Supporting information

A Photocatalyst-Free, SET-Mediated Photochemical Approach for the Synthesis of Dumbbell-Like Amine-Functionalized Bis-C60 Fullerene through C–C Bond Formation

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1. General procedures

The corresponding primary amines 1-4 (1- 5823 mg, 2- 6586 mg, 3- 6801 mg, 4- 7455 mg, 54.35 mmol) was taken in acetonitrile (120 mL), added K$_2$CO$_3$ (11266 mg, 81.52 mmol) under argon. The reaction mixture heated at 70 0C for 1 h and iodomethyltrimethylsilane 5 (969 7 mg, 45.29 mmol) was added dropwise. The reaction mixture stirred for 7 h at 70 0C. After completion of reaction (checked by TLC), the mixture concentrated in vacuo to give residues that were partitioned between water and CH$_2$Cl$_2$. The CH$_2$Cl$_2$ layers were dried and concentrated in vacuo to afford residues that were subjected to silica gel column chromatography (EtOAc/hexane = 1:1) to yield the corresponding Secondary N-Trimehtylsilylmethyl-N-benzylamines 6 (8197 mg, 78%), 7 (9580 mg, 85%), 8 (6317 mg, 55%) and 9 (9712 mg, 80%). The spectral data exactly matching with reported one.

General Procedure for Synthesis of bis α-trimethylsilyl-substituted tertiary amines 13-16.
The corresponding secondary amines 6-9 (6- 1160 mg, 7- 1244 mg, 8- 1268 mg, 9- 1340 mg, 6 mmol) was taken in acetonitrile (120 mL), added K$_2$CO$_3$ (1243 mg, 9 mmol) under argon. The reaction mixture heated at 70 0C for 1 h and 2,2'-oxybis (ethane-2,1-diyl) bis (2-bromoacetate) 12 (1043 mg, 3 mmol) was added dropwise. The reaction mixture stirred for 7 h at 70 0C. After completion of reaction (checked by TLC), the mixture concentrated in vacuo to give residues that were partitioned between water and CH$_2$Cl$_2$. The CH$_2$Cl$_2$ layers were dried and concentrated in vacuo to afford residues that were subjected to silica gel column chromatography (diethyl ether/hexane = 1:8) to yield the corresponding symmetrical molecules 13 (1288 mg, 75%), 14 (1442 mg, 80%), 15 (1095 mg, 60%) and 16 (1481 mg, 78%).

2, 2'-oxybis (ethane-2,1-diyl) bis (2 (benzyl ((trimethylsilyl) methyl) amino) acetate) 13. $^1$H NMR δ 0.08 (s, 18H), 2.23 (s, 4H), 3.32 (s, 4H), 3.66 (t, $J=12.30$Hz, 4H), 3.78 (s, 4H), 4.34 (t, $J=12.24$Hz, 4H), 7.37-7.21 (m, 10H); $^{13}$C NMR δ -1.5, 41.4, 45.6, 56.7, 61.3, 63.5, 126.9, 128.1, 128.7, 139.2, 170.8.

2, 2'-oxybis (ethane-2,1-diyl) bis (2- (4-methylbenzyl) ((trimethylsilyl) methyl) amino)acetate) 14. $^1$H NMR δ 0.10 (s, 18H), 2.23 (s, 4H), 3.31 (s, 4H), 3.66 (t, $J=12.30$Hz, 4H), 3.74 (s, 4H), 4.33 (t, $J=12.22$Hz, 4H), 7.12 (d, $J=9$Hz, 4H), 7.25 (d, $J=6.24$Hz, 4H); $^{13}$C NMR δ -1.5, 21.0, 41.4, 45.6, 56.6, 60.9, 63.4, 128.6, 128.8, 136.1, 134.6, 170.8.

2, 2'-oxybis (ethane-2,1-diyl) bis (2- (4-fluorobenzyl) ((trimethylsilyl) methyl) amino)acetate) 15. $^1$H NMR δ 0.04 (s, 18H), 2.17 (s, 4H), 3.28 (s, 4H), 3.70-3.64 (m, 8H), 4.32 (t, $J=12.22$Hz, 4H), 6.96 (t, $J=18.16$Hz, 4H), 7.31-7.26 (m, 4H); $^{13}$C NMR δ -1.5, 41.5, 45.5, 56.6, 60.6, 63.5, 114.9 (d, $J_{CF} = 84$Hz), 130.2 (d, $J_{CF} = 30$Hz), 135.0 (d, $J_{CF} = 12$Hz), 161.9 (d, $J_{CF} = 972$ Hz), 170.5.

2, 2'-oxybis (ethane-2,1-diyl) bis (2- (4-methoxybenzyl) ((trimethylsilyl) methyl) amino)acetate)
\[ ^1H \text{NMR} \delta 0.06 (s, 18H), 2.19 (s, 4H), 3.27 (s, 4H), 3.68-3.62 (m, 8H), 3.75 (s, 6H), 4.30 (t, J=12.24Hz, 4H), 6.82 (d, J= 12Hz, 4H), 7.24 (d, J= 6.28Hz, 4H); ^{13}C \text{NMR} \delta-1.6, 41.4, 45.4, 54.9, 56.4, 60.5, 63.3, 113.4, 129.7, 131.1, 158.5, 170.7. \]

**General Procedure for Photoreactions of C\(_{60}\) with bis \(\alpha\)-trimethylsilyl-substituted tertiary benzyl amines.** Preparative photochemical reactions were conducted using an apparatus consisting of a 450 W Hanovia medium vapor pressure mercury lamp surrounded by a flint glass filter (>300 nm) in a water-cooled quartz immersion well surrounded by a solution consisting of 10% EtOH-toluene of C\(_{60}\) (201.78 mg, 0.28 mmol), and bis \(\alpha\)-trimethylsilyl-substituted tertiary amines (13-320.81 mg, 14-336.52 mg, 15-340.96 mg, 16-354.44 mg, 0.56 mmol). Each solution was purged with nitrogen before and during irradiation, which was carried out for the time periods given for each substance below. The photoproduct were concentrated, and the generated residues were triturated with CHCl\(_3\) to recover C\(_{60}\). The triturates were concentrated in vacuo to generate residues that were subjected to silica gel column chromatography (eluants given below) to obtain photoproducts.

**Photoreaction of C\(_{60}\) with 13.** In N\(_2\) saturated condition: 90 min irradiation, 89% conversion, column chromatography (CS\(_2\):CHCl\(_3\)= 5:1) to yield 17 (256 mg, 49%) and 21 (22 mg, 4%). O\(_2\) saturated condition: 120 min irradiation, 90% conversion, column chromatography (CS\(_2\):CHCl\(_3\)= 5:1) to yield 17 (10 mg, 2%) and 21 (286 mg, 51%).

\[ ^1H \text{NMR} \delta 3.76 (t, 4H, J= 9.45Hz), 4.00 (s, 4H), 4.48-4.53 (m, 8H), 4.76 (s, 4H), 6.90 (s, 2H), 7.30-7.42 (m, 6H), 7.62 (d, 4H, J= 6.60Hz); ^{13}C \text{NMR} \delta 41.6, 55.7, 58.0, 59.8, 64.17, 67.3, 68.4, 127.8, 128.7, 129.4, 136.0, 136.1, 138.15, 140.0, 140.2, 141.6 (2C), 141.7, 141.9, 142.0, 142.3, 142.5 (2C), 143.2, 144.4, 144.6, 145.3 (3C), 145.4, 145.8, 146.1 (2C), 146.3 (2C), 146.8, 147.2, 147.3, 154.3, 154.7, 171.1; HRMS (FAB) m/z 1872.9016 (M + 1, C\(_{144}\)H\(_{35}\)N\(_2\)O\(_5\) requires 1872.8212). \]

\[ ^1H \text{NMR} \delta 0.51 (s, 18H), 3.57-3.68 (m, 4H), 4.37-4.45 (m, 2H), 4.47-4.55 (m, 2H), 4.60 (d, 2H, J=12.15Hz), 5.28 (d, 2H, J=12.18Hz), 5.39 (s, 2H), 5.51 (s, 2H), 7.28-7.48 (m, 6H), 7.65 (d, J=6.30Hz); ^{13}C \text{NMR} \delta 0.7, 41.3, 56.2, 64.5, 70.0, 77.2, 77.6, 77.9, 127.8, 128.6, 128.9, 134.9, 135.5, 135.6, 136.3, 138.7, 139.2, 139.6, 139.7, 140.1, 141.6, 141.7, 141.8, 141.9, 142.0, 142.1 (2C), 142.2, 142.3, 142.4, 142.6, 142.7, 143.0, 143.1, 144.2, 144.3, 144.4, 144.5, 144.9, 145.1, 145.2, 145.3, 145.5, 145.8, 145.9, 146.1 (2C), 146.2, 146.6, 146.9, 147.0, 152.4, 154.7, 156.4, 156.9, 170.3; HRMS (FAB) m/z 2013.2318 (M + 1, C\(_{150}\)H\(_{47}\)N\(_2\)O\(_5\)SiO\(_2\) requires 2013.1516). \]

**Photoreaction of C\(_{60}\) with 14.** In N\(_2\) saturated condition: 80 min irradiation, 85% conversion, column chromatography (CS\(_2\):CHCl\(_3\)= 5:1) to yield 18 (271 mg, 51%) and 20 (17 mg, 3%). O\(_2\) saturated condition: 120 min irradiation, 90% conversion, column chromatography (CS\(_2\):CHCl\(_3\)= 5:1) to yield 18 (20 mg, 4%) and 22 (233 mg, 50%).
18: \(^1\)H NMR \(\delta\) 2.35 (s, 6H), 3.90 (t, 4H, \(J = 9.24\) Hz), 3.98 (s, 4H), 4.37 (t, 4H, \(J = 9.22\) Hz), 4.49 (s, 4H), 4.75 (s, 4H), 6.93 (s, 2H), 7.19 (d, 4H, \(J = 9.30\) Hz), 7.49 (d, 4H, \(J = 6.32\) Hz); \(^{13}\)C NMR \(\delta\) 21.2, 41.6, 55.6, 58.1, 59.5, 64.1, 67.4, 68.4, 129.4 (2C), 135.0, 136.0, 136.1, 137.4, 140.0, 140.2, 141.6 (2C), 141.8, 141.9, 142.0, 142.3, 142.5 (2C), 143.2, 144.5, 144.6, 145.3 (2C), 145.4, 145.8, 146.1, 146.2, 146.3, 146.8, 147.2, 147.3, 154.4, 154.7, 162.2, 171.1; HRMS (FAB) m/z 1900.6023 (M + 1, \(C_{146}H_{39}N_2O_5\) requires 1900.8743).

22: \(^1\)H NMR \(\delta\) 0.51 (s, 18H), 2.40 (s, 6H), 3.59-3.65 (m, 4H), 4.37-4.58 (m, 6H), 5.24 (d, 2H, \(J = 12.42\) Hz), 5.38 (s, 2H), 5.52 (s, 2H), 7.25 (d, 4H, \(J = 6.12\) Hz), 7.53 (d, 4H, \(J = 9.18\) Hz); \(^{13}\)C NMR \(\delta\) 0.7, 21.2, 28.1, 55.9, 64.3, 70.0, 76.4, 77.2, 77.6, 77.9, 128.5, 129.6, 134.9, 135.5, 135.6, 137.5, 139.2, 139.5, 139.7, 140.1, 141.6, 141.7, 141.8, 141.9, 142.0, 142.1, 142.2, 142.3, 142.4, 142.6, 142.7, 143.0, 143.1, 143.2, 144.3, 144.4, 144.5, 144.9, 145.1, 145.2, 145.3, 145.5, 145.8, 145.9, 146.1(2C), 146.2, 146.3, 146.6, 146.9, 147.0, 152.5, 154.8, 156.5, 157.0, 170.3; HRMS (FAB) m/z 2041.5231 (M + 1, \(C_{152}H_{51}N_2O_5SiO_2\) requires 2041.2048).

Photoreaction of \(C_{60}\) with 15. In \(N_2\) saturated condition: 120 min irradiation, 70% conversion, column chromatography (CS\(_2\):CHCl\(_3\) = 5:1) to yield 19 (181 mg, 34%) and 23 (28 mg, 5%). \(O_2\) saturated condition: 150 min irradiation, 72% conversion, column chromatography (CS\(_2\):CHCl\(_3\) = 5:1) to yield 19 (2 mg, traces) and 23 (183 mg, 55%).

19: \(^1\)H NMR \(\delta\) 3.60 (t, 4H, \(J = 12.44\) Hz), 3.97 (s, 4H), 4.49 (s, 4H), 4.57 (t, 4H, \(J = 12.32\) Hz), 4.75 (s, 4H), 6.86 (s, 2H), 7.07 (t, 4H, \(J = 18.12\) Hz), 7.55-7.60 (m, 4H); \(^{13}\)C NMR \(\delta\) 55.6, 58.0, 59.0, 64.0, 67.2, 68.4, 115.5 (d, \(J_{C-F} = 84\) Hz), 130.9 (d, \(J_{C-F} = 30\) Hz), 133.8, 136.0 (d, \(J_{C-F} = 25.2\) Hz), 140.0, 140.2, 141.6 (2C), 141.7, 141.9, 142.0, 142.3, 142.5 (2C), 143.2, 144.4, 144.6, 145.3 (2C), 145.4, 145.7, 146.1, 146.2, 146.3 (2C), 146.7, 147.1, 147.2, 147.3, 154.2, 154.5, 162.3 (d, \(J_{C-F} = 978\) Hz), 170.9; HRMS (FAB) m/z 1908.8743 (M + 1, \(C_{144}H_{33}F_2N_2O_5\) requires 1908.8021).

23: \(^1\)H NMR \(\delta\) 0.50 (s, 18H), 3.38-3.52 (m, 4H), 4.66-4.47 (m, 6H), 5.25 (d, 2H, \(J = 12.22\) Hz), 5.38 (s, 2H), 5.46 (s, 2H), 7.14 (t, 4H, \(J = 18.02\) Hz), 7.60-7.64 (m, 4H); \(^{13}\)C NMR \(\delta\) 0.7, 29.6, 55.4, 64.4, 70.0, 77.2, 77.5, 77.8, 115.8 (d, \(J_{C-F} = 84.9\) Hz), 130.1 (d, \(J_{C-F} = 31.5\) Hz), 134.4 (d, \(J_{C-F} = 12\) Hz), 134.9, 135.5, 136.4, 139.2, 139.6, 139.7, 140.1, 141.6, 141.7, 141.8 (2C), 141.9, 142.0, 142.1, 142.2 (3C), 142.4, 142.6 (2C), 142.7, 143.0, 143.1, 144.2, 144.3, 144.4, 144.5, 144.9, 145.1, 145.2 (3C), 145.4, 145.8, 145.9 (3C), 146.1, 146.2 (2C), 146.3, 146.6, 146.9, 147.0, 152.3, 154.6, 156.3, 156.9, 162.4 (d, \(J_{C-F} = 978.3\) Hz), 170.2; HRMS (FAB) m/z 2049.2915 (M + 1, \(C_{150}H_{45}F_2N_2O_5SiO_2\) requires 2049.1326).

Photoreaction of \(C_{60}\) with 16. In \(N_2\) saturated condition: 90 min irradiation, 84% conversion, column chromatography (CS\(_2\):CHCl\(_3\) = 5:1) to yield 20 (286 mg, 53%) and 24 (11 mg, 2%). \(O_2\) saturated condition: 120 min irradiation, 88% conversion, column chromatography (CS\(_2\):CHCl\(_3\) = 5:1) to yield 20 (16 mg, 3%) and 24 (220 mg, 47%).

20: \(^1\)H NMR \(\delta\) 3.75-3.84 (m, 10H), 3.98 (s, 4H), 4.46-4.54 (m, 8H), 4.74 (s, 4H), 6.89 (s, 2H), 6.92
(d, 4H, $J=8.70\text{Hz}$), 7.52 (d, 4H, $J=8.70\text{Hz}$); $^{13}\text{C NMR } \delta 41.7, 55.3, 55.5, 58.0, 59.1, 64.1, 67.3, 68.2, 114.0, 130.0, 130.6, 136.0, 136.1, 139.9, 140.2, 141.6 (2C), 141.7, 141.9, 142.0, 142.3, 142.5 (2C), 143.0, 143.1, 144.4, 144.6, 145.2, 145.3, 145.4, 145.7, 146.1 (2C), 146.3 (2C), 146.8, 147.2, 147.3, 154.3, 154.7, 159.2, 171.1; HRMS (FAB) m/z 1932.6059 (M + 1, C$_{146}$H$_{39}$N$_2$O$_7$ requires 1932.8731).

24: $^1\text{H NMR } \delta 0.50$ (s, 18H), 3.59-3.65 (m, 4H), 3.84 (s, 6H), 4.36-4.54 (m, 6H), 5.21 (d, 2H, $J=13.20\text{Hz}$), 5.36 (s, 2H), 5.50 (s, 2H), 6.97 (d, 4H, $J=8.40\text{Hz}$), 7.56 (d, 4H, $J=8.40\text{Hz}$); $^{13}\text{C NMR } \delta 0.7, 41.3, 55.3, 55.5, 64.5, 69.9, 76.3, 77.2, 77.5, 77.9, 129.8, 130.7, 134.9, 135.6 (2C), 136.3, 139.2, 139.5, 139.7, 140.1, 141.6, 141.6, 141.7, 141.8 (2C), 141.9, 142.0, 142.1, 142.2 (2C), 142.3, 142.4, 142.6, 142.7, 143.0 (2C), 143.1, 144.2, 144.3, 144.4, 144.5, 145.0, 145.1, 145.2 (3C), 145.3, 145.5 (2C), 145.8, 145.9 (2C), 146.1 (2C), 146.2, 146.3, 146.7, 146.9, 147.0, 152.5, 154.8, 156.5, 157.0, 159.2, 170.4; HRMS (FAB) m/z 2073.2654 (M + 1, C$_{152}$H$_{51}$N$_2$O$_5$SiO$_2$ requires 2073.2036).
3. $^1$H and $^{13}$C NMR spectra of the compounds