Electronic Supplementary Information (ESI)

Multifunctionalization of C_{70} at the two polar regions with a high regioselectivity via oxazolination and benzylation reactions

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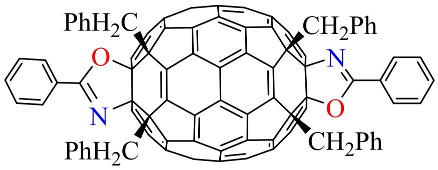
Experimental Section

General Methods. All reactions were carried out under an atmosphere of Ar. All reagents were obtained commercially and used without further purification, unless otherwise noted. Benzonitrile (PhCN) was distilled over P_2O_5 under vacuum at 305 K prior to use. Tetra-*n*-butylammonium perchlorate (TBAP) was recrystallized from absolute ethanol and dried under vacuum at 313 K prior to use. ^1H NMR spectra were recorded on a 600 MHz spectrometer and ^{13}C NMR spectra were recorded on a 150 MHz spectrometer. Accurate MS measurement was performed using an ESI electrospray ionization Fourier transform ion cyclotron resonance mass spectrometer (ESI FT-ICR MS).

For CV measurements, a three-electrode cell was used and a glassy carbon, a platinum wire were used as working electrode and counter electrode, and a saturated calomel electrode (SCE) was used as reference electrode.

Preparation of Compound 1. Typically, 155.4 mg of C_{70} (185.0 μmol) were put into a 1:1 (v:v) mixture of PhCN:*o*-DCB degassed with argon at 50 ºC. Then 2.1-fold TBAOH (1.0 M in methanol, 389 μL, 0.39 mmol) was added into the solution and the reaction was allowed to proceed for 2 h, and was then quenched with sixty-fold $PhCH_2Br$ (1.32 mL, 11.1 mmol). The solvent was removed under reduced pressure, and the residue was washed with methanol to remove TBAOH and $PhCH_2Br$. The crude product was put into toluene, and the soluble part was purified with toluene over a semi-preparative Buckyprep-M COSMOSIL Packed Column (10 mm × 250 mm) at a flow rate of 4.0 mL/min with the detector wavelength set at 380 nm, which afforded compound **1** with an isolated yield of 61% (128.4 mg) and 8.1 mg of unreacted C_{70}. The identity of compound **1** was confirmed by the ^1H NMR and UV-vis characterizations as compared with previous work.

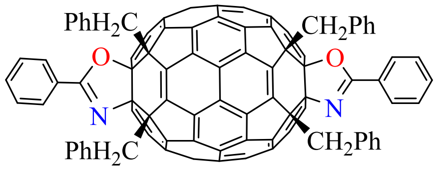
Preparation of Compound 2 and 3. Typically, 65.0 mg of compound **1** (57.0 μmol) were put into 50 mL of freshly distilled benzonitrile solution at 50 ºC, which was degassed with argon for 20 min under vigorous stirring. Then 3-fold of TBAOH (1.0 M in methanol, 171 μL, 0.17 mmol) was added into the solution and the reaction was allowed to proceed for 5 h, and was then quenched with sixty-fold $PhCH_2Br$ (406 μL, 3.4 mmol). The solvent was removed under reduced pressure, and the residue was washed with methanol to remove TBAOH and $PhCH_2Br$. The crude product was put into toluene, and the soluble part was eluted with toluene over a semi-preparative Buckyprep-M COSMOSIL Packed Column (10 mm × 250 mm) at a flow rate of 4.0 mL/min with the detector wavelength set at 380 nm, which afforded a mixture of **2** and **3** and 7.9 mg of unreacted compound **1** (12%). The mixture of **2** and **3** was purified by eluting with 60:40 v/v toluene/hexane mixture over a semi-preparative COSMOSIL Packed Column 5SL-Ⅱ (10 mm × 250 mm), and it afforded 20.3 mg of **2** (25%) and 20.1 mg of **3** (25%).



2

Spectral Characterization of 2: Positive ESI FT-ICR MS, *m*/*z* calcd for $C_{112}H_{39}N_2O_2^+$ [M + H]$^+$ 1443.30060, found 1443.30309; ^1H NMR (600 MHz,*o*-DCB-*d*$_4$) δ ppm, 8.28-8.27 (m, 4H), 7.49-7.48 (m, 6H), 7.15 (m, 7H), 6.98-6.89 9 (m, 13H), 3.89, 3.73 (ABq, J_{AB} = 13 Hz, 4H), 3.29, 3.26 (ABq, J_{AB} = 13 Hz, 4H); ^{13}C NMR (150 MHz, *o*-DCB-*d*$_4$) δ ppm, 166.10 (2C), 164.37 (2C), 162.84 (2C), 154.86 (2C), 154.32 (2C), 153.23 (2C), 152.28 (2C), 151.91 (2C), 151.80 (2C), 151.27 (2C), 151.19 (2C), 150.96 (2C), 150.55 (2C), 150.27 (2C), 149.34 (2C), 147.56 (2C), 147.42 (2C), 147.38 (2C), 146.84 (2C), 144.25 (2C), 143.60 (2C), 142.03(2C), 141.88 (2C), 139.94 (2C), 139.82 (2C), 139.57 (2C), 139.43 (2C), 138.27 (2C), 138.06 (2C), 137.56 (2C), 137.04 (2C), 135.39 (2C), 132.77 (4C, Ph), 132.35 (4C, Ph), 132.17 (2C, Ph), 131.86 (2C, Ph), 130.48 (4C, Ph), 129.84 (4C, Ph), 129.13(2C, Ph), 128.99 (2C, Ph), 128.00(2C, Ph), 127.83 (2C, Ph), 127.63 (4C, Ph), 126.98 (4C, Ph), 94.45 (2C, sp^3, C_{70}–O), 87.24 (2C, sp^3, C_{70}–N), 59.29 (2C, sp^3, C_{70}–CH$_2$), 58.63 (2C, sp^3, C_{70}–CH$_2$), 43.42 (2C, CH$_2$), 42.57 (2C, CH$_2$); UV-vis (toluene): $\lambda_{\max}$ 394, 475, 542 and 598 nm.

X-ray Single-Crystal Diffraction of 2. Black crystals of **2** were obtained by slowly diffusing ethanol into a carbon disulfide solution of **2** at room temperature. Single-crystal X-ray diffraction data were collected on an instrument equipped with a CCD area detector using graphite-monochromated Mo Kα radiation (λ = 0.71073 Å) in the scan range 1.73° < θ < 25.05°. The structure was solved with the direct method of SHELXS-97 and refined with full-matrix least-squares techniques using the SHELXL-97 program within WINGX. Crystal data of **2**•CS$_2$; $C_{113}H_{38}N_2O_2S_2$, M_w = 1519.57, Monoclinic, space group $C2/c$, a = 21.845(3) Å, b = 16.430(2) Å, c = 20.014(3) Å, α = 90°, β = 107.937(2), γ = 90°, V = 6834.1(16) Å^3, Z = 4, D_{calcd} = 1.477 Mg • m^{-3}, μ= 0.146 mm^{-1}, T = 187(2) K, crystal size 0.21 × 0.19 × 0.11 mm; reflections collected 19743, independent reflections 6041; 3323 with $I > 2\sigma(I)$; $R1$ = 0.0817 [$I > 2\sigma(I)$], w$R2$ = 0.1779 [$I > 2\sigma(I)$]; $R1$ = 0.1549 (all data), w$R2$ = 0.2145 (all data), GOF (on F^2) = 1.039.



3

Spectral Characterization of 3: Positive ESI FT-ICR MS, m/z calcd for $C_{112}H_{39}N_2O_2^+$ [M + H]$^+$ 1443.30060, found 1443.29934; ^{1}H NMR (600 MHz, o-DCB-d_4) δ ppm, 8.29-8.28 (m, 4H), 7.50-7.49 (m, 6H), 7.15(m, 7H), 6.99-6.90 (m, 13H), 3.89, 3.74 (ABq, J_{AB} = 13 Hz, 4H), 3.32, 3.25 (ABq, J_{AB} = 13 Hz, 4H); ^{13}C NMR (150 MHz, o-DCB-d_4) δ ppm, 165.96 (2C), 164.56 (2C), 162.84

(2C), 154.86 (2C), 154.68 (2C), 152.94 (2C), 152.32 (2C), 152.18 (2C), 151.65 (2C), 151.24 (2C), 151.17 (2C), 151.10 (2C), 151.05 (2C), 150.72 (2C), 150.27 (2C), 149.36 (2C), 147.55 (2C), 147.31 (2C), 147.12 (2C), 146.87 (2C), 144.20 (2C), 143.58 (2C), 142.02 (2C), 141.95 (2C), 140.08 (2C), 139.84 (2C), 139.57 (2C), 139.02 (2C), 138.26 (4C), 137.76 (2C), 137.50 (2C), 132.77 (4C, Ph), 132.35 (4C, Ph), 132.16 (2C, Ph), 131.88 (2C, Ph), 130.48 (4C, Ph), 129.84 (4C, Ph), 129.13 (2C, Ph), 128.99 (2C, Ph), 128.00 (2C, Ph), 127.82 (2C, Ph), 127.62 (4C, Ph), 126.98 (4C, Ph), 94.40 (2C, sp^3, C_{70}–O), 87.23 (2C, sp^3, C_{70}–N), 59.33 (2C, sp^3, C_{70}–CH_2), 58.60 (2C, sp^3, C_{70}–CH_2), 43.40 (2C, CH_2), 42.57 (2C, CH_2); UV-vis (toluene): λ_{max} 394, 475, 542 and 598 nm.

Quantum Computational Methods. The structure of **1** was optimized with Gaussian09 at the B3LYP/6-31G level, followed by harmonic frequency calculations at the same level to confirm them as the energy minima. The NBO charge distribution and the energy of **1** was obtained at the B3LYP/6-311G(d) level.

Device Fabrication. Patterned ITO substrates (15 × 15 mm) with a sheet resistance of 6 Ω sq^{-1} (Kuramoto Co., Ltd.) were used. The substrates were sonicated sequentially in cleaning surfactant (Semi Clean, M-Lo), water, acetone and 2-isopropanol for 15 min each. The substrates were then dried in an oven at 70 °C. Subsequently, ITO substrates were exposed to UV/O_3 for 15 min before depositing PEDOT:PSS dispersed in water (Clevios P VP, Heraeus Precious Metals GmbH & Co.) at a spin speed of 5000 rpm for 30 s.

For P3HT:acceptor photoactive layer deposition, P3HT and the sample mixture of 20 mg mL^{-1} concentration in *o*-dichlorobenzene (anhydrous, 99%, Sigma-Aldrich) was prepared with a donor:acceptor ratio of 1:1. The solution was stirred for 4 h at 60 °C. The photoactive layer solution was spin coated on the substrates at 2000 rpm for 60 s.

A 1-nm-thick LiF layer was deposited on top of the active layer as an interfacial layer. An approximately 100-nm-thick Al layer was thermally evaporated at a pressure of 2×10^{-4} Pa with a shadow mask, which defined the device active area as 0.09 cm^2.

Characterization. The *J–V* characteristics were measured by using a software-controlled source meter (2400, Keithley) under dark conditions and 1 sun AM 1.5 G simulated sunlight irradiation (100 mW cm^{-2}) with a solar simulator (EMS-35AAA, Ushio Spax Inc.), which was calibrated by using a silicon diode (BS-520BK, Bunkokeiki).

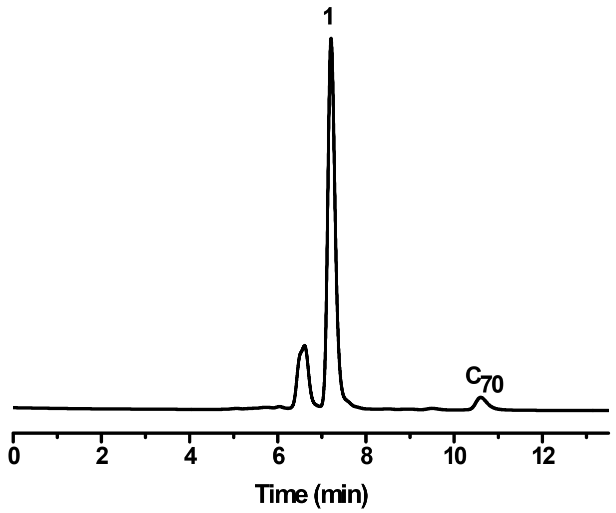


Figure 1. HPLC trace of the crude reaction mixture formed from the reaction of OH^{-} with C_{70} and PhCN quenched with $PhCH_2Br$. The crude product was eluted with toluene over a semi-preparative Buckyprep-M column at a flow rate of 4.0 mL/min with the detector wavelength set at 380 nm.

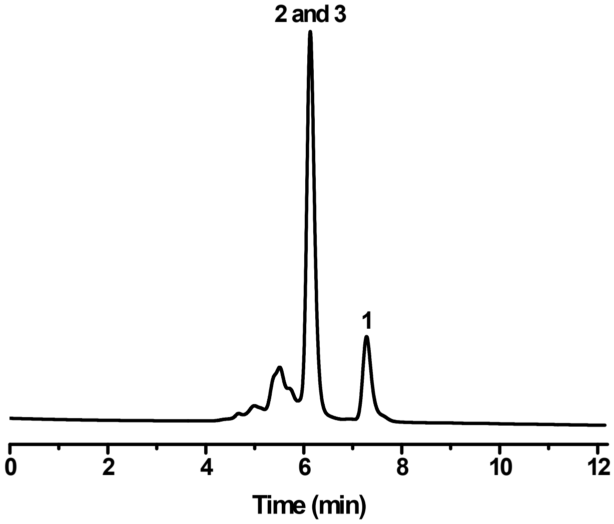


Figure S2. HPLC trace of the crude reaction mixture formed from the reaction of OH^- with **1** and PhCN quenched with $PhCH_2Br$. The crude product was eluted with toluene over a semi-preparative Buckyprep-M column at a flow rate of 4.0 mL/min with the detector wavelength set at 380 nm.

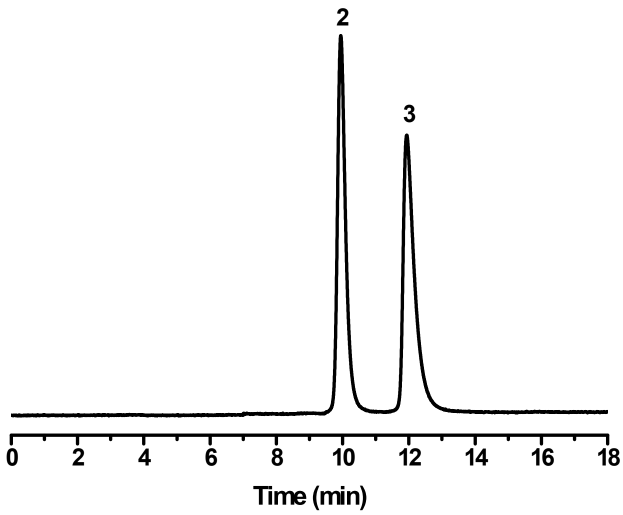
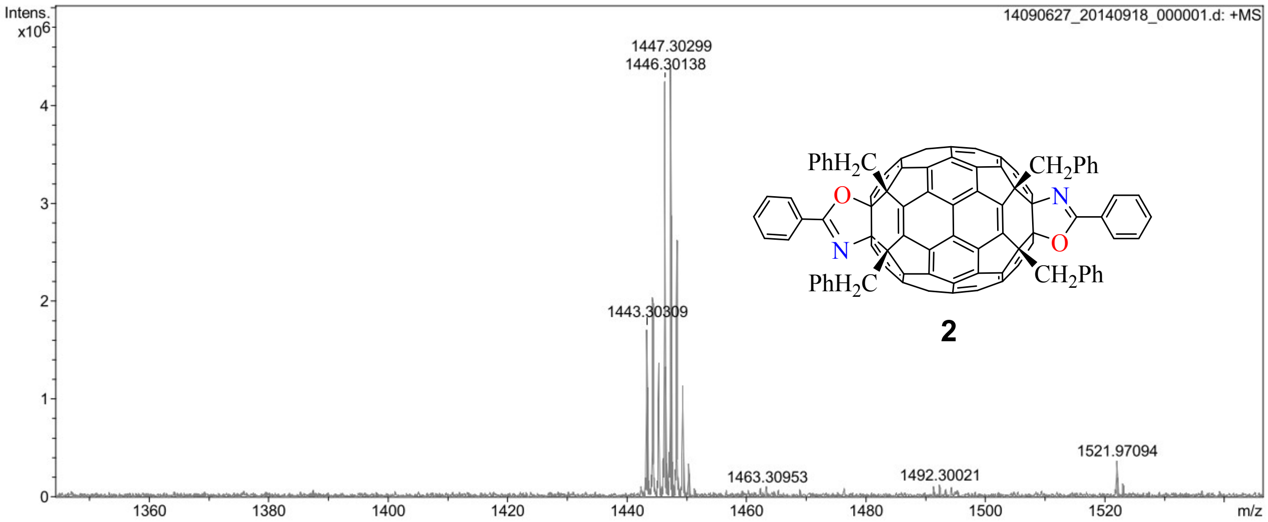
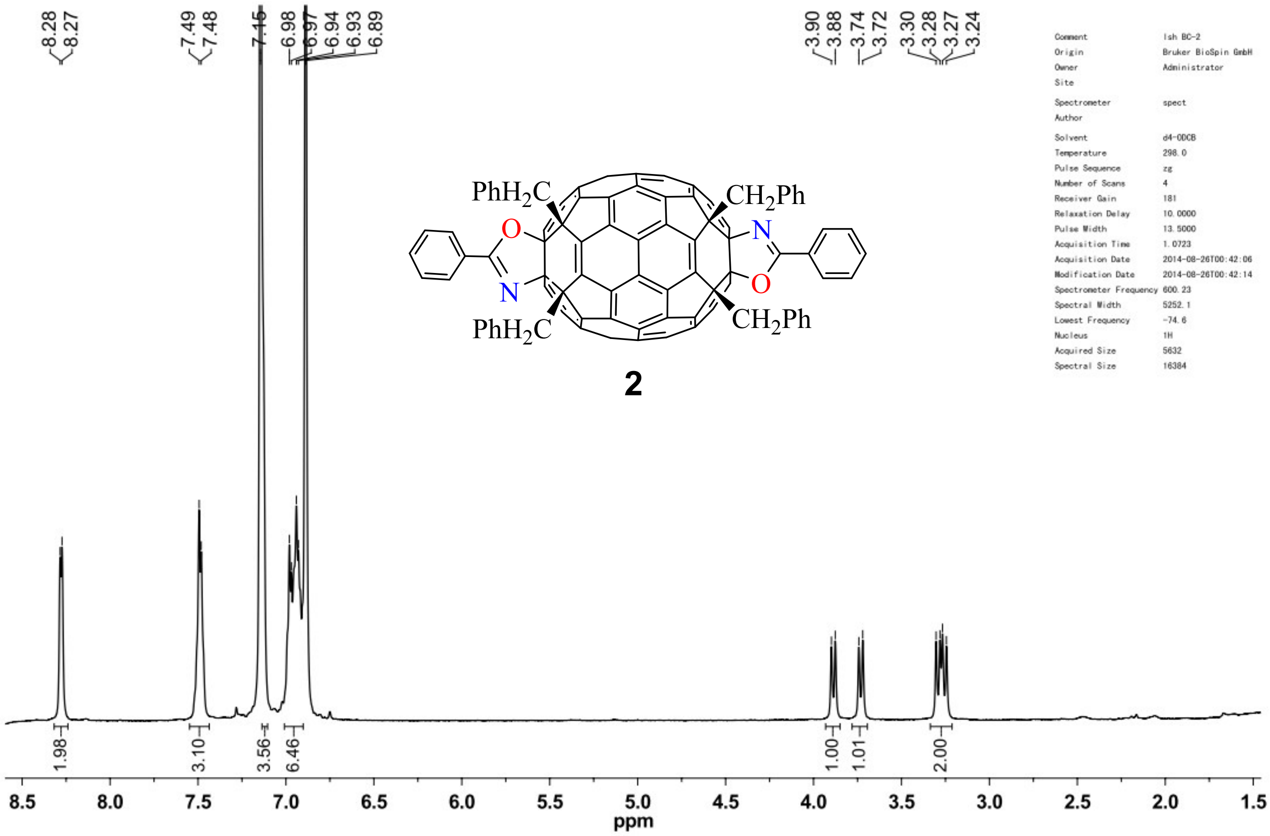


Figure S3. HPLC purification of the mixture of **2** and **3** over a semi-preparative column 5SL-II eluted with a 60:40 v/v mixture of toluene/hexane at a flow rate of 4.0 mL/min with detector wavelength set at 380 nm.



Meas. m/z	I	Formula	m/z	err [mDa]	err [ppm]	mSigma	rdb	e⁻ Conf	N-Rule
1443.30309	1763530	C 112 H 39 N 2 O 2	1443.30060	-2.49	-1.72	609.6	94.5	even	ok
1446.30138	4262858	C 96 H 169 N 2 O 6	1446.29752	-3.86	-2.67	33.5	13.5	even	ok
		C 107 H 40 N 3 O 5	1446.29625	-5.13	-3.55	38.9	89.5	even	ok
		C 112 H 40 N O 3	1446.30027	-1.11	-0.76	51.8	93.5	even	ok

Figure S4. Positive ESI FT-ICR MS of compound **2**.



2

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Origin                     Bruker BioSpin GmbH
Owner                      Administrator
Site

Spectrometer               spect
Author

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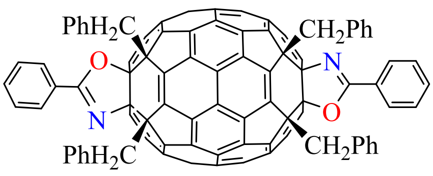
Figure S5. ^{1}H NMR spectrum (600 MHz) of compound **2** recorded in *o*-DCB-d_4.



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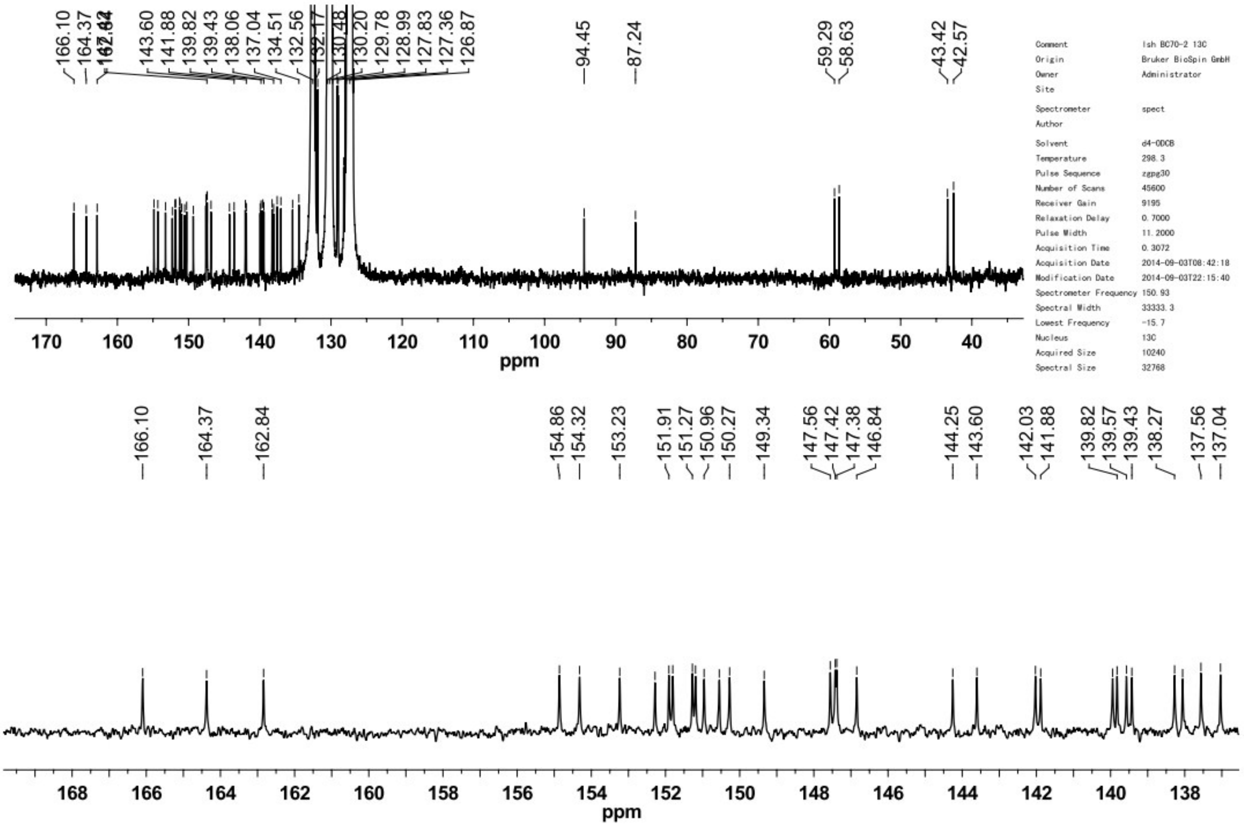
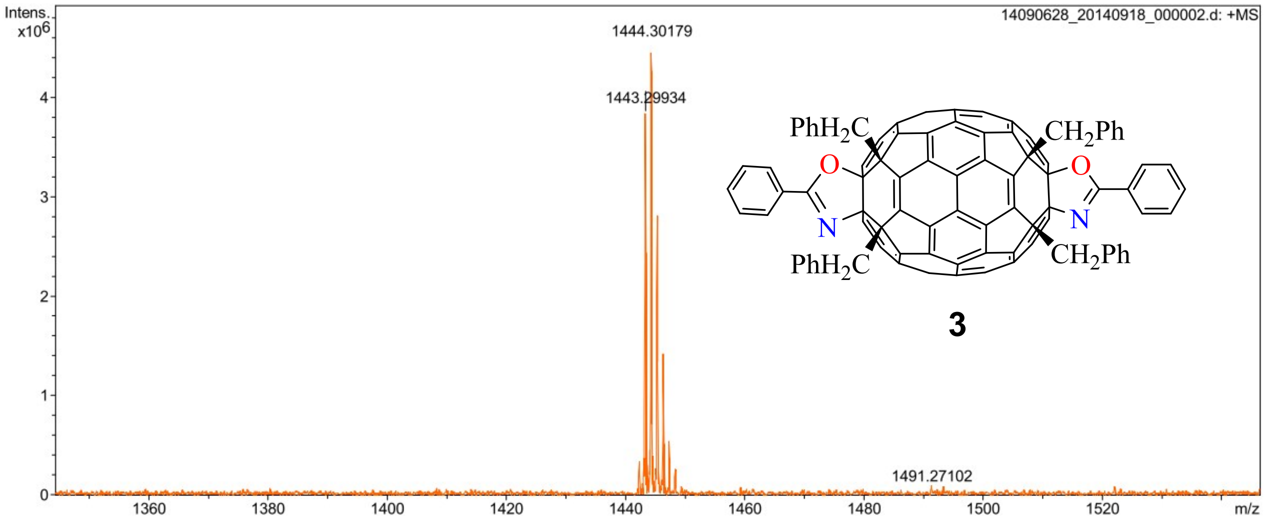
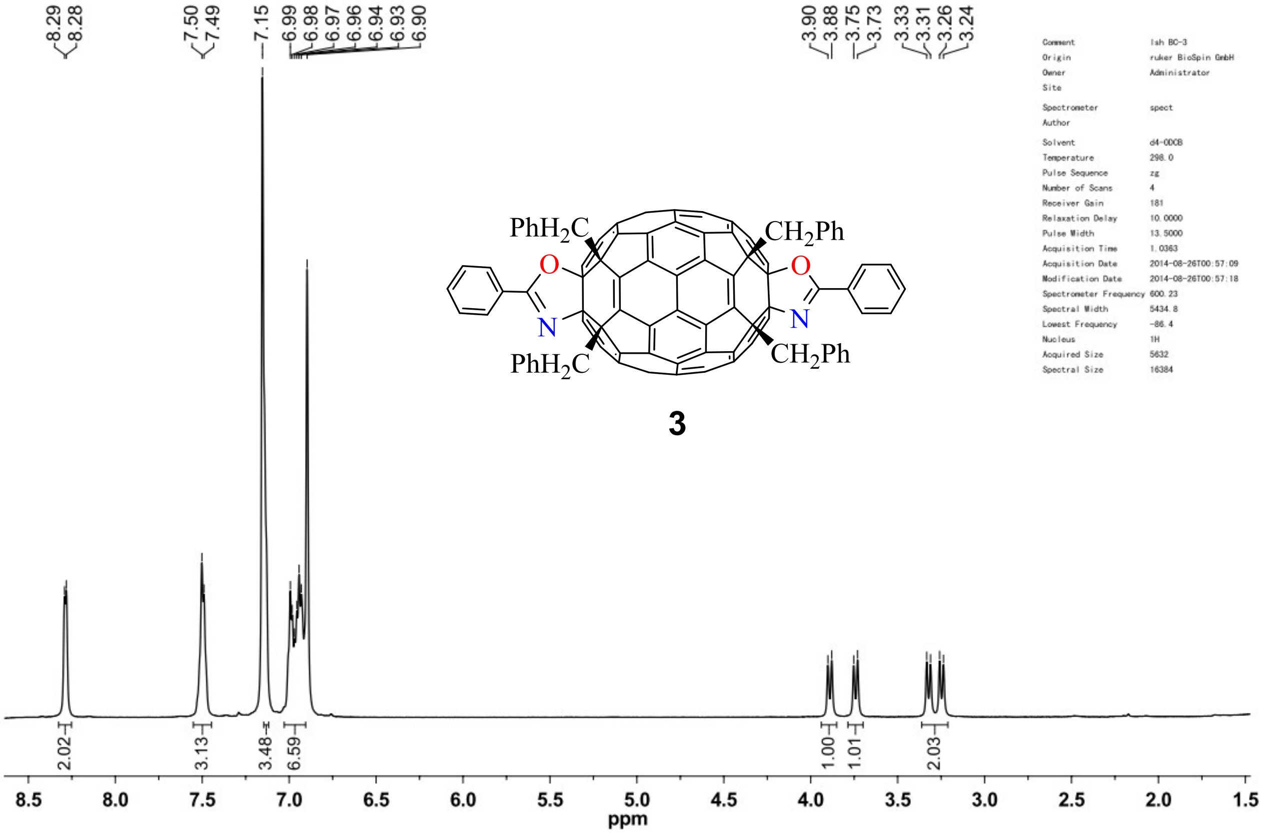


Figure S6. ^{13}C NMR spectrum (150 MHz) of compound **2** recorded in *o*-DCB-d_4.



Meas. m/z	I	Formula	m/z	err [mDa]	err [ppm]	mSigma	rdb	e⁻ Conf	N-Rule
1443.29934	3991794	C 112 H 39 N 2 O 2	1443.30060	1.26	0.88	42.7	94.5	even	ok

Figure S7. Positive ESI FT-ICR MS of compound **3**.



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Author	
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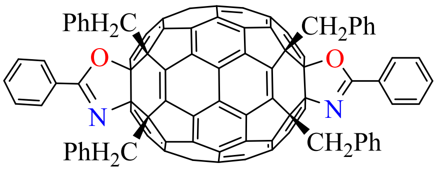
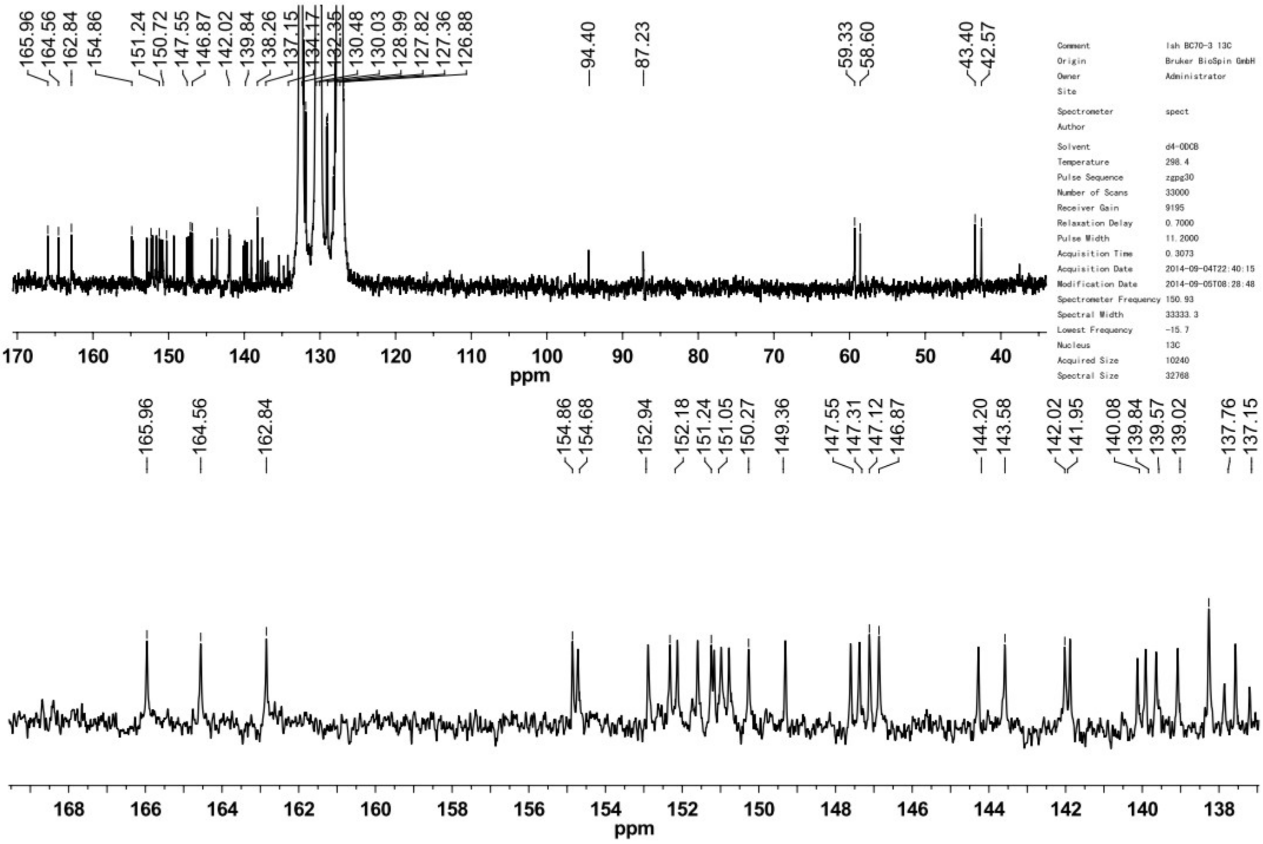
Spectral Size	16384

Figure S8. ^{1}H NMR spectrum (600 MHz) of compound **3** recorded in *o*-DCB-*d*$_4$.



3



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Author	
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Figure S9. ^{13}C NMR spectrum (150 MHz) of compound **3** recorded in *o*-DCB-d_4.

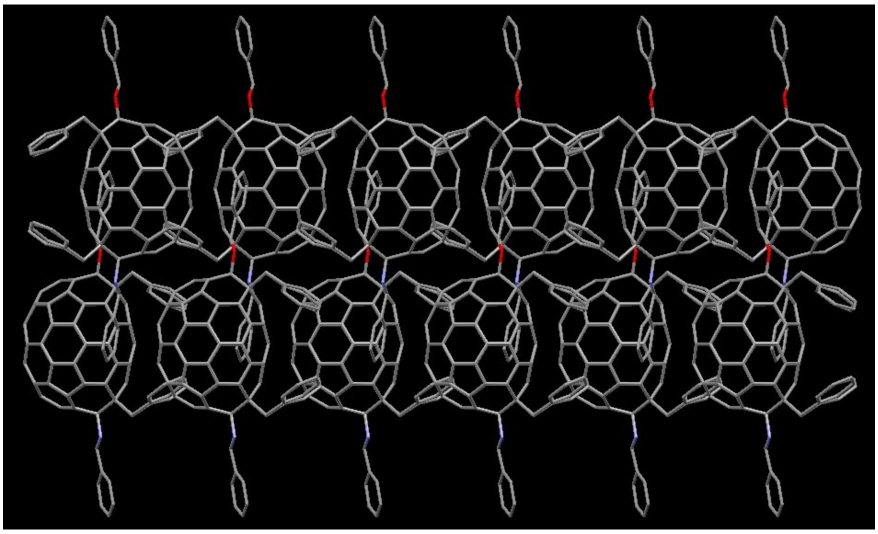

Figure S10. Packing diagram of **2** viewed along the *bc* plane. The solvent molecules and hydrogen atoms were removed for clarity.

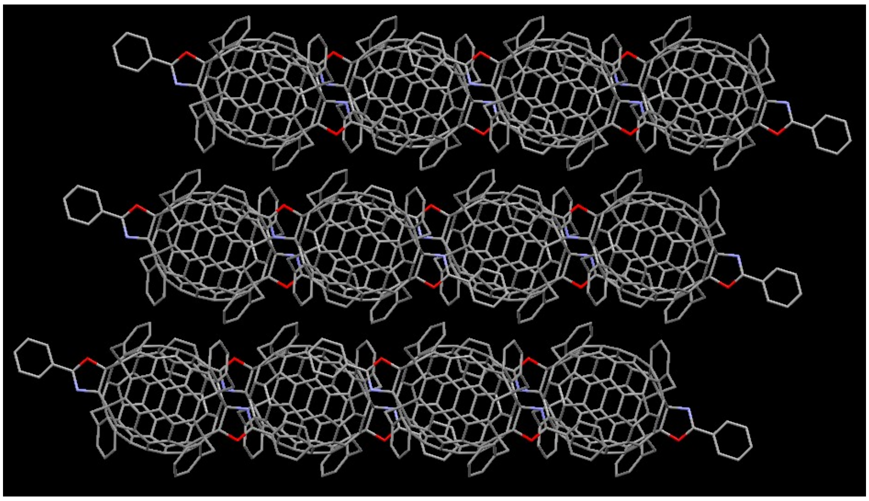

Figure S11. Packing diagram of **2** viewed along the *ac* plane. The solvent molecules and hydrogen atoms were removed for clarity.

Cartesian coordinates, the lowest frequency and total energy of **1** obtained with Gaussian09 at B3LYP/6-31G level.

Geometry of **1**
Charge = 0 Multiplicity = 1

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C	6.78493200	-2.03076700	-1.93197900
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C	7.97466500	-3.22638900	0.30544200
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H	6.10308900	-2.83833000	1.31256900
C	3.58356600	1.54833600	-1.94718500
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C	3.40812000	3.01058000	-2.29889100
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C	3.28848800	2.91186400	5.64777000
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C	-0.30664200	-2.20486000	-3.15353500
C	-5.09414500	-2.20401900	0.53167800
C	1.37504000	-2.82977900	-0.98184700
C	-4.22008700	-2.59799900	-1.60463000
C	0.58065700	-0.03404200	-3.21867100
C	-1.89921500	1.31634000	3.19855900
C	-4.20668100	-3.06179900	-0.24238000
C	-0.81225200	0.02438200	-3.63459500
C	-1.99459400	-3.97385200	-0.57529200
C	-2.67533300	-3.25598600	1.71628500
C	-0.26368500	-3.67081800	1.15379900
C	1.16594400	-0.71724600	2.50172900
C	-3.38968500	2.79544800	-1.75631800
C	-0.35310300	2.43901500	1.60096600
C	-3.86698300	-0.16135200	3.17075500
C	-2.80432300	2.92612100	1.75599900

C	-3.52010800	-2.35308700	2.42076400
C	-1.59868500	3.33425400	-0.35279900
C	0.23448800	-3.62556400	-1.24039000
C	-0.74721900	-2.20042400	2.90427500
C	-2.00818000	-3.51057500	-1.93829300
C	-3.34063700	1.12588200	3.15142300
C	-5.89167600	0.09605900	0.08854100
C	-4.80276600	-0.38101300	-2.50841000
C	-3.03582700	-3.63127100	0.33266100
C	-0.60478000	-4.03808800	-0.14617700
C	0.59803600	2.36656900	-0.67155400
C	-0.62680600	-3.29267200	-2.34428700
C	0.26281400	2.04288300	-2.02547700
C	-2.97205700	-1.30775400	3.24392300
C	-3.91124900	2.13197300	2.26691800
C	-3.93823000	3.05000100	-0.43178300
C	-4.99946300	2.27809300	0.05061900
C	0.31200000	0.38874600	2.84055700
C	0.63705000	-1.98404500	2.51274600
C	-5.03048600	0.98072600	-2.05292900
C	-1.94827600	2.98349400	-1.70320000
C	-5.67416400	-1.21376700	-0.35915800
C	-3.06369200	-2.69179100	-2.42934200
C	-1.56500100	-1.14022400	3.38736900
C	0.89648800	-1.43647100	-2.91148100
C	0.62437400	1.47201400	1.95745300
C	-1.63263700	1.15417600	-3.35695100
C	-1.57180300	2.41921500	2.33526100
C	-5.53907800	0.45911500	1.45448300
C	1.74033800	-2.49763100	0.35950400

Lowest frequency = 17.31 cm^{-1}
Total energy = –3608.0482 hartree (1 hartree = 627.51 kcal/mol)

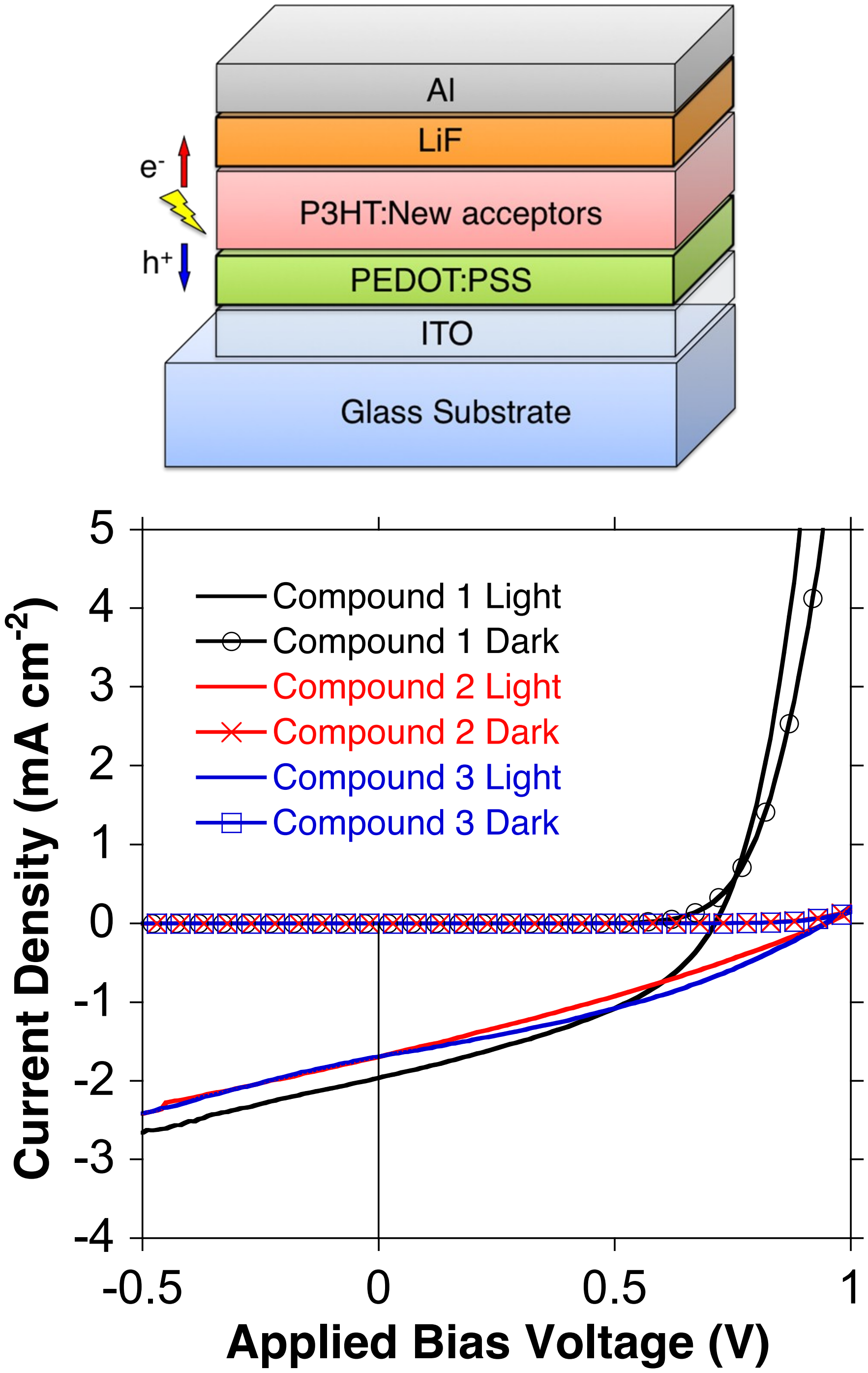

Figure S12. The solar cell device structure used for this manuscript and the corresponding *J*–*V* curves under 1 sun (100 mW cm^{-2}) and in dark.

Table S1. Optimized photovoltaic parameters of the solar cell devices fabricated using the organofullerene acceptor compounds (ITO/PEDOT:PSS/P3HT: organofullerenes/LiF/Al)

Acceptors	**V_{OC} (V)**	**J_{SC} (mA•cm^{-2})**	***FF***	**R_S (Ω)**	**R_{SH} (Ω)**	**PCE (%)**
Compound **1**	0.71	1.96	0.39	3.7×10^1	1.2×10^7	0.54
Compound **2**	0.95	1.69	0.29	1.3×10^3	3.0×10^5	0.46
Compound **3**	0.95	1.69	0.34	1.6×10^3	1.3×10^7	0.55