Electronic Supplementary Information for

Dual Electron Transfer Pathways from the Excited C$_{60}$ Radical Anion: Enhanced Reactivities due to Photoexcitation of Reaction Intermediates

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Synthesis of dyad compounds

Materials. 1,2,4,5-Benzenetetracarboxylic dianhydride, 2-ethyl-1-hexylamine, aminoacetaldehyde diethylacetal, and ethyl acetate were purchased from Aldrich. Trifluoroacetic acid was supplied from Wako Chemicals. Dichloromethane and toluene were purchased from Kishida. Hexane and acetic anhydride were supplied from Nacalai Tesque. Sarcosine, C_{60}, and 1,4,5,8-Naphthalenetricarboxylic dianhydride Tokyo Chemical Industry. All substances were used without further purification.

Measurements. $^1$H NMR spectra were recorded on a JEOL JMN LA-400 spectrometer operating at 400 MHz, at a constant temperature of 25 °C using SiMe$_4$ as reference. MALDI-TOF mass spectrometry (MS) was carried with BRUKER Ultraflex III

Synthesis of C$_{60}$-PI.

Scheme S1. Synthesis of C$_{60}$-PI.

1a. 1,2,4,5-Benzenetetracarboxylic dianhydride (10 g, 46 mmol) was placed in 175 mL of DMF and heated. 2-Ethyl-1-hexylamine (5.9 g, 46 mmol) dissolved in 75 mL of DMF was added drop wise to the reaction flask. The reaction mixture was refluxed for 16 hr under argon
atmosphere. The reaction mixture was cooled to room temperature, and evaporated in vacuo. After treatment with acetic anhydride, purification with column chromatography (dichloromethane) provided 1a as white powder (0.75 g, 2.3 mmol).

1H NMR (400 MHz, CDCl₃): δ 0.86-0.94 (m, 6H), 1.28-1.35 (m, 8H), 1.81-1.89 (m, 1H), 3.67 (d, J = 7.3 Hz, 2H), 8.44 (s, 2H).

1b. 1a (0.75 g, 2.3 mmol) was dissolved in 40 mL of DMF and heated. Aminoacetaldehyde diethylacetal (0.30 g, 2.3 mmol) dissolved in 25 mL of DMF was added drop wise, and the reaction mixture was refluxed for 24 hr under argon atmosphere. The reaction mixture was cooled to room temperature, and evaporated in vacuo. The purification with column chromatography afforded 1b as white powder (0.70 g, 1.6 mmol).

1H NMR (400 MHz, CDCl₃): δ 0.85-0.94 (m, 6H), 1.16 (t, J = 6.8 Hz, 6H), 1.23-1.38 (m, 8H), 1.80-1.86 (m, 1H), 3.55 (dq, J = 6.8, 9.1 Hz, 2H), 3.62 (d, J = 7.3 Hz, 2H), 3.74 (dq, J = 6.8, 9.1 Hz, 2H), 3.89 (d, J = 5.5 Hz, 2H), 4.88 (t, J = 5.5 Hz, 1H), 8.28 (s, 2H).

1c. To 1b (0.70 g, 1.6 mmol) dissolved in 100 mL of dichloromethane, 10 mL of trifluoroacetic acid was added. After stirring for 5 hr under argon environment, the reaction mixture was evaporated in vacuo. 1c was obtained as white powder (0.46 g, 1.2 mmol).

1H NMR (400 MHz, CDCl₃): δ 0.87-0.94 (m, 6H), 1.24-1.39 (m, 8H), 1.82-1.88 (m, 1H), 3.65 (d, J = 7.3 Hz, 2H), 4.66 (s, 2H), 8.32 (s, 2H), 9.67 (s, 1H).

C₆₀-PI. 1c (0.25 g, 0.67 mmol), sarcosine (25 mg, 0.28 mmol), and C₆₀ (0.10 g, 0.14 mmol) were dissolved in 130 mL of toluene, and refluxed for 6 hr under argon atmosphere. The reaction mixture was cooled to room temperature, and evaporated in vacuo. The purification with column chromatography (toluene:ethylacetate = 19:1) and crystallization from dichloromethane and hexane afforded C₆₀-PI as brown powder (28 mg, 0.025 mmol).
\(^{1}\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\) 0.87-0.95 (m, 6H), 1.29-1.36 (m, 8H), 1.83-1.96 (m, 1H), 3.08 (s, 3H), 3.66 (d, \(J = 6.8 \text{ Hz}\), 2H), 4.33 (d, \(J = 10 \text{ Hz}\), 1H), 4.74 (d, \(J = 12 \text{ Hz}\), 2H), 4.86 (t, \(J = 12 \text{ Hz}\), 1H), 4.89 (d, \(J = 10 \text{ Hz}\), 1H), 8.34 (s, 2H). MALDI MS: calcd. 1117.20, found 1117 (M).

**Synthesis of C\(_{60}\)-NDI.**

Scheme S2. Synthesis of C\(_{60}\)-NDI.

2a. 1,4,5,8-Naphthalenetetracarboxylic dianhydride (12 g, 45 mmol) was placed in 260 mL of DMF and heated. 2-Ethyl-1-hexylamine (5.8 g, 45 mmol) dissolved in 70 mL of DMF was added drop wise to the reaction flask. The reaction mixture was refluxed for 18 hr under argon atmosphere. The reaction mixture was cooled to room temperature, and evaporated in vacuo. After treatment with acetic anhydride, purification with column chromatography (dichloromethane) provided 2a as pink powder (5.0 g, 13 mmol)

\(^{1}\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\) 0.88 (t, \(J = 7.3 \text{ Hz}\), 3H), 0.94 (t, \(J = 7.7 \text{ Hz}\), 3H), 1.24-1.41 (m, 8H), 1.81-1.89 (m, 1H), 4.15 (ddd, \(J = 6.8, 7.7, 12.8 \text{ Hz}\), 2H), 8.82 (s, 4H).

2b. 2a (5.0 g, 13 mmol) was dissolved in 225 mL of DMF and heated. Aminoacetaldehyde diethylacetal (1.7 g, 13 mmol) dissolved in 150 mL of DMF was added drop wise, and the
reaction mixture was refluxed for 17 hr under argon atmosphere. The reaction mixture was cooled to room temperature, and evaporated in vacuo. The purification with column chromatography (dichloromethane) afforded 2b as light brown powder (4.5 g, 9.2 mmol).

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 0.88 (t, $J = 7.3$ Hz, 3H), 0.94 (t, $J = 7.3$ Hz, 3H), 1.15 (t, $J = 6.8$ Hz, 6H), 1.29-1.42 (m, 8H), 1.90-1.98 (m, 1H), 3.57 (dq, $J = 6.8$, 9.6 Hz, 2H), 3.77 (dq, $J = 6.8$, 9.6 Hz, 2H), 4.14 (ddd, $J = 7.3$, 7.7, 12.8 Hz, 2H), 4.41 (d, $J = 5.9$ Hz, 2H), 5.01 (t, $J = 5.9$ Hz, 1H), 8.77 (s, 4H).

2c. To 2b (0.49 g, 0.99 mmol) dissolved in 100 mL of dichloromethane, 10 mL of trifluoroacetic acid was added. After stirring for 5 hr under argon environment, the reaction mixture was evaporated in vacuo. 2c was obtained as orange powder (0.37 g, 0.88 mmol).

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 0.88 (t, $J = 7.3$ Hz, 3H), 0.94 (t, $J = 7.3$ Hz, 3H), 1.29-1.42 (m, 8H), 1.90-1.98 (m, 1H), 4.17 (d, $J = 7.3$ Hz, 2H), 5.12 (s, 2H), 8.78 (s, 4H), 9.76 (s, 1H).

C$_{60}$-NDI. 2c (0.46 g, 1.1 mmol), sarcosine (39 mg, 0.43 mmol), and C$_{60}$ (0.16 g, 0.21 mmol) were dissolved in 130 mL of toluene, and refluxed for 6 hr under argon atmosphere. The reaction mixture was cooled to room temperature, and evaporated in vacuo. The purification with column chromatography (toluene:ethylacetate = 19:1) and crystallization from dichloromethane and hexane afforded C$_{60}$-NDI as brown powder (36 mg, 0.030 mmol).

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 0.89 (t, $J = 7.3$ Hz, 3H), 0.94 (t, $J = 7.3$ Hz, 3H), 1.26-1.43 (m, 8H), 1.92-1.99 (m, 1H), 3.10 (s, 3H), 4.17 (d, $J = 6.8$ Hz, 2H), 4.36 (d, $J = 10.5$ Hz, 1H), 4.89 (dd, $J = 3.2$, 8.7 Hz, 1H), 4.97 (d, $J = 10.5$ Hz, 1H), 5.20 (dd, $J = 8.7$, 13.7 Hz, 1H), 5.43 (dd, $J = 3.2$, 13.7 Hz, 1H), 8.34 (s, 2H). MALDI MS: calcd. 1167.21, found 1167 (M).

Synthesis of C$_{60}$-PDI.
3b. 3a was synthesized according to the reported procedure.1 3a (154 mg, 0.268 mmol) was dissolved in 15 mL of DMF and heated. Aminoacetaldehyde diethylacetal (0.1 mL) was added to the reaction mixture, and the reaction mixture was refluxed for 24 hr under argon atmosphere. The reaction mixture was cooled to room temperature, and evaporated in vacuo. The purification with column chromatography (dichloromethane) afforded 3b as red powder (183 mg, 0.265 mmol).

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 0.90 (m, 6H), 1.15 (t, $J = 6.87$ Hz, 6H) 1.35 (m, 16H), 1.88 (m, 2H), 2.25 (m, 2H), 3.60 (dq, $J = 9.16$, 7.33 Hz, 2H), 3.80 (dq, $J = 9.16$, 7.33 Hz, 2H), 4.40 (d, $J = 5.95$ Hz, 2H) 5.19 (m, 1H), 8.57 (m, 8H).

3c. To 3b (183 mg, 0.265 mmol) dissolved in 50 mL of dichloromethane, 4 mL of trifluoroacetic acid was added. After stirring for 21 hr under argon environment, the reaction mixture was evaporated in vacuo. 3c was obtained as red powder (154 mg, 0.251 mmol).

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 0.83 (m, 6H), 1.28 (m, 16H), 1.87 (m, 2H), 2.26 (m, 2H), 5.11 (s, 2H), 5.18 (m, 1H), 8.70 (m, 8H), 9.77 (s, 1H).

C$_{60}$-PDI. 3c (154 mg, 0.25 mmol), sarcosine (67 mg, 0.75 mmol), and C$_{60}$ (0.20 g, 0.28 mmol) were dissolved in 200 mL of toluene, and refluxed for 15 hr under argon atmosphere. The
reaction mixture was cooled to room temperature, and evaporated in vacuo. The purification with column chromatography (toluene:ethylacetate = 19:1) and crystallization from dichloromethane and hexane afforded C$_{60}$-NDI as brown powder (135 mg, 0.099 mmol).

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 0.91 (m, 6H), 1.35 (m, 16H), 1.87 (m, 2H), 2.26 (m, 2H), 3.10 (s, 3H), 4.33 (d, $J$ = 10.5 Hz, 1H), 4.89 (dd, $J$ = 3.2, 8.7 Hz, 1H), 4.94 (d, $J$ = 10.5 Hz, 1H), 5.20 (m, 1H), 5.26 (dd, $J$ = 3.2, 14.2 Hz, 1H), 5.41 (dd, $J$ = 8.8, 14.2 Hz, 1H), 8.71 (m, 8H). MALDI MS: calcd. 1362.47, found 1361 (M).

**Absorption peaks**

Table S1. Absorption peak positions of the radical anions in the D$_0$, D$_1$, and D$_0^{\text{hot}}$ states in this study.$^a$

<table>
<thead>
<tr>
<th></th>
<th>D$_0$</th>
<th>D$_1$ $^b$</th>
<th>D$_0^{\text{hot}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>C$_{60}^-$</td>
<td>1078</td>
<td>651 ($\sim$1080)</td>
<td>622, 1136</td>
</tr>
<tr>
<td>C$_{60}$H$^-$</td>
<td>1003</td>
<td>651 (1178)</td>
<td>643, 1064</td>
</tr>
<tr>
<td>PI$^-$</td>
<td>720</td>
<td>$-$ $^c$</td>
<td>$-$ $^c$</td>
</tr>
<tr>
<td>NDI$^-$</td>
<td>475, 610, 691, 766</td>
<td>570, 649, 720</td>
<td>615, 700, &gt;760</td>
</tr>
<tr>
<td>PDI$^-$</td>
<td>717, 770, 801, 961</td>
<td>470, 620 ($\sim$971, 1127, 1336)</td>
<td>$-$ $^c$</td>
</tr>
</tbody>
</table>

$^a$ unit: nm $^b$ numbers in the parenthesis indicate the peak position of stimulated emission. $^c$ not observed in this study.
**Figure S1.** Steady state absorption spectra of $C_{60}$-NDI (0.20 mM) in the presence of TDAE in Ar-saturated BN. Inset: TDAE-concentration dependence of absorbance at 1000 and 610 nm.

**Figure S2.** Steady state absorption spectra of $C_{60}$-PDI (0.20 mM) in the presence of TDAE in Ar-saturated BN.
Figure S3. (Top panel) Transient absorption spectra at various times after a 715 nm femtosecond laser pulse excitation during the laser flash photolysis of PDI in BN in the presence of TDAE. (Bottom panel) Kinetic traces of ΔO.D. at 972 and 1127 nm. Red lines are fitted result.
Figure S4. Schematic energy diagrams for ET in (a) D-S-A and (b) D-S_m-A molecules, where D, S, and A, denote for donor, spacer, and acceptor, respectively.

Reference