

Photoinduced Electron Transfer Reactivity of Aza[60]fullerene. Three Discrete Functionalization Pathways with a Single Substrate

Georgios C. Vougioukalakis, and Michael Orfanopoulos*

Department of Chemistry, University of Crete, 71409 Iraklion, Greece

Supporting Information

Experimental Section

General Considerations. ^1H NMR and ^{13}C NMR spectra were recorded on a 500 MHz spectrometer. Chemical shifts are reported in ppm downfield from Me_4Si , by using the residual solvent peak as internal standard. FT-IR spectra were recorded on a fourier transform infrared spectrometer, using KBr pellets. UV-vis spectra were performed on a UV/Visible spectrometer. HPLC analyses have been carried out on C_{18} reverse phase columns with detection at 326 nm. A mixture of toluene/acetonitrile (55/45) was used as eluent at 1, or 4 ml/min flow rates. TLC was carried out on SiO_2 (silica gel F₂₅₄). Photochemical reactions were carried out by a 300-W xenon lamp as the light source, using a pyrex filter.

Synthesis of aza[60]fullerene derivative 5. $(\text{C}_{59}\text{N})_2$ (30 mg, 0.02 mmoles) together with a 20-fold excess of toluene-*p*-sulfonic acid (44 mg, 0.4 mmoles) were dissolved in 18 ml of an ODCB/benzyltrimethylsilane mixture (9/1). The reaction mixture was irradiated for 40 min at 0 °C, while a constant, slow air stream was maintained over the solution (all reactions were monitored by HPLC). Consecutively, a 100-fold excess of triethylamine was added, the solvent was distilled from the reaction mixture under reduced pressure at 57 °C, and the remaining crude product was washed and centrifuged five times with acetonitrile HPLC grade. The isolated product was further purified by semi-preparative HPLC (4 ml/min flow rate) to afford 9.3 mg (yield: 28%) of **5** as a brown solid. m.p. > 360 °C; IR (KBr): ν (cm^{-1}) = 523, 700, 752, 800, 1023, 1093, 1261, 1421, 1458, 1497, 1550, 1584, 2845, 2913, 2957;

UV-vis (CHCl_3): λ_{max} (nm)= 260, 322, 438, 602, 728; MS (FAB): m/z 830 (MH^+), 722 (C_{59}N^+); ^1H NMR (500 MHz, $\text{CS}_2\text{-CDCl}_3$): δ 7.85 (d, J = 7.5 Hz, 2H), 7.54 (t, J = 7.5 Hz, 2H), 7.45 (t, J = 7.5 Hz, 1H), 5.98 (s, 2H); ^{13}C NMR (125 MHz, $\text{CS}_2\text{-CDCl}_3$): δ 154.32, 147.70, 147.48, 147.44, 147.42, 146.51, 146.48, 146.34, 146.04, 146.02, 145.88, 145.43, 145.22, 145.13, 144.61, 144.36, 143.74, 143.40, 143.25, 142.73, 142.63, 142.01, 141.88, 141.65, 141.44, 140.01, 137.67, 137.38, 136.06, 129.27, 128.73, 125.76, 69.04, 30.45.

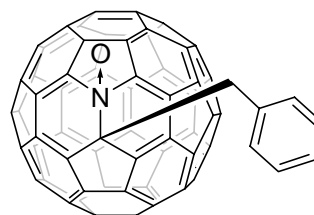
Synthesis of aza[60]fullerene derivative 7. (C_{59}N)₂ (30 mg, 0.02 mmol) together with a 20-fold excess of toluene-*p*-sulfonic acid (44 mg, 0.4 mmol) were dissolved in 18 ml of an ODCB/benzyltrimethylsilane mixture (9/1). The reaction mixture was stirred at 150 °C for 1.5 hours, while a constant, slow air stream was maintained over the solution. After the reaction was cooled down to room temperature, a 100-fold excess of triethylamine was added, the solvent was distilled from the reaction mixture under reduced pressure at 57 °C, and the remaining crude product was washed and centrifuged five times with acetonitrile HPLC grade. The isolated product was further purified by semi-preparative HPLC (4 ml/min flow rate) to afford 23.0 mg (yield: 65%) of **7** as a brown solid. m.p. > 360 °C; IR (KBr): ν (cm^{-1})= 523, 693, 718, 752, 850, 897, 965, 1088, 1146, 1180, 1205, 1244, 1314, 1409, 1420, 1504, 1546, 1605; UV-vis (CHCl_3): λ_{max} (nm)= 256, 320, 446, 600, 730, 818; MS (FAB): m/z 886 (MH^+), 722 (C_{59}N^+); ^1H NMR (500 MHz, $\text{CS}_2\text{-CDCl}_3$): δ 8.70 (d, J = 8.0 Hz, 2H), 7.52 (d, J = 8.0 Hz, 2H), 2.41 (s, 2H), 0.24 (s, 9H); ^{13}C NMR (125 MHz, $\text{CS}_2\text{-CDCl}_3$): δ 155.09, 149.69, 148.44, 148.29, 148.25, 147.92, 147.90, 147.25, 147.04, 146.87, 146.52, 146.48, 146.30, 145.68, 145.21, 144.95, 144.65, 143.78, 143.39, 143.03, 142.72, 142.45, 142.21, 142.06, 141.63, 141.52, 140.42, 138.22, 137.33, 133.60, 130.04, 127.84, 124.81, 83.51, 28.12, -1.10.

Synthesis of aza[60]fullerene derivative 6. (C_{59}N)₂ (30 mg, 0.02 mmol) were dissolved in 18 ml of a thoroughly degassed (6 vacuum-argon cycles) ODCB/benzyltrimethylsilane mixture (9/1). The reaction mixture was stirred at 160 °C for 4 hours under argon. The solvent was distilled from the reaction mixture under reduced pressure at 57 °C, and the product was purified by semipreparative HPLC (4 ml/min flow rate) to afford **6** as a brown solid (yield: < 8%). Unfortunately, due to the very low yield of these free radical reactions, we did not manage to purify enough quantity of **6** for characterization with ^{13}C NMR and FT-IR; however, all other data

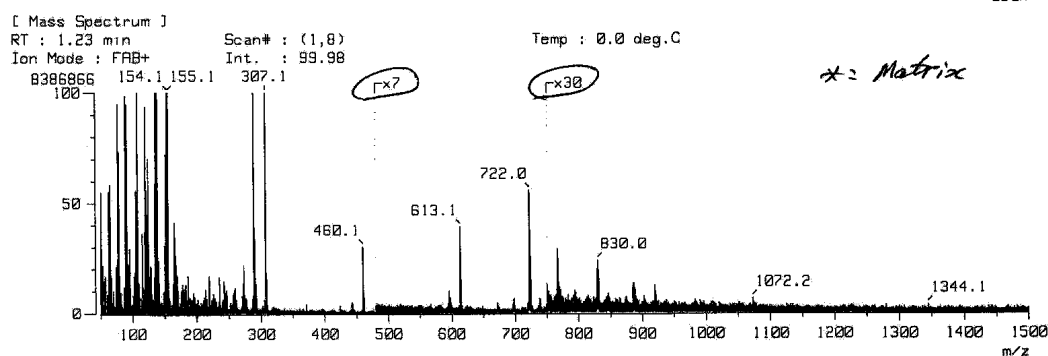
support the proposed structure. m.p. > 360 °C; UV-vis (CHCl₃): λ_{max} (nm)= 255, 322, 446, 601, 729, 816; MS (MALDI): m/z 813 (M⁺), 722 (C₅₉N⁺); ¹H NMR (500 MHz, CS₂-CDCl₃): δ 7.86 (d, J = 7.5 Hz, 2H), 7.55 (t, J = 7.5 Hz, 2H), 7.46 (t, J = 7.5 Hz, 1H), 5.99 (s, 2H). The same adduct was also derived by photochemical treatment of (C₅₉N)₂ in a ODCB/benzyltrimethylsilane mixture (9/1) under argon at 0 °C.

Spectral Data

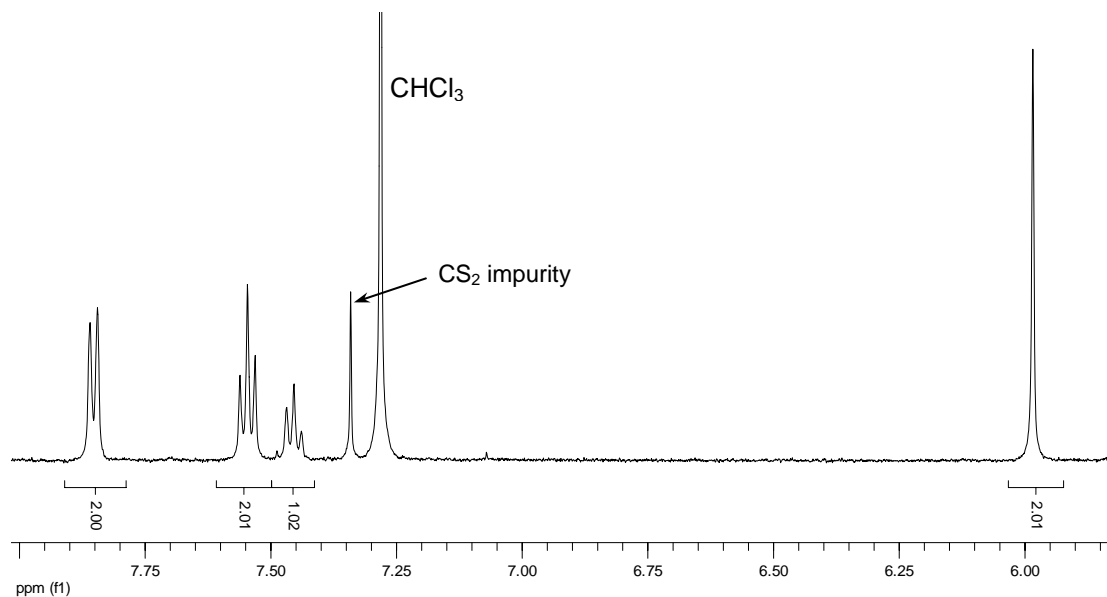
A) Aza[60]fullerene adduct 5



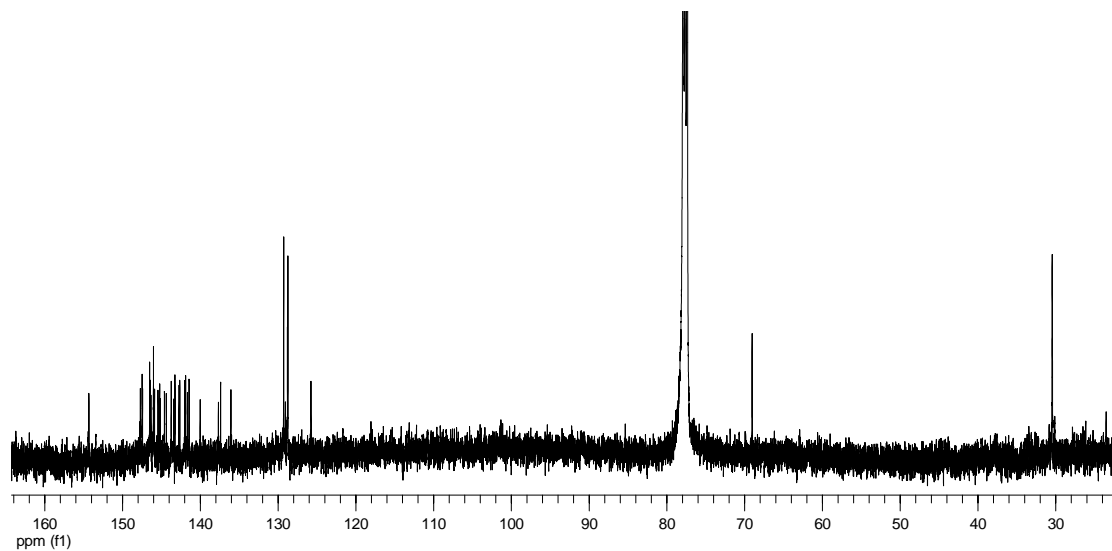
1) FAB-MS, (MH⁺) = 830



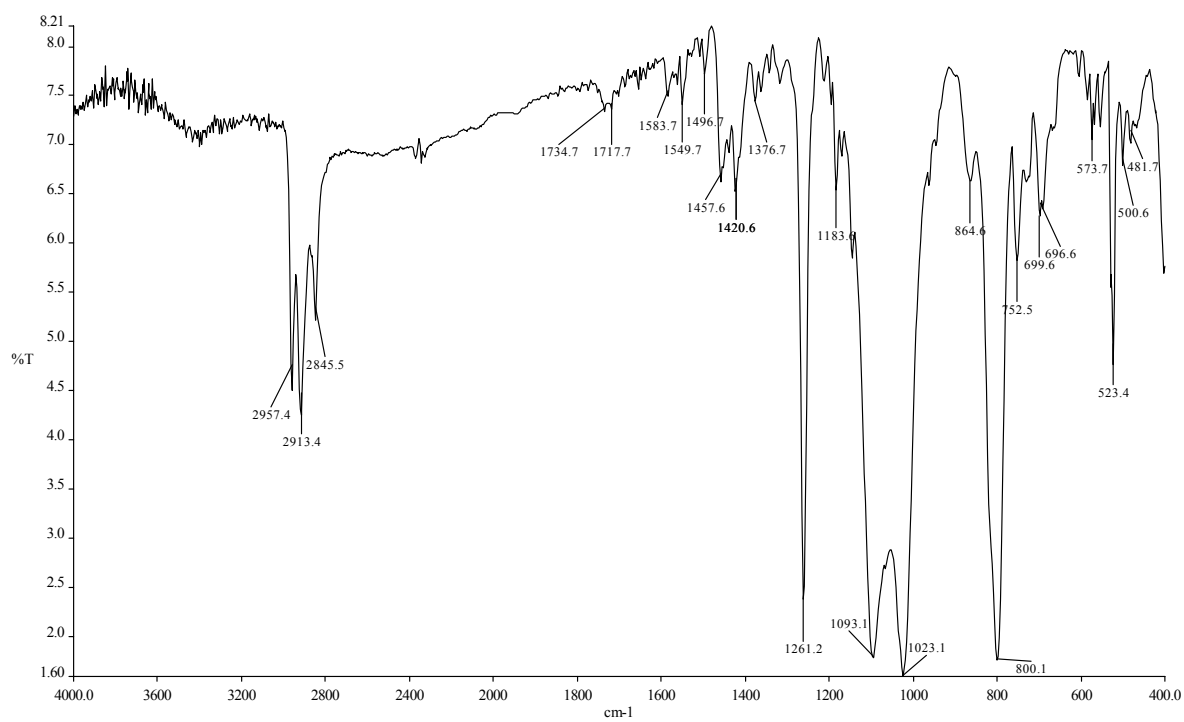
2) ¹H NMR (500 MHz, CDCl₃-CS₂)



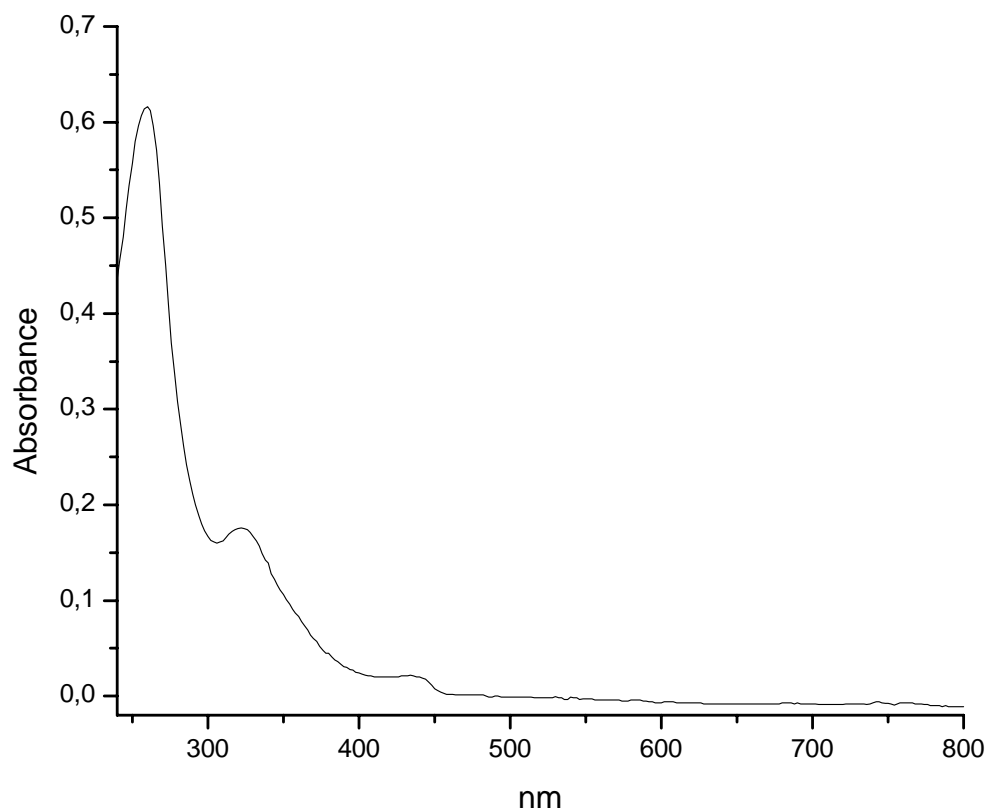
3) ^{13}C NMR (125 MHz, $\text{CDCl}_3\text{-CS}_2$)



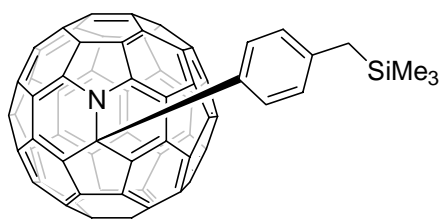
4) FT-IR



5) UV-vis

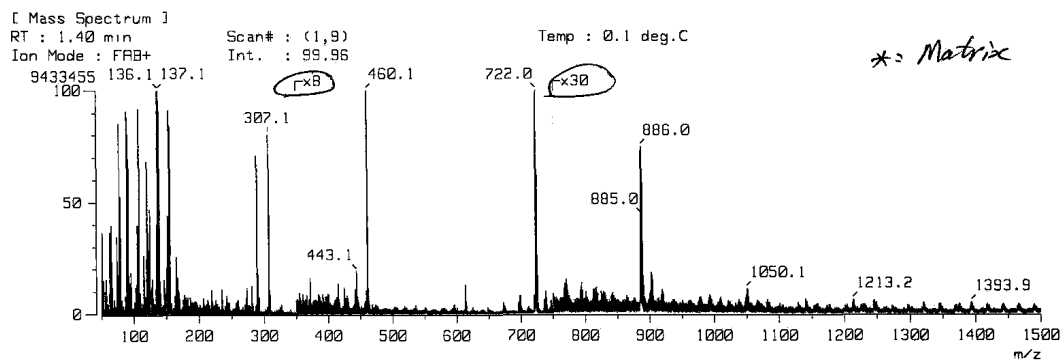


B) Aza[60]fullerene adduct 7

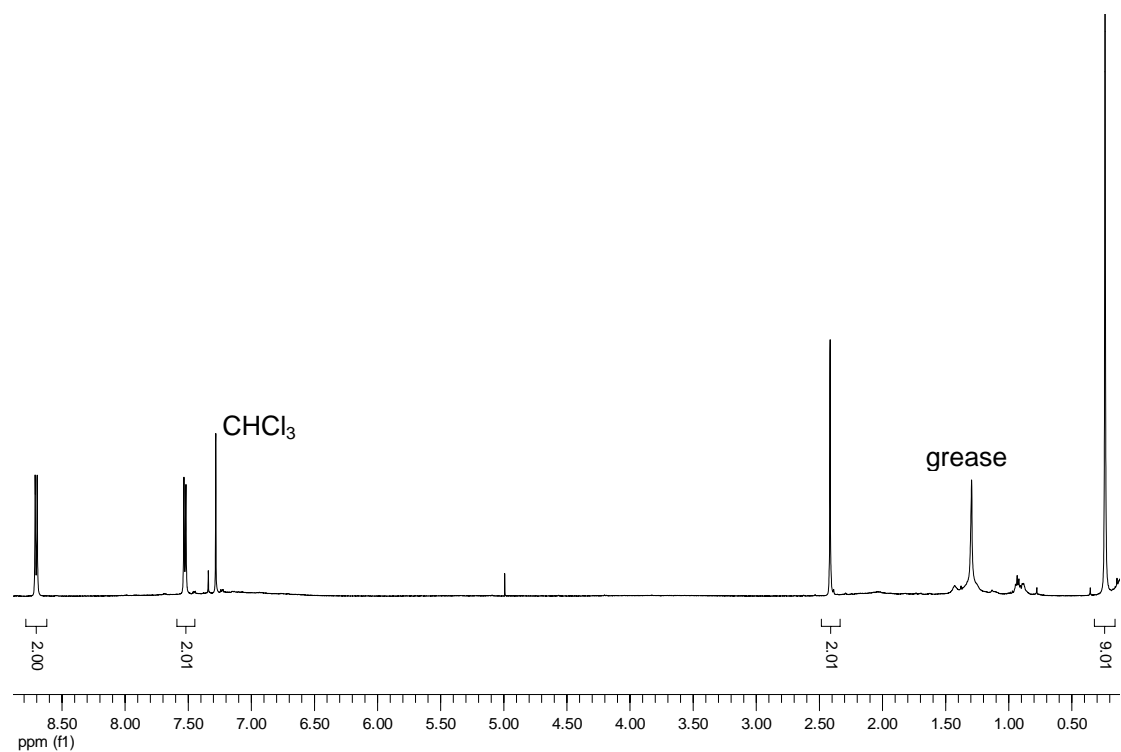


7

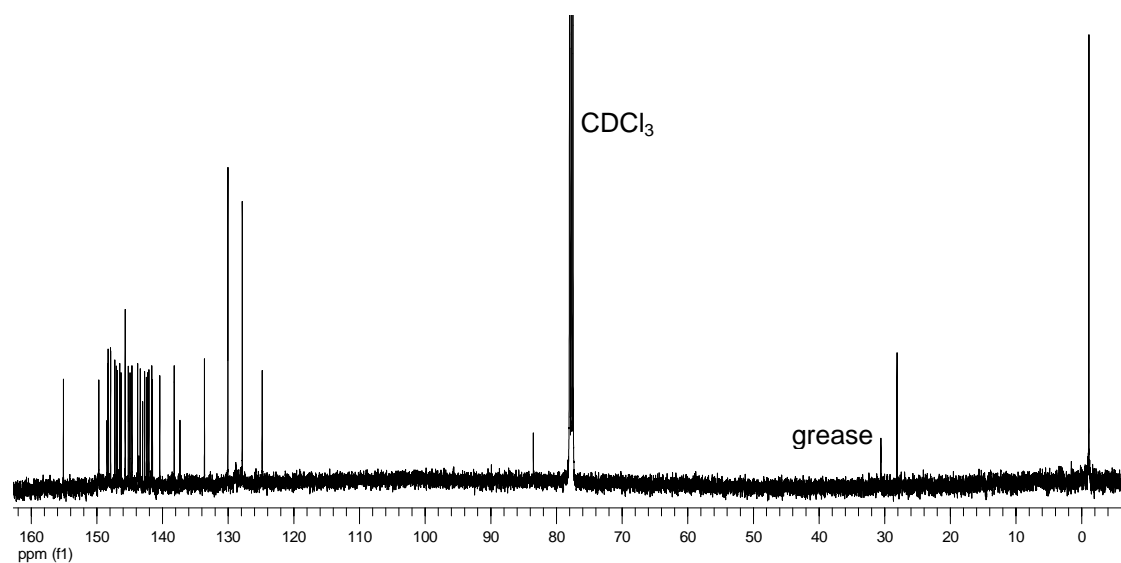
1) FAB-MS, (MH⁺) = 886



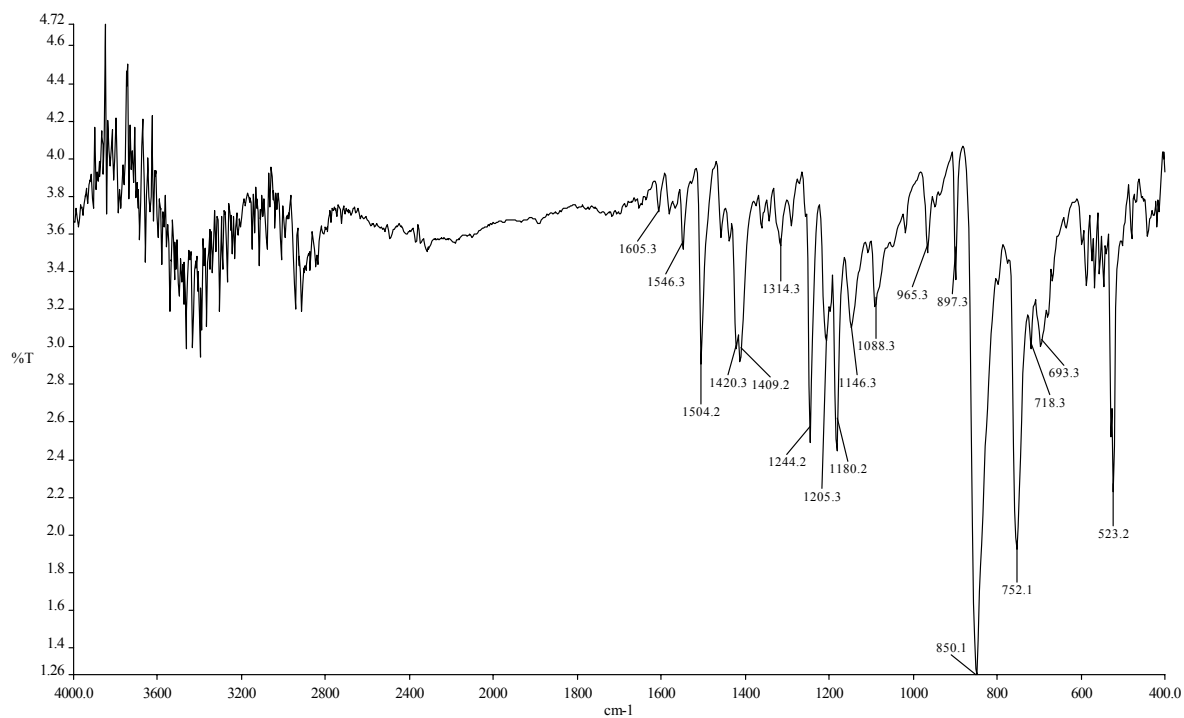
2) ^1H NMR (500 MHz, $\text{CDCl}_3\text{-CS}_2$)



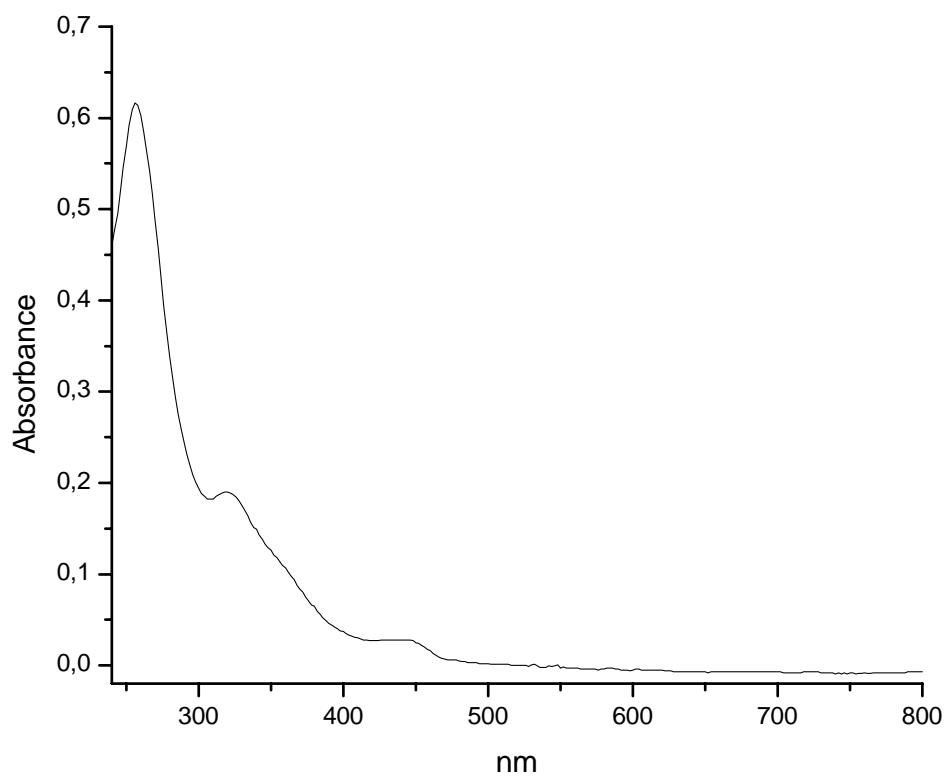
3) ^{13}C NMR (125 MHz, $\text{CDCl}_3\text{-CS}_2$)



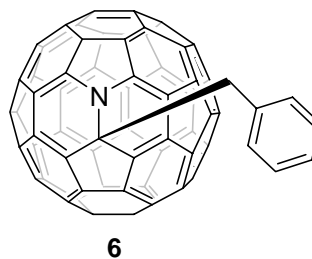
4) FT-IR



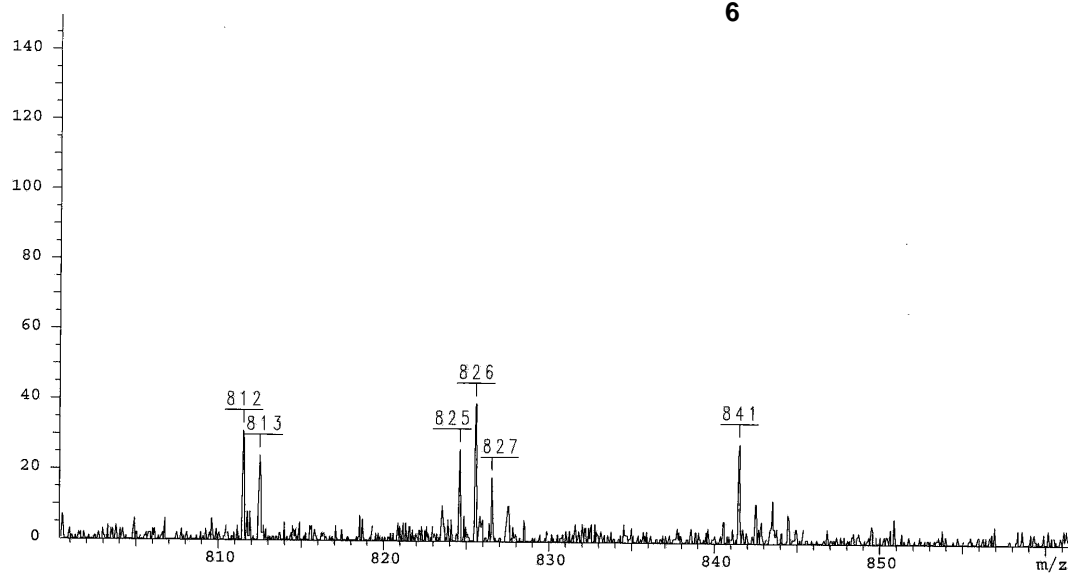
5) UV-vis



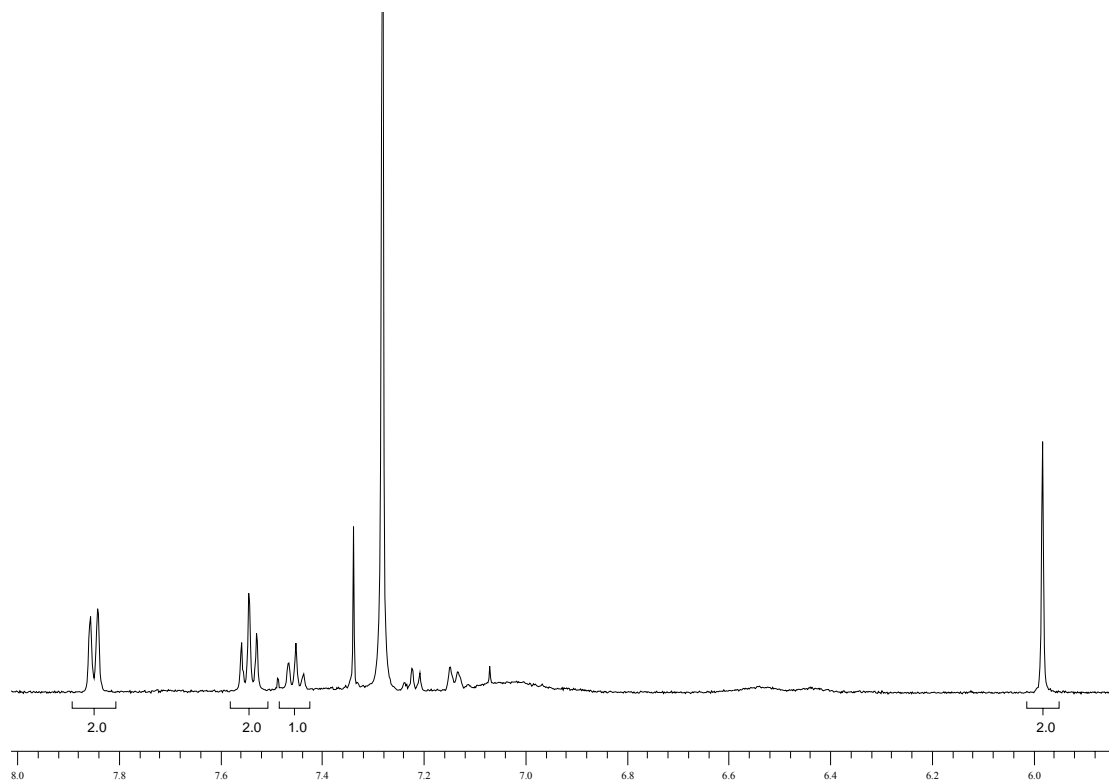
C) Aza[60]fullerene adduct 6



1) MALDI, (M^+) = 813



2) ^1H NMR (500 MHz, $\text{CDCl}_3\text{-CS}_2$)



3) UV-vis

