Electronic Supplementary Information (ESI) for the manuscript:

High LUMO energy pyrrolidinofullerenes as promising electron-acceptor materials for organic solar cells

A. V. Mumyatov, F. A. Prudnov, L. N. Inasaridze, O. A. Mukhacheva, and P. A. Troshin

Contents

Materials and instrumentation

All solvents and reagents were purchased from Sigma-Aldrich or Acros Organics and used as received or purified according to standard procedures. AFM images were obtained using NTEGRA PRIMA instrument (NT-MDT, Russia). ESI MS spectra were obtained using Shimadzu LCMS 2020. PL spectra were obtained using Avantes AvaSpec-2048 optical fiber spectrometer.

Synthetic procedures and spectral data

Compound 2 was synthesized according to the literature procedure.[i] To a round-bottomed flask containing a solution of 2-(2-methoxyphenyl)acetic acid (10.0 g, 60 mmol) in CCl_4 (50 mL) N-bromosuccinimide (NBS, 13.3 g, 74 mmol) and 2,2′-azobis(2-methylpropionitrile) (AIBN, 1.4 g, 9.0 mmol) were added. The mixture was heated at reflux for 3 h and then stirred overnight at room temperature. The precipitate was separated by filtration, while the filtrate was concentrated in vacuum. Purification of then oily residue by flash column chromatography (silica gel, 40-60 μm, 60Å, 20-25% EtOAc in hexane) afforded the title compound as a white solid (7.5 g, 50%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.63 – 7.60 (m, 1H, aromatic), 7.35 (m, 1H, aromatic), 7.00 (m, 1H, aromatic), 6.90 (m, 1H, aromatic), 5.89 (s, 1H, C*H*Ph), 3.89 (s, 3H, OCH_3).

Compound 3. 2-Ethylhexylamine (7.4 g, 57 mmol) was dissolved in a mixture of 25 ml of ethanol and 13 ml of water and this solution was cooled in an ice bath. Bromoacetic acid (2 g, 14 mmol) was added in small portions at 0°C. The reaction mixture was stirred for 20 hours, slowly warmed to room temperature and then was poured into 100 ml of cold acetone. A white precipitate was filtered, washed with acetone and dried under vacuum (1.83 g, 68%). ^{1}H NMR (500 MHz, $CDCl_3$ + DMSO-d6) δ 2.98 (s, 2H), 2.42 (d, J = 6.6 Hz, 2H), 1.31 (m, 1H), 1.15 – 0.80 (m, 10H), 0.50 (m, 6H, terminal CH_3).

Compound 4. Compound **2** (3 g, 12 mmol) was dissolved in THF (50 mL*)*. Then a solution of 2-ethylhexylamine (1.6 g, 12 mmol) and triethylamine (2.7 g, 27 mmol) in THF (20 mL) was added dropwise. Reaction mixture was stirred overnight and filtered. The filtrate was concentrated in vacuum and the crude solid material was purified by flash column chromatography (eluent: methanol/ethyl acetate 1:1; silica gel, 40-60 μm, 60Å) which afforded yellowish solid (1.18 g, 32%) which represented a 1:1 mixture of two isomers of **4**. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.40 (m, 2H, aromatic), 7.29 (m, 2H, aromatic), 6.96 (t, J = 7.5 Hz, 2H, aromatic), 6.86 (m, 2H, aromatic), 4.87 (s, 1H, C*H*Ph), 4.86 (s, 1H, C*H*Ph), 3.82 (m, 6H, OCH_3), 2.86 (m, 2H, N-C*Ha*), 2.38 (m, 2H, N-C*Hb*), 1.72 – 1.59 (m, 2H, alkyl), 1.47 – 1.02 (m, 16H, alkyl), 0.90 – 0.68 (m, 12H, terminal CH_3).

General procedure for the synthesis of pyrrolidinofullerenes F1-F4

Fullerene C_{60} (0.3 g, 0.4 mmol) and 2 eq. of the corresponding amino acid **3-4**, 1 eq. of the appropriate aldehyde and 60 mL of 1,2-DCB were introduced in the listed here sequence into a round-bottom two-necked flask equipped with a reversed condenser. The reaction mixture was deaerated using repeating cycles of freezing in liquid nitrogen, evacuation, filling with argon, and heating up to the room temperature. The mixture of reagents was heated at 120 ^{0}C for two hours with intense stirring, then cooled down and

the solvent was removed in vacuum. The crude solid material was purified by flash column chromatography (eluent: petroleum ether/toluene 7:3; silica gel, 40-60 μm, 60Å).

Compound F1. Yield 37% (160 mg). Obtained as a mixture of 2 isomers. ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.17 (s, 1H, aromatic), 6.17 (s, 1H, aromatic), 6.11 (m, 2H, aromatic), 5.77 (s, 1H, C*H*Ph), 5.76 (s, 1H, C*H*Ph), 5.01 (s, 1H, C*Ha*H), 4.99 (s, 1H, C*Ha*H), 3.90 (m, 2H, C*Hb*H), 3.81 (s, 6H, OCH_3), 3.75 (m, 6H, OCH_3), 3.70 (m, 6H, OCH_3), 2.92 (dt, J = 18.5, 11.4 Hz, 2H, N-C*Ha*), 2.44 (m, 2H, N-C*Hb*), 2.1-1.2 (m, 18H, alkyl), 1.07 (t, J = 7.3 Hz, 3H, terminal CH_3), 1.03 – 0.94 (m, 9H, terminal CH_3). ^{13}C NMR (126 MHz, $CDCl_3$): δ= 161.34, 160.92, 160.70, 160.69, 157.78, 156.11, 156.09, 155.60, 155.51, 147.41, 147.32, 147.09, 147.08, 146.93, 146.92, 146.64, 146.63, 146.41, 146.27, 146.20, 146.10, 146.06, 146.05, 146.02, 145.97, 145.82, 145.60, 145.38, 145.35, 145.33, 145.24, 145.16, 145.15, 144.99, 144.97, 144.87, 144.83, 144.61, 144.55, 143.25, 143.17, 142.71, 142.68, 142.64, 142.57, 142.55, 142.52, 142.46, 142.23, 142.20, 142.18, 141.91, 141.81, 141.80, 141.73, 141.49, 140.07, 140.01, 139.93, 139.28, 137.10, 136.79, 136.77, 136.05, 136.03, 134.62, 134.58, 105.43, 105.38, 91.31, 91.24, 90.82, 90.78, 76.16, 76.15, 74.76, 74.71, 69.98, 69.96, 67.26, 67.18, 58.12, 57.77, 56.16, 55.32, 54.53, 54.43, 38.76, 38.19, 32.38, 32.27, 29.83, 29.31, 26.11, 24.71, 23.76, 23.36, 14.53, 14.37, 12.00, 10.77 ppm.

Compound F2. Yield 21% (100 mg). Obtained as a mixture of 5 stereoisomers. ^{1}H NMR (500 MHz, $CDCl_3$) δ= 8.32-8.27 (m, 2H, aromatic), 8.22-8.18 (m, 1H, aromatic), 7.98-7.95 (m, 1H, aromatic), 7.20-7.14 (m, 7H, aromatic), 7.0-6.85 (m, 6H, aromatic), 6.3-5.9 (m, 13H aromatic + 6H C*H*Ph), 4.17-4.15 (m, 4H, C*H*Ph), 3.9-3.66 (m, 6H, OCH_3), 3.2-2.58 (m, 10H, NCH_2), 1.9-1.0 (m, 45H, alkyl), 0.9-0.65 (m, 30H, terminal CH_3). ^{13}C NMR (126 MHz, $CDCl_3$) δ 161.82, 161.68, 161.40, 161.37, 161.28, 161.25, 161.08, 161.05, 160.91, 160.85, 160.67, 160.61, 160.52, 159.59, 159.54, 159.31, 158.89, 158.72, 158.69, 158.47, 158.44, 158.08, 158.03, 156.98, 156.95, 156.76, 156.74, 156.71, 156.36, 156.32, 156.22, 156.15, 155.83, 155.31, 155.10, 154.62, 154.56, 154.40, 154.31. 147.99, 147.97, 147.46, 147.43, 147.41, 147.40, 147.37, 147.31, 147.30, 147.26, 146.85, 146.81, 146.80, 146.78, 146.74, 146.72, 146.70, 146.67, 146.64, 146.59, 146.38, 146.35, 146.31, 146.26, 146.20, 146.18, 146.14, 146.12, 146.10, 146.00, 145.96, 145.94, 145.92, 145.90, 145.88, 145.85, 145.83, 145.79, 145.72, 145.71, 145.67, 145.35, 145.33, 145.32, 145.29, 145.26, 145.22, 145.16, 145.14, 145.12, 145.11, 145.10, 145.08, 145.06, 145.04, 144.94, 144.88, 144.84, 144.81, 144.73, 144.69, 144.66, 144.55, 144.53, 144.51, 144.49, 144.45, 143.19, 143.06, 143.03, 143.01, 142.77, 142.68, 142.65, 142.63, 142.61, 142.59, 142.57, 142.53, 142.49, 142.45, 142.44, 142.41, 142.37, 142.35, 142.34, 142.32, 142.27, 142.24, 142.17, 142.13, 142.11, 142.10, 142.02, 142.00, 141.90, 141.86, 141.78, 141.69, 141.67, 141.64, 141.61, 141.54, 141.53, 141.48, 141.43, 141.39, 140.00, 139.96, 139.92, 139.90, 139.88, 139.87, 139.83, 139.63, 139.60, 139.58, 139.55, 139.42, 139.40, 139.37, 139.34, 139.27, 139.22, 139.16, 139.12, 139.04, 139.03, 138.01, 137.02, 136.97, 136.95, 136.90, 136.85, 136.83, 136.55, 136.47, 135.91, 135.88, 135.76, 135.74, 134.76, 134.69, 134.56, 134.53, 134.48, 134.46, 134.45, 134.39, 133.60, 133.58, 132.68, 132.51, 131.86, 131.71, 130.71, 130.67, 130.22, 130.08, 129.63, 129.47, 129.18, 128.76, 128.75, 128.49, 128.47, 128.37, 127.37, 127.32, 125.44, 124.91, 124.78, 121.26, 121.20, 121.10, 121.00, 120.94, 120.82, 117.62, 111.40, 110.94, 110.90, 108.61, 108.59, 106.83, 106.70, 102.60, 102.43, 94.39, 91.39, 91.33, 91.25, 91.18, 90.94, 90.91, 90.73, 90.68, 90.62, 90.36, 90.32, 75.84, 75.81, 75.53, 75.43, 75.36, 75.29, 74.85, 74.73, 74.65, 74.44, 74.29, 74.17, 74.13, 73.98, 73.57, 73.35, 72.33, 72.23, 71.46, 65.94, 65.78, 58.35, 57.80, 56.47, 56.26, 56.19, 56.07, 56.06, 55.73, 55.61, 55.57, 55.53, 55.51, 55.50, 55.46, 55.45, 55.41, 55.37, 55.33, 55.32, 54.94, 54.91, 54.56, 54.48, 51.80, 37.72, 37.59, 36.64, 36.57, 35.13, 34.24, 34.21, 33.37, 33.08, 32.87, 32.08, 31.67, 31.62, 29.35, 29.21, 29.06, 29.02, 28.85, 28.74, 26.92, 26.30,

26.02, 25.43, 25.12, 24.75, 23.47, 23.43, 23.18, 23.12, 22.88, 21.61, 14.59, 14.46, 14.39, 14.37, 14.34, 14.29, 11.60, 11.50, 11.16, 11.06, 11.00, 10.69.

Compound F3. Yield 42% (177 mg). Obtained as a mixture of 2 isomers. ^{1}H NMR (500 MHz, $CDCl_3$) δ= 7.89 (m, 2H, aromatic), 6.6 (m, 2H, aromatic), 6.48 (m, 2H, aromatic), 5.58 (s, 1H, C*H*Ph), 5.57 (s, 1H, C*H*Ph), 5.05 (m, 2H, C*Ha*H), 4.06 (m, 2H, C*Hb*H), 3.81 (s, 6H, OCH_3), 3.70 (s, 6H, OCH_3), 3.02 (m, 2H, N-C*Ha*), 2.45 (m, 2H, N-C*Hb*), 2.12-1.20 (m, 18H, alkyl), 0.94-1.12 (m, 12H, terminal CH_3). ^{13}C NMR (126 MHz, $CDCl_3$) δ= 160.45, 159.46, 159.43, 157.51, 155.49, 154.84, 154.42, 147.42, 146.99, 146.79, 146.64, 146.37, 146.34, 146.30, 146.22, 146.19, 146.06, 146.04, 145.89, 145.88, 145.80, 145.73, 145.67, 145.42, 145.40, 145.39, 145.36, 145.21, 145.19, 145.15, 144.78, 144.72, 144.58, 144.52, 143.19, 143.12, 142.77, 142.75, 142.70, 142.66, 142.50, 142.48, 142.32, 142.30, 142.23, 142.11, 142.03, 142.01, 141.85, 141.82, 141.70, 140.30, 140.22, 139.66, 139.58, 136.72, 136.52, 136.28, 134.68, 134.66, 131.21, 118.43, 105.24, 105.16, 98.73, 98.70, 76.43, 74.73, 74.67, 69.33, 67.28, 67.18, 57.84, 57.75, 55.43, 38.50, 38.11, 31.94, 31.46, 29.85, 29.66, 28.56, 25.62, 24.45, 23.59, 23.33, 14.54, 14.35, 11.92, 10.73 ppm.

Compound F4. Yield 41% (173 mg). Obtained as a mixture of 2 isomers. ^{1}H NMR (500 MHz, $CDCl_3$) δ= 7.62 (m, 2H, aromatic), 7.13 (t, 2H, *J* = 8.1 Hz, aromatic), 6.86 (m, 2H, aromatic), 5.61 (s, 2H, C*H*Ph), 5.07 (m, 2H, C*Ha*H), 4.07 (m, 2H, C*Hb*H), 3.88 (s, 6H, OCH_3), 3.87 (s, 6H, OCH_3), 2.90 (m, 2H, N-C*Ha*), 2.45 (m, 2H, N-C*Hb*), 2.05-1.88 (m, 4H), 1.75-1.22 (m, 14H, alkyl), 1.07 – 0.92 (m, 12H, terminal CH_3). ^{13}C NMR (126 MHz, $CDCl_3$) δ= 152.74, 148.97, 148.94, 147.44, 147.42, 146.80, 146.73, 146.40, 146.36, 146.34, 146.24, 146.21, 146.19, 146.08, 146.06, 145.91, 145.89, 145.76, 145.72, 145.66, 145.47, 145.43, 145.42, 145.41, 145.36, 145.30, 145.28, 145.23, 144.80, 144.76, 144.58, 144.50, 143.24, 143.23, 143.12, 142.76, 142.72, 142.70, 142.67, 142.49, 142.47, 142.43, 142.32, 142.26, 142.25, 142.18, 142.13, 142.12, 142.03, 142.01, 141.90, 141.83, 141.73, 140.26, 140.11, 139.58, 139.57, 136.16, 136.15, 135.29, 135.27, 124.15, 124.10, 122.71, 122.69, 111.84, 76.27, 75.36, 75.31, 69.47, 67.23, 67.12, 61.41, 57.81, 57.69, 55.74, 38.42, 37.96, 31.85, 31.34, 29.66, 28.35, 25.56, 24.28, 23.56, 23.29, 14.51, 14.32, 11.91, 10.46.

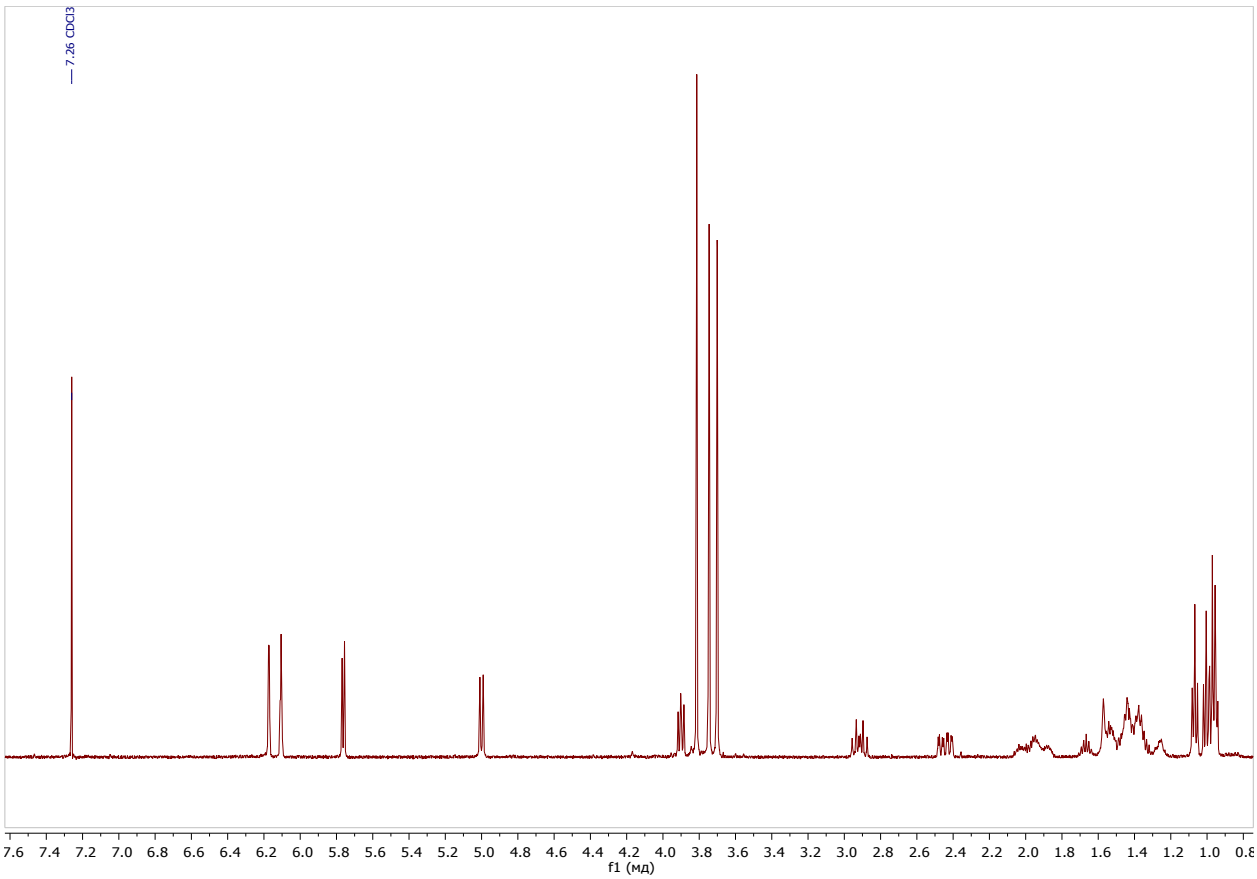

Figure S1. ^{1}H NMR spectrum of pyrrolidinofullerene **F1** (2 isomers)

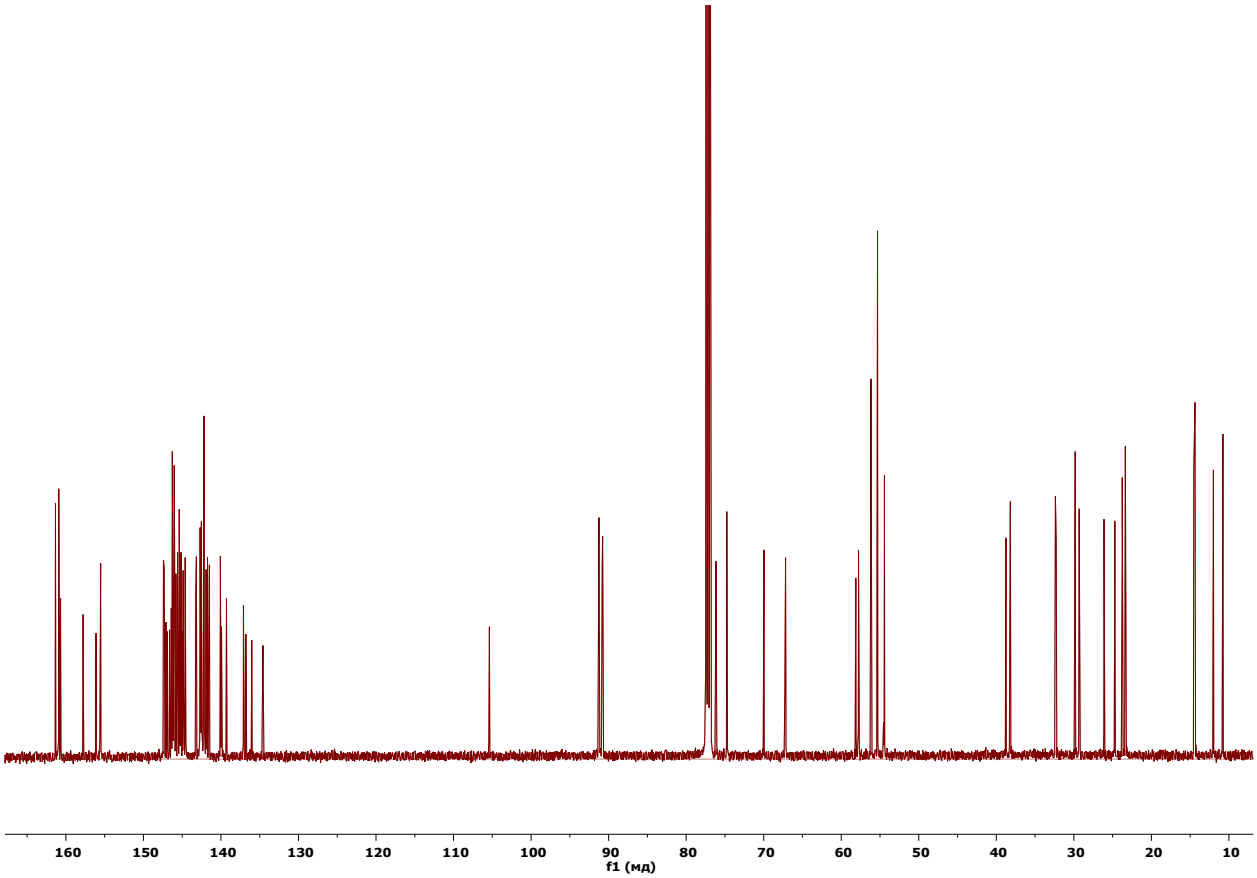

Figure S2. ^{13}C NMR spectrum of pyrrolidinofullerene **F1** (2 isomers)

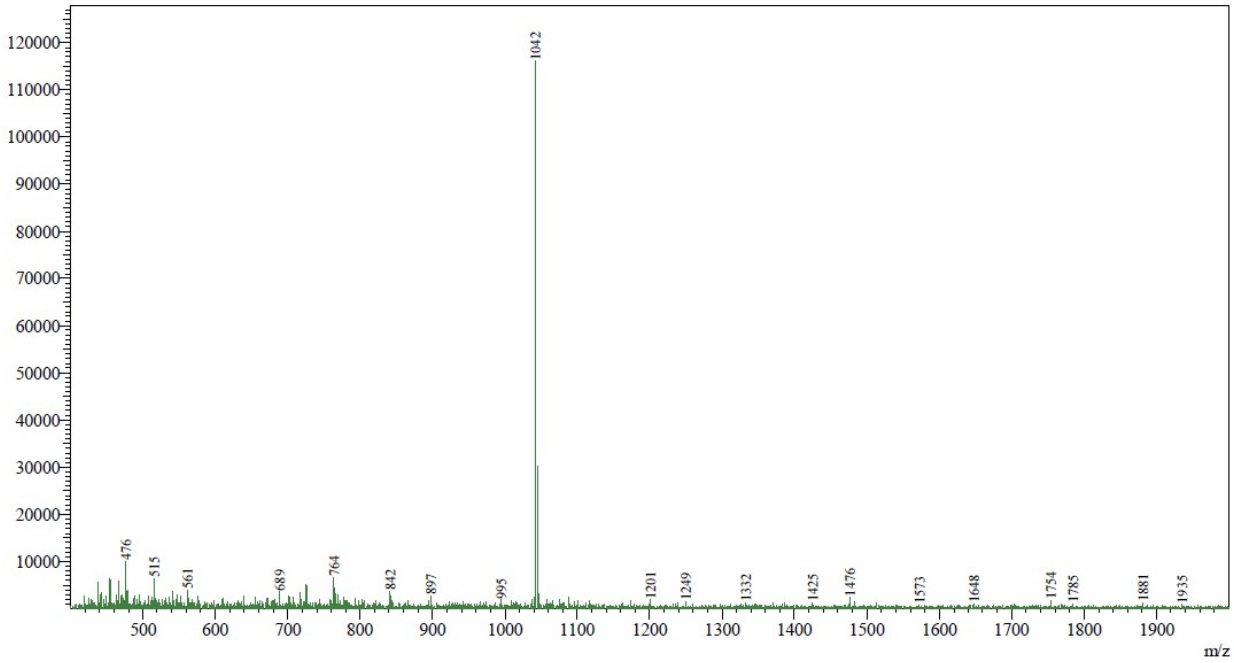

Figure S3. Electrospray MS spectrum of pyrrolidinofullerene **F1**, $(M+H)^+$=1042

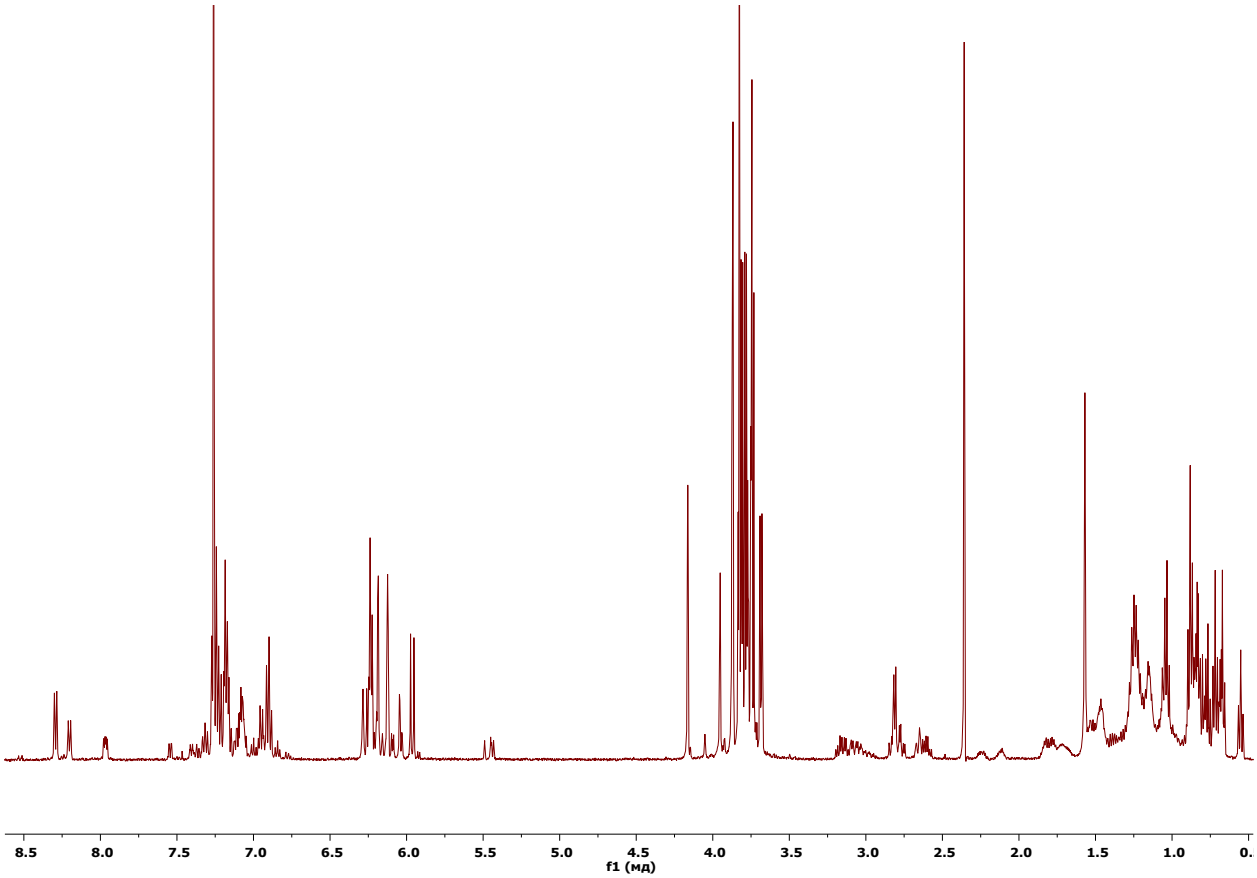

Figure S4. ^{1}H NMR spectrum of pyrrolidinofullerene **F2** ($CDCl_3$)

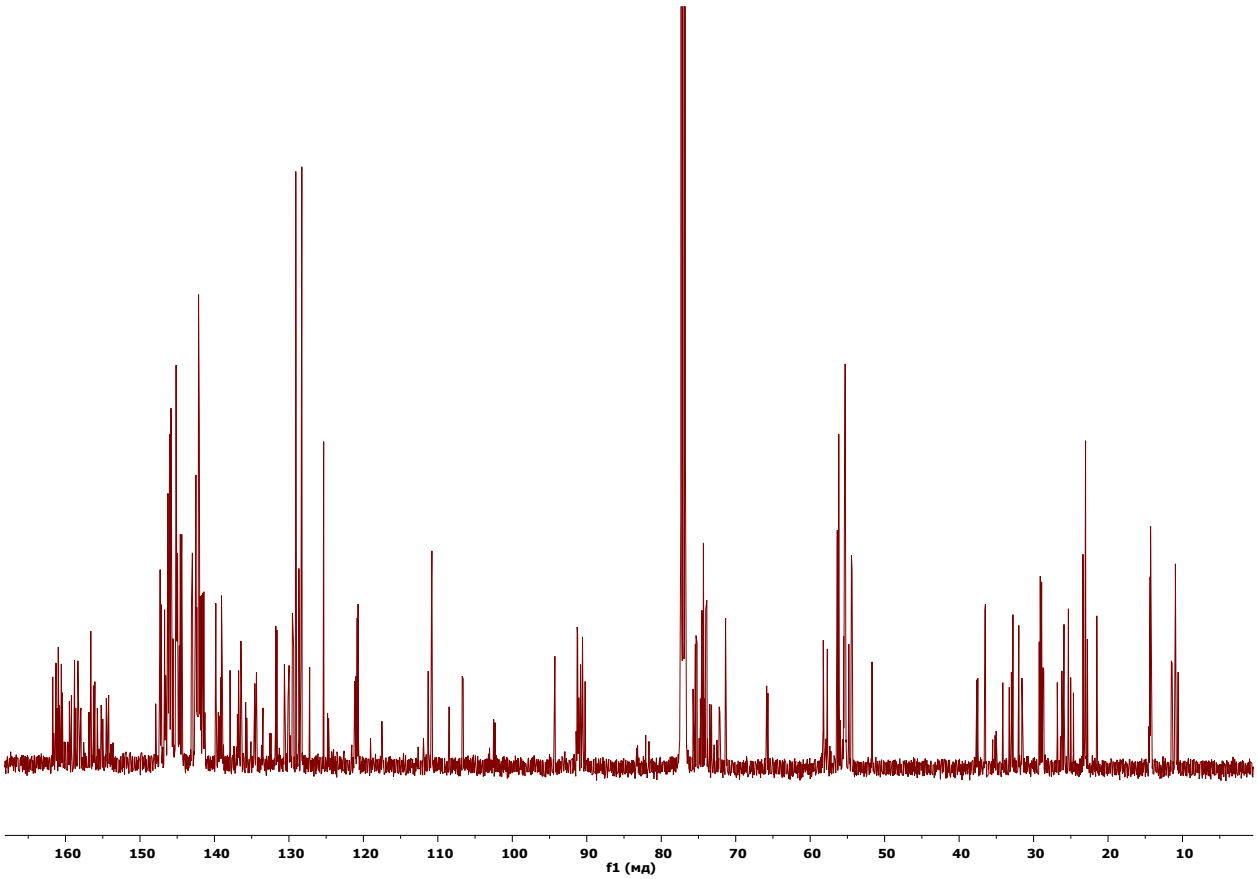

Figure S5. ^{13}C NMR spectrum of pyrrolidinofullerene **F2**

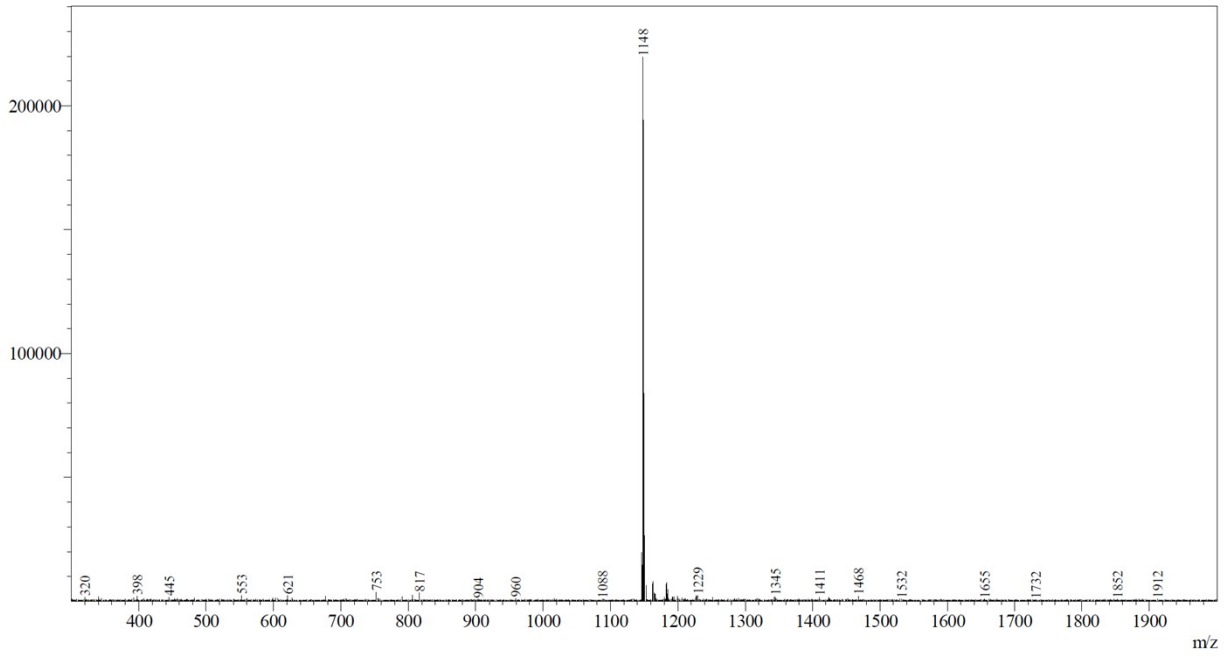

Figure S6. Electrospray MS spectrum of pyrrolidinofullerene **F2**, $(M+H)^+$=1148

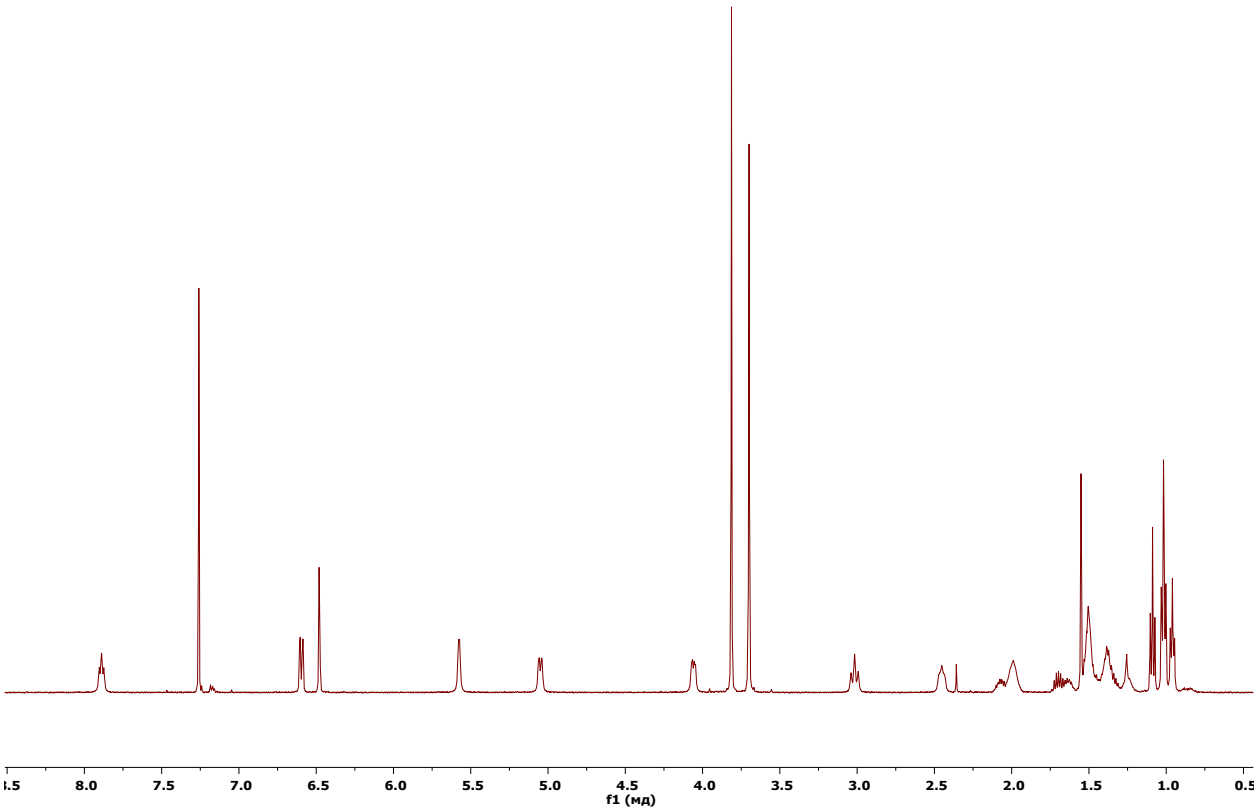

Figure S7. ^{1}H NMR spectrum of pyrrolidinofullerene **F3** (2 isomers)

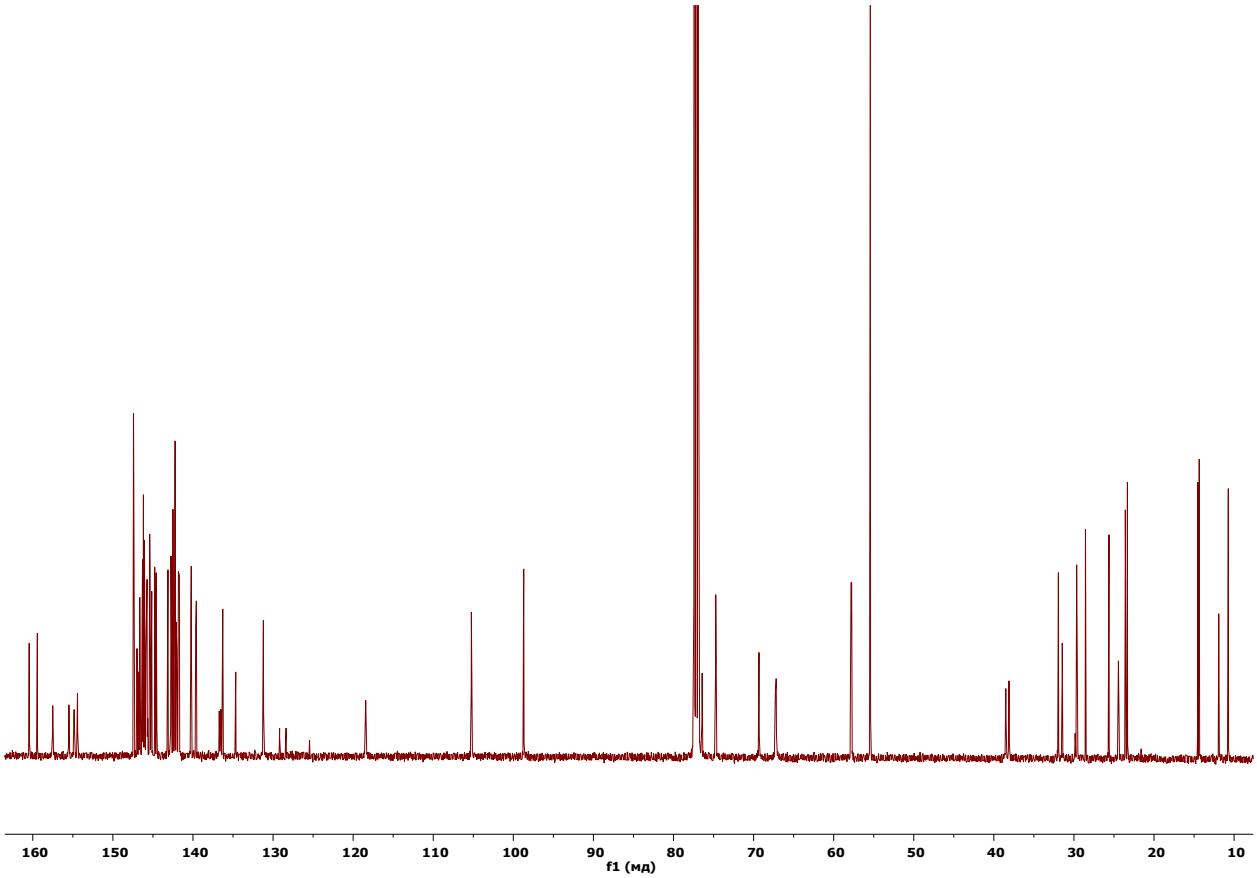

Figure S8. ^{13}C NMR spectrum of pyrrolidinofullerene **F3** (2 isomers)

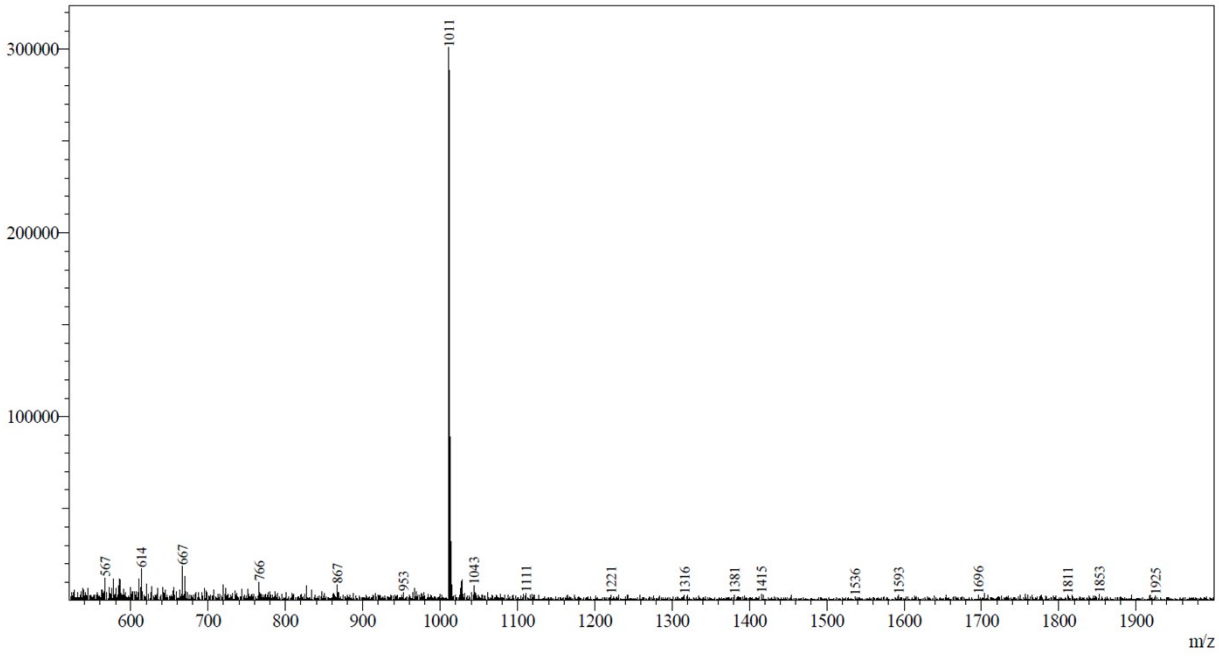

Figure S9. Electrospray MS spectrum of pyrrolidinofullerene **F3**, M^-=1011

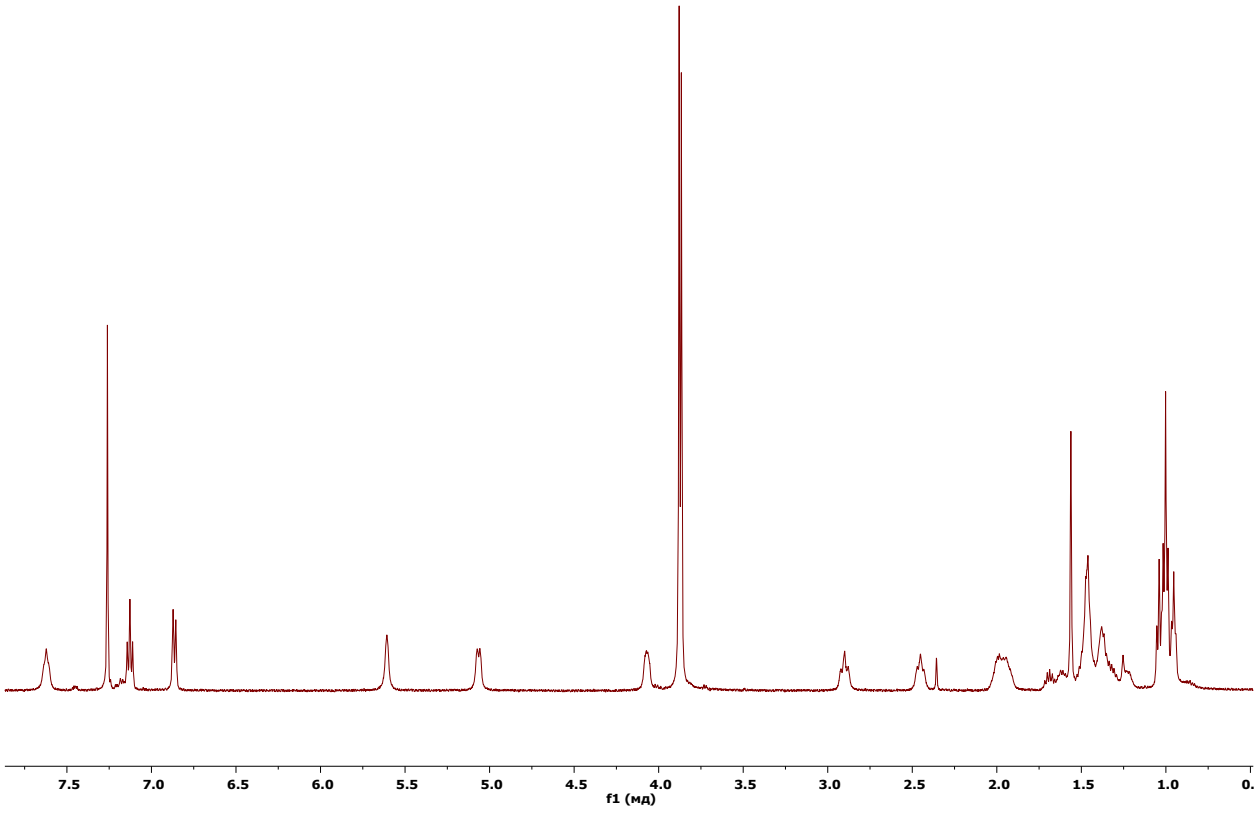

Figure S10. ^{1}H NMR spectrum of pyrrolidinofullerene **F4** (2 isomers)

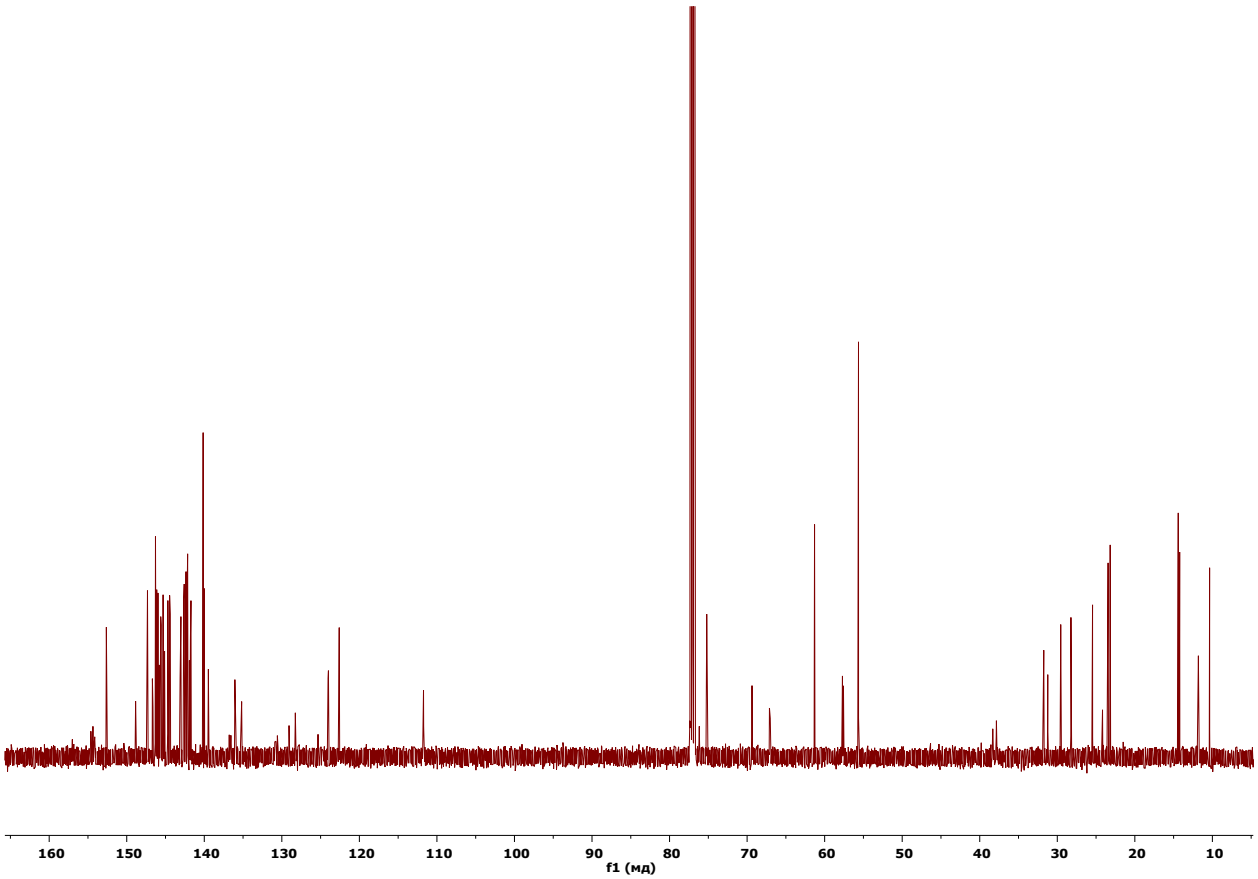

Figure S11. ^{13}C NMR spectrum of pyrrolidinofullerene **F4** (2 isomers)

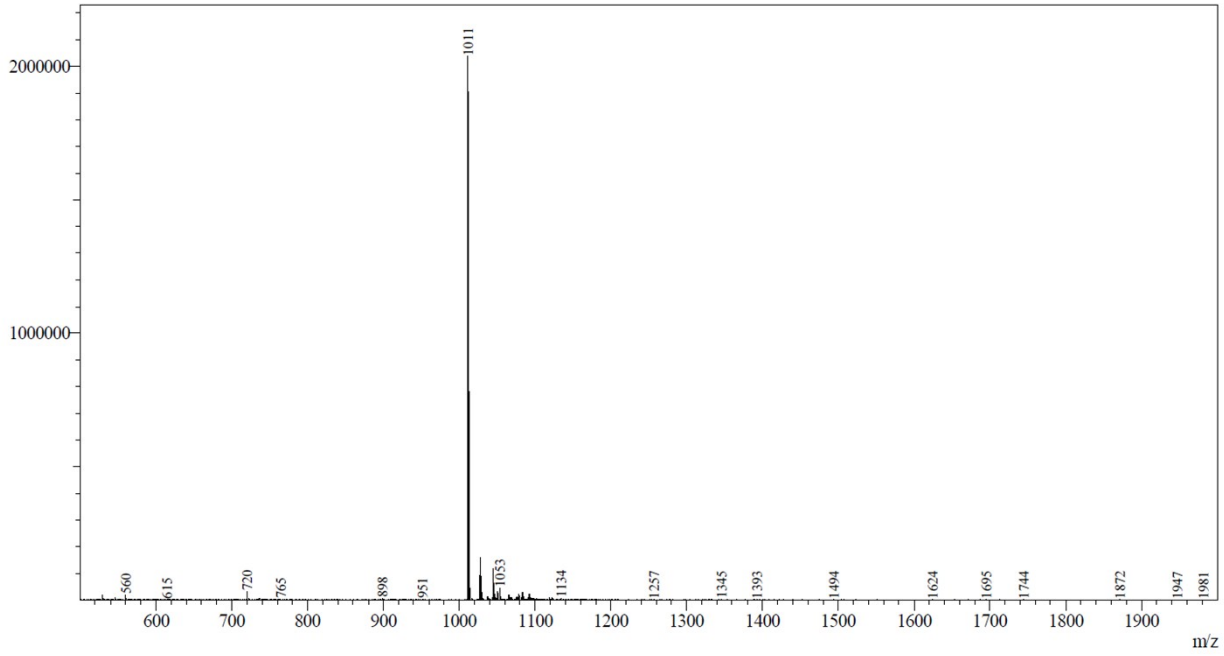

Figure S12. Electrospray MS spectrum of pyrrolidinofullerene **F4**, M^-=1011

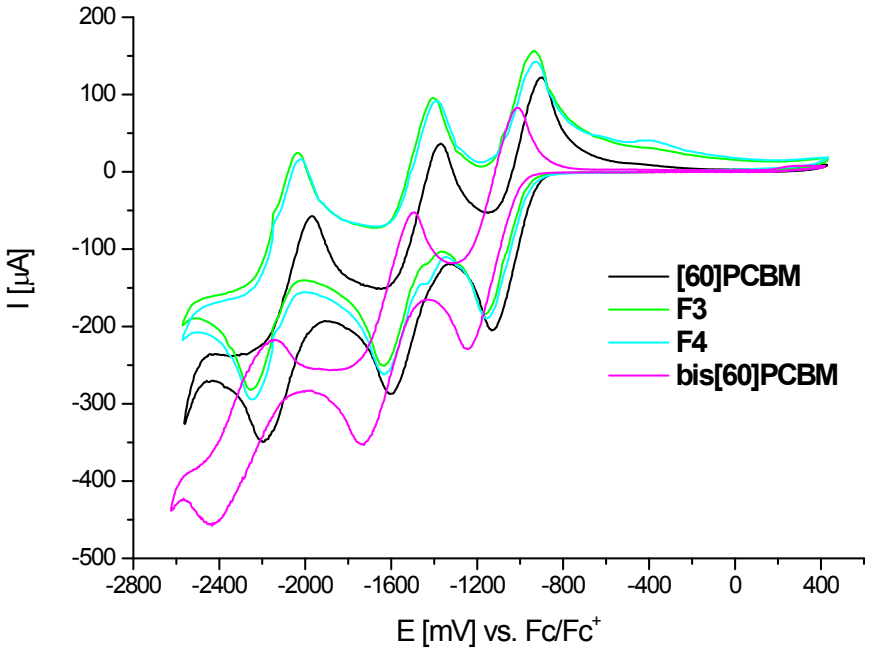

Figure S13. Cyclic voltammograms of the pyrrolidinofullerenes **F3**,**F4,** [60]PCBM and bis[60]PCBM

Table S1. Photovoltaic performance of **F1**-**F4** with P3HT and PCDTBT

Composite	Ratio	Anneal	V_{OC}, mV	J_{SC}, mA/cm^2	FF, %	η, %
P3HT/ [60]PCBM	1:0.5	165 ^{0}C, 3 min	599	8.5	60	3.0
P3HT/ **F1**	1:0.7	90 ^{0}C, 15 min	747	7.7	59	3.4
P3HT/ **F2**		140 ^{0}C, 3 min	772	8.6	55	3.7
P3HT/ **F3**	1:0.5	165 ^{0}C, 3 min	735	9.1	53	3.5
P3HT/ **F4**			709	8.5	55	3.3
PCDTBT/ [60]PCBM	1:4	90 ^{0}C, 15 min	871	7.8	60	4.1
PCDTBT/ **F1**	1:2		849	4.0	34	1.1
PCDTBT/ **F2**			981	3.6	29	1.0
PCDTBT/ **F3**	1:2		983	8.9	47	4.1
PCDTBT/ **F4**	1:3		957	8.3	52	4.1

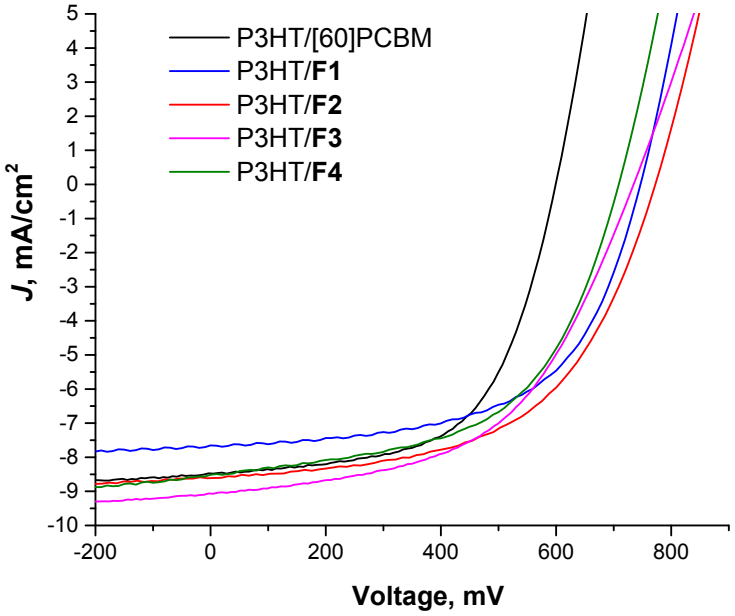

Figure S14. J-V curves of the solar cells based on the composites of the fullerene derivatives **F1**- **F4** with P3HT

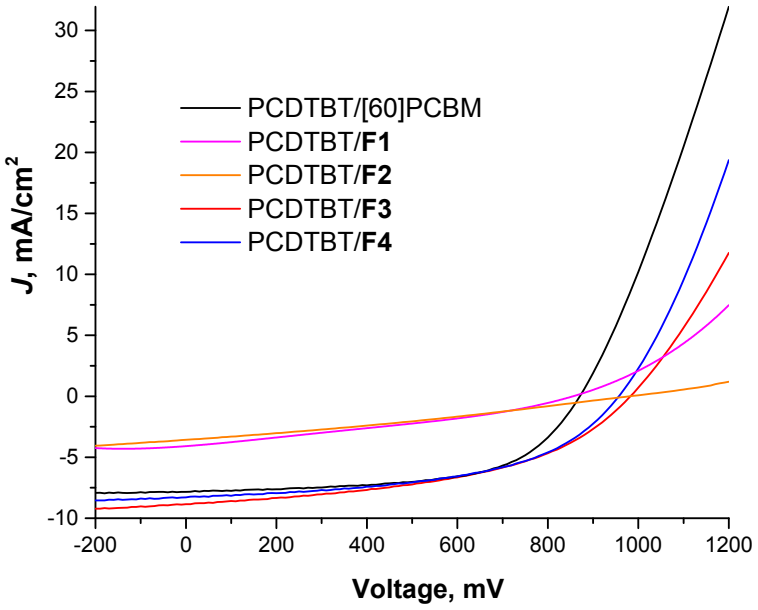

Figure S15. J-V curves of the solar cells based on the composites of the fullerene derivatives **F1**- **F4** with PCDTBT

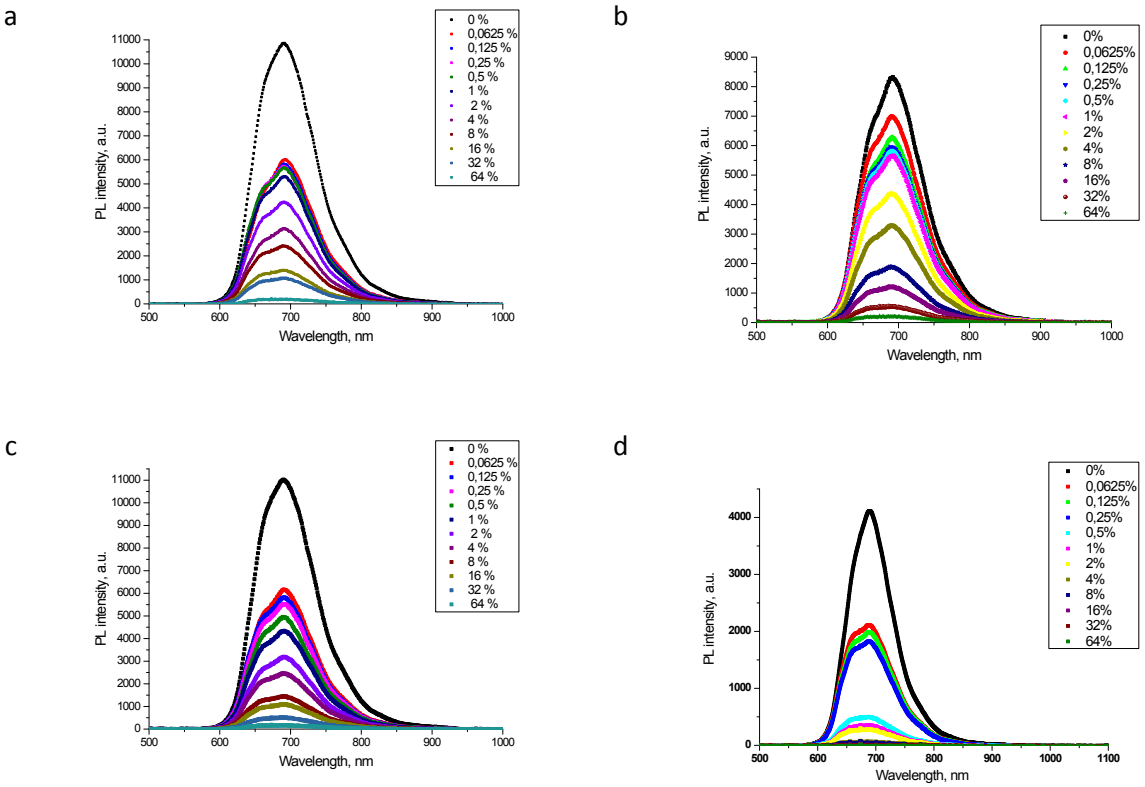

Figure S16. PL quenching of PCDTBT by fullerene derivatives **F1 (a)**, **F2 (b)**, **F3 (c) and F4 (d**)

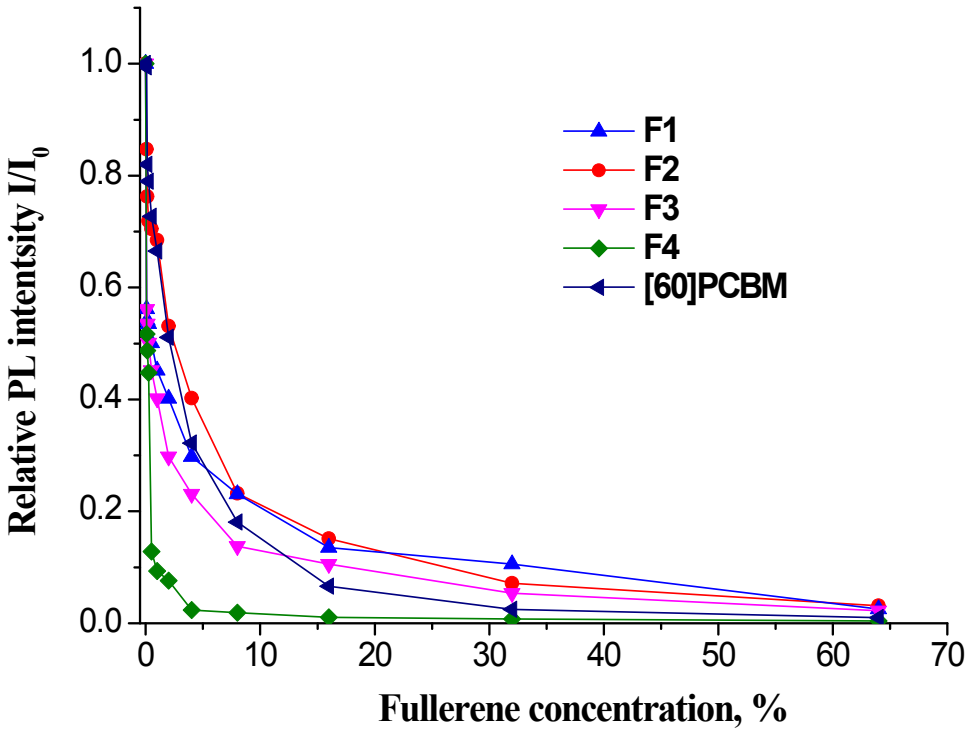

Figure S17. Relative intensity of the PCDTBT photoluminescence in thin films as a function of the fullerene derivatives concentration

[i] C. Fotsch, M. D. Bartberger, E. A. Bercot, M. Chen, R. Cupples, M. Emery, J. Fretland, A. Guram, C. Hale, N. Han, D. Hickman, R. W. Hungate, M. Hayashi, R. Komorowski, Q. Liu, G. Matsumoto, D. J. St. Jean, S. Ursu, M. Véniant, G. Xu, Q. Ye, C. Yuan, J. Zhang, X. Zhang, H. Tu and M. Wang, *J. Med. Chem.,* 2008, **51**, 7953–7967.