Electronic Supplementary Material (ESI) for Nanoscale.

Supporting Information

Diazonium Functionalized Fullerenes: A New Class of Efficient Molecular Catalysts for the Hydrogen Evolution Reaction

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Experimental Section

General procedures

All chemicals were reagent grade, purchased from Sigma Aldrich. Silica gel (Redisep silica, 40-60 μ, 60 Å) was used to separate the products. MALDI-TOF mass spectrometric measurements were obtained on a Bruker Microflex LRF mass spectrometer on reflector positive mode. The UV/Vis-NIR spectra were taken using a Cary 5000 UV/Vis-NIR spectrophotometer using toluene or chloroform solutions. The NMR spectra were recorded using a JEOL 600 MHz spectrometer. FTIR spectra were recorded in solid state in a Bruker Tensor 27 in transmittance mode.

Electrochemical measurements

The HER performances of the diazonium fullerene derivatives as well as fulleropyrrolidine derivatives and pure C_{60}, C_{70} and $Sc_3N@I_hC_{80}$, were performed on an electrochemical workstation (CHI 660D) with a three-electrode system. Glassy carbon, Ag/AgCl (3 M KCl) and graphite rod electrodes were used as the working, reference and counter electrodes, respectively, for the HER reactions. 0.5 M H_2SO_4 was used as electrolyte for the HER reaction. To create the working electrode, 1 mg of the catalysts were dispersed in 1 mL of toluene and, subsequently, 10 μL of ink were deposited on the surface of the glassy carbon electrode. Linear sweep voltammetry (LSV) was carried out in 0.5 M H_2SO_4 solutions at 2 mV s^{-1} for HER reaction. The electrochemical impedance spectroscopy (EIS) were performed at -0.7 V vs RHE from 10^{-1} to 10^5 Hz.

General synthesis of fulleropyrrolidine amine derivatives

In a round bottom flask, the fullerene, pulverized 4-aminobenzaldehyde and sarcosine were added and dissolved in *o*-dichlorobenzene (*o*-DCB). The reaction was left to stir under reflux for 30-40 min. After this time, the mixture was chromatographed using silica gel with the following eluents: carbon disulfide, carbon disulfide/chloroform (1:1) and hexanes/chloroform (1:2).

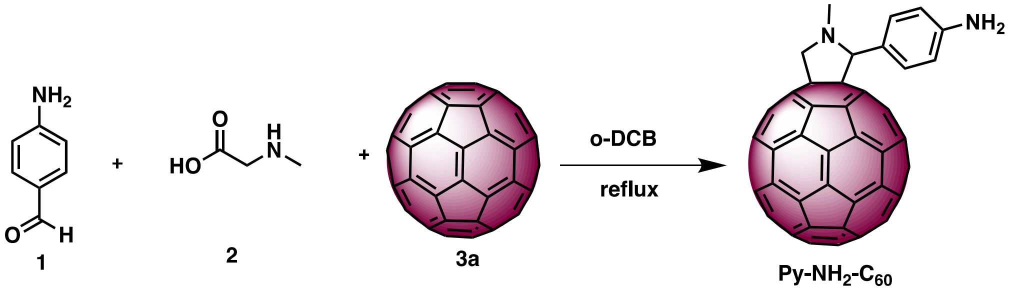
General synthesis of fulleropyrrolidine diazonium derivatives

In a round bottom flask, the obtained fulleropyrrolidine derivatives and HBF_4 48 wt % in H_2O were added and dissolved in acetic acid/carbon disulfide (2:1). Isoamyl nitrite (21 μL, 0.14 mmol) was added dropwise and the reaction left at room temperature for 30 min. After this time, diethyl ether was added, and the reaction was left to stir at about -20 °C for 16 h. Finally, sample was washed with cooled ether.

General synthesis of fulleropyrrolidine derivatives

In a round bottom flask, the fullerene, paraformaldehyde and sarcosine were added and dissolved in *o*-dichlorobenzene (*o*-DCB). The reaction was left to stir under reflux for 30-50 min. After this time, the mixture was chromatographed using silica gel with toluene.

Synthesis of 4-aminobenzyl C_{60} derivative (Py-NH_2-C_{60})



In a round bottom flask, C_{60} (**3a**)(72.1 mg, 0.100 mmol), pulverized 4-aminobenzaldehyde (**1**) (24.8 mg, 0.201 mmol) and sarcosine (**2**) (18.6 mg, 0.204 mmol) were added and dissolved in *o*-dichlorobenzene (o-DCB) after sonication. The reaction was left to stir under reflux for 40 min. After this time, the mixture was chromatographed using silica gel with the following eluents: carbon disulfide, carbon disulfide/chloroform (1:1) and hexanes/chloroform (1:2). **Py-NH_2-C_{60}** was obtained as a brown solid with 55% of isolated yield. Figures S1-S2 illustrate the characterization of **Py-NH_2-C_{60}. ^{1}H-NMR (600 MHz, $CDCl_3$) δ:** 7.57 (m, 2H), 6.71 (d, *J* = 8.4 Hz, 2H), 4.95 (d, *J* = 9.0 Hz, 1H), 4.82 (s, 1H), 4.21 (d, *J* = 9.0 Hz, 1H), 3.80 – 3.65 (m, 2H), 2.78 (s, *J* = 16.8 Hz, 3H). **^{13}C-NMR (150 MHz, $CDCl_3$) δ:** 192.8, 156.7, 154.4, 154.1, 146.0, 142.5, 140.4, 140.2, 139.8, 136.8, 136.0, 135.9, 130.6, 130.6, 115.4, 115.4, 83.7, 70.2, 40.2, 30.2. **MALDI-TOF HRMS** (m/z) calc for [M^-] =868.85; found: 867.57. **IR (cm^{-1}):** 3483-3388, 2956, 2922, 2853, 2782, 1713, 1629, 1594, 1523, 1442, 1298, 1284, 1236, 1169, 1132, 829, 769.

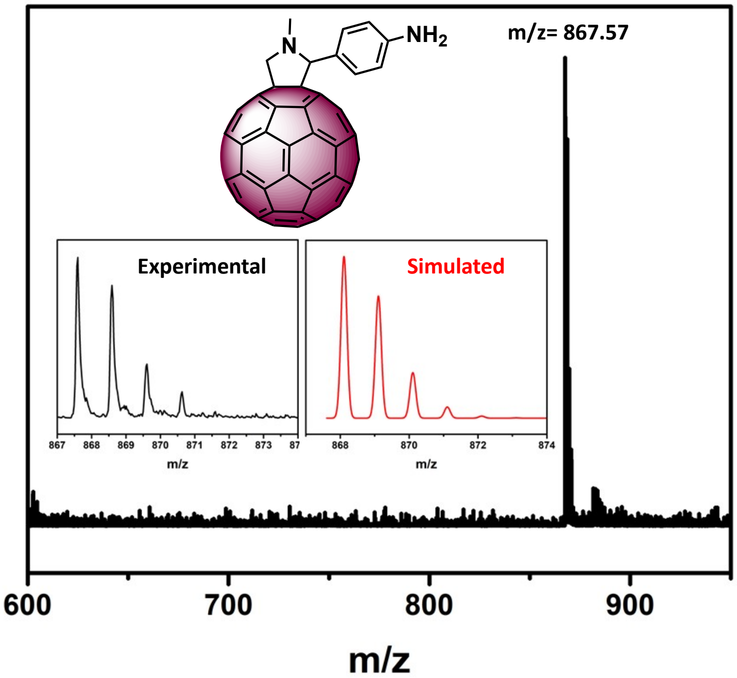


Figure S1. MALDI-TOF mass spectrum of Py-NH_2-C_{60}

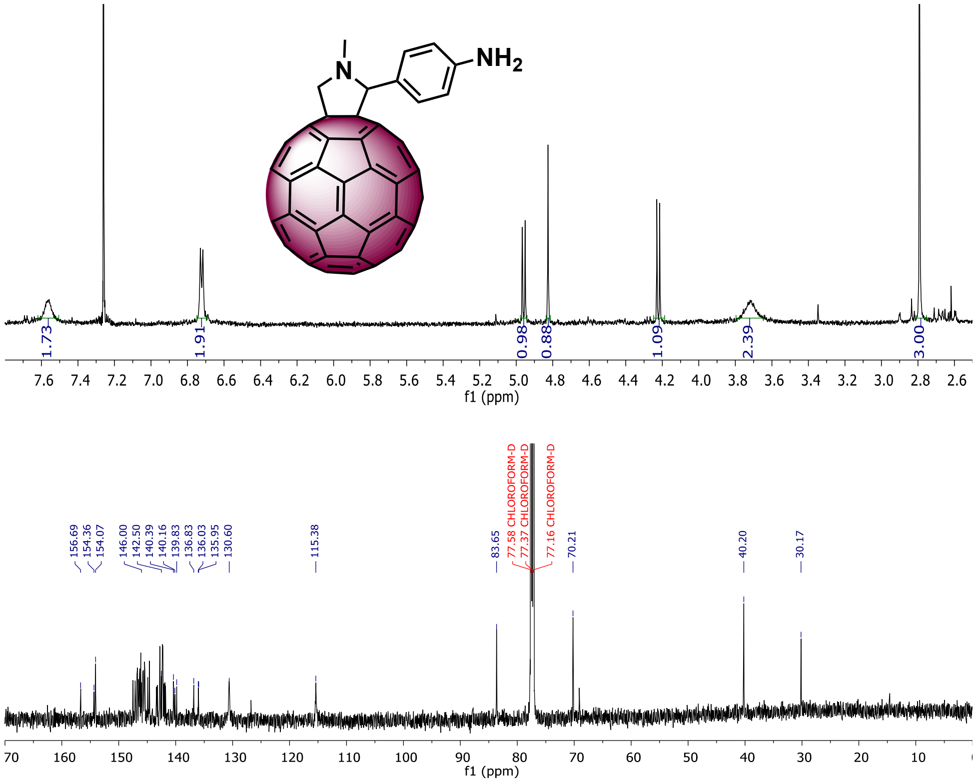
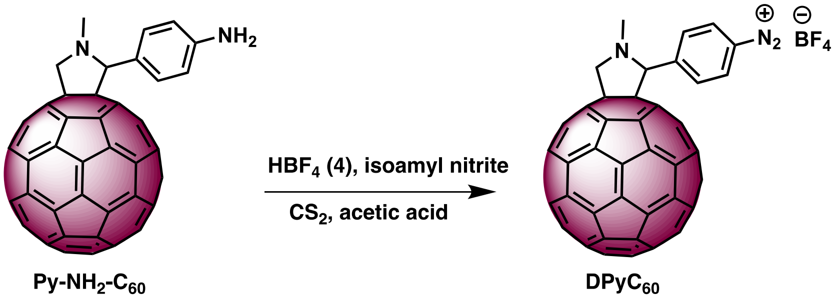


Figure S2. ^{1}H-NMR (600 MHz) and ^{13}C-NMR (150 MHz) spectra of Py-NH_2-C_{60} in $CDCl_3$.

Synthesis of diazonium salt fulleropyrrolidine C_{60} derivative ($DPyC_{60}$).



In a round bottom flask, **Py-NH$_2$-C$_{60}$** (17.6 mg, 20.2 μmol) and HBF_4 48 wt % in H_2O (**4**) (20 μL, 0.30 mmol) were added and dissolved in acetic acid/carbon disulfide (2:1) after sonication. Isoamyl nitrite (21 μL, 0.14 mmol) was added dropwise and left the reaction at room temperature for 30 min. After this time, diethyl ether was added, and the reaction was left to stir at about -20 °C for 16 h. Finally, sample was washed with cooled ether. The pure **DPyC$_{60}$** was obtained as a brown solid with 86% of yield and was characterized by FT-IR as shown in Figure S3. **IR (cm^{-1}):** 3653-3397, 3108, 2934, 2843, 2778, 2285, 1720, 1688, 1587, 1584, 1520, 1465, 1424, 1312, 1288, 1047, 846, 754.

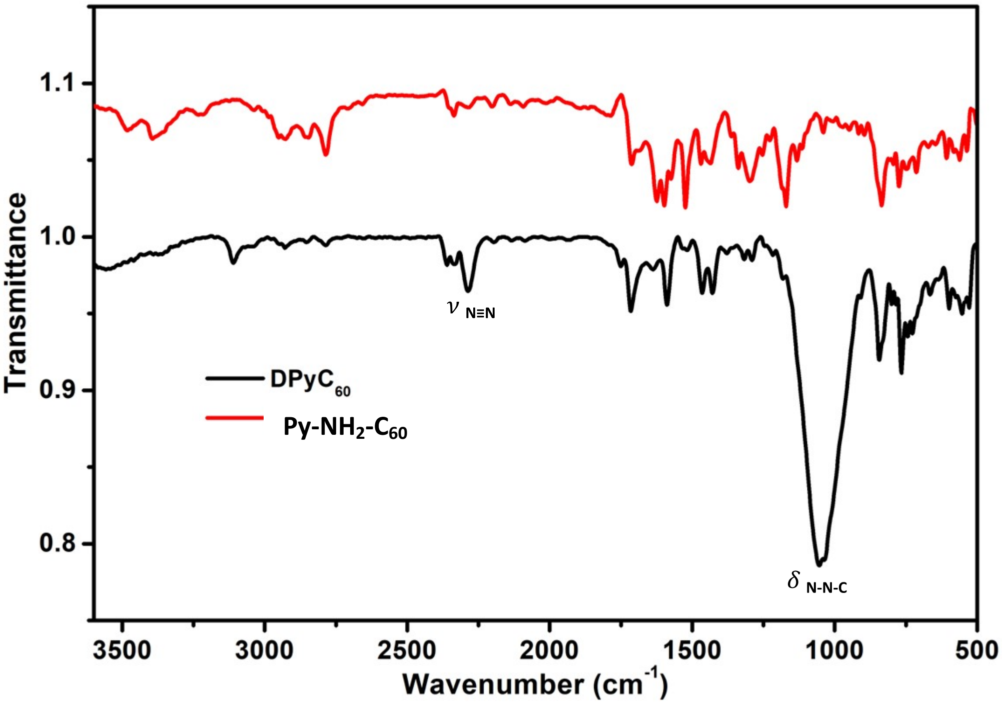
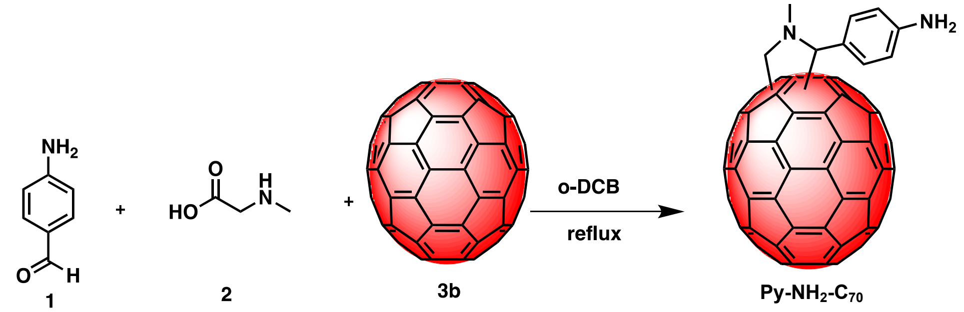


Figure S3. ATR-FT-IR spectra of Py-NH$_2$-C$_{60}$ and DPyC$_{60}$.

Synthesis of 4-aminobenzyl C$_{70}$ derivative (Py-NH$_2$-C$_{70}$)



In a round bottom flask, C$_{70}$ (**3b**) (83.5 mg, 0.0993 mmol), pulverized **1** (24.6 mg, 0.200 mmol) and **2** (20.0 mg, 0.220 mmol) were added and dissolved in *o*-DCB after sonication. The reaction was left to stir under reflux for 50 min. After this time, the mixture was chromatographed using silica gel with the following eluents: carbon disulfide and carbon disulfide/chloroform (1:1). **Py-NH$_2$-C$_{70}$** was obtained as a mixture of isomers in the form of a brown solid with 74% of isolated yield. Figures S4-S5 illustrate the characterization of **Py-NH$_2$-C$_{70}$.** **^{1}H-NMR (600 MHz, CDCl$_3$) δ**: 7.60 – 7.55 (m, 2H), 7.10 – 6.99 (m, 2H), 6.87 (dd, *J* = 14.5, 9.8 Hz, 2H), 6.65 (s, 2H), 6.52 (d, *J* = 26.4 Hz, 2H), 6.45 (d, *J* = 5.2 Hz, 2H), 4.68 – 4.62 (m, 2H), 4.30 – 4.14 (m, 4H), 4.07 (d, *J* = 14.9 Hz, 2H), 3.87 (s, *J* = 11.5 Hz, 1H), 3.70 (s, 2H), 3.50 – 3.45 (m, 1H), 3.40 – 3.34 (m, 1H), 3.19 – 3.15 (m, 1H), 3.06 (d, *J* = 5.3 Hz, 1H), 2.51 (s, 3H), 2.43 (s, 3H), 2.34 (s, 3H). **^{13}C-NMR (150 MHz, CDCl$_3$) δ**: 167.8, 151.7, 151.5, 151.4, 150.8, 150.6, 150.4, 149.9, 149.4, 149.3, 149.2, 148.3, 147.4, 147.1, 146.9, 146.7, 146.3, 145.8, 145.3, 144.7, 143.6, 142.9, 140.3, 138.0, 137.7, 134.0, 133.7, 133.1, 132.5, 132.2, 131.7, 131.4, 131.0, 129.6, 129.1, 128.9, 128.3, 126.9, 125.4, 80.2, 77.3, 77.1, 76.9, 68.3, 38.8, 30.4, 29.8, 29.0, 23.8, 23.1, 14.1, 11.1. **MALDI-TOF HRMS** (m/z) calc for [M$^-$]: 988.95; found: 987.44. **IR (cm^{-1}):** 3471-3380, 2926, 2852, 2773, 1739, 1613, 1513, 1452, 1425, 1269, 1208, 1164, 1084, 1028, 936, 830, 797, 741, 667.

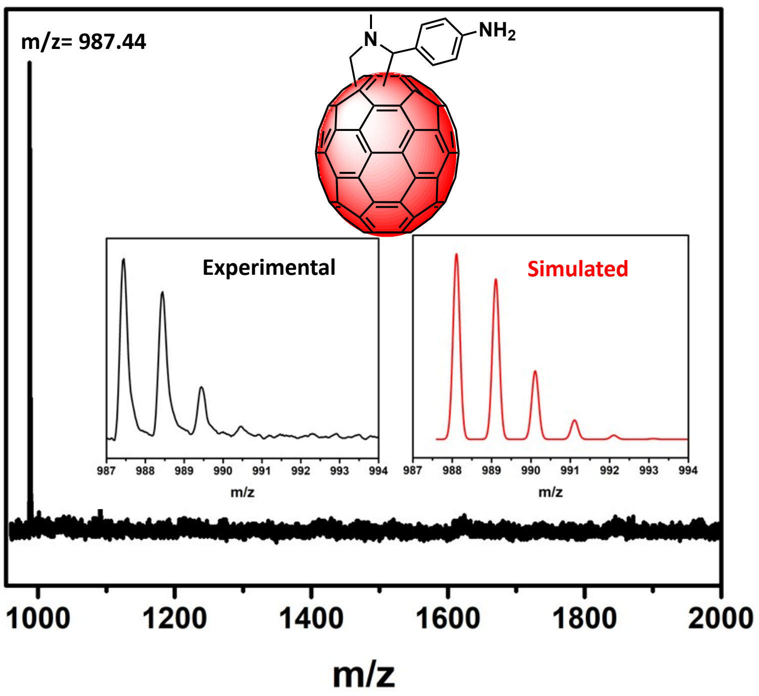


Figure S4. MALDI-TOF mass spectrum of Py-NH_2-C_{70}.

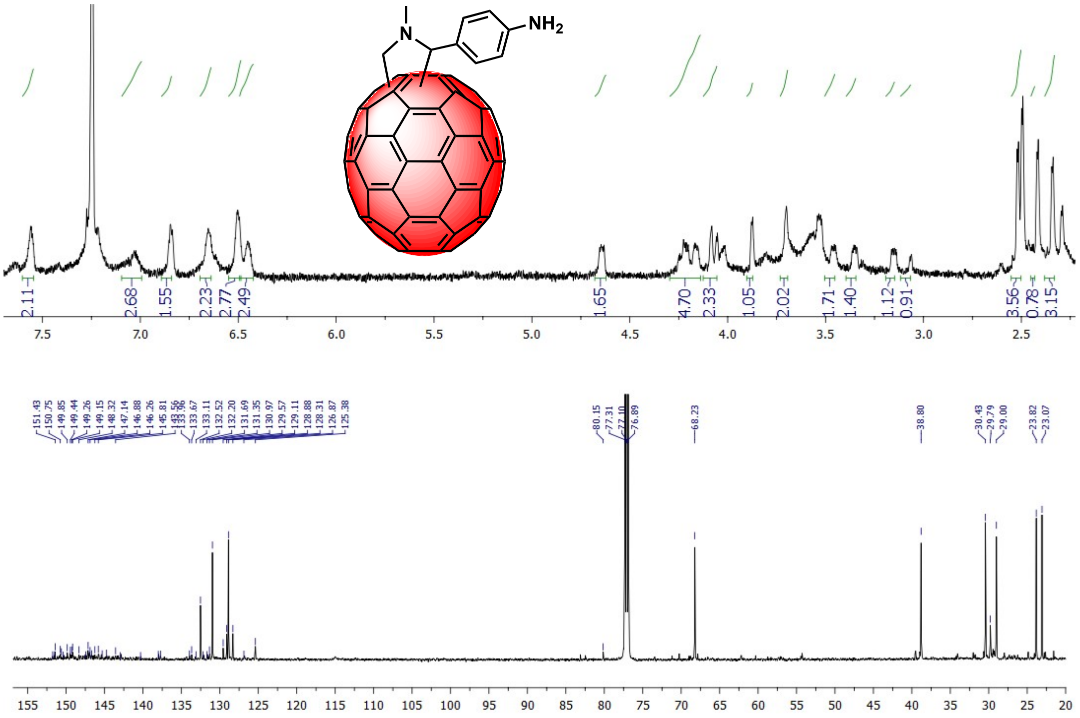
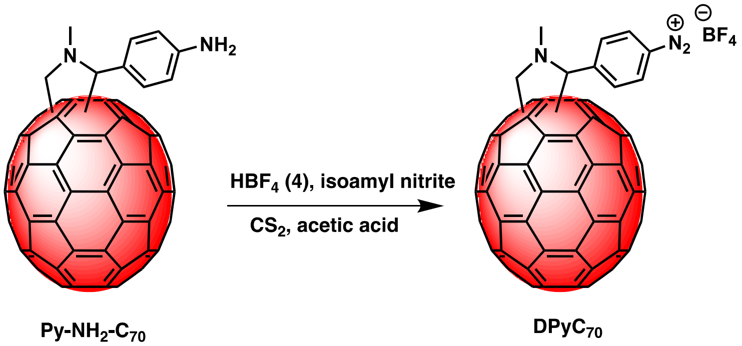


Figure S5. ^{1}H-NMR (400 MHz) and ^{13}C-NMR (150 MHz) spectra of Py-NH_2-C_{70} in $CDCl_3$.

Synthesis of diazonium salt fulleropyrrolidine C_{70} derivative (DPyC_{70}).



In a round bottom flask, **Py-NH_2-C_{70}** (14.6 mg, 14.9 µmol) and **4** (14 µL, 0.21 mmol) were added and dissolved in acetic acid/carbon disulfide (2:1) after sonication. Isoamyl nitrite (21 µL, 0.14 mmol) was added dropwise and left the reaction at room temperature for 50 min. After this time, diethyl ether was added, and the reaction was left to stir at about -20 °C for 20 h. Finally, sample was washed with cooled ether. The pure **DPyC_{70}** was obtained as a brown solid with 37% of yield and was characterized by FT-IR technique as shown in Figure S6. **IR (cm^{-1}):** 3681-3410, 3099, 2931, 2781, 2355, 2334, 2276, 1737, 1697, 1628, 1588, 1431, 1424, 1327, 1019, 829, 799, 673.

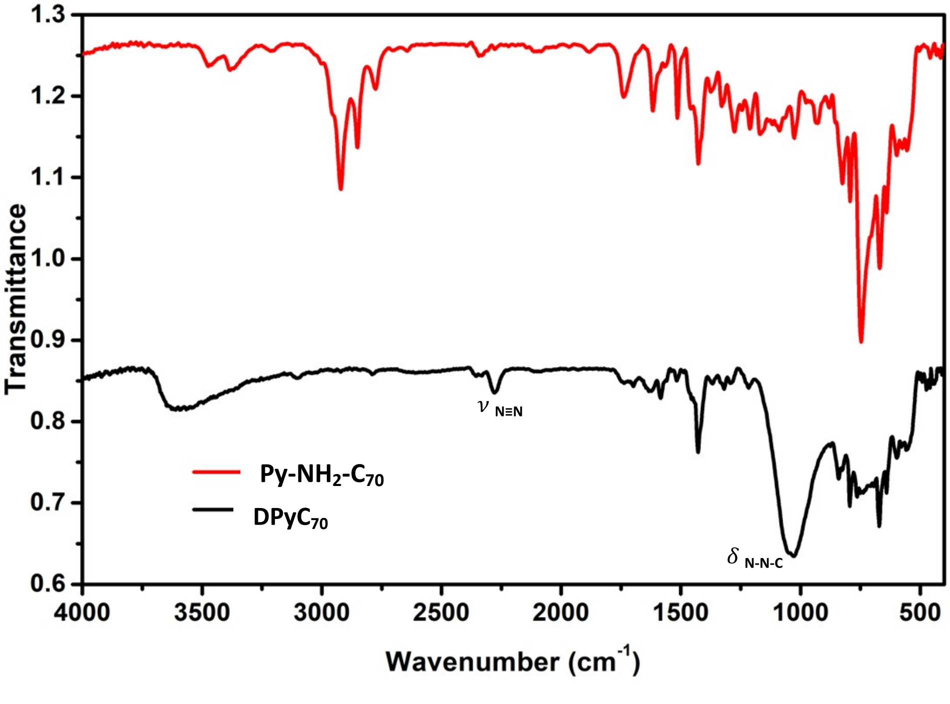
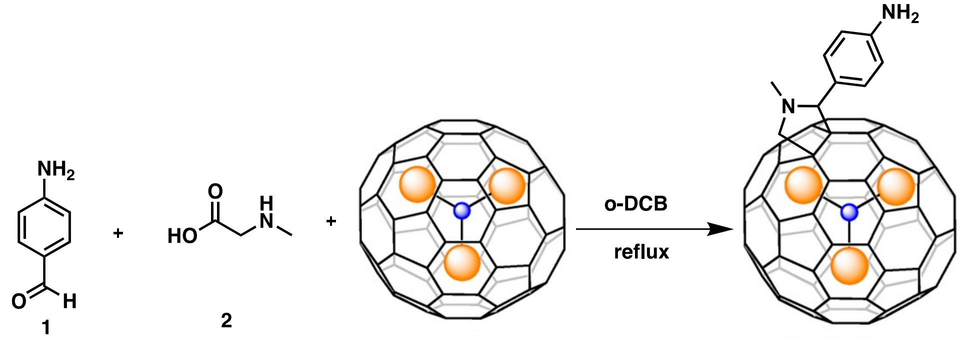


Figure S6. ATR-FT-IR spectra of Py-NH_2-C_{70} and DPyC_{70}.

Synthesis of 4-aminobenzyl $Sc_3N@I_hC_{80}$ derivative (Py-NH_2-$Sc_3N@I_hC_{80}$).



In a round bottom flask, $Sc_3N@I_hC_{80}$ (**3c**) (3 mg, 0.0027 mmol), pulverized 4-aminobenzaldehyde (**1**) (1.7 mg, 0.0135 mmol) and sarcosine (**2**) (1.3 mg, 0.0135 mmol) were added and dissolved in *o*-dichlorobenzene (*o*-DCB) after sonication. The reaction was left to stir under reflux for 40 min. After this time, the mixture was chromatographed using silica gel with the following eluents: carbon disulfide, carbon disulfide/chloroform (1:1) and hexanes/chloroform (1:2). **Py-NH_2-$Sc_3N@I_hC_{80}$** was obtained as a brown solid with 55% of isolated yield. Figure S7 illustrates the characterization of **Py-NH_2-$Sc_3N@I_hC_{80}$.** **^{1}H-NMR (600 MHz, $CDCl_3$) δ**: 7.79 (d, *J* = 8.8 Hz, 1H), 7.68 (d, *J* = 8.2 Hz, 1H), 7.16 (d, *J* = 7.5 Hz, 1H), 6.69 (d, *J* = 7.9 Hz, 1H), 5.14 (s, 2H), 5.10 (s, 1H), 3.64 (s, 2H), 3.34 (s, 3H), 2.34 (s, 2H). **IR (cm^{-1}):** 3483-3391, 2952, 2876, 2890, 1733, 1621, 1518, 1477, 1452, 1349, 1222, 776.

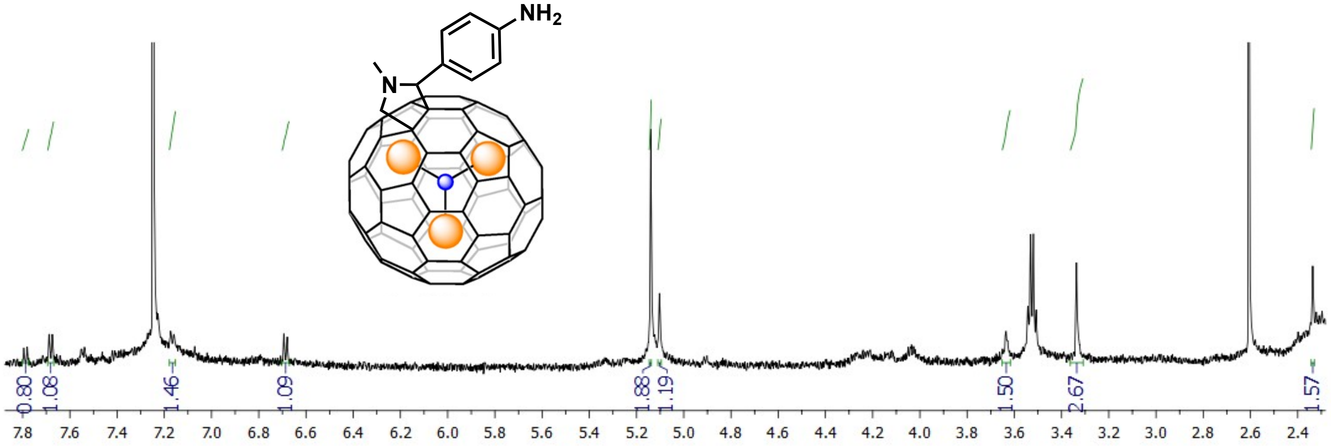
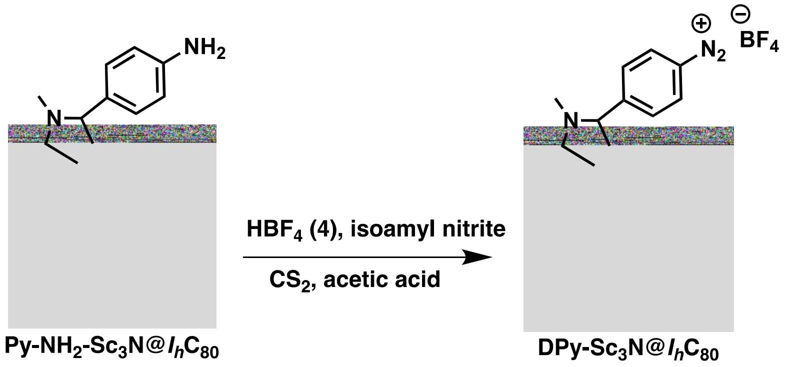


Figure S7. ^{1}H-NMR (600 MHz) spectrum of Py-NH$_2$-Sc$_3$N@I_hC$_{80}$ in CDCl$_3$.

Synthesis of diazonium salt fulleropyrrolidine Sc$_3$N@I_hC$_{80}$ derivative (DPySc$_3$N@I_hC$_{80}$).



In a round bottom flask, **Py-NH$_2$-Sc$_3$N@I_hC$_{80}$** (1 mg, 0.8 µmol) and **4** (0.8 µL, 0.012 mmol) were added and dissolved in acetic acid/carbon disulfide (2:1) after sonication. Isoamyl nitrite (0.8 µL, 0.006 mmol) was added dropwise and left the reaction at room temperature for 50 min. After this time, diethyl ether was added, and the reaction was left to stir at about -20 °C for 20 h. Finally, sample was washed with cooled ether. The pure **DPySc$_3$N@I_hC$_{80}$** was obtained as a yellow solid with 15% of yield and was characterized by FT-IR technique as shown in Figure S8. **IR (cm^{-1}):** 3275, 2955, 2873, 2891, 2259, 1736, 1641, 1538, 1482, 1465, 1349, 1022, 837, 789.

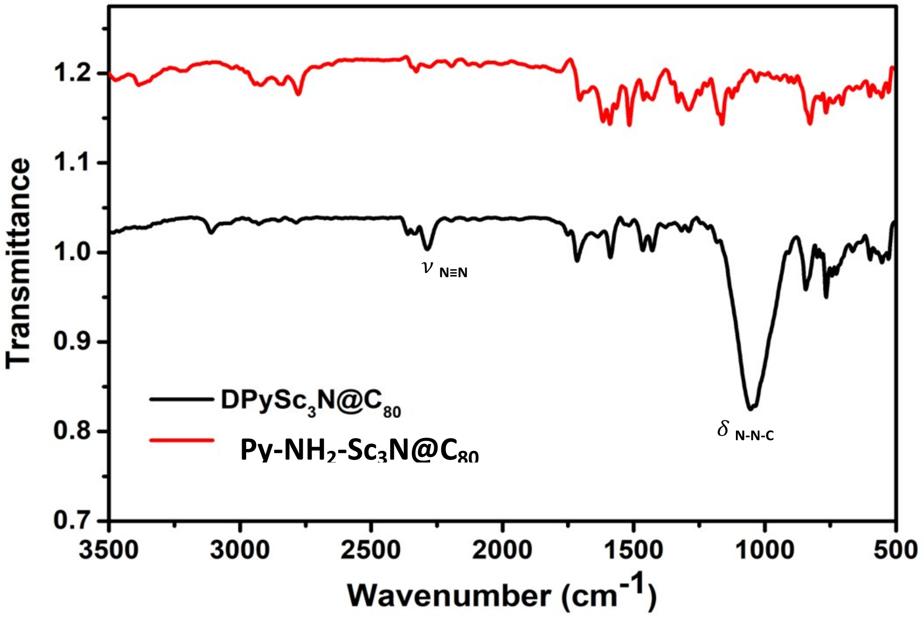
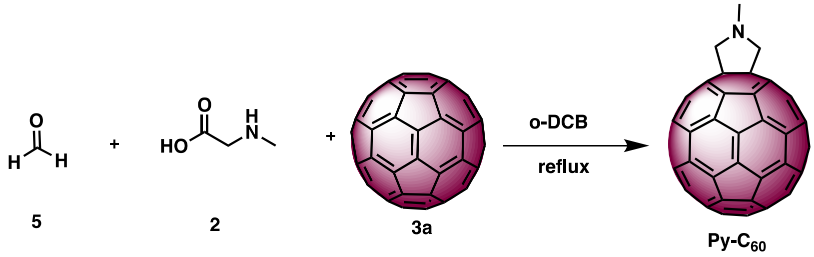


Figure S8. ATR-FT-IR spectra of Py-NH$_2$-Sc$_3$N@I_hC$_{80}$ and DPySc$_3$N@I_hC$_{80}$.

Synthesis of pyrrolidine C$_{60}$ derivative (PyC$_{60}$)



In a round bottom flask, C$_{60}$ (**3a**) (72 mg, 0.1 mmol), paraformaldehyde (**5)** (4.5 mg, 0.15 mmol) and **2** (13.3 mg, 0.15 mmol) were added and dissolved in *o*-DCB after sonication. The reaction was left to stir under reflux for 30 min. After this time, the mixture was chromatographed using silica gel with CS$_2$ and toluene. **PyC$_{60}$** was obtained as a brown solid with 89% of isolated yield. Figure S9 illustrates the characterization of **PyC$_{60.}$ ^{1}H-NMR (400 MHz, CDCl$_3$) δ:** 4.44 (s, 4H), 3.03 (s, 3H). **^{13}C-NMR (100 MHz, CDCl$_3$) δ:** 154.9, 147.4, 146.3, 146.1, 146.1, 145.5, 145.3, 144.6, 143.1, 142.7, 142.3, 142.1, 141.9, 140.2, 136.3, 70.1, 41.7, 30.9.

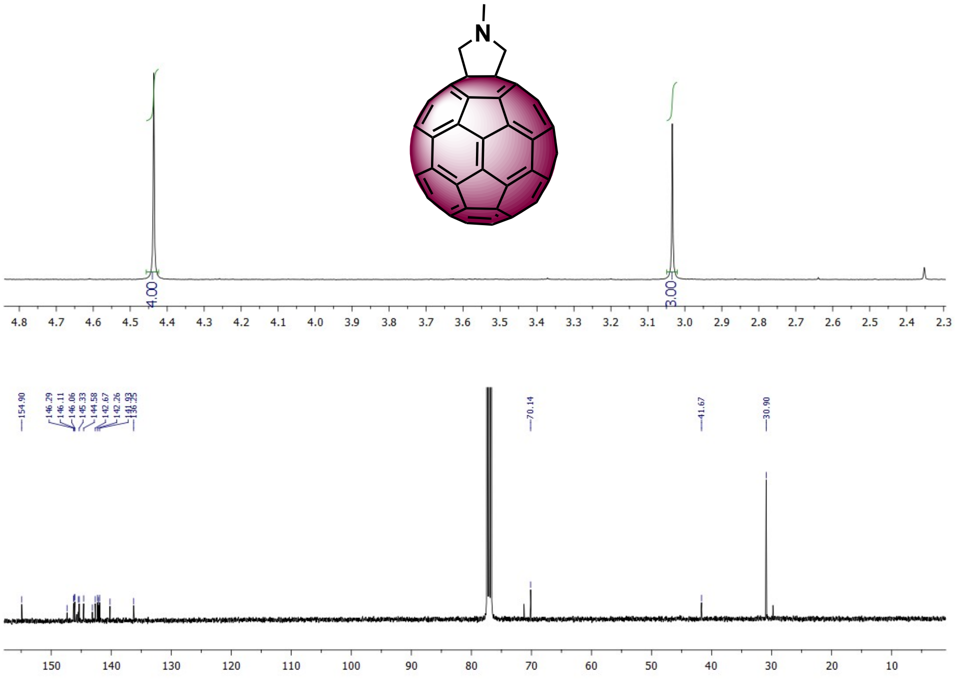
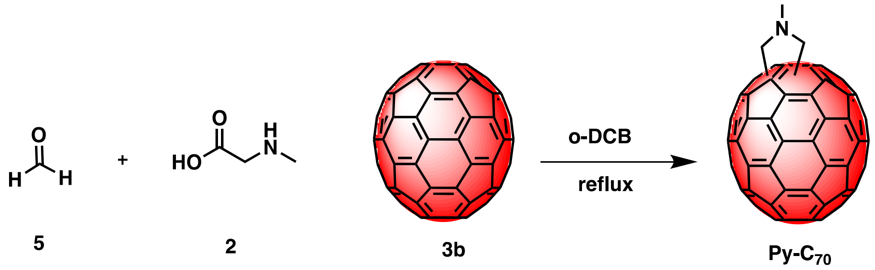


Figure S9. ^{1}H-NMR (400 MHz) and ^{13}C-NMR (100 MHz) spectra of PyC$_{60}$ in CDCl$_3$.

Synthesis of pyrrolidine C$_{70}$ derivative (PyC$_{70}$)



In a round bottom flask, C$_{70}$ (**3b**) (84 mg, 0.1 mmol), **5** (4.5 mg, 0.15 mmol) and **2** (13.3 mg, 0.15 mmol) were added and dissolved in *o*-DCB after sonication. The reaction was left to stir under reflux for 30 min. After this time, the mixture was chromatographed using silica gel with CS$_2$ and toluene. **PyC$_{70}$** was obtained as a mixture of isomers in the form of a brown solid with 86% of isolated yield. Figure S10 illustrate the characterization of **PyC$_{70}$.** **^{1}H-NMR (400 MHz, CDCl$_3$) δ:** 4.04 (d, *J* = 9.9 Hz, 1H), 3.94 (s, 2H), 3.70 (d, *J* = 9.7 Hz, 2H), 3.60 (s, 2H), 3.51 (s, 4H), 3.46 (d, *J* = 9.7 Hz, 2H), 2.76 (s, 3H), 2.63 (s, 3H), 2.54 (s, 1H), 2.31 (d, *J* = 9.6 Hz, 1H). **^{13}C-NMR (100 MHz, CDCl$_3$) δ:** 166.1, 146.9, 145.8, 145.4, 145.3, 145.3, 145.2, 145.1, 144.8, 144.7, 144.7, 144.6, 144.5, 144.5, 143.9, 143.7, 143.1, 143.0, 143.0, 142.9, 142.8, 142.3, 142.2, 142.2, 142.1, 141.0, 141.0, 139.2, 138.3, 138.0, 134.0, 132.0, 131.4, 127.0, 125.8, 124.3, 123.8, 75.1, 66.9, 54.7, 29.3.

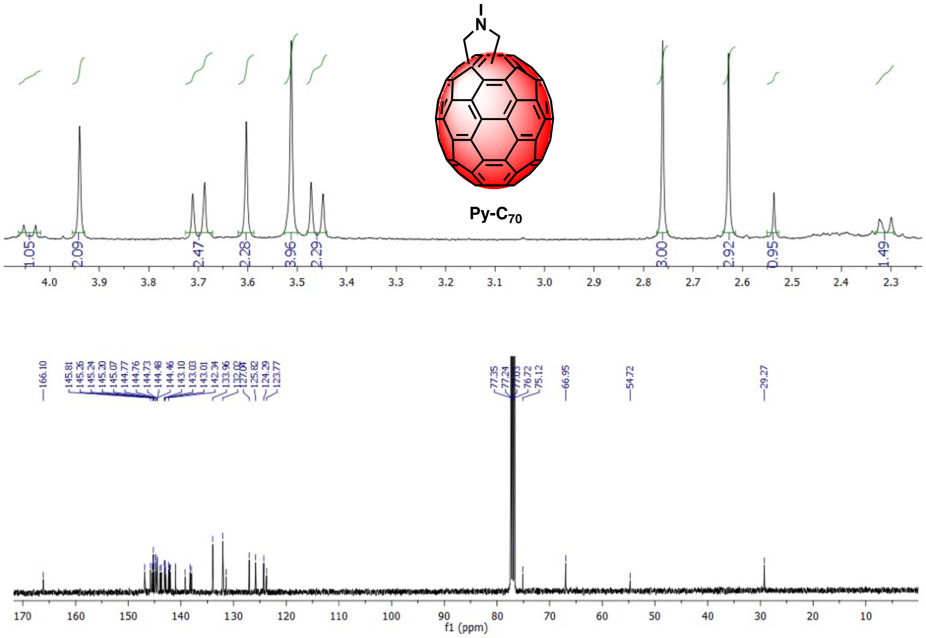
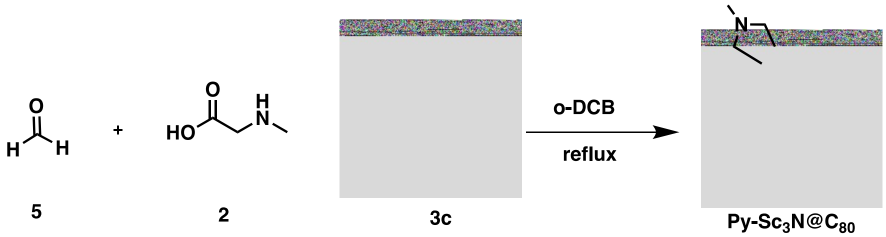


Figure S10. ^{1}H-NMR (400 MHz) and ^{13}C-NMR (100 MHz) spectra of PyC$_{70}$ in CDCl$_3$.

Synthesis of pyrrolidine Sc$_3$N@I_hC$_{80}$ derivative (PySc$_3$N@I_hC$_{80}$)



In a round bottom flask, C$_{70}$ (**3c**) (3 mg, 0.003 mmol), **5** (0.3 mg, 0.01 mmol) and **2** (0.89 mg, 0.01 mmol) were added and dissolved in *o*-DCB after sonication. The reaction was left to stir under reflux for 40 min. After this time, the mixture was chromatographed using silica gel with CS$_2$ and toluene. **Py-Sc$_3$N@I_hC$_{80}$** was obtained as a yellow solid with 53% of isolated yield. Figure S11 illustrates the characterization of **Py-Sc$_3$N@I_hC$_{80}$. ^{1}H-NMR (600 MHz, DMSO-D6) δ:** 4.03 (d, *J* = 7.2 Hz, 2H), 3.86 (s, 3H), 3.81 (d, *J* = 7.2 Hz, 2H).

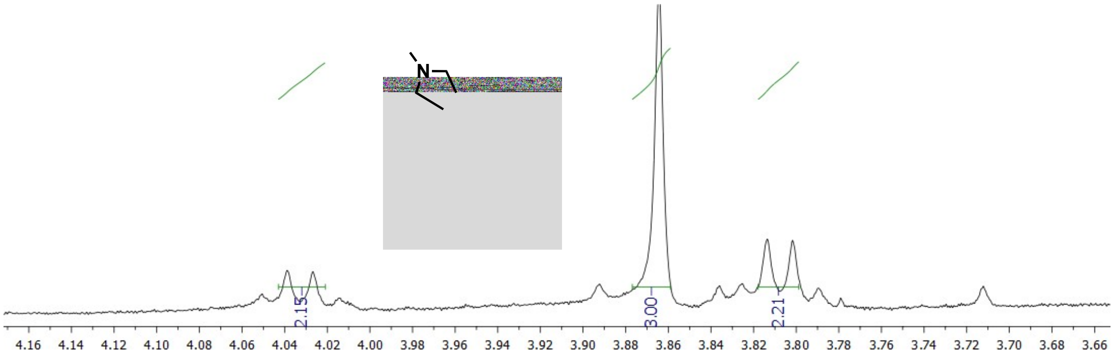
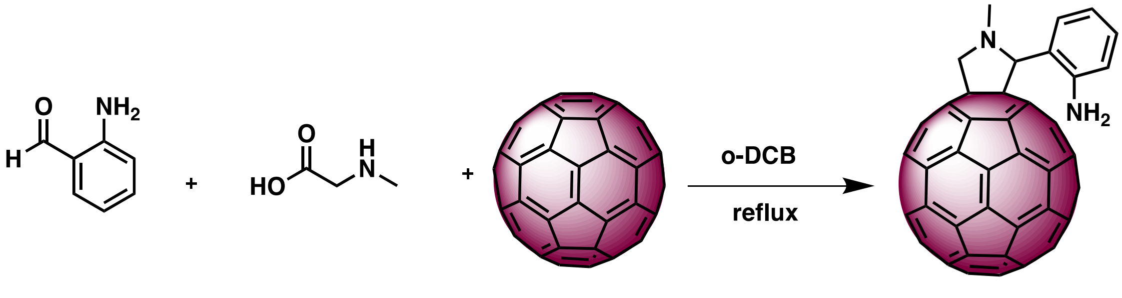


Figure S11. ^{1}H-NMR (400 MHz) spectrum of Py-$Sc_3N@I_hC_{80}$ in $CDCl_3$.

Synthesis of 2-aminobenzyl C_{60} derivative (ortho-Py-NH_2-C_{60})



ortho-Py-NH_2-C_{60}

In a round bottom flask, C_{60} (72.1 mg, 0.100 mmol), pulverized 2-aminobenzaldehyde (24.8 mg, 0.201 mmol) and sarcosine (18.6 mg, 0.204 mmol) were added and dissolved in *o*-dichlorobenzene (*o*-DCB) after sonication. The reaction was left to stir under reflux for 40 min. After this time, the mixture was chromatographed using silica gel with the following eluents: carbon disulfide, carbon disulfide/chloroform (1:1) and hexanes/chloroform (1:2). **ortho-Py-NH_2-C_{60}** was obtained as a brown solid with 57% of isolated yield. Figures S12-S13 illustrate the characterization of **ortho-Py-NH_2-C_{60}.** **^{1}H-NMR (400 MHz, $CDCl_3$) δ:** 7.36 (s, 2H), 7.12 (t, J = 7.6 Hz, 1H), 6.70 (t, J = 7.6 Hz, 2H), 6.64 (d, J = 8.1 Hz, 1H), 5.03 (s, 1H), 5.00 (d, J = 3.7 Hz, 2H), 4.30 (d, J = 9.6 Hz, 1H), 4.20 (d, J = 9.1 Hz, 1H), 2.93 (d, J = 12.7 Hz, 3H). **^{13}C-NMR (101 MHz, $CDCl_3$) δ:** 193.9, 192.6, 164.7, 156.7, 154.1, 153.9, 152.16, 149.9, 148.7, 147.3, 146.9, 146.7, 146.2, 146.1, 145.9, 145.8, 145.6, 145.3, 145.2, 144.6, 144.4, 143.1, 142.6, 142.2, 142.1, 141.9, 141.8, 141.7, 141.6, 140.2, 140.1, 139.6, 136.6, 135.9, 135.7, 135.3, 135.2, 134.7, 132.3, 130.0, 129.6, 129.3, 129.2, 129.1, 128.8, 128.3, 127.5, 126.2, 124.5, 124.2, 120.2, 119.2, 118.9, 117.6, 116.5, 116.4, 116.0, 115.8, 77.4, 77.3, 77.1, 76.8, 69.8, 69.4, 55.9, 39.9, 32.1, 29.8, 22.9, 14.3. **IR (cm^{-1}):** 3502-3208, 2937, 2920, 2845, 2777, 1709, 1626, 1587, 1515, 1428, 1336, 1293, 1235, 1162, 1037, 833, 766.

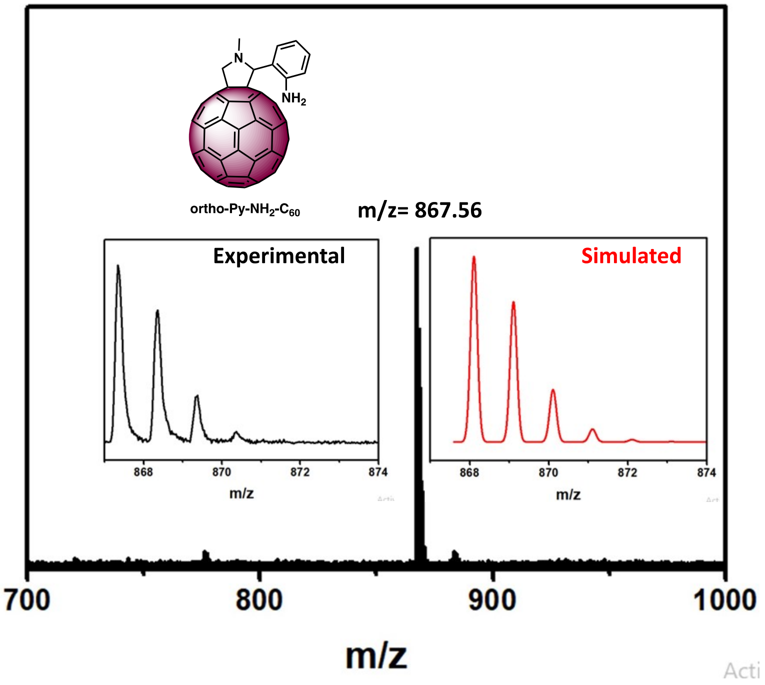


Figure S12. MALDI-TOF mass spectrum of ortho-Py-NH_2-C_{60}.

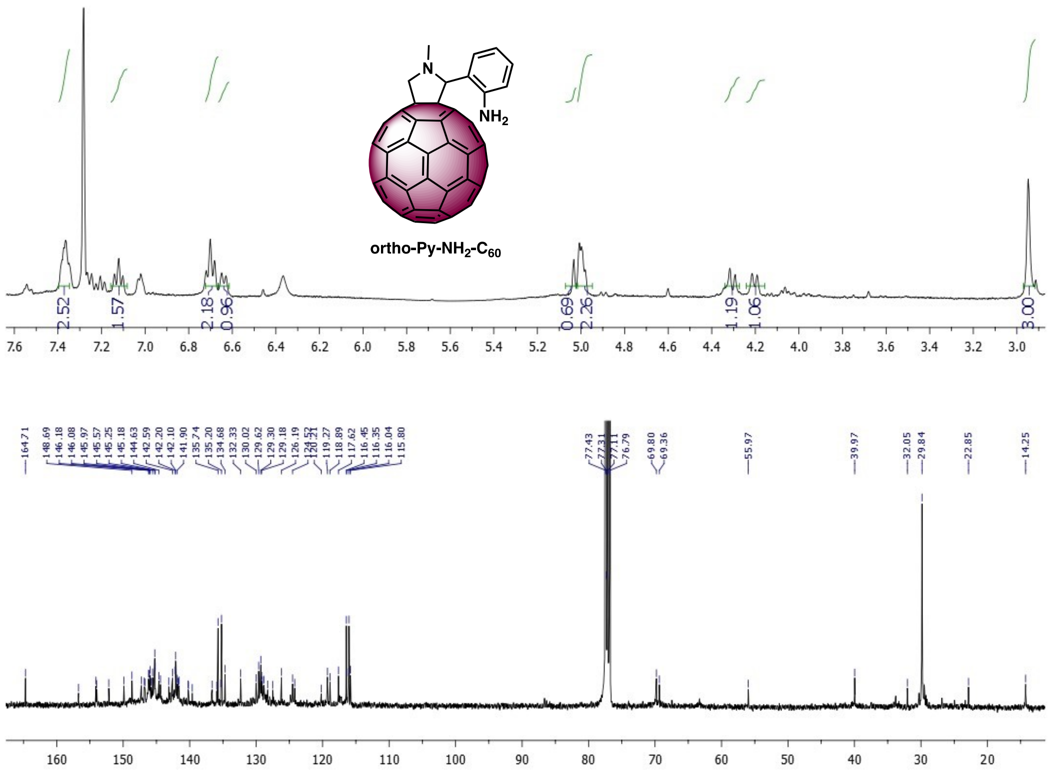
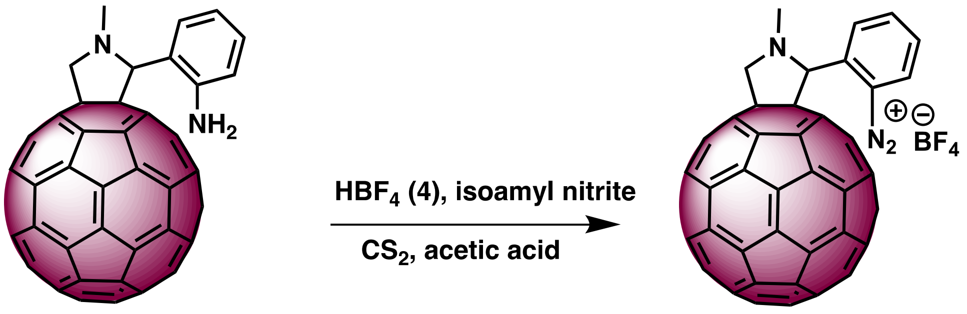


Figure S13. ^{1}H-NMR (101 MHz) and ^{13}C-NMR (101 MHz) spectra of ortho-Py-C$_{60}$ in CDCl$_3$.

Synthesis of diazonium salt fulleropyrrolidine C$_{60}$ derivative (ortho-DPyC$_{60}$).



ortho-Py-NH$_2$-C$_{60}$

ortho-DPyC$_{60}$

In a round bottom flask, **ortho-Py-NH$_2$-C$_{60}$** (17.6 mg, 20.2 μmol) and HBF$_4$ 48 wt % in H$_2$O (20 μL, 0.30 mmol) were added and dissolved in acetic acid/carbon disulfide (2:1) after sonication. Isoamyl nitrite (21 μL, 0.14 mmol) was added dropwise and left the reaction at room temperature for 30 min. After this time, diethyl ether was added, and the reaction was left to stir at about -20 °C for 16 h. Finally, sample was washed with cooled ether. The pure **ortho-DPyC$_{60}$** was obtained as a brown solid with 83% of yield and was characterized by FT-IR as shown in Figure S14. **IR (cm^{-1}):** 3543-3390, 3113, 2945, 2852, 2777, 2271, 1722, 1694, 1580, 1583, 1520, 1456, 1422, 1315, 1299, 1035, 856, 742.

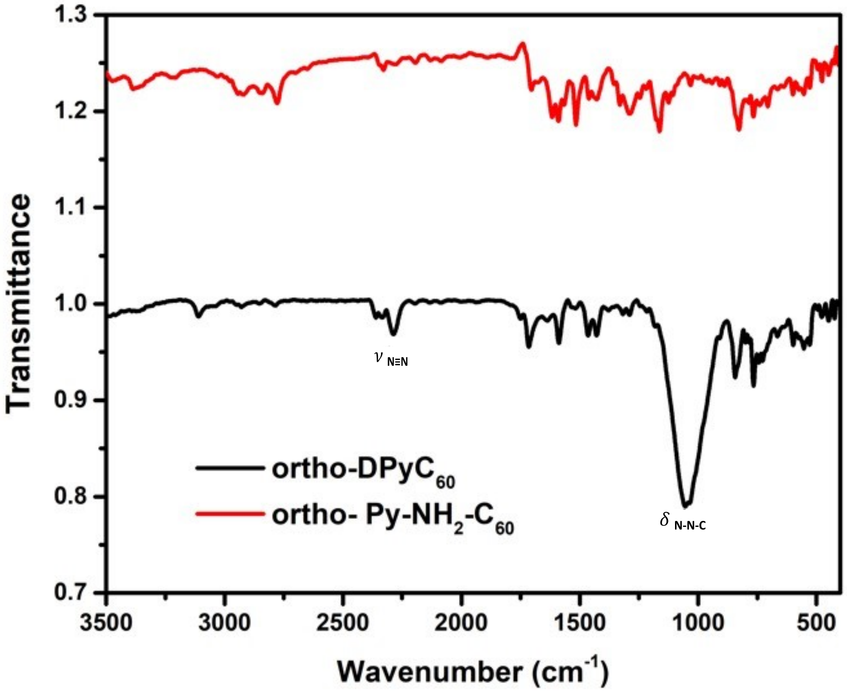


Figure S14. ATR-FT-IR spectra of ortho-Py-NH$_2$-C$_{60}$ and ortho-DPyC$_{60}$.

Electrochemical measurements

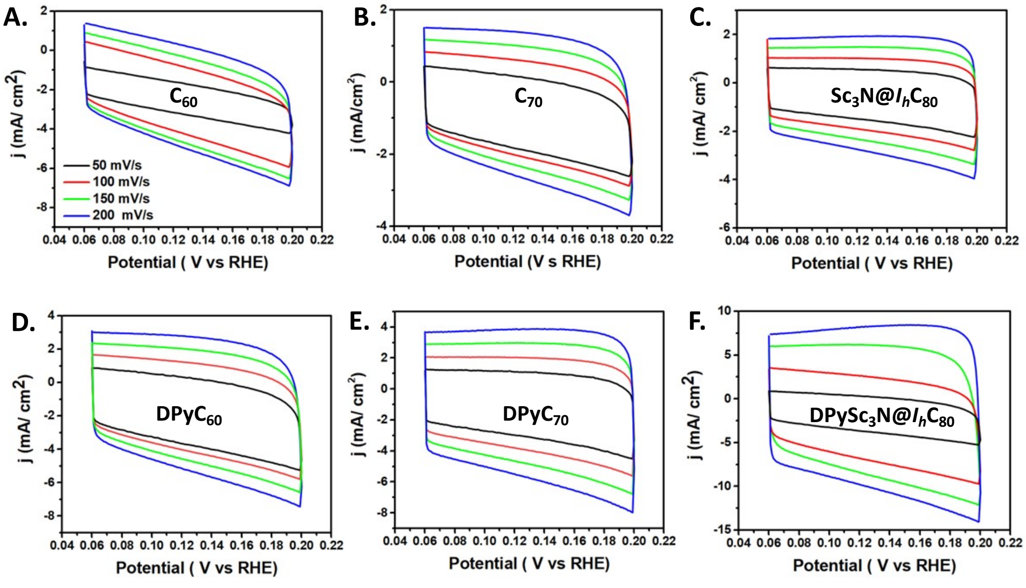


Figure S15. Double capacitance measurements for the synthesized fullerenes and their respective starting materials.

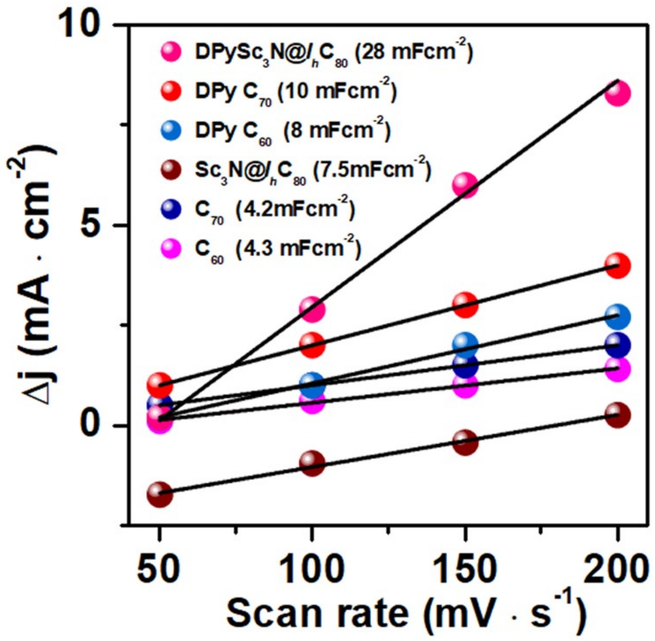


Figure S16. Linear dependency of the current with the scan rate

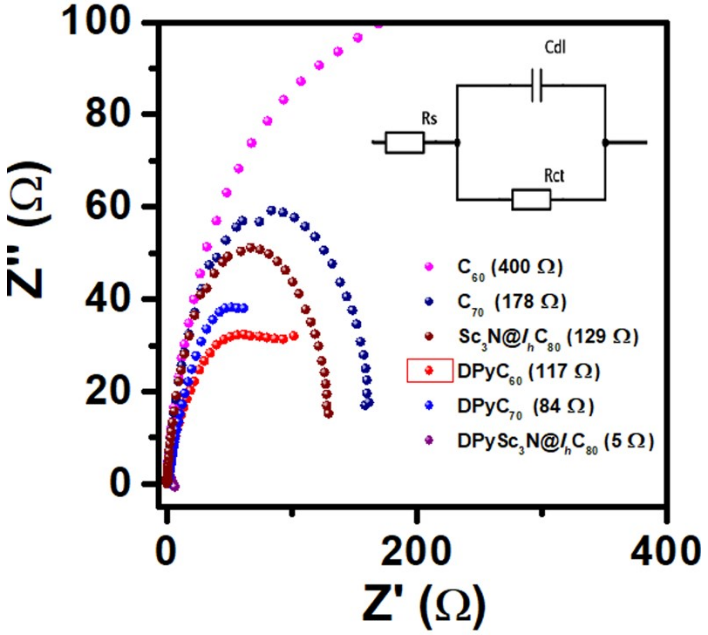


Figure S17. EIS measurements for the diazonium functionalized fullerene derivatives and their starting materials

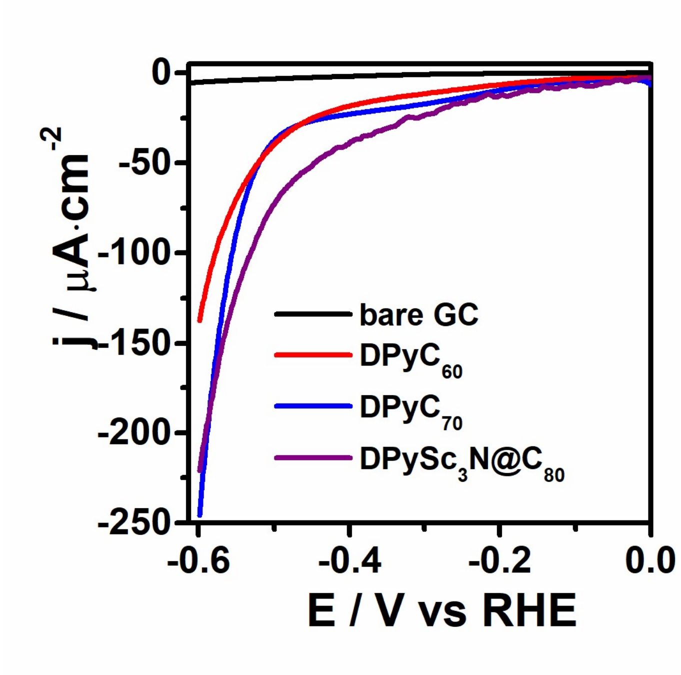


Figure S18. Comparison of the catalytic activity of the diazonium functionalized fullerene derivatives with bare glassy carbón electrode.

Table S1: Onset potential of the top-ranked carbon-nanomaterials electrocatalysts

Materials	Onset potential (mV)	Tafel slope [mV dec^{-1}]	Reference
MoS_2/N-doped CNT forest	−75	40	[1]
$MoSe_2$/rGO hybrid	**-**11	69	[2]
$MoSe_2$/GN nanosheets	−50	61	[3]
Nanoporous Mo_2C nanowires (carbide)	−70	53	[4]
NiMoNx/C (nitrides)	−157	35.9	[5]
$DPySc_3N@I_hC_{80}$	-25	115	This Work

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