New Efficient (Thio)acetalized Fullerene Monoadducts for Organic Solar Cells: Characterization Based on Solubility, Mobility Balance, and Dark Current

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**Experimental.**

**Materials and Synthesis.** Regioregular P3HT, fullerenes (C\textsubscript{60} and PCBM), and solvents were purchased from Aldrich Inc., Frontier Carbon Inc., and Kishida Chemical Inc., respectively, and were used as received. Acetalized fullerenes SAF and SAF\textsubscript{n} (n = 5-7) were synthesized in the same way with our previous report.\[^{[S1]}\] Thioacetalized fullerene STAF\textsubscript{n} (n = 5-7) was synthesized by the reaction of 2 equivalent of the dithiols HS(CH\textsubscript{2})\textsubscript{n}SH (n = 2, 3, 4) with cyclohexanone-fused fullerene 1 in presence of TiCl\textsubscript{4} as the catalyst. The structures of STAF\textsubscript{n} (n = 5-7) were determined by \textsuperscript{1}H and \textsuperscript{13}C NMR analysis and MALDI-TOF-MS spectroscopy. Reduction potentials \(E_{1}^{\text{red}}\) standardized by Fc/Fc\textsuperscript{+} couple were evaluated by cyclic voltammetry using an Ag/AgCl electrode and Pt as the working and counter electrode in \(o\)-dichlorobenzene (DCB), respectively. The lowest unoccupied molecular orbital (LUMO) levels were calculated from \(E_{1}\) using LUMO level = \(-e (E_{1}^{\text{red}} + 4.8)\).\[^{[S2]}\]

**Thioacetalized fullerene with 5-membered ring: STAF\textsubscript{5}**

\textsuperscript{1}H NMR (270 MHz, CS\textsubscript{2}/CDCl\textsubscript{3}) \(\delta=3.47-3.63\) (m, 2H, 2H, 4H), 4.15 (s, 2H); \textsuperscript{13}C NMR (150 MHz, oDCB-d\textsubscript{4}) \(\delta=37.35\), 41.26, 44.04, 54.14, 64.74, 64.82, 66.36, 136.27, 136.34, 140.93, 140.96, 142.29, 142.72, 142.74, 142.75, 142.77, 143.21, 145.37, 145.39, 145.98, 146.05, 146.07, 146.12, 146.23, 146.55, 146.90, 147.08, 147.11, 147.17, 148.31, 148.35, 156.81, 157.53; FAB MS, calculated for C\textsubscript{66}H\textsubscript{10}S\textsubscript{2}[M]\textsuperscript{+}, 866.0224, found 866.0206.

**Thioacetalized fullerene with 6-membered ring: STAF\textsubscript{6}**

\textsuperscript{1}H NMR (270 MHz, CS\textsubscript{2}/CDCl\textsubscript{3}) \(\delta=2.23\) (tt, 2H), 3.20 (m, 4H), 3.42 (m, 2H), 3.53 (m, 2H), 4.14 (s, 2H); \textsuperscript{13}C NMR (150 MHz, oDCB-d\textsubscript{4}) \(\delta=25.40\), 27.62, 35.34, 38.63, 49.41, 50.00, 63.31, 64.86, 135.64, 135.76, 140.22, 141.56, 141.59, 141.95, 142.02, 142.06, 142.48, 142.54, 143.21, 144.70, 145.11, 145.37, 145.39, 145.43, 145.52, 145.89, 146.16, 146.20, 146.35, 146.44, 147.62, 147.67, 156.22, 157.07; FAB MS, calculated for C\textsubscript{67}H\textsubscript{12}S\textsubscript{2}[M]\textsuperscript{+}, 880.0451, found 880.0480.

**Thioacetalized fullerene with 7-membered ring: STAF\textsubscript{7}**

\textsuperscript{1}H NMR (270 MHz, CS\textsubscript{2}/CDCl\textsubscript{3}) \(\delta=2.13\) (m, 4H), 3.03 (m, 4H), 3.23 (m, H), 3.48 (m, 2H), 3.80 (s, 2H); \textsuperscript{13}C NMR (67.5 MHz, oDCB-d\textsubscript{4}) \(\delta=23.95\), 32.83, 35.93, 40.88, 52.48, 60.24, 63.13, 136.28, 140.88, 140.91, 142.23, 142.25, 142.70, 142.75, 143.17, 143.20, 143.24, 243.92, 145.37, 145.41, 145.80, 145.99, 146.05, 146.08, 146.11, 146.24, 146.61, 146.86, 146.87, 147.04, 147.11, 148.30, 148.35, 157.07, 158.19; FAB MS, calculated for C\textsubscript{68}H\textsubscript{14}S\textsubscript{2}[M]\textsuperscript{+}, 894.0583, found 894.0560.
Organic photovoltaic cell (OPV).

Normal cell.\[^{[53]}\] P3HT and S(T)AFs were dissolved in 1.5 wt% DCB solution separately (1:1 wt ratio, 1.95 g / mL for each). A PEDOT:PSS layer was cast onto the cleaned ITO layer by spin-coating after passing through a 0.45 μm filter. The substrate was annealed on a hot plate at 120 °C for 10 min. After the substrate was annealed on a hot plate at 180 °C for 10 min, the DCB solution was then casted on top of the PEDOT:PSS buffer layer in a nitrogen glove box by spin-coating at 1400 rpm for 15 s after passing through a 0.2 mm filter. The thickness was around 200 nm. A cathode consisting of 20 nm Ca and 100 nm Al layers was sequentially deposited through a shadow mask on top of the active layers by thermal evaporation in a vacuum chamber. The resulting device configuration was ITO (120-160 nm)/PEDOT:PSS (45-60 nm)/active layer (ca. 200 nm)/Ca (20 nm)/Al (100 nm) with an active area of 7.1 mm\(^2\).

Inverted cell. \[^{[54, 55]}\] A ZnO layer was fabricated onto a cleaned ITO layer by spin-coating of ZnO precursor solution (0.1 g/ml zinc acetate dihydrate and 0.028 g/ml ethanolamine in 2-methoxyethanol). The substrate was annealed on a hot plate at 200 °C for 30 min. An active layer consisting of polymer and fullerene was cast on top of the ZnO layer in a nitrogen glove box by spin-coating. The thickness was controlled by changing the rotation speed and measured by a surface profiler, an ULVAC model Dektak 150. An anode consisting of 10 nm MoO\(_x\) and 100 nm Ag layers was sequentially deposited through a shadow mask on top of the active layers by thermal evaporation in a vacuum chamber. The resulting device configuration was ITO (120-160 nm)/ZnO(30 nm)/active layer /MoO\(_x\) (10 nm)/Ag (100 nm) with an active area of 7.1 mm\(^2\).

Evaluation. Current-voltage (\(J-V\)) curves were measured using a source-measure unit (ADCMT Corp., 6241A) under AM 1.5 G solar illumination at 100 mW cm\(^{-2}\) (1 sun, monitored by a calibrated standard cell, Bunko Keiki SM-250KD) from a 300 W solar simulator (SAN-EI Corp., XES-301S). The EQE spectra were measured by a Bunko Keiki model BS-520BK equipped with a Keithley model 2401 source meter. The monochromated light power was calibrated by a silicon photovoltaic cell, Bunko Keiki model S1337-1010BQ. Atomic force microscopy (AFM) observations were performed by a Seiko Instruments Inc. model Nanocute OP and Nanonavi II.
**Space-charge limited current (SCLC).** The device structures of SCLC were the ITO/PEDOT:PSS/active layer (ca. 200 nm)/Au for hole, and Al/Active layer (ca. 230 nm)/LiF/Al for electron, respectively. The other procedures are same with the OPV device fabrication. The active layer (blend of P3HT and fullerene) was prepared under the optimized condition. The hole or electron mobility was determined by fitting the J-V curve into Mott-Gurney law:[S6-S8]

\[
j = \frac{9 \varepsilon_0 \mu V^2}{8d^3}
\]

(S1)

where \(\varepsilon_0\) is the permittivity of free space, \(\varepsilon_r\) is the dielectric constant of the material, \(\mu\) is the hole (or electron) mobility, \(V\) is the voltage drop across the device, and \(d\) is the thickness of the layer.

**Surface energy (SE).** Contact angles (\(\theta\)) of fullerenes and P3HT were measured using water and glycerol droplets. The surface free energy (SFE) was calculated according to Kaelble–Uy theory[S9] given by

\[
\gamma_L (1 + \cos \theta) = 2 \sqrt{\gamma_S \gamma_L} + 2 \sqrt{\gamma_L \gamma_p}
\]

(S1)

where \(\gamma_L\) and \(\gamma_S\) are SFEs of liquid and solid, respectively.
Crystallographic Data by Single Crystal X-Ray Diffraction (XRD).

A brown platelet crystal of C_{68}H_{14}S_{2} having approximate dimensions of 0.40 x 0.15 x 0.05 mm was mounted on a glass fiber. All measurements were made on a Rigaku RAXIS RAPID imaging plate area detector with graphite monochromated Cu-K\(\alpha\) radiation.

Indexing was performed from 3 oscillations that were exposed for 150 seconds. The crystal-to-detector distance was 127.40 mm.

Cell constants and an orientation matrix for data collection corresponded to a primitive orthorhombic cell with dimensions:

\[
a = 9.97592(18) \text{ Å} \\
b = 19.8174(4) \text{ Å} \\
c = 20.1513(4) \text{ Å} \\
V = 3983.85(13) \text{ Å}^3
\]

For \(Z = 4\) and F.W. = 894.98, the calculated density is 1.492 g/cm\(^3\). The systematic absences of:

- h00: \(h \pm 2n\)
- 0k0: \(k \pm 2n\)
- 00l: \(l \pm 2n\)

uniquely determine the space group to be: P2\(_1\)2\(_1\)2\(_1\) (#19)

The data were collected at a temperature of -150 \(+1^\circ\)C to a maximum 2\(\theta\) value of 143.5\(^\circ\). A total of 96 oscillation images were collected. A sweep of data was done using \(\omega\) scans from 80.0 to 260.0\(^\circ\) in 15.0\(^\circ\) step, at \(\chi=54.0^\circ\) and \(\phi = 0.0^\circ\). The exposure rate was 30.0 [sec./\(^\circ\)]. A second sweep was performed using \(\omega\) scans from 80.0 to 260.0\(^\circ\) in 15.0\(^\circ\) step, at \(\chi=54.0^\circ\) and \(\phi = 60.0^\circ\). The exposure rate was 30.0 [sec./\(^\circ\)]. Another sweep was performed using \(\omega\) scans from 80.0 to 260.0\(^\circ\) in 15.0\(^\circ\) step, at \(\chi=54.0^\circ\) and \(\phi = 120.0^\circ\). The exposure rate was 30.0 [sec./\(^\circ\)]. Another sweep was performed using \(\omega\) scans from 80.0 to 260.0\(^\circ\) in 15.0\(^\circ\) step, at \(\chi=54.0^\circ\) and \(\phi = 180.0^\circ\). The exposure rate was 30.0 [sec./\(^\circ\)].
Another sweep was performed using $\omega$ scans from 80.0 to 260.0$^\circ$ in 15.0$^\circ$ step, at $\chi$=54.0$^\circ$ and $\phi$ = 240.0$^\circ$. The exposure rate was 30.0 [sec./$^\circ$]. Another sweep was performed using $\omega$ scans from 80.0 to 260.0$^\circ$ in 15.0$^\circ$ step, at $\chi$=54.0$^\circ$ and $\phi$ = 320.0$^\circ$. The exposure rate was 30.0 [sec./$^\circ$]. Another sweep was performed using $\omega$ scans from 80.0 to 260.0$^\circ$ in 15.0$^\circ$ step, at $\chi$=20.0$^\circ$ and $\phi$ = 20.0$^\circ$. The exposure rate was 30.0 [sec./$^\circ$]. Another sweep was performed using $\omega$ scans from 80.0 to 260.0$^\circ$ in 15.0$^\circ$ step, at $\chi$=20.0$^\circ$ and $\phi$ = 120.0$^\circ$. The exposure rate was 30.0 [sec./$^\circ$]. The crystal-to-detector distance was 127.40 mm. Readout was performed in the 0.100 mm pixel mode.

Empirical Formula
C$_{68}$H$_{14}$S$_2$•C$_7$H$_8$

Formula Weight
987.12

Crystal Color, Habit
brown, platelet

Crystal Dimensions
0.40 X 0.15 X 0.05 mm

Crystal System
orthorhombic

Lattice Type
Primitive

Indexing Images
3 oscillations @ 150.0 seconds

Detector Position
127.40 mm

Pixel Size
0.100 mm

Lattice Parameters
a = 9.97592(2) Å
b = 19.8174(4) Å
c = 20.1513(4) Å
V = 3983.85(2) Å$^3$

Space Group
P2$_1$2$_1$2$_1$ (#19)

Z value
4

D$_{calc}$
1.492 g/cm$^3$

F$_{000}$
1816.00

$\mu$(CuK$\alpha$)
16.124 cm$^{-1}$

Residuals: R1 (I>2.00$\sigma$(I))
0.0693

Residuals: R (All reflections)
0.0981

Residuals: wR2 (All reflections)
0.1923
Supporting References.


Supporting Tables.

Table S1. Reduction potentials of SDOFₙ in DCB.

<table>
<thead>
<tr>
<th>Compound</th>
<th>$E_{1\text{red}}$ / V [a]</th>
<th>$E_{2\text{red}}$ / V [a]</th>
<th>$E_{3\text{red}}$ / V [a]</th>
<th>LUMO / eV [b]</th>
</tr>
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<tbody>
<tr>
<td>STAF₅</td>
<td>-1.20</td>
<td>-1.57</td>
<td>-2.09</td>
<td>-3.60</td>
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<tr>
<td>STAF₆</td>
<td>-1.22</td>
<td>-1.58</td>
<td>-2.08</td>
<td>-3.58</td>
</tr>
<tr>
<td>STAF₇</td>
<td>-1.22</td>
<td>-1.58</td>
<td>-2.09</td>
<td>-3.58</td>
</tr>
</tbody>
</table>

[a] Reduction potentials $E_{\text{red}} = 0.5 \left( E_{\text{ox}}^{p} + E_{\text{red}}^{p} \right)$ were measured versus Ag/AgCl reference electrode and standardized to Fc/Fc⁺ couple $E_{\text{Fc/Fc⁺}} = +0.224$ V versus Ag/Ag⁺ (DCB) in 0.1 mM DCB with 0.1 M nBu₄PF₆ as supporting electrolyte. Scan rate was 100 mV/s. [b] Calculated from $E_{1}$ using LUMO level $= -e \left( E_{\text{1red}} + 4.8 \right)$.

Table S2. Influence of polymer:fullerene (D/A) ratios on photovoltaic properties of the P3HT:SAF₇ devices.

<table>
<thead>
<tr>
<th>Ratio (P3HT:SAF₇)</th>
<th>$J_{\text{sc}}$ / mAm⁻²</th>
<th>$V_{\text{oc}}$ / V</th>
<th>FF</th>
<th>PCE / %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1:0.8</td>
<td>7.87</td>
<td>0.66</td>
<td>0.62</td>
<td>3.22</td>
</tr>
<tr>
<td>1:1</td>
<td>8.43</td>
<td>0.64</td>
<td>0.66</td>
<td>3.52</td>
</tr>
<tr>
<td>1:1.2</td>
<td>7.62</td>
<td>0.49</td>
<td>0.46</td>
<td>1.70</td>
</tr>
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</table>

Table S3. Contact angle (CA) and surface energy (SE) measurements.

<table>
<thead>
<tr>
<th>Films</th>
<th>CA$_{\text{glycerol}}$ / °</th>
<th>CA$_{\text{water}}$ / °</th>
<th>SE / mJ cm⁻²</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>80.98</td>
<td>95.99</td>
<td>25.5</td>
</tr>
<tr>
<td>SAF₅</td>
<td>27.16</td>
<td>40.75</td>
<td>57.6</td>
</tr>
<tr>
<td>SAF₆</td>
<td>68.83</td>
<td>74.54</td>
<td>29.9</td>
</tr>
<tr>
<td>SAF₇</td>
<td>70.71</td>
<td>84.14</td>
<td>29.8</td>
</tr>
<tr>
<td>STAF₅</td>
<td>59.72</td>
<td>70.07</td>
<td>35.9</td>
</tr>
<tr>
<td>STAF₆</td>
<td>61.12</td>
<td>64.98</td>
<td>36.9</td>
</tr>
<tr>
<td>STAF₇</td>
<td>59.82</td>
<td>65.31</td>
<td>37.0</td>
</tr>
<tr>
<td>PCBM</td>
<td>61.93</td>
<td>75.02</td>
<td>35.0</td>
</tr>
<tr>
<td>P3HT</td>
<td>101.73</td>
<td>106.6</td>
<td>10.1</td>
</tr>
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</table>
### Table S4. OPV outputs of PTB7:SAF$_7$ (best values) processed from CB with DIO.

<table>
<thead>
<tr>
<th>Cell</th>
<th>DIO / vol%</th>
<th>$J_{sc}$ / mAcm$^{-2}$</th>
<th>$V_{oc}$ / V</th>
<th>FF</th>
<th>PCE / %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Inverted $^a$</td>
<td>0</td>
<td>5.46</td>
<td>0.74</td>
<td>0.35</td>
<td>1.41</td>
</tr>
<tr>
<td>Inverted $^a$</td>
<td>1</td>
<td>8.57</td>
<td>0.74</td>
<td>0.39</td>
<td>2.48</td>
</tr>
<tr>
<td>Inverted $^a$</td>
<td>3</td>
<td>13.34</td>
<td>0.76</td>
<td>0.57</td>
<td>5.84</td>
</tr>
<tr>
<td>Inverted $^a$</td>
<td>5</td>
<td>11.91</td>
<td>0.78</td>
<td>0.60</td>
<td>5.56</td>
</tr>
<tr>
<td>Inverted $^a$</td>
<td>7</td>
<td>11.95</td>
<td>0.78</td>
<td>0.61</td>
<td>5.65</td>
</tr>
<tr>
<td>Inverted $^a$</td>
<td>10</td>
<td>11.47</td>
<td>0.77</td>
<td>0.56</td>
<td>4.95</td>
</tr>
<tr>
<td>Normal $^b$</td>
<td>7</td>
<td>6.03</td>
<td>0.83</td>
<td>0.38</td>
<td>1.91</td>
</tr>
</tbody>
</table>

$^a$ Inverted cell (glass/ITO/ZnO/BHJ/MoO$_x$/Ag).  
$^b$ Normal cell (glass/ITO/PEDOT:PSS/BHJ/Ca/Al).
Figure S1. $^1$H (upper) and $^{13}$C NMR spectra (lower) of STAF$_5$. 

Supporting Figures.
Figure S2. $^1$H (upper) and $^{13}$C NMR spectra (lower) of STAF$_6$. 
Figure S3. $^1$H (upper) and $^{13}$C NMR spectra (lower) of STAF$_7$. 
Figure S4. Purity of STAFs evaluated by HPLC.
Figure S5. Cyclic voltammograms of STAFₙ.
**Figure S6.** $J-V$ curves of P3HT:SAF$_7$ = 1:0.8 (solid line), 1:1 (double line), and 1:1.2 (dotted line) normal cells processed from DCB under AM1.5G (100 mW cm$^{-2}$).

**Figure S7.** Atomic force microscopy (AFM) topological (upper) and phase images (bottom) of P3HT:fullerenes at the best condition. The image size is $2 \times 2 \mu$m$^2$. 
Figure S8. Optical microscope of the blend film of fullerenes $\text{SAF}_5$ and $\text{STAF}_5$ with P3HT.
Figure S9. Examples of contact angle measurement pictures.
Figure S10. SCLC $J-V$ curves of P3HT:fullerenes (1:1 in wt%) under dark conditions using optimized device condition. (a) Hole- and (b) electron-only devices.
Figure S11. a) Dark currents of P3HT:SAF$_7$ (1:1 in wt%) device at low temperature. b) Temperature dependence of dark current of P3HT:fullerene (1:1 in wt%) OPV.
Figure S12. OPV output of PTB7:PCBM (1:1.5 wt%) inverted cell processed from CB with 3vol% DIO. (a) $JV$ curves under AM1.5G (100 mW cm$^{-2}$, solid line) and dark (dotted line). The chemical structures are superimposed. (b) External quantum efficiency (EQE) spectrum of the corresponding device. The calculated $J_{sc}$ is 14.23 mA cm$^{-2}$, consistent with the $J_{sc}$ under one sun (13.96 mA cm$^{-2}$).
Figure S13. (a) $J-V$ curve of PTB7:SAF$_7$ (1:1.5 wt%) inverted cells processed from CB with various DIO concentration under AM1.5G (100 mW cm$^{-2}$). (b) AFM phase images ($2 \times 2 \mu$m$^2$) of the films. The values indicate the DIO concentration.