Supporting Information

A pyridine-functionalized pyrazolinofullerene used as a buffer layer in polymer solar cells

Pingao Yang,‡ [a,b] Shan Chen,‡ [b] Yu Liu,* [a] Zuo Xiao* [b] and Liming Ding* [b]

[a] Key Lab of Environment-Friendly Chemistry and Applications of the Ministry of Education, College of Chemistry, Xiangtan University, Xiangtan 411105, China; E-mail: liuyu03b@126.com
[b] National Center for Nanoscience and Technology, Beijing 100190, China;
E-mail: OPV.CHINA@yahoo.com, xiaoz@nanoctr.cn
‡ These authors contributed equally to this work.

Content

1. General characterization

^{1}H NMR spectra were measured on a Bruker AVANCE-400 spectrometer. ^{13}C NMR spectrum was measured on a Bruker AVANCE III 500 spectrometer. Mass spectrum was measured on a Bruker APEX IV instrument. Single-crystal XRD was performed on a Rigaku MM007HF diffractometer with Saturn724+ CCD detector. UV-Vis absorption spectrum was recorded on a SHIMADZU UV-1800 spectrophotometer. Cyclic voltammetry (CV) was performed using a SHANGHAI CHENHUA CHI620D voltammetric analyzer. The CV measurement was carried out in a cell under Ar, equipped with a glassy-carbon working electrode, a platinum wire counter electrode, and an Ag/Ag^+ reference electrode. Measurement was 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 (TGA) was carried out on a Perkin-Elmer Diamond TG/DTA thermal analyzer.

2. Solar cell fabrication and measurements

A patterned ITO glass with a sheet resistance of 8-10 Ω sq^{-1} was ultrasonically cleaned using detergent, distilled water, acetone, and isopropanol sequentially and then given UV-ozone treatment. ZnO precursor was prepared according to a literature.[1] ZnO precursor solution was spin-coated (4000 rpm for 30 s) onto ITO-glass substrate. The film was annealed at 200 °C for 30 min in air. ZnO film thickness is about 30 nm, determined by a KLA Tencor D-120 profilometer. ZnO substrate was immersed in an ODCB solution of **1** (0.1 mg/mL) for 2 h. Then, the substrates were taken out from the solution and heated at 150 °C for 10 min in N_2 to form the self-assembly of **1** on ZnO surface. Finally, the substrates were rinsed with ODCB to remove those physically adsorbed fullerene molecules. A P3HT/$PC_{61}BM$ blend in ODCB (1:1 w/w, 24 mg/mL) was spin-coated (1200 rpm for 60 s) onto ZnO and the film was annealed at 130 °C for 10 min. MoO_3 (~7 nm) and Ag (~100 nm) were thermally evaporated under a shadow mask (pressure: ca. 10^{-4} Pa). The effective area for the devices is 4 mm^2. *J-V* curves were measured on a computerized Keithley 2420 SourceMeter. Device characterization was done in air under 100 mW/cm^2 irradiation (calibrated with a NREL certified standard silicon cell (4 cm^2)) from a xenon-lamp-based solar simulator (Newport Oriel Solar Simulator, Model 91159A). For bilayer heterojunction devices, the fabrication process is similar except for P3HT coating. A P3HT solution (12 mg/mL in ODCB) was spin-coated (1200 rpm for 60 s) onto ZnO and the film was annealed at 130 °C for 10 min.

3. Synthetic procedures and spectra data

C_{60} (99.9%) was purchased from YongXin Co. (China). Reagent and chemicals were purchased from Alfa-Aesar Co., TCI Co., or other commercial suppliers and used as received.

3,6-Di(2-pyridyl)-1,2,4,5-tetrazine. Hydrazine monohydrate (1.16 g, 43.2 mmol) was added dropwise to a solution of picolinonitrile (3.00 g, 28.8 mmol) and sulfur (0.64 g, 20.1 mmol) in ethanol (8 mL). The reaction mixture was stirred at room temperature for 10 minutes and then heated to reflux for 2 h. The mixture was cooled and filtered. The solid was dried in vacuum to afford 3.12 g crude 1,4-dihydro-3,6-di(pyridin-2-yl)-1,2,4,5-tetrazine. A portion of this crude material (3.00 g, 12.6 mmol) was dissolved in CH_2Cl_2 (10 mL), and a solution of sodium nitrite (2.60 g, 37.7 mmol) in water was added to the mixture. The mixture was cooled to 0 °C and acetic acid (1.81 g, 30.2 mmol) was added dropwise into it. The reaction mixture was stirred at room temperature for 5 h. CH_2Cl_2 was removed under reduced pressure and the precipitate was filtered, washed with cold water and dried under vacuum. The crude product was purified by silica gel column chromatography with CH_2Cl_2:ethyl acetate (7:1) as the eluent to give 3,6-di(2-pyridyl)-1,2,4,5-tetrazine as a red solid (0.94 g, yield: 29%). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 9.00 (dd, J = 3.9, 0.8 Hz, 2H), 8.77 (dd, J = 7.9, 0.7 Hz, 2H), 8.03 (m, 2H), 7.60 (m, 2H).

Compound 1. Ten drops of water were added into a solution of C_{60} (300 mg, 0.416 mmol) and 3,6-di(2-pyridyl)-1,2,4,5-tetrazine (103 mg, 0.436 mmol) in 200 mL o-dichlorobenzene under N_2. The mixture was irradiated with a sunlamp and was heated to reflux for 2.5 h. The mixture was cooled down and directly submitted to silica gel column chromatography. Firstly, CS_2 was used as the eluent to remove the unreacted C_{60}. Then, the eluent was changed to CS_2:ethyl acetate (7:1) to give compound **1** as a brown solid (165 mg, yield: 42%). ^{1}H NMR (400 MHz, $CDCl_3/CS_2$): δ (ppm) 8.92 (d, J = 4.5 Hz, 1H), 8.78 (d, J = 4.4 Hz, 1H), 8.19 (d, J = 8.0 Hz, 1H), 8.15-7.97 (m, 2H), 7.89-7.76 (m, 1H), 7.71-7.62 (m, 1H), 7.41 (dd, J = 6.7, 4.8 Hz, 1H), 6.70-6.59 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3/CS_2$): δ (ppm) 165.43, 154.03, 153.57, 151.54, 150.57, 150.25, 149.31, 148.93, 148.80, 148.46, 148.13, 147.49, 147.41, 147.17, 147.12, 146.78, 146.38, 145.87, 145.76, 145.58, 145.25, 144.99, 144.95, 144.62, 144.54, 144.46, 144.37, 144.27, 144.13, 143.90, 143.62, 143.33, 143.21, 142.94, 142.61, 142.55, 142.17, 142.01, 141.80, 141.48, 141.04, 139.84, 139.01, 138.69, 137.48, 137.37, 136.50, 125.21, 124.75, 124.30, 123.16, 80.18, 70.81, 55.76, 54.25. ESI-HRMS: $C_{72}H_{11}ON_4$ ($M + H^+$) calcd 947.0933, found 947.0939.

4. NMR spectra

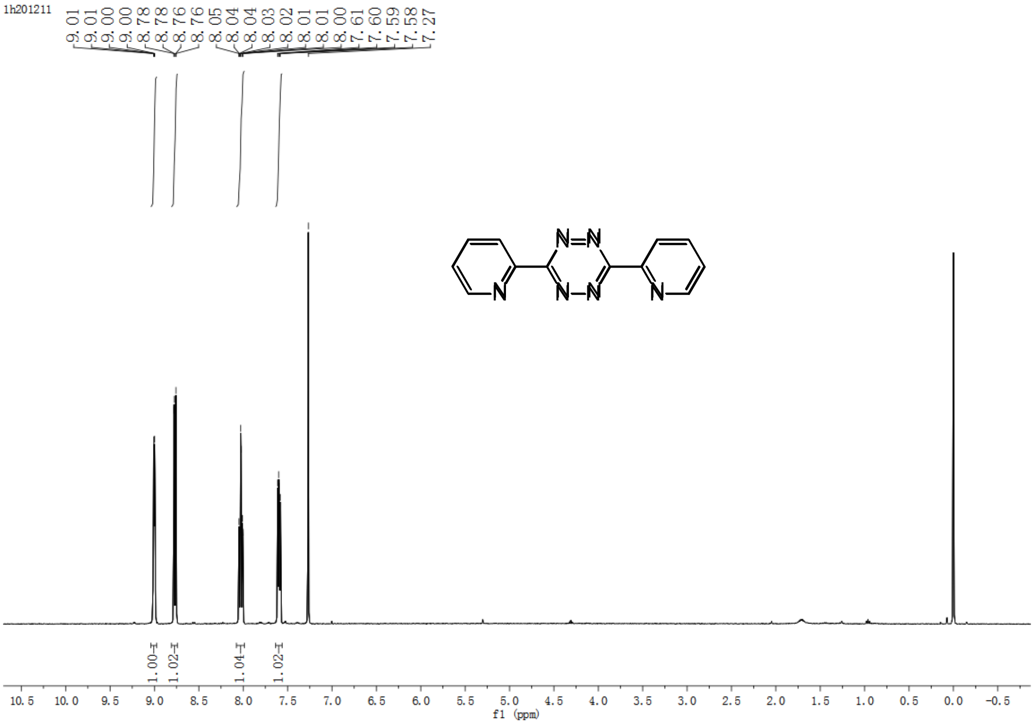


Figure S1 ^{1}H NMR spectrum for 3,6-di(2-pyridyl)-1,2,4,5-tetrazine.

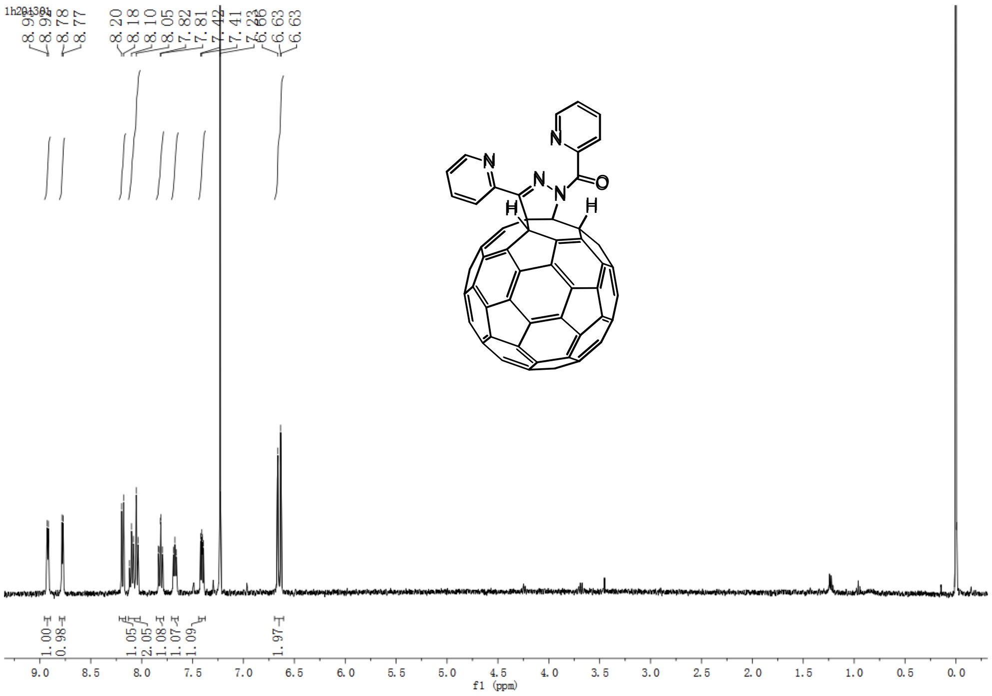


Figure S2 ^{1}H NMR spectrum for **1**.

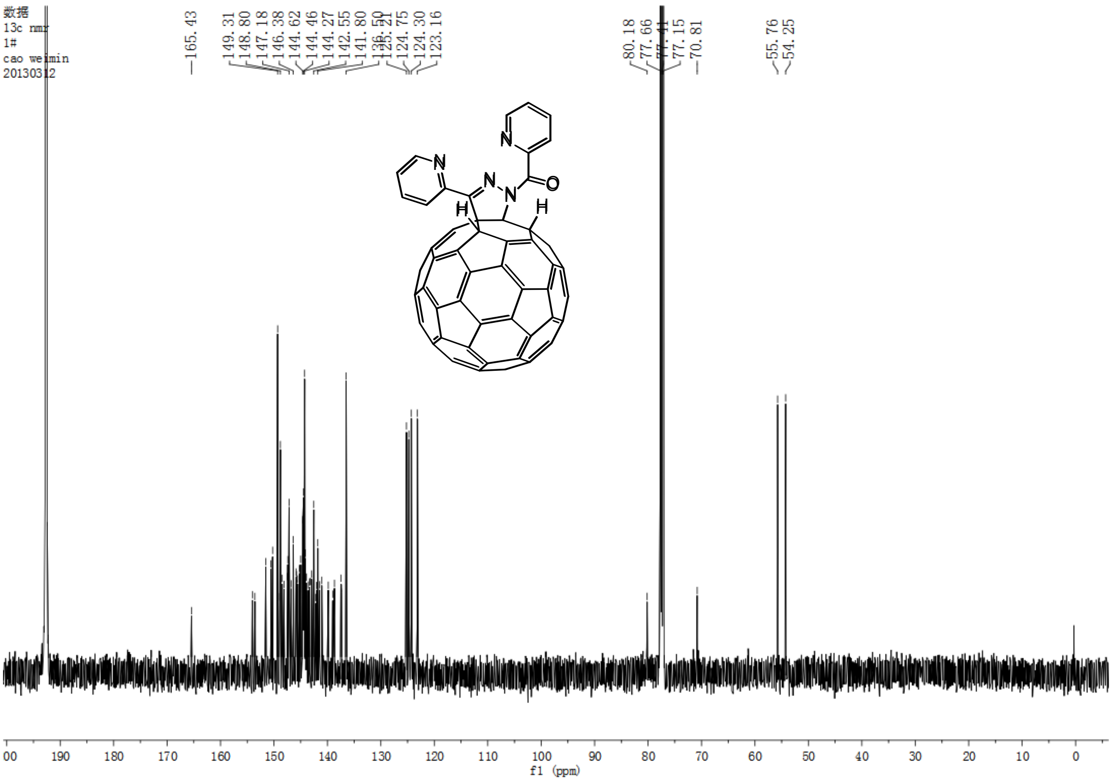
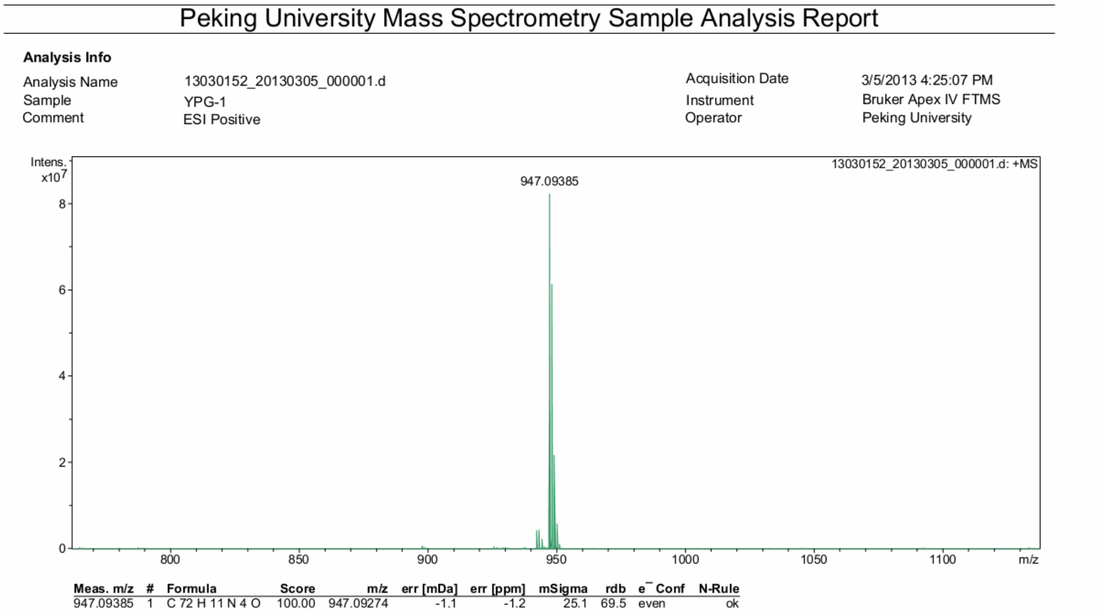


Figure S3 ^{13}C NMR spectrum for **1**.

5. Mass spectrum for 1


Peking University Mass Spectrometry Sample Analysis Report

Analysis Info

Analysis Name	13030152_20130305_000001.d	Acquisition Date	3/5/2013 4:25:07 PM
Sample	YPG-1	Instrument	Bruker Apex IV FTMS
Comment	ESI Positive	Operator	Peking University

Meas. m/z	#	Formula	Score	m/z	err [mDa]	err [ppm]	mSigma	rdb	e⁻ Conf	N-Rule
947.09385	1	C 72 H 11 N 4 O	100.00	947.09274	-1.1	-1.2	25.1	69.5	even	ok

Figure S4 Mass spectrum for **1**.

6. Absorption spectrum for 1

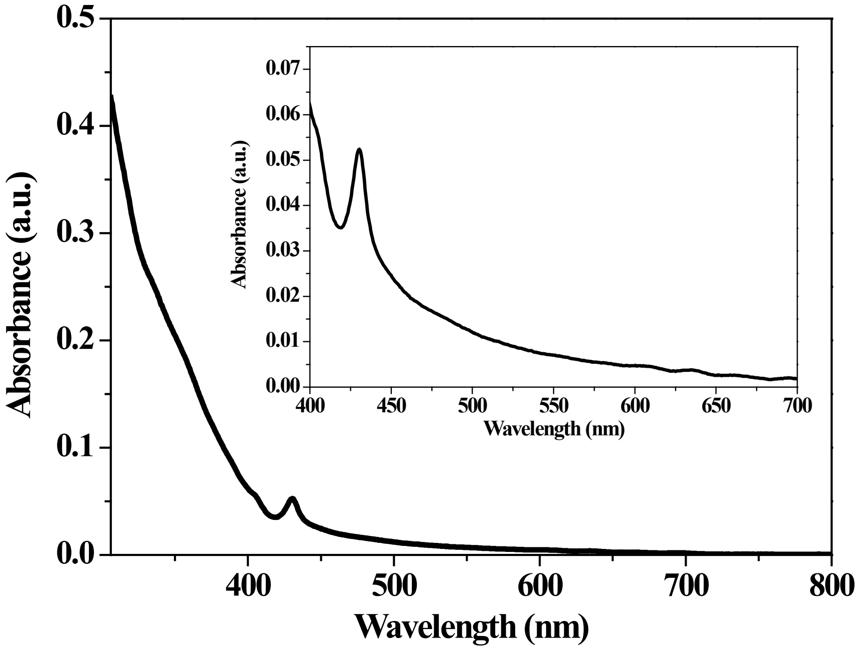


Figure S5 Absorption spectrum for **1** in $CHCl_3$ (10^{-5} mol/L). Inset: enlarged absorption spectrum in the visible region (400-700nm).

7. CV measurement for 1

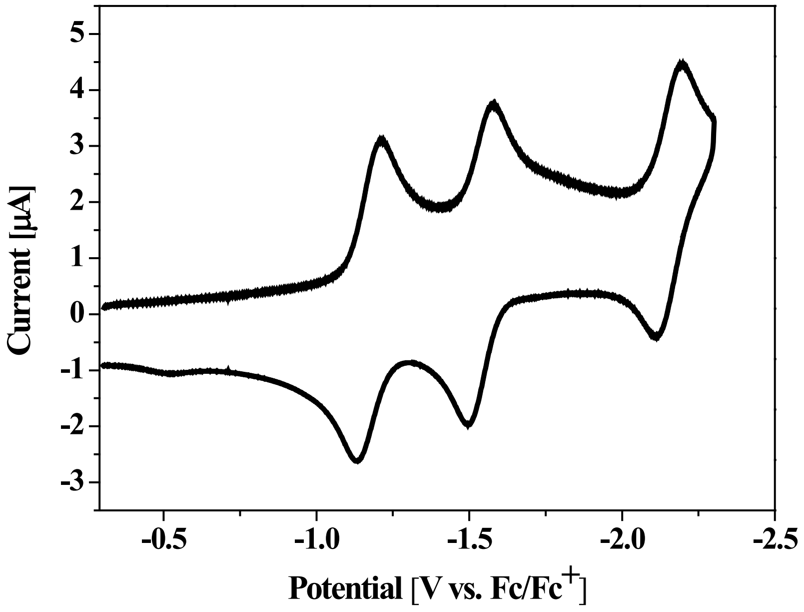


Figure S6 Cyclic voltammogram for **1**.

$E_{1/2}^{red1}$ (V)	$E_{1/2}^{red2}$ (V)	$E_{1/2}^{red3}$ (V)	E_{red}^{onset} (V)	LUMO (eV)
-1.17	-1.54	-2.15	-1.10	-4.00

8. TGA measurement for 1

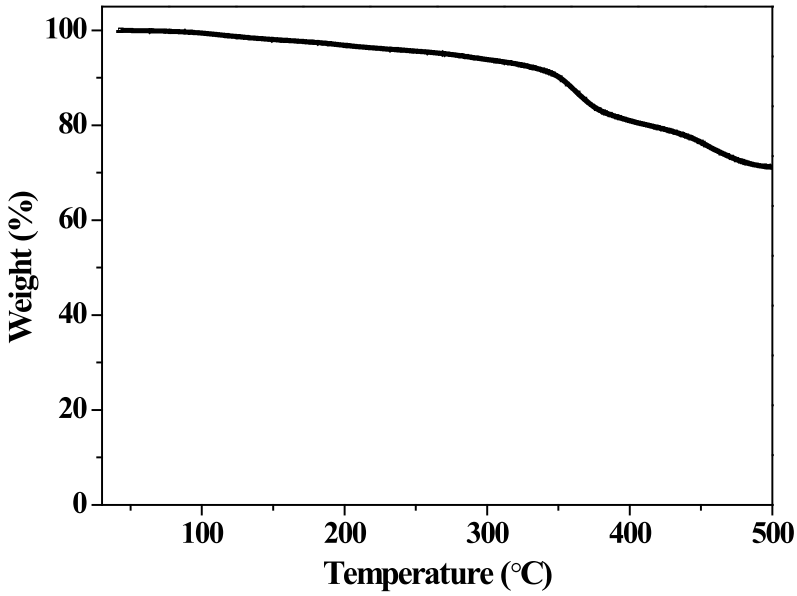


Figure S7 TGA curve for **1**.

9. EQE spectra for devices A and B

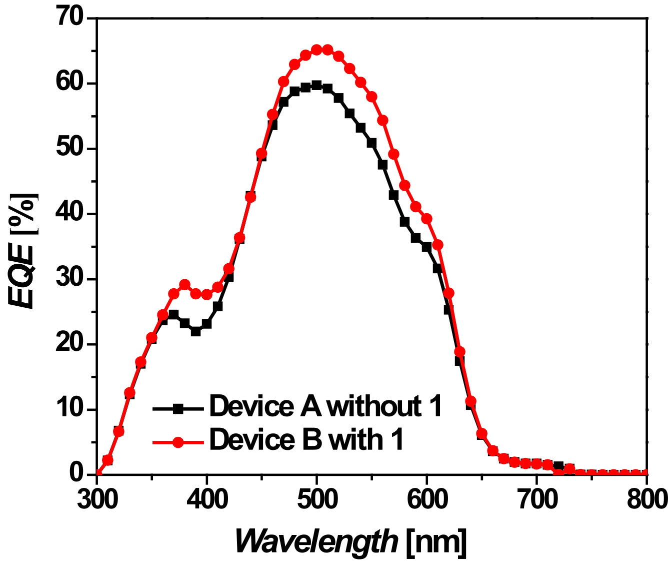


Figure S8 EQE spectra for devices A and B.

Reference

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