

**Remote Control on the Photochemical Rearrangement of 1,6-(*N*-Aryl)aza-[60]fulleroids to 1,2-(*N*-Arylaziridino)-[60]fullerenes by *N*-Substituted Aryl Groups**

**- Supporting Information -**

Akihiko Ouchi,\* Bahlul Z. S. Awen, Ryota Hatsuda, Reiko Ogura, Tadahiro Ishii, Yasuyuki Araki, and Osamu Ito\*

**Contents**

Page S2-3: Preparation of phenylazide, 1- and 2-naphthyl azides, and 1-pyrenylazide.

Page S4-8: Synthesis of 1,6-(*N*-aryl)aza-[60]fulleroids (**1a-d**) and 1,2-(*N*-arylaziridino)-[60]fullerenes (**2a-d**).

Page S9: Derivation of eq 2 from eq 1.

Page S10: **Figure S1.** Results on the photochemical rearrangement of **1a-d** under air-saturated conditions.

Page S11: **Figure S2.** Results on the photochemical rearrangement of **1a-c** under nitrogen-purged conditions.

Page S12: **Figure S3.** Results on the photochemical rearrangement of **1a-d** with > 450-nm light under degassed condition.

Page S13: **Figure S4.** The effects of **2b** addition in photochemical rearrangement **1b** → **2b** with > 600-nm light.

**Figure S5.** The effects of **2b-d** and C<sub>60</sub> addition in photochemical rearrangement **1a** → **2a** with > 290-nm light.

Page S14: **Figure S6.** The effects of **2a,c,d** and C<sub>60</sub> addition in photochemical rearrangement **1b** → **2b** with > 290-nm light.

**Figure S7.** The effects of **2a,b,d** and C<sub>60</sub> addition in photochemical rearrangement **1c** → **2c** with > 290-nm light.

Page S15: **Figure S8.** The decay profiles of the transient absorption peaks of **1a** and **2a** in the absence and presence of oxygen gas.

**Figure S9.** Curve fitting of the data on the consumption of **1a-d** by > 600-nm light irradiation according to eq 2.

Page S16: **Table S1.** PM3 calculation on the ground-state heats of formation and the charges on the nitrogen atom for 1,6-(*N*-aryl)aza-[60]fulleroids (**1**) and 1,2-(*N*-arylaziridino)-[60]fullerenes (**2**).

#### **References and notes.**

#### **Preparation of arylazides.**

**General Aspects.** NMR spectra<sup>S1</sup> were recorded on a Bruker AC-200 with CDCl<sub>3</sub> as solvent. As internal standards, TMS ( $\delta$  0.0 ppm) was used for <sup>1</sup>H NMR and CDCl<sub>3</sub> ( $\delta$  77.0 ppm) for <sup>13</sup>C NMR analyses. Infrared spectra were measured on a Shimadzu FTIR-4000 spectrophotometer and melting points were taken on a Yanagimoto Seisakusho Micro Melting Point Apparatus. Mass spectral measurements<sup>S1</sup> were carried out in the Spectrum Data Base System at the National Institute of Materials and Chemical Research or by direct injection method using Shimadzu GCMS-QP5050A mass spectrometer. Solvents and commercially available chemicals were purified and dried by standard procedures or used as bought. 1-Aminonaphthalene, 2-naphthoic acid, and 1-aminopyrene were purchased from Tokyo Kasei Kogyo Co., Ltd., aniline from Kanto Chemical Co., Inc., sodium azide and sodium nitrite from Nakarai Chemicals Ltd. 2-Aminonaphthalene was prepared from 2-naphthoic acid by the reported procedure.<sup>S2</sup>

**General procedure.** Aryl azides were synthesized from corresponding arylamines according to the reported procedure<sup>S3</sup> and purified by silica gel column chromatography (hexane).

**Phenylazide.** Yield, 84 %; colorless oil.  $^1\text{H}$  NMR ( $\text{CDCl}_3/\text{TMS}$ ): 7.02 (dd, 2H,  $J=7.6$ , 1.3 Hz), 7.14 (tt, 1H,  $J=7.3$ , 1.3 Hz), 7.35 (dt, 2H,  $J=7.3$ , 7.6 Hz);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ): 118.99, 124.84, 129.73, 139.94; IR (neat): 2028, 2018, 1595, 1492, 1395, 750, 685, 670  $\text{cm}^{-1}$ ; MS (EI),  $m/e$  (relative intensity): 38 (22), 41 (14), 51 (14), 63 (37), 64 (82), 65 (19), 91 (100), 119 (49,  $\text{M}^+$ ).

**1-Naphthylazide.** Yield, 80 %; pale yellow oil.  $^1\text{H}$  NMR ( $\text{CDCl}_3/\text{TMS}$ ): 7.17 (dd, 1H,  $J=7.4$ , 0.9 Hz), 7.36 (d, 1H,  $J=8.9$  Hz), 7.38-7.48 (m, 2H), 7.57 (d, 1H,  $J=8.9$  Hz), 7.74-7.79 (m, 1H), 8.04-8.09 (m, 1H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ): 113.81, 122.48, 124.39, 125.36, 126.04, 126.32, 126.79, 127.64, 134.26, 136.40; IR (neat): 2215, 2112, 2047, 1628, 1593, 1576, 1507, 1462, 1391, 1346, 1289, 1258, 1217, 1165, 1076, 1005, 862, 791, 770, 656  $\text{cm}^{-1}$ ; MS (EI),  $m/e$  (relative intensity): 39 (16), 50 (13), 51 (11), 57 (14), 62 (17), 63 (28), 70 (17), 87 (11), 88 (12), 113 (31), 114 (63), 115 (13), 140 (89), 141 (100), 142 (13), 169 (45,  $\text{M}^+$ ).

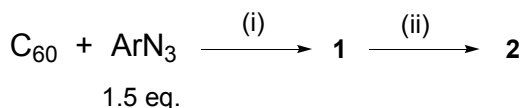
**2-Naphthylazide.** Yield, 73 %; pale yellow solid, m. p. 32.2 - 32.7  $^{\circ}\text{C}$  [lit.<sup>S4</sup> 33  $^{\circ}\text{C}$ ].  $^1\text{H}$  NMR ( $\text{CDCl}_3/\text{TMS}$ ): 7.15 (dd, 1H,  $J=8.7$ , 2.3 Hz), 7.39 (dd, 1H,  $J=6.9$ , 1.5 Hz), 7.42-7.45 (m, 1H), 7.50 (dd, 1H,  $J=6.8$ , 1.5 Hz), 7.72-7.63 (m, 3H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ): 115.75, 118.72, 125.38, 126.96, 127.82, 129.86, 130.99, 133.94, 137.46; IR (KBr): 2107, 1626, 1599, 1550, 1464, 1285, 1237, 849, 808, 747, 470  $\text{cm}^{-1}$ ; MS (EI),  $m/e$  (relative intensity): 63 (18), 70 (21), 114 (43), 140 (59), 141 (100), 169 (43,  $\text{M}^+$ ).

**1-Pyrenylazide.** Yield, 33 %; pale yellow solid, m. p. 124.0 - 124.5  $^{\circ}\text{C}$  [lit.<sup>S5</sup> 119-120  $^{\circ}\text{C}$ ].  $^1\text{H}$  NMR ( $\text{CDCl}_3/\text{TMS}$ ): 7.82 (d, 1H,  $J=10.3$  Hz), 7.97-8.10 (m, 4H), 8.15-8.20 (m, 3H), 8.30 (d, 1H,  $J=11.5$  Hz);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ): 115.43, 121.50, 122.55, 124.48, 125.09, 125.24, 125.50, 125.61, 126.47, 126.80, 127.11, 127.60, 128.34, 131.32, 131.52, 133.23; IR (KBr): 2162, 2133, 2106, 1599, 1504, 1435, 1323, 1291, 831, 750, 708  $\text{cm}^{-1}$ ; MS (EI),  $m/e$  (relative intensity): 93 (38), 94 (30), 107 (34), 287 (13), 214 (82), 215 (100), 243 (23,  $\text{M}^+$ ).

### Synthesis of 1,6-(*N*-aryl)aza-[60]fulleroids (**1a-d**) and 1,2-(*N*-arylaziridino)-[60]fullerenes (**2a-d**).

Compounds **1** and **2** were synthesized from C<sub>60</sub> and the corresponding aryl azides as shown in Scheme S1. Instead of the reported two-step synthesis of **1**,<sup>S6</sup> we have used one-step synthesis. This improvement gave higher yield of **1** in shorter preparation time using less amount of starting aryl azides. Compound **1a** obtained by our method was the same as that obtained by separate experiments using the reported two-step procedure via triazoline. The preparation time and the amount of phenyl azide used in our one-step synthesis were ca. 1/3 and 1/27 of those in the two-step procedure, and the total yield of **1a** obtained by our method was > 3.5-fold higher than the two-step synthesis.

Scheme S1



Ar : **a, b, c, d**

(i) 1,2-Dichlorobenzene, 80 °C, N<sub>2</sub>.

(ii) toluene,  $h\nu$  (>290 nm), room temperature, N<sub>2</sub>.

The photochemical rearrangement of **1** to **2** was conducted in toluene solutions similar to the reported procedure.<sup>S6</sup>

### Synthesis of 1,6-(*N*-aryl)aza-[60]fulleroids (**1**)

**General Aspects.** NMR spectra were recorded on a Bruker AC-200 or on a JEOL JNM-LA500 with CS<sub>2</sub>: acetone-d<sub>6</sub> (10 : 1) as solvent. As internal standards, acetone-d<sub>6</sub> was used for <sup>1</sup>H NMR (δ: 2.05 ppm) and <sup>13</sup>C NMR (δ: 29.9 ppm) analyses. UV absorption spectra

were recorded on a Shimadzu UV-265 or on a Shimadzu UV-2400PC spectrophotometer, infrared spectra were measured on a Shimadzu FTIR-4000 spectrophotometer, and melting points were taken on a Yanagimoto Seisakusho Micro Melting Point Apparatus.

MALDI-TOFMS spectra were measured on a Shimadzu/KRATOS AXIMA-CFR spectrophotometer at the analytical center of the Shimadzu Co. Elemental analyses were carried out at the analytical center of the National Institute of Advanced Industrial Science and Technology. Solvents and commercially available chemicals were purified and dried by standard procedures or used as bought. Fullerene C<sub>60</sub> (99.5 %) was purchased from Southern Chemical Group, LLC, toluene from Wako Chemicals, 1,2-dichlorobenzene from Tokyo Kasei Kogyo Co., Ltd., spectral grade toluene from Kanto Chemical Co., Inc.

**1,6-(*N*-phenyl)aza-[60]fulleroid (1a).**<sup>S6</sup> Reaction time: 20 h; yield: 37 % (recovered C<sub>60</sub>: 39 %)<sup>S7a</sup>; black powder; m. p. 120 - 130 °C (decomposition). <sup>1</sup>H NMR (δ: 200.13 MHz; CS<sub>2</sub>: acetone-d<sub>6</sub> = 10 : 1): 7.06 (tt, 1H, J = 7.2, 1.2 Hz), 7.35 (dd, 2H, J = 7.9, 7.2 Hz), 7.52 (dt, 2H, J = 7.9, 1.2 Hz) ppm; <sup>13</sup>C NMR (δ: 50.32 MHz; CS<sub>2</sub>: acetone-d<sub>6</sub> = 10 : 1): 116.71, 123.56, 129.86, 135.45, 137.43, 138.01, 138.24, 138.45, 139.16, 140.18, 140.30, 140.84, 141.85, 142.24, 142.30, 143.30, 143.50, 143.52, 143.76, 143.83, 143.89, 143.94, 143.97, 144.17, 144.27, 144.42 (× 2), 144.62 (× 2), 144.74, 144.77, 145.06 (× 2), 145.15, 148.07, 148.11 ppm; IR (KBr): 2920, 2855, 1597, 1493, 1429, 1183, 747, 687, 526, 457 cm<sup>-1</sup>; MALDI-TOFMS (m/e, relative intensity): 720 (100), 811 (4, M<sup>-</sup>) (negative ion); 720 (100), 811 (8, M<sup>+</sup>) (positive ion); elemental analysis: C: 97.757 %, H: 0.650 %, N: 1.593 % (observed); C: 97.654 %, H: 0.621 %, N: 1.725 % (calculated).

**1,6-(*N*-1-naphthyl)aza-[60]fulleroid (1b).** Reaction time: 19.5 h; yield, 23 % (recovered C<sub>60</sub>: 40 %)<sup>S7a</sup>; black powder; m. p. 140 - 150 °C (decomposition). <sup>1</sup>H NMR (δ: 200.13 MHz; CS<sub>2</sub>: acetone-d<sub>6</sub> = 10 : 1): 7.40 - 7.55 (m, 3H), 7.45 (d, 1H, J = 8.2 Hz), 7.82 - 7.89 (m, 1H), 7.96 (dd, 1H, J = 7.6, 1.0 Hz), 8.53 - 8.60 (m, 1H) ppm; <sup>13</sup>C NMR (δ: 125.40 MHz; CS<sub>2</sub>: acetone-d<sub>6</sub> = 10 : 1): 114.17, 124.94, 125.55, 125.92, 126.76, 126.81, 126.97, 129.61, 135.54,

136.14, 137.18, 138.36, 138.52, 138.57, 139.34, 140.06, 140.54, 141.29, 141.92, 142.02, 142.21, 142.37, 143.39, 143.51, 143.63 ( $\times 2$ ), 143.64, 143.67, 143.68, 143.86, 143.95, 144.00, 144.23, 144.47, 144.52, 144.63, 144.68, 144.79, 144.87, 144.91, 145.27, 147.99 ppm; IR (KBr): 3050, 2950, 2910, 2860, 1595, 1574, 1508, 1462, 1439, 1429, 1400, 1342, 1287, 1177, 787, 766, 540  $\text{cm}^{-1}$ ; MALDI-TOFMS ( $m/e$ , relative intensity): 720 (100), 861 (2,  $M^-$ ) (negative ion); 720 (100), 811 (16,  $M^+$ ) (positive ion); elemental analysis: C: 97.314 %, H: 1.237 %, N: 1.449 % (observed); C: 97.556 %, H: 0.819 %, N: 1.625 % (calculated).

**1,6-(*N*-2-naphthyl)aza-[60]fulleroid (1c).** Reaction time: 21.5 h; yield, 35 % (recovered  $C_{60}$ : 33 %) <sup>S7a</sup>; black powder; m. p. 150 - 160 °C (decomposition).  $^1\text{H}$  NMR ( $\delta$ : 200.13 MHz;  $\text{CS}_2$ : acetone- $d_6$  = 10 : 1): 7.42 (dd, 1H,  $J$  = 6.9, 1.4 Hz), 7.31 (dd, 1H,  $J$  = 6.9, 1.4 Hz), 7.70 (dd, 1H,  $J$  = 8.9, 2.3 Hz), 7.71 - 7.77 (m, 2H), 7.42 (d, 1H, 8.9 Hz), 7.31 (d, 1H,  $J$  = 2.3 Hz) ppm;  $^{13}\text{C}$  NMR ( $\delta$ : 125.40 MHz;  $\text{CS}_2$ : acetone- $d_6$  = 10 : 1): 112.35, 118.57, 125.19, 127.66, 127.67, 128.49, 130.03, 130.80, 131.08 ( $\times 2$ ), 134.58, 135.45, 137.54, 137.96, 138.20, 138.60, 139.22, 140.22, 140.33, 140.91, 141.87, 142.29, 142.30, 143.37, 143.57 ( $\times 2$ ), 143.63, 143.81, 143.95, 143.99, 144.01, 144.23, 144.30, 144.48, 144.70, 144.80, 144.86, 145.13, 145.15, 145.24, 145.54, 148.16 ppm; IR (KBr): 3040, 2924, 2860, 1628, 1510, 1468, 843, 804, 741, 524  $\text{cm}^{-1}$ ; MALDI-TOFMS ( $m/e$ , relative intensity): 720 (100), 861 (1,  $M^-$ ) (negative ion); 720 (100), 811 (9,  $M^+$ ) (positive ion); elemental analysis: C: 97.400 %, H: 1.156 %, N: 1.444 % (observed); C: 97.556 %, H: 0.819 %, N: 1.625 % (calculated).

**1,6-(*N*-1-pyrenyl)aza-[60]fulleroid (1d).** Reaction time: 29 h; yield, 17 % (recovered  $C_{60}$ : 33 %) <sup>S7a</sup>; black powder; m. p. 155 - 160 °C (decomposition).  $^1\text{H}$  NMR ( $\delta$ : 499.10 MHz;  $\text{CS}_2$ : acetone- $d_6$  = 10 : 1): 7.95 (d, 1H,  $J$  = 9.0 Hz), 7.98 (dd, 1H,  $J$  = 7.9, 7.4 Hz), 8.01 (d, 1H,  $J$  = 9.0 Hz), 8.09 (d, 1H,  $J$  = 9.5 Hz), 8.12 (d, 1H,  $J$  = 7.4 Hz), 8.12 (d, 1H,  $J$  = 7.9 Hz), 8.17 (d, 1H,  $J$  = 8.2 Hz), 8.56 (d, 1H,  $J$  = 8.2 Hz), 8.78 (d, 1H,  $J$  = 9.5 Hz) ppm;  $^{13}\text{C}$  NMR ( $\delta$ : 125.40 MHz;  $\text{CS}_2$ : acetone- $d_6$  = 10 : 1): 115.99, 122.37, 123.67, 125.60, 125.67, 125.77, 126.02, 127.03, 127.21, 127.36, 128.12, 128.26, 128.86, 131.54, 132.29, 135.70, 137.25, 138.39, 138.56, 138.60, 139.39, 140.21, 140.49, 140.55, 141.25, 142.04, 142.38, 142.46, 143.40, 143.58, 143.63, 143.68 ( $\times 2$ ),

143.73, 143.87, 143.96, 143.99, 144.02, 144.24, 144.29, 144.52, 144.66, 144.73, 144.86, 144.90, 144.97, 145.29, 148.02 ppm; IR (KBr): 3050, 2920, 1599, 1510, 1435, 1344, 1284, 1186, 838, 709, 528 cm<sup>-1</sup>; MALDI-TOFMS (m/e, relative intensity): 720 (100), 935 (4, M<sup>-</sup>) (negative ion); 720 (37), 935 (100, M<sup>+</sup>) (positive ion); elemental analysis: C: 97.647 %, H: 1.019 %, N: 1.334 % (observed); C: 97.534 %, H: 0.969 %, N: 1.497 % (calculated).

### Synthesis of 1,2-(*N*-arylaziridino)-[60]fullerenes (**2**)

**1,2-(*N*-Phenylaziridino)-[60]fullerene (**2a**).**<sup>S6</sup> 0.049 g of 1,6-(*N*-phenyl)aza- [60]fulleroid (**1a**) in 80 mL toluene was irradiated with the xenon lamp for 10.5 h after bubbling nitrogen gas into the solution for 0.75 h. Yield, 37 %;<sup>S7b</sup> black powder, m. p. 125 - 130 °C (decomposition). <sup>1</sup>H NMR (δ: 200.13 MHz; CS<sub>2</sub>: acetone-d<sub>6</sub> = 10 : 1): 7.17 - 7.24 (m, 1H), 7.42 - 7.50 (m, 2H), 7.60 - 7.65 (m, 2H) ppm; <sup>13</sup>C NMR (δ: 50.32 MHz; CS<sub>2</sub>: acetone-d<sub>6</sub> = 10 : 1): 84.13, 122.01, 124.89, 129.80, 141.26, 141.48, 142.74, 142.77, 143.38, 143.63 (× 2), 144.39, 144.64, 145.09, 145.24, 145.29, 145.35, 145.36, 145.67, 145.76, 146.05 ppm; IR (KBr): 2924, 2344, 1597, 1489, 1429, 1387, 1318, 1184, 754, 704, 688, 526 cm<sup>-1</sup>; MALDI-TOFMS (m/e, relative intensity): 720 (100), 811 (13, M<sup>-</sup>) (negative ion); elemental analysis: C: 97.244 %, H: 1.291 %, N: 1.465 % (observed); C: 97.654 %, H: 0.621 %, N: 1.725 % (calculated).

**1,2-(*N*-1-Naphthylaziridino)-[60]fullerene (**2b**).** 0.057 g of 1,6-(*N*-1-naphthyl)aza-[60]fulleroid (**1b**) in 70 mL toluene was irradiated with the xenon lamp for 1.0 h after bubbling nitrogen gas into the solution for 1.0 h. Yield, 88 %;<sup>S7b</sup> black powder, m. p. 150 - 160 °C (decomposition). <sup>1</sup>H NMR (δ: 200.13 MHz; CS<sub>2</sub>: acetone-d<sub>6</sub> = 10 : 1): 7.50 - 7.73 (m, 5H), 7.95 (dd, 1H, J = 7.9, 1.5 Hz), 8.88 (d, 1H, J = 8.5 Hz) ppm; <sup>13</sup>C NMR (δ: 50.32 MHz; CS<sub>2</sub>: acetone-d<sub>6</sub> = 10 : 1): 83.63, 119.95, 123.08, 125.44, 125.88, 127.27 (× 2), 127.49, 129.84, 135.30, 140.85, 141.39, 141.48, 142.67, 142.82, 143.36, 143.61 (× 2), 144.45, 144.61, 145.11, 145.24, 145.36, 145.48, 145.59, 145.71, 145.83 ppm; IR (KBr): 3061, 2920, 2853, 1626, 1595, 1976, 1509, 1462, 1399, 1383, 1183, 789, 768, 527 cm<sup>-1</sup>; MALDI-TOFMS (m/e, relative intensity): 720 (100), 861 (97, M<sup>-</sup>) (negative ion); elemental analysis: C: 97.445 %, H: 1.011 %, N: 1.465 % (observed); C: 97.654 %, H: 0.621 %, N: 1.725 % (calculated).

N: 1.544 % (observed); C: 97.556 %, H: 0.819 %, N: 1.625 % (calculated).

**1,2-(*N*-2-Naphthylaziridino)-[60]fullerene (2c).** 0.082 g of 1,6-(*N*-2-naphthyl)aza-[60]fulleroid (**1c**) in 80 mL toluene was irradiated with the xenon lamp for 13 h after bubbling nitrogen gas into the solution for 0.5 h. Yield, 58 %;<sup>S7b</sup> black powder, m. p. 150 - 160 °C (decomposition). <sup>1</sup>H NMR (δ: 200.13 MHz; CS<sub>2</sub>: acetone-d<sub>6</sub> = 10 : 1): 7.37 (m, 2H), 7.81 - 7.96 (m, 5H) ppm; <sup>13</sup>C NMR (δ: 50.32 MHz; CS<sub>2</sub>: acetone-d<sub>6</sub> = 10 : 1): 84.22, 118.90, 121.86, 125.96, 127.61, 127.91, 128.55, 130.08, 131.31, 134.24, 141.29, 141.48, 142.71, 142.76, 143.22, 143.39, 143.62 (× 2), 144.37, 144.61, 145.06, 145.21, 145.26 (× 2), 145.33, 145.64, 145.74 ppm; IR (KBr): 3040, 2930, 2870, 1628, 1512, 1466, 1383, 806, 741, 525 cm<sup>-1</sup>; MALDI-TOFMS (m/e, relative intensity): 720 (100), 861 (11, M<sup>-</sup>) (negative ion); elemental analysis: C: 97.640 %, H: 0.822 %, N: 1.538 % (observed); C: 97.556 %, H: 0.819 %, N: 1.625 % (calculated).

**1,2-(*N*-1-Pyrenylaziridino)-[60]fullerene (2d).** 0.048 g of 1,6-(*N*-1-pyrenyl)aza-[60]fulleroid (**1d**) in 100 mL toluene was irradiated with the xenon lamp for 15 h after bubbling nitrogen gas into the solution for 2.0 h. Yield, 67 %;<sup>S7b</sup> black powder, m. p. 160 - 170 °C (decomposition). <sup>1</sup>H NMR (δ: 499.10 MHz; CS<sub>2</sub>: acetone-d<sub>6</sub> = 10 : 1): 8.01 (t, 1H, J = 7.6 Hz), 8.03 (d, 1H, J = 8.8 Hz), 8.09 (d, 1H, J = 8.8 Hz), 8.18 (d, 1H, J = 7.6 Hz), 8.19 (d, 1H, J = 7.6 Hz), 8.255 (d, 1H, J = 9.2 Hz), 8.261 (d, 1H, J = 8.0 Hz), 8.29 (d, 1H, J = 8.0 Hz), 9.11 (d, 1H, J = 9.2 Hz) ppm; <sup>13</sup>C NMR (δ: 125.40 MHz; CS<sub>2</sub>: acetone-d<sub>6</sub> = 10 : 1): 83.96, 121.33, 122.29, 123.63, 125.56, 125.64, 126.07, 126.30, 126.50, 127.22, 127.42, 128.12, 128.86, 129.00, 131.75, 132.14, 141.44, 141.57, 142.71, 142.85, 143.38, 143.63, 143.64, 143.67, 144.49, 144.61, 145.09, 145.13, 145.33, 145.41, 145.55, 145.75, 145.87 ppm; IR (KBr): 3050, 2922, 2853, 1630, 1599, 1514, 1507, 1433, 1408, 1385, 1183, 839, 526 cm<sup>-1</sup>; MALDI-TOFMS (m/e, relative intensity): 720 (99), 935 (100, M<sup>-</sup>) (negative ion); elemental analysis: C: 97.624 %, H: 1.060 %, N: 1.316 % (observed); C: 97.534 %, H: 0.969 %, N: 1.497 % (calculated).



### Derivation of eq 2 from eq 1.

Equation 1 is

$$-\frac{d[\mathbf{1}]_t}{dt} = k_d[\mathbf{1}]_t + k_s[\mathbf{1}]_t[\mathbf{2}]_t \quad (1)$$

By substituting  $[\mathbf{2}]_t = [\mathbf{1}]_0 - [\mathbf{1}]_t$  to eq 1, eq 1 becomes

$$\frac{d[\mathbf{1}]_t}{dt} + (k_d + k_s[\mathbf{1}]_0)[\mathbf{1}]_t = k_s[\mathbf{1}]_t^2 \quad (1')$$

Equation 1' is a Bernoulli's differential equation, which can be solved as

$$\frac{1}{[\mathbf{1}]_t} = \{C_1 - k_s \int \exp(-W) dt\} \exp W \quad (3)$$

where

$$W = (k_d + k_s[\mathbf{1}]_0) \int dt = (k_d + k_s[\mathbf{1}]_0)t + C_2 \quad (4)$$

and  $C_1$  and  $C_2$  are constants. From eqs 3 and 4

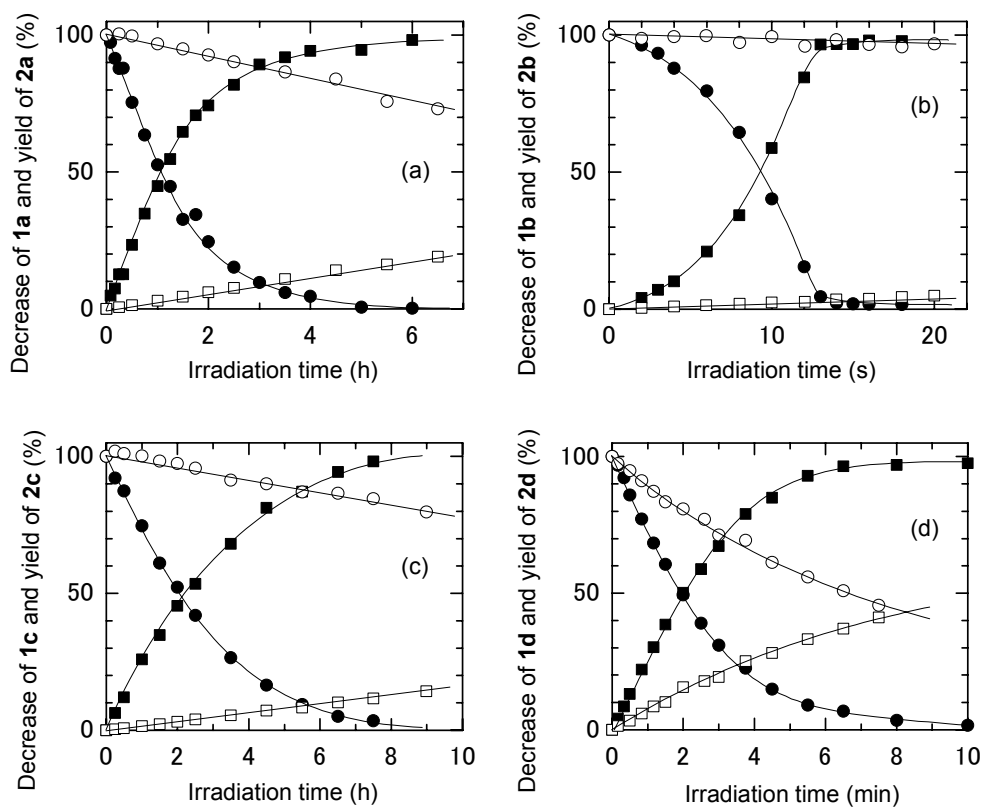
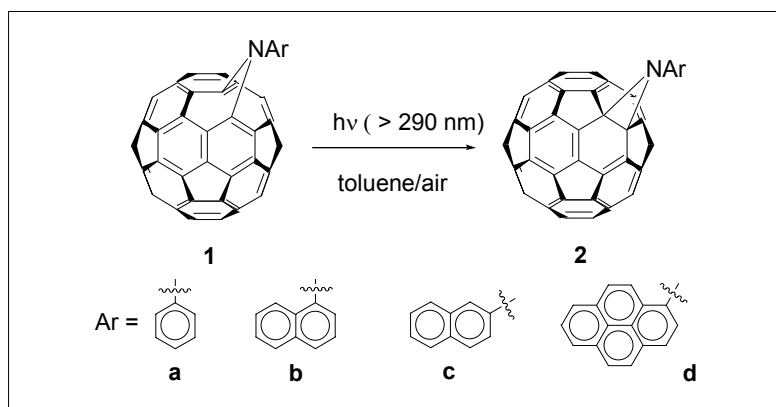
$$\begin{aligned} \frac{1}{[\mathbf{1}]_t} &= [C_1 - k_s \int \exp\{-(k_d + k_s[\mathbf{1}]_0)t - C_2\} dt] \exp\{(k_d + k_s[\mathbf{1}]_0)t + C_2\} \\ &= C_1 \exp C_2 \exp(k_d + k_s[\mathbf{1}]_0)t + \frac{k_s}{k_d + k_s[\mathbf{1}]_0} \end{aligned} \quad (5)$$

At  $t = 0$ ,  $[\mathbf{1}]_t$  is  $[\mathbf{1}]_0$ , so that from eq 5

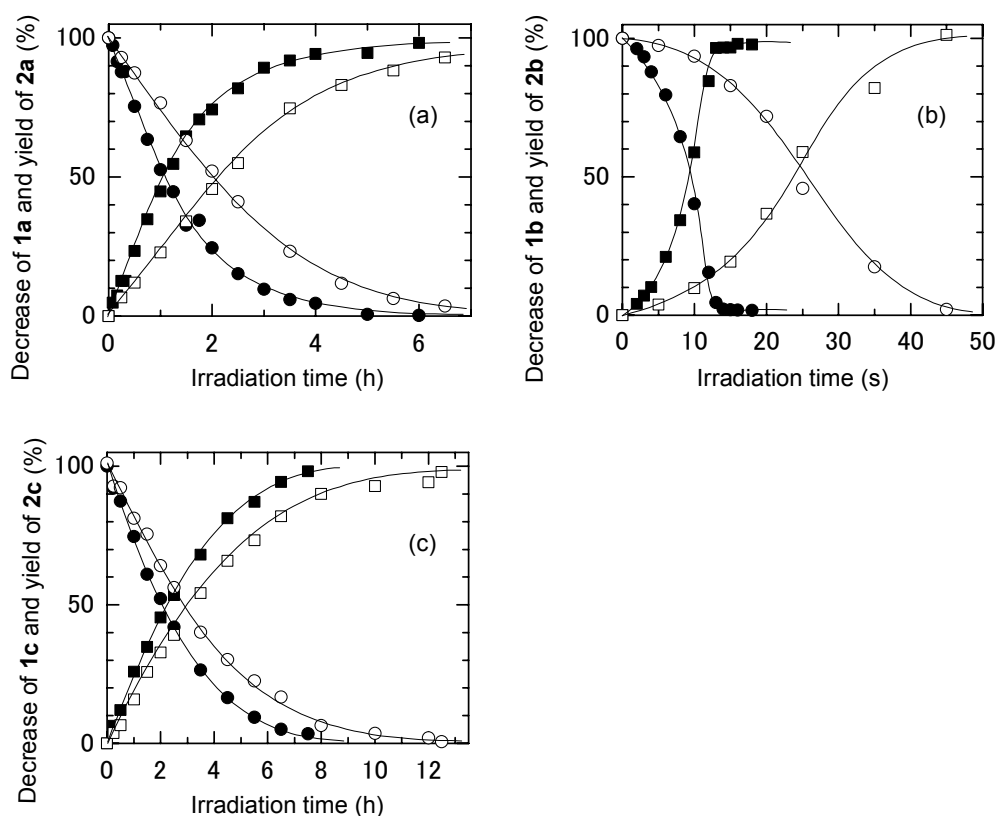
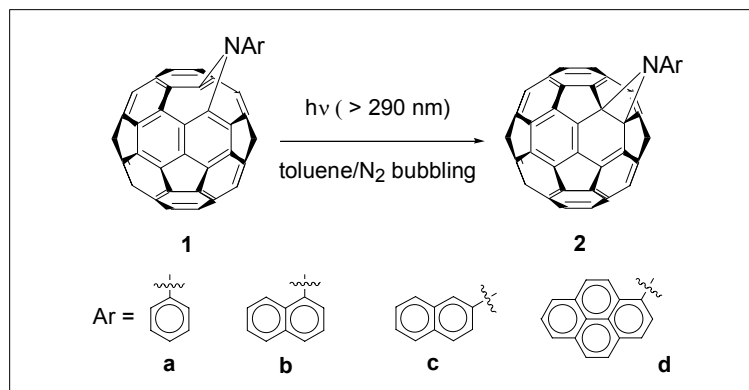
$$\begin{aligned} \frac{1}{[\mathbf{1}]_0} &= C_1 \exp C_2 + \frac{k_s}{k_d + k_s[\mathbf{1}]_0} \\ \therefore C_1 \exp C_2 &= \frac{1}{[\mathbf{1}]_0} - \frac{k_s}{k_d + k_s[\mathbf{1}]_0} \end{aligned} \quad (6)$$

By substituting eq 6 to eq 5

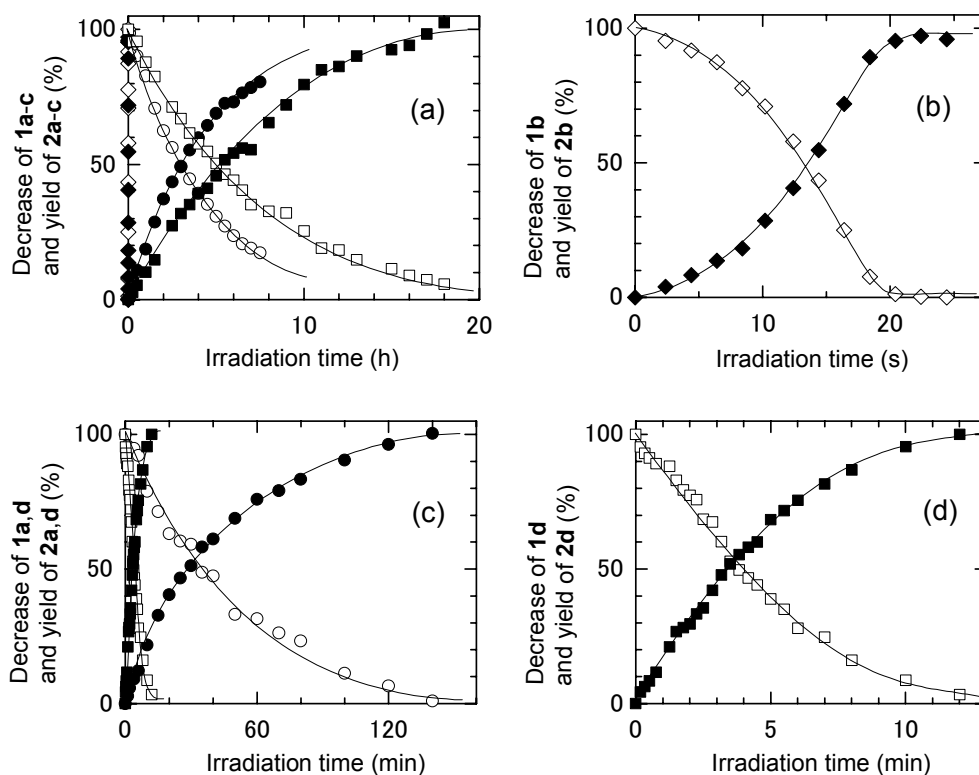
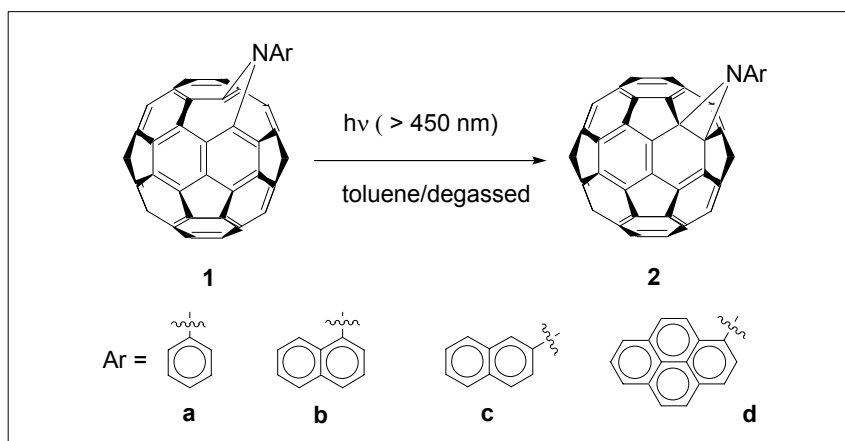
$$\begin{aligned} \frac{1}{[\mathbf{1}]_t} &= \left\{ \frac{1}{[\mathbf{1}]_0} - \frac{k_s}{k_d + k_s[\mathbf{1}]_0} \right\} \exp\{(k_d + k_s[\mathbf{1}]_0)t\} + \frac{k_s}{k_d + k_s[\mathbf{1}]_0} \\ \therefore [\mathbf{1}]_t &= \frac{1}{\left( \frac{1}{[\mathbf{1}]_0} - \frac{k_s}{k_d + k_s[\mathbf{1}]_0} \right) \exp\{(k_d + k_s[\mathbf{1}]_0)t\} + \frac{k_s}{k_d + k_s[\mathbf{1}]_0}} \end{aligned} \quad (2)$$



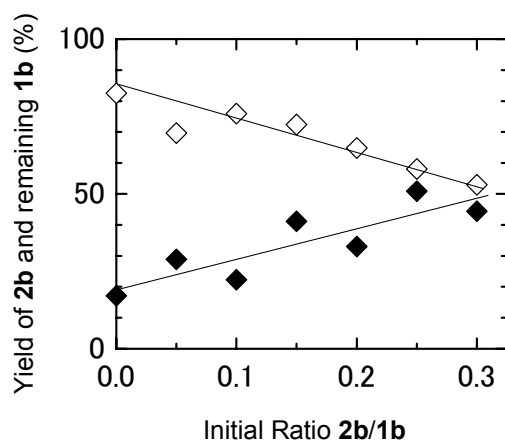
**Figure S1.** Decrease of **1a-d** (○, ●) and formation of **2a-d** (□, ■) in degassed (solid symbols) and air-saturated (open symbols) conditions. (a) **1a**, **2a**; (b) **1b**, **2b**; (c) **1c**, **2c**; (d) **1d**, **2d**. Concentration: (a, b, c)  $5 \times 10^{-4} \text{ M}$  and (d)  $1 \times 10^{-5} \text{ M}$  **1** in toluene; light source: 500-W Xe lamp, fitted with a water filter and a Toshiba UV-29 filter ( $> 290\text{-nm}$  light). The results of the degassed experiments were obtained from the average of (a, c, d) three or (b) four independent runs and those of the air-saturated experiments (a, b, c) from the average of two independent runs and (d) from a single run.



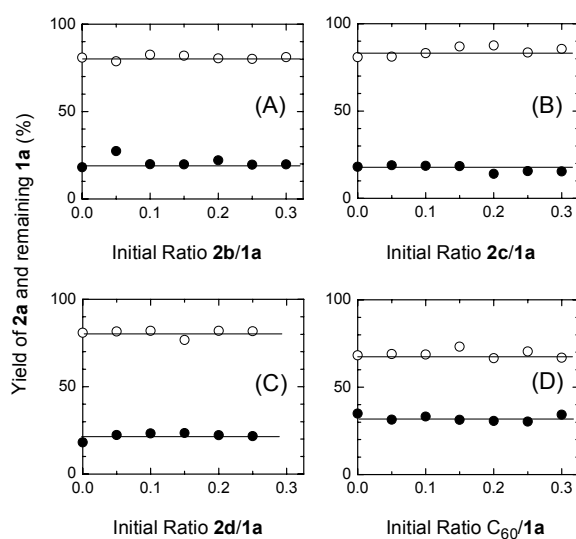
**Figure S2.** Decrease of **1a-c** (○, ●) and formation of **2a-c** (□, ■) in degassed (solid symbols) and nitrogen bubbling (open symbols) conditions. (a) **1a**, **2a**; (b) **1b**, **2b**; (c) **1c**, **2c**. Concentration: (a, b, c)  $5 \times 10^{-4}$  M **1** in toluene; light source: 500-W Xe lamp, fitted with a water filter and a Toshiba UV-29 filter ( $> 290$ -nm light). The results of the degassed experiments were obtained from the average of (a, c) three or (b) four independent runs and those of the nitrogen-purged experiments from the average of (a) four or (b, c) two independent runs.



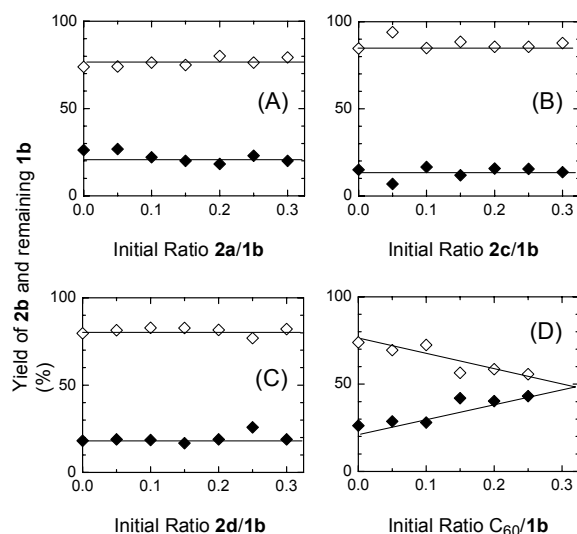
**Figure S3.** (a) Decrease of **1a-c** and formation of **2a-c**, (b) decrease of **1b** and formation of **2b**, (c) decrease of **1a,d** and formation of **2a,d** in degassed solution as a function of irradiation time. Codification of substrates **1a** ( $\circ$ ), <sup>S8a</sup> **1b** ( $\diamond$ ), <sup>S8b</sup> **1c** ( $\square$ ), <sup>S8a</sup> **1d** ( $\triangle$ ), <sup>S8a</sup> and products **2a** ( $\bullet$ ), <sup>S8a</sup> **2b** ( $\blacklozenge$ ), <sup>S8b</sup> **2c** ( $\blacksquare$ ), <sup>S8a</sup> **2d** ( $\blacktriangle$ ). Concentration: (a, b)  $5 \times 10^{-4}$  M and (c, d)  $1 \times 10^{-5}$  M **1** in toluene; light source: 500-W xenon lamp, fitted with a water filter and a Toshiba Y-45 filter ( $> 450$ -nm light).



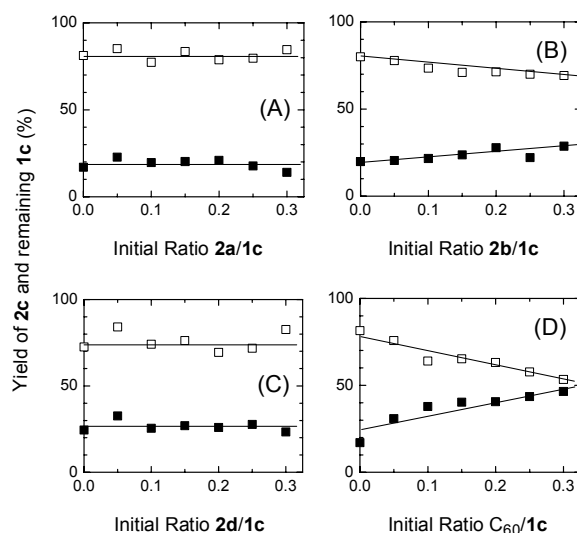
**Figure S4.** Yield of **2b** and remaining **1b** in degassed solutions as a function of the ratio of the amount of initially added authentic **2b** to **1b**.<sup>S8a</sup> Codification of substrate **1b** (◇) and product **2b** (◆). Irradiation time: 6 s. Concentration:  $5 \times 10^{-4}$ . Light source: 500-W Xe lamp, fitted with a water filter and a Toshiba R-60 filter ( $> 600$ -nm light).



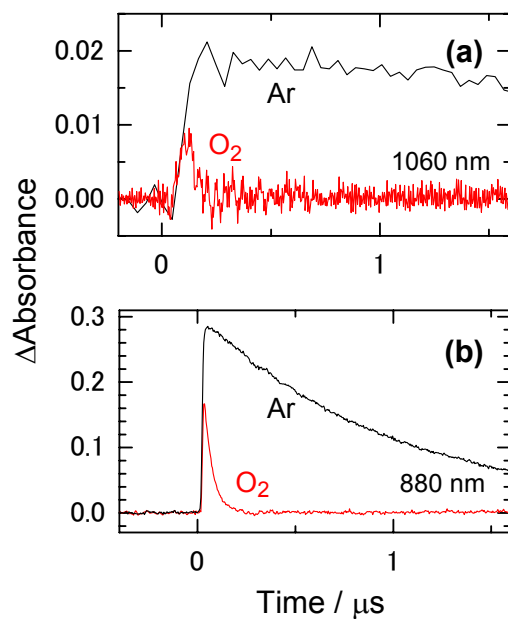
**Figure S5.** Yield of **2a** and remaining **1a** in degassed solutions as a function of the ratio of the amount of initially added authentic **2b** to **1a** (A),<sup>S8a</sup> **2c** to **1a** (B),<sup>S8a</sup> **2d** to **1a** (C),<sup>S8a</sup> and **C<sub>60</sub>** to **1a** (D).<sup>S8b</sup> Codification of substrate **1a** (○) and product **2a** (●). Irradiation time: 20 min (A-C), 30 min (D). Concentration:  $5 \times 10^{-4}$  M **1a** in toluene. Light source: 500-W Xe lamp fitted with a water filter and a Toshiba UV-29 filter ( $> 290$ -nm light).



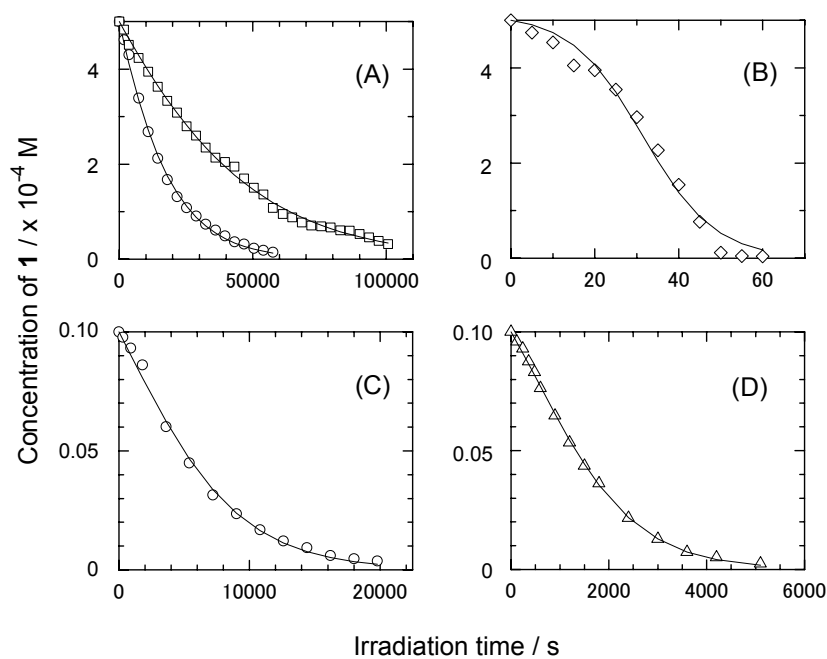
**Figure S6.** Yield of **2b** and remaining **1b** in degassed solutions as a function of the ratio of the amount of initially added authentic **2a** to **1b** (A),<sup>S8a</sup> **2c** to **1b** (B),<sup>S8c</sup> **2d** to **1b** (C),<sup>S8a</sup> and **C<sub>60</sub>** to **1b** (D).<sup>S8a</sup> Codification of substrate **1b** (◇) and product **2b** (◆). Irradiation time: 6 s. Concentration:  $5 \times 10^{-4}$  M **1a** in toluene. Light source: 500-W Xe lamp, fitted with a water filter and a Toshiba UV-29 filter (> 290-nm light).



**Figure S7.** Yield of **2c** and remaining **1c** in degassed solutions as a function of the ratio of the amount of initially added authentic **2a** to **1c** (A),<sup>S8a</sup> **2b** to **1c** (B),<sup>S8a</sup> **2d** to **1c** (C),<sup>S8b</sup> and **C<sub>60</sub>** to **1c** (D).<sup>S8a</sup> Codification of substrate **1c** (□) and product **2c** (■). Irradiation time: 1 h. Concentration:  $5 \times 10^{-4}$  M **1c** in toluene. Light source: 500-W Xe lamp, fitted with a water filter and a Toshiba UV-29 filter (> 290-nm light).



**Figure S8.** The decay profiles of the transient absorption peaks of **1a** (a) and **2a** (b) in the absence and presence of oxygen gas. Excitation wavelength: 530 nm. Concentration:  $10^{-4}$  M in toluene.



**Figure S9.** Decrease of **1a-d** as a function of irradiation time with curve fitting according to eq 2. Codification of substrate; **1a** ( $\circ$ ), **1b** ( $\diamond$ ), **1c** ( $\square$ ), **1d** ( $\triangle$ ). Initial concentration ( $[\mathbf{1}]_0$ ):  $5 \times 10^{-4}$  (A, B) and  $1 \times 10^{-5}$  M (C, D) in toluene; light source: 500-W Xe lamp, fitted with a water filter and a Toshiba R-60 filter ( $> 600\text{-nm}$  light).

**Table S1.** Ground-state heats of formation and the charges on the nitrogen atom for 1,6-(*N*-aryl)aza-[60]fulleroids (**1**) and 1,2-(*N*-arylaziridino)-[60]fullerenes (**2**).<sup>a</sup>

Substituent	Fulleroids <b>1</b>		Fullerenes <b>2</b>	
	$\Delta H_f^b$ (kJ/mol)	Charge <sup>c</sup>	$\Delta H_f^b$ (kJ/mol)	Charge <sup>c</sup>
<b>a</b>	3548	0.137	3558	0.121
<b>b</b>	3634	0.128	3643	0.113
<b>c</b>	3620	0.137	3630	0.121
<b>d</b>	3732	0.133	3737	0.125

<sup>a</sup> Calculated by MOPAC using PM3 Hamiltonian. <sup>b</sup> Heat of formation. <sup>c</sup> Charge on the nitrogen atom.

## References and notes

- S1. Some of the original spectra can be seen in the web site of the Spectrum Data Base System (SDBS) (<http://www.aist.go.jp/RIODB/SDBS/>).
- S2. Snyder, H. R.; Elston, C. T.; Kellon, D. B. *J. Am. Chem. Soc.*, **1953**, 75, 2014-2015.
- S3. Mendenhall, G. D.; Smith, P. A. S., *Org. Synth., Coll. Vol. 5*, John Wiley & Sons, New York, 1973, pp. 829-833.
- S4. Hodgson, H. H.; Norris, W. H. H. *J. Chem. Soc.*, **1949**, 762-763.
- S5. Schrock, A. K.; Schuster, G. B. *J. Am. Chem. Soc.*, **1984**, 106, 5234-5240.
- S6. Averdung, J.; Mattay, J. *Tetrahedron* **1996**, 52, 5407-5420.
- S7. (a) The yields of **1** and recovered C<sub>60</sub> are based on the amount of initially used C<sub>60</sub>. (b) The yields of **2** are based on the amount of initially used **1**. The yields of **2** have not been optimized.
- S8. The results were obtained from (a) one independent run or (b) from the average of two or (c) three independent runs.