Supporting Information

An azafullerene acceptor for organic solar cells

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1. General characterization

NMR spectra were measured on a Bruker Avance-400 spectrometer or a Bruker Avance-500 spectrometer. High resolution ESI mass spectra were measured by using 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/CH₃CN (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).

2. Synthetic procedures and spectral data

99.9% pure C_{60} was purchased from YongXin Co. (China). Reagents and chemicals were purchased from J&K Co., Alfa-Aesar Co., Aladdin Co., or other commercial suppliers and used as received. Fullerene ketolactam **1** and 1,4-dihydrobenzo[d][1,2]oxathiine 3-oxide were prepared according to literature.^{1,2}

ThC₅₉N. To a solution of 1 (100 mg, 0.12 mmol) and thiophene (2.97 g, 35.4 mmol) in 15 mL ODCB was added *p*-TsOH (110 mg, 0.64 mmol). The mixture was stirred in a preheated oil bath at 150 °C with a slow steady stream of air over the solution. The reaction was monitored by TLC. After 15 min the mixture was cooled to room temperature, and purified by silica gel column chromatography (eluent: CS₂). The first green band was collected to give ThC₅₉N (21 mg, yield: 22%). ¹H NMR (400 MHz, CDCl₃/CS₂): δ (ppm) 8.31-8.32 (m, 1H, Ar), 7.79-7.80 (m, 1H, Ar), 7.49-7.51 (m, 1H, Ar). ¹³C NMR (125 MHz, CDCl₃/CS₂): δ (ppm) 153.49, 147.76, 147.49, 147.29, 147.20, 147.08, 146.39, 146.32, 146.17, 145.97, 145.58, 145.52, 145.43,

145.07, 144.80, 144.71, 144.36, 144.07, 143.71, 142.90, 142.54, 141.87, 141.57, 141.26, 141.17, 140.86, 140.69, 139.72, 137.15, 132.51, 128.02, 127.34, 126.50, 123.66, 99.36. ESI-HRMS (+): $C_{63}H_4SN [M + H^+]$ calc. 806.0064, found 806.0076.

OQThC₅₉N. To a solution of ThC₅₉N (90 mg, 0.11 mmol) in ODCB (20 mL) was added 1,4-dihydrobenzo[d][1,2]oxathiine 3-oxide (23 mg, 0.137 mmol). The mixture was degassed with argon three times and stirred at 80 °C for 10 h. Then, the reaction mixture was cooled to room temperature and poured into methanol. The crude product was collected by filtration and purified by silica gel column chromatography (eluent: CS₂/petroleum ether = 1:1). The second band was collected to give OQThC₅₉N (36 mg, yield: 36%). ¹H NMR (400 MHz, CDCl₃/CS₂): δ (ppm) 7.34-8.46 (m, 7H, Ar), 3.73-4.98 (m, 4H, CH₂). ¹³C NMR (100 MHz, CDCl₃/CS₂): δ (ppm) 162.16, 159.31, 158.64, 158.40, 157.75, 150.58, 150.36, 149.82, 148.92, 148.11, 147.78, 146.73, 145.85, 145.41, 145.09, 144.80, 144.21, 143.48, 142.83, 142.16, 141.40, 141.12, 140.25, 139.56, 138.87, 138.04, 137.95, 137.80, 128.23, 128.17, 128.07, 127.99, 127.87, 127.77, 127.36, 127.26, 127.01, 126.53, 126.47, 126.19, 65.70, 65.28, 65.12, 64.95, 64.79, 64.72, 64.40, 45.38, 45.34, 45.08, 44.39, 44.25. ESI-HRMS (+): C₇₁H₁₂SN [M + H⁺] calc. 910.0691, found 910.0704.

3. NMR spectra



Figure S1. ¹H NMR spectrum for ThC₅₉N in CDCl₃/CS₂.



Figure S2. ¹³C NMR spectrum for ThC₅₉N in CDCl₃/CS₂.



Figure S3. ¹H NMR spectrum for OQThC₅₉N in CDCl₃/CS₂.



Figure S4. ¹³C NMR spectrum for OQThC₅₉N in CDCl₃/CS₂.

4. 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 sulfonate (PEDOT:PSS, CleviosTM 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 N₂-filled glovebox. 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 110 °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 devices is 4 mm². 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/cm²). 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.).

Electron-only devices

The structure of electron-only devices is 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 110 °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 in dark using a computerized Keithley 2420 SourceMeter.

5. Device optimization

| D:A | V _{oc} | $J_{ m sc}$ | FF | PCE^{b} |
|-------|-----------------|----------------|-------|-----------|
| (w/w) | [V] | $[mA cm^{-2}]$ | [%] | [%] |
| 1:0.4 | 0.78 | 6.84 | 61.46 | 3.28 |
| 1:0.6 | 0.78 | 7.57 | 69.20 | 4.09 |
| 1:0.8 | 0.76 | 6.81 | 70.05 | 3.63 |

Table S1. D/A ratio optimization.^a

^{*a*}Annealing temperature: 110 °C; film thickness: 100 nm. ^{*b*}The highest PCEs.

| Table S2. Thickness optimization | . <i>a</i> |
|--|------------|
|--|------------|

| Thickness | V _{oc} | $J_{ m sc}$ | FF | PCE^{b} |
|-----------|-----------------|----------------|-------|-----------|
| [nm] | [V] | $[mA cm^{-2}]$ | [%] | [%] |
| 80 | 0.77 | 7.72 | 63.42 | 3.77 |
| 90 | 0.76 | 7.72 | 65.67 | 3.85 |
| 100 | 0.76 | 7.98 | 66.57 | 4.04 |
| 110 | 0.76 | 7.52 | 65.32 | 3.73 |

^{*a*}Annealing temperature: 110 °C; D/A ratio: 1:0.6. ^{*b*}The highest PCEs.

 Table S3. Annealing temperature optimization. a

| Annealing | $V_{ m oc}$ | $J_{ m sc}$ | FF | PCE^{b} |
|------------------|-------------|----------------|-------|-----------|
| temperature (°C) | [V] | $[mA cm^{-2}]$ | [%] | [%] |
| 0 °C | 0.77 | 6.15 | 53.48 | 2.53 |
| 70 °C | 0.78 | 6.69 | 65.04 | 3.39 |
| 90 °C | 0.77 | 6.96 | 68.69 | 3.68 |
| 110 °C | 0.78 | 7.57 | 69.20 | 4.09 |
| 130 °C | 0.76 | 6.82 | 68.71 | 3.56 |

^{*a*} Film thickness: 100 nm; D/A ratio: 1:0.6. ^{*b*} The highest PCEs.

6. External quantum efficiency (EQE) spectra



Figure S5. EQE spectra for OQThC₅₉N:P3HT and PC₆₁BM:P3HT cells.

7. Film absorption spectra



Figure S6. Absorption spectra for OQThC $_{59}$ N:P3HT and PC $_{61}$ BM:P3HT blend films.

References

1 J. C. Hummelen, B. Knight, J. Pavlovich, R. Gonzalez, F. Wudl, Science, 1995, 269, 1554.

2 X. Meng, W. Zhang, Z. Tan, C. Du, C. Li, Z. Bo, Y. Li, X. Yang, M. Zhen, F. Jiang, J. Zheng, T. Wang, L. Jiang, C. Shu, C. Wang, *Chem. Commun.*, 2012, **48**, 425.