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Fullerene-based carboxylic acids for improving performance and stability of perovskite solar cells

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Experimental

1. General

Synthesis: all solvents and reagents were purchased from commercial suppliers (Acros Organics, Sigma-Aldrich) and used as received or purified following the standard methods. All obtained compounds were purified to achieve the purity of at least 99.5% according to HPLC or NMR spectroscopy. The ^{1}H, ^{13}C and 2D NMR spectra in CS_2-acetone-d6 solutions were obtained using Bruker AVANCE III 500 instrument. MALDI mass spectra were obtained using an Axima Confidence time-of-flight spectrometer (Shimadzu Biotech) equipped with a reflectron detector operating in high resolution mode, utilizing a nitrogen laser (λ = 337.1 nm, maximum pulse frequency 50 Hz). Negative ions were recorded. A MALDI matrix trans-2-[3-(4-tert-Butylphenyl)-2-methyl-2-propenylidene]malononitrile (DCTB, Sigma Aldrich) was used for analysis.

To prepare the matrix solution, a concentration of 10 mg/ml was achieved by dissolving DCTB in chlorobenzene (99%, ITW Reagents (PanReac AppliChem)). All sample solutions were also prepared in chlorobenzene at a concentration of 1 mg/ml. Each sample solution was pre-mixed with the matrix solution (1:10, v/v) in an Eppendorf tube and 1 μl of the resulting mixture was applied onto the stainless steel MALDI MS target for analysis.

Device fabrication: PbI_2 (99.9%) was purchased from LANHIT. Anhydrous N,N-dimethylformamide (DMF) (99.8%), N-Methyl-2-pyrrolidone (NMP) (99.5%), and toluene (99.8%) were received from ACROS. PCBA, PTA and methylammonium iodide (CH_3NH_3I) were purchased from FOMaterials Ltd., Russia. SnO_2 layers were prepared using the solution of tin (IV) oxide (15 wt. % in H_2O, colloidal dispersion, Alfa Aesar. V_2O_5 (99.6 %) was received from Aldrich. Contact angle measurements were performed using drop shape analyzer DSA25S Kruss (Germany) in a sessile drop mode.

2. Synthesis of fullerene derivatives F1-F3

Fullerene derivative (**1**, **2** or **3**) (100 mg) was dissolved in toluene (20 mL) in a two-necked round bottom flask equipped with a condenser, thermometer, and PTFE-coated magnetic stirring bar. Acetic acid (20 mL) and hydrochloric acid (5 mL) were added to the reaction mixture. The reaction mixture was heated at 70^{o}C for a week and then allowed to cool down to room temperature. The reaction mixture was concentrated using the rotary evaporator, and residue was washed with methanol and dried in air. Fullerene derivatives **F1-F3** were obtained with 93–97% yields as brown powders.

3. Perovskite solar cell fabrication and characterization

The perovskite solar cells were assembled in the ITO/SnO_2/PCBA or NDI/$CH_3NH_3PbI_3$/PTA/VO_x/Ag (or Al). ITO substrates (15 Ohm/sq., Kintec, China) were cleaned sequentially with detergent, deionized water, acetone, and isopropyl alcohol followed by drying with N_2 and RF plasma treatment for 5 min. SnO_2 (10% in H_2O colloidal dispersion) was deposited twice on ITO at 4000 rpm for 30 s and the films were annealed at 170 °C for 15 min. The SnO_2 films were transferred into the nitrogen filled glove box for spin-coating of PCBA (0.2 mg mL^{-1} in toluene) or **F1-F3** (0.1 mg mL^{-1} in chlorobenzene) at 3000-3500 rpm for 30 s and following annealing at 100 °C for 10 min.

$MAPbI_3$ precursor solution contained 1.45 M PbI_2 and 1.40 M MAI in anhydrous DMF:NMP 85:15 (v/v). The perovskite films were grown by spin coating the $MAPbI_3$ solution at 4000 rpm for 40 s. Toluene (160 μL) was dripped as an antisolvent quencher 12 s after starting the spin coating process. The $MAPbI_3$ films were annealed at 85 °C for 5 min. After the perovskite annealing, the substrates were cooled down for few minutes and the PTA solution (5 mg mL^{-1} in chlorobenzene) was deposited above the absorber layer by spin-coating at 1000 rpm for 30 s. Finally, a hole-selective and electron-blocking interfacial layer of V_2O_{5-x} (30 nm) and Ag (or Al) electrode (~120 nm) were deposited by thermal evaporation of vanadium (V) oxide and the corresponding metals under a vacuum of ~5×10^{-6} mbar through a shadow mask.

The device characterization was performed inside MBraun glove box under nitrogen atmosphere using simulated AM 1.5G irradiation (K.H. Steuernagel Lichttechnik GmbH) at 100 mW/cm^2 using Advantest R6240A source-measurement units. The light flux was calibrated by a silicon diode with a known spectral response. The external quantum efficiency (EQE) spectra were obtained using a home-made setup with 300 W Xenon lamp as a light source and automatic monochromator from LOMO instruments, Russia. The signal detection and processing were performed using SR510 lock-in amplifier combined with SR540 optical chopper (both from Stanford Research Instruments, USA).

Spectral data for the synthesized compounds

Compound **F1**. ^{1}H NMR (500 MHz, CS_2+$(CD_3)_2CO$) δ 8.04 – 7.99 (m, 2H), 7.62 – 7.56 (m, 2H), 7.55 – 7.48 (m, 1H), 3.26 – 3.17 (m, 2H), 2.87 – 2.75 (m, 2H). ^{13}C NMR (126 MHz, CS_2+$(CD_3)_2CO$) δ 172.28, 148.98, 147.93, 146.12, 145.38, 145.27, 145.24, 145.23, 145.14, 145.00, 144.84, 144.75, 144.56, 144.52, 144.18, 143.86, 143.15, 143.12, 143.06, 143.01, 142.40, 142.27, 142.25, 142.16, 141.04, 140.79, 138.33, 136.32, 132.28, 128.69, 128.55, 79.97, 31.25, 29.89. MALDI MS: m/z=882.50 ($[M]^-$), calculated for $C_{70}H_{10}O_2$ ($[M]^-$): 882.07.

Compound **F2**. ^{1}H NMR (500 MHz, CS_2+$(CD_3)_2CO$) δ 7.52 – 7.48 (m, 2H), 7.15 (dd, *J* = 5.0, 3.7 Hz, 1H), 3.01 – 2.94 (m, 2H), 2.51 (t, *J* = 7.3 Hz, 2H), 2.25 – 2.15 (m, 2H). ^{13}C NMR (126 MHz, CS_2+$(CD_3)_2CO$) δ 174.07, 148.36, 147.61, 145.79, 145.30, 145.27, 145.25, 145.24, 144.87, 144.85, 144.81, 144.72, 144.63, 144.59, 144.33, 143.90, 143.88, 143.15, 143.13, 143.08, 143.03, 143.02, 142.25, 142.23, 142.19, 141.06, 140.80, 139.15, 138.43, 138.39, 132.01, 126.55, 126.35, 80.05, 46.21, 34.24, 33.40. MALDI MS: m/z=902.50 ($[M]^-$), calculated for $C_{69}H_{10}O_2S$ ($[M]^-$): 902.04.

Compound **F3**. ^{1}H NMR (500 MHz, CS_2+$(CD_3)_2CO$) δ 4.08 – 3.98 (m, 2H), 2.91 – 2.81 (m, 2H), 2.38 – 2.32 (m, 2H), 1.78 – 1.71 (m, 2H). ^{13}C NMR (126 MHz, CS_2+$(CD_3)_2CO$) δ 173.73, 148.56, 145.98, 145.23, 145.14, 144.79, 144.40, 144.24, 143.78, 143.12, 143.03, 142.30, 142.26, 140.85, 137.82, 51.83, 32.36, 30.20, 28.86, 24.55. MALDI MS: m/z=878.52 ($[M]^-$), calculated for $C_{67}H_{10}O_4$ ($[M]^-$): 878.06.

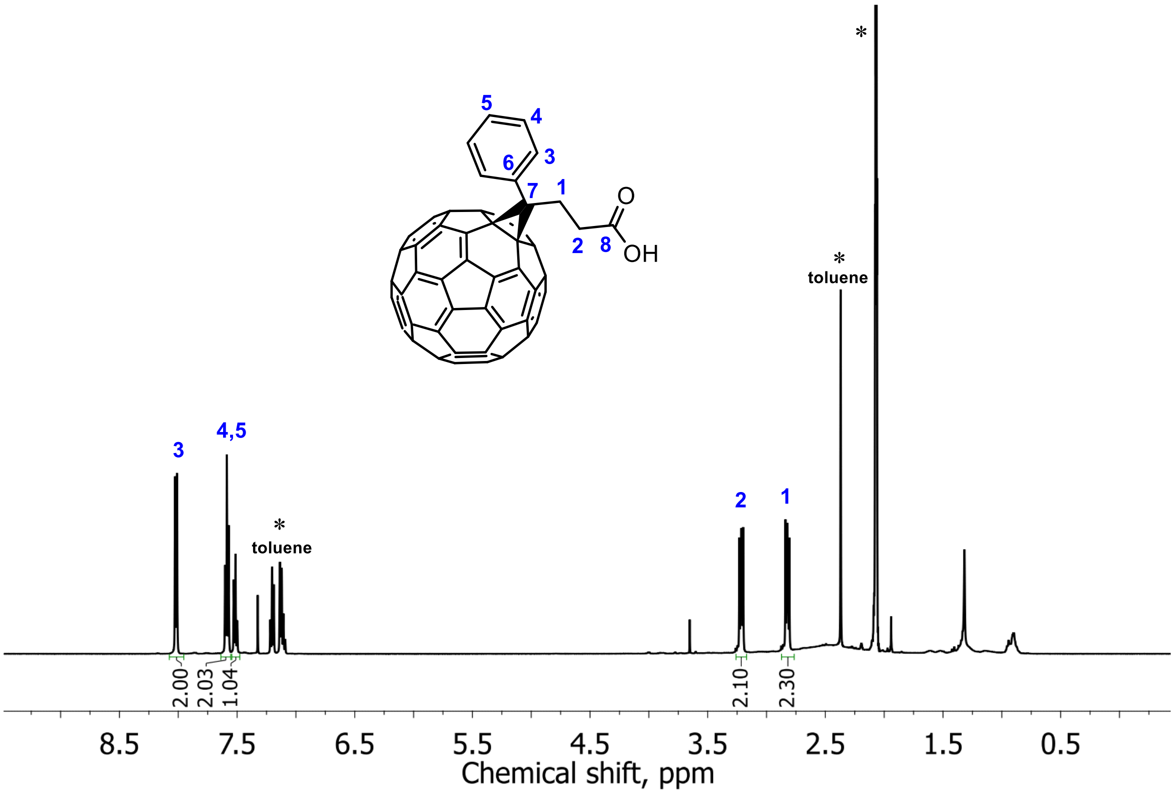

Figure S1. ^{1}H NMR spectrum of compound **F1**. * Denotes signals of toluene and acetone.

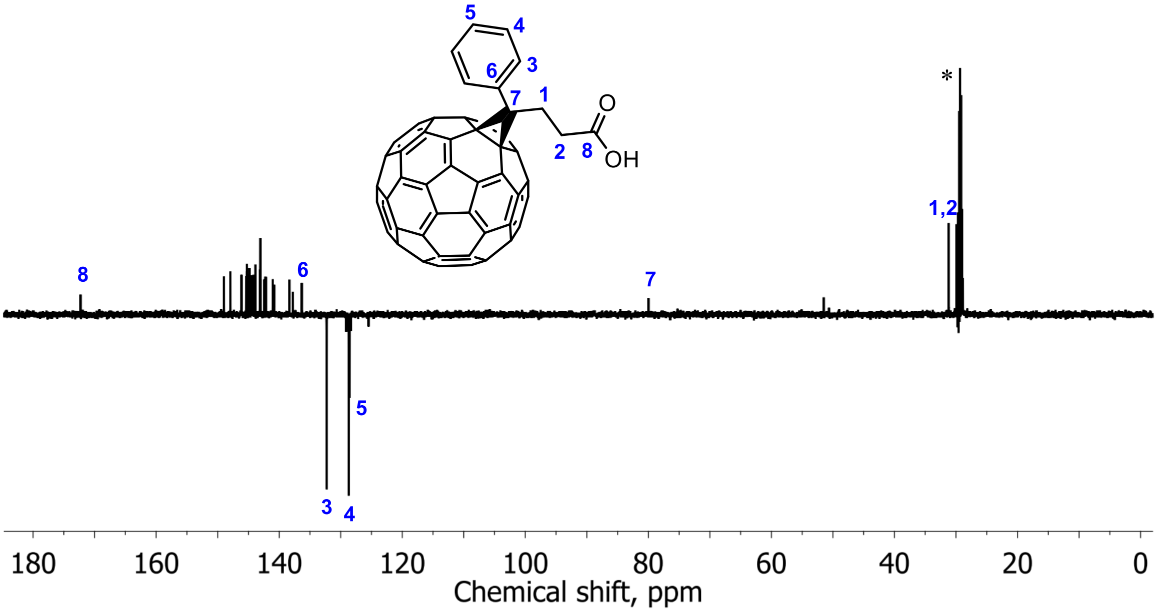

Figure S2. *J*-modulated spin-echo ^{13}C NMR spectrum of compound **F1**. * Denotes signals of acetone.

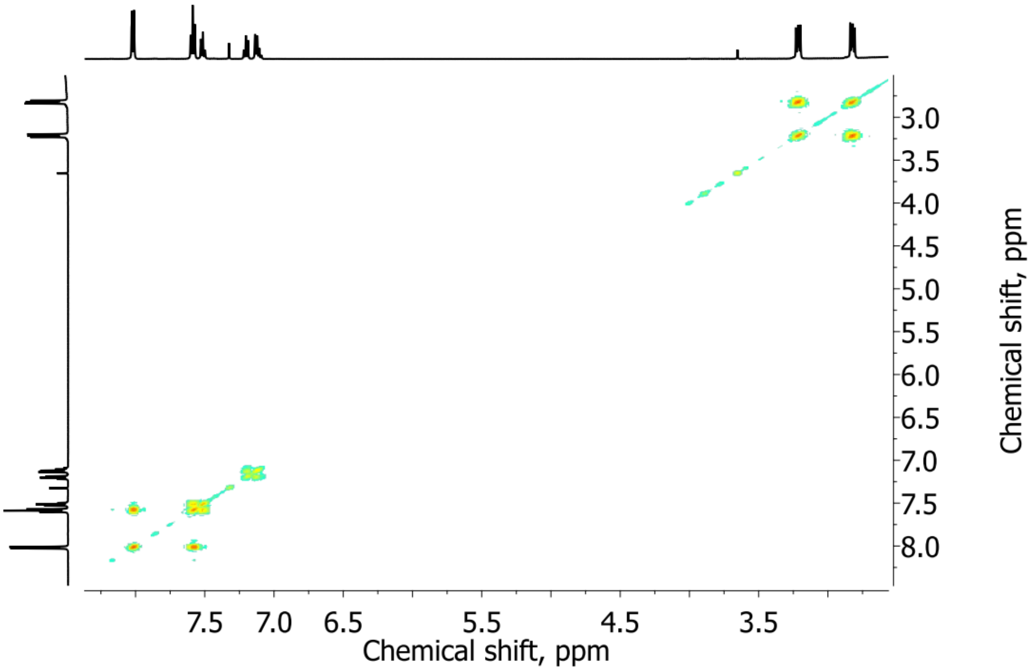

Figure S3. ^{1}H-^{1}H COSY NMR spectrum of compound **F1**.

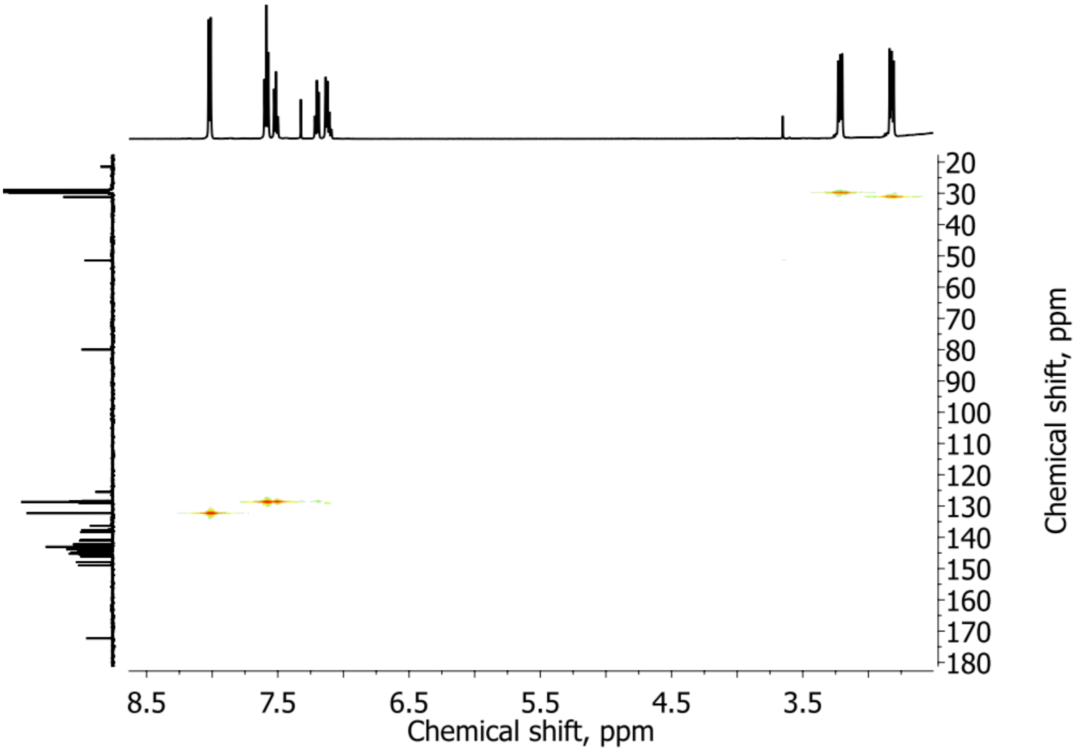

Figure S4. ^{1}H-^{13}C HSQC NMR spectrum of compound **F1**.

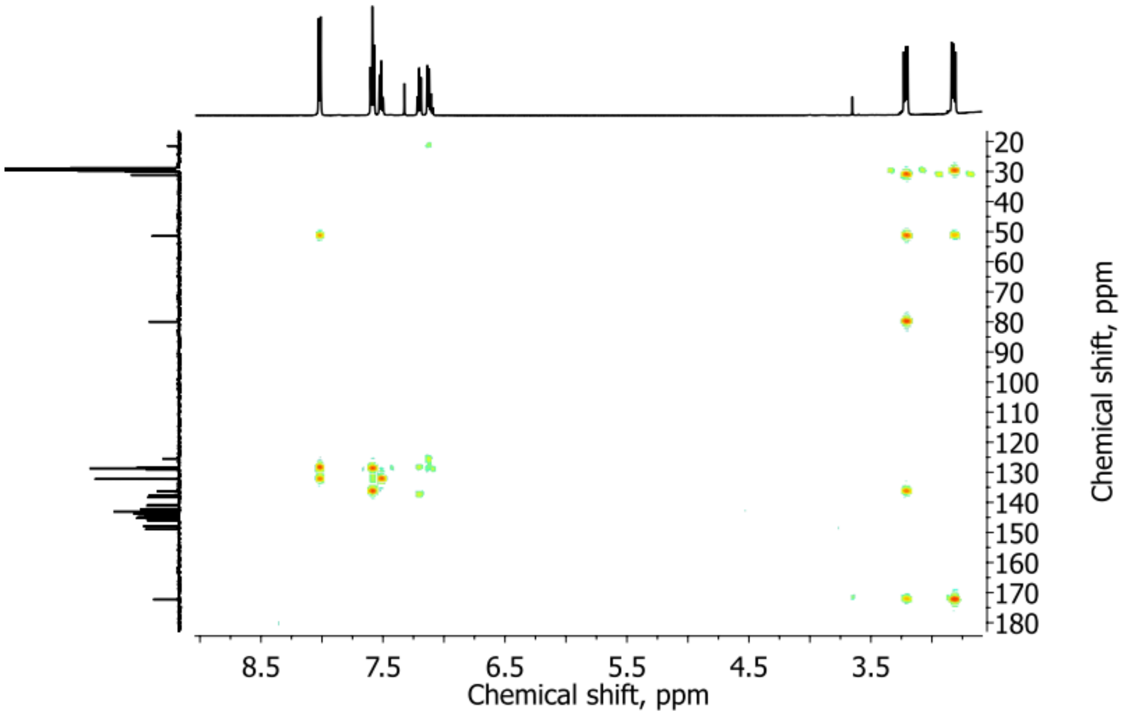

Figure S5. ^{1}H-^{13}C HMBC NMR spectrum of compound **F1**.

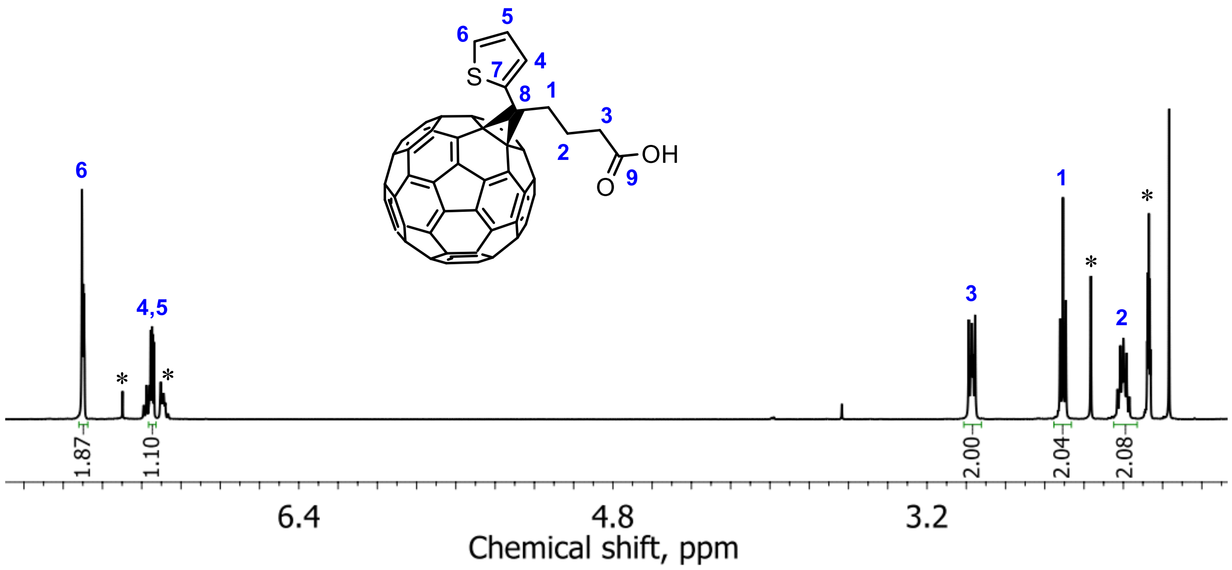

Figure S6. ^{1}H NMR spectrum of compound **F2**. * Denotes signals of toluene and acetone.

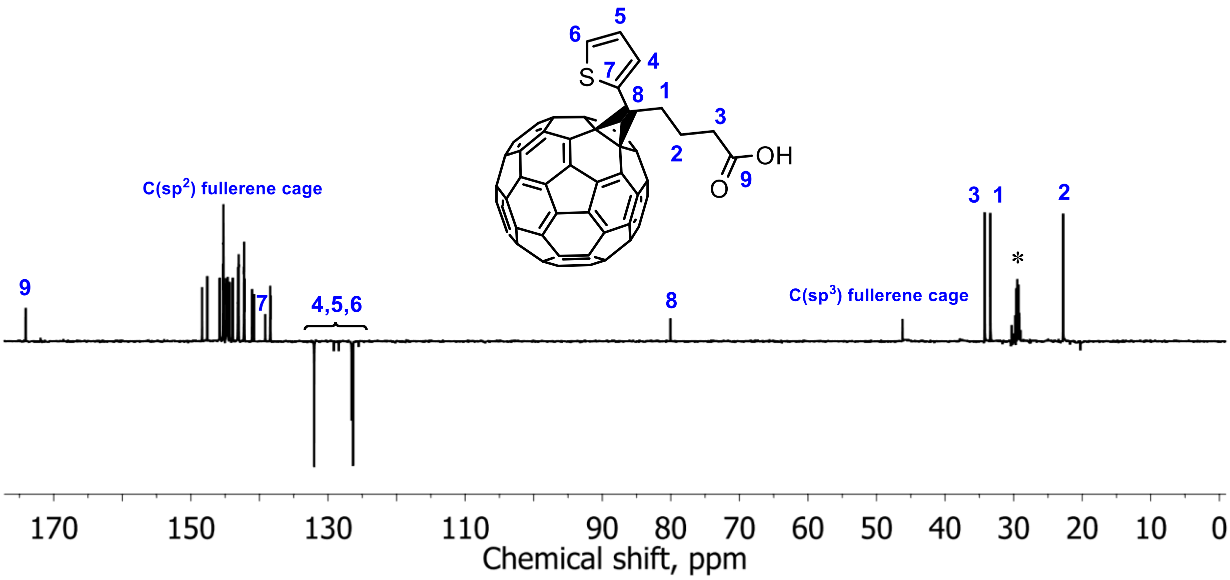

Figure S7. *J*-modulated spin-echo ^{13}C NMR spectrum of compound **F2**. * Denotes signals of acetone.

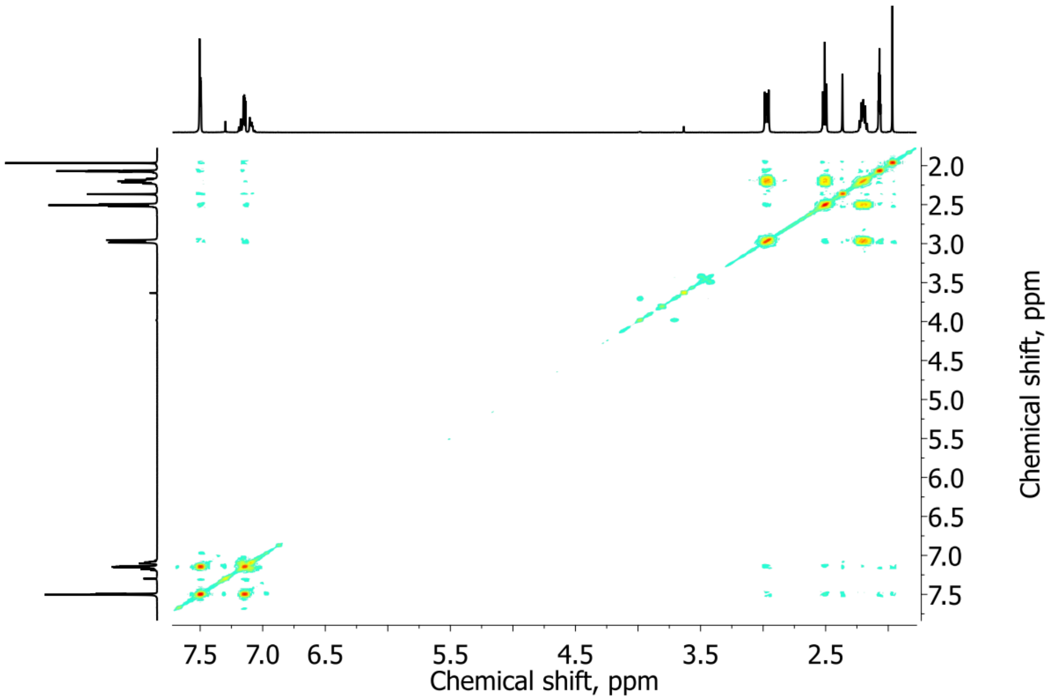

Figure S8. ^{1}H-^{1}H COSY NMR spectrum of compound **F2**.

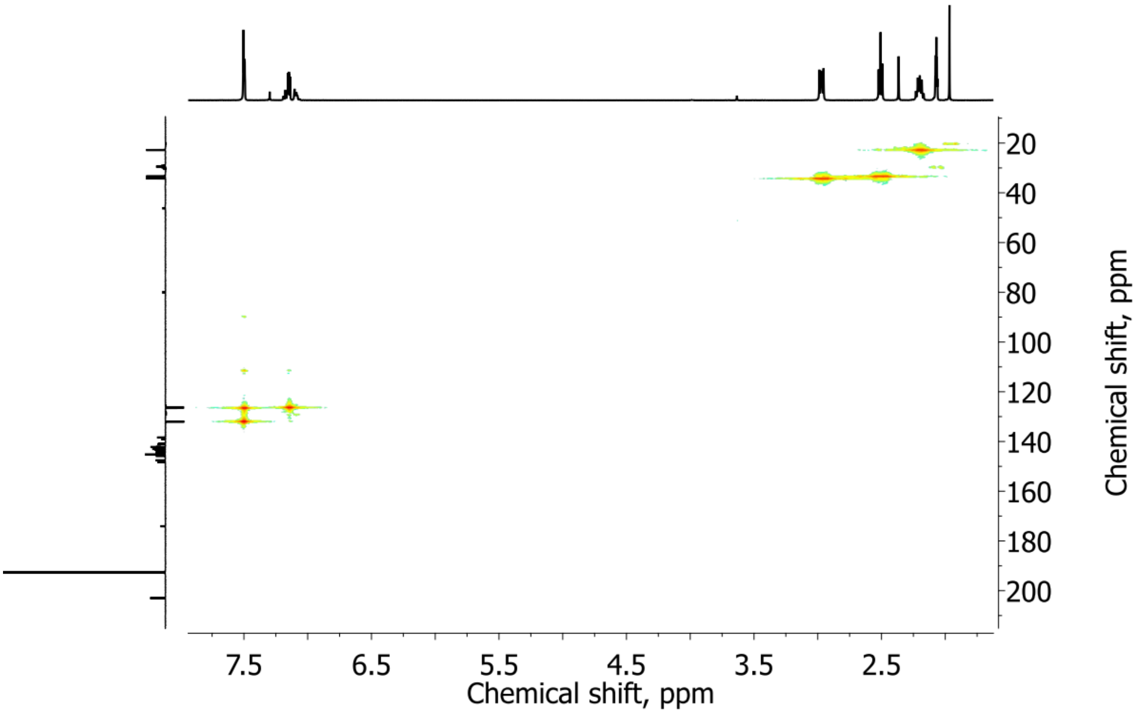

Figure S9. ${}^{1}H$-${}^{13}C$ HSQC NMR spectrum of compound **F2**.

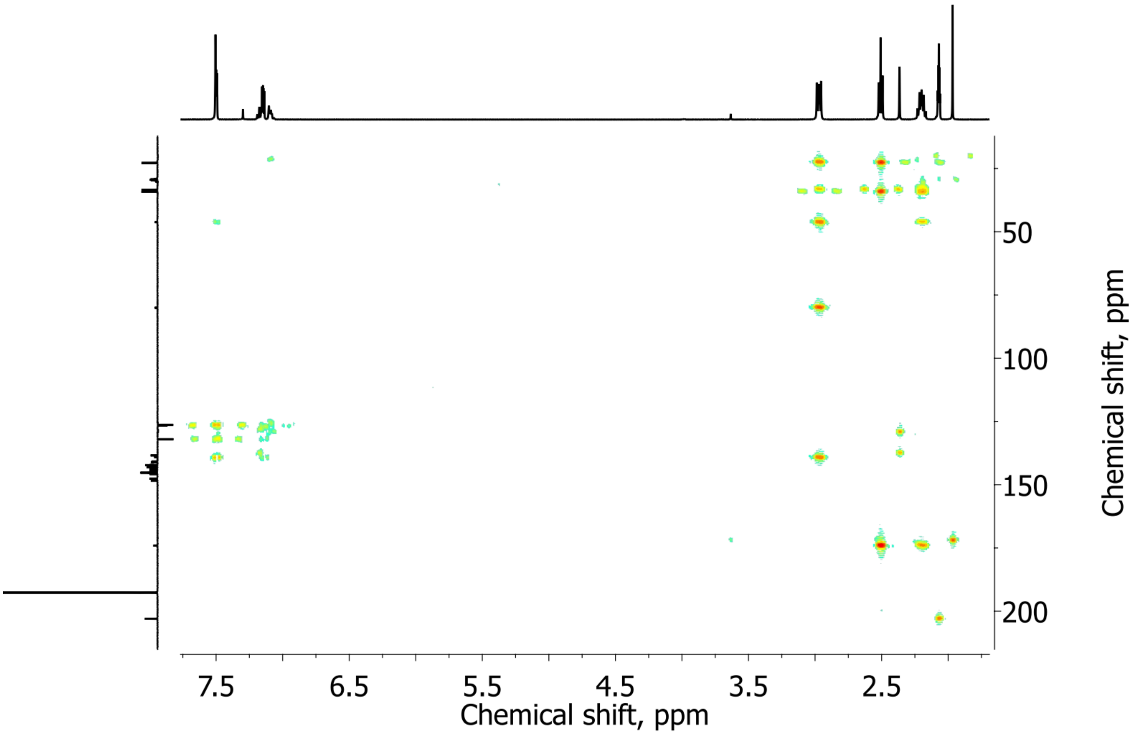

Figure S10. ${}^{1}H$-${}^{13}C$ HMBC NMR spectrum of compound **F2**.

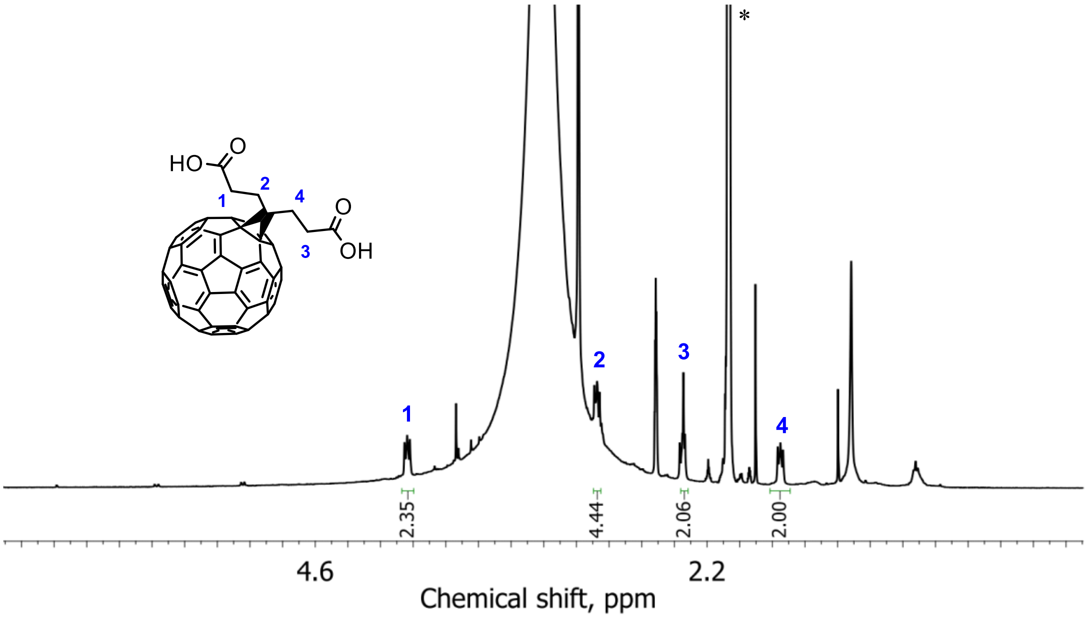

Figure S11. ^{1}H NMR spectrum of compound **F3**. * Denotes signals of acetone.

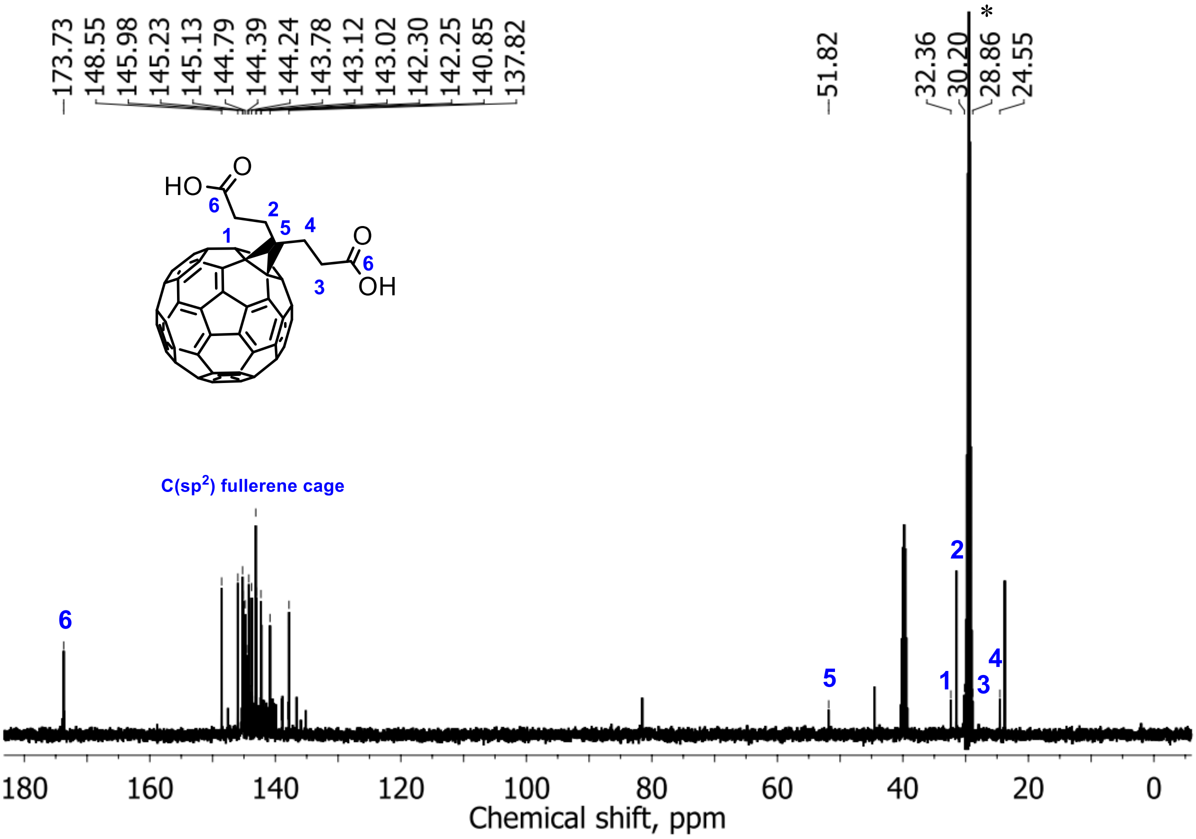

Figure S12. ^{13}C NMR spectrum of compound **F3**. * Denotes signals of acetone.

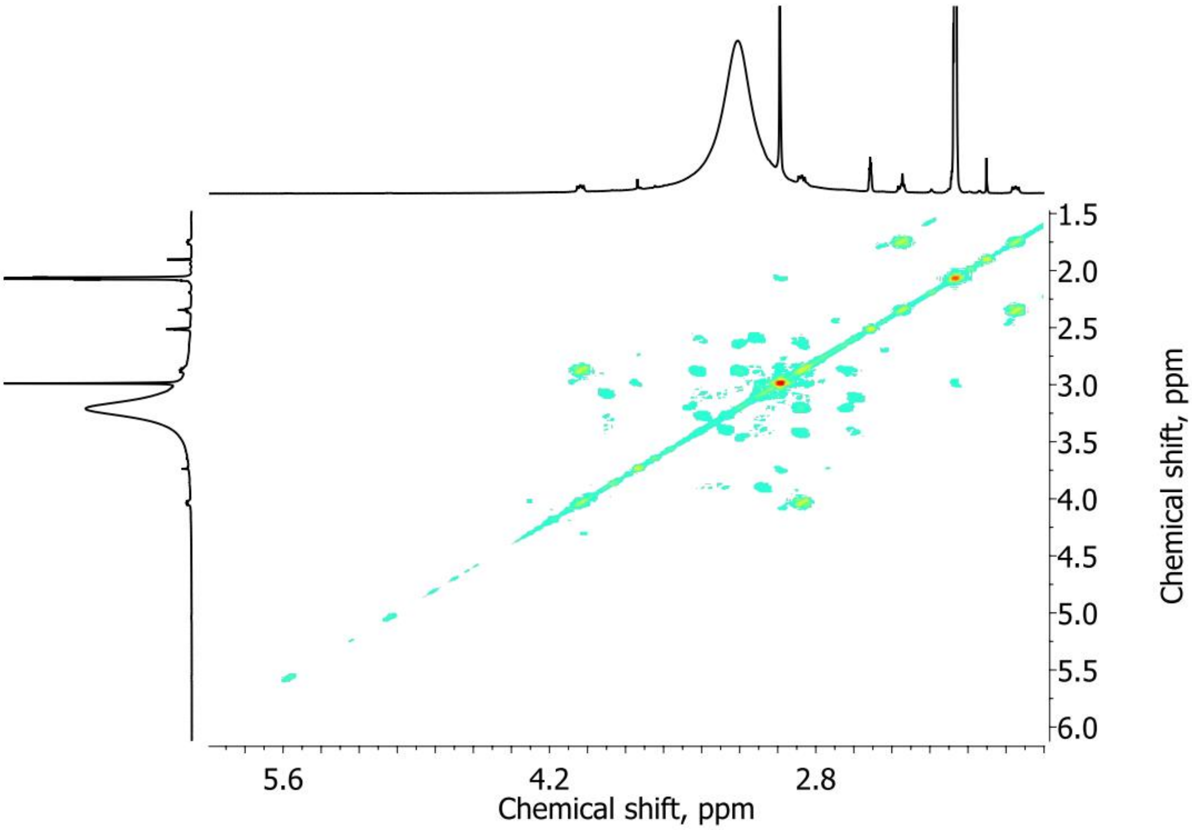

Figure S13. ^{1}H-^{1}H COSY NMR spectrum of compound **F3**.

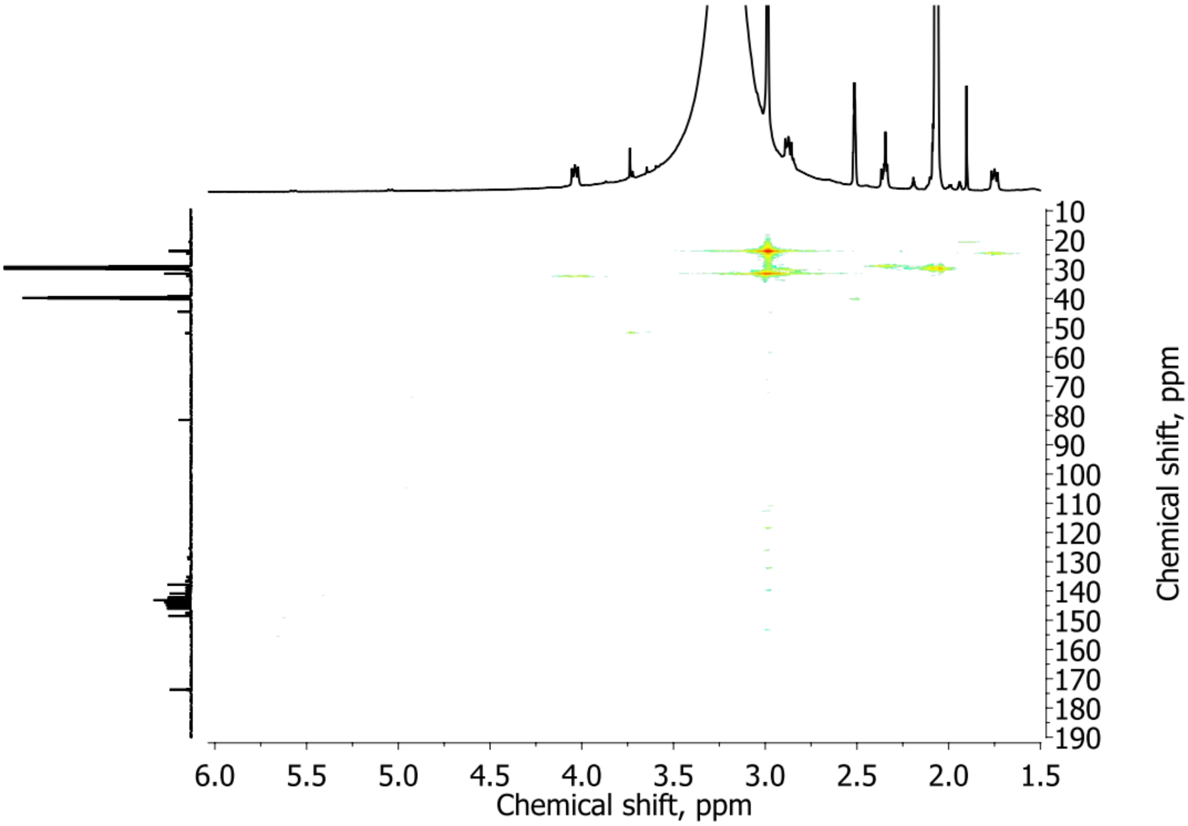

Figure S14. ^{1}H-^{13}C HSQC NMR spectrum of compound **F3**.

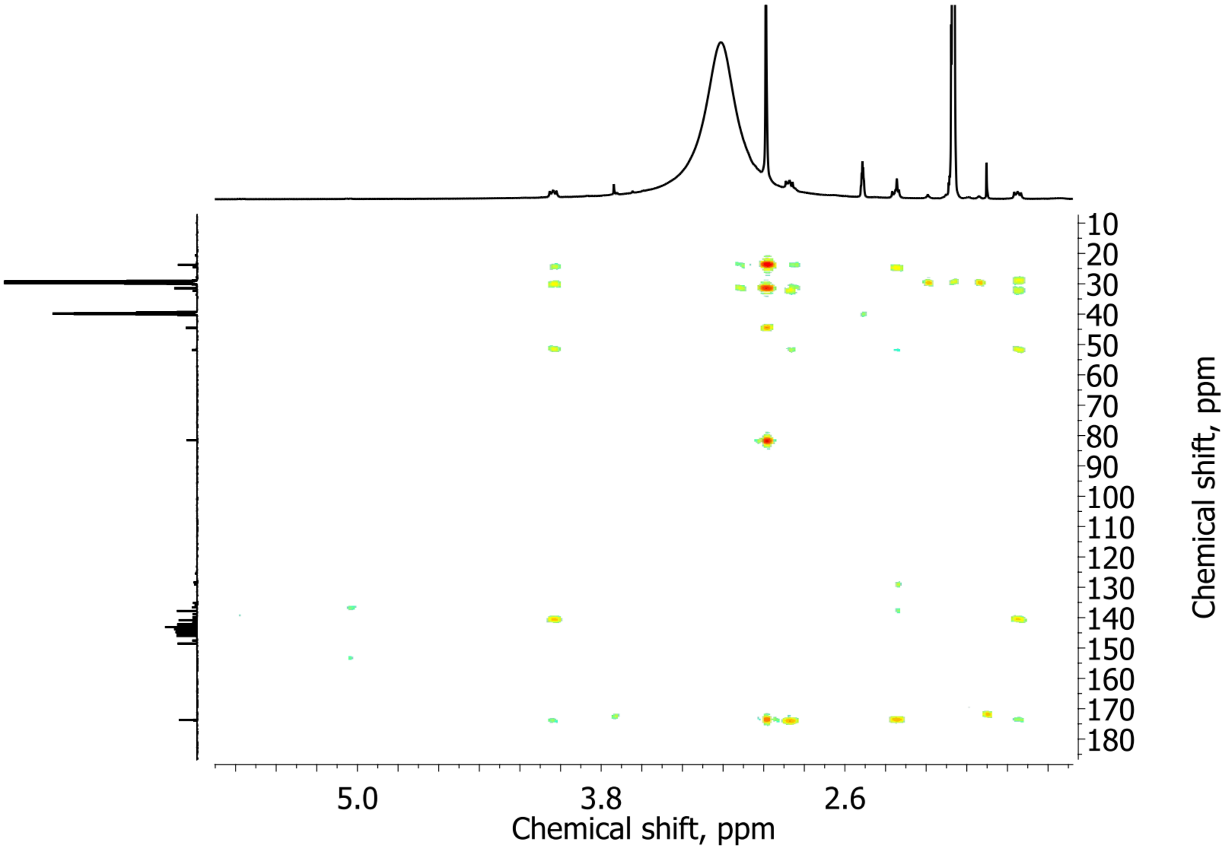

Figure S15. ^{1}H-^{13}C HMBC NMR spectrum of compound **F3**.

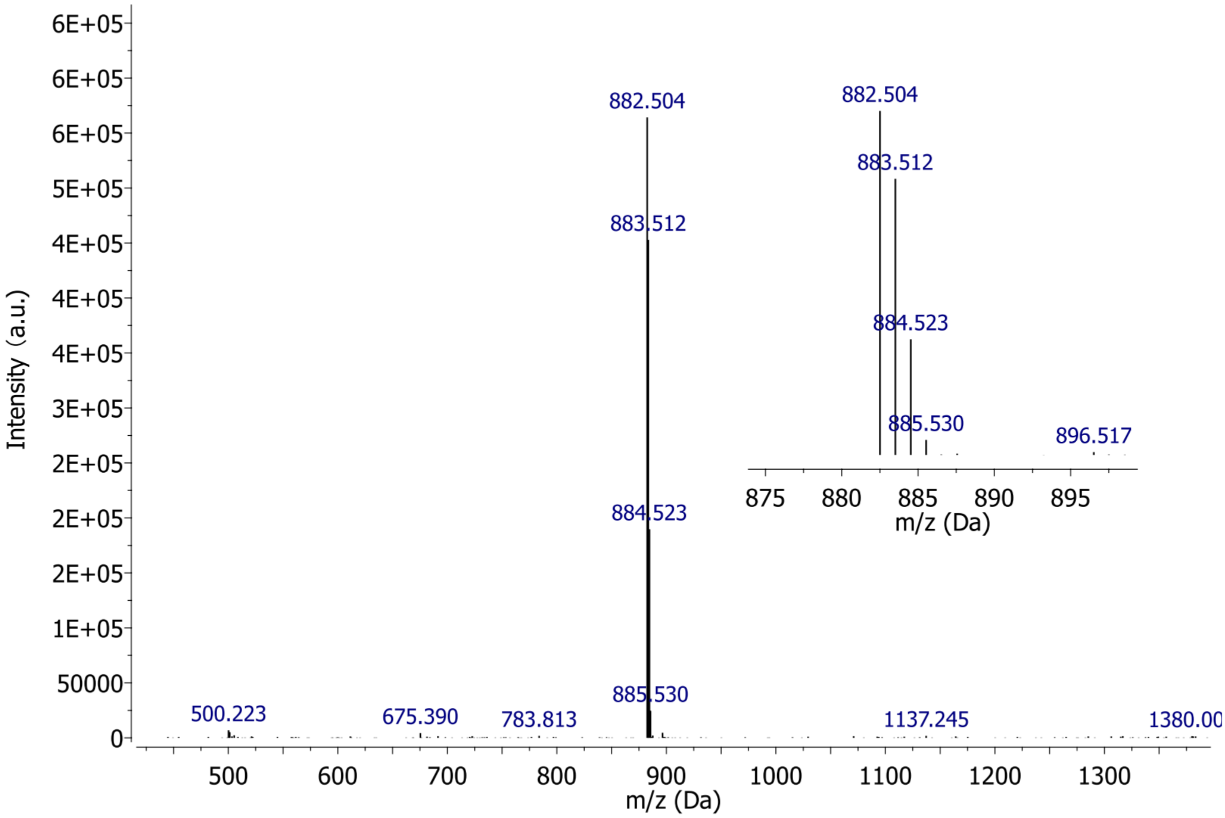

Figure S16. MALDI mass spectrum of compound **F1**.

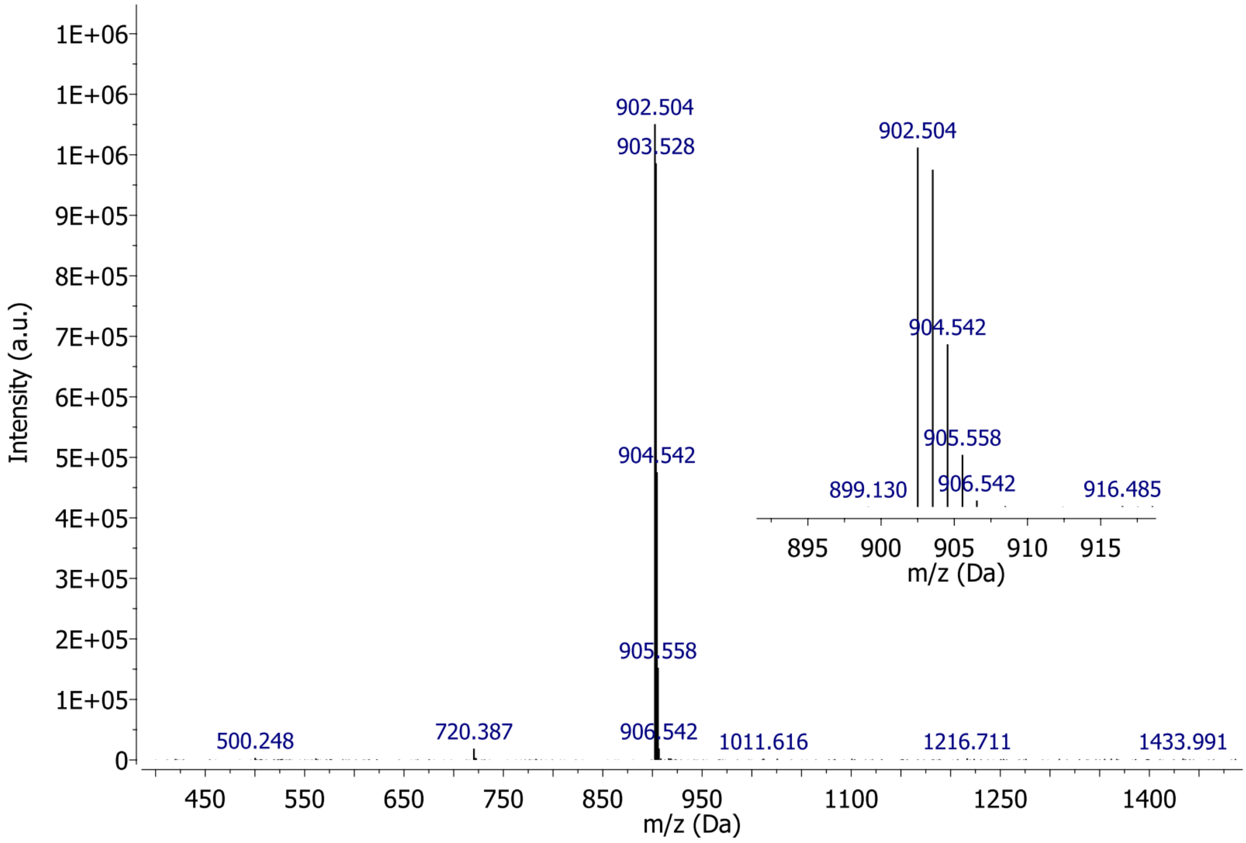

Figure S17. MALDI mass spectrum of compound **F2**.

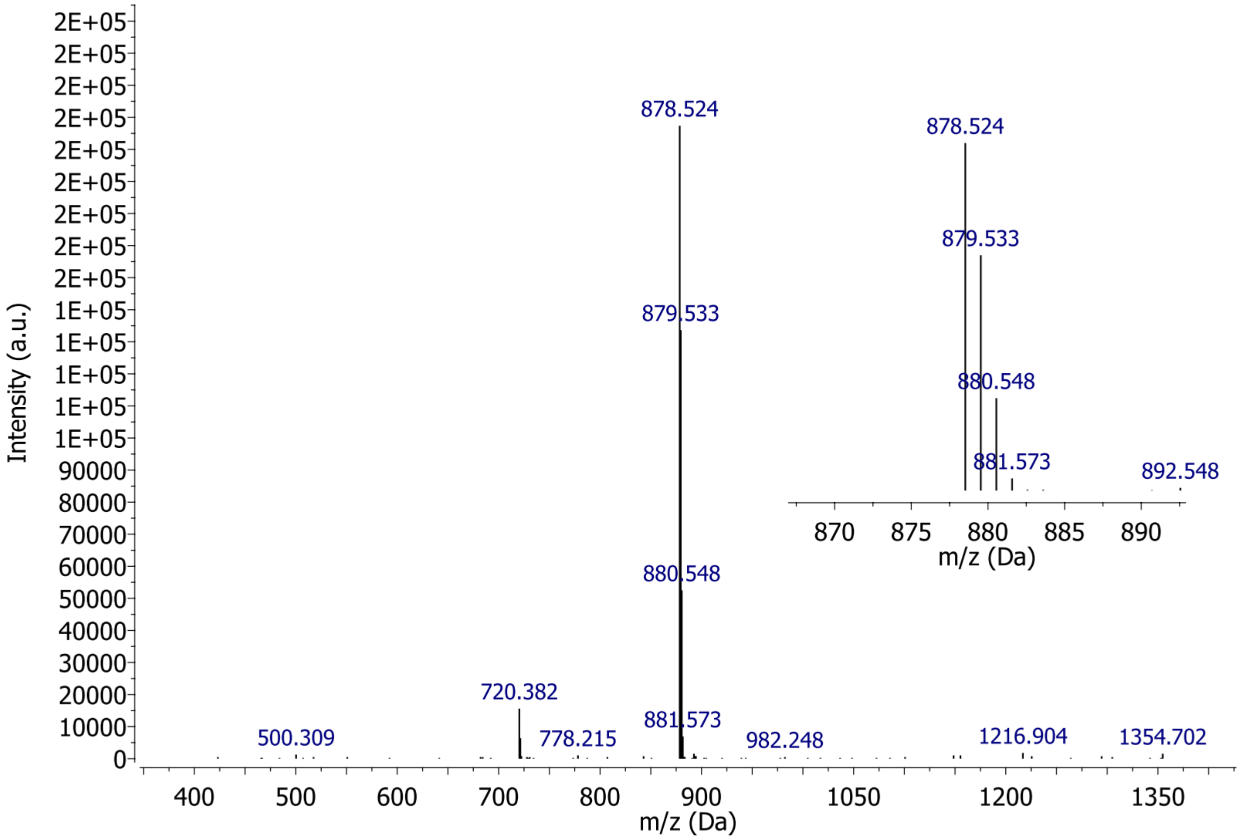

Figure S18. MALDI mass spectrum of compound **F3**.

Table S1. Surface properties of bare SnO_2 films and modified with **F1-F3**.

Sample*	**Contact angle [°]**			**Total surface energy**	**Dispersive component**	**Polar component**
	H_2O	**CH_2I_2**	**$MAPbI_3$ in DMF**	**[mN/m]**	**[mN/m]**	**[mN/m]**
SnO_2	19.2	38.2	31.9	73.6	40.5	33.1
SnO_2/PCBA (s)	*73.9*	*24.1*	*36.7*	*50.7*	*46.5*	*4.2*
SnO_2/PCBA (c, 3500 rpm)	59.9	21.4	39.5	57.3	47.4	10.0
SnO_2/**F1** (s)	57.1	31.1	34.6	56.3	43.8	12.6
SnO_2/**F1** (c, 3000 rpm)	55.6	26.9	34.0	58.2	45.4	12.7
SnO_2/**F2** (s)	63.7	29.5	49.2	53.4	44.4	9.0
SnO_2/**F2** (c, 3000 rpm)	64.8	21.0	36.8	55.1	47.5	7.6
SnO_2/**F3** (s)	59.4	27.6	29.6	56.0	45.2	10.9
SnO_2/**F3** (c, 3000 rpm)	62.6	25.3	37.2	55.1	46.1	9.0

* "s" denotes the samples prepared using soaking approach, whereas "c" stands for the samples processed by spin-coating (deposition frequency is given in rotations per minute, rpm).