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Strategic end-halogenation of π-conjugated small molecules enabling fine morphological control and enhanced performance of organic solar cells

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Instrumentation and Measurements.

^{1}H and ^{13}C NMR spectra were recorded on an Avance III 400 spectrometer (Bruker). Chemical shifts of ^{1}H and ^{13}C NMR signals were quoted to tetramethylsilane (δ = 0.00) and $CDCl_3$ (δ = 77.0) as internal standards, respectively. Matrix-assisted laser desorption ionization time-of-flight (MALDI-TOF) mass spectra were collected on an Autoflex III spectrometer (Bruker Daltonics) using dithranol as a matrix. Elemental analyses were carried out using an MT-5 analyzer (Yanaco). Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) were performed using a TG/DTA7300 analyzer (Hitach High-Tech Science) and a DSC7000X analyzer (Hitachi High-Tech Science), respectively, and under N_2 atmosphere. Film thickness was measured using a Surfcorder ET150 profilometer (Kosaka Laboratory). UV–vis absorption spectra were measured with a V-670Y spectrometer (Jasco). The HOMO energy levels were determined using an AC-2 ultraviolet photoelectron yield spectrometer (Riken Keiki). The LUMO energy levels were estimated by subtracting the optical energy gap (E_g) from the measured HOMO energy levels; the E_g values were determined from the onset position of the absorption spectra. The DFT calculations were performed with the Gaussian 16 program package. Geometry optimization was carried out using the B3LYP functional with the 3-21G* basis set. The lowest excited singlet states were computed using the optimized structures with time-dependent DFT (TD-DFT) at the same level. X-ray diffraction (XRD) patterns were obtained using a SmartLab (Rigaku) with Ni-filtered CuKα radiation. Transmission electron microscopy (TEM) images were obtained using a JEM-2010 transmission electron microscope (JEOL) at an accelerating voltage of 120 keV. The spin-coated thin films on mica were peeled from substrates by soaking in water and then transferred onto copper grids for the TEM observations. The spin-coated thin films on mica were peeled from the substrates by soaking in water and then transferred onto copper grids for the TEM observations. Contact angle measurements were conducted on a DMs-401 contact angle meter (Kyowa Interface Science). A liquid droplet (1 μL) of each probe solvent was applied on the surface of the thin-film sample on a quartz substrate and left 1 s before measuring. The contact angles were averaged over five different measurements.

Materials.

All commercially available reagents and solvents were used without further purification unless otherwise noted. PFN-Br was purchased from 1-Material. Ethanolamine and 2-methoxyethanol were purchased from Sigma-Aldrich, and zinc acetate was purchased from Fujifilm Wako Pure Chemical Corp. $PC_{71}BM$ was purchased from Frontier Carbon Corp. PEDOT:PSS (Clevios AI 4083) was purchased from Heraeus. 2,6-Bis(trimethylstannyl)-4,8-bis[5-(2-butyloctyl)thiophen-2-yl]benzo[1,2-*b*:4,5-*b*']dithiophene (**6**) was purchased from SunaTech Inc. 5'-Bromo-3,4'-

dihexyl-[2,2'-bithiophene]-5-carbaldehyde (**7**) was prepared according to our previous work.[S1] All reactions were carried out under a nitrogen atmosphere in dry solvents using standard Schlenk techniques.

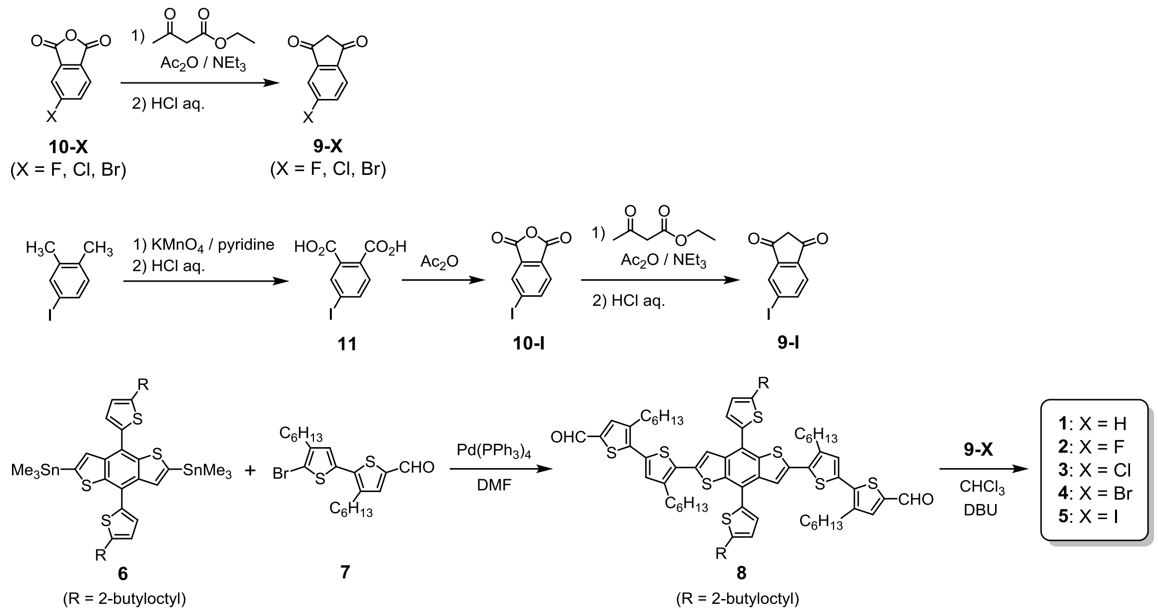
OSC Device Fabrication and Evaluation.

Prepatterned ITO-coated glass substrates were cleaned sequentially by sonicating in detergent solution, deionized water, acetone, and isopropyl alcohol for 10 min each, and then subjected to UV/ozone treatment for 15 min. A thin layer (~30 nm) of ZnO was prepared by spin-coating (at 5000 rpm for 60 s) a precursor solution of zinc acetate (1.00 g) and ethanolamine (0.28 g) in 2-methoxyethanol (10 mL) through a 0.20 µm polyethylene membrane filter, followed by baking at 200 °C for 10 min under air. A solution of PFN-Br in methanol (1.0 mg mL^{-1}) was spin-coated (at 5000 rpm for 60 s) on the ZnO surface to form an interfacial layer. The photoactive layer was then deposited by spin-coating from a chloroform solution containing a donor (9.3 mg mL^{-1}) and $PC_{71}BM$ (4.6 mg mL^{-1}) after passing through a 0.45 µm poly(tetrafluoroethylene) membrane filter. The thickness of the photoactive layer was ca. 70–80 nm, measured with a profilometer. The thin films were then loaded into an E-200 vacuum evaporation system (ALS Technology). Finally, 10-nm-thick MoO_3 and 100-nm-thick Ag layers were sequentially vacuum-deposited on top of the photoactive layer under high vacuum ($<5.0 \times 10^{-4}$ Pa) through a shadow mask, defining an active area of 0.04 cm^2 for each device. The current density–voltage (*J*–*V*) characteristics and EQE spectra of the fabricated OSCs were measured with a computer-controlled Keithley 2400 source measure unit in air, under simulated AM 1.5G solar illumination at 100 mW cm^{-2} (1 sun) conditions, using a Xe lamp-based SRO-25GD solar simulator and IPCE measurement system (Bunko Keiki). The light intensity was calibrated using a certified silicon photovoltaic reference cell. For testing the OSCs under various light intensities (0.01–1 sun), the intensity of the incident light was modulated with a set of neutral density filters.

Carrier Mobility Measurements.

The mobility measurements on the pristine neat films and BHJ blend films were carried out using the following diode structure: ITO/PEDOT:PSS (30 nm)/**1–5** or **1–5**:$PC_{71}BM$ layer/MoO_x (10 nm)/Ag (100 nm) for hole mobility; dark *J*−*V* curves were recorded over a voltage range of 0–10 V. The charge carrier mobilities were calculated using the SCLC model: $J = (9/8)\varepsilon_0\varepsilon_r\mu(V^2/L^3)$, where ε_0 is the permittivity of free space (8.85×10^{-14} C V^{-1} cm^{-1}), ε_r is the relative dielectric constant of the transport medium (assumed to be 3.0), μ is the hole mobility, and L is the thickness of the active layer.

Synthesis.



Scheme S1 Synthetic routes for **1–5**.

5-Fluoroindan-1,3-dione (9-F): To a stirred solution of 5-fluorophthalic anhydride (**10-F**, 6.98 g, 42.0 mmol) in acetic anhydride (16.8 mL) and triethylamine (9.1 mL) was added ethyl acetoacetate (6.01 g, 46.2 mmol). The mixture was stirred overnight at room temperature. The reaction mixture was then slowly poured into a mixture of ice-water (20 mL) and concentrated HCl (48 mL). After that, the mixture was stirred for 20 min at 80 °C. After cooling to room temperature, the product was extracted with chloroform. The combined organic layer was dried over anhydrous Na_2SO_4. After filtration and evaporation, the product was purified by silica gel column chromatography (eluent: chloroform), recrystallized from chloroform/hexane, and dried under vacuum to afford **9-F** as a pale yellow solid (yield = 3.63 g, 53%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.03–8.00 (m, 1H), 7.61–7.59 (m, 1H), 7.53 (td, J = 8.5, 2.3 Hz, 1H), 3.28 (s, 2H). MS (MALDI-TOF): *m*/*z* calcd 163.02 $[M-H]^-$; found 162.38.

5-Chloroindan-1,3-dione (9-Cl): This compound was prepared by a similar method to that of **9-F**, using 5-chlorophthalic anhydride (**10-Cl**, 7.30 g, 40.0 mmol) and ethyl acetoacetate (5.73 g, 44.0 mmol). The product was purified by silica gel column chromatography (eluent: chloroform), recrystallized from chloroform/hexane, and dried under vacuum to afford **9-Cl** as a pale yellow solid (yield = 5.14 g, 71%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.94 (s, 1H), 7.93 (d, J = 9.8 Hz 1H), 7.80 (dd, J = 8.2, 1.9 Hz, 1H), 3.27 (s, 2H). MS (MALDI-TOF): *m*/*z* 178.99 $[M-H]^-$; found 178.55.

5-Bromoindan-1,3-dione (9-Br): This compound was prepared by a similar method to that of **9-F**, using 5-bromophthalic anhydride (**10-Br**, 6.81 g, 30.0 mmol) and ethyl acetoacetate (4.29 g, 33.0 mmol). The product was purified by silica gel column chromatography (eluent: chloroform), recrystallized from chloroform/hexane, and dried under vacuum to afford **9-Br** as a pale yellow solid (yield = 5.06 g, 75%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.12 (d, J = 1.8 Hz, 1H), 7.96 (dd, J = 8.0, 1.8 Hz, 1H), 7.85 (d, J = 8.0 Hz, 1H), 3.26 (s, 2H). MS (MALDI-TOF): *m*/*z* 222.94 $[M-H]^-$; found 222.62.

4-Iodophthalic acid (11): To a stirred solution of 4-iodo-1,2-dimethylbenzene (3.48 g, 15.0 mmol) in pyridine (31.5 mL) and distilled water (66 mL) was added potassium permanganate ($KMnO_4$, 23.7 g, 150 mmol). The mixture was refluxed for 24 h. The hot reaction mixture was filtered, and the residual solid was washed with KOH aq. (1 M, 100 mL). The filtrate was acidified with concentrated HCl to pH 1–2. The product was extracted with ethyl acetate, and the organic layer was dried over anhydrous Na_2SO_4. After filtration and evaporation, **11** was obtained as a white solid (yield = 3.58 g, 82%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.22 (d, J = 1.8 Hz, 1H), 7.99 (dd, J = 8.3, 1.8 Hz, 1H), 7.64 (d, J = 8.0 Hz, 1H). MS (MALDI-TOF): *m*/*z* 290.92 $[M-H]^-$; found 290.81.

5-Iodophthalic anhydride (10-I): The mixture of **11** (3.42 g, 11.7 mmol) in acetic anhydride (50 mL) was stirred overnight at 100 °C. After removal of the solvent, **10-I** was obtained as a yellow solid without any other purifications (yield = 2.94 g, 92%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.38 (d, J = 1.0 Hz, 1H), 8.26 (dd, J = 8.0, 1.5 Hz, 1H), 7.73 (d, J = 8.3 Hz, 1H). MS (MALDI-TOF): *m*/*z* 272.91 $[M-H]^-$; found 272.50.

5-Iodoindan-1,3-dione (9-I): This compound was prepared by a similar method to that of **9-F**, using **10-I** (1.51 g, 5.50 mmol) and ethyl acetoacetate (0.787 g, 6.05 mmol). The product was purified by silica gel column chromatography (eluent: chloroform), recrystallized from chloroform/hexane, and dried under vacuum to afford **9-I** as a pale yellow solid (yield = 1.06 g, 71%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.36 (t, J = 0.8 Hz, 1H), 8.18 (dd, J = 8.0, 1.5 Hz, 1H), 7.70 (dd, J = 8.0, 0.5 Hz, 1H), 3.23 (s, 2H). MS (MALDI-TOF): *m*/*z* 270.93 $[M-H]^-$; found 269.84.

5',5'''-(4,8-bis(5-(2-butyloctyl)thiophen-2-yl)benzo[1,2-b:4,5-b']dithiophene-2,6-diyl)bis(3,4'-dihexyl-[2,2'-bithiophene]-5-carbaldehyde) (8): To a stirred solution of 2,6-Bis(trimethylstannyl)-4,8-bis[5-(2-butyloctyl)thiophen-2-yl]benzo[1,2-*b*:4,5-*b*']dithiophene (**6**, 1.83 g, 1.80 mmol) and 5'-bromo-3,4'-dihexyl-[2,2'-bithiophene]-5-carbaldehyde (**7**,[S1] 1.67 g, 3.78 mmol) in dry DMF (20 mL) were added Pd(PPh$_3$)$_4$ (83 mg, 0.072 mmol). The solution was N$_2$-bubbled for 5 min and then stirred overnight at 80 °C. After cooling to room temperature, the reaction mixture was poured into methanol, and the formed precipitate was collected by filtration. The product was purified by silica gel column chromatography (eluent: chloroform), recrystallized from chloroform/methanol, and dried under vacuum to afford **8** as a red solid (yield = 2.20 g, 87%). ^{1}H NMR (400 MHz, CDCl$_3$): δ 9.83 (s, 2H), 7.70 (s, 2H), 7.59 (s, 2H), 7.35 (d, J = 3.5 Hz, 2H), 7.14 (s, 2H), 6.91 (d, J = 3.5 Hz, 2H), 2.88–2.80 (m, 12H), 1.72–1.65 (m, 10H), 1.38–1.28 (m, 56H), 0.92–0.84 (m, 24H). MS (MALDI-TOF): *m*/*z* 1411.67 [M+H]$^+$; found 1411.14.

BDT-ID-H (1): To a stirred solution of **8** (212 mg, 0.15 mmol) and 1,3-indandione (**9-H**, 46 mg, 0.31 mmol) in chloroform (3 mL) was added 1,8-diazabicyclo[5.4.0]undec-7-ene (1 drop). The mixture was stirred overnight at 60 °C. After cooling to room temperature, the reaction mixture was directly purified by silica gel column chromatography (eluent: chloroform), recrystallized from chloroform/methanol, and dried under vacuum to afford **1** as a black solid. This material was further purified by recycling preparative GPC (eluent: chloroform) prior to use (yield = 229 mg, 91%). ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.98–7.94 (m, 4H), 7.88 (s, 2H), 7.79–7.76 (m, 6H), 7.72 (s, 2H), 7.38 (d, J = 3.5 Hz, 2H), 7.32 (s, 2H), 6.94 (d, J = 3.5 Hz, 2H), 2.90–2.84 (m, 12H), 1.76–1.67 (m, 10H), 1.44–1.28 (m, 56H), 0.93–0.84 (m, 24H). ^{13}C NMR (125 MHz, CDCl$_3$): δ 190.53, 189.91, 146.20, 145.57, 145.02, 142.20, 142.06, 141.08, 140.68, 139.30, 137.16, 136.94, 136.72, 135.86, 135.11, 134.90, 134.79, 134.48, 133.80, 131.14, 128.06, 125.72, 123.96, 123.69, 123.10, 122.92, 122.21, 40.20, 34.91, 33.62, 33.20, 32.11, 31.84, 31.82, 30.74, 30.18, 29.90, 29.83, 29.52, 29.36, 29.07, 26.84, 23.24, 22.88, 22.85, 22.80, 14.38, 14.33, 14.31, 14.29. MS (MALDI-TOF): *m*/*z* 1667.72 [M+H]$^+$; found 1667.22. Anal. calcd (%) for $C_{102}H_{122}O_4S_8$: C 73.42, H 7.37; found: C 73.53, H 7.42.

BDT-ID-F (2): This compound was prepared by a similar method to that of **1**, using **8** (706 mg, 0.50 mmol) and **9-F** (181 mg, 1.10 mmol). The product was purified by silica gel column chromatography (eluent: chloroform), recrystallized from chloroform/methanol, and dried under vacuum to afford **2** as a black solid. This material was further purified by recycling preparative GPC (eluent: chloroform) prior to use (yield = 592 mg, 69%). ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.98–7.94 (m, 2H), 7.86 (d, J = 4.0 Hz, 2H), 7.79 (d, J = 4.3 Hz, 2H), 7.72 (s, 2H), 7.59–7.56 (m, 2H), 7.42 (tt, J = 8.5, 2.6 Hz, 2H), 7.38 (d, J = 3.5 Hz, 2H), 7.32 (s, 2H), 6.94 (d, J = 3.3 Hz, 2H), 2.90–2.84 (m, 12H), 1.76–1.67 (m, 10H), 1.44–1.28 (m, 56H), 0.93–0.84 (m, 24H). ^{13}C NMR

(125 MHz, $CDCl_3$): δ 189.23, 188.97, 188.49, 188.42, 166.15, 166.02, 146.23, 145.96, 145.83, 145.65, 145.48, 142.12, 141.23, 141.20, 139.32, 138.30, 137.17, 136.91, 136.76, 136.69, 136.23, 136.15, 134.70, 134.56, 134.38, 134.02, 131.26, 128.08, 125.73, 123.77, 123.71, 122.52, 122.33, 122.26, 122.16, 110.04, 109.93, 109.86, 109.75, 40.21, 34.91, 33.63, 33.20, 32.11, 31.85, 31.82, 30.74, 30.16, 29.90, 29.83, 29.53, 29.36, 29.07, 26.85, 23.25, 22.88, 22.85, 22.80, 14.38, 14.33, 14.31, 14.29. MS (MALDI-TOF): *m*/*z* 1703.70 $[M+H]^+$; found 1703.58. Anal. calcd (%) for $C_{102}H_{120}F_2O_4S_8$: C 71.87, H 7.10; found: C 71.80, H 7.13.

BDT-ID-Cl (3): This compound was prepared by a similar method to that of **1**, using **8** (706 mg, 0.50 mmol) and **9-Cl** (199 mg, 1.10 mmol). The product was purified by silica gel column chromatography (eluent: chloroform), recrystallized from chloroform/methanol, and dried under vacuum to afford **3** as a black solid. This material was further purified by recycling preparative GPC (eluent: chloroform) prior to use (yield = 307 mg, 35%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.89–7.85 (m, 6H), 7.79 (d, *J* = 4.3 Hz, 2H), 7.72–7.68 (m, 4H), 7.38 (d, *J* = 3.3 Hz, 2H), 7.31 (s, 2H), 6.94 (d, *J* = 3.3 Hz, 2H), 2.90–2.83 (m, 12H), 1.76–1.67 (m, 10H), 1.44–1.28 (m, 56H), 0.93–0.84 (m, 24H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 189.25, 189.17, 188.62, 188.40, 146.22, 146.03, 145.95, 145.85, 145.78, 143.47, 142.09, 141.98, 141.72, 141.55, 141.25, 141.22, 140.19, 139.26, 138.68, 137.16, 136.91, 136.67, 136.49, 135.07, 134.89, 134.69, 134.64, 134.32, 134.11, 131.31, 128.09, 125.72, 124.37, 124.20, 123.68, 123.40, 123.21, 123.08, 122.20, 40.21, 34.92, 33.64, 33.21, 32.12, 31.85, 31.82, 30.72, 30.13, 29.92, 29.88, 29.55, 29.37, 29.08, 26.86, 23.26, 22.89, 22.87, 22.82, 14.39, 14.34, 14.32. MS (MALDI-TOF): *m*/*z* 1735.64 $[M+H]^+$; found 1736.04. Anal. calcd (%) for $C_{102}H_{120}Cl_2O_4S_8$: C 70.51, H 6.96; found: C 70.29, H 6.96.

BDT-ID-Br (4): This compound was prepared by a similar method to that of **1**, using **8** (706 mg, 0.50 mmol) and **9-Br** (236 mg, 1.05 mmol). The product was purified by silica gel column chromatography (eluent: chloroform), recrystallized from chloroform/methanol, and dried under vacuum to afford **4** as a black solid. This material was further purified by recycling preparative GPC (eluent: chloroform) prior to use (yield = 490 mg, 54%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.06 (t, *J* = 1.6 Hz, 2H), 7.89–7.85 (m, 4H), 7.82–7.78 (m, 4H), 7.72 (d, *J* = 1.0 Hz, 2H), 7.38 (d, *J* = 3.5 Hz, 2H), 7.32 (s, 2H), 6.94 (d, *J* = 3.5 Hz, 2H), 2.90–2.83 (m, 12H), 1.76–1.67 (m, 10H), 1.44–1.28 (m, 55H), 0.93–0.84 (m, 24H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 189.43, 189.07, 188.80, 188.29, 146.22, 146.06, 145.97, 145.90, 145.84, 143.41, 142.09, 141.93, 141.26, 141.23, 140.56, 139.26, 139.05, 137.96, 137.78, 137.16, 136.91, 136.67, 136.56, 134.70, 134.67, 134.31, 134.13, 131.32, 130.28, 130.08, 128.10, 126.26, 126.14, 125.72, 124.45, 124.30, 123.68, 123.21, 122.21, 40.21, 34.93, 33.64, 33.21, 32.12, 31.85, 31.82, 30.71, 30.12, 29.92, 29.88, 29.56, 29.37, 29.08, 26.86, 23.26, 22.89, 22.87, 22.82, 14.39, 14.34, 14.32. MS (MALDI-TOF): *m*/*z* 1823.54 [M+H]$^+$; found 1822.94. Anal. calcd (%) for $C_{102}H_{120}Br_2O_4S_8$: C 67.08, H 6.62; found: C 67.13, H 6.62.

BDT-ID-I (5): This compound was prepared by a similar method to that of **1**, using **8** (636 mg, 0.450 mmol) and **9-I** (269 mg, 0.990 mmol). The product was purified by silica gel column chromatography (eluent: chloroform), recrystallized from chloroform/methanol, and dried under vacuum to afford **5** as a black solid. This material was further purified by recycling preparative GPC (eluent: chloroform) prior to use (yield = 806 mg, 93%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.30 (q, *J* = 1.5 Hz, 2H), 8.11–8.08 (m, 2H), 7.88 (q, *J* = 1.5 Hz, 2H), 7.81 (s, 2H), 7.72 (d, *J* = 2.5 Hz, 2H), 7.66 (m, 2H), 7.38–7.37 (m, 2H), 7.32 (d, *J* = 1.3 Hz, 2H), 6.94 (d, *J* = 5.8 Hz, 2H), 2.90–2.84 (m, 12H), 1.73 (dd, *J* = 15.1, 7.0 Hz, 10H), 1.44–1.28 (m, 56H), 0.93–0.84 (m, 24H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 189.76, 189.11, 189.04, 188.26, 146.22, 146.06, 145.96, 145.88, 145.84, 143.88, 143.69, 143.07, 142.09, 141.59, 141.27, 141.11, 139.58, 139.26, 137.16, 136.92, 136.68, 136.59, 136.54, 134.75, 134.33, 134.14, 132.27, 132.20, 131.34, 128.10, 125.73, 124.31, 124.16, 123.68, 122.97, 122.21, 102.88, 102.62, 40.21, 34.92, 33.63, 33.20, 32.12, 31.85, 31.82, 30.71, 30.12, 29.92, 29.88, 29.55, 29.36, 29.07, 26.85, 23.26, 22.89, 22.87, 22.81, 22.70, 14.39, 14.32, 14.30. MS (MALDI-TOF): *m*/*z* 1920.51 [M+H]$^+$; found 1920.97. Anal. calcd (%) for $C_{102}H_{120}I_2O_4S_8$: C 63.80, H 6.30; found: C 63.80, H 6.24.

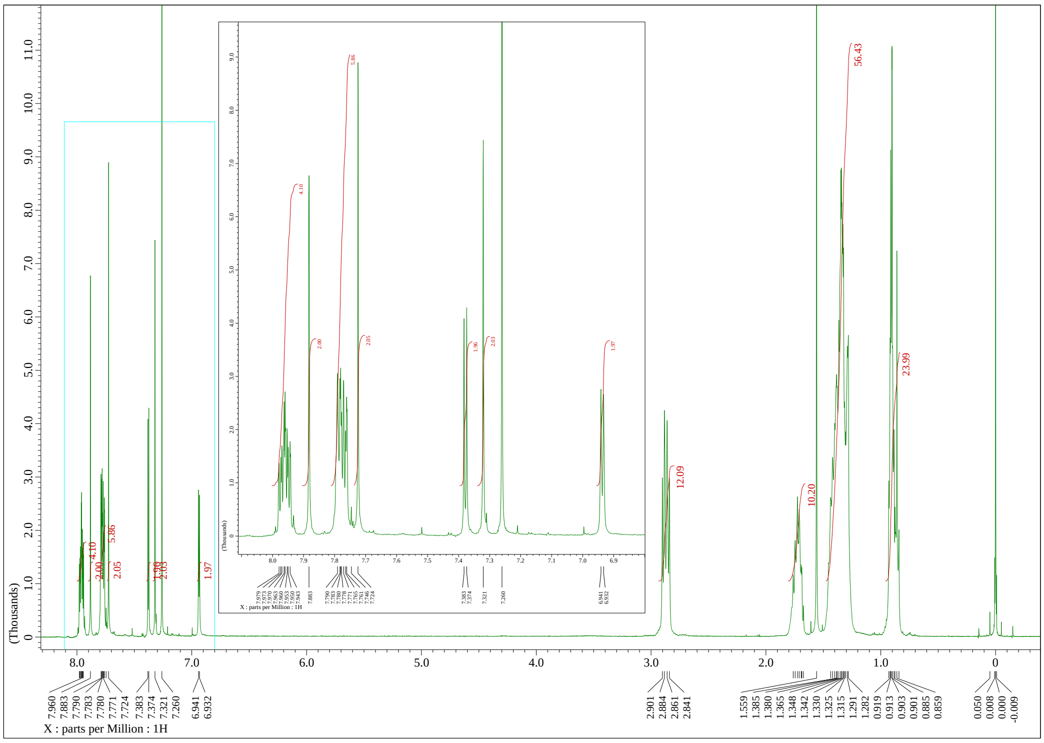


Fig. S1 ^{1}H NMR spectrum of **1** in $CDCl_3$.

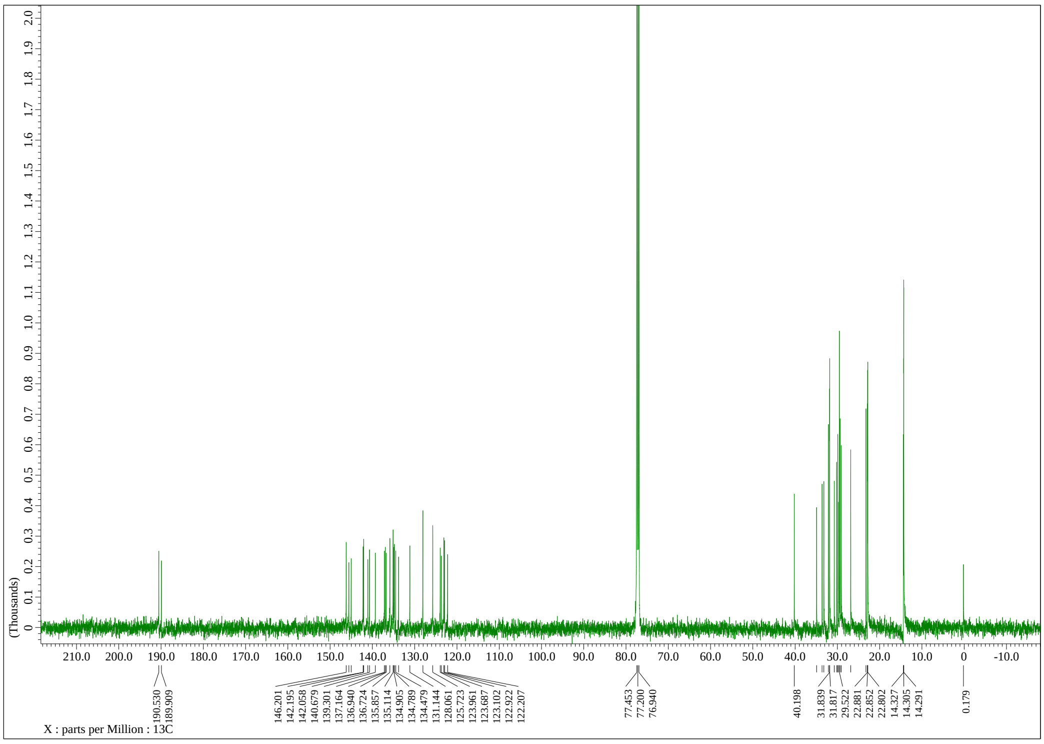


Fig. S2 ^{13}C NMR spectrum of **1** in $CDCl_3$.

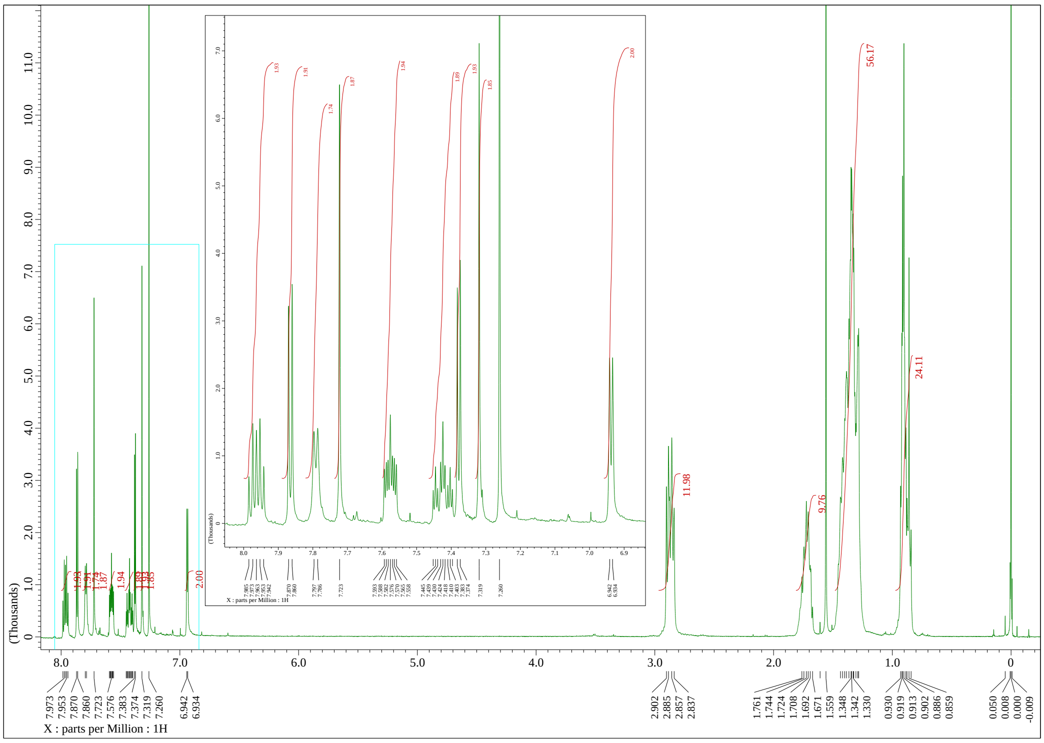


Fig. S3 ^{1}H NMR spectrum of **2** in $CDCl_3$.

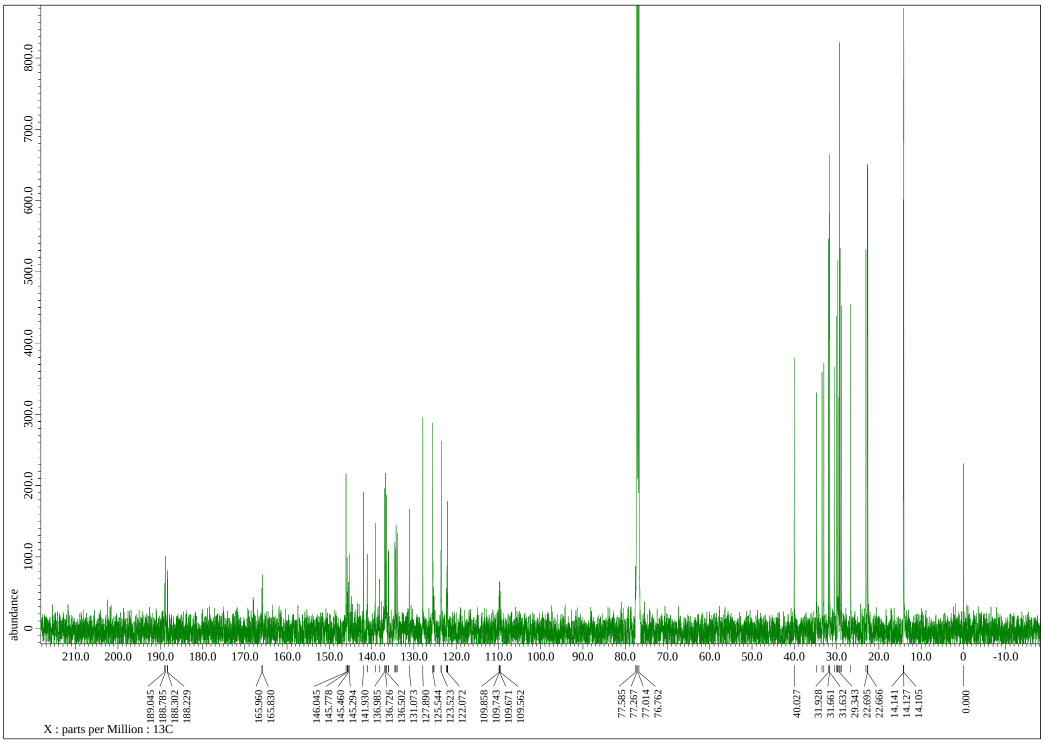


Fig. S4 ^{13}C NMR spectrum of **2** in $CDCl_3$.

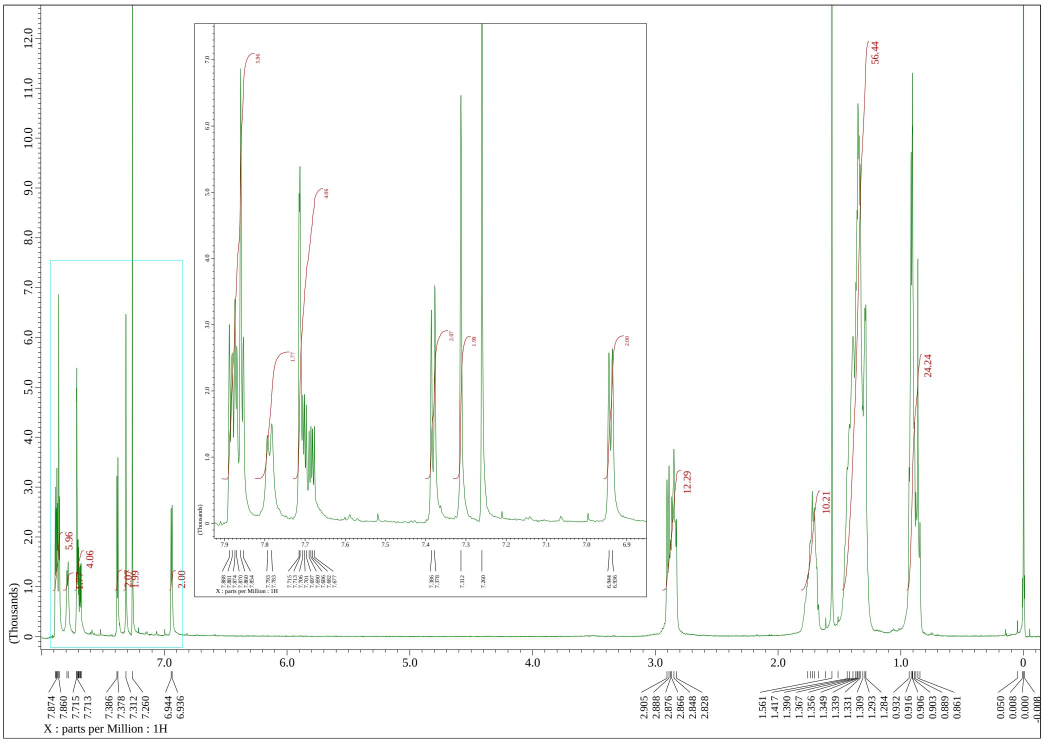


Fig. S5 ^{1}H NMR spectrum of **3** in $CDCl_3$.

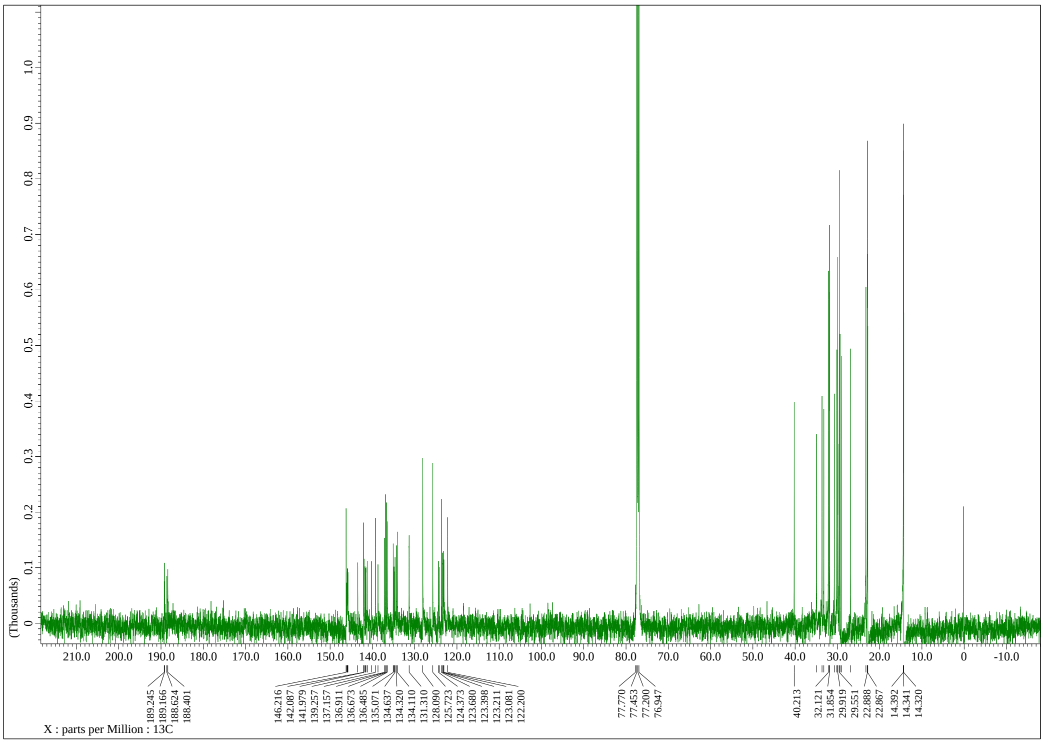


Fig. S6 ^{13}C NMR spectrum of **3** in $CDCl_3$.

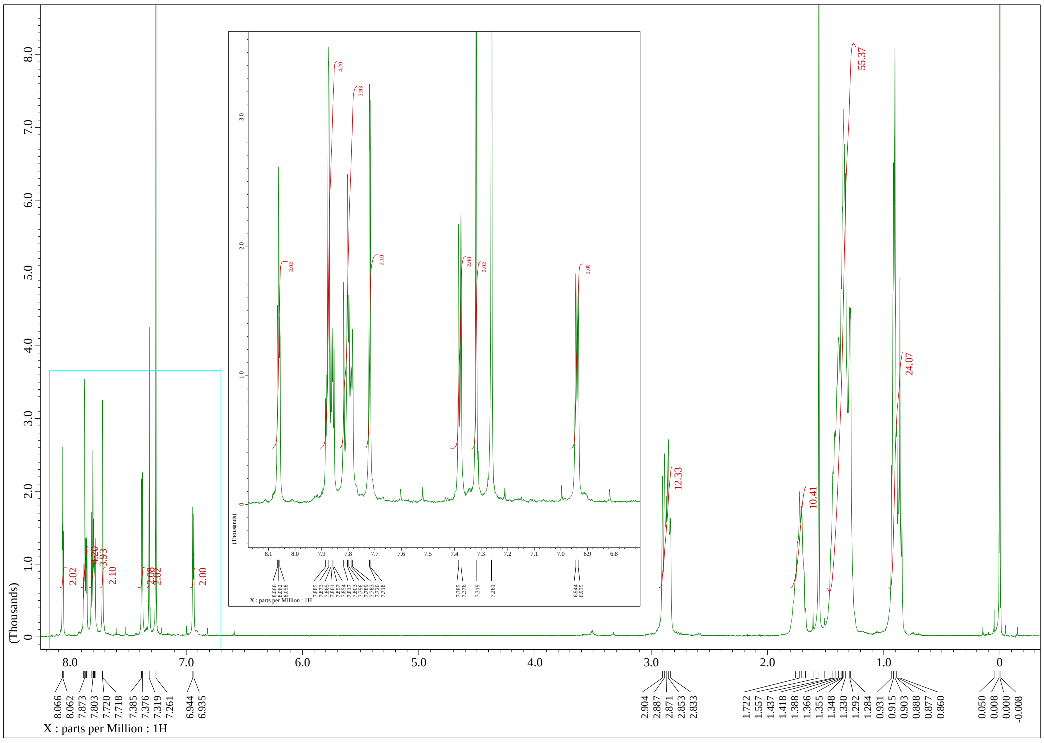


Fig. S7 ^{1}H NMR spectrum of **4** in $CDCl_3$.

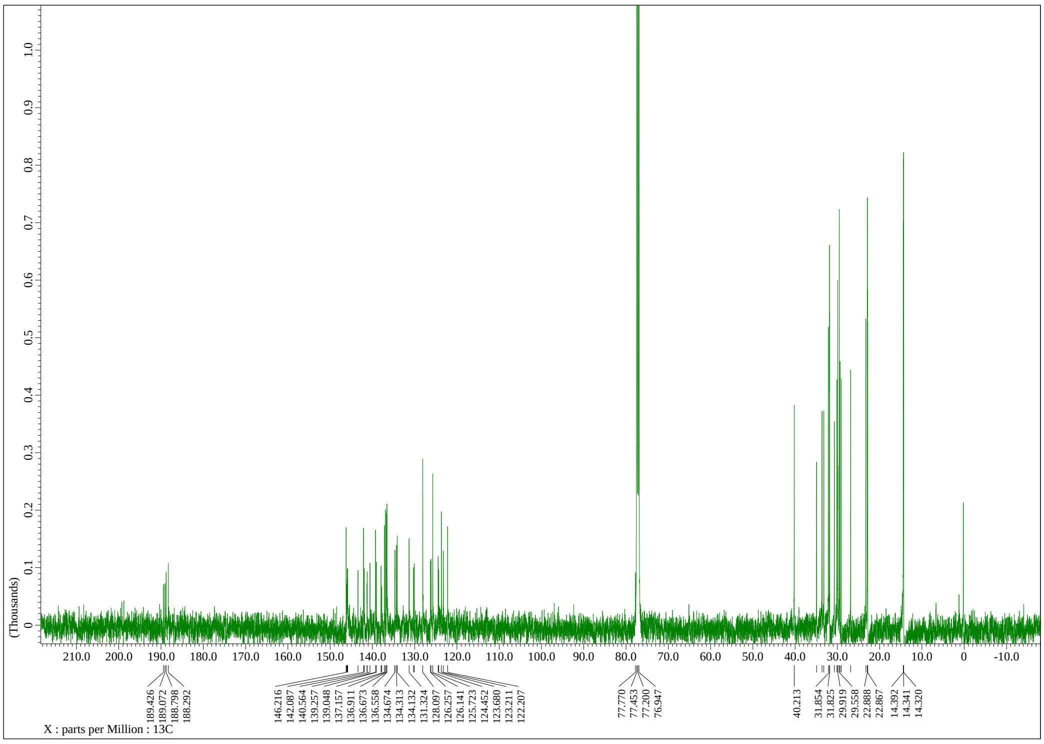


Fig. S8 ^{13}C NMR spectrum of **4** in $CDCl_3$.

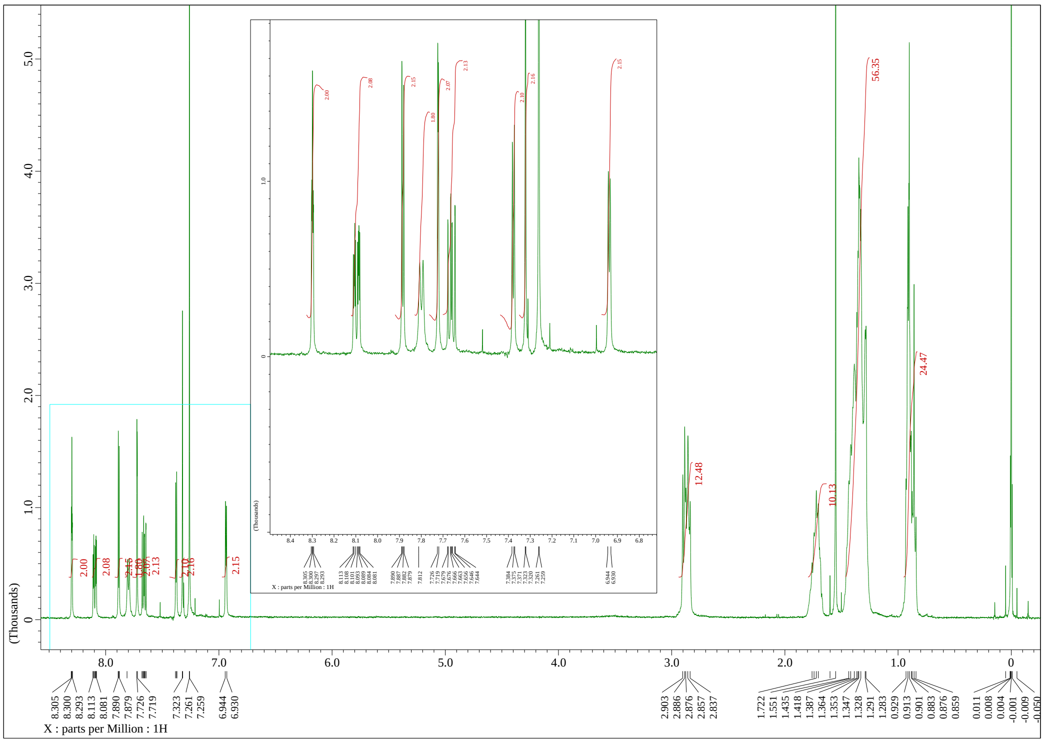


Fig. S9 ^{1}H NMR spectrum of **5** in CDCl$_3$.

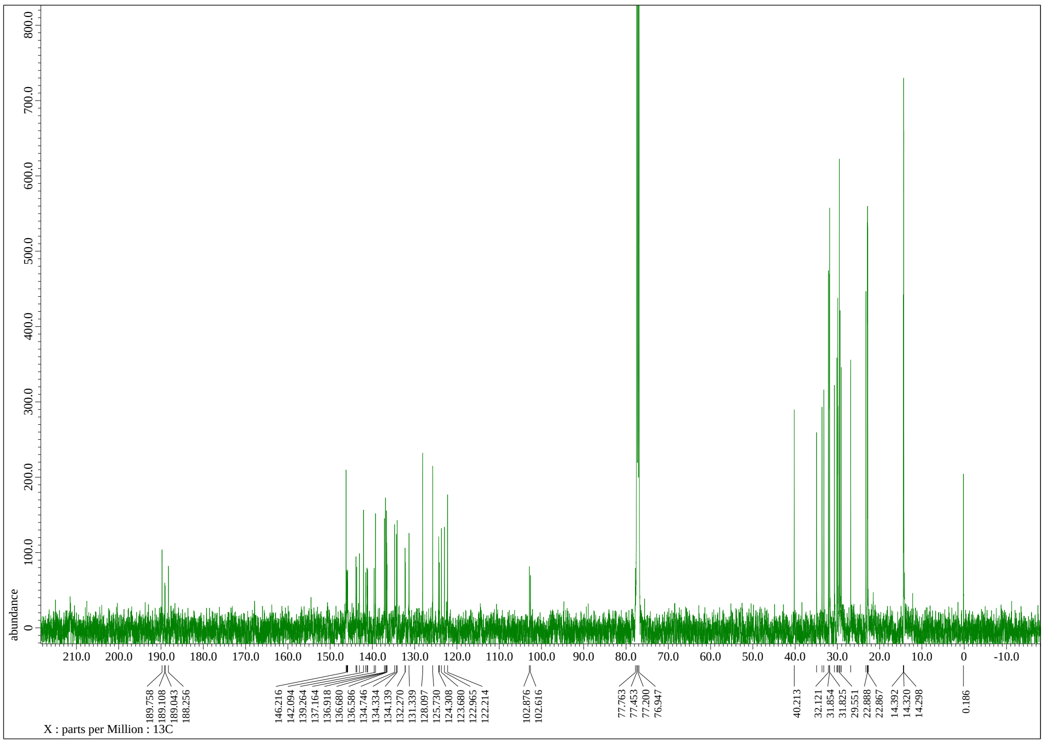


Fig. S10 ^{13}C NMR spectrum of **5** in CDCl$_3$.

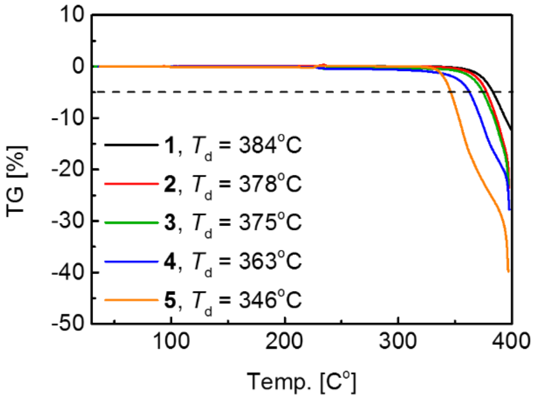


Fig. S11 TGA curves of **1–5** at a scanning rate of 10 °C min^{-1} under N$_2$.

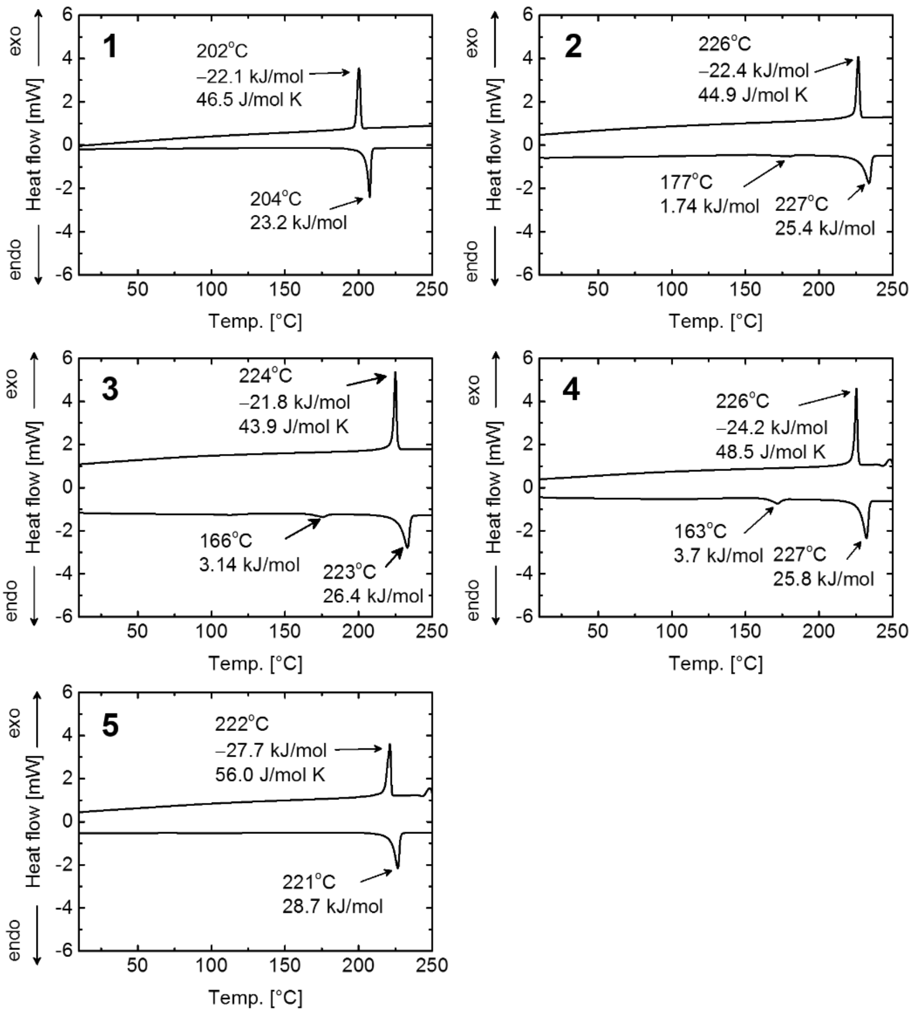


Fig. S12 DSC thermograms of **1–5** at a scanning rate of 10 °C min^{-1} under N$_2$.

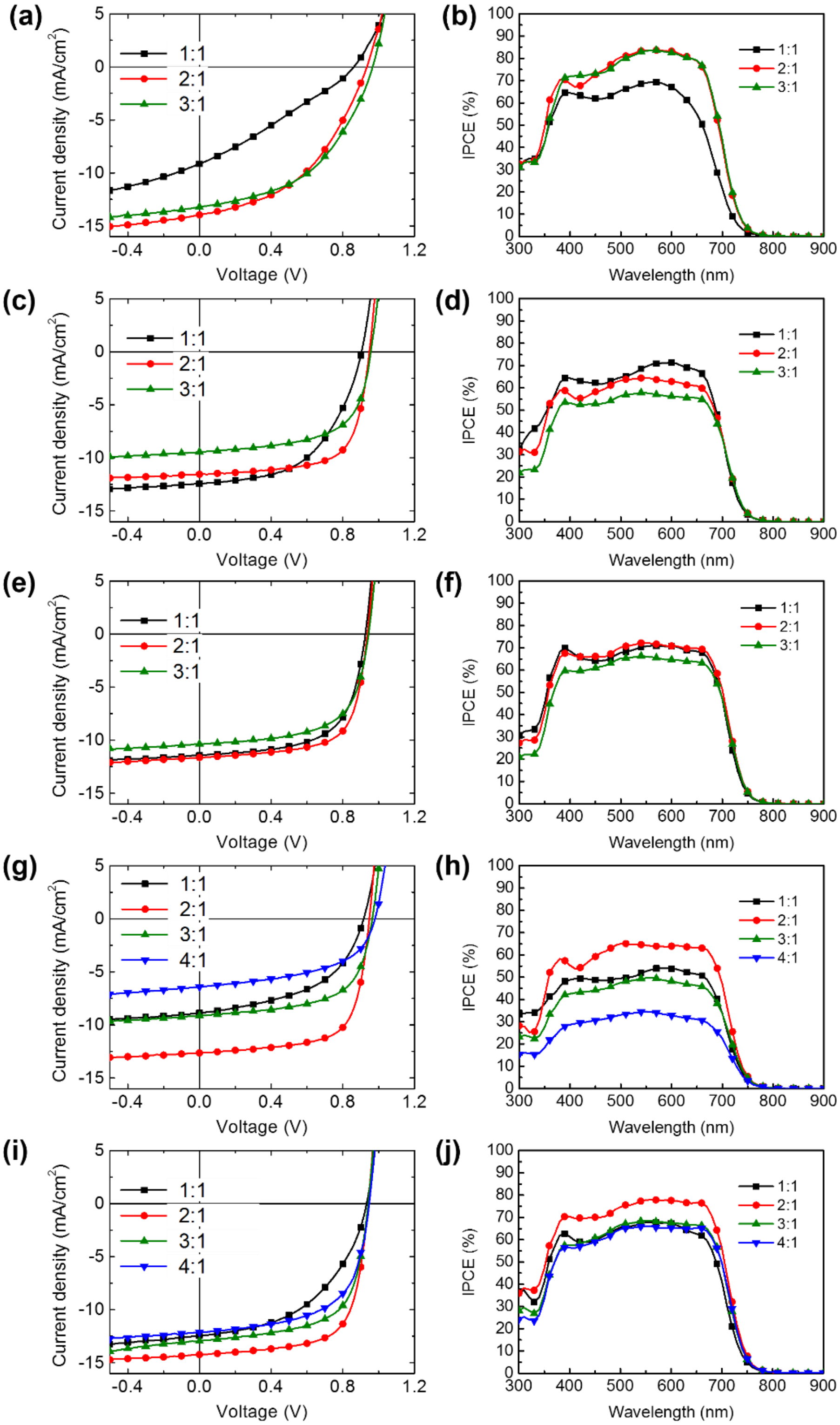


Fig. S12 *J*–*V* characteristics under one sun illumination (left panels) and IPCE spectra (right panels) for SM-OSCs based on (a,b) **1**:PC$_{71}$BM, (c,d) **2**:PC$_{71}$BM, (e,f) **3**:PC$_{71}$BM, (g,h) **4**:PC$_{71}$BM, and (I,j) **5**:PC$_{71}$BM with different D/A blend ratios (w/w).

Table S1 Photovoltaic parameters for SM-OSCs based on **1–5**:PC$_{71}$BM with different D/A blend ratios (w/w) under one sun illumination (100 mW/cm^2, AM 1.5G)

donor[a]	D:A[b]	thickness [nm]	J_{sc} [mA cm^{-2}]	V_{oc} [V]	FF [%]	PCE [%)]
1	1:1	72	9.1	0.86	28	2.2
	2:1	77	14.0	0.93	45	5.9
	3:1	68	13.3	0.96	48	6.1
2	1:1	74	12.4	0.90	53	6.0
	2:1	77	11.5	0.94	68	7.5
	3:1	67	9.4	0.96	62	5.6
3	1:1	61	11.4	0.93	63	6.6
	2:1	80	11.6	0.94	68	7.4
	3:1	66	10.4	0.94	63	6.1
4	1:1	85	8.9	0.92	50	4.1
	2:1	74	12.6	0.95	69	8.2
	3:1	82	9.1	0.96	62	5.4
	4:1	79	6.4	0.98	52	3.3
5	1:1	65	12.5	0.93	49	5.7
	2:1	78	14.2	0.94	68	9.2
	3:1	77	13.0	0.94	64	7.8
	4:1	64	12.1	0.95	60	6.9

[a] Device structure: ITO/ZnO (30 nm)/PFN-Br/donor:PC$_{71}$BM/MoO$_x$ (10 nm)/Ag (100 nm); [b] Donor/acceptor blend ratio (w/w).

Table S2 XRD data for neat films of **1–5** (left) and blend films of **1–5**:PC$_{71}$BM (2:1, w/w; right)

film	index	q [Å^{-1}]	d [Å]	L[a] [nm]	film	index	q [Å^{-1}]	d [Å]	L[a] [nm]
1	(100)	0.331	19.0	30	**1**:PC$_{71}$BM	(100)	0.343	18.3	18
	(200)	0.666	9.4	-		(200)	0.680	9.2	-
	(300)	1.00	6.2	-		(300)	1.02	6.1	-
2	(100)	0.324	19.4	14	**2**:PC$_{71}$BM	(100)	0.329	19.1	14
3	(100)	0.320	19.6	13	**3**:PC$_{71}$BM	(100)	0.328	19.2	14
4	(100)	0.329	19.1	12	**4**:PC$_{71}$BM	(100)	0.334	18.8	14
5	(100)	0.329	19.1	12	**5**:PC$_{71}$BM	(100)	0.343	18.3	13

[a] Coherence length (or crystallite size) of lamellar domains estimated using the Sherrer equation: $L = (K\lambda)/(\beta\cos\theta)$, where K is the shape factor (assumed to be 0.89), λ is the incident X-ray wavelength, β is full-width at half-maximum (FWHM) in radians, and θ is the diffraction angle.

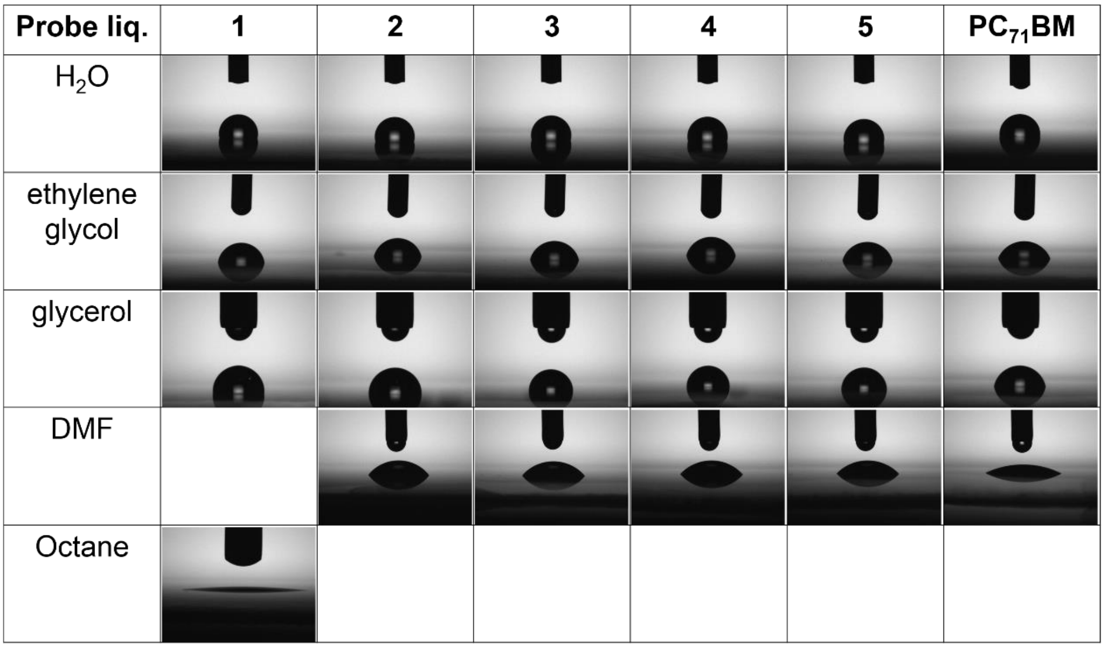


Fig. S14 Optical images of the contact angles between neat films of **1**–**5** (or PC$_{71}$BM) and the droplet of different probe liquid.

Table S3 Summary of the contact angle data

probe liquid	γ_{L} a) [mJ m^{-2}]		contact angle b) [°]					
	$\gamma_{\mathrm{L}}^{\mathrm{d}}$	$\gamma_{\mathrm{L}}^{\mathrm{p}}$	**1**	**2**	**3**	**4**	**5**	PC$_{71}$BM
H_2O	21.8	51.0	102.9	103.8	103.7	103.4	102.0	94.1
ethylene glycol	29.0	19.0	79.8	75.0	74.6	74.0	73.0	61.6
glycerol	34.0	30.0	94.5	88.8	89.3	88.0	86.9	77.1
DMF	32.4	4.9	– c)	50.4	48.4	46.7	45.3	25.3
octane	21.8	0.0	5.3	– c)	– c)	– c)	– c)	– c)

a) Surface free energy of each probe liquid consisting of dispersive and polar components ($\gamma_{\mathrm{L}}^{\mathrm{d}}$ and $\gamma_{\mathrm{L}}^{\mathrm{p}}$), see ref. S2; b) Average values over five different measurements. c) Not determined.

References

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[S2] (a) D. K. Owens and R. C. Wendt, *J. Appl. Polym. Sci.*, 1969, **13**, 1741; (b) M. Mantel and J. P. Wightman, *Surf. Interface Anal.*, 1994, **21**, 595.