Electronic Supplementary Information

Isobenzofulvene-Fullerene Mono-adduct for Photovoltaic Applications

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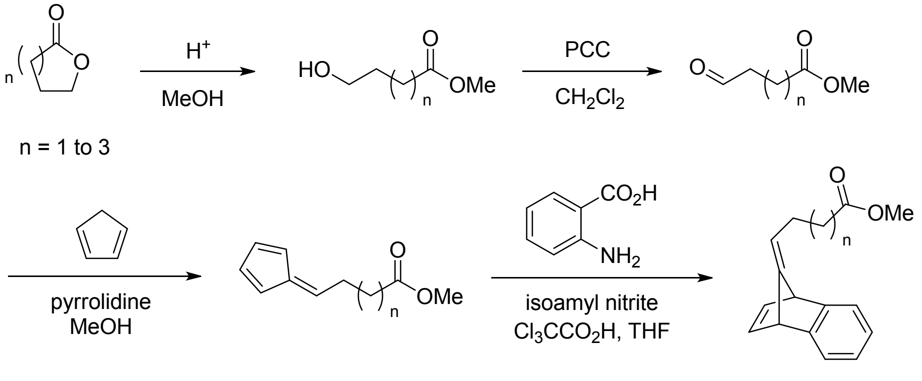
Experimental:

Methanol, ethanol, dichloromethane, ethyl acetate, toluene, *n*-hexane, and *o*-dichlorobenzene were used as received from Merck Millipore, Macorn, or RCI labscan. All reagents were used as received from Sigma-Aldrich or J&K Scientific unless otherwise indicated. Analytical thin layer chromatography was performed with Merck Millipore normal phase 0.25 mm aluminum backed TLC plates (Merck Millipore 1.05554.0001). Purification of reaction products was generally done by flash chromatography with Merck Millipore 70-230 or 230-400 mesh silica gel 60. All experiments were performed under anhydrous conditions under an atmosphere of nitrogen unless otherwise noted.

^{1}H, and ^{13}C spectra were recorded using Varian Mercury 300 MHz spectrometer. ^{1}H spectra were referenced to tetramethylsilane (TMS, 0 ppm) and ^{13}C spectra were referenced to solvent carbons ($CDCl_3$, 77.0 ppm). High resolution mass spectra were obtained on GCT Premier mass spectrometer operated in EI or CI mode or MALDI micro MX mass spectrometer operated in MALDI-TOF mode. Electrochemical cyclic voltammetry was conducted on a Autolab PGSTAT302N electrochemical workstation with glassy carbon disk, Pt wire, and Ag wire as working electrode, counter electrode, and reference electrode, respectively, in a 0.1 mol/L tetrabutylammonium hexafluorophosphate (Bu_4NPF_6) odichlorobenzene/acetonitrile (5:1) solution. AFM measurements were performed by using a Scanning Probe Microscope-Dimension 3100 in tapping mode. All film samples were spin casted on ITO/ZnO substrates.



Scheme S1. Synthetic route of Bicyclo precursors.

Synthesis of C2-bicyclo. The C2-bicyclo was prepared according to the previously reported procedure.[21] Using the reaction condition described in literature with methyl 4-(cyclopenta-2,4-dien-1-ylidene)butanoate (1.62 g, 9.87

mmol) as starting material, followed by chromatography on silica gel using 5% EtOAc in hexane ($R_f = 0.33$) gave title compound (1.36 g, 57%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.26-7.17 (m, 2H), 7.00-6.93 (m, 2H), 6.93-6.86 (m, 2H), 4.48-4.40 (m, 2H), 4.10 (s, 1H), 3.56 (s, 3H), 2.33-2.21 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 173.5, 167.5, 149.8, 149.4, 142.8, 142.3, 124.7, 124.6, 121.2, 121.0, 98.7, 53.7, 51.5, 49.5, 34.3, 23.2. HRMS (CI) Calcd for $C_{16}H_{16}O_2$ [M^+] 240.1150, found 240.1156.Using the reaction condition described in literature with methyl 4-(cyclopenta-2,4-dien-1-ylidene)butanoate (1.62 g, 9.87 mmol) as starting material, followed by chromatography on silica gel using 5% EtOAc in hexane ($R_f = 0.33$) gave title compound (1.36 g, 57%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.26-7.17 (m, 2H), 7.00-6.93 (m, 2H), 6.93-6.86 (m, 2H), 4.48-4.40 (m, 2H), 4.10 (s, 1H), 3.56 (s, 3H), 2.33-2.21 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 173.5, 167.5, 149.8, 149.4, 142.8, 142.3, 124.7, 124.6, 121.2, 121.0, 98.7, 53.7, 51.5, 49.5, 34.3, 23.2. HRMS (CI) Calcd for $C_{16}H_{16}O_2$ [M^+] 240.1150, found 240.1156.

Synthesis of C3-bicyclo. The C3-bicyclo was prepared according to the previously reported procedure.[21] Using the reaction condition described in literature with methyl 5-(cyclopenta-2,4-dien-1-ylidene)pentanoate (1.45 g, 8.14 mmol) as starting material, followed by chromatography on silica gel using 5% EtOAc in hexane ($R_f = 0.30$) gave title compound (1.82 g, 88%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.28-7.14 (m, 2H), 7.00-6.83 (m, 4H), 4.42 (t, $J = 7.5$ Hz, 1H), 4.35 (s, 1H), 4.10 (s, 1H), 3.63 (s, 3H), 2.21 (t, $J = 7.5$ Hz, 2H), 2.05-1.88 (m, 2H), 1.68-1.54 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ174.1, 167.6, 149.9, 149.5, 142.9, 142.3, 124.6, 124.5, 121.0, 120.9, 99.5, 53.8, 51.4, 49.5, 33.0, 26.6, 25.0. HRMS (CI) Calcd for $C_{17}H_{18}O_2$ [M^+] 254.1307, found 254.1310.

Synthesis of C4-bicyclo. The C4-bicyclo was prepared according to the previously reported procedure.[21] Using the reaction condition described in literature with methyl 6-(cyclopenta-2,4-dien-1-ylidene)hexanoate (1.56 g, 8.14 mmol) as starting material, followed by chromatography on silica gel using 2% EtOAc in hexane gave title compound (984 mg, 45%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.25-7.18 (m, 2H), 6.99-6.86 (m, 4H), 4.44 (t, $J = 7.3$ Hz, 1H), 4.36 (s, 1H), 4.10 (s, 1H), 3.64 (s, 3H), 2.25 (t, $J = 7.5$ Hz, 2H), 1.56-1.48 (m, 2H), 1.36-1.24 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 174.1, 167.0, 150.1, 149.6, 143.0, 142.4, 124.6, 124.5, 121.0, 120.9, 100.3, 53.9, 51.4, 49.6, 33.9, 29.3, 26.9, 24.3. HRMS (CI) Calcd for $C_{18}H_{20}O_2$ [M^+] 268.1463, found 268.1473.

Synthesis of $IC_{60}MA$-2C. To a solution of fullerene (0.25 mmol) in 18 mL of *o*-dichlorobenzene at 25 °C was added tetrazine (0.55 mmol) and C2-bicyclo (0.50 mmol), and the resulting mixture was stirred at 45 °C for 16 h. The solvent was then removed in *vacuo*, followed by chromatography on silica gel to afford the corresponding isobenzofulvene fullerene monoadduct from second color band of the chromatography (Yield: 56%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.75-7.58 (m, 2H), 7.52-7.41 (m, 2H), 5.90 (t, $J = 7.3$ Hz, 1H), 5.42 (s, 1H), 5.04 (s, 1H), 3.67 (s, 3H), 2.93-2.75 (m, 2H), 2.69-2.57 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ173.3, 155.53, 155.47, 153.5, 153.4, 149.0, 147.3, 146.3, 146.22, 146.18, 146.14, 146.11, 146.08, 146.05, 146.01, 145.7, 145.6, 145.44, 145.38, 145.31, 145.27, 145.15, 145.10, 145.05, 144.74, 144.66, 144.61, 144.44, 144.40, 143.0, 142.8, 142.63, 142.61, 142.51, 142.48, 142.45, 142.3, 142.2, 142.0, 141.9, 141.8, 141.70, 141.66, 139.99, 139.95, 139.7, 138.0, 137.9, 137.6, 137.4, 127.6, 127.5, 123.7, 123.5, 115.7, 74.9, 74.7, 60.9, 56.9, 51.8, 34.6, 29.7, 24.7. HRMS (MALDI) Calcd for $C_{74}H_{16}O_2$ [M^+] 934.0994, found 934.1069.

Synthesis of IC$_{60}$MA-3C. To a solution of fullerene (0.25 mmol) in 18 mL of *o*-dichlorobenzene at 25 °C was added tetrazine (0.55 mmol) and C3-bicyclo (0.50 mmol), and the resulting mixture was stirred at 45 °C for 16 h. The solvent was then removed in *vacuo*, followed by chromatography on silica gel to afford the corresponding isobenzofulvene fullerene monoadduct from second color band of the chromatography (Yield: 61%). 1H NMR (300 MHz, CDCl3): δ 7.72-7.58 (m, 2H), 7.53-7.37 (m, 2H), 5.86 (t, J = 7.3 Hz, 1H), 5.38 (s, 1H), 5.05 (s, 1H), 3.66 (s, 3H), 2.69-2.41 (m, 4H), 2.06-1.86 (m, 2H); 13C NMR (75 MHz, CDCl3): δ173.9, 155.6, 155.5, 153.7, 153.5, 148.5, 147.3, 146.3, 146.2, 146.15, 146.11, 146.08, 146.0, 145.7, 145.6, 145.4, 145.35, 145.28, 145.24, 145.22, 145.11, 145.07, 144.8, 144.65, 144.58, 144.41, 144.39, 143.0, 142.7, 142.6, 142.51, 142.49, 142.4, 142.3, 142.2, 142.0, 141.9, 141.79, 141.77, 141.7, 141.6, 139.9, 139.70, 139.68, 138.0, 137.8, 137.6, 137.5, 130.5, 129.0, 128.2, 127.5, 127.4, 125.3, 123.6, 123.5, 116.7, 74.9, 74.7, 61.0, 56.9, 51.62, 51.60, 33.4, 29.7, 28.5, 25.4. HRMS (MALDI) Calcd for C75H16O2 [M+] 948.1150, found 948.1180.

Synthesis of IC$_{60}$MA-4C. To a solution of fullerene (0.25 mmol) in 18 mL of *o*-dichlorobenzene at 25 °C was added tetrazine (0.55 mmol) and C4-bicyclo (0.50 mmol), and the resulting mixture was stirred at 45 °C for 16 h. The solvent was then removed in *vacuo*, followed by chromatography on silica gel to afford the corresponding isobenzofulvene fullerene monoadduct from second color band of the chromatography (Yield: 50%). 1H NMR (300 MHz, CDCl3): δ 7.72-7.58 (m, 2H), 7.51-7.40 (m, 2H), 5.88 (t, J = 7.3 Hz, 1H), 5.38 (s, 1H), 5.05 (s, 1H), 3.66 (s, 3H), 2.65-2.43 (m 2H), 2.38 (s, J = 7.3 Hz, 2H), 1.89-1.73 (m, 2H), 1.73-1.61 (m, 2H); 13C NMR (75 MHz, CDCl3): δ174.0, 155.7, 155.5, 153.7, 153.6, 147.8, 147.3, 146.3, 146.22, 146.16, 146.13, 146.05, 145.7, 145.6, 145.5, 145.41, 145.37, 145.32, 145.26, 145.13, 145.08, 144.9, 144.7, 144.6, 144.44, 144.41, 143.0, 142.8, 142.6, 142.54, 142.51, 142.4, 142.3, 142.2, 142.0, 141.9, 141.81, 141.78, 141.7, 141.6, 139.9, 139.7, 138.0, 137.7, 137.64, 137.56, 130.5, 127.7, 127.5, 127.4, 123.6, 123.5, 117.4, 75.0, 74.8, 61.0, 56.9, 51.6, 34.0, 29.7, 28.8, 24.6. HRMS (MALDI) Calcd for C76H18O2 [M+] 962.1307, found 962.1339.

Fabrication and Characterization of Polymer Solar Cell Devices: The ITO-coated glass substrates were washed by sequential ultrasonication in water/detergent, water, acetone, and isopropanol for 30 min in each solvent. The washed substrates were further treated with a UV-O_3 cleaner (Novascan, PSD Series digital UV ozone system) for 30 min. A topcoat layer of ZnO (The diethylzinc solution wt15% in toluene, diluted by tetrahydrofuran) was spin-coated onto the ITO substrate at a spinning rate of 5000 rpm for 30 s and then annealed in air at 150 °C for 20 min. A blend of PTB7:IC$_{60}$MA at a concentration of 10 mg/mL in Chlorobenzene (CB) with 3% DIO as additive was prepared by stiring at 80°C overnight. Before spincoating, the solution of polymer blend was cooled to room temperature then spin-coated on the top of ZnO layer at different spin rate from 1300–1700 rpm to achieve an optimal film thickness. All dried thin film was thermally annealed at 100°C for 10 min inside a N_2-filled glove box. The thickness of active layer is typically 90 nm. After that, a Molybdenum oxide interlayer (MoO_3, 20 nm) and an aluminum electrode (Al, 100 nm) were vacuum-deposited at 2.0×10^{-6} torr. The current density–voltage (J–V) characteristics were measured in air under simulated AM 1.5 solar irradiation (100 mW cm^{-2}, Newport: Oriel model 94021A). The light intensity was adjusted by using a standard silicon reference cell. The J–V characteristics of the photovoltaic cells were recorded with a $J - V$ measurement system (Keithley 236). The configuration of the shadow mask afforded four independent devices on each substrate, and each device had an active layer of ~7 mm^2. Charge-carrier mobilities (μ) were calculated from the J–V characteristics using the space-charge-limited current

(SCLC) method with the Mott-Gurney equation for the current density J_{SCLC} expressed as $J = \frac{9\varepsilon_r\varepsilon_0\mu V^2}{8L^3}$, where ε_0 is the vacuum permittivity, ε_r is the dielectric constant of the film ($\varepsilon_r = 3$ was assumed), and L is the thickness of the active layer.

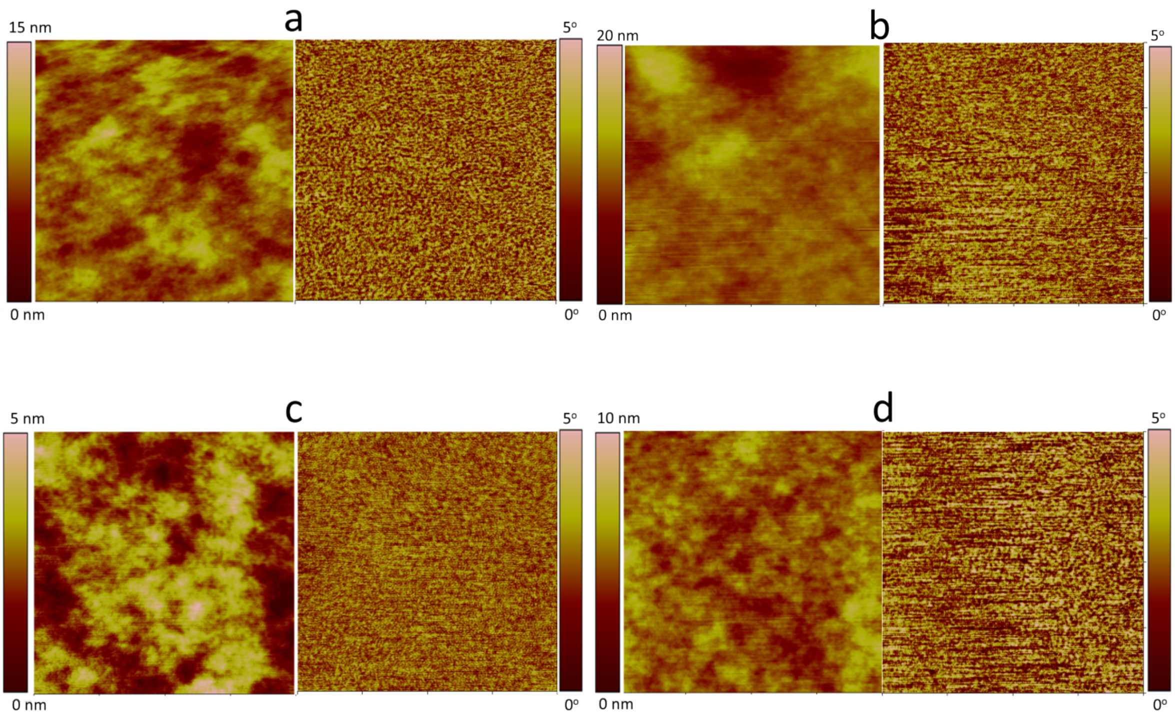


Fig S1. AFM images (1 μm x1μm) of (a) PTB7:$PC_{60}BM$ (b) PTB7:$IC_{60}MA$-2C (c) PTB7:$IC_{60}MA$-3C and (d) PTB7:$IC_{60}MA$-4C.