Electronic Supplementary Information

Regioselective Acylation and Carboxylation of [60]Fulleroidinoline via Electrochemical Synthesis

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**General Methods**

All electrochemical reactions were performed under argon atmosphere using a SHANGHAI CHENHUA CH1630D workstation. Tetra-n-butylammonium perchlorate (TBAP) was recrystallized from absolute ethanol and dried in a vacuum at 313 K prior to use. All the chemicals were obtained commercially. Among these chemicals, liquid chemicals such as acetyl chloride, benzoic chloride, and ethyl chloroformate were distilled at each boiling point prior to use, due mainly to their high sensitivity towards humidity, others were used without further purification. Controlled potential electrolysis (CPE) was carried out on a potentiostat/galvanostat using an “H” type cell consisting of two platinum gauze electrodes (serving as working and counter electrodes, respectively) and a saturated calomel reference electrode (SCE). The SCE was separated from the bulk of the solution by a fritted-glass bridge of low porosity, which contained the solvent/supporting electrolyte mixture.

**Synthesis of the dianion 1^{2−}:** 26.0 mg (0.030 mmol) of [60]fulleroindoline 1 was dissolved in 25.0 mL of anhydrous o-dichlorobenzene (ODCB) solution containing 0.1 M TBAP. Then the solution was electroreduced at −1.1 V vs SCE under an argon atmosphere at room temperature. When the theoretical number of coulombs required for a full conversion of 1 to 1^{2−} was reached, the electrolysis was terminated after about 5.0 h, and a dark-green solution of 1^{2−} was obtained.

**Experimental procedures and spectral data for products 3a−3g.**

**Synthesis of compound 3a:** After the electrolysis of the 1 (26.0 mg, 0.030 mmol), the dianion 1^{2−} reacted with benzoyl chloride (17.5 μL, 0.150 mmol) and NaH (57–63% oil dispersion, 12.0 mg, 0.300 mmol). After being stirred at 0 °C for 5 h, the resulting mixture was directly filtered through a silica gel (200–300 mesh) plug with CS₂/CH₂Cl₂ (1:1 v/v) to remove the supporting electrolyte and insoluble materials, and then evaporated in vacuo to remove the solvent. Next, the residue was further separated on a silica gel column (400–500 mesh) with CS₂/CH₂Cl₂ (4:1 v/v) as the eluent to afford product 3a (17.5 mg, 60%) as an amorphous brown solid along with unreacted 1 (0.6 mg, 2%). If the dianion 1^{2−} reacted with benzoyl chloride in the absence of NaH under the same conditions, then the 1,2,3,4-adduct 4 (5.9 mg, 23%) and product 3a (11.2 mg, 38%) were obtained along with unreacted 1 (1.1 mg, 4%).$^{1}H$ NMR (400 MHz, CS₂/CDCl₃) δ 8.39 (d, $J = 8.0$ Hz, 2H), 7.60 (t, $J = 7.4$ Hz, 1H), 7.50 (t, $J = 7.7$ Hz, 2H), 7.41 (d, $J = 7.8$ Hz, 1H), 7.29 (s, 1H), 7.04 (d, $J = 7.8$ Hz, 1H), 5.95 (s, 1H), 2.76 (s, 3H), 2.52 (s, 3H);$^{13}C$ NMR (100 MHz, CS₂/CDCl₃, all 1C unless indicated) δ 196.06 (C=O), 167.78 (C=O), 152.39, 152.08, 151.38, 150.04, 149.83, 149.22, 148.81, 148.52, 148.26, 147.93,
147.86, 147.73, 147.36, 147.18, 147.14 (2C), 146.91, 146.86, 146.41, 146.40, 145.99 (2C), 145.95, 145.92, 145.53, 145.37, 145.33, 144.82 (2C), 144.80, 144.72, 144.54, 144.42, 144.31, 144.14, 143.84, 143.65, 143.42, 143.31, 143.05, 142.13, 141.93, 141.79, 141.72 (2C), 141.69, 141.55, 141.35, 141.24, 141.10, 140.63, 140.14, 139.93 (aryl C), 138.84, 137.70, 137.54 (aryl C), 137.47, 137.38, 135.44 (aryl C), 133.14 (aryl C), 129.16 (2C, aryl C), 128.72 (2C, aryl C), 128.61 (aryl C), 125.80 (aryl C), 125.42 (aryl C), 115.11 (aryl C), 83.58 (sp³-C of C₆₀), 69.89 (sp³-C of C₆₀), 62.42 (sp³-C of C₆₀), 56.81 (sp³-C of C₆₀), 26.84, 22.25; UV-vis (CHCl₃) λ_max nm (log ε) 251.0 (5.1), 318.5 (4.6), 403.5 (4.0), 440.0 (3.9), 525.5 (3.2), 703.5 (2.5); FT-IR ν/cm⁻¹ (KBr) 2922, 2860, 1668, 1599, 1499, 1439, 1366, 1304, 1236, 1180, 1086, 1020, 964, 858, 802, 748, 691, 604, 528; MALDI-TOF MS m/z calcd for C₇₆H₆₂NO₂ [M+H]^+ 974.1176, found 974.1165.

**Synthesis of compound 3b:** After the electrolysis of the 1 (26.0 mg, 0.030 mmol), the dianion 1² reacted with p-anisoyl chloride (20.5 μL, 0.150 mmol) and NaH (57–63% oil dispersion, 12.0 mg, 0.300 mmol). After being stirred at 0 °C for 5 h, the resulting mixture was directly filtered through a silica gel (200–300 mesh) plug with CS₂/CH₂Cl₂ (1:1 v/v) to remove the supporting electrolyte and insoluble materials, and then evaporated in vacuo to remove the solvent. Next, the residue was further separated on a silica gel (400–500 mesh) column with CS₂/CH₂Cl₂ (4:1 v/v) as the eluent to afford product 3b (17.9 mg, 59%) as an amorphous brown solid along with unreacted 1 (1.1 mg, 4%). ¹H NMR (400 MHz, TCE-d₂) δ 8.55 (d, J = 8.9 Hz, 2H), 7.32 (d, J = 7.8 Hz, 1H), 7.29 (s, 1H), 7.04 (d, J = 7.8 Hz, 1H), 7.00 (d, J = 8.9 Hz, 2H), 5.92 (s, 1H), 3.83 (s, 3H), 2.74 (s, 3H), 2.45 (s, 3H); ¹³C NMR (100 MHz, TCE-d₂), all 1C unless indicated) δ 194.79 (C=O), 169.08 (C=O), 164.29 (aryl C), 152.98, 152.71, 152.50, 150.47, 150.05, 149.56, 149.05, 148.77, 148.49, 148.21, 148.06, 147.90, 147.62, 147.56, 147.49, 147.47, 147.17 (2C), 146.64, 146.60, 146.26, 146.20, 146.19, 146.17, 145.72, 145.61, 145.53, 145.09, 145.03, 144.98, 144.92, 144.75, 144.64, 144.56, 144.25, 144.08, 143.67, 143.56, 143.46, 143.11, 142.46, 142.11, 141.99, 141.88, 141.79, 141.75, 141.72, 141.57, 141.40, 141.36, 141.12, 140.62 (aryl C), 140.31, 139.30, 137.95, 137.53, 137.51, 135.81 (aryl C), 132.45 (2C, aryl C), 129.82 (aryl C), 128.86 (aryl C), 125.91 (aryl C), 125.68 (aryl C), 115.65 (aryl C), 114.60 (2C, aryl C), 83.78 (sp³-C of C₆₀), 69.99 (sp³-C of C₆₀), 62.59 (sp³-C of C₆₀), 57.00 (sp³-C of C₆₀), 56.07, 27.60, 22.55; UV-vis (CHCl₃) λ_max nm (log ε) 253.5 (5.1), 325.0 (4.8), 403.5 (4.2), 443.5 (4.0), 522.0 (3.5), 706.0 (3.1); FT-IR ν/cm⁻¹ (KBr) 2960, 2920, 1660, 1590, 1500, 1440, 1370, 1340, 1300, 1260, 1170, 1110, 1030, 964, 860, 802, 748, 702, 683, 609, 561, 528; MALDI-TOF MS m/z calcd for C₇₇H₇₁NO₃Na [M+Na]^+ 1026.1101, found 1026.1114.
**Synthesis of compound 3c:** After the electrolysis of the 1 (26.0 mg, 0.030 mmol), the dianion $1^2$ reacted with $p$-nitrobenzoyl chloride (27.8 mg, 0.150 mmol) and NaH (57–63% oil dispersion, 120.0 mg, 3.000 mmol). After being stirred at 0 °C for 2 h, the resulting mixture was directly 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, and then evaporated in vacuo to remove the solvent. However, further purification on a silica gel (400–500 mesh) column would cause product 3c to completely decompose. Accordingly, the residue was purified by semi-preparative HPLC on a Buckyprep column (10 × 250 mm, eluent: toluene, 5 mL/min flow rate, detection at 325 nm) to afford product 3c (14.8 mg, 48%) as an amorphous brown solid along with unreacted 1 (1.0 mg, 4%). If the dianion $1^2$ reacted with $p$-nitrobenzoyl chloride in the presence of 10 equiv of NaH under the same conditions, then the 1,2,3,4-adduct 4 (14.1 mg, 54%) was exclusively obtained along with unreacted 1 (1.1 mg, 4%). $^1$H NMR (400 MHz, TCE-$d_2$) δ 8.42 (d, $J = 8.9$ Hz, 2H), 8.31 (d, $J = 8.9$ Hz, 2H), 7.38 (d, $J = 7.7$ Hz, 1H), 7.33 (s, 1H), 7.12 (d, $J = 7.7$ Hz, 2H), 5.96 (s, 1H), 2.75 (s, 3H), 2.49 (s, 3H); $^{13}$C NMR (100 MHz, TCE-$d_2$, all 1C unless indicated) δ 197.27 (C=O), 169.08 (C=O), 152.49, 150.88, 150.70, 150.34, 150.22 (aryl C), 150.17, 149.48, 149.12, 148.88, 148.53, 148.22, 148.10, 147.71, 147.53, 147.46, 147.42, 147.41, 147.05, 146.84, 146.77, 146.69, 146.32, 146.29, 146.20, 146.17, 145.70, 145.58, 145.52, 145.14, 145.12, 145.06, 145.00, 144.84, 144.67, 144.59, 144.55, 144.48, 144.17, 143.68, 143.48, 143.24, 142.83, 142.22, 142.15, 142.14, 142.02, 141.89, 141.85, 141.82, 141.74, 141.63, 141.42, 141.04, 140.94, 140.42, 137.89, 137.71, 137.67, 137.48, 136.40 (aryl C), 130.06 (2C, aryl C), 128.76 (aryl C), 125.97 (aryl C), 125.37 (aryl C), 124.35 (2C, aryl C), 115.84 (aryl C), 83.89 (sp$^2$-C of C$_{60}$), 69.75 (sp$^3$-C of C$_{60}$), 62.70 (sp$^3$-C of C$_{60}$), 57.04 (sp$^3$-C of C$_{60}$), 27.59, 22.58; UV-vis (CHCl$_3$) $\lambda_{max}$ nm (log ε) 254.5 (5.0), 321.0 (4.6), 402.5 (4.0), 439.0 (3.9), 521.0 (3.4), 705.5 (3.0); FT-IR ν/cm$^{-1}$ (KBr) 2922, 2852, 1668, 1599, 1525, 1498, 1435, 1369, 1342, 1302, 1248, 1223, 1178, 1130, 1093, 1032, 1011, 964, 847, 820, 746, 702, 604, 561, 528; MALDI-TOF MS $m/z$ calcd for C$_{76}$H$_{13}$N$_2$O$_4$ [M–H]$^+$ 1017.0870, found 1017.0882.
Synthesis of compound 3d: After the electrolysis of the 1 (26.0 mg, 0.030 mmol), the dianion \(1^2\) reacted with acetyl chloride (10.5 µL, 0.150 mmol) and NaH (57–63% oil dispersion, 120.0 mg, 3.000 mmol). After being stirred at 0 °C for 5 h, the resulting mixture was directly filtered through a silica gel (200–300 mesh) plug with \(\text{CS}_2/\text{CH}_2\text{Cl}_2\) (1:1 v/v) to remove the supporting electrolyte and insoluble materials, and then evaporated in vacuo to remove the solvent. Next, the residue was further separated on a silica gel (400–500 mesh) column with \(\text{CS}_2/\text{CH}_2\text{Cl}_2\) (4:1 v/v) as the eluent to afford product 3d (10.9 mg, 40%) as an amorphous brown solid along with unreacted 1 (2.1 mg, 8%). \(\text{H NMR (400 MHz, CDCl}_3\) δ 7.62 (d, \(J = 7.8\) Hz, 1H), 7.38 (s, 1H), 7.24 (d, \(J = 7.8\) Hz, 1H), 6.01 (s, 1H), 2.98 (s, 3H), 2.82 (s, 3H), 2.57 (s, 3H); \(\text{C NMR (100 MHz, CDCl}_3\) all 1C unless indicated) δ 202.61 (C=O), 168.82 (C=O), 152.89, 152.32, 150.31, 150.28, 150.17, 149.55, 149.09, 148.78, 148.54, 148.22, 148.02, 147.62, 147.50, 147.45 (2C), 147.31, 147.08, 147.00, 146.86, 146.64, 146.31 (2C), 146.27, 146.24, 145.74, 145.57, 145.44, 145.19, 145.05, 144.93, 144.96, 144.81, 144.66, 144.55, 144.37, 144.09, 143.70, 143.69, 143.17, 142.39, 142.28, 142.21, 142.12, 141.99, 141.84, 141.75 (2C), 141.57, 141.47, 140.98, 140.44 (aryl C), 140.38, 138.74, 138.12, 137.53, 137.42, 135.28 (aryl C), 129.21 (aryl C), 125.96 (aryl C), 125.93 (aryl C), 115.39 (aryl C), 83.84 (sp\(^3\)-C of C\(_6\)0), 71.44 (sp\(^3\)-C of C\(_6\)0), 57.04 (sp\(^3\)-C of C\(_6\)0), 27.49, 27.35, 22.40; UV-vis (CHCl\(_3\)) \(\lambda_{\text{max}}\) nm (log ε) 251.0 (5.0), 318.5 (4.6), 401.5 (4.0), 446.0 (3.8), 524.0 (3.2), 702.5 (2.3); FT-IR \(\nu/cm^{-1}\) (KBr) 2920, 2855, 1717, 1665, 1603, 1501, 1435, 1362, 1302, 1256, 1169, 1086, 1036, 802, 606, 527; MALDI-TOF MS \(m/z\) calcd for C\(_{71}H_{14}NO_2\) [M+H]\(^+\) 912.1019, found 912.1002.

![Diagram](image_url)

Synthesis of compound 3e: After the electrolysis of the 1 (26.0 mg, 0.030 mmol), the dianion \(1^2\) reacted with isobutyl chloride (15.5 µL, 0.150 mmol) and NaH (57–63% oil dispersion, 12.0 mg, 0.300 mmol). After being stirred at 0 °C for 5 h, the resulting mixture was directly filtered through a silica gel (200–300 mesh) plug with \(\text{CS}_2/\text{CH}_2\text{Cl}_2\) (1:1 v/v) to remove the supporting electrolyte and insoluble materials, and then evaporated in vacuo to remove the solvent. Next, the residue was further separated on a silica gel (400–500 mesh) column with \(\text{CS}_2/\text{CH}_2\text{Cl}_2\) (4:1 v/v) as the eluent to afford product 3e (11.1 mg, 39%) as an amorphous brown solid along with unreacted 1 (1.5 mg, 5%). \(\text{H NMR (400 MHz, TCE-}d_2\) δ 7.44 (d, \(J = 7.8\) Hz, 1H), 7.31 (s, 1H), 7.17 (d, \(J = 7.8\) Hz, 1H), 5.93 (s, 1H), 3.98 (hept, \(J = 6.6\) Hz, 1H), 2.75 (s, 3H), 2.49 (s, 3H), 1.36 (d, \(J = 6.7\) Hz, 3H), 1.30 (d, \(J = 6.7\) Hz, 3H); \(\text{C NMR (100 MHz, TCE-}d_2\), all 1C unless indicated) δ 209.84 (C=O), 169.09 (C=O), 153.12, 151.95, 150.40, 150.27, 150.15, 149.68, 149.03, 148.72, 148.52, 148.22, 147.98, 147.80, 147.57, 147.54, 147.49, 147.33, 147.14, 147.09, 146.79, 146.60, 146.29 (2C), 146.23 (2C), 145.66, 145.56, 145.43, 145.04 (2C),
144.93 (2C), 144.91, 144.77, 144.67, 144.53, 144.32, 144.07, 143.74, 143.65, 143.19, 142.47, 142.24, 142.20, 142.12, 141.85, 141.77, 141.69, 141.62, 141.52, 141.49, 141.11, 140.70 (aryl C), 140.35, 139.19, 138.36, 137.75, 137.46, 134.84 (aryl C), 129.20 (aryl C), 125.98 (aryl C), 125.82 (aryl C), 115.68 (aryl C), 83.70 (sp$^3$-C of C$_{60}$), 71.31 (sp$^3$-C of C$_{60}$), 62.68 (sp$^3$-C of C$_{60}$), 57.04 (sp$^3$-C of C$_{60}$), 37.54, 27.64, 22.59, 20.86, 20.77; UV-vis (CHCl$_3$) $\lambda_{\text{max}}$ (log $\varepsilon$) 252.0 (5.0), 318.5 (4.6), 401.5 (4.0), 437.0 (3.9), 526.5 (3.4), 704.5 (3.1); FT-IR ν/cm$^{-1}$ (KBr) 2962, 2922, 2854, 1714, 1668, 1599, 1498, 1439, 1371, 1342, 1302, 1259, 1174, 1093, 1036, 964, 858, 802, 698, 604, 561, 530; MALDI-TOF MS $m/z$ calcd for C$_{73}$H$_{18}$NO$_2$ [M+H]$^+$ 940.1338, found 940.1332.

Synthesis of compound 3f: After the electrolysis of the 1 (26.0 mg, 0.030 mmol), the dianion 1$^2$ reacted with ethyl chloroformate (14.5 μL, 0.150 mmol) and NaH (57–63% oil dispersion, 12.0 mg, 0.300 mmol). After being stirred at 25 °C for 24 h, the resulting mixture was directly 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, and then evaporated in vacuo to remove the solvent. Next, the residue was further separated on a silica gel (400–500 mesh) column with CS$_2$/CH$_2$Cl$_2$ (4:1 v/v) as the eluent to afford product 3f (8.6 mg, 30%) as an amorphous brown solid along with unreacted 1 (9.5 mg, 37%). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.90 (d, $J = 7.7$ Hz, 1H), 7.38 (s, 1H), 7.23 (d, $J = 7.7$ Hz, 1H), 6.00 (s, 1H), 4.59 (q, $J = 7.1$ Hz, 2H), 2.82 (s, 3H), 2.57 (s, 3H), 1.49 (t, $J = 7.1$ Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$, all 1C unless indicated) $\delta$ 169.32 (C=O), 168.78 (C=O), 152.82, 152.34, 150.18, 150.07, 149.91, 149.29, 149.02, 148.69, 148.47, 148.19, 147.89, 147.44, 147.38, 147.35, 147.32, 147.23 (2C), 146.98, 146.75, 146.62, 146.37, 146.30, 146.17, 146.12, 145.62, 145.47, 145.37, 145.02, 144.99, 144.96, 144.82, 144.77, 144.74, 144.61, 144.49, 144.17, 144.01, 143.59 (2C), 142.99, 142.34, 142.24, 142.07 (2C), 141.87, 141.76, 141.65, 141.60, 141.58, 141.20, 140.94, 140.41 (aryl C), 140.23, 138.14, 138.11, 137.33, 137.00, 135.34 (aryl C), 129.09 (aryl C), 126.13 (aryl C), 125.76 (aryl C), 115.43 (aryl C), 83.83 (sp$^3$-C of C$_{60}$), 63.64, 62.71 (sp$^3$-C of C$_{60}$), 61.83 (sp$^3$-C of C$_{60}$), 57.00 (sp$^3$-C of C$_{60}$), 27.34, 22.41, 14.52; UV-vis (CHCl$_3$) $\lambda_{\text{max}}$ (nm) (log $\varepsilon$) 251.0 (5.0), 318.0 (4.6), 403.0 (4.0), 443.5 (3.8), 524.5 (3.2), 699.5 (2.4); FT-IR ν/cm$^{-1}$ (KBr) 2951, 2920, 2855, 1734, 1667, 1594, 1499, 1438, 1369, 1341, 1300, 1220, 1093, 1021, 858, 845, 791, 605, 562, 529; MALDI-TOF MS $m/z$ calcd for C$_{72}$H$_{16}$NO$_3$ [M+H]$^+$ 942.1125, found 942.1114.
Synthesis of compound 3g: After the electrolysis of the 1 (26.0 mg, 0.030 mmol), the dianion 1\(^2\) reacted with phenyl chloroformate (18.5 μL, 0.150 mmol) and NaH (57–63\% oil dispersion, 12.0 mg, 0.300 mmol). After being stirred at 25 °C for 24 h, the resulting mixture was directly filtered through a silica gel (200–300 mesh) plug with CS\(_2/\text{CH}_2\text{Cl}_2\) (1:1 \(\text{v/v}\)) to remove the supporting electrolyte and insoluble materials, and then evaporated in vacuo to remove the solvent. Next, the residue was further separated on a silica gel (400–500 mesh) column with CS\(_2/\text{CH}_2\text{Cl}_2\) (4:1 \(\text{v/v}\)) as the eluent to afford product 3g (7.7 mg, 26\%) as an amorphous brown solid along with unreacted 1 (11.7 mg, 45\%). \(^1\)H NMR (400 MHz, TCE-\(d_2\)) \(\delta\) 7.84 (d, \(J = 7.7\) Hz, 1H), 7.46 (t, \(J = 7.8\) Hz, 2H), 7.36–7.26 (m, 4H), 7.18 (d, \(J = 7.8\) Hz, 1H), 5.96 (s, 1H), 2.75 (s, 3H), 2.51 (s, 3H); \(^{13}\)C NMR (100 MHz, TCE-\(d_2\), all 1C unless indicated) \(\delta\) 169.10 (C=O), 168.41 (C=O), 152.89, 151.51, 150.97, 150.49, 149.34, 149.32, 149.09, 148.80, 148.52, 148.26, 147.97, 147.47, 147.44, 147.41, 147.38, 147.29 (2C), 146.98, 146.76, 146.69, 146.38, 146.37, 146.24 (2C), 145.61, 145.54, 145.43, 145.16, 145.12, 145.10, 145.04, 144.98, 144.83, 144.68, 144.57, 144.54, 144.33, 144.11, 143.65, 143.59, 143.10, 142.32, 142.28, 142.18, 142.01, 141.90, 141.81, 141.76, 141.73, 141.71, 141.33, 141.08, 140.88 (aryl C), 140.31, 138.04, 137.48, 137.42, 137.38, 135.87 (aryl C), 130.20 (2C, aryl C), 128.94 (aryl C), 127.13 (aryl C), 126.07 (aryl C), 125.86 (aryl C), 121.59 (2C, aryl C), 115.76 (aryl C), 83.86 (sp\(^3\)-C of C\(_6\)O), 62.76 (sp\(^3\)-C of C\(_6\)O), 61.48 (sp\(^3\)-C of C\(_6\)O), 57.09 (sp\(^3\)-C of C\(_6\)O), 27.60, 22.62; UV-vis (CHCl\(_3\)) \(\lambda_{\text{max}}\) nm (log \(\varepsilon\)) 252.5 (5.0), 319.0 (4.6), 403.5 (4.0), 440.0 (3.8), 524.0 (3.0), 729.5 (2.9); FT-IR \(\nu/\text{cm}^{-1}\) (KBr) 2922, 2852, 1755, 1666, 1597, 1495, 1437, 1371, 1302, 1254, 1188, 1088, 1036, 987, 827, 742, 701, 687, 604, 565, 530; MALDI-TOF MS m/z calcd for C\(_{76}H_{15}NO_3\) [M]+ 989.1046, found 989.1055.

Synthesis of 2a in the presence of NaH or molecular sieves before electrolysis. NaH (57–63\% oil dispersion, 12.0 mg, 0.300 mmol) or 4 \(\AA\) molecular sieves (1.5 g) was added before the electrolysis process. After the electrolysis of 1 (26.0 mg, 0.030 mmol), the dianion 1\(^2\) reacted with benzoyl chloride (17.5 μL, 0.150 mmol). After being stirred at 0 °C for 5 h, the resulting mixture was directly filtered through a silica gel (200–300 mesh) plug with CS\(_2/\text{CH}_2\text{Cl}_2\) (1:1 \(\text{v/v}\)) to remove the supporting electrolyte and insoluble materials, and then evaporated in vacuo to remove the solvent. Next, the residue was further separated on a silica gel (400–500 mesh) column with CS\(_2/\text{CH}_2\text{Cl}_2\) (4:1 \(\text{v/v}\)) as the eluent to afford product 3a (16.8 mg, 58\% in the presence of NaH; 11.7 mg, 40\% in the presence of molecular sieves), 1,2,3,4-adduct 4 (0.8 mg, 3\% in the presence of NaH; 5.7 mg, 22\% in the presence of molecular sieves) along with unreacted 1 (1.1 mg, 4\%).
Investigation of possible proton source from the Hofmann elimination of electrolyte. After the electrolysis of 1 (26.0 mg, 0.030 mmol), the solution of 1<sup>2-</sup> was vigorously stirred at 0 °C under an argon atmosphere for 36 h. After that, the resulting mixture was directly filtered through a silica gel (200–300 mesh) plug with CS<sub>2</sub>/CH<sub>2</sub>Cl<sub>2</sub> (1:1 v/v) to remove the supporting electrolyte and insoluble materials, and then evaporated in vacuo to remove the solvent to recover unreacted 1 (21.3 mg, 82%).

**Reaction of 1<sup>2-</sup> with 2a quenched by D<sub>2</sub>O.** After the electrolysis of 1 (26.0 mg, 0.030 mmol), the dianion 1<sup>2-</sup> reacted with benzoyl chloride (17.5 μL, 0.150 mmol) and NaH (57–63% oil dispersion, 12.0 mg, 0.300 mmol). After being stirred at 0 °C for 5 h, then quenched by D<sub>2</sub>O (60.0 μL, 3.0 mmol) for 30 mins. The resulting mixture was directly filtered on a silica gel (200–300 mesh) plug column with CS<sub>2</sub>/CH<sub>2</sub>Cl<sub>2</sub> (1:1 v/v) to remove the supporting electrolyte and insoluble materials, and then evaporated in vacuo to remove the solvent. Next, the residue was further separated on a silica gel (400–500 mesh) column with CS<sub>2</sub>/CH<sub>2</sub>Cl<sub>2</sub> (4:1 v/v) as the eluent to afford product 3a (17.0 mg, 58%) as an amorphous brown solid along with unreacted 1 (0.8 mg, 3%).

**Reaction of 1<sup>2-</sup> with 2a quenched by CD<sub>3</sub>COOD.** After the electrolysis of 1 (26.0 mg, 0.030 mmol), the dianion 1<sup>2-</sup> reacted with benzoyl chloride (17.5 μL, 0.150 mmol) and NaH (57–63% oil dispersion, 12.0 mg, 0.300 mmol). After being stirred at 0 °C for 5 h, then quenched by CD<sub>3</sub>COOD (180.0 μL, 3.0 mmol) for 30 min. The resulting mixture was directly filtered through a silica gel (200–300 mesh) plug column with CS<sub>2</sub>/CH<sub>2</sub>Cl<sub>2</sub> (1:1 v/v) to remove the supporting electrolyte and insoluble materials, and then evaporated in vacuo to remove the solvent. Next, the residue was further separated on a silica gel (400–500 mesh) column with CS<sub>2</sub>/CH<sub>2</sub>Cl<sub>2</sub> (4:1 v/v) as the eluent to afford product 3a-H(D) (17.1 mg, 59%) as an amorphous brown solid along with unreacted 1 (1.0 mg, 4%).

**Reaction of 1<sup>2-</sup> with 2c in the presence of TEMPO.** After the electrolysis of 1 (26.0 mg, 0.030 mmol), the dianion 1<sup>2-</sup> reacted with p-nitrobenzoyl chloride 2c (27.8 mg, 0.150 mmol), NaH (57–63% oil dispersion, 120.0 mg, 3.000 mmol) and 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO) (10.3 mg, 0.06 mmol). After being stirred at 0 °C for 2 h, the resulting mixture was directly filtered through a silica gel (200–300 mesh) plug with CS<sub>2</sub>/CH<sub>2</sub>Cl<sub>2</sub> (1:1 v/v) to remove the supporting electrolyte and insoluble materials, and then evaporated in vacuo to remove the solvent. The residue further was purified by semi-preparative HPLC on a Buckyprep column (10 × 250 mm, eluent: toluene, 5 mL/min flow rate, detection at 325 nm) to afford product 3c (13.3 mg, 43%) along with unreacted 1 (1.2 mg, 5%).

**Treatment of 3b under basic conditions.** Ketone 3b (6.0 mg, 6.0 μmol) and NaOH (4.8 mg, 0.12 mmol) were added in a 15-mL reaction vessel containing a magnetic stirring bar. Then, the solid mixture was thoroughly degassed through five freeze-pump-thaw cycles, and subsequently filled with argon or oxygen. Next, the degassed toluene (4.0 mL) and CH<sub>3</sub>CN (0.75 mL) were added into the vessel. The resulting mixture was stirred
vigorously at ambient temperature (25 °C) under argon or oxygen atmosphere. After the color of the solution turned to brown (argon: 21 h; oxygen: 5 h), the resulting solution was neutralized with 1N HCl and then evaporated in vacuo. Next, the residue was dissolved in toluene and filtrated to remove the insoluble salts. Finally, [60]fulleroindoline 1 and p-methoxybenzoic acid were monitored by HPLC and GC-MS analysis, respectively. Column chromatography of the residue on silica gel (CS₂/CH₂Cl₂ 4:1 v/v) provided 1 (2.1 mg, 41% under argon atmosphere; 3.7 mg, 71% under oxygen atmosphere).

**Attempted conversion of 3b to 3a under basic conditions.** Ketone 3b (10.3 mg, 10.0 μmol) and NaOH (8.0 mg, 0.05 mmol) were added in a 15-mL reaction vessel containing a magnetic stirring bar. Then, the solid mixture was thoroughly degassed through five freeze-pump-thaw cycles, and subsequently filled with argon. Next, the degassed anhydrous ODCB (4.0 mL) and CH₃CN (1.0 mL) were added into the vessel. The resulting mixture was stirred vigorously at ambient temperature (25 °C) under argon for 10 min. Later, benzoyl chloride (12.0 μL, 0.1 mmol) was added, the resulting mixture immediately turned into brownish from dark green. After 5 h, the solvent was directly removed under vacuum. Further separation was performed on a silica gel column (CS₂/CH₂Cl₂ 4:1 v/v), providing 1 (5.2 mg, 52%) along with recovered 3b (2.4 mg, 23%).

**Treatment of 3c under acidic conditions.** Ketone 3c (6.0 mg, 6.0 μmol) and trifluoroacetic acid (4.8 μL, 0.06 mmol) were added in a 15-mL reaction vessel containing a magnetic stirring bar. Then the solid mixture was thoroughly degassed by performing five freeze-pump-thaw cycles, and subsequently filled with argon. Next, the degassed toluene (4.0 mL) was added into the vessel. The resulting mixture was stirred vigorously at ambient temperature (25 °C) under argon atmosphere. After the reaction was over, the resulting solution was evaporated under reduce pressure. The residue was purified by flash column chromatography on silica gel (CS₂/CH₂Cl₂ 1:1 v/v), affording 1,2,3,4-adduct 4 (4.5 mg, 88%). ¹H NMR of compound 4 (400 MHz, CS₂/CDCl₃) δ 7.97 (d, J = 7.6 Hz, 1H), 7.41 (s, 1H), 7.27 (d, J = 7.6 Hz, 1H), 6.35 (d, J = 1.7 Hz, 1H), 6.32 (d, J = 1.7 Hz, 1H), 2.87 (s, 3H), 2.59 (s, 3H).
$^1$H NMR and $^{13}$C NMR spectra of compounds 3a–3g.
Expanded $^{13}$C NMR (100 MHz, CD$_2$Cl$_2$) of compound 3a

$^1$H NMR (400 MHz, TCE-d$_2$) of compound 3b
Expanded $^{13}$C NMR (100 MHz, TCE-d$_2$) of compound 3e
$^1$H NMR (400 MHz, CS$_2$/CDCl$_3$) of resulting mixture quenched by CD$_2$COOD

**Non-fullerene impurities**

$^1$H NMR (400 MHz, CS$_2$/CDCl$_3$) of compound 3a-H(D)

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UV-vis spectra of compounds 3a–3g.

UV-vis spectrum of compound 3a in CHCl₃

UV-vis spectrum of compound 3b in CHCl₃
UV-vis spectrum of compound 3e in CHCl₃

Absorption vs. Wavelength (nm)

- 252.0 nm
- 437.0 nm
- 318.5 nm
- 526.5 nm
- 704.5 nm
- 401.5 nm

UV-vis spectrum of compound 3f in CHCl₃

Absorption vs. Wavelength (nm)

- 251.0 nm
- 443.5 nm
- 318.0 nm
- 524.5 nm
- 699.5 nm
- 403.0 nm
UV-vis spectrum of compound 3g in CHCl₃

- 252.5 nm
- 319.0 nm
- 403.5 nm
- 440.0 nm
- 524.0 nm
- 729.5 nm

3g