Electronic Supplementary Information

NBS-Promoted oxidation of fullerene monoradicals leading to regioselective 1,4-difunctional fullerenes

Weili Si, Shirong Lu, Naoki Asao, Ming Bao, Yoshinori Yamamoto, and Tienan Jin*

a WPI-Advanced Institute for Materials Research (WPI-AIMR), Tohoku University, Sendai 980-8577, Japan
b State Key Laboratory of Fine Chemicals, Dalian University of Technology, Dalian 116023, China

tjin@m.tohoku.ac.jp

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**General Information.** ^1^H NMR and ^1^C NMR spectra were recorded on JEOL JMTC-270/54/SS (JASTEC, 400 MHz) spectrometers. ^1^H NMR spectra are reported as follows: chemical shift in ppm (δ) relative to the chemical shift of CDCl₃ at 7.26 ppm, integration, multiplicities (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet and br = broadened), and coupling constants (Hz). ^1^C NMR spectra reported in ppm (δ) relative to the central line of triplet for CDCl₃ at 77 ppm. High-resolution mass spectra were obtained on a BRUKER APEXIII spectrometer. Preparative recycling HPLC was used a LC-2000 Plus instrument equipped with a Buckyprep column (4.6 mm x 250 mm, nakarai Tesque). HPLC analysis performed using toluene as an elution at 0.6 mL/min flow rate, detection at 320 nm in 16 °C. Column chromatography was carried out employing Slica gel 60 N (spherical, neutral, 40~100 m, KANTO Chemical Co.). Analytical thin-layer chromatography (TLC) was performed on 0.2 mm precoated plate Kieselgel 60 F₂₅₄ (Merk).

**Materials.** Anhydrous 1,2-dichlorobenzene (Aldrich), toluene, carbon disulfide, DMF (WAKO), copper catalysts (Aldrich), C₆₀ (Aldrich), amines (Aldrich) were purchased and used as received. The singly bonded fullerene dimers 1 were prepared following the reported papers. The structure of products were determined by using ^1^H NMR, ^1^C NMR, HMRS, and UV-vis spectra.

**References:**

**Procedure for synthesis of 2a**
To a mixture of 1,2-dichlorobenzene (20 mL), DMF (2 mL), and single-bonded fullerene dimer 1a (87 mg, 0.05 mmol) was added NBS (0.20 mmol, 36 mg) under an air atmosphere at rt. The reaction mixture was stirred at 50 °C for 1 h. After monitoring by HPLC and TLC, the reaction mixture was purified directly through a silica gel chromatography using toluene as an eluent. The obtained product was washed with methanol and dried, affording the expected product 2a in 64% yield (58.2 mg) as a dark brown solid.

**Procedure for synthesis of 3a**
To a mixture of 1,2-dichlorobenzene (20 mL), CH₃OH (100 µL), and single-bonded fullerene dimer 1a (87 mg, 0.05 mmol) was added NBS (0.11 mmol, 19.6 mg) under an air atmosphere at rt. The reaction mixture was stirred at 50 °C for 2.5 h. After monitoring by HPLC and TLC, the reaction mixture was purified directly through a silica gel chromatography using toluene as an eluent. The obtained product was washed with methanol and dried, affording the expected product 3a in 91% yield (84 mg) as a dark brown solid.

**Procedure for synthesis of 4a**
To a mixture of 1,2-dichlorobenzene (20 mL), CH₃OH (100 µL), single-bonded fullerene dimer 1a (87
mg, 0.05 mmol), and NBS (0.20 mmol, 36 mg) was added anisole (5.0 mmol, 0.54 mL) under an air atmosphere at rt. The reaction mixture was stirred at 70 °C for 6 h. After monitoring by HPLC and TLC, the reaction mixture was purified directly through a silica gel chromatography using toluene as an eluent. The obtained product was washed with methanol and dried, affording the expected product 4a in 73% yield (72.9 mg) as a dark brown solid.

**UV-vis absorption of products 2a, 3a, and 4a**

![Figure S1 UV-vis absorption of the amine-substituted 1,4-bisadducts in chloroform.](image)

**Analytic data**

![Chemical structure of 2a](image)

2a: Dark brown solid; 1H NMR (400 MHz, CDCl3/CS2 = 1/4) δ 2.18 (1H, s), 4.00 (3H, s), 4.39 (1H, d, J = 12.8 Hz), 4.44 (1H, d, J = 12.8 Hz), 7.72 (1H, dd, J = 7.6 Hz, 7.6 Hz), 7.92 (1H, d, J = 7.6 Hz), 8.19 (1H, d, J = 7.6 Hz), 8.36 (1H, s); 13C NMR (100 MHz, CDCl3/CS2 = 1/4) δ 47.95, 51.72, 59.07, 74.72, 128.15, 128.62, 128.90, 130.42, 131.69, 134.83, 136.03, 137.25, 138.05, 138.17, 139.36, 140.72, 141.66, 141.79, 142.13, 142.20, 142.31, 142.44, 142.53, 142.77, 142.81, 142.92, 143.04, 143.11, 143.47, 143.52, 143.59, 143.62, 143.83, 143.90, 144.04, 144.58, 145.12, 145.15, 145.28, 145.33, 146.25, 146.41, 146.47, 146.58, 146.68, 148.02, 148.44, 149.03, 150.08, 150.41, 151.94, 154.19, 164.98. HRMS (ESI, positive) calcd for C69H10O3 [M+Na]+: 909.0522, found 909.0522.
3a: Dark brown solid; soluble solvents: CHCl₃, toluene, ODCB; ¹H NMR (400 MHz, CDCl₃/CS₂ = 1/4) δ 3.94 (3H, s), 4.07 (3H, s), 4.37 (1H, d, J = 12.8 Hz), 4.43 (1H, d, J = 12.8 Hz), 7.54 (1H, dd, J = 7.6 Hz, 7.6 Hz), 7.80 (1H, d, J = 7.6 Hz), 8.05 (1H, d, J = 7.6 Hz), 8.22 (1H, s); ¹³C NMR (100 MHz, CDCl₃/CS₂ = 1/4) δ 48.43, 51.61, 54.03, 59.31, 80.72, 127.20, 128.11, 128.46, 130.08, 131.4, 134.76, 135.43, 138.24, 139.37, 139.56, 140.40, 141.07, 141.68, 141.84, 142.15, 142.17, 142.2, 142.48, 142.51, 142.53, 142.63, 142.8, 142.84, 142.86, 142.91, 143.00, 143.34, 143.55, 143.60, 143.63, 143.80, 143.81, 143.85, 144.05, 144.12, 144.49, 144.63, 145.14, 145.31, 145.95, 146.16, 146.29, 146.44, 146.54, 146.58, 146.71, 146.80, 146.87, 147.22, 148.01, 148.49, 149.03, 153.01, 153.98, 165.65. HRMS (ESI, positive) calcd for C₇₀H₁₂O₃[M+Na]⁺: 923.0679, found 923.0672.

3b: Dark brown solid; ¹H NMR (400 MHz, CDCl₃/CS₂ = 1/4) δ 1.59 (3H, t, J = 6.8, 7.2 Hz), 3.92 (3H, s), 4.37 (1H, d, J = 12.8 Hz), 4.44 (1H, d, J = 12.8 Hz), 4.47-4.54 (2H, m), 7.52 (1H, dd, J = 7.6, 7.6 Hz), 7.99 (1H, d, J = 8.0 Hz), 8.03 (1H, d, J = 7.6 Hz), 8.2 (1H, s); ¹³C NMR (100 MHz, CDCl₃/CS₂ = 1/4) δ 16.05, 48.49, 51.42, 59.16, 62.42, 80.22, 128.00 128.45, 130.06, 131.31, 134.54, 135.37, 137.12, 138.18, 139.21, 139.24, 140.29, 140.46, 141.42, 141.62, 141.78, 141.91, 142.1, 142.12, 142.14, 142.43, 142.5, 142.57, 142.77, 142.81, 142.84, 142.93, 143.33, 143.48, 143.54, 143.56, 143.57, 143.61, 143.69, 143.71, 143.74, 143.99, 144.05, 144.09, 144.43, 144.56, 145.08, 145.18, 145.22, 145.86, 146.1, 146.21, 146.38, 146.47, 146.5, 146.63, 146.74, 147.15, 147.22, 147.94, 148.39, 149.59, 151.55, 152.84, 153.86, 165.13. HRMS (ESI, positive) calcd for C₇₁H₁₄O₃[M+Na]⁺: 937.0835, found 937.0833.
3c: Dark brown solid; $^1$H NMR (400 MHz, CDCl$_3$/CS$_2$ = 1/4) δ 0.96 (3H, t, $J = 7.2$ Hz), 1.38-1.42 (4H, m), 1.46-1.53 (2H, m), 1.76-1.84 (2H, m), 4.10 (3H, s), 4.30 (2H, t, $J = 6.4$ Hz), 4.37 (1H, d, $J = 12.8$ Hz), 4.44 (1H, d, $J = 12.4$ Hz), 7.64 (2H, d, $J = 8.4$ Hz), 8.07 (2H, d, $J = 8.0$ Hz); $^{13}$C NMR (100 MHz, CDCl$_3$/CS$_2$ = 1/4) δ 14.3, 22.97, 25.96, 28.97, 31.69, 48.67, 53.98, 59.11, 64.56, 80.67, 129.34, 129.51, 130.27, 137.11, 139.28, 139.51, 139.75, 140.37, 140.48, 140.99, 141.61, 141.79, 141.9, 142.08, 142.13, 142.43, 142.45, 142.48, 142.75, 142.79, 142.84, 142.87, 142.94, 143.28, 143.5, 143.53, 143.57, 143.63, 143.69, 143.73, 144, 144.02, 144.05, 144.42, 144.57, 145.08, 145.25, 145.3, 146.1, 146.23, 146.4, 146.49, 146.52, 146.63, 146.74, 147.04, 147.15, 147.95, 148.42, 148.97, 151.9, 152.95, 153.77, 164.77; HRMS (ESI, positive) calcd for C$_{75}$H$_{22}$O$_3$Na [M+Na]$^+$: 993.1461, found 993.1457.

3d: Dark brown solid; $^1$H NMR (400 MHz, CDCl$_3$/CS$_2$ = 1/4) δ 2.59-2.68 (2H, m), 3.18 (2H, t, $J = 8.0$ Hz), 3.84 (2H, t, $J = 6.0$ Hz), 4.26 (3H, s), 4.63 (2H, s), 7.24-7.37 (5H, m); $^{13}$C NMR (100 MHz, CDCl$_3$/CS$_2$ = 1/4) δ 27.64, 38.93, 53.93, 58.53, 69.67, 72.79, 80.82, 127.07, 127.14, 127.99, 136.93, 137.87, 138.03, 139.47, 139.57, 140.32, 140.47, 140.57, 141.66, 141.79, 142.05, 142.11, 142.16, 142.37, 142.43, 142.57, 142.68, 142.71, 142.8, 142.87, 142.95, 143.38, 143.56, 143.63, 143.71, 143.77, 143.8, 143.94, 144.06, 144.13, 144.46, 144.51, 145.02, 145.2, 145.26, 145.99, 146.03, 146.18, 146.35, 146.45, 146.47, 146.65, 146.69, 147.21, 147.29, 147.89, 148.41, 149.09, 152.89, 154, 155.35; HRMS (ESI, positive) calcd for C$_{71}$H$_{16}$O$_2$Na [M+Na]$^+$: 923.1043, found 923.1038.
**4a:** Dark brown solid; soluble solvents: CHCl₃, toluene, ODCB; ¹H NMR (400 MHz, CDCl₃/CS₂ = 1/4) δ 3.92 (3H, s), 3.97 (3H, s), 4.26 (1H, d, J = 13.2 Hz), 4.32 (1H, d, J = 13.2 Hz), 7.08 (2H, d, J = 8.8 Hz), 7.35 (1H, dd, J = 7.6 Hz, 7.6 Hz), 7.68 (1H, d, J = 7.6 Hz), 7.84 (1H, d, J = 7.6 Hz), 8.05 (1H, d, J = 7.6 Hz), 8.11 (1H, s); ¹³C NMR (100 MHz, CDCl₃/CS₂ = 1/4) δ 47.79, 51.41, 54.74, 59.59, 114.62, 127.52, 127.89, 128.40, 129.9, 131.08, 132.48, 134.33, 135.43, 138.06, 141.91, 142.04, 142.17, 142.64, 142.77, 142.81, 143.57, 143.62, 143.64, 143.71, 143.91, 144.41, 146.49, 146.55, 146.59, 148.19, 148.26, 150.92, 158.98, 165.22. HRMS (ESI, positive) calcd for C₇₈H₁₆O₃Na [M+Na]⁺: 999.0992, found 999.0992.

![Image 4a](attachment:image4a.png)

**4b:** Dark brown solid; ¹H NMR (400 MHz, CDCl₃/CS₂ = 1/4) δ 3.93 (3H, s), 3.97 (3H, s), 4.01 (3H, s), 4.14 (3H, s), 4.22 (1H, d, J = 12.8 Hz), 4.27 (1H, d, J = 12.8 Hz), 6.76 (1H, d, J = 8.8 Hz), 7.36 (1H, dd, J = 7.6, 7.6 Hz), 7.60 (1H, d, J = 8.8 Hz), 7.69 (1H, d, J = 7.2 Hz), 7.84 (1H, d, J = 7.6 Hz), 8.2 (1H, s); ¹³C NMR (100 MHz, CDCl₃/CS₂ = 1/4) δ 47.44, 51.47, 55.36, 59.24, 59.38, 60.01, 60.27, 106.9, 122.83, 127.79, 128.28, 129.9, 131.22, 134.36, 135.69, 137.9, 138.03, 138.11, 138.24, 140.32, 141.35, 141.63, 141.73, 142.09, 142.25, 142.29, 142.45, 142.63, 142.69, 142.72, 142.73, 142.84, 143.28, 143.38, 143.41, 143.55, 143.61, 143.66, 143.85, 143.87, 143.91, 144.04, 144.13, 144.16, 144.26, 144.49, 144.65, 144.77, 145.02, 145.05, 145.5, 146.36, 146.44, 146.49, 146.52, 146.57, 146.7, 146.77, 146.8, 148.07, 148.11, 148.15, 149.97, 152.7, 153.7, 155.63, 156.03, 165.31. HRMS (ESI, positive) calcd for C₇₈H₁₂₀O₃Na [M+Na]⁺: 1059.1203, found 1059.1200.

![Image 4b](attachment:image4b.png)

**4c:** Dark brown solid; soluble solvents: CHCl₃, toluene, ODCB; ¹H NMR (400 MHz, CDCl₃/CS₂ = 1/4) δ 3.92 (3H, s), 4.38 (1H, d, J = 12.8 Hz), 4.51 (1H, d, J = 12.8 Hz), 7.25-7.27 (1H, m), 7.43 (1H, dd, J = 7.6, 8.0 Hz), 7.52-7.53 (1H, m), 7.68-7.69 (1H, m), 7.79 (1H, d, J = 7.6 Hz), 7.95 (1H, d, J = 7.6 Hz), 8.20 (1H, s); ¹³C NMR (100 MHz, CDCl₃/CS₂ = 1/4) δ 48.00, 51.40, 56.85, 59.48, 125.39, 125.42, 127.49, 127.92, 128.44, 129.98, 131.20, 134.43, 135.37, 136.64, 137.92, 138.17, 138.71, 140.59, 141.53, 141.66.
HRMS (ESI, positive) calcd for C\textsubscript{73}H\textsubscript{12}O\textsubscript{2}S\textsubscript{Na} [M+Na]	extsuperscript{+}: 975.0450, found 975.0450.

4d: Dark brown solid; \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}/CS\textsubscript{2} = 1/4) \( \delta \) 0.86-0.95 (6H, m), 1.26-1.39 (12H, m), 1.64-1.74 (4H, m), 2.64-2.72 (4H, m), 3.88 (3H, s), 4.40 (1H, d, \( J = 12.8 \) Hz), 4.56 (1H, d, \( J = 12.8 \) Hz), 7.00 (1H, d, \( J = 5.2 \) Hz), 7.33 (1H, d, \( J = 5.2 \) Hz), 7.44 (1H, dd, \( J = 7.6, 7.6 \) Hz), 7.57 (1H, s), 7.81 (1H, d, \( J = 7.6 \) Hz), 7.97 (1H, d, \( J = 7.6 \) Hz), 8.2 (1H, s); \textsuperscript{13}C NMR (100 MHz, CDCl\textsubscript{3}/CS\textsubscript{2} = 1/4) \( \delta \) 8.19, 14.33, 22.93, 22.97, 22.98, 29.06, 29.31, 29.42, 29.53, 30.88, 30.92, 31.82, 31.88, 48.08, 51.4, 59.42, 125.64, 127.12, 127.71, 127.97, 128.36, 129.05, 129.97, 131.27, 134.43, 135.43, 136.92, 137.98, 138.32, 138.71, 140.61, 141.67, 141.82, 141.98, 142.05, 142.13, 142.26, 142.59, 142.69, 142.74, 142.91, 143.29, 143.43, 143.47, 143.62, 143.68, 143.82, 143.85, 143.91, 144, 144.06, 144.42, 144.71, 144.87, 145.15, 145.58, 146.15, 146.5, 146.58, 146.73, 148.28, 150.4, 155, 155.12, 165.15. HRMS (MALDI) calcd for C\textsubscript{89}H\textsubscript{38}O\textsubscript{2}S\textsubscript{2} [M]\textsuperscript{+}: 1202.2308, found 1202.2260.

4e: Dark brown solid; soluble solvents: CHCl\textsubscript{3}, toluene, ODCB; \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}/CS\textsubscript{2} = 1/4) \( \delta \) 3.84 (3H, s), 3.94 (3H, s), 3.95 (3H, s), 4.35 (1H, d, \( J = 12.4 \) Hz), 4.39 (1H, d, \( J = 12.4 \) Hz), 7.10 (2H, d, \( J = 8.4 \) Hz), 7.45-7.49 (2H, m), 7.55 (1H, d, \( J = 7.6 \) Hz), 8.12 (2H, d, \( J = 8.8 \) Hz); \textsuperscript{13}C NMR (100 MHz, CDCl\textsubscript{3}/CS\textsubscript{2} = 1/4) \( \delta \) 42.06, 51.91, 55.10, 55.18, 59.55, 60.93, 111.61, 114.66, 121.95, 127.81, 129.43, 130.51, 131.93, 133.27, 136.39, 137.56, 140.59, 142.11, 142.32, 142.43, 142.50, 142.86, 142.96, 143.56, 143.69, 143.77, 143.86, 143.90, 143.99, 144.09, 144.17, 144.21, 144.42, 144.75, 144.80, 145.27, 145.36, 145.97, 146.32, 146.32, 146.65, 146.68, 146.76, 146.82, 146.86, 148.18, 148.42, 148.61, 150.92, 157.49.
159.15, 165.08. HRMS (ESI, positive) calcd for C_{79}H_{14}O_{6}Na [M+Na]^+: 1029.1097, found 1029.1098.

4f: Dark brown solid; \(^1H\) NMR (400 MHz, CDCl\(_3)/CS_2 = 1/4\) δ 3.88 (3H, s), 3.91 (3H, s), 3.97 (3H, s), 4.10 (3H, s), 4.29 (1H, d, J = 12.4 Hz), 4.33 (1H, d, J = 12.0 Hz), 6.70 (1H, dd, J = 8.8, 3.2 Hz), 7.43-7.45 (2H, m), 7.51 (1H, d, J = 7.6 Hz), 7.58 (1H, dd, J = 8.8, 6.0 Hz); \(^{13}C\) NMR (100 MHz, CDCl\(_3)/CS_2 = 1/4\) δ 41.49, 51.29, 54.77, 55.25, 59.09, 59.19, 59.74, 60.04, 106.76, 111.42, 121.79, 122.83, 127.36, 129.18, 130.19, 131.57, 137.16, 137.64, 141.67, 141.75, 142.11, 142.16, 142.21, 142.24, 142.35, 142.57, 142.59, 142.69, 142.77, 143.33, 143.35, 143.37, 143.59, 143.69, 143.48, 143.89, 143.92, 143.94, 144.11, 144.24, 144.54, 144.56, 144.95, 144.97, 146.27, 146.39, 146.51, 146.53, 146.64, 146.69, 147.55, 148.01, 148.11, 148.22, 150.77, 152.56, 153.51, 156.25, 156.75, 157.09, 164.97. HRMS (ESI, positive) calcd for C_{79}H_{14}O_{6}Na [M+Na]^+: 1089.1309, found 1089.1309.

4g: Dark brown solid; \(^1H\) NMR (400 MHz, CDCl\(_3)/CS_2 = 1/4\) δ 3.87 (3H, s), 3.94 (3H, s), 4.48 (1H, d, J = 12.4 Hz), 4.55 (1H, d, J = 12.8 Hz), 7.25-7.29 (1H, m), 7.52-7.55 (3H, m), 7.62 (1H, d, J = 7.6 Hz), 7.73 (1H, s); \(^{13}C\) NMR (100 MHz, CDCl\(_3)/CS_2 = 1/4\) δ 42.05, 51.39, 54.67, 59.19, 111.42, 121.75, 125.27, 125.33, 127.31, 128.88, 130.59, 131.79, 136.66, 137.26, 137.83, 140.52, 141.54, 141.83, 142, 142.11, 142.16, 142.25, 142.72, 142.74, 142.77, 143.28, 143.38, 143.47, 143.49, 143.62, 143.76, 143.82, 143.85, 143.88, 143.94, 144.09, 144.16, 144.4, 144.51, 144.79, 145.04, 145.14, 146.01, 146.23, 146.43, 146.47, 146.49, 146.58, 146.65, 146.73, 147.57, 147.89, 149.14, 150.57, 156.26, 157.18, 165.09. HRMS (ESI, positive) calcd for C_{74}H_{13}O_{3}SNa [M+Na]^+: 1005.0556, found 1005.0556.
NMR spectra

2a

OH

CO₂Me

2a

OH

CO₂Me

NMR spectra