Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.


## Supporting Information

# A highly efficient fullerene acceptor for polymer solar cells

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## 1. General characterization

All reagents were purchased from Aladdin Co., Acros Co. and other commercial suppliers. NMR spectra were measured on a Bruker Avance-400 spectrometer. High resolution ESI mass spectra were measured by a Bruker Apex IV FTMS spectrometer. Absorption spectra were recorded on a Shimadzu UV-1800 spectrophotometer. Cyclic voltammetry (CV) was conducted on a Shanghai Chenhua CHI620D voltammetric analyzer. All measurements were carried out in a one-compartment cell under argon, 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 (0.1 M) as a supporting electrolyte at 25 °C with a scan rate of 0.1 V/s. All potentials were corrected against $Fc/Fc^+$. AFM was performed on a Dimension 3100 microscope (Veeco) (tapping mode). X-ray diffraction (XRD) was performed using a 2 kW Rigaku D/max-2500 X-ray diffractometer in reflection mode (40 kV, 200 mA, Cu K$\alpha$ radiation).

## 2. Synthetic procedures and spectral data

**OQMF70 and bis-OQMF70.** To a solution of $C_{70}CH_2$ (650 mg, 0.76 mmol) in ODCB (130 mL) was added 1,4-dihydrobenzo[d][1,2]oxathiine 3-oxide (325 mg, 1.93 mmol). The mixture was stirred at 100 °C for 4 h. Then the reaction solution was cooled to room temperature and poured into methanol. The crude product was collected by filtration and purified through a silica gel column with $CS_2$:hexane (1:1) as the eluent. The first band was the unreacted $C_{70}CH_2$. The second band was collected to give OQMF70 (380 mg, yield: 52%). The third band was collected to give bis-OQMF70 (276 mg, yield: 34%).

**OQMF70.** $^1H$ NMR (400 MHz, $CDCl_3$): δ (ppm) 7.10-7.55 (m, 4H, Ar), 2.42-4.14 (m, 6H, C$H_2$). ESI-HRMS (+): $C_{79}H_{10}$ [$M^+$] calc. 958.0783, found 958.0754.

**bis-OQMF70.** $^{1}$H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.21-7.65 (m, 8H, Ar), 2.15-4.12 (m, 10H, C$H_2$). ESI-HRMS (+): $C_{87}H_{18}$ [$M^+$] calc. 1062.1409, found 1062.1435.

## 3. Device fabrication and measurements

### Conventional solar cells

Patterned ITO glass with a sheet resistance of 15 Ω $sq^{-1}$ was cleaned by ultrasonics in detergent, deionized water, acetone, isopropanol sequentially and then treated with UV-ozone for 10 min. A 30 nm thick poly(3,4-ethylenedioxythiophene)-polystyrene sulfonic acid (PEDOT:PSS, Clevios™ P VP AI 4083) layer was formed on ITO substrates by spin coating an aqueous dispersion onto ITO glass (4000 rpm for 30 s). PEDOT:PSS coated substrates were dried at 150 °C for 10 min, and then the substrates were transferred into a $N_2$-filled glove box. A P3HT:fullerene (w/w, 1:0.6) blend in ODCB (24 mg/mL) was spin-coated onto PEDOT:PSS layer (1200 rpm for 60 s). Then the films were annealed at 150 °C for 10 min. The thicknesses of the active layers (~100 nm) were measured by a 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). The effective area for the device is 4 $mm^2$. *J-V* curves were measured using a computerized Keithley 2420 SourceMeter. Device characterization was done in air using a Xenon-lamp-based solar simulator (Newport, 91159A, AM 1.5G, 100 $mW/cm^2$). Solar simulator illumination intensity was determined using a monocrystalline silicon cell (Oriel 91150, 2 × 2 cm) calibrated by NREL. The external quantum efficiency (EQE) was measured using a QE-R3011 measurement system (Enli Technology, Inc.).

### Inverted solar cells

ZnO precursor was prepared according to literature.[1] ZnO precursor solution was spin-coated onto ITO glass (4000 rpm for 30 s). The films were annealed at 200 °C for 30 min in air. The thickness of ZnO film is about 30 nm. A P3HT:fullerene (w/w, 1:0.6) blend in ODCB (24 mg/mL) was spin-coated onto ZnO layer (1200 rpm for 60

s). Then the films were annealed at 150 °C for 10 min. $MoO_3$ (~6 nm) and Ag (~80 nm) was successively evaporated onto the active layer under a shadow mask (pressure ca. $10^{-4}$ Pa).

**Electron-only devices**

The structure of electron-only devices is ITO/Al/active layer/Ca/Al. Al (~100 nm) was first evaporated onto glass substrates. A P3HT:fullerene (w/w, 1:0.6) blend in ODCB (24 mg/mL) was spin-coated onto Al (1200 rpm for 60 s). Then the films were annealed at 150 °C for 10 min. Ca (~10 nm) and Al (~100 nm) were thermally evaporated under a shadow mask (pressure ca. $10^{-4}$ Pa). *J-V* curves were measured using a computerized Keithley 2420 SourceMeter.

**4. NMR spectra**

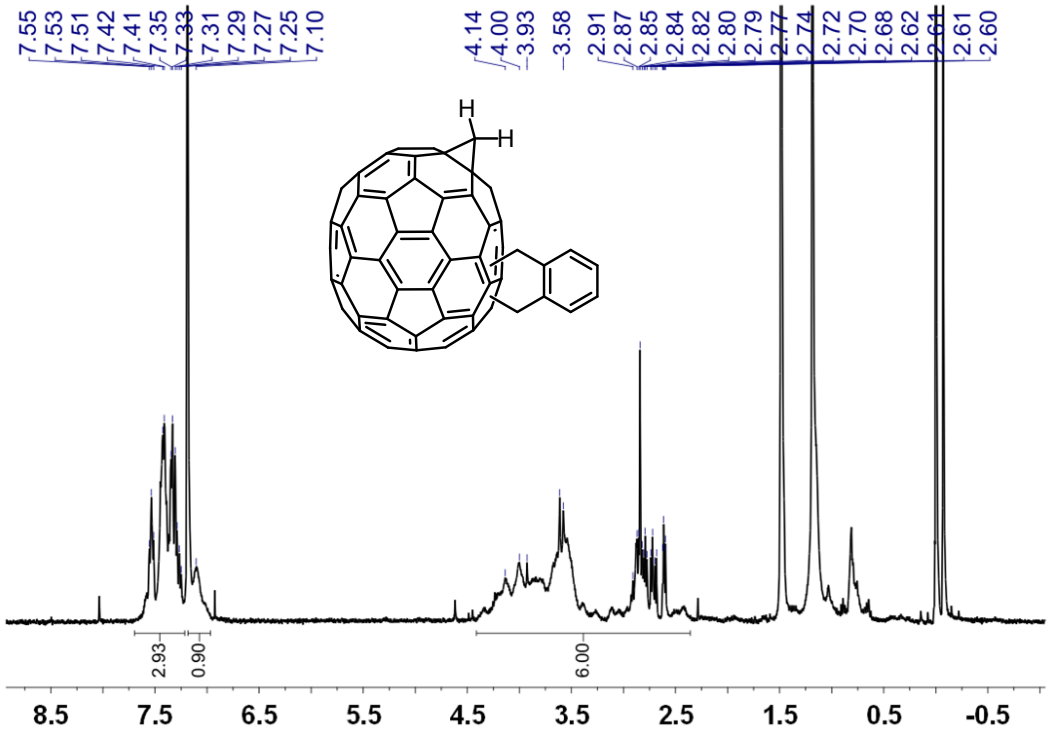


**Figure S1.** $^1$H NMR spectrum for OQMF70 in $CDCl_3$.

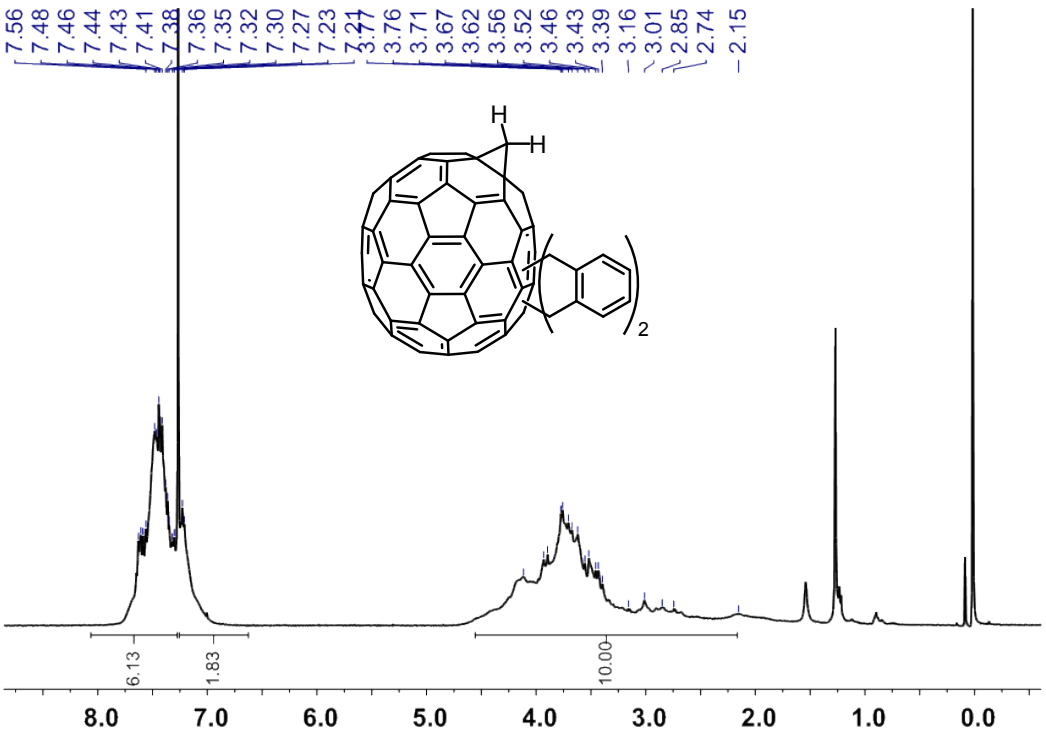


**Figure S2.** $^{1}$H NMR spectrum for bis-OQMF70 in $CDCl_3$.

## 5. *J-V* curves

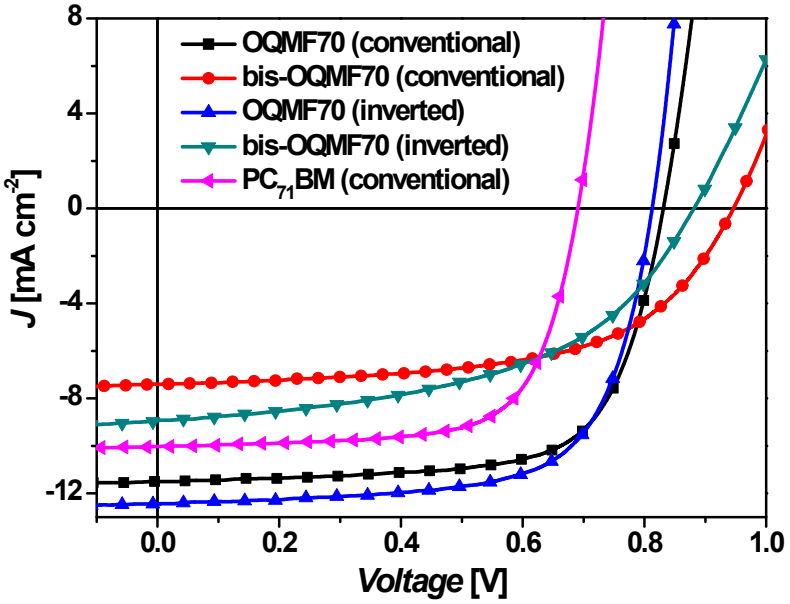


**Figure S3.** *J–V* curves for OQMF70:P3HT and bis-OQMF70:P3HT cells ($PC_{71}BM$:P3HT cells shown as reference).

## 6. Space charge limited current (SCLC) measurements

Charge carrier mobility was measured by SCLC method. The mobility was determined by fitting the dark current to the model of a single carrier SCLC, which is described by:

$$J = \frac{9}{8}\varepsilon_0\varepsilon_r\mu\frac{V^2}{d^3}$$

where $J$ is the current density, $\mu$ is the zero-field mobility of electrons, $\varepsilon_0$ is the permittivity of the vacuum, $\varepsilon_r$ is the relative permittivity of the material, $d$ is the thickness of the blend film, and $V$ is the effective voltage, $V = V_{appl} - V_{bi}$, where $V_{appl}$ is the applied voltage, and $V_{bi}$ is the built-in potential determined by electrode workfunction difference. Figure S4 (a) shows $J$-$V$ curves for the electron-only devices. The mobility was calculated from the slope of $J^{1/2}$-$V$ curves.

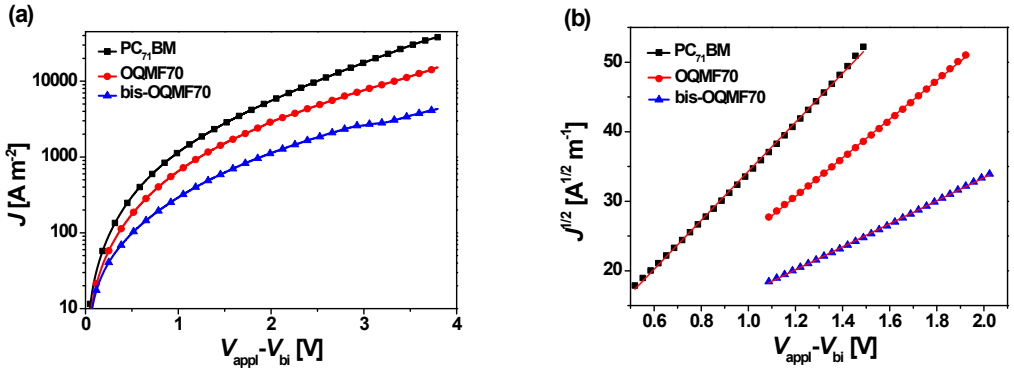


**Figure S4.** $J$-$V$ curves (a) and the corresponding $J^{1/2}$-$V$ curves (b) for electron-only devices (in dark). The thicknesses for $PC_{71}BM$:P3HT, OQMF70:P3HT and bis-OQMF70:P3HT blend films are 94 nm, 100 nm and 97 nm, respectively.

## 7. External quantum efficiency (EQE) spectra

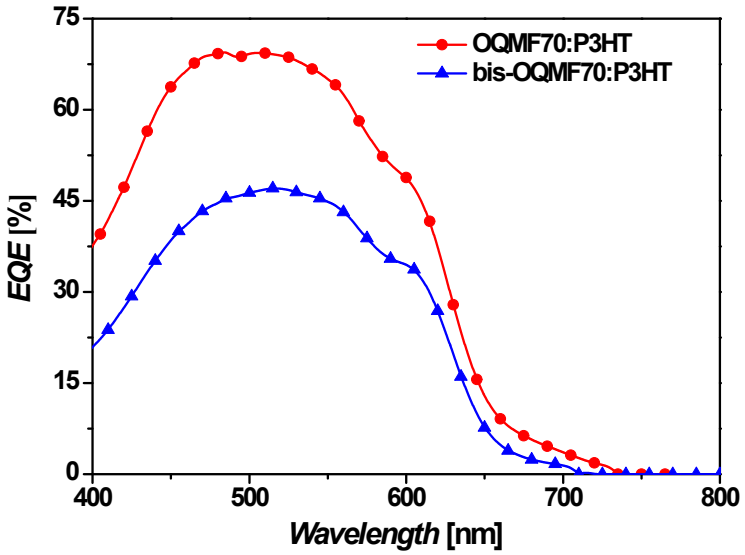


**Figure S5.** EQE spectra for OQMF70:P3HT and bis-OQMF70:P3HT solar cells.

Reference

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