Electronic Supplementary Information

Copper-mediated synthesis of fullerooxazoles from [60]fullerene and

N-hydroxybenzimidoyl cyanides

Qing-Song Liu, Wen-Jie Qiu, Wen-Qiang Lu and Guan-Wu Wang* 

aHefei National Laboratory for Physical Sciences at Microscale and Department of Chemistry, University of Science and Technology of China, Hefei, Anhui 230026, P. R. China 
E-mail: gwang@ustc.edu.cn; Fax: +86 551 3607864; Tel: +86 551 3607864

bState Key Laboratory of Applied Organic Chemistry, Lanzhou University, Lanzhou, Gansu 730000, P. R. China

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1. General information
Anhydrous 1,2-dichlorobenzene (1,2-C₆H₄Cl₂) was freshly distilled, N-hydroxybenzimidoyl cyanides 1a–r were synthesized by the literature procedure.¹ Other chemicals were purchased from commercial sources and used as received. ¹H NMR and ¹³C NMR spectra were recorded on a Bruker ASCEND III–400 or a Bruker ASCEND III–500 or a JEOL JNM-ECZ600R/SI spectrometer at room temperature. ¹H NMR chemical shifts were determined relative to TMS. ¹³C NMR chemical shifts were determined relative to TMS or residual DMSO (δ 39.03 ppm). Abbreviations for signal couplings are: s, singlet; d, doublet; t, triplet; m, multiplet. High resolution mass spectra were obtained on a Bruker UltrafleXtreme MALDI-TOF/TOF instrument. UV-vis spectra were obtained on a SHIMADZU UV-3600PLUS instrument. IR spectra were obtained on a Thermo Scientific Nicolet 6700 instrument. Electrochemical reaction was performed under an argon atmosphere at 0 °C using a Shanghai Chenhua CHI630D workstation.

2. General procedure for the reaction of C₆₀ with substrates 1
A mixture of C₆₀ (0.05 mmol), 1 (0.15 mmol) (0.25 mmol for 1c, 1f and 1m), CuBr₂ (0.05 mmol) and Na₂HPO₄ (0.10 mmol) was completely dissolved in anhydrous 1,2-C₆H₄Cl₂ (6 mL) and the reaction was performed in a sealed tube. After being stirred in an oil bath at 150 °C (160 °C for 1i) for 1 h, the resulting solution was evaporated in vacuo and subsequently separated on a silica gel column (300–400 mesh) with carbon disulfide (CS₂) as the eluent to give recovered C₆₀ and then the desired products 2.

Products 2a–c, 2g–j, 2p and 2q were known compounds, and their spectra were consistent with those reported in the literature.²a–f

3. Synthesis and spectral data of compounds 2a–r and 3a

![Synthesis and spectral data of 2a](image_url)  

**Synthesis and spectral data of 2a:** by following the general procedure, the reaction of C₆₀ (36.8 mg, 0.05 mmol) with 1a (21.9 mg, 0.15 mmol), CuBr₂ (11.4 mg, 0.05 mmol) and Na₂HPO₄ (14.5 mg, 0.10 mmol) at 150 °C for 1 h afforded recovered C₆₀ (16.8 mg, 46%) and 2a²a,c–f (12.7 mg, 30%): amorphous brown solid; ¹H NMR (400 MHz, CS₂ with DMSO-d₆ as the external deuterium lock) δ 8.44–8.37 (m, 2H), 7.70–7.64 (m, 1H), 7.64–7.58 (m, 2H).
Synthesis and spectral data of 2b: by following the general procedure, the reaction of C$_{60}$ (36.3 mg, 0.05 mmol) with 1b (24.3 mg, 0.15 mmol), CuBr$_2$ (11.0 mg, 0.05 mmol) and Na$_2$HPO$_4$ (14.2 mg, 0.10 mmol) at 150 °C for 1 h afforded recovered C$_{60}$ (20.9 mg, 58%) and 2b$^{2a,e,f}$ (11.0 mg, 26%): amorphous brown solid; $^1$H NMR (400 MHz, 1:1 CS$_2$/CDCl$_3$) δ 8.35 (d, $J$ = 8.0 Hz, 2H), 7.43 (d, $J$ = 8.0 Hz, 2H), 2.55 (s, 3H).

Synthesis and spectral data of 2c: by following the general procedure, the reaction of C$_{60}$ (35.9 mg, 0.05 mmol) with 1c (44.3 mg, 0.25 mmol), CuBr$_2$ (11.8 mg, 0.05 mmol) and Na$_2$HPO$_4$ (14.5 mg, 0.10 mmol) at 150 °C for 1 h afforded recovered C$_{60}$ (16.9 mg, 47%) and 2c$^{2a-f}$ (10.4 mg, 24%): amorphous brown solid; $^1$H NMR (500 MHz, 1:1 CS$_2$/CDCl$_3$) δ 8.38 (d, $J$ = 8.9 Hz, 2H), 7.10 (d, $J$ = 8.9 Hz, 2H), 3.96 (s, 3H).

Synthesis and spectral data of 2d: by following the general procedure, the reaction of C$_{60}$ (35.9 mg, 0.05 mmol) with 1d (26.6 mg, 0.15 mmol), CuBr$_2$ (11.1 mg, 0.05 mmol) and Na$_2$HPO$_4$ (14.5 mg, 0.10 mmol) at 150 °C for 1 h afforded recovered C$_{60}$ (15.2 mg, 42%) and 2d (9.8 mg, 22%): amorphous brown solid; $^1$H NMR (400 MHz, CS$_2$ with DMSO-$d_6$ as the external deuterium lock) δ 7.96 (d, $J$ = 7.6 Hz, 1H), 7.89 (dd, $J$ = 2.6, 1.6 Hz, 1H), 7.48 (t, $J$ = 7.9 Hz, 1H), 7.15 (ddd, $J$ = 8.3, 2.7, 1.0 Hz, 1H), 3.96 (s, 3H); $^{13}$C NMR (101 MHz, CS$_2$ with DMSO-$d_6$ as the external deuterium lock and reference, all 2C unless indicated) δ 164.40 (1C, C=N), 159.04 (1C, aryl C), 147.55 (1C), 147.49, 147.14 (1C), 145.75 (4C), 145.61, 145.46, 145.40, 145.12, 144.98, 144.83, 144.59, 144.48, 144.22, 143.97, 143.65, 143.02, 142.18, 142.15, 142.07, 141.75 (4C), 141.66, 141.51, 141.39 (4C), 139.85, 139.01, 137.21, 135.51, 129.30 (1C, aryl C), 127.56 (1C,
Synthesis and spectral data of 2e: by following the general procedure, the reaction of C₆₀ (36.3 mg, 0.05 mmol) with 1e (30.5 mg, 0.15 mmol), CuBr₂ (11.5 mg, 0.05 mmol) and Na₂HPO₄ (14.0 mg, 0.10 mmol) at 150 °C for 1 h afforded recovered C₆₀ (18.3 mg, 50%) and 2e (8.5 mg, 19%): amorphous brown solid; ¹H NMR (400 MHz, CS₂ with DMSO-d₆ as the external deuterium lock) δ 8.30 (d, J = 8.4 Hz, 2H), 7.59 (d, J = 8.4 Hz, 2H), 1.46 (s, 9H); ¹³C NMR (101 MHz, CS₂ with DMSO-d₆ as the external deuterium lock and reference, all 2C unless indicated) δ 164.37 (1C, C=N), 154.85 (1C, aryl C), 147.70, 147.56 (1C), 147.14 (1C), 145.75, 145.74, 145.60, 145.46, 145.40, 145.12, 145.04, 144.86, 144.59, 144.48, 144.26, 143.99, 143.66, 143.21, 142.17, 142.16, 142.06, 141.77 (4C), 141.66, 141.52, 141.40 (4C), 139.82, 139.00, 137.23, 135.49, 128.72 (aryl C), 125.23 (aryl C), 123.67 (1C, aryl C), 96.58 (1C, sp³-C of C₆₀), 91.72 (1C, sp³-C of C₆₀), 34.26 (1C), 30.80 (3C); FT-IR ν/cm⁻¹ (KBr) 1641, 1324, 1111, 1085, 984, 932, 843, 774, 686, 661, 603, 576, 563, 525; UV-vis (CHCl₃) λmax nm (log ε) 257 (5.03), 316 (4.56), 418 (3.34), 453 (3.09), 684 (1.97); MALDI-TOF MS m/z calcd for C₆₈H₇NO₂ [M] 869.0482, found 869.0474.

Synthesis and spectral data of 2f: by following the general procedure, the reaction of C₆₀ (35.5 mg, 0.05 mmol) with 1f (53.5 mg, 0.25 mmol), CuBr₂ (11.3 mg, 0.05 mmol) and Na₂HPO₄ (14.3 mg, 0.10 mmol) at 150 °C for 1 h afforded recovered C₆₀ (17.3 mg, 49%) and 2f (10.6 mg, 23%): amorphous brown solid; ¹H NMR (400 MHz, CS₂ with DMSO-d₆ as the external deuterium lock) δ 8.46 (dd, J = 8.3, 1.6 Hz, 2H), 7.79 (dd, J = 8.3, 1.6 Hz, 2H), 7.69–7.61 (m, 2H), 7.50–7.41 (m, 2H), 7.41–7.34 (m, 1H); ¹³C NMR (101 MHz, CS₂ with DMSO-d₆ as the external deuterium lock and reference, all 2C unless indicated) δ 164.46 (1C, C=N), 147.74 (3C), 147.31 (1C), 145.93 (4C), 145.78,
145.64, 145.58, 145.31, 145.02, 144.77 (3C including 1 aryl C), 144.66, 144.41, 144.16, 143.83, 143.26, 142.35 (4C), 142.24, 141.94 (4C), 141.84, 141.69, 141.57 (4C), 140.02, 139.58 (1C, aryl C), 139.19, 137.41, 135.68, 129.52 (aryl C), 128.81 (aryl C), 127.97 (1C, aryl C), 127.13 (aryl C), 127.02 (aryl C), 96.89 (1C, sp$^3$-C of C$_{60}$), 91.91 (1C, sp$^3$-C of C$_{60}$); FT-IR ν/cm$^{-1}$ (KBr) 1638, 1511, 1322, 1088, 982, 931, 847, 766, 730, 694, 661, 603, 575, 563, 525; UV-vis (CHCl$_3$) λ$_{max}$ nm (log ε) 258 (5.04), 314 (4.75), 413 (3.52), 454 (3.22), 689 (2.34); MALDI-TOF MS m/z caled for C$_{73}$H$_9$NO [M] 915.0690, found 915.0684.

Synthesis and spectral data of 2g: by following the general procedure, the reaction of C$_{60}$ (35.8 mg, 0.05 mmol) with 1g (27.4 mg, 0.15 mmol), CuBr$_2$ (11.1 mg, 0.05 mmol) and Na$_2$HPO$_4$ (14.5 mg, 0.10 mmol) at 150 ºC for 1 h afforded recovered C$_{60}$ (15.6 mg, 44%) and 2g$_{2h-d,f}$ (12.6 mg, 29%): amorphous brown solid; $^1$H NMR (500 MHz, 1:1 CS$_2$/CDCl$_3$) δ 8.40 (d, $J$ = 8.5 Hz, 2H), 7.60 (d, $J$ = 8.5 Hz, 2H).

Synthesis and spectral data of 2h: by following the general procedure, the reaction of C$_{60}$ (36.1 mg, 0.05 mmol) with 1h (27.6 mg, 0.15 mmol), CuBr$_2$ (11.4 mg, 0.05 mmol) and Na$_2$HPO$_4$ (14.5 mg, 0.10 mmol) at 150 ºC for 1 h afforded recovered C$_{60}$ (10.1 mg, 28%) and 2h$_{2e}$ (9.4 mg, 21%): amorphous brown solid; $^1$H NMR (500 MHz, 1:1 CS$_2$/CDCl$_3$) δ 8.46 (t, $J$ = 2.0 Hz, 1H), 8.36 (dt, $J$ = 8.0, 1.3 Hz, 1H), 7.69–7.62 (m, 1H), 7.58 (t, $J$ = 8.0 Hz, 1H).

Synthesis and spectral data of 2i: by following the general procedure, the reaction of
C_{60} (36.2 mg, 0.05 mmol) with 1i (27.2 mg, 0.15 mmol), CuBr\textsubscript{2} (11.1 mg, 0.05 mmol) and Na\textsubscript{2}HPO\textsubscript{4} (14.1 mg, 0.10 mmol) at 160 °C for 1 h afforded recovered C_{60} (16.2 mg, 45%) and 2j\textsuperscript{2e,f} (8.0 mg, 18%): amorphous brown solid; \textsuperscript{1}H NMR (500 MHz, 1:1 CS\textsubscript{2}/CDCl\textsubscript{3}) \(δ = 8.37 \ (d, \ J = 7.6 \ Hz, 1H), 7.67 \ (d, \ J = 8.0 \ Hz, 1H), 7.67 \ (d, \ J = 8.0, 7.6 \ Hz, 1H), 7.54 \ (t, \ J = 7.5 \ Hz, 1H).

\[ \text{Synthesis and spectral data of 2j:} \]

by following the general procedure, the reaction of C_{60} (36.2 mg, 0.05 mmol) with 1j (34.4 mg, 0.15 mmol), CuBr\textsubscript{2} (11.2 mg, 0.05 mmol) and Na\textsubscript{2}HPO\textsubscript{4} (14.2 mg, 0.10 mmol) at 150 °C for 1 h afforded recovered C_{60} (13.6 mg, 38%) and 2j\textsuperscript{2a} (11.7 mg, 25%): amorphous brown solid; \textsuperscript{1}H NMR (400 MHz, CS\textsubscript{2} with DMSO-d\textsubscript{6} as the external deuterium lock) \(δ = 8.30 \ (d, \ J = 8.4 \ Hz, 2H), 7.75 \ (d, \ J = 8.4 \ Hz, 2H).

\[ \text{Synthesis and spectral data of 2k:} \]

by following the general procedure, the reaction of C_{60} (36.0 mg, 0.05 mmol) with 1k (25.0 mg, 0.15 mmol), CuBr\textsubscript{2} (11.3 mg, 0.05 mmol) and Na\textsubscript{2}HPO\textsubscript{4} (14.2 mg, 0.10 mmol) at 150 °C for 1 h and afforded recovered C_{60} (16.8 mg, 47%) and 2k (13.1 mg, 31%): amorphous brown solid; \textsuperscript{1}H NMR (500 MHz, CS\textsubscript{2} with DMSO-d\textsubscript{6} as the external deuterium lock) \(δ = 8.44 \ (dd, \ J = 8.4, 5.5 \ Hz, 2H), 7.28 \ (t, \ J = 8.3 \ Hz, 2H); \textsuperscript{13}C NMR (126 MHz, CS\textsubscript{2} with DMSO-d\textsubscript{6} as the external deuterium lock, all 2C unless indicated) \(δ = 164.29 \ (1C, \text{aryl C, d, J = 255.5 Hz}), 163.06 \ (1C, \text{C=N}), 147.10 \ (1C), 146.90, 146.68 \ (1C), 145.29 \ (4C), 145.15, 145.00, 144.95, 144.67, 144.48, 144.33, 144.13, 144.02, 143.68, 143.50, 143.17, 142.41, 141.72, 141.69, 141.61, 141.28, 141.25, 141.18, 141.04, 140.92, 140.87, 139.37, 138.55, 136.75, 135.00, 130.61 \ (aryl C, d, J = 8.8 Hz), 122.24 \ (1C, \text{aryl C, d, J = 3.2 Hz}), 114.93 \ (aryl C, d, J = 21.8 Hz), 96.41 \ (1C, \text{sp\textsuperscript{3}-C of C_{60}})), 91.16 \ (1C, \text{sp\textsuperscript{3}-C of C_{60}}); \text{FT-IR} ν/cm\textsuperscript{-1} (KBr) 1638, 1604, 1510, 1459, 1426, 1341, 1270, 1178, 748, 563, 527; \text{UV-vis} (CHCl\textsubscript{3}) \(λ_{\text{max}} \text{nm (log ε)} = 256 \ (5.01), 317 \ (4.56), 416 \ (3.52), 458 \ (3.27), 684 \ (2.65); \text{MALDI-TOF MS} m/z \text{calcd for C_{67}H_{44}NOF [M]} = 857.0282, \text{found} 857.0286.}
Synthesis and spectral data of 2l: by following the general procedure, the reaction of C_{60} (35.7 mg, 0.05 mmol) with 1l (22.2 mg, 0.15 mmol), CuBr₂ (11.5 mg, 0.05 mmol) and Na₂HPO₄ (14.6 mg, 0.10 mmol) at 150 °C for 1 h afforded recovered C_{60} (13.0 mg, 36%) and 2l (11.5 mg, 27%): amorphous brown solid; ¹H NMR (500 MHz, CS₂ with DMSO-d₆ as the external deuterium lock) δ 8.25–8.20 (m, 1H), 8.13–8.06 (m, 1H), 7.61 (td, J = 7.9, 5.6 Hz, 1H), 7.38–7.32 (m, 1H); ¹³C NMR (126 MHz, CS₂ with DMSO-d₆ as the external deuterium lock and reference, all 2C unless indicated) δ 163.05 (1C, C=N, d, J = 3.0 Hz), 161.56 (1C, aryl C, d, J = 248.8 Hz), 147.11 (1C, 146.69 (3C), 145.32, 145.31, 145.17, 145.02, 144.96, 144.70, 144.49, 144.33, 144.15, 144.03, 143.68, 143.49, 143.17, 142.24, 141.74, 141.69, 141.62, 141.30, 141.23, 141.20, 141.06, 140.93, 139.39, 138.58, 136.74, 135.05, 129.39 (1C, aryl C, J = 7.7 Hz), 128.20 (1C, aryl C, d, J = 8.2 Hz), 123.91 (1C, aryl C, d, J = 3.1 Hz), 118.34 (1C, aryl C, d, J = 21.1 Hz), 115.24 (1C, aryl C, d, J = 23.5 Hz), 96.46 (1C, sp³-C of C_{60}), 91.10 (1C, sp³-C of C_{60}); FT-IR ν/cm⁻¹ (KBr) 1644, 1452, 1316, 1086, 982, 936, 883, 848, 789, 713, 564, 526; UV-vis (CHCl₃) λₘₐₓ nm (log ε) 256 (5.11), 316 (4.67), 412 (3.62), 454 (3.36), 683 (2.61); MALDI-TOF MS m/z calcd for C_{67}H_{41}NOF [M]^+ 857.0282, found 857.0285.

Synthesis and spectral data of 2m: by following the general procedure, the reaction of C_{60} (36.2 mg, 0.05 mmol) with 1m (37.0 mg, 0.25 mmol), CuBr₂ (11.1 mg, 0.05 mmol) and Na₂HPO₄ (14.5 mg, 0.10 mmol) at 150 °C for 1 h afforded recovered C_{60} (11.4 mg, 31%) and 2m (10.4 mg, 24%): amorphous brown solid; ¹H NMR (500 MHz, 1:1 CS₂/CDCl₃) δ 8.45 (td, J = 7.4, 1.6 Hz, 1H), 7.72–7.62 (m, 1H), 7.42 (t, J = 7.6 Hz, 1H), 7.35 (dd, J = 10.1, 8.9 Hz, 1H); ¹³C NMR (126 MHz, 1:1 CS₂/CDCl₃, all 2C unless indicated) δ 162.81 (1C, C=N, d, J = 5.4 Hz), 161.62 (1C, aryl C, d, J = 261.6 Hz), 148.15 (1C), 147.74 (1C), 147.53, 146.34 (4C), 146.22, 146.04, 145.99, 145.76, 145.60, 145.40, 145.16, 145.06, 144.78, 144.50, 144.19, 143.22, 142.73, 142.68, 142.62, 142.31, 142.20 (4C), 142.06, 141.94, 141.88, 140.34, 139.58, 137.79, 136.25, 134.18 (1C, aryl C, d, J = 8.7 Hz), 131.95 (1C, aryl C), 124.32 (1C, aryl C, d, J = 3.8 Hz), 117.14 (1C, aryl C, d, J = 21.6 Hz), 115.16 (1C, aryl C, d, J = 10.2 Hz), 97.01 (1C, sp³-
C of C₆₀), 91.98 (1C, sp³-C of C₆₀); FT-IR ν/cm⁻¹ (KBr) 1641, 1495, 1456, 1330, 1229, 1066, 982, 932, 822, 763, 740, 658, 603, 563, 526; UV-vis (CHCl₃) λmax nm (log ε) 256 (5.02), 317 (4.57), 417 (3.53), 454 (3.30), 684 (2.52); MALDI-TOF MS m/z calcd for C₆₀H₃NOF [M] 857.0282, found 857.0289.

![2n](image)

**Synthesis and spectral data of 2n:** by following the general procedure, the reaction of C₆₀ (35.8 mg, 0.05 mmol) with 1n (27.8 mg, 0.15 mmol), CuBr₂ (11.2 mg, 0.05 mmol) and Na₂HPO₄ (14.2 mg, 0.10 mmol) at 150 °C for 1 h afforded recovered C₆₀ (13.2 mg, 37%) and 2n (11.1 mg, 26%): amorphous brown solid; ¹H NMR (500 MHz, 1:1 CS₂/CDCl₃) δ 8.34–8.28 (m, 1H), 8.28–8.24 (m, 1H), 7.47–7.40 (m, 1H); ¹³C NMR (126 MHz, 1:1 CS₂/CDCl₃, all 2C unless indicated) δ 163.93 (1C, C=bez), 153.23 (1C, aryl C, dd, J = 256.9, 12.7 Hz), 150.34 (1C, aryl C, d, dd, J = 250.9, 13.1 Hz), 148.18 (1C), 147.77 (1C), 147.36, 146.37 (4C), 146.23, 146.07, 146.02, 145.77, 145.39, 145.35, 144.19, 145.09, 144.61, 144.49, 144.19, 143.01, 142.77, 142.71, 142.66, 142.30, 142.21, 142.19, 142.08, 141.95, 141.83, 140.41, 139.61, 137.81, 136.19, 126.01 (1C, aryl C, dd, J = 7.1, 3.7 Hz), 123.88 (1C, aryl C, dd, J = 6.4, 3.8 Hz), 118.60 (1C, aryl C, d, J = 19.6 Hz), 117.85 (1C, aryl C, d, J = 17.9 Hz), 97.84 (1C, sp³-C of C₆₀), 91.95 (1C, sp³-C of C₆₀); FT-IR ν/cm⁻¹ (KBr) 1641, 1512, 1495, 1339, 1323, 1268, 1195, 1141, 1080, 983, 937, 823, 794, 776, 720, 563, 526; UV-vis (CHCl₃) λmax nm (log ε) 256 (5.07), 317 (4.61), 416 (3.45), 452 (3.20), 683 (2.42); MALDI-TOF MS m/z calcd for C₆₀H₃NOF₂ [M] 875.0188, found 875.0182.

![2o](image)

**Synthesis and spectral data of 2o:** by following the general procedure, the reaction of C₆₀ (35.8 mg, 0.05 mmol) with 1o (27.3 mg, 0.15 mmol), CuBr₂ (11.9 mg, 0.05 mmol) and Na₂HPO₄ (14.1 mg, 0.10 mmol) at 150 °C for 1 h afforded recovered C₆₀ (14.2 mg, 40%) and 2o (8.8 mg, 20%): amorphous brown solid; ¹H NMR (500 MHz, 1:1 CS₂/CDCl₃) δ 8.03–7.96 (m, 2H), 7.12 (tt, J = 8.5, 2.4 Hz, 1H); ¹³C NMR (126 MHz, 1:1 CS₂/CDCl₃, all 2C unless indicated) δ 163.89 (1C, C=bez, t, J = 3.6 Hz), 162.99 (aryl C, dd, J = 250.7, 12.1 Hz), 148.19 (1C), 147.77 (1C), 147.13, 146.39, 146.37, 146.24, 146.08, 146.02, 145.79, 145.38, 145.33, 145.19, 145.09, 144.60, 144.48, 144.18,
142.81, 142.77, 142.70, 142.66, 142.30, 142.21, 142.16, 142.08, 141.95, 141.81, 140.42, 139.63, 137.80, 136.23, 129.92 (1C, aryl C, t, J = 10.2 Hz), 112.31 (aryl C, dd, J = 20.9, 6.9 Hz), 107.88 (1C, aryl C, t, J = 25.1 Hz), 97.88 (1C, sp\(^3\)-C of C\(_{60}\)), 91.89 (1C, sp\(^3\)-C of C\(_{60}\); FT-IR ν/cm\(^{-1}\) (KBr) 1648, 1619, 1593, 1437, 1354, 1123, 987, 938, 873, 853, 717, 561, 526; UV-vis (CHCl\(_3\)) \(\lambda_{\text{max}}\) nm (log \(\varepsilon\)) 254 (5.06), 318 (4.59), 415 (3.48), 457 (3.22), 682 (2.50); MALDI-TOF MS \(m/z\) calcd for C\(_{67}H_3NOF_2\) [M]\(^-\) 875.0188, found 875.0185.

Synthesis and spectral data of 2p: by following the general procedure, the reaction of C\(_{60}\) (35.7 mg, 0.05 mmol) with 1p (30.7 mg, 0.15 mmol), CuBr\(_2\) (11.2 mg, 0.05 mmol) and Na\(_2\)HPO\(_4\) (14.3 mg, 0.10 mmol) at 150 °C for 1 h afforded recovered C\(_{60}\) (10.8 mg, 30%) and 2p\(^{2b,e}\) (10.1 mg, 23%): amorphous brown solid; \(^1\)H NMR (500 MHz, 1:1 CS\(_2\)/CDCl\(_3\)) \(\delta\) 8.54 (d, \(J = 7.8\) Hz, 2H), 8.29 (d, \(J = 7.8\) Hz, 2H), 4.00 (s, 3H).

Synthesis and spectral data of 2q: by following the general procedure, the reaction of C\(_{60}\) (35.6 mg, 0.05 mmol) with 1q (25.4 mg, 0.15 mmol), CuBr\(_2\) (12.4 mg, 0.05 mmol) and Na\(_2\)HPO\(_4\) (14.4 mg, 0.10 mmol) at 150 °C for 1 h afforded recovered C\(_{60}\) (9.7 mg, 27%) and 2q\(^{2b}\) (10.4 mg, 24%): amorphous brown solid; \(^1\)H NMR (500 MHz, 1:1 CS\(_2\)/CDCl\(_3\)) \(\delta\) 8.59 (d, \(J = 8.3\) Hz, 2H), 7.93 (d, \(J = 8.3\) Hz, 2H).

Synthesis and spectral data of 2r: by following the general procedure, the reaction of C\(_{60}\) (36.1 mg, 0.05 mmol) with 1r (22.4 mg, 0.15 mmol), CuBr\(_2\) (11.5 mg, 0.05 mmol) and Na\(_2\)HPO\(_4\) (14.4 mg, 0.10 mmol) at 150 °C for 1 h afforded recovered C\(_{60}\) (24.9 mg,
69%) and 2r (4.7 mg, 14%); amorphous brown solid; \(^1\)H NMR (500 MHz, 1:1 CS\(_2\)/CDCl\(_3\)) \(\delta\) 8.95 (d, \(J = 6.0\) Hz, 2H), 8.28 (d, \(J = 6.0\) Hz, 2H); \(^{13}\)C NMR (151 MHz, 1:1 CS\(_2\)/CDCl\(_3\), all 2C unless indicated) \(\delta\) 164.14 (1C, C=N), 150.63 (aryl C), 148.15 (1C), 147.74 (1C), 146.97, 146.37 (4C), 146.22, 146.05, 146.00, 145.77, 145.36, 145.29, 145.17, 145.08, 144.57, 144.44, 144.15, 142.76, 142.69 (4C), 142.65, 142.28, 142.19, 142.13, 142.06, 141.93, 141.79, 140.42, 139.63, 137.72, 136.19, 134.13 (1C, aryl C), 122.44 (aryl C), 97.76 (1C, sp\(^3\)-C of C\(_{60}\)), 91.91 (1C, sp\(^3\)-C of C\(_{60}\)); FT-IR \(\nu/cm^{-1}\) (KBr) 3416, 1668, 1639, 1577, 1515, 1464, 1427, 1269, 1250, 707, 688, 551, 527; UV-vis (CHCl\(_3\)) \(\lambda_{\text{max}}\) nm (log \(\varepsilon\)) 255 (5.04), 317 (4.58), 416 (3.49), 449 (3.26), 684 (2.39); MALDI-TOF MS \(m/z\) calcd for C\(_{66}\)H\(_2\)N\(_2\)O [M] 840.0329, found 840.0315.

\[
\begin{align*}
3a
\end{align*}
\]

**Synthesis and spectral data of 3a:** 16.8 mg (0.02 mmol) of 2a was electroreduced by controlled potential electrolysis (CPE) at \(-1.07\) V vs saturated calomel electrode (SCE) in 15 mL of 1,2-C\(_2\)H\(_4\)Cl\(_2\) containing 0.1 M n-butylammonium perchlorate (TBAP) under an argon atmosphere at 0 °C. CPE was carried out on a potentiostat/galvanostat using an “H” type cell which consisted of two platinum gauze electrodes (serving as working and counter electrodes, respectively) separated by a sintered glass frit. The SCE was used as reference electrode and separated from the bulk of the solution by a fritted-glass bridge of low porosity, which contained the solvent/supporting electrolyte mixture. The electrolysis was terminated when the theoretical number of coulombs required for a full conversion of 2a to 2a\(^{-}\) was reached. Then, the dianionic 2a\(^{-}\) was reacted with trifluoroacetic acid (7.6 \(\mu\)L, 0.10 mmol) at 0 °C for 10 min. The reaction mixture was filtered through a silica gel (200–300 mesh) plug with CS\(_2\)/CH\(_2\)Cl\(_2\) (1:1, v/v) to remove the supporting electrolyte and insoluble materials. After evaporation in vacuo, the residue was separated on a silica gel (300–400 mesh) column with CS\(_2\)/CH\(_2\)Cl\(_2\) (4:1, v/v) to afford product 3a (8.5 mg, 50%) as an amorphous brown solid; \(^1\)H NMR (400 MHz, CDCl\(_3\)/CDCl\(_2\)) \(\delta\) 8.52 (s, 1H), 8.23–8.14 (m, 2H), 7.68–7.63 (m, 1H), 7.63–7.56 (m, 2H), 6.91 (s, 1H); \(^{13}\)C NMR (151 MHz, 2:1 CDCl\(_3\)/CDCl\(_2\)/CS\(_2\), all 2C unless indicated) \(\delta\) 166.99 (1C, C=O), 151.84, 147.98, 146.90 (1C), 146.15 (1C), 145.59, 145.48, 145.23, 145.09, 145.06, 145.03, 144.64, 144.37, 144.24, 144.20 (4C), 143.88, 143.33, 142.05, 141.62, 141.51, 141.35, 141.17, 141.00, 140.81, 140.50, 140.17, 139.25, 138.74, 137.64, 135.45, 132.40 (1C, aryl C), 131.67 (1C, aryl C), 128.09 (aryl C), 126.47 (aryl C), 71.75 (1C, sp\(^3\)-C of C\(_{60}\)), 59.53 (1C, sp\(^3\)-C of C\(_{60}\)); FT-IR \(\nu/cm^{-1}\) (KBr) 3416, 1668, 1639, 1577, 1515, 1464, 1427, 1269, 1250, 707, 688, 551, 527; UV-vis (CHCl\(_3\)) \(\lambda_{\text{max}}\) nm (log \(\varepsilon\)) 258 (5.03), 328 (4.52), 405 (3.77), 431 (3.62), 697 (2.87); MALDI-TOF MS \(m/z\) calcd for C\(_{67}\)H\(_3\)NO [M] 841.0533, found 841.0541.
Synthesis and spectral data of 3a-D: 8.4 mg (0.01 mmol) of 2a was electroreduced by controlled potential electrolysis (CPE) at −1.07 V vs saturated calomel electrode (SCE) in 15 mL of 1,2-C_6H_4Cl_2 containing 0.1 M n-butylammonium perchlorate (TBAP) under an argon atmosphere at 0 °C. The electrolysis was terminated when the theoretical number of coulombs required for a full conversion of 2a to 2a^{2−} was reached. Then, the dianionic 2a^{2−} was reacted with CF_3COOD (73.2 μL, 1.00 mmol) at 0 °C for 10 min. After removal of volatiles in vacuo, the residue was dissolved in CS_2. Subsequent filtration to remove TBAP and insoluble impurities. Evaporation of the resulting filtrate to remove CS_2 and then washing with methanol provided product 3a-D along with decomposition product C_{60} as an amorphous brown solid (Figure S1); ^1H NMR (500 MHz, CDCl_3CDCl_3) δ 8.54 (s, 0.85H), 8.20 (d, J = 7.6 Hz, 2H), 7.69–7.64 (m, 1H), 7.64–7.57 (m, 2H), 6.91 (s, 0.44H). The ^1H NMR spectrum of 3a-D showed all expected signals of 3a except that the fullerenyl proton at 6.91 ppm had an integral of 0.44 and the amide proton at 8.54 ppm had an integral of 0.85, hinting partial H-D exchange during the workup process.

Figure S1. Reaction of 2a^{2−} and CF_3COOD.
4. Attempted reaction of $2a^{2-}$ with Mel or D$_2$O

**Attempted reaction of $2a^{2-}$ with Mel:** 8.4 mg (0.01 mmol) of $2a$ was electroreduced by controlled potential electrolysis (CPE) at $-1.07$ V vs saturated calomel electrode (SCE) in 15 mL of 1,2-C$_6$H$_4$Cl$_2$ containing 0.1 M $n$-butylammonium perchlorate (TBAP) under an argon atmosphere at 0 °C. The electrolysis was terminated when the theoretical number of coulombs required for a full conversion of $2a$ to $2a^{2-}$ was reached. Then, the dianionic $2a^{2-}$ was reacted with Mel (32.0 μL, 0.50 mmol) at 0 °C for 6 h. It was found that $2a$ was partially decomposed to C$_{60}$ (Figure S2).

![](image)

**Figure S2.** Reaction of $2a^{2-}$ and Mel.

**Attempted reaction of $2a^{2-}$ with D$_2$O:** 8.4 mg (0.01 mmol) of $2a$ was electroreduced by controlled potential electrolysis (CPE) at $-1.07$ V vs saturated calomel electrode (SCE) in 15 mL of 1,2-C$_6$H$_4$Cl$_2$ containing 0.1 M $n$-butylammonium perchlorate (TBAP) under an argon atmosphere at 0 °C. The electrolysis was terminated when the theoretical number of coulombs required for a full conversion of $2a$ to $2a^{2-}$ was reached. Then, the dianionic $2a^{2-}$ was reacted with D$_2$O (10.0 μL, 0.50 mmol) at 0 °C for 6 h. It was found that $2a$ was partially decomposed to C$_{60}$ (Figure S3).
5. Control experiments
A mixture of C₆₀ (36.1 mg, 0.05 mmol), 1a (21.8 mg, 0.15 mmol) and CuBr₂ (11.4 mg, 0.05 mmol), Na₂HPO₄ (14.4 mg, 0.10 mmol) and TEMPO (3.9 mg, 0.025 mmol) was completely dissolved in 1,2-C₆H₄Cl₂. After being stirred in an oil bath at 150 °C for 1 h, the resulting solution was evaporated in vacuo and subsequently separated on a silica gel column (300–400 mesh) with CS₂ as the eluent to give recovered C₆₀ (24.5 mg, 68%) and the product 2a (4.4 mg, 10%). While adding 1 equiv. of TEMPO (7.8 mg, 0.05 mmol), there was no desired product, and the radical coupling product 4 between TEMPO and 1a radical was successfully detected by ESI-MS. ESI-MS m/z calcd for C₁₇H₂₄N₃O [M+H]+ 286.1914, found 286.1919.
Figure S4. HRMS of product 4.

6. Reaction mechanism leading to fulleroisoxazoles

![Reaction mechanism diagram]

Scheme S1. Reaction mechanism for the formation of fulleroisoxazoles 2'.

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7. References
Figure S5. $^1$H NMR (400 MHz, CS$_2$/DMSO-$d_6$) of 2a.
Figure S6. $^1$H NMR (400 MHz, 1:1 CS$_2$/CDCl$_3$) of 2b.
Figure S7. $^1$H NMR (500 MHz, 1:1 CS$_2$/CDCl$_3$) of 2c.
Figure S8. $^1$H NMR (400 MHz, CS$_2$/DMSO-$_d_6$) of 2d.
Figure S9. $^{13}$C NMR (101 MHz, CS$_2$/DMSO-$d_6$) of 2d.
Figure S10. Expanded $^{13}$C NMR (101 MHz, CS$_2$/DMSO-$d_6$) of 2d.
Figure S11. $^1$H NMR (400 MHz, CS$_2$/DMSO-$d_6$) of 2e.
Figure S12. $^{13}$C NMR (101 MHz, CS$_2$/DMSO-$d_6$) of 2e.
Figure S13. Expanded $^{13}$C NMR (101 MHz, CS$_2$/DMSO-$_d_6$) of 2e.
Figure S14. $^1$H NMR (400 MHz, CS$_2$/DMSO-$d_6$) of 2f.
Figure S15. $^{13}$C NMR (101 MHz, CS$_2$/DMSO-$d_6$) of 2f.
Figure S16. Expanded $^{13}$C NMR (101 MHz, CS$_2$/DMSO-$d_6$) of 2f.
Figure S17. $^1$H NMR (500 MHz, 1:1 CS$_2$/CDCl$_3$) of 2g.
Figure S18. $^1$H NMR (500 MHz, 1:1 CS$_2$/CDCl$_3$) of 2h.
Figure S19. $^1$H NMR (500 MHz, 1:1 CS$_2$/CDCl$_3$) of 2i.
Figure S20. $^1$H NMR (400 MHz, CS$_2$/DMSO-$d_6$) of 2j.
Figure S21. $^1$H NMR (500 MHz, CS$_2$/DMSO-$d_6$) of 2k.
Figure S22. $^{13}$C NMR (126 MHz, CS$_2$/DMSO-$d_6$) of 2k.
Figure S23. Expanded $^{13}$C NMR (126 MHz, CS$_2$/DMSO-$d_6$) of 2k.
Figure S24. $^1$H NMR (500 MHz, CS$_2$/DMSO-$d_6$) of 2l.
Figure S25. $^{13}$C NMR (126 MHz, CS$_2$/DMSO-$d_6$) of 21.
Figure S26. Expanded $^{13}$C NMR (126 MHz, CS$_2$/DMSO-$d_6$) of 21.
Figure S27. $^1$H NMR (500 MHz, 1:1 CS$_2$/CDCl$_3$) of 2m.
Figure S28. $^{13}$C NMR (126 MHz, 1:1 CS$_2$/CDCl$_3$) of 2m.
Figure S29. Expanded $^{13}$C NMR (126 MHz, 1:1 CS$_2$/CDCl$_3$) of 2m.
Figure S30. $^1$H NMR (500 MHz, 1:1 CS$_2$/CDCl$_3$) of 2n.
Figure S31. $^{13}$C NMR (126 MHz, 1:1 CS$_2$/CDCl$_3$) of 2n.
Figure S32. Expanded $^{13}$C NMR (126 MHz, 1:1 CS$_2$/CDCl$_3$) of 2n.
Figure S33. $^1$H NMR (500 MHz, 1:1 CS$_2$/CDCl$_3$) of 2o.
Figure S34. $^{13}$C NMR (126 MHz, 1:1 CS$_2$/CDCl$_3$) of 2o.
Figure S35. Expanded $^{13}$C NMR (126 MHz, 1:1 CS$_2$/CDCl$_3$) of 2o.
Figure S36. $^1$H NMR (500 MHz, 1:1 CS$_2$/CDCl$_3$) of 2p.
Figure S37. $^1$H NMR (500 MHz, 1:1 CS$_2$/CDCl$_3$) of 2q.
Figure S38. $^1$H NMR (500 MHz, 1:1 CS$_2$/CDCl$_3$) of 2r.
Figure S39. $^{13}$C NMR (151 MHz, 1:1 CS$_2$/CDCl$_3$) of 2r.
**Figure S40.** Expanded $^{13}$C NMR (151 MHz, 1:1 CS$_2$/CDCl$_3$) of 2r.
Figure S41. $^1$H NMR (400 MHz, CDCl$_2$CDCl$_2$) of 3a.
Figure S42. $^{13}$C NMR (151 MHz, 2:1 CDCl$_3$/CDCl$_2$/CS$_2$) of 3a.
Figure S43. Expanded $^{13}$C NMR (151 MHz, 2:1 CDCl$_2$CDCl$_2$/CS$_2$) of 3a.
Figure S44. $^1$H NMR (500 MHz, CDCl$_2$/CDCl$_2$) of 3a-D.
9. UV-vis Spectra of Compounds 2d–f, 2k–o, 2r and 3a

Figure S45. UV-vis absorption of compound 2d.  
Figure S46. UV-vis absorption of compound 2e.

Figure S47. UV-vis absorption of compound 2f.  
Figure S48. UV-vis absorption of compound 2k.

Figure S49. UV-vis absorption of compound 2l.  
Figure S50. UV-vis absorption of compound 2m.
Figure S51. UV-vis absorption of compound 2a.

Figure S52. UV-vis absorption of compound 2o.

Figure S53. UV-vis absorption of compound 2r.

Figure S54. UV-vis absorption of compound 3a.