Supporting Information

Efficient and thermal-stable polymer solar cells based on a 54\(\pi\)-electron fullerene acceptor

Shan Chen,\(^a\)\(^\dagger\)\(^a\)\(^,b\) Gang Ye,\(^a\)\(^\dagger\)\(^a\) Zuo Xiao\(^*\)\(^a\) and Liming Ding\(^*\)\(^a\)

\(^a\) National Center for Nanoscience and Technology, Beijing 100190, China

E-mail: OPV.CHINA@yahoo.com, xiaoz@nanoctr.cn

\(^b\) University of Chinese Academy of Sciences, Beijing 100049, China

\(^\dagger\) S. Chen and G. Ye contributed equally to this work.
1. General characterization

NMR spectra were measured on a Bruker AVANCE-400 spectrometer. Mass spectra were measured on a Bruker Apex IV FIMS spectrometer. UV-Vis absorption spectra were recorded on a SHIMADZU UV-1800 spectrophotometer. Cyclic voltammetry (CV) was performed using a SHANGHAI CHENHUA CHI620D voltammetric analyzer. CV measurements were carried out in a cell under Ar gas, equipped with a glassy-carbon working electrode, a platinum wire counter electrode, and a Ag/Ag⁺ reference electrode. Measurements were performed in ODCB/CH₃CN (9:1) solution containing tetrabutylammonium hexafluorophosphate (TBAPF₆, 0.1 M) as a supporting electrolyte with a scanning rate of 0.1 V/s. All potentials were corrected against Fe/Fe⁺. Thermogravimetric analysis (TGA) was carried out by a PerkinElmer Diamond TG/DTA thermal analyzer. Differential scanning calorimetry (DSC) was carried out by a PerkinElmer thermal analyzer (Diamond). AFM characterization was carried out on a Dimension 3100 microscope (Veeco) (tapping mode). TEM was performed on a FEI Tecnai G2 F20 electron microscope operated at 200 kV. Optical microscopy images were obtained by using a DM4000 microscope (Leica).
2. Synthetic procedures and spectra data for bis-TOQMF and tris-TOQC

99.9% pure C\textsubscript{60} was purchased from YongXin Co. (China). Reagents and chemicals were purchased from Alfa-Aesar Co., TCI Co., or other commercial suppliers and used as received. Methano[60]fullerene (C\textsubscript{60}CH\textsubscript{2}), 2,3-bis(chloromethyl)thiophene, and P3HT were prepared according to literature.\textsuperscript{1-3}

Synthesis of bis-TOQMF

To a solution of methano[60]fullerene (C\textsubscript{60}CH\textsubscript{2}) (140 mg, 0.19 mmol) in ODCB (14 mL) was added 2,3-bis(chloromethyl)thiophene (70 mg, 0.38 mmol), potassium iodide (315 mg, 1.90 mmol) and 18-crown-6 (250 mg, 0.95 mmol). The mixture was degassed with Ar three times and was put into a 110 °C oil bath with stirring for 30 min. Then, the reaction mixture was cooled to room temperature and poured into methanol. The solid was collected by filtration. Silica gel column chromatography (eluent: CS\textsubscript{2}/petroleum ether = 1:1) afforded the band of bis-TOQMF (45 mg, yield: 25%) after the band of monoadducts.

\textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}/CS\textsubscript{2}): \(\delta\) (ppm) 2.00-5.00 (m, 10H, CH\textsubscript{2}), 6.80-7.50 (m, 4H, Ar). \textsuperscript{13}C NMR (100 MHz, CDCl\textsubscript{3}/CS\textsubscript{2}): \(\delta\) (ppm) 23.30, 26.87, 28.21, 29.77, 39.79, 40.19, 40.24, 40.48, 40.72, 40.93, 41.06, 41.35, 41.64, 41.84, 56.91, 60.46, 64.39, 64.58, 64.69, 64.85, 65.01, 65.24, 65.40, 65.57, 65.88, 68.30, 68.44, 69.01, 69.60, 122.85, 123.03, 123.11, 123.23, 123.34, 123.40, 126.52, 126.56, 126.63, 126.68, 126.72, 126.79, 127.23, 127.62, 130.48, 132.61, 135.24, 135.40, 135.49, 135.66, 135.78, 137.21, 137.63, 137.97, 138.16, 140.59, 141.15, 141.81, 142.52, 142.79,
Synthesis of tris-TOQC

To a solution of C\textsubscript{60} (100 mg, 0.14 mmol) in ODCB (10 mL) was added 2,3-bis(dichloromethyl)thiophene (50 mg, 0.28 mmol), potassium iodide (231 mg, 1.40 mmol) and 18-crown-6 (183 mg, 0.70 mmol). The mixture was degassed with Ar three times and was placed into a 110 °C oil bath for 30 min. Then, the reaction mixture was cooled to room temperature and poured into methanol. The solid was collected by filtration. Silica gel column chromatography (eluent: CS\textsubscript{2}/n-hexane=1:1) afforded the band of tris-TOQC (14 mg, yield: 9%) after the bands of mono-adducts and bis-adducts.

\(^1\text{H} \text{NMR (400 MHz, CDCl\textsubscript{3}/CS\textsubscript{2})}: \delta (\text{ppm}) 3.75-4.70 (m, \text{12H, CH}_2), 7.00-7.45 (m, 6H, Ar). \(^{13}\text{C} \text{NMR (100 MHz, CDCl\textsubscript{3}/CS\textsubscript{2})}: \delta (\text{ppm}) 39.22, 39.45, 39.65, 39.78, 39.93, 40.01, 40.15, 40.24, 40.34, 40.50, 40.61, 40.71, 40.76, 40.87, 41.05, 41.27, 41.49, 41.55, 41.85, 41.99, 63.64, 63.71, 63.84, 64.01, 64.08, 64.22, 64.34, 64.43, 64.58, 64.71, 64.77, 64.96, 65.05, 65.11, 65.19, 65.41, 65.52, 65.91, 66.26, 66.57, 123.21, 123.31, 123.37, 123.47, 123.51, 126.85, 126.94, 127.02, 127.12, 127.29, 127.83, 129.41, 130.70, 132.08, 133.18, 133.84, 135.17, 135.73, 137.47, 138.53, 139.38, 140.08, 141.13, 141.79, 142.22, 143.35, 144.12, 144.98, 145.57, 146.07, 146.85, 147.80, 148.49, 149.79, 150.84, 152.22, 153.08, 153.47, 155.11, 155.60, 157.51.
158.47, 160.48, 162.67, 163.41, 164.30. ESI-HRMS: C$_{78}$H$_{18}$S$_{3}$ (M$^+$) calc. 1050.05706, found 1050.05690.
3. Spectra of bis-TOQMF and tris-TOQC

Figure S1. $^1$H NMR spectrum of bis-TOQMF.

Figure S2. $^{13}$C NMR spectrum of bis-TOQMF.
Figure S3. $^1$H NMR spectrum of tris-TOQC.

Figure S4. $^{13}$C NMR spectrum of tris-TOQC.
Figure S5. Mass spectra of bis-TOQMF (above) and tris-TOQC (below).
Figure S6. Absorption spectra for PC₆₁BM, bis-TOQMF, and tris-TOQC: (a) in CHCl₃ (10⁻⁵ mol/L. Inset: enlarged absorption spectra (300-600 nm)) and (b) as thin films.
4. CV measurements for bis-TOQMF and tris-TOQC

Figure S7. Cyclic voltammograms of fullerenes (0.001 mol/L) in ODCB/CH₃CN (9:1) solution containing TBAPF₆ (0.1 mol/L) at a scanning rate of 100 mV/s.

Table S1 Optical and electrochemical properties of PC₆₁BM.

<table>
<thead>
<tr>
<th>Acceptor</th>
<th>λ_onset (nm)</th>
<th>E_g opt (eV)</th>
<th>E_{1/2}^{Red1} (V)</th>
<th>E_{1/2}^{Red2} (V)</th>
<th>LUMO (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PC₆₁BM</td>
<td>715</td>
<td>1.73</td>
<td>-1.12</td>
<td>-1.51</td>
<td>-3.68</td>
</tr>
</tbody>
</table>

\(^{a} E_g = \frac{1240}{\lambda_{onset}}\)
\(^{b} \text{Potential in volts vs Fc/Fc}^+\)
\(^{c} \text{LUMO energy levels were calculated using the following equation:} \)
\[ \text{LUMO level} = -(E_{1/2}^{\text{Red1}} + 4.8) \text{ eV}. \]
5. Thermal properties of bis-TOQMF and tris-TOQC

![TGA curves of bis-TOQMF and tris-TOQC.](image)

Figure S8. TGA curves of bis-TOQMF and tris-TOQC.
Figure S9. DSC curves of bis-TOQMF and tris-TOQC.
6. Device optimization

Figure S10. Effect of D/A ratio on performance of P3HT/bis-TOQMF solar cells: a) PCE; b) $V_{oc}$; c) $J_{sc}$; d) FF. Device fabrication parameters: blend concentration: 24 mg/mL in ODCB; annealing temperature: 150 °C.
Figure S11. Effect of film thickness on performance of P3HT/bis-TOQMF solar cells: a) PCE; b) $V_{oc}$; c) $J_{sc}$; d) FF. Device fabrication parameters: D/A ratio: 1:0.6; annealing temperature: 150 °C.
Figure S12. Effect of annealing temperature on performance of P3HT/bis-TOQMF solar cells: a) PCE; b) $V_{oc}$; c) $J_{sc}$; d) FF. Device fabrication parameters: blend concentration: 24 mg/mL in ODCB; D/A ratio: 1:0.6.
7. Morphology of bis-TOQMF/P3HT and tris-TOQC/P3HT blend films

Figure S13. AFM height images (1μm×1μm) for bis-TOQMF/P3HT blend films: (a) without additive, (b) with α-CN, (c) with DIO; and tris-TOQC/P3HT blend films: (d) without additive, (e) with α-CN, (f) with DIO.
Figure S14. TEM images for bis-TOQMF/P3HT blend films: (a) without additive, (b) with α-CN, (c) with DIO; and tris-TOQC/P3HT blend films: (d) without additive, (e) with α-CN, (f) with DIO.
8. Space charge limited current (SCLC) measurements for bis-TOQMF and tris-TOQC

Charge carrier mobility was measured by the SCLC method. The mobility was
determined by fitting the dark current to the model of a single carrier SCLC, which is
described by

\[ J = \frac{9}{8} \varepsilon_0 \varepsilon_r \mu \left( \frac{V}{d} \right)^2 \]

where \( J \) is the current density, \( \mu \) is the zero-field mobility of electrons (\( \mu_e \)) or holes
(\( \mu_h \)), \( \varepsilon_0 \) is the permittivity of the vacuum, \( \varepsilon_r \) is the relative permittivity of the material,
\( d \) is the thickness of the blend film, and \( V \) is the effective voltage, \( V = V_{\text{appl}} - V_{\text{bi}} \),
where \( V_{\text{appl}} \) is the applied voltage, and \( V_{\text{bi}} \) is the built-in potential which results from
the difference in the work function of the anode and the cathode. Figure S15 shows
\( J-V \) curve of the electron-only device based on PC_{61}BM/P3HT blend in dark. Figure
S16 shows \( J-V \) curves of the hole-only devices based on bis-TOQMF/P3HT and
tris-TOQC/P3HT blends in dark. The mobilities were calculated from the slopes for
\( J^{1/2}-V \) curves and listed in Table S2.
Figure S15. (a) $J-V$ curve for the electron-only device based on PC$_{61}$BM/P3HT blend film in dark; the thickness for the blend film is 105 nm. (b) The corresponding $J^{1/2}-V$ curve.
Figure S16. (a) $J-V$ curves for the hole-only devices based on bis-TOQMF/P3HT and tris-TOQC/P3HT blend films in dark; the thicknesses for the blend films are 125 nm and 135 nm, respectively. (b) The corresponding $J^{1/2}-V$ curves.

Table S2 Mobility data for bis-TOQMF/P3HT, tris-TOQC/P3HT, and PC$_6$BM/P3HT blend films.

<table>
<thead>
<tr>
<th>Active layer</th>
<th>$\mu_e$ (cm$^2$ V$^{-1}$ s$^{-1}$)</th>
<th>$\mu_h$ (cm$^2$ V$^{-1}$ s$^{-1}$)</th>
<th>$\mu_h/\mu_e$</th>
</tr>
</thead>
<tbody>
<tr>
<td>bis-TOQMF:P3HT</td>
<td>$1.68\times10^{-5}$</td>
<td>$1.91\times10^{-4}$</td>
<td>11</td>
</tr>
<tr>
<td>tris-TOQC:P3HT</td>
<td>$1.52\times10^{-6}$</td>
<td>$2.40\times10^{-4}$</td>
<td>158</td>
</tr>
<tr>
<td>PC$_6$BM:P3HT</td>
<td>$1.78\times10^{-4}$</td>
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<td>--</td>
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</table>
9. Thermal stability of PSCs based on bis-TOQMF/P3HT and PC$_{61}$BM/P3HT blends

Figure S17. PCE changes for solar cells based on bis-TOQMF/P3HT and PC$_{61}$BM/P3HT blends under heating at 130 °C.

Figure S18. Polarizing microscopy image for PC$_{61}$BM/P3HT blend film after being heated at 130 °C for 45 h.
References

