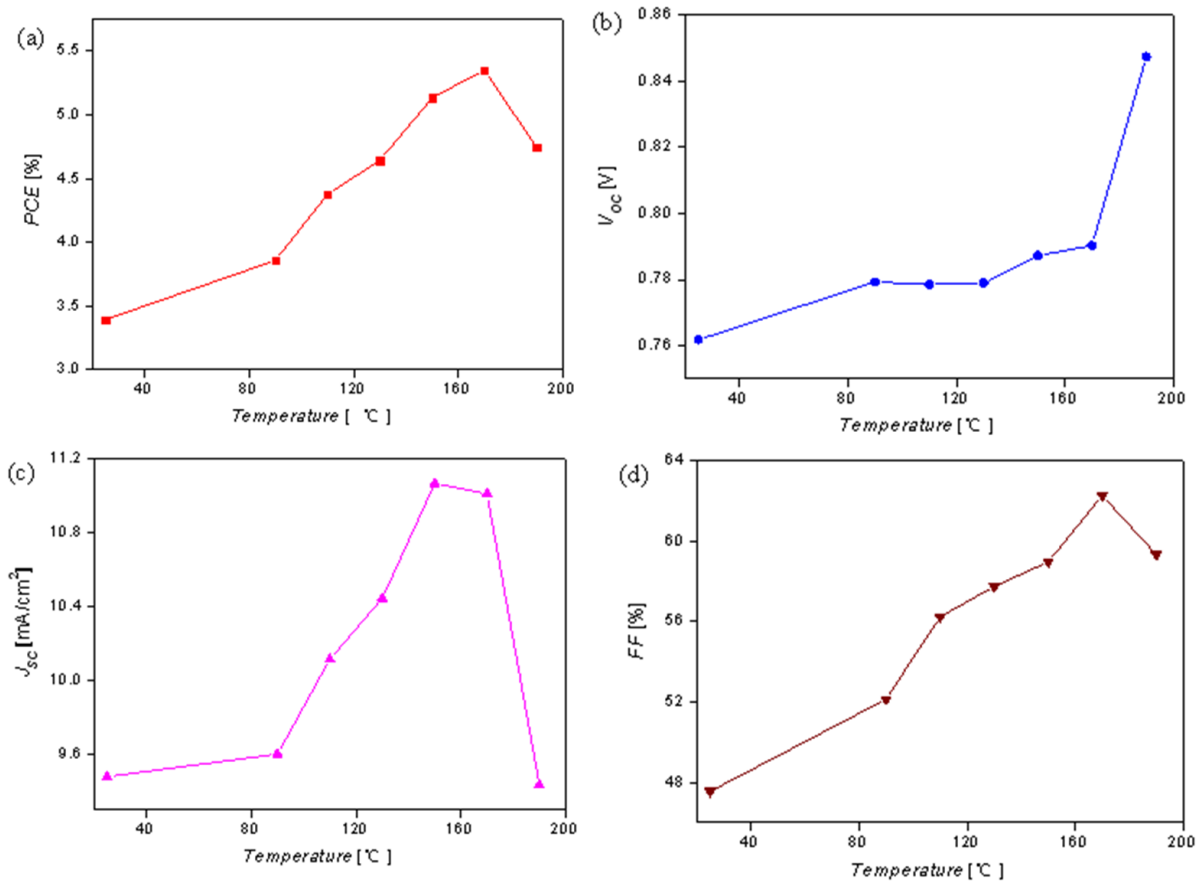

Figure S8. Effect of annealing temperature on performance of P3HT:OQMF solar cells: a) PCE; b) V_{oc}; c) J_{sc}; d) FF. Device fabrication parameters: blend concentration: 24 mg/mL in ODCB; D/A ratio: 1:0.6.

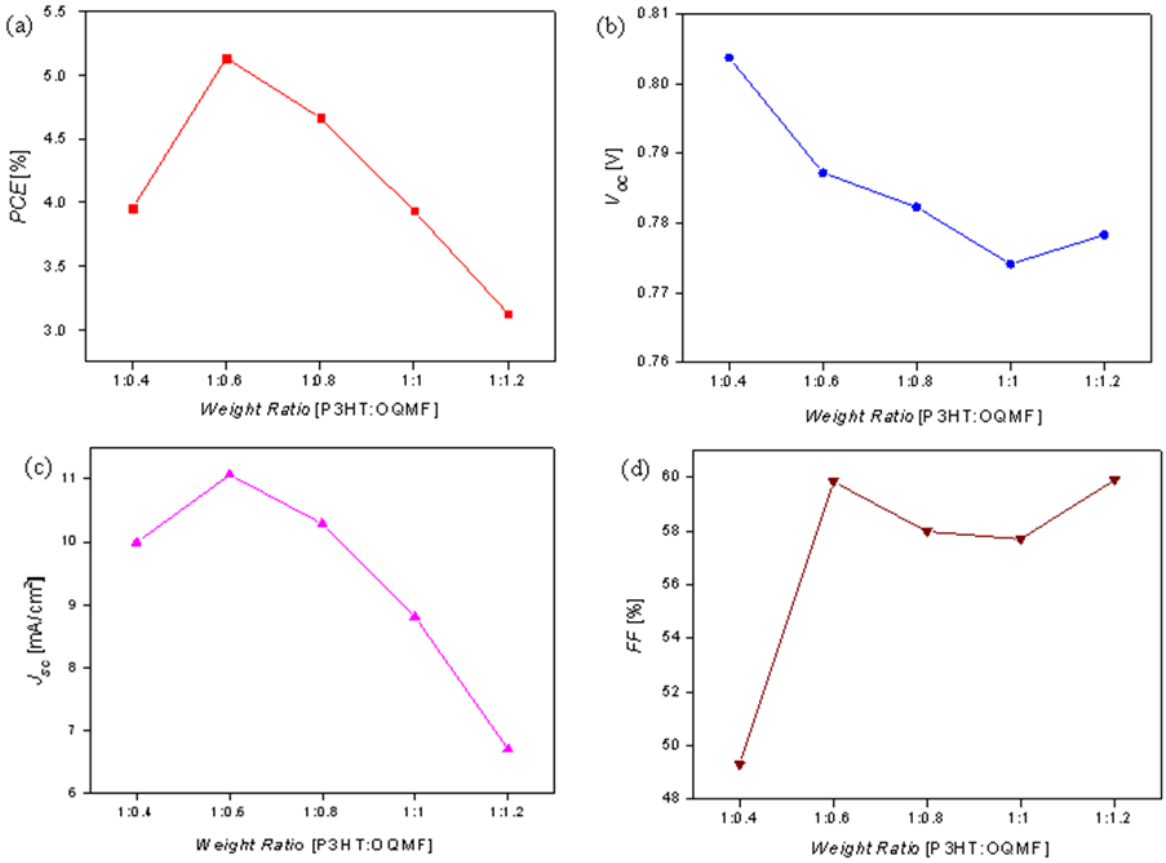

Figure S9. Effect of D/A ratio on performance of P3HT:OQMF solar cells: a) PCE; b) V_{oc}; c) J_{sc}; d) FF. Device fabrication parameters: blend concentration: 24 mg/mL in ODCB; annealing temperature: 170□.

8. Space charge limited current (SCLC) measurements for OQMF and TOQMF

Electron mobilities of P3HT:$PC_{61}BM$, P3HT:OQMF, and P3HT:TOQMF blend films (1:0.6, w/w) were measured by SCLC method. The cell structure is Al/active layer/Ca/Al.[4] The SCLC can be written as:

$$J = \frac{9}{8}\varepsilon_r \varepsilon_0 \mu_e \frac{V^2}{L^3}$$

where J is current density, ε_r is dielectric constant of the fullerene derivatives, ε_0 is the permittivity of vacuum, μ_e is electron mobility, L is film thickness, $V=V_{appl} - V_{bi}$, V_{appl} is the applied potential, and V_{bi} is the built-in potential resulting from workfunction difference between two electrodes (in this device, V_{bi}=0 V). Figure S10 shows J–V curves for P3HT:$PC_{61}BM$, P3HT:OQMF, and P3HT:TOQMF cells. Electron mobilities were calculated from the slopes of $J^{1/2}$-V lines.

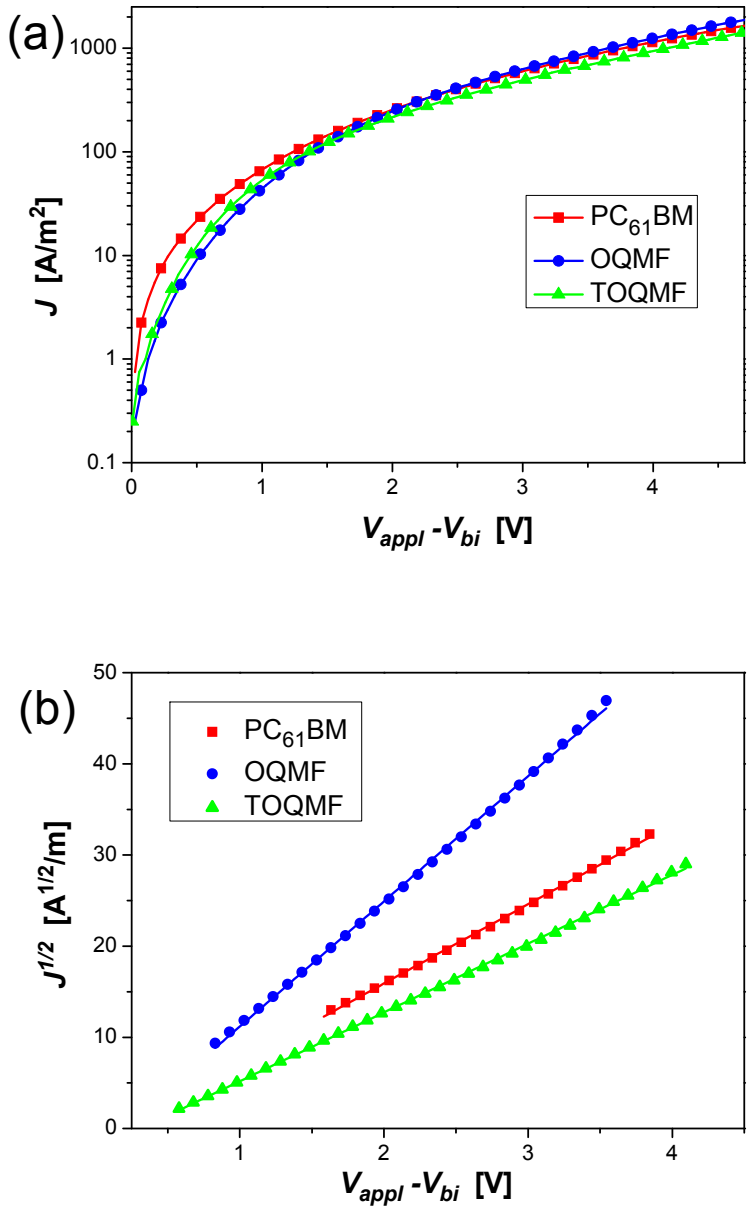

Figure S10. (a) *J-V* curves for the electron-only cells based on P3HT:$PC_{61}BM$ (141 nm), P3HT:OQMF (110 nm), and P3HT:TOQMF (155 nm) blend films in the dark; (b) the corresponding $J^{1/2}$-*V* curves.

[1] Y. Sun, J. H. Seo, C. J. Takacs, J. Seifter, A. J. Heeger, *Adv. Mater.*, 2011, **23**, 1679.

[2] (a) Y. Zhang, Y. Matsuo, C. Z. Li, H. Tanaka, E. Nakamura, *J. Am. Chem. Soc.*, 2011, **133**, 8086; (b) C. Z. Li, S. C. Chien, H. L. Yip, C. C. Chueh, F. C. Chen, Y. Matsuo, E. Nakamura, A. K. Y. Jen, *Chem. Commun.*, 2011, **47**, 10082.

[3] K. Hammer, T. Benneche, H. Hope, K. Undheim, *Acta Chem. Scand.*, 1997, **51**, 392.

[4] Z. He, C. Zhong, X. Huang, W. Y. Wong, H. Wu, L. Chen, S. Su, Y. Cao, *Adv. Mater.*, 2011, **23**, 4636.