

Supporting Information

Deterioration of Bulk Heterojunction Organic Photovoltaic Devices by a Minute Amount of Oxidized Fullerene

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1. Synthetic procedure

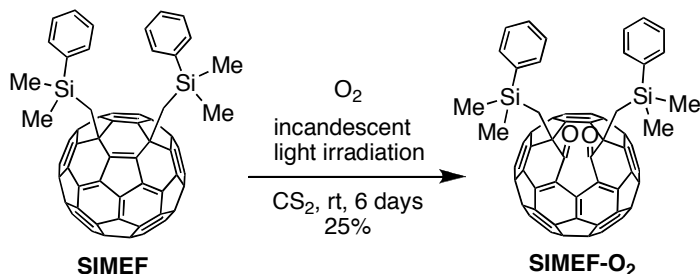
General. The reaction was carried out under air atmosphere. Incandescent lamp equipped with a 60 W, 110 V bulb was used in this study. Analysis with high pressure liquid chromatography (HPLC) was performed on a Shimadzu LC-10A system equipped with SPD-M10A diode array detector and RPFULLERENE column (Nomura Chemical, 4.6 mm ID × 250 mm). Preparative HPLC was performed on an RPFULLERENE column (Nomura Chemical, 20 mm ID × 250 mm) using toluene/acetonitrile (55/45) as eluent (flow rate 8 mL/min, detected at 350 nm with an UV spectrophotometric detector, Shimadzu SPD-6A). NMR spectra were measured on JEOL ECA-500 spectrometer. Spectra were reported in parts per million from tetramethylsilane (δ 0.00 ppm) for ^1H NMR, from solvent carbon (e.g., δ 77.00 ppm for chloroform) for ^{13}C NMR. Open silica gel column chromatography was performed on silica gel 60 N (Kanto, spherical and neutral, 140–325 mesh). High-resolution mass spectra (HR-MS) were measured by APCI using a time-of-flight mass analyzer on a JEOL JMS-T100LC (AccuTOF) spectrometer with a calibration standard of C_{60} (MW 720.00).

Materials. Unless otherwise noted, materials were purchased from Tokyo Kasei Co., Aldrich Inc., and other commercial suppliers and used after appropriate purification before use. Anhydrous solvents (stabilizer-free) were purchased from WAKO Pure Chemical and purified by a solvent purification system (GlassContour) equipped with columns of activated alumina and supported copper catalyst (Q-5) prior to use. Synthesis of SIMEF was conducted by following the procedure described in the literature.¹

¹ Matsuo, Y.; Iwashita, A.; Abe, Y.; Li, C. Z.; Matsuo, K.; Hashiguchi, M.; Nakamura, E. *J. Am. Chem. Soc.* **2008**, *130*, 15429.

**6,9-Bis(dimethylphenylsilylmethyl)-6,9-dihydro-1,5-dioxo-1,5-seco(C₆₀-I_h)
[5,6]fullerene (SIMEF-O₂)**

Optimization of Reaction Condition.



entry	solvent	reaction time [day]	yield [%] ^a	recovery [%] ^a
1	CS ₂	1	14.3	82
2	CS ₂	6	32.4	54
3	Toluene	1	1.0	98
4	Benzene	1	0.4	94
5	CH ₂ Cl ₂	1	1.8	97
6	C ₆ F ₆ +CS ₂	1	15.5	79
7	CH ₂ Cl ₂	1	4.5	94
8	CHCl ₃	1	2.7	95
9	— (solid) ^b	1	7.7	90

^a HPLC area ratio yield. ^b a thin-film formed on glass plate by drop-casting of CS₂ solution

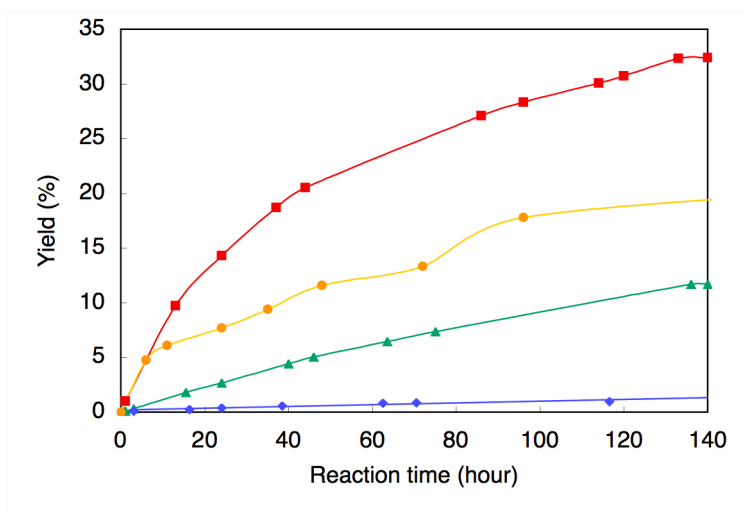


Fig. S1 The kinetic profile of the oxidation reaction (HPLC area ratio, CS₂: red, CHCl₃: green, benzene: blue, solid: orange)

Synthesis. The solution of SIMEF (201.9 mg, 0.198 mmol) in CS₂ (267 mL) was irradiated with an incandescent lamp (60 W), while bubbling through a gentle stream of oxygen. The temperature was maintained at 35~40 °C. After 6 days, the solvent was removed by rotary-evaporation. The solid was purified by silica gel column chromatography (eluent: toluene/hexane = 1/1) or preparative HPLC separation (RPFULLERENE column, eluent: toluene/acetonitrile = 55/45). The first fraction was collected as the recovered SIMEF (109.6 mg, 54% yield). The second fraction was collected as the SIMEF derivative (52.7 mg, 25% yield). A minor unidentified product was also collected in the third fraction (9.3 mg). The experiments in other solvents were performed under the same conditions.

¹H NMR (500 MHz, CDCl₃): δ 0.42 (s, 6H, SiCH₃), 0.46 (s, 6H, SiCH₃), 2.44 (d, 2H, ²J = 14.4 Hz, CH₂), 3.44 (d, 2H, ²J = 14.4 Hz, CH₂), 7.19-7.22 (m, 6H, Ph), 7.47-7.49 (m, 4H, Ph).

¹³C NMR (500 MHz, CDCl₃): δ -1.79 (2C, SiCH₃), -1.13 (2C, SiCH₃), 29.58 (2C, CH₂), 71.66 (2C, C₆₀CH₂), 127.75 (4C, Ph), 129.21 (2C, Ph), 131.65 (1C, C₆₀), 134.09 (4C, Ph), 134.91 (1C, C₆₀), 135.07 (2C, C₆₀), 136.06 (2C, C₆₀), 138.12 (2C, Ph), 138.47 (2C, C₆₀), 139.70 (2C, C₆₀), 139.82 (2C, C₆₀), 140.66 (2C, C₆₀), 141.06 (2C, C₆₀), 141.96 (2C, C₆₀), 142.96 (4C, C₆₀), 143.15 (2C, C₆₀), 143.40 (1C, C₆₀), 143.48 (1C, C₆₀), 143.74 (2C, C₆₀), 143.84 (2C, C₆₀), 144.77 (2C, C₆₀), 144.88 (2C, C₆₀), 145.05 (2C, C₆₀), 145.58 (2C, C₆₀), 146.13 (2C, C₆₀), 146.40 (2C, C₆₀), 147.07 (2C, C₆₀), 147.28 (2C, C₆₀), 147.89 (2C, C₆₀), 149.33 (2C, C₆₀), 149.39 (2C, C₆₀), 155.35 (2C, C₆₀), 200.07 (2C, C₆₀O₂).

APCI-HRMS (-): *m/z* calcd. for C₆₉H₁₃Si (M-H⁺), 1050.1471; found, 1050.1463.

2. HPLC analysis in the synthesis of SIMEF-O₂

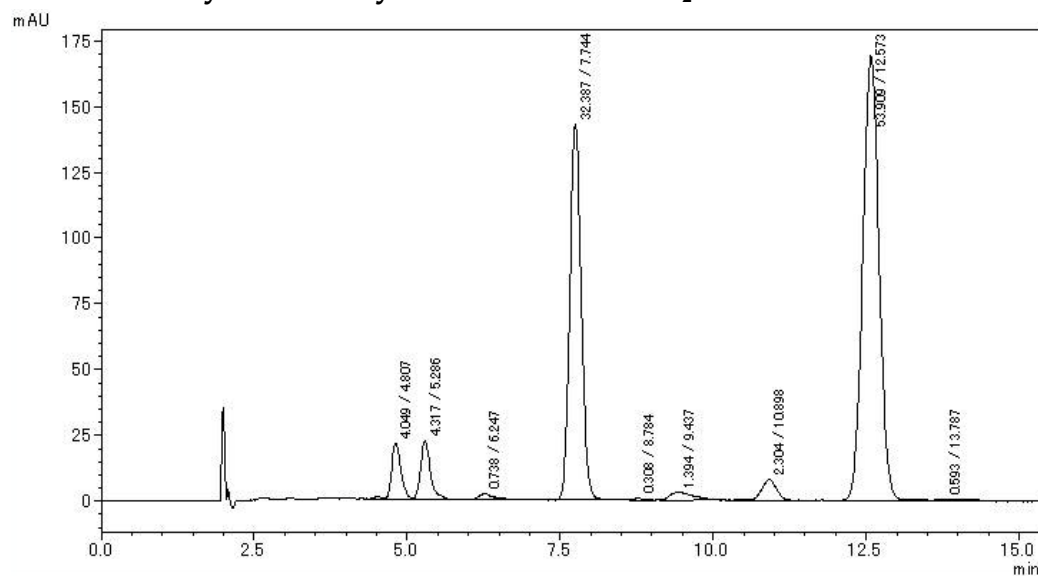


Fig. S2 HPLC chromatogram of the crude reaction product, using an RPFULLERENE column. Mobile phase conditions: toluene/acetonitrile (5/5), monitored at 350 nm. SIMEF-O₂ was detected at 7.7 min, and SIMEF was detected at 12.6 min.

3. DSC Measurement of Thermotropic Properties

The samples were analyzed under nitrogen atmosphere at a scanning rate of 10 °C/min by applying two heating and cooling cycles (Figure S4). The differential scanning calorimetry (DSC) measurements indicated that the SIMEF-O₂ shows glass transition temperature (T_g) and crystallization temperature (T_c) at 163 °C and 114 °C, respectively. It is similar to SIMEF expect absence of melting point.¹

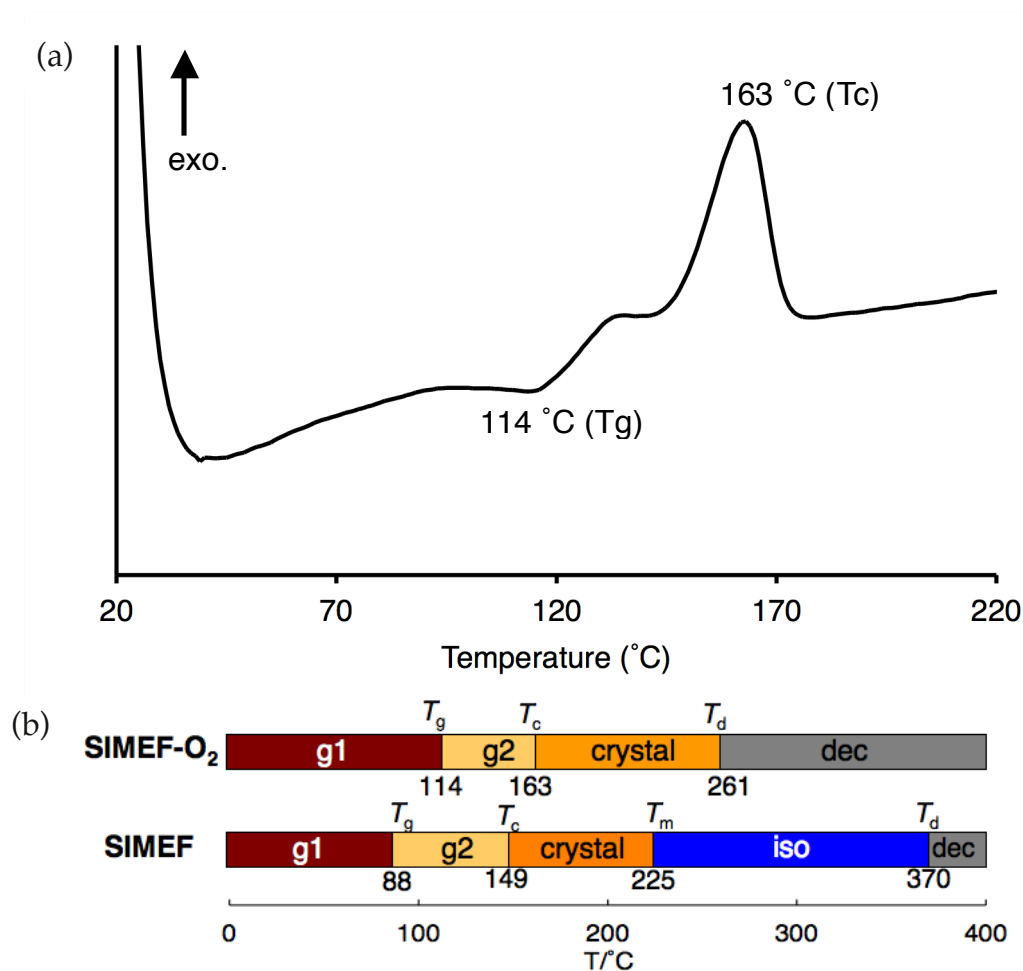


Fig. S3 (a) DSC curve of SIMEF-O₂, (b) Summary of the thermal properties of SIMEF-O₂ and SIMEF¹

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4. Electrochemical properties

Cyclic voltammetry (CV) was performed on a HOKUTO DENKO HZ-5000 voltammetric analyzer. All measurements were carried out in a one-compartment cell under Ar gas, equipped with a glassy-carbon working electrode, a platinum wire counter electrode, and an Ag/Ag⁺ reference electrode. Measurements were performed in THF solution containing tetrabutylammonium perchlorate (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⁺.

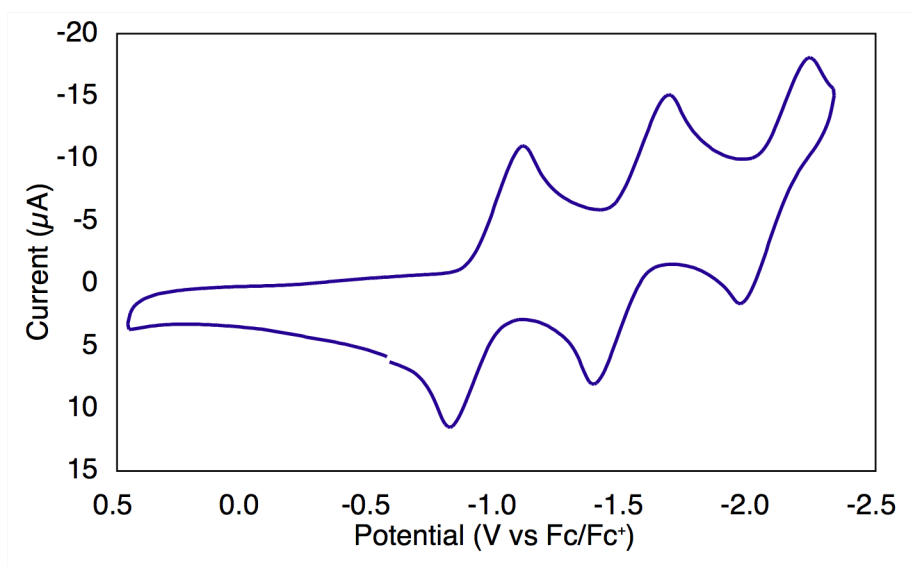


Fig. S4 Cyclic Voltammogram of SIMEF-O₂ in THF solution containing Bu₄N⁺PF₆⁻ (0.1 M) as a supporting electrolyte at 25 °C

5. Device Fabrications and Characterization

A 145-nm-thick, patterned indium-tin oxide (ITO) glass with a sheet resistance of 8Ω /square was used as the substrate. A conducting poly(3,4- ethylenedioxythiophene)-poly(styrenesulfonate) (PEDOT:PSS, Clevios AI4083) layer was formed on the glass/ITO substrate to obtain a 30-nm-thick thin film. Poly(3-hexylthiophene), P3HT (10 mg) and electron-accepting materials (10 mg) composed of different ratios of SIMEF and SIMEF-O₂ were dissolved in 1 ml chlorobenzene. A P3HT:SIMEF:SIMEF-O₂ active layer was formed by spin-coating method to obtain a 220-nm-thick layer. LiF (0.15 nm) was deposited in vacuum (3×10^{-4} Pa) on top of active layer as an exciton blocking layer, followed by the deposition of an aluminum electrode (Al, 80 nm) in vacuum and annealing at 150 °C for 10 minutes. The devices were encapsulated in a glove box in nitrogen atmosphere. The photocurrent of the fabricated OPV devices was investigated with a sweeping voltage using a Keithley 2400 source measurement unit controlled by a computer under simulated solar light using an AM1.5G light source with a 100 mW/cm² intensity. Incident light intensity was calibrated to 1 sun (100 mW/cm²) with a standard Si photodiode (Bunko-Keiki, BS-520). The current density vs voltage (*J-V*) characteristics were measured for an area of 0.04 cm². The incident photon to current efficiency (IPCE) was measured under a constant power generated by monochromatized photons using a xenon lamp.

6. UV-vis absorption spectra of bulk-heterojunction thin-film

UV-vis absorption spectra were measured on JASCO V-570 spectrometer (Nihon bunko).

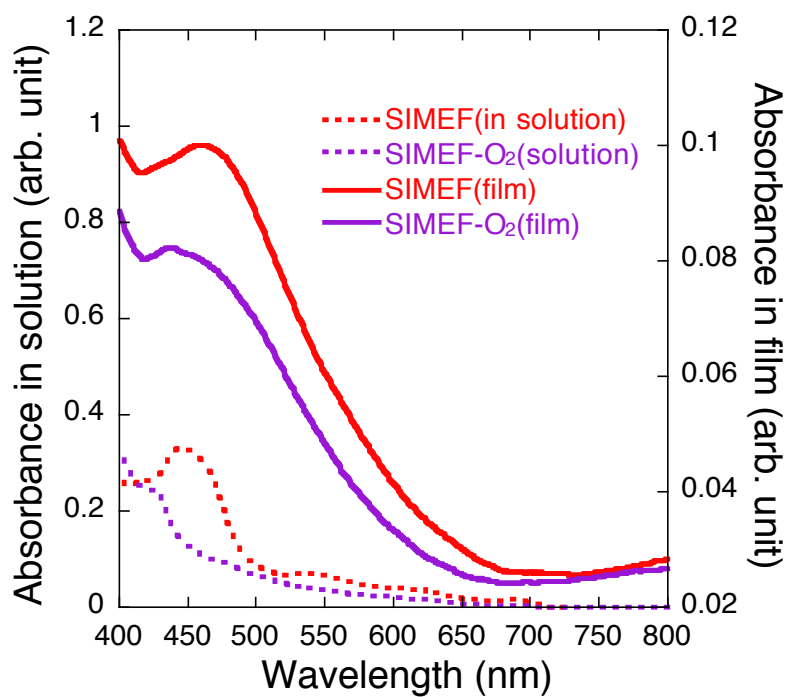


Fig. S5 UV-vis absorption spectra of SIMEF (red line) and SIMEF-O₂ (blue line). (a) In solution in CH₂Cl₂ (concentration: 4.97×10^{-5} mol dm⁻³). (b) As solid thin-film on glass/ITO/PEDOT:PSS (thickness: 50 nm).

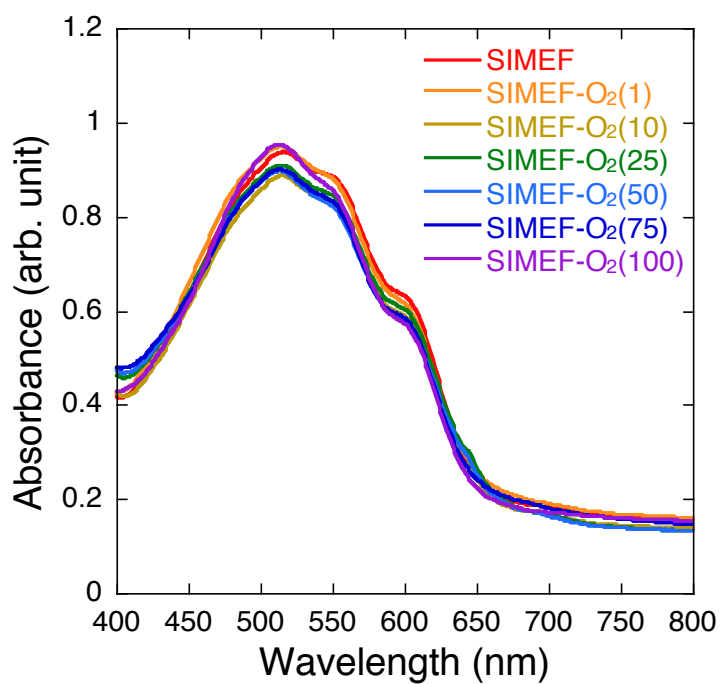


Fig. S6 Light absorption spectra of a bulk-heterojunction film composed of P3HT and electron-accepting materials at different ratios of SIMEF ($100 - x$) and SIMEF-O₂(x) (x = weight ratio of SIMEF-O₂ to the total amount of SIMEF and SIMEF-O₂); (a) $x = 0$, (b) $x = 1$, (c) $x = 10$, (d) $x = 25$, (e) $x = 50$, and (f) $x = 100$. The substrates; glass/ITO/PEDOT:PSS.

7. Electron mobility

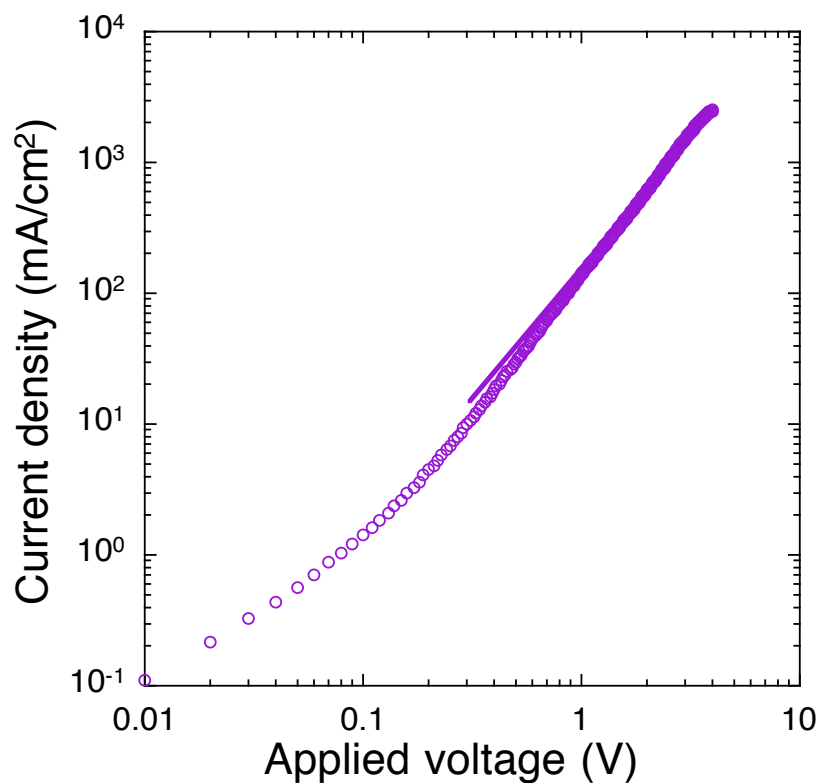


Fig. S7 J - V characteristics of electron-only device of glass/Al (110 nm)/SIMEF-O₂ (94 nm)/LiF (0.6 nm)/Al (110 nm) structure for electron mobility of SIMEF-O₂ estimated by space-charge limited current (SCLC) model. Solid line shows $J \sim V^2$.

8. IPCE spectra in BHJ solar cells

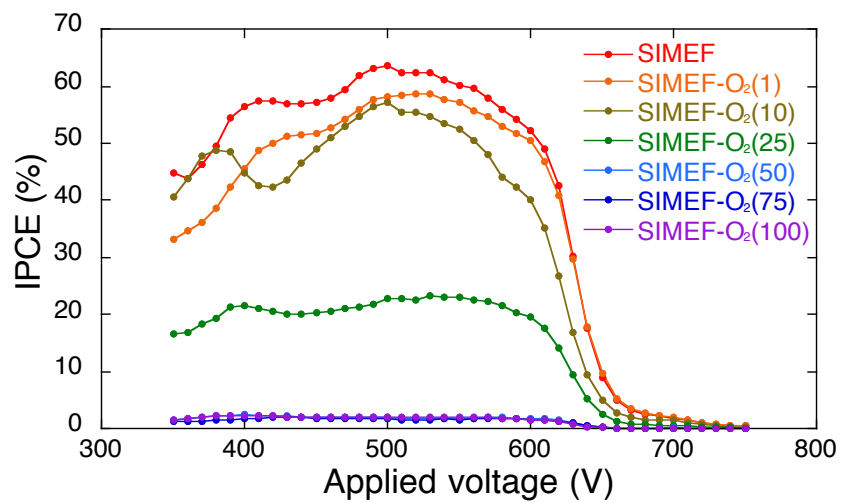


Fig. S8 IPCE spectra as function of wavelength of OPV devices with different weight ratio of SIMEF-O₂ to total amount of SIMEF and SIMEF-O₂.

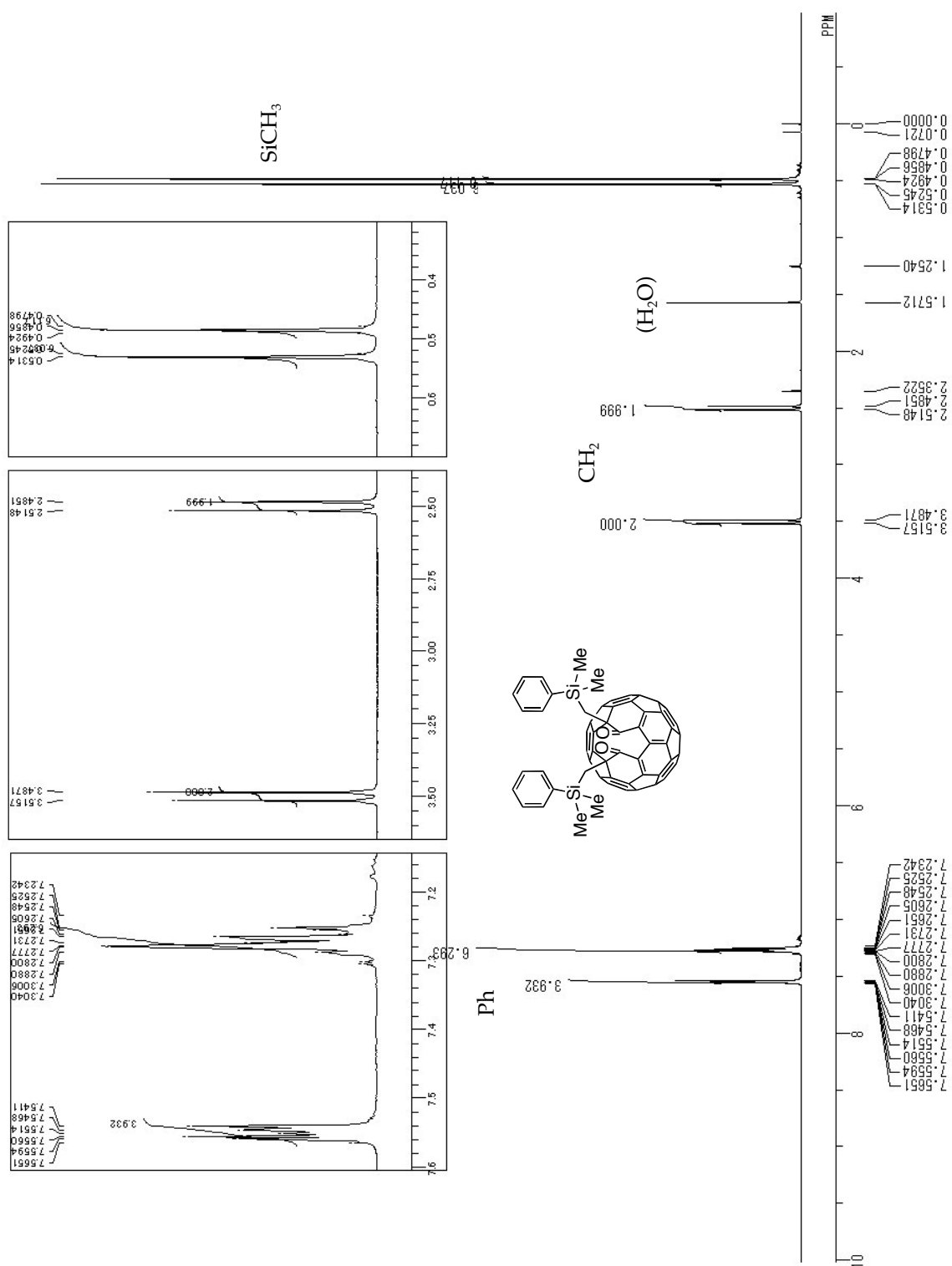


Fig. S9 ¹H NMR spectrum of SIMEF-O₂.

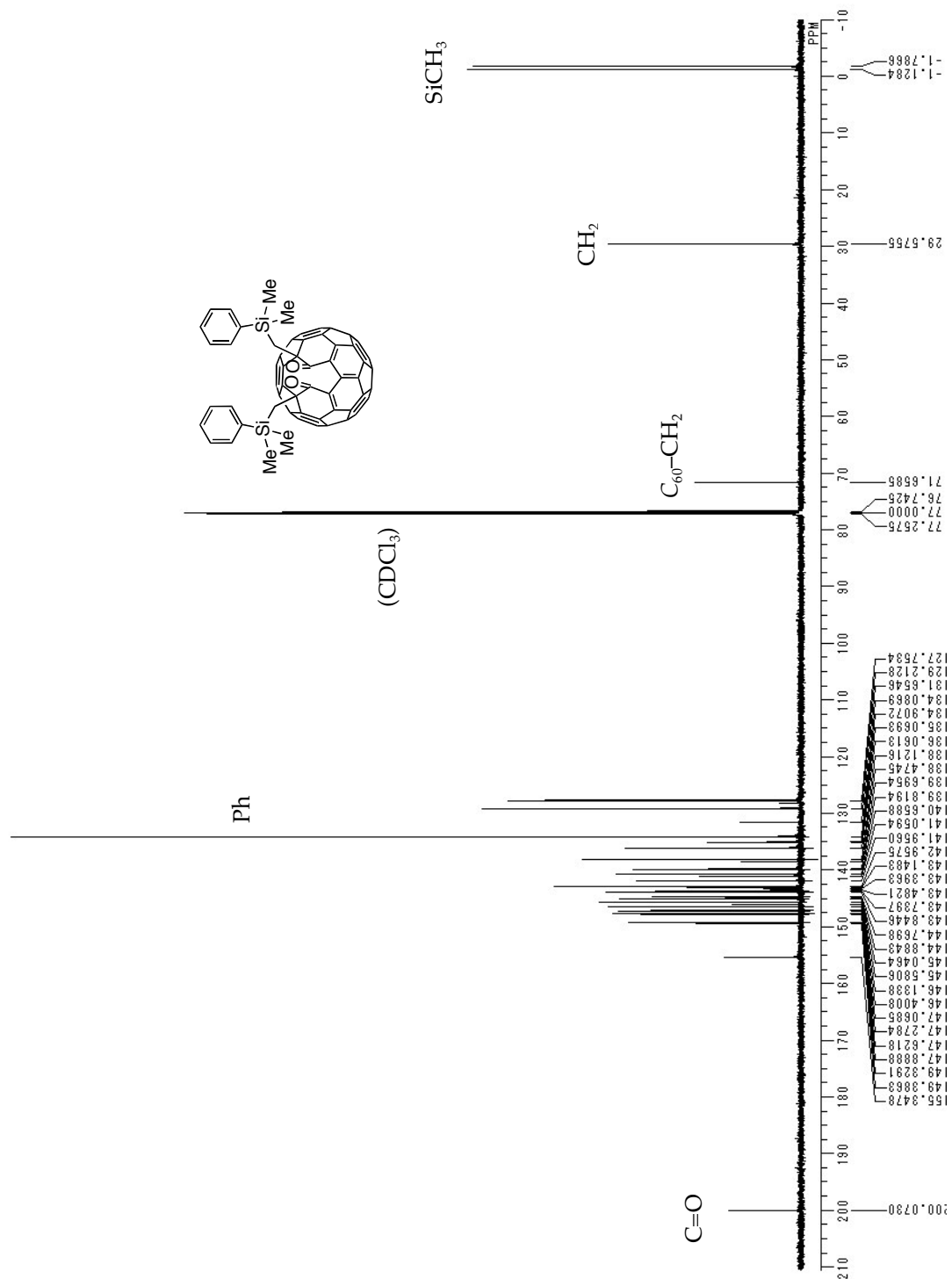


Fig. S10 ^{13}C NMR spectrum of SIMEF- O_2 .

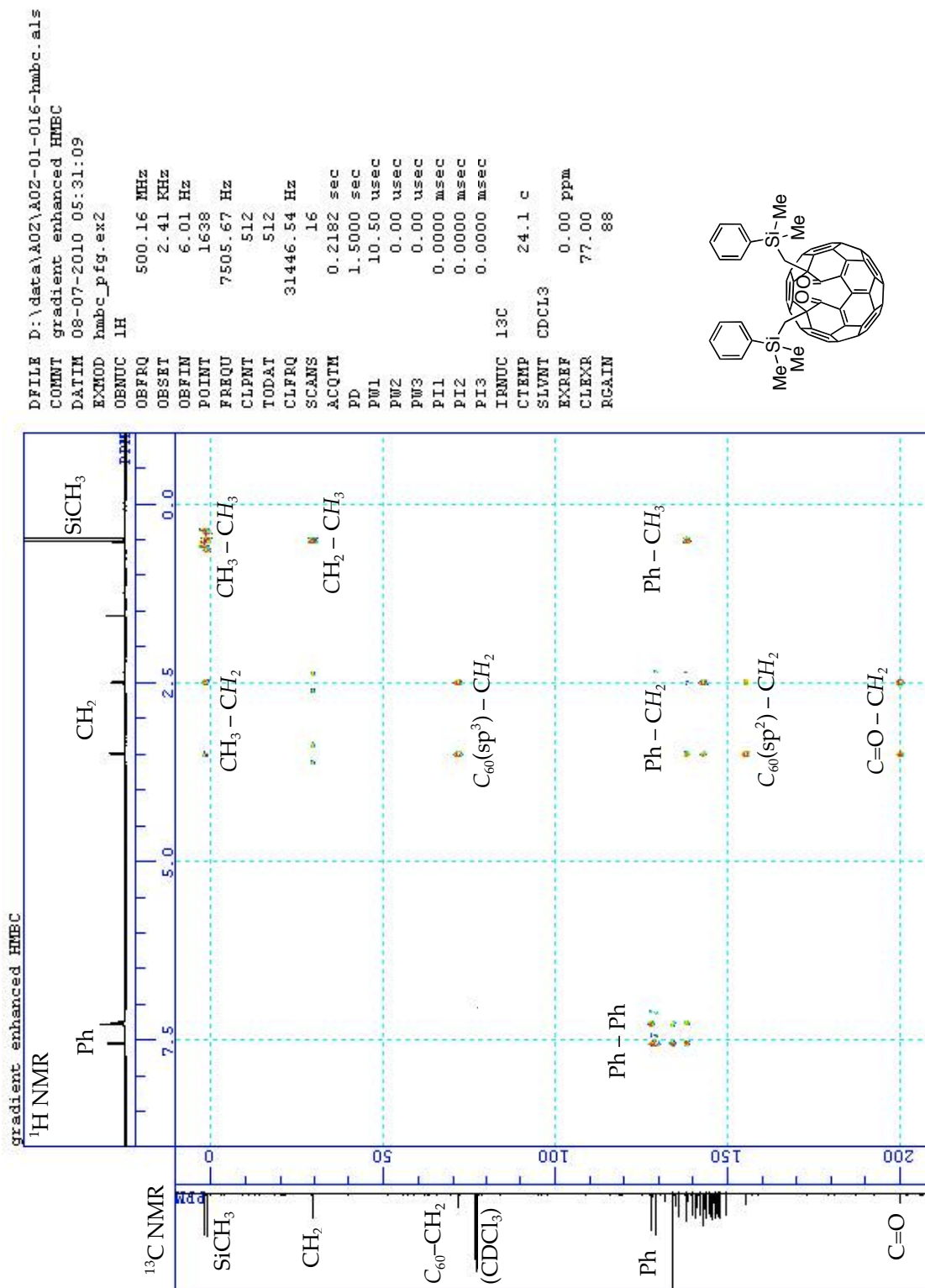


Fig. S11 HMBC spectra of SIMEF-O₂.