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 13C NMR. Open silica gel column chromatography was performed on silica gel 60 N (Kanto, spherical and neutral, 140–250 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 C60 (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

6,9-Bis(dimethylphenylsilylmethyl)-6,9-dihydro-1,5-dioxo-1,5-seco(C_{60}-I_h) [5,6]fullerene (SIMEF-O_2)

Optimization of Reaction Condition.

<table>
<thead>
<tr>
<th>entry</th>
<th>solvent</th>
<th>reaction time [day]</th>
<th>yield [%]</th>
<th>recovery [%]</th>
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<tr>
<td>1</td>
<td>CS_2</td>
<td>1</td>
<td>14.3</td>
<td>82</td>
</tr>
<tr>
<td>2</td>
<td>CS_2</td>
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<td>32.4</td>
<td>54</td>
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<tr>
<td>3</td>
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<td>98</td>
</tr>
<tr>
<td>4</td>
<td>Benzene</td>
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<td>0.4</td>
<td>94</td>
</tr>
<tr>
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<td>CH_3Cl</td>
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<td>97</td>
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<tr>
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<td>C_6F_6+CS_2</td>
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<td>15.5</td>
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<td>7</td>
<td>CH_2Cl_2</td>
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<td>94</td>
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<tr>
<td>8</td>
<td>CHCl_3</td>
<td>1</td>
<td>2.7</td>
<td>95</td>
</tr>
<tr>
<td>9</td>
<td>— (solid)^b</td>
<td>1</td>
<td>7.7</td>
<td>90</td>
</tr>
</tbody>
</table>

^a^ HPLC area ratio yield. ^b^ a thin-film formed on glass plate by drop-casting of CS_2 solution

**Fig. S1** The kinetic profile of the oxidation reaction (HPLC area ratio, CS_2: red, CHCl_3: green, benzene: blue, solid: orange)
**Synthesis.** The solution of SIMEF (201.9 mg, 0.198 mmol) in CS$_2$ (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.

$^1$H NMR (500 MHz, CDCl$_3$): δ 0.42 (s, 6H, SiC$_3$H$_3$), 0.46 (s, 6H, SiC$_3$H$_3$), 2.44 (d, 2H, $^2$J = 14.4 Hz, CH$_2$), 3.44 (d, 2H, $^2$J = 14.4 Hz, CH$_2$), 7.19-7.22 (m, 6H, Ph), 7.47-7.49 (m, 4H, Ph).

$^{13}$C NMR (500 MHz, CDCl$_3$): δ -1.79 (2C, SiCH$_3$), -1.13 (2C, SiCH$_3$), 29.58 (2C, CH$_2$), 71.66 (2C, C$_{60}$CH$_2$), 127.75 (4C, Ph), 129.21 (2C, Ph), 131.65 (1C, C$_{60}$), 134.09 (4C, Ph), 134.91 (1C, C$_{60}$), 135.07 (2C, C$_{60}$), 136.06 (2C, C$_{60}$), 138.12 (2C, Ph), 138.47 (2C, C$_{60}$), 139.70 (2C, C$_{60}$), 139.82 (2C, C$_{60}$), 140.66 (2C, C$_{60}$), 141.06 (2C, C$_{60}$), 141.96 (2C, C$_{60}$), 142.96 (4C, C$_{60}$), 143.15 (2C, C$_{60}$), 143.40 (1C, C$_{60}$), 143.48 (1C, C$_{60}$), 143.74 (2C, C$_{60}$), 143.84 (2C, C$_{60}$), 144.77 (2C, C$_{60}$), 144.88 (2C, C$_{60}$), 145.05 (2C, C$_{60}$), 145.58 (2C, C$_{60}$), 146.13 (2C, C$_{60}$), 146.40 (2C, C$_{60}$), 147.07 (2C, C$_{60}$), 147.28 (2C, C$_{60}$), 147.89 (2C, C$_{60}$), 149.33 (2C, C$_{60}$), 149.39 (2C, C$_{60}$), 155.35 (2C, C$_{60}$), 200.07 (2C, C$_{60}$O$_2$).

APCI-HRMS (−): m/z calcd. for C$_{60}$H$_{13}$Si (M–H$^-$), 1050.1471; found, 1050.1463.
2. HPLC analysis in the synthesis of SIMEF-O$_2$

![HPLC chromatogram](image)

**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-O$_2$ 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 (Tg) and crystallization temperature (Tc) at 163 °C and 114 °C, respectively. It is similar to SIMEF except absence of melting point.¹

![DSC curve of SIMEF-O₂](image)

**Fig. S3** (a) DSC curve of SIMEF-O₂, (b) Summary of the thermal properties of SIMEF-O₂ and SIMEF.¹

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⁺.

![Cyclic Voltammogram of SIMEF-O₂ in THF solution containing Bu₄N⁺PF₆⁻ (0.1 M) as a supporting electrolyte at 25 °C](image-url)

**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 8 \( \Omega /\text{square} \) 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-O\(_2\) were dissolved in 1 ml chlorobenzene. A P3HT:SIMEF:SIMEF-O\(_2\) active layer was formed by spin-coating method to obtain a 220-nm-thick layer. LiF (0.15 nm) was deposited in vacuum (3 \times 10^{-4} \text{ 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/cm\(^2\) intensity. Incident light intensity was calibrated to 1 sun (100 mW/cm\(^2\)) 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 cm\(^2\). 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

![Graph showing J-V characteristics](image)

**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

![Graph showing 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. 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 $^1$H NMR spectrum of SIMEF-O$_2$. 
Fig. S10 $^{13}$C NMR spectrum of SIMEF-O$_2$. 
Fig. S11 HMBC spectra of SIMEF-O2.

**1H NMR**

- SiCH3
- CH2
- Ph
- CH3 – CH3
- C60 – CH2 – C60
- Ph – Ph
- Ph – CH2
- Ph – CH3
- C60(sp3) – CH2
- C60(sp3) – CH2

**13C NMR**

- SiCH3
- CH2
- C60 – CH2 – C60
- Ph
- C60(sp3) – CH2
- C60(sp3) – CH2

**Spectroscopy Parameters**

- **DSPEC** 500.15 MHz
- **DSQ** 2.41 KHz
- **DSF** 6.01 Hz
- **DS** 1638
- **FRQ** 7505.67 Hz
- **CL** 312
- **TOT** 612
- **CLFROQ** 31446.54 Hz
- **SCANS** 16
- **ACQIM** 0.2102 sec
- **PD** 1.5000 sec
- **P01** 10.58 usec
- **P02** 0.00 usec
- **P03** 0.00 usec
- **DIL** 0.0000 msec
- **PIZ** 0.0000 msec
- **PI3** 0.0000 msec
- **EIMUC** 13C
- **CFEMP** 24.1 c
- **SLVNT** CDCl3
- **EEOV** 0.00 ppm
- **CLEVR** 77.00
- **ROAM** 88

Electronic Supplementary Material (ESI) for Chemical Communications

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