

Supporting information

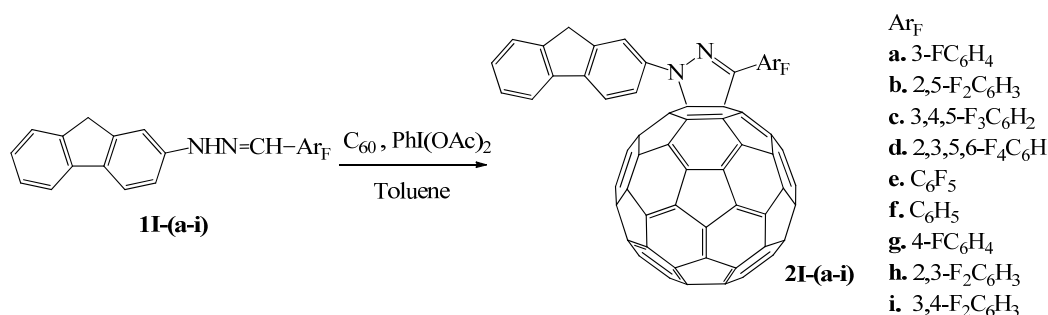
SYNTHESIS AND PHOTOPHYSICAL PROPERTIES OF NEW PYRAZOLINO[60]FULLERENES WITH FLUORENYL AND FLUORINATED PHENYL SUBSTITUENTS

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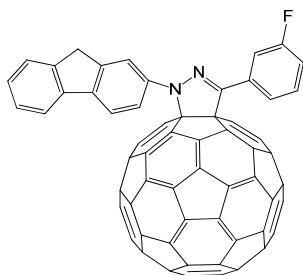
General description of the experimental techniques.

1. Synthesis of 2I-(a-i)



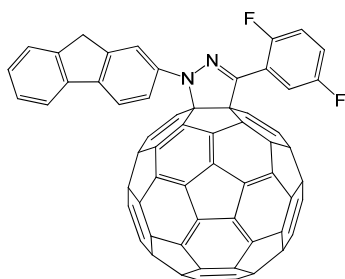
Typical procedure for the synthesis of pyrazolines: A mixture of C₆₀ (72 mg, 0.1 mmol), hydrazones **1I-(a-i)** (0.2 mmol) and PhI(OAc)₂ (64 mg, 0.2 mmol) were dissolved in 40 mL of toluene and stirred at 30 °C for 5h. The solvent was then evaporated in vacuum and the residue was separated on a silica gel column using CS₂ or CS₂-toluene as the eluent to afford unreacted C₆₀ and adduct **2I-(a-i)**.

1-(*N*-Fluorenyl)-3-(3'-fluorophenyl)pyrazolino[C₆₀]fullerene (2I-a).



Brown solid; IR (KBr, cm⁻¹): ν 3455, 2919, 2850, 1605, 1578, 1047, 574, 526; ¹H NMR (500 MHz, CS₂-CDCl₃): δ 8.32–8.29 (m, 2H), 8.06 (s, 1H), 7.95 (d, J = 8.0 Hz, 1H), 7.81 (d, J = 8.0 Hz, 1H), 7.74 (d, J = 7.5 Hz, 1H), 7.52 (d, J = 7.5 Hz, 1H), 7.36 (t, J = 7.5 Hz, 1H), 7.28 (t, J = 7.5 Hz, 1H), 7.21 (t, J = 8.5 Hz, 2H), 3.98 (s, 2H); ¹⁹F NMR (470 MHz, CS₂-CDCl₃): δ -109.02 (s, 1F); ¹³C NMR (125 MHz, CS₂-CDCl₃): δ 162.50 (d, J = 246.25 Hz), 147.23, 146.85, 146.03, 145.92, 145.64, 145.59, 145.53, 145.46, 145.43, 145.14, 144.90, 144.82, 144.80, 144.17, 143.94, 143.93, 143.08, 142.83, 142.81, 142.59, 142.53, 142.12, 142.06, 141.93, 141.84, 141.58, 141.41 (d, J = 2.5 Hz); 140.83, 139.99, 139.47, 139.06, 137.17, 136.21, 135.95, 134.45 (d, J = 8.75 Hz), 130.01 (d, J = 8.75 Hz), 128.74, 128.00, 126.76, 126.50, 125.11, 124.79, 123.93, 123.90, 122.97, 120.78, 120.03, 119.63, 115.82 (d, J = 21.25 Hz), 115.44 (d, J = 22.5 Hz), 92.30 (sp³ C of C₆₀), 80.83 (sp³ C of C₆₀), 37.05; MALDI-FTICR-MS: [M]⁺ Calculated for C₈₀H₁₃N₂F₁: 1020.1073; found 1020.10573.

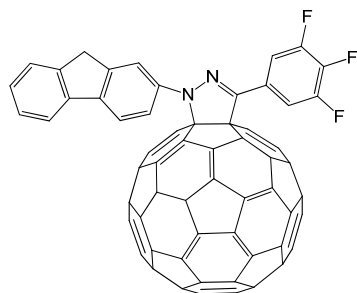
1-(*N*-Fluorenyl)-3-(2',5'-difluorophenyl)pyrazolino[C₆₀]fullerene (2I-b).



Brown solid; IR (KBr, cm⁻¹): ν 3474, 2918, 2847, 1611, 1512, 1495, 1049, 575, 526; ¹H NMR (500 MHz, CS₂-CDCl₃): δ 8.04 (s, 1H), 7.94 (d, J = 8.0 Hz, 1H), 7.81 (d, J = 8.5 Hz, 1H), 7.73 (d, J = 8.0 Hz, 1H), 7.64 - 7.60 (m, 1H), 7.52 (d, J = 8.0 Hz, 1H), 7.35 (t, J = 7.5 Hz, 1H), 7.27 (t, J = 7.5 Hz, 1H), 7.28–7.24 (m, 1H), 7.21–7.16 (m, 1H), 3.98 (s, 2H); ¹⁹F NMR (470 MHz, CS₂-CDCl₃): δ -114.98 to -115.05 (m, 1F), δ -115.97 to -116.03 (m, 1F); ¹³C NMR (125 MHz, CS₂-CDCl₃): 158.19 (d, J = 243.50 Hz), 157.06 (d, J = 246.63 Hz), 147.46, 147.02, 146.15, 146.05, 145.81, 145.73, 145.53, 145.45, 145.24, 145.21, 145.12, 145.04, 144.99, 144.58, 144.44, 144.31, 144.23, 144.17, 144.09, 143.99, 143.85, 143.52, 143.46, 143.07, 142.94, 142.67, 142.62, 142.53, 142.33, 142.18, 142.06, 141.94, 141.90, 141.78, 141.02, 140.87, 140.46, 139.57, 139.20, 138.59, 136.16, 136.12, 128.32, 127.18, 126.81, 126.54, 125.12 (d, J =

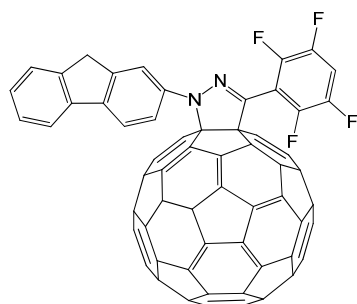
17.50 Hz), 124.19, 122.97, 120.97, 120.70, 120.20, 199.72, 199.10, 118.16-117.49 (m, 3C), 91.50 (sp³ C of C₆₀), 82.18 (sp³ C of C₆₀), 37.11; MALDI-FTICR-MS: [M+H]⁺ Calculated for C₈₀H₁₃N₂F₂: 1039.1084; found 1039.10413.

1-(*N*-Fluorenyl)-3-(3',4',5'-trifluorophenyl)pyrazolino[C₆₀]fullerene (2I-c).



Brown solid; IR (KBr, cm⁻¹): ν 3443, 2960, 2919, 2848, 1699, 1659, 1583, 1338, 1261, 1101, 1025, 849, 802, 526; ¹H NMR (500 MHz, CS₂-CDCl₃): δ 8.02 (s, 1H), 7.92 (d, *J* = 8.0 Hz, 1H), 7.71 (d, *J* = 7.5 Hz, 1H), 7.51 (d, *J* = 7.5 Hz, 1H), 7.79 (d, *J* = 8.5 Hz, 1H), 7.72 (d, *J* = 7.5 Hz, 1H), 7.52 (d, *J* = 7.5 Hz, 1H), 7.34 (t, *J* = 8.0 Hz, 1H), 7.27 (t, *J* = 7.5 Hz, 1H), 7.15-7.09 (m, 2H), 3.98 (s, 2H); ¹⁹F NMR (470 MHz, CS₂-CDCl₃): δ -128.87 to -129.16 (m, 2F), -155.76 (t, *J* = 18.8 Hz, 1F); ¹³C NMR (125 MHz, CS₂-CDCl₃): δ 151.59 (ddd, *J* = 2.5, 10.0, 253.75 Hz), 150.23 (ddd, *J* = 3.75, 11.25, 251.25 Hz, 2C), 147.25, 146.84, 145.98, 145.87, 145.64, 145.58, 145.54, 145.33, 145.10, 145.07, 144.93, 144.86, 144.79, 144.19, 143.88, 143.81, 143.13, 142.79, 142.52, 142.48, 142.02, 141.99, 141.95, 141.87, 141.73, 141.60, 140.79, 140.28, 139.43, 139.07, 137.07 (d, *J* = 13.75 Hz), 136.02, 135.94, 128.73, 127.99, 126.75, 126.51, 125.10, 124.78, 122.70, 120.48, 120.06, 119.63, 117.50 (d, *J* = 2.5 Hz), 111.93 (dd, *J* = 3.75, 17.5 Hz, 2C), 91.33 (sp³ C of C₆₀), 81.90 (sp³ C of C₆₀), 37.03; MALDI-FTICR-MS: [M+H]⁺ Calculated for C₈₀H₁₂N₂F₃: 1057.0922; found 1057.09452.

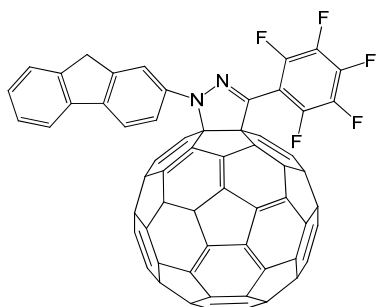
1-(*N*-Fluorenyl)-3-(2',3',5',6'-tetrafluorophenyl)pyrazolino[C₆₀]fullerene (2I-d).



Brown solid; IR (KBr, cm⁻¹): ν 3441, 2919, 2849, 1609, 1509, 1477, 11453, 1025, 1101, 574, 525; ¹H NMR (500 MHz, CS₂-CDCl₃): δ 8.02 (s, 1H), 7.93 (d, *J* = 8.5 Hz, 1H), 7.83 (d, *J* = 8.0 Hz, 1H), 7.74 (d, *J* = 7.5 Hz, 1H), 7.53 (d, *J* = 7.5 Hz, 1H), 7.36 (t, *J* = 7.5 Hz, 1H), 7.30-7.24 (m, 2H), 3.99 (s, 2H); ¹⁹F

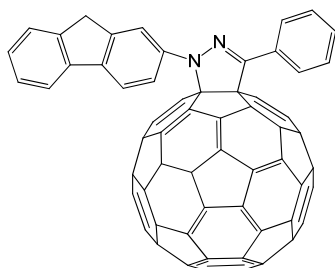
NMR (470 MHz, CS₂-CDCl₃): δ -131.42 to -131.49 (m, 2F), -135.96 to -136.04 (m, 2F); ¹³C NMR (125 MHz, CS₂-CDCl₃): 147.40, 146.94, 146.02, 145.97, 145.73, 145.70, 145.60, 145.39, 145.18, 144.91, 144.85, 144.55, 144.33, 143.99, 143.85, 143.53, 142.96, 142.94, 142.85, 142.56, 142.51, 142.07, 142.02, 141.76, 141.68, 140.81, 140.55, 139.47, 136.20, 135.99, 132.98, 126.79, 126.62, 124.85, 122.99, 120.16, 119.72, 107.58 (t, J = 22.50 Hz), 91.42 (sp³ C of C₆₀), 81.93 (sp³ C of C₆₀), 37.06; MALDI-FTICR-MS: [M]⁺ Calculated for C₈₀H₁₀N₂F₄: 1074.0782; found 1074.07746.

1-(*N*-Fluorenyl)-3-perfluorophenylpyrazoline[C₆₀]fullerene (2I-e).



Brown solid; IR (KBr, cm⁻¹): ν 3440, 2963, 2919, 2851, 1608, 1582, 1509, 1261, 1097, 802, 573, 525; ¹H NMR (500 MHz, CS₂-CDCl₃): δ 8.00 (s, 1H), 7.92 (d, J = 8.0 Hz, 1H), 7.83 (d, J = 8.0 Hz, 1H), 7.74 (d, J = 7.5 Hz, 1H), 7.53 (d, J = 7.5 Hz, 1H), 7.36 (t, J = 7.5 Hz, 1H), 7.28 (t, J = 7.5 Hz, 1H), 3.99 (s, 2H); ¹⁹F NMR (470 MHz, CS₂-CDCl₃): δ -135.11 (dd, J = 7.05, 23.5 Hz, 2F), -149.09 (t, J = 21.15 Hz, 1F), -158.88 to -158.98 (m, 2F); ¹³C NMR (125 MHz, CS₂-CDCl₃): δ 147.40, 146.94, 146.03, 145.97, 145.74, 145.70, 145.60, 145.34, 145.19, 144.92, 144.80, 144.63, 144.43, 144.32, 143.97, 143.84, 143.36, 142.91, 142.86, 142.77, 142.57, 142.52, 142.05, 141.99, 141.76, 141.69, 140.74, 140.58, 139.57, 139.50, 136.15, 136.01, 128.78, 128.03, 126.81, 126.67, 125.13, 124.84, 122.98, 120.77, 120.17, 119.73, 91.45 (sp³ C of C₆₀), 81.79 (sp³ C of C₆₀), 37.05; MALDI-FTICR-MS: [M]⁺ Calculated for C₈₀H₉N₂F₅: 1092.0707; found 1093.06804.

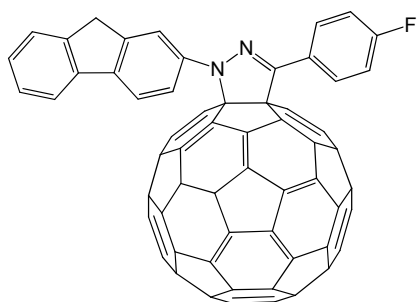
1-(*N*-Fluorenyl)-3-phenylpyrazoline[C₆₀]fullerene (2I-f).



Brown solid; IR (KBr, cm⁻¹): ν 3449, 2919, 2852, 1636, 1486, 1453, 573, 526; ¹H NMR (500 MHz, CS₂-CDCl₃): δ 8.41 (s, 1H), 8.28 (d, J = 8.0 Hz, 1H), 7.85 (d, J = 8.0 Hz, 1H), 7.81 (d, J = 8.5 Hz, 1H), 7.78 (d, J = 8.0 Hz, 1H), 7.69 (d, J = 11.0 Hz, 1H), 7.55 (d, J = 7.5 Hz, 1H), 7.41-7.31 (m, 4H), 6.88 (dt,

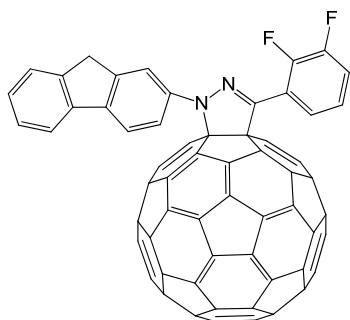
$J = 2.5, 8.5$ Hz, 1H), 4.016 (s, 2H); ^{13}C NMR (125 MHz, $\text{CS}_2\text{-CDCl}_3$): δ 147.37, 146.98, 146.15, 146.03, 145.83, 145.77, 145.71, 145.64, 145.61, 145.23, 145.21, 145.03, 145.01, 144.96, 144.35, 144.10, 144.06, 143.69, 143.60, 143.02, 142.95, 142.92, 142.69, 142.63, 142.25, 142.19, 142.11, 142.08, 141.96, 141.69, 141.06, 140.09, 139.57, 138.98, 136.25, 136.08, 132.29, 130.42, 129.20, 128.73, 128.67, 128.09, 126.79, 126.46, 125.18, 124.88, 124.83, 123.09, 120.82, 120.12, 119.67, 92.23 (sp^3 C of C_{60}), 81.46 (sp^3 C of C_{60}), 37.11; MALDI-FTICR-MS: $[\text{M}]^+$ Calculated for $\text{C}_{80}\text{H}_{14}\text{N}_2$: 1002.1135; found 1002.11515.

1-(*N*-Fluorenyl)-3-(4'-fluorophenyl)pyrazolino[C_{60}]fullerene (2I-g).



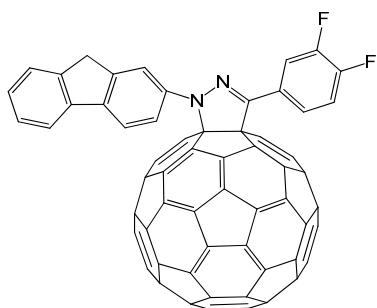
Brown solid; IR (KBr, cm^{-1}): ν 3446, 2954, 2918, 2849, 1699, 1598, 1022, 573, 525; ^1H NMR (500 MHz, $\text{CS}_2\text{-CDCl}_3$): δ 8.34 (d, $J = 5.5$ Hz, 1H), 8.32 (d, $J = 5.0$ Hz, 1H), 8.05 (s, 1H), 7.94 (d, $J = 8.0$ Hz, 1H), 7.79 (d, $J = 8.5$ Hz, 1H), 7.72 (d, $J = 7.5$ Hz, 1H), 7.52 (d, $J = 7.5$ Hz, 1H), 7.35 (t, $J = 7.5$ Hz, 1H), 7.35 (t, $J = 7.5$ Hz, 1H), 7.28 (t, $J = 3.0$ Hz, 1H), 7.21 (t, $J = 8.0$ Hz, 1H), 3.99 (s, 2H); ^{19}F NMR (470 MHz, $\text{CS}_2\text{-CDCl}_3$): δ -108.45 (t, $J = 7.05$ Hz, 1F); ^{13}C NMR (125 MHz, $\text{CS}_2\text{-CDCl}_3$): δ 163.32 (d, $J = 250.0$ Hz), 147.63, 147.24, 146.43, 146.30, 146.18, 146.04, 145.98, 145.93, 145.87, 145.83, 145.50, 145.47, 145.30, 145.22, 144.53, 144.34, 143.79, 143.24, 143.17, 142.98, 142.93, 142.49, 142.47, 142.41, 142.36, 142.33, 142.24, 141.96, 141.27, 140.40, 139.85, 139.31, 136.58, 136.30, 130.82 (d, $J = 7.25$ Hz, 2C), 128.79 (d, $J = 2.75$ Hz, 2C), 127.15, 126.86, 125.17, 123.31, 121.07, 120.41, 120.00, 116.08, 115.91, 92.50 (sp^3 C of C_{60}), 81.54 (sp^3 C of C_{60}), 37.45; MALDI-FTICR-MS: $[\text{M}]^+$ Calculated for $\text{C}_{80}\text{H}_{13}\text{N}_2\text{F}_1$: 1020.1023; found 1020.10573.

1-(*N*-Fluorenyl)-3-(2',3'-difluorophenyl)pyrazolino[C_{60}]fullerene (2I-h).



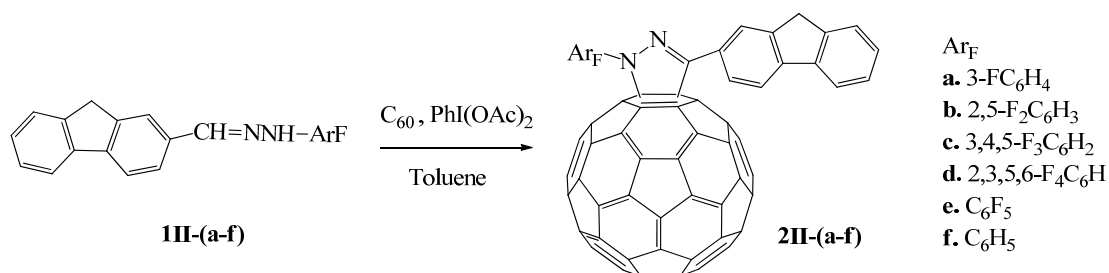
Brown solid; IR (KBr, cm^{-1}): ν 3459, 2917, 2846, 1612, 1471, 1454, 1044, 574, 526; ^1H NMR (500 MHz, $\text{CS}_2\text{-CDCl}_3$): δ 8.05 (s, 1H), 7.94 (d, $J = 8.0$ Hz, 1H), 7.81 (d, $J = 8.5$ Hz, 1H), 7.72 (d, $J = 7.5$ Hz, 1H), 7.73–7.69 (m, 1H), 7.52 (d, $J = 7.0$ Hz, 1H), 7.36–7.31 (m, 2H), 7.30–7.24 (m, 2H), 3.98 (s, 2H); ^{19}F NMR (470 MHz, $\text{CS}_2\text{-CDCl}_3$): δ -133.96 (d, $J = 12.2$ Hz, 1F), -134.43 (d, $J = 21.6$ Hz, 2F); ^{13}C NMR (125 MHz, $\text{CS}_2\text{-CDCl}_3$): δ 150.84 (dd, $J = 11.25, 248.75$ Hz); 149.13 (dd, $J = 12.5, 251.25$ Hz), 147.26, 146.85, 145.99, 145.89, 145.65, 145.59, 145.55, 145.39, 144.34, 145.10, 145.07, 144.87, 144.83, 144.22, 144.07, 143.92, 143.83, 143.32, 142.84, 142.79, 142.52, 142.48, 142.04, 141.99, 141.92, 141.76, 141.61, 140.86, 140.26, 139.42, 139.00, 137.80, 136.01, 135.99, 126.74, 126.47, 125.82, 125.79, 124.79, 123.91 (t, $J = 5.0$ Hz), 122.74, 122.01 (d, $J = 11.25$ Hz), 120.52, 120.06, 119.62, 118.21 (d, $J = 16.25$ Hz), 91.32 (sp^3 C of C_{60}), 82.09 (sp^3 C of C_{60}), 37.05; MALDI-FTICR-MS: $[\text{M}]^+$ Calculated for $\text{C}_{80}\text{H}_{12}\text{N}_2\text{F}_2$: 1038.0960; found 1038.09613.

1-(*N*-Fluorenyl)-3-(3',4'-difluorophenyl)pyrazolino[C_{60}]fullerene (2I-i).



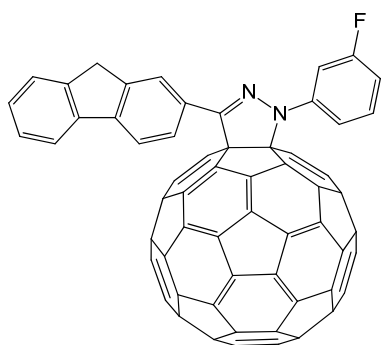
Brown solid; IR (KBr, cm^{-1}): ν 3451, 2919, 1605, 1557, 1512, 1046, 574, 526; ^1H NMR (500 MHz, $\text{CS}_2\text{-CDCl}_3$): δ 8.17 (dd, $J = 2.5, 11.5$ Hz, 1H), 8.12–8.10 (m, 1H), 8.04 (s, 1H), 7.94 (d, $J = 8.0$ Hz, 1H), 7.81 (d, $J = 8.0$ Hz, 1H), 7.73 (d, $J = 7.5$ Hz, 1H), 7.53 (d, $J = 7.5$ Hz, 1H), 7.36 (t, $J = 7.5$ Hz, 1H), 7.30 (t, $J = 10.0$ Hz, 1H), 7.32 - 7.26 (m, 1H), 3.98 (s, 2H); ^{19}F NMR (470 MHz, $\text{CS}_2\text{-CDCl}_3$): δ -134.45 (d, $J = 20.0$ Hz, 1F), -134.74 (d, $J = 18.8$ Hz, 1F); ^{13}C NMR (125 MHz, $\text{CS}_2\text{-CDCl}_3$): δ 150.59 (dd, $J = 15.0, 254.25$ Hz); 150.18 (dd, $J = 25.0, 261.25$ Hz), 147.30, 146.92, 146.10, 145.98, 145.72, 145.66, 145.59, 145.44, 145.42, 145.31, 145.21, 144.98, 144.88, 144.86, 144.79, 144.25, 144.00, 143.97, 143.03, 142.90, 142.87, 142.82, 142.65, 142.60, 142.14, 142.11, 141.95, 141.90, 141.63, 140.83, 140.76, 140.10, 139.55, 139.22, 137.26, 136.34, 135.94, 129.48 (dd, $J = 3.75, 6.25$ Hz), 128.79, 128.04, 126.81, 126.59, 125.14, 124.84, 124.54 (dd, $J = 3.75, 6.25$ Hz), 123.08, 120.86, 120.10, 119.69, 117.63 (d, $J = 18.75$ Hz), 92.38 (sp^3 C of C_{60}), 80.71 (sp^3 C of C_{60}), 37.57; MALDI-FTICR-MS: $[\text{M}+\text{H}]^+$ Calculated for $\text{C}_{80}\text{H}_{13}\text{N}_2\text{F}_2$: 1039.1084; found 1039.10413.

2. Synthesis of 2II-(a-f)



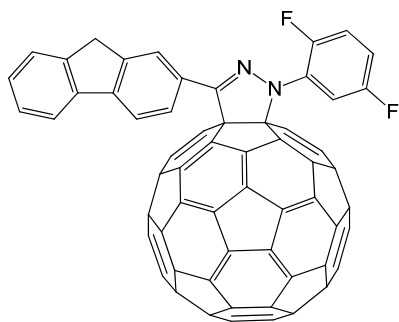
Typical procedure for the synthesis of fulleropyrazolines: A mixture of C₆₀ (72 mg, 0.1 mmol), hydrazones **1III-(a-f)** (0.2 mmol), and PhI(OAc)₂ (64 mg, 0.2 mmol) was dissolved in 40 mL of toluene and stirred at 40 °C for 5 h. The solvent was then evaporated in vacuum and the residue was separated on a silica gel column using CS₂ or CS₂-toluene as the eluent to afford unreacted C₆₀ and adduct **2II-(a-f)**.

1-(*N*-3'-Fluorophenyl)-3-fluorenylpyrazolino[C₆₀]fullerene (**2II-a**).



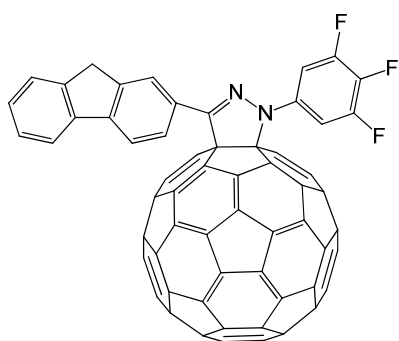
Brown solid; IR (KBr, cm⁻¹): ν 3453, 2921, 2851, 1605, 1578, 1047, 573, 525; ¹H NMR (500 MHz, CS₂-CDCl₃): δ 8.41 (s, 1H), 8.28 (d, J = 7.5 Hz, 1H), 7.86 (d, J = 8.0 Hz, 1H), 7.80 (d, J = 8.0 Hz, 1H), 7.78 (d, J = 7.5 Hz, 1H), 7.70 (td, J = 2.0, 10.5 Hz, 1H), 7.55 (d, J = 7.5 Hz, 1H), 7.41–7.37 (m, 2H), 7.33 (t, J = 7.0 Hz, 1H), 7.70 (dt, J = 2.0, 8.0 Hz, 1H), 4.01 (s, 2H); ¹⁹F NMR(470 MHz, CS₂-CDCl₃): δ -109.06 to -109.11(m, 1F); ¹³C NMR (125 MHz, CS₂-CDCl₃): δ 163.06 (d, J = 246.25 Hz), 147.31, 146.89, 146.18, 146.11, 146.01, 145.73, 145.69, 145.65, 145.49, 145.13, 144.95, 144.93, 144.74, 144.48, 144.05, 143.97, 143.42, 143.38, 142.93, 142.90, 142.84, 142.66, 142.61, 142.18 (d, J = 1.25 Hz), 142.01, 141.95, 141.92, 141.63, 140.65, 140.06, 139.40, 137.29, 136.27, 136.06, 130.21, 129.95 (d, J = 8.25 Hz), 128.79, 128.04, 127.52, 127.33, 126.88, 125.67, 125.14, 124.97, 120.22, 119.86, 117.96 (d, J = 2.5 Hz), 110.88 (d, J = 21.25 Hz), 109.79 (d, J = 23.75 Hz), 91.24 (sp³ C of C₆₀), 81.87 (sp³ C of C₆₀), 37.04; MALDI-FTICR-MS: [M+H]⁺ Calculated for C₈₀H₁₄N₂F: 1021.1156; found 1021.11355.

1-(*N*-2',5'-Difluorophenyl)-3-fluorenylpyrazolino[C₆₀]fullerene (2II-b).



Brown solid; IR (KBr, cm⁻¹): ν 3443, 2920, 2851, 1727, 1615, 1500, 1048, 574, 525; ¹H NMR (500 MHz, CS₂-CDCl₃): δ 8.36 (s, 1H), 8.24 (d, J = 8.0 Hz, 1H), 7.82 (d, J = 8.0 Hz, 1H), 7.74 (d, J = 7.5 Hz, 1H), 7.56–7.53 (m, 1H), 7.51 (d, J = 7.0 Hz, 1H), 7.34 (t, J = 7.5 Hz, 1H), 7.28 (t, J = 7.5 Hz, 1H), 7.18–7.14 (m, 1H), 7.03–6.98 (m, 1H), 3.96 (s, 2H); ¹⁹F NMR (470 MHz, CS₂-CDCl₃): δ -114.92 to -114.97 (m, 1F), -119.38 to -119.44 (m 1F); ¹³C NMR (125 MHz, CS₂-CDCl₃): δ 158.34 (d, J = 245 Hz), 154.50 (d, J = 245 Hz), 147.31, 146.91, 146.58, 146.09, 145.96, 145.86, 145.69, 145.66, 145.57, 145.40, 145.21, 144.95, 144.94, 144.87, 144.54, 144.53, 144.02, 143.93, 143.45, 143.42, 143.10, 142.85, 142.82, 142.58, 142.56, 142.12, 142.09, 142.01, 141.97, 141.95, 141.54, 140.65, 139.99, 139.50, 136.21, 135.78, 133.63 (dd, J = 8.75, 13.75 Hz), 130.89, 130.06, 129.07, 127.47, 127.35, 126.87, 125.66, 124.97, 120.25, 119.88, 117.33 (dd, J = 10.0, 22.5 Hz), 115.90 (d, J = 25.0 Hz), 114.82 (dd, J = 7.5, 23.75 Hz), 92.06 (sp³ C of C₆₀), 81.06 (sp³ C of C₆₀), 37.02; MALDI-FTICR-MS: [M]⁺ Calculated for C₈₀H₁₂N₂F₂: 1038.0959; found 1038.09631.

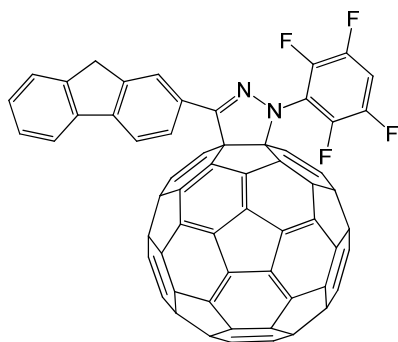
1-(*N*-3',4',5'-Trifluorophenyl)-3-fluorenylpyrazolino[C₆₀]fullerene (2II-c).



Brown solid; IR (KBr, cm⁻¹): ν 3444, 2919, 2849, 1728, 1634, 1600, 1500, 1042, 574, 526; ¹H NMR (500 MHz, CS₂-CDCl₃): δ 8.36 (s, 1H), 7.99 (d, J = 7.5 Hz, 2H), 7.85 (d, J = 8.0 Hz, 1H), 7.78 (d, J = 7.5 Hz, 1H), 7.37 (d, J = 7.5 Hz, 1H), 7.32 (t, J = 7.0 Hz, 1H), 6.88 (t, J = 8.0 Hz, 1H), 4.00 (s, 2H); ¹⁹F NMR (470 MHz, CS₂-CDCl₃): δ -104.14 (t, J = 7.5 Hz, 1F), -109.76 (t, J = 7.0 Hz, 2F), ¹³C NMR (125 MHz, CS₂-CDCl₃): δ 161.89 (dd, J = 13.75, 250.00 Hz), 161.23 (ddd, J = 3.75, 13.75, 262.50 Hz, 2C), 147.32, 146.95, 146.07, 145.95, 145.67, 145.56, 145.40, 145.38, 145.24, 144.97, 144.87, 144.16, 144.01, 143.96,

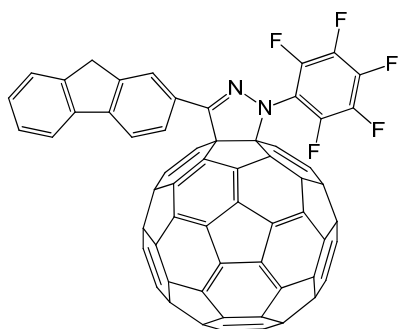
143.46, 143.43, 143.01, 142.84, 142.58, 142.54, 142.11, 142.07, 142.04, 141.97, 141.55, 140.71, 139.99, 139.82, 136.34, 135.84, 132.97, 131.36, 130.86, 130.09, 129.06, 128.82, 128.05, 127.40, 127.30, 126.85, 125.59, 124.97, 120.23, 119.88, 114.88, 101.09 (d, $J = 53.75$ Hz), 91.76 (sp^3 C of C_{60}), 80.75 (sp^3 C of C_{60}), 37.00; MALDI-FTICR-MS: $[\text{M}+\text{H}]^+$ Calculated for $\text{C}_{80}\text{H}_{12}\text{N}_2\text{F}_3$: 1057.0922; found 1057.09471.

1-(*N*-2',3',5',6'-Tetrafluorophenyl)-3-fluorenylpyrazolino[C_{60}]fullerene (2II-d).



Brown solid; IR (KBr, cm^{-1}): ν 3444, 2920, 2850, 1639, 1503, 1473, 1049, 574, 527; ^1H NMR (500 MHz, $\text{CS}_2\text{-CDCl}_3$): δ 8.36 (s, 1H), 8.25 (d, $J = 8$ Hz, 1H), 7.87 (d, $J = 7.5$ Hz, 1H), 7.79 (d, $J = 7.5$ Hz, 1H), 7.57 (d, $J = 7.5$ Hz, 1H), 7.39 (t, $J = 7.0$ Hz, 1H), 7.33 (t, $J = 7.0$ Hz, 1H), 7.22–7.19 (m, 1H), 4.00 (s, 2H); ^{19}F NMR (470 MHz, $\text{CS}_2\text{-CDCl}_3$): δ -136.51 to -136.60 (m, 2F), -141.47 to -141.60 (m, 2F); ^{13}C NMR (125 MHz, $\text{CS}_2\text{-CDCl}_3$): δ 147.54, 147.47, 147.08, 146.20, 146.08, 145.96, 145.81, 145.76, 145.44, 145.37, 145.10, 145.02, 144.48, 144.09, 144.06, 143.67, 143.59, 143.42, 142.94, 142.70, 142.67, 142.21, 142.17, 142.12, 142.10, 141.67, 140.72, 140.17, 139.96, 137.57, 136.40, 136.06, 129.77, 128.90, 128.12, 127.50, 127.44, 126.92, 125.74, 125.20, 125.07, 120.34, 120.02, 105.85 (t, $J = 21.25$ Hz), 91.67 (sp^3 C of C_{60}), 81.03 (sp^3 C of C_{60}), 37.05; MALDI-FTICR-MS: $[\text{M}+\text{H}]^+$ Calculated for $\text{C}_{80}\text{H}_{11}\text{N}_2\text{F}_4$: 1075.0863; found 1075.08529.

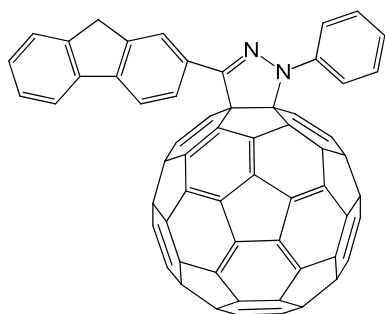
1-(*N*-Perfluorophenyl)-3-fluorenylpyrazolino[C_{60}]fullerene (2II-e).



Brown solid; IR (KBr, cm^{-1}): ν 3485, 2920, 2847, 1516, 1506, 1048, 574, 527; ^1H NMR (500 MHz, $\text{CS}_2\text{-CDCl}_3$): δ 8.43 (s, 1H), 8.23 (d, $J = 8$ Hz, 1H), 7.85 (d, $J = 8.0$ Hz, 1H), 7.77 (d, $J = 7.0$ Hz, 1H), 7.54 (d, $J = 7.5$ Hz, 1H), 7.37 (t, $J = 7.5$ Hz, 1H), 7.32 (t, $J = 7.5$ Hz, 1H), 4.00 (s, 2H); ^{19}F NMR (470

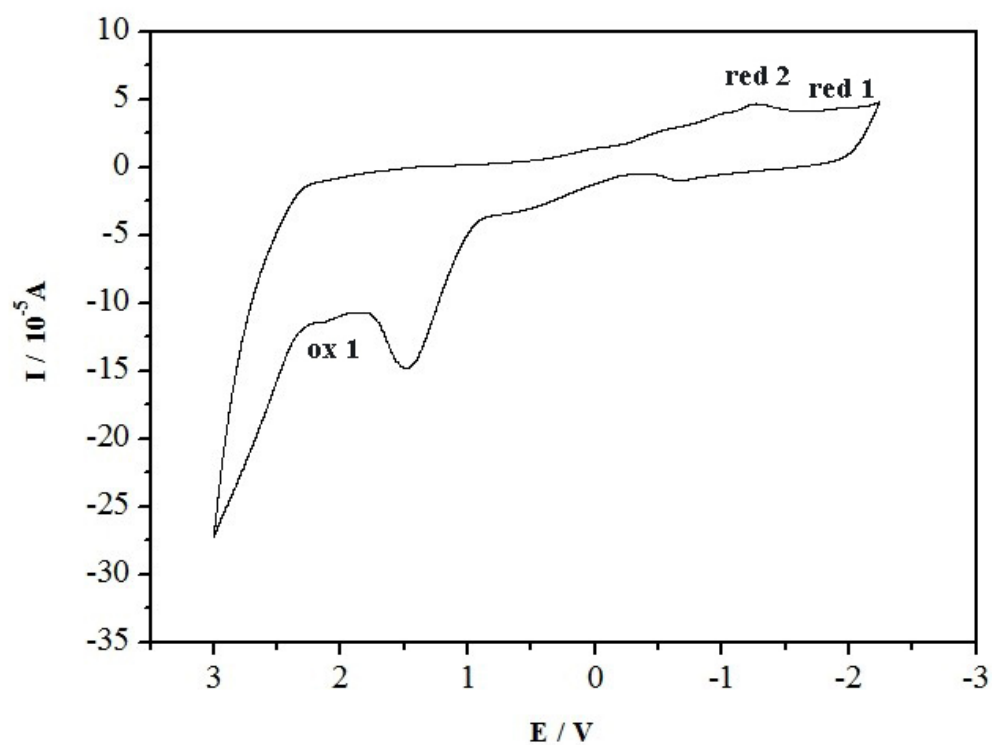
MHz, CS₂-CDCl₃): δ -140.86 (d, J = 22.6 Hz, 2F), -164.52 (t, J = 22.1 Hz, 1F), -159.64 (t, J = 22.0 Hz, 2F), ¹³C NMR (125MHz, CS₂-CDCl₃): δ 147.26, 147.08, 146.87, 146.02, 145.89, 145.74, 145.62, 145.51, 145.21, 145.19, 144.89, 144.83, 144.14, 143.89, 143.86, 143.71, 143.38, 143.31, 143.29, 142.77, 142.54, 142.50, 142.03, 141.94, 141.87, 141.47, 140.50, 139.97, 139.85, 137.21, 137.18, 136.15, 135.91, 129.83, 129.54, 128.74, 128.00, 127.42, 126.86, 125.56, 125.10, 124.93, 120.24, 119.86, 199.27(dt, J = 3.75, 13.75 Hz), 91.43 (sp³ C of C₆₀), 80.76 (sp³ C of C₆₀), 36.97; MALDI-FTICR-MS: [M+H]⁺ Calculated for C₈₀H₁₀N₂F₅: 1093.0767; found 1093.07586.

1-(*N*-Phenyl)-3-fluorenylpyrazolino[C₆₀]fullerene (2II-f).

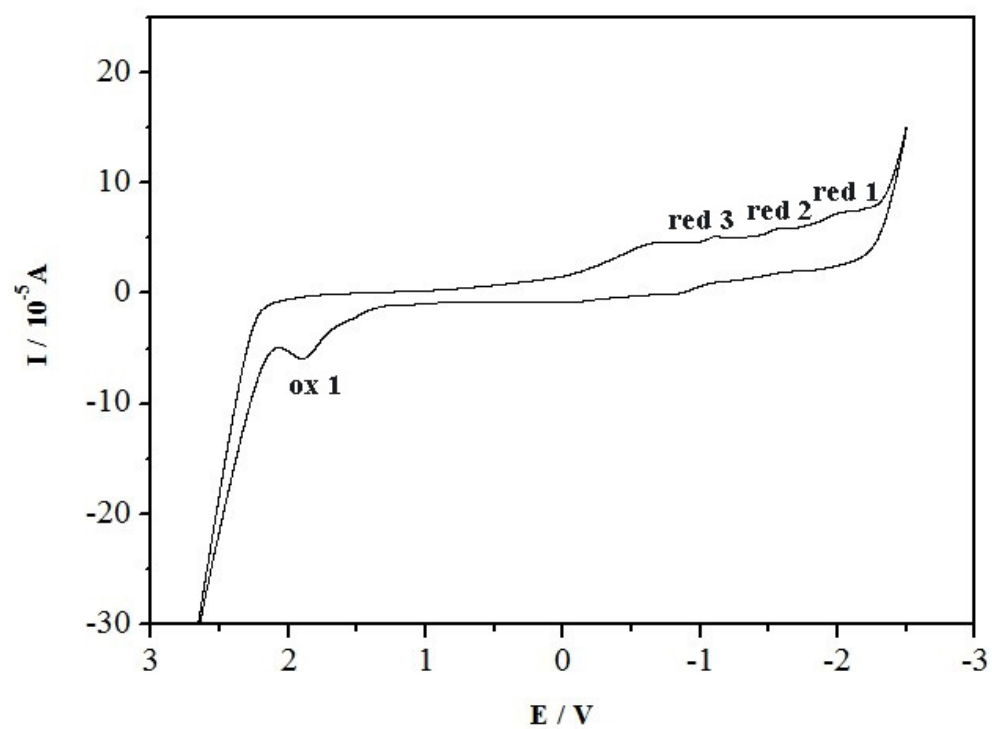


Brown solid; IR (KBr, cm⁻¹): ν 3442, 2920, 2851, 1592, 1490, 1027, 577, 525; ¹H NMR (500 MHz, CS₂-CDCl₃): δ 8.43 (s, 1H), 8.30 (d, J = 8.0 Hz, 1H), 7.94 (d, J = 7.5 Hz, 1H), 7.84 (d, J = 8.0 Hz, 1H), 7.77 (d, J = 7.5 Hz, 1H), 7.54 (d, J = 7.5 Hz, 1H), 7.45 (t, J = 8.0 Hz, 1H), 7.37 (t, J = 7.5 Hz, 1H), 7.32 (t, J = 7.0 Hz, 1H), 7.13–7.09 (m, 1H), 4.00 (s, 2H); ¹³C NMR (125 MHz, CS₂-CDCl₃): δ 147.34, 146.93, 146.26, 146.13, 146.01, 145.84, 145.74, 145.68, 145.62, 145.59, 145.20, 145.17, 144.99, 144.98, 144.93, 144.74, 144.07, 144.04, 143.85, 143.46, 142.92, 142.89, 142.74, 142.67, 142.62, 142.22, 142.18, 142.10, 142.05, 141.96, 141.65, 140.78, 140.06, 139.49, 137.41, 136.18, 136.11, 132.94, 130.59, 129.10, 128.84, 128.07, 127.45, 127.25, 126.86, 125.62, 125.16, 124.99, 124.88, 123.59, 120.21, 119.87, 144.98, 91.81 (sp³ C of C₆₀), 81.67 (sp³ C of C₆₀), 37.05; MALDI-FTICR-MS: [M]⁺ Calculated for C₈₀H₁₄N₂: 1002.1128; found 1002.11515.

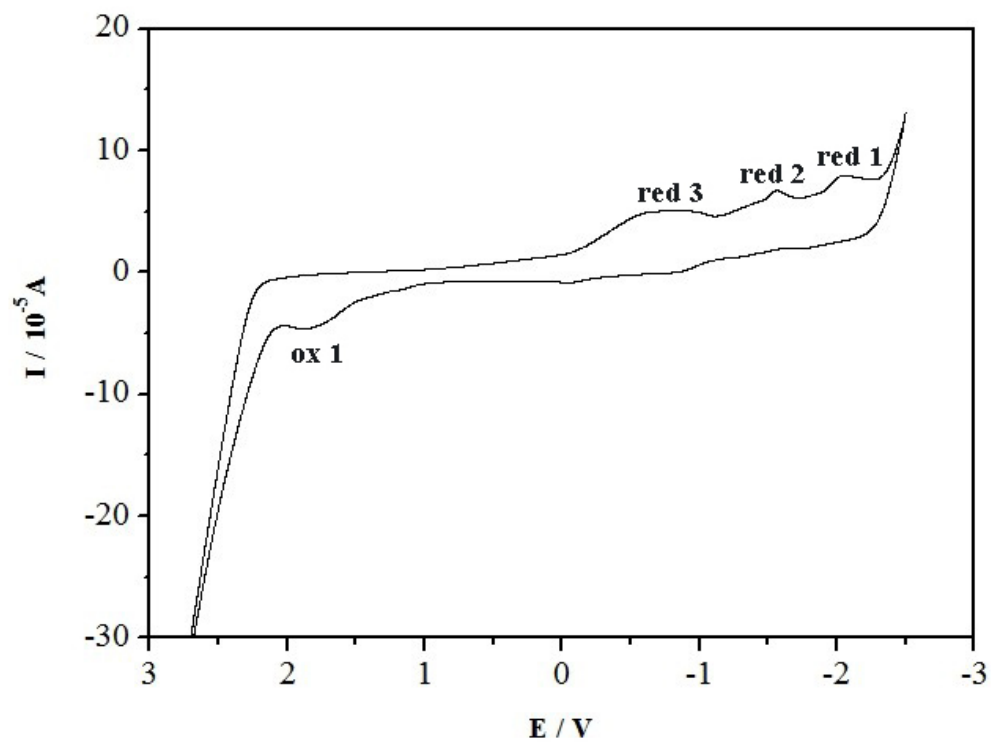
1-(N-fluorenyl)-3-(3'-fluorophenyl)pyrazolino[C60]fullerene (2I-a).



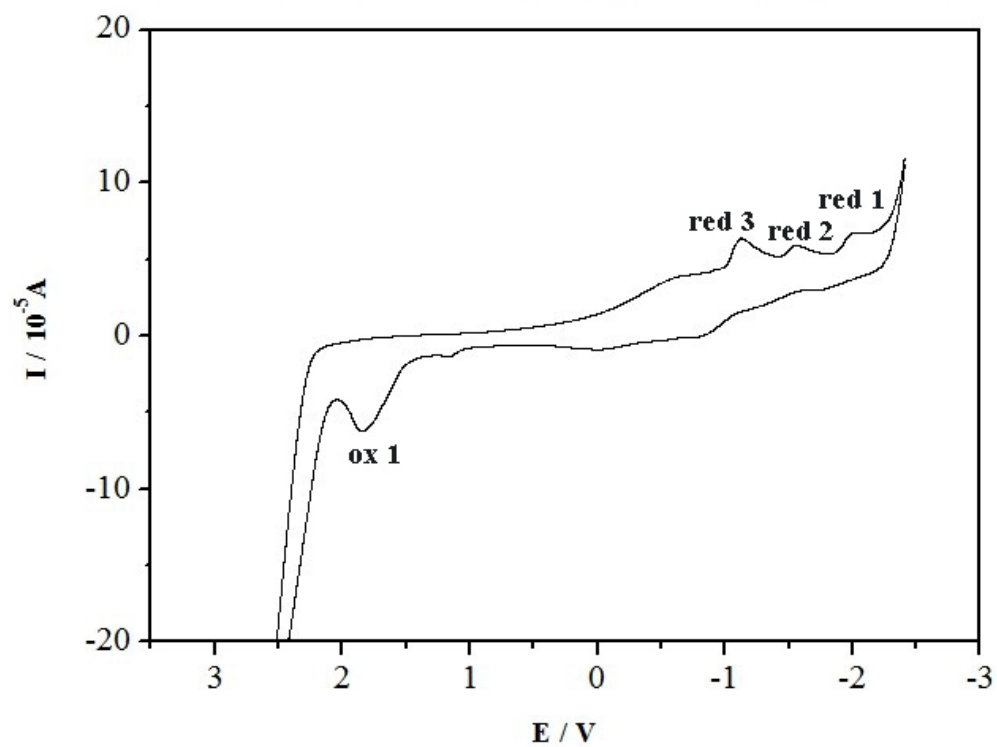
1-(N-fluorenyl)-3-(2',3',5',6'-tetrafluorophenyl)pyrazolino[C60]fullerene (2I-d).



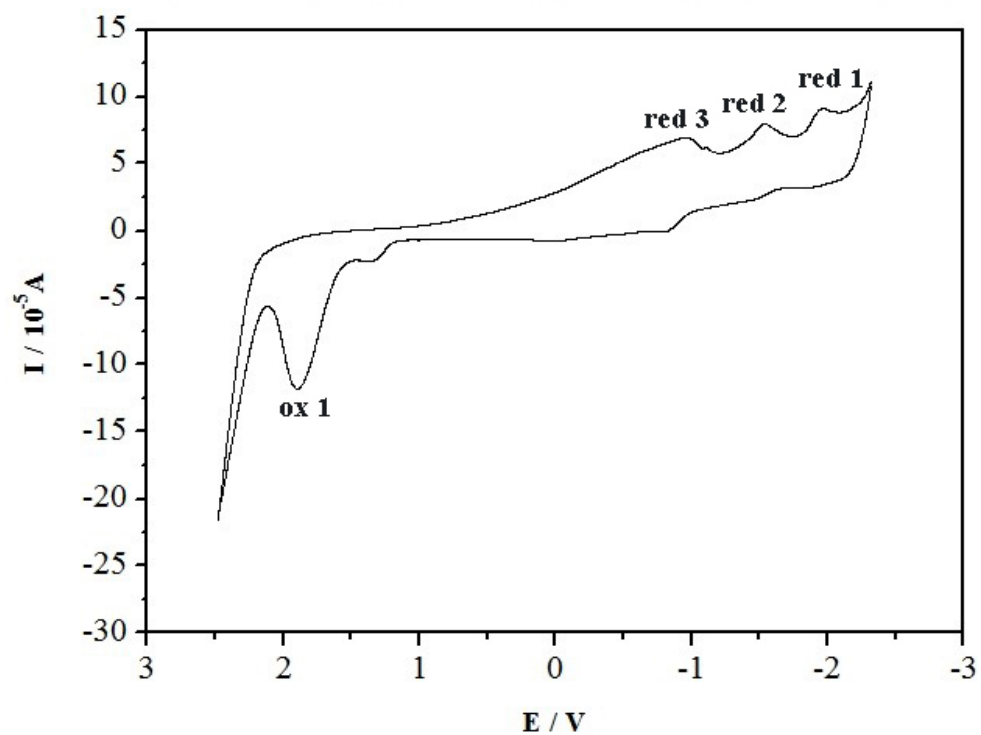
1-(N-fluorenyl)-3-(2',3'-difluorophenyl)pyrazolino[C60]fullerene (2I-h).



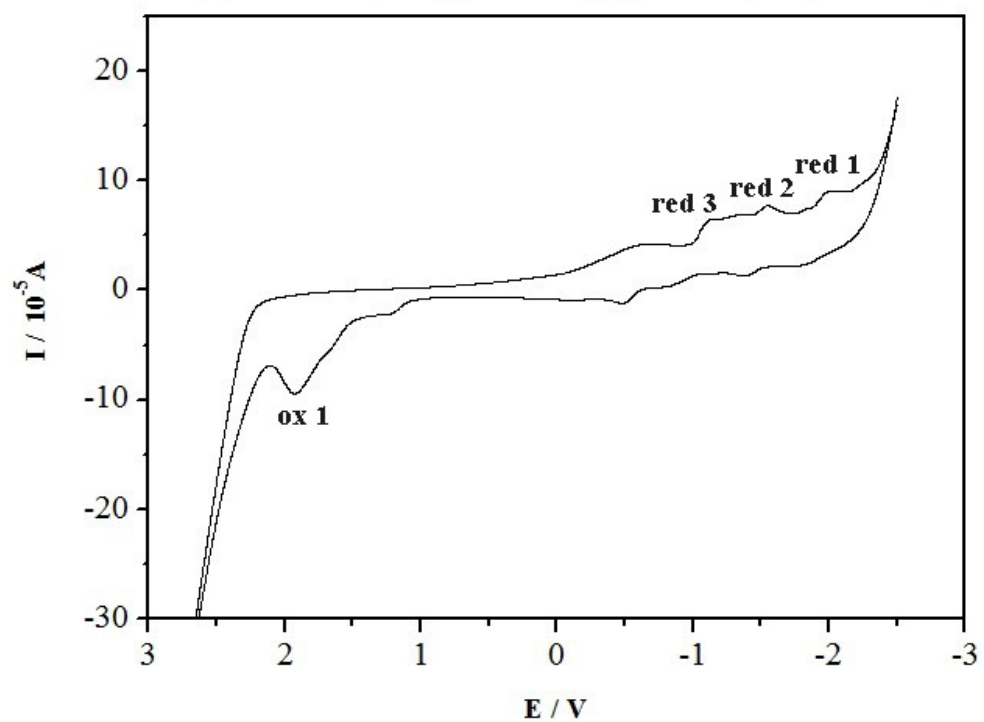
1-(N-fluorenyl)-3-(3',4'-difluorophenyl)pyrazolino[C60]fullerene (2I-i).



1-(N-3'-fluorophenyl)-3-fluorenylpyrazolino[C60]fullerene (2II-a).



1-(N-3',4',5'-trifluorophenyl)-3-fluorenylpyrazolino[C60]fullerene (2II-c).



1-(N-2',3',5',6'-tetrafluorophenyl)-3-fluorenylpyrazolino[C60]fullerene (2II-d).

