Electronic supplementary materials *Mendeleev Commun.*, 2025, **35**, 386–389

Naphthalenediimides with carboxyl anchoring groups as promising components of the electron transport layer in n-i-p perovskite solar cells

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Experimental

1. General

Synthesis and characterization: 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 DMSO-d_6 solutions were obtained using Bruker AVANCE III 500 instrument. LDI mass spectra were registered 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.

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 NDIs 1-4

Naphthalenetetracarboxylic dianhydride (1 g, 3.73 mmol, 1 eq.), alkylamine (3.73 mmol, 1 eq.), and amino acid (3.73 mmol, 1 eq.) were suspended in 20 mL of dimethylformamide in a three-necked round bottom flask equipped with a condenser, thermometer, stopper, and PTFE-coated magnetic stirring bar. The system was degassed and filled with argon. The reaction mixture was heated at reflux for 24 hours and then allowed to cool down to room temperature. The residue was washed with distilled water, dried, and then dissolved in chloroform. The solution was poured on the top of the silica gel column. The reaction mixture was eluted using chloroform and chloroform-methanol mixtures. Target nonsymmetrical NDIs were eluted with 2-10 vol% of methanol in chloroform. The resulting chloroform/methanol solutions were concentrated using the rotary evaporator, and residues were dried in air. NDIs **1-4** were obtained with 23–35% yields and appeared as yellowish 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) configuration. 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 NDIs (0.2 mg mL^{-1} in chlorobenzene – acetonitrile 90:10 v/v mixture) at 4500 rpm for 30 s and following annealing at 100 °C for 10 min. Alternatively, the SnO_2 films were immersed into the solutions of PCBA (0.2 mg mL^{-1} in toluene) or NDIs (0.2 mg mL^{-1} in chlorobenzene – acetonitrile 90:10 v/v mixture) for 30-60 min. After the soaking, samples were taken out, washed with pure chlorobenzene, dried and used for deposition of the perovskite absorber layer.

$MAPbI_3$ 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 $\sim5\times10^{-6}$ 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).

4. Spectral data for the synthesized compounds

1. ^{1}H NMR (500 MHz, $(CD_3)_2SO$, δ, ppm): 8.67 (s, 4H), 4.30 – 4.25 (m, 2H), 4.10 – 3.89 (m, 2H), 2.67 – 2.58 (m, 2H), 1.94 – 1.73 (m, 1H), 1.40 – 1.21 (m, 8H), 0.88 (t, *J* = 7.4 Hz, 3H), 0.84 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (126 MHz, $(CD_3)_2SO$, δ, ppm): 172.87, 163.47, 163.01, 131.02, 130.92, 126.78, 126.76, 126.66, 44.16, 37.69, 36.57, 32.52, 30.57, 28.55, 24.00, 22.87, 14.38, 10.91. LDI MS: m/z=450.17 ($[M]^-$), calculated for $C_{25}H_{26}N_2O_6$ ($[M]^-$): 450.18.

2. ^{1}H NMR (500 MHz, $(CD_3)_2SO$, δ, ppm): 8.64 – 8.59 (m, 4H), 4.93 – 4.84 (m, 1H), 4.32 – 4.23 (m, 2H), 2.67 – 2.60 (m, 2H), 2.48 – 2.36 (m, 2H), 1.93 – 1.81 (m, 2H), 1.80 – 1.72 (m, 3H), 1.48 – 1.24 (m, 3H). ^{13}C NMR (126 MHz, $(CD_3)_2SO$, δ, ppm): 172.86, 163.37, 162.97, 130.88, 130.80, 126.52, 126.39, 53.87, 36.54, 32.45, 29.02, 26.53, 25.61. LDI MS: m/z=420.17 ($[M]^-$), calculated for $C_{23}H_{20}N_2O_6$ ($[M]^-$): 420.13.

3. ^{1}H NMR (500 MHz, $(CD_3)_2SO$, δ, ppm): 8.67 – 8.58 (m, 4H), 4.10 – 3.90 (m, 4H), 2.23 (t, *J* = 7.3 Hz, 2H), 1.90 – 1.80 (m, 1H), 1.74 – 1.60 (m, 2H), 1.61 – 1.51 (m, 2H), 1.42 – 1.19 (m, 10H), 0.93 – 0.80 (m, 6H). ^{13}C NMR (126 MHz, $(CD_3)_2SO$, δ, ppm): 174.87, 163.37, 163.33, 162.99, 162.96, 131.00, 130.89, 126.68, 126.64, 126.54, 126.51, 44.11, 37.70, 33.93, 30.56, 28.54, 27.60, 26.46, 24.67, 23.98, 22.89, 14.39, 10.89. LDI MS: m/z=492.25 ($[M]^-$), calculated for $C_{28}H_{32}N_2O_6$ ($[M]^-$): 492.23.

4. ^{1}H NMR (500 MHz, $(CD_3)_2SO$, δ, ppm): 8.64 (s, 4H), 4.12 – 3.88 (m, 4H), 2.17 (t, *J* = 7.3 Hz, 2H), 1.97 – 1.76 (m, 1H), 1.69 – 1.56 (m, 2H), 1.53 – 1.43 (m, 2H), 1.40 – 1.19 (m, 20H), 0.96 – 0.76 (m, 6H). ^{13}C NMR (126 MHz, $(CD_3)_2SO$, δ, ppm): 174.96, 163.41, 163.02, 131.01, 130.90, 126.73, 126.59, 44.12, 37.70, 34.12, 30.56, 29.31, 29.18, 29.00, 28.78, 28.54, 27.81, 26.94, 24.95, 24.04, 23.98, 22.94, 22.89, 14.39, 10.90. LDI MS: m/z=562.36 ($[M]^-$), calculated for $C_{33}H_{42}N_2O_6$ ($[M]^-$): 562.30.

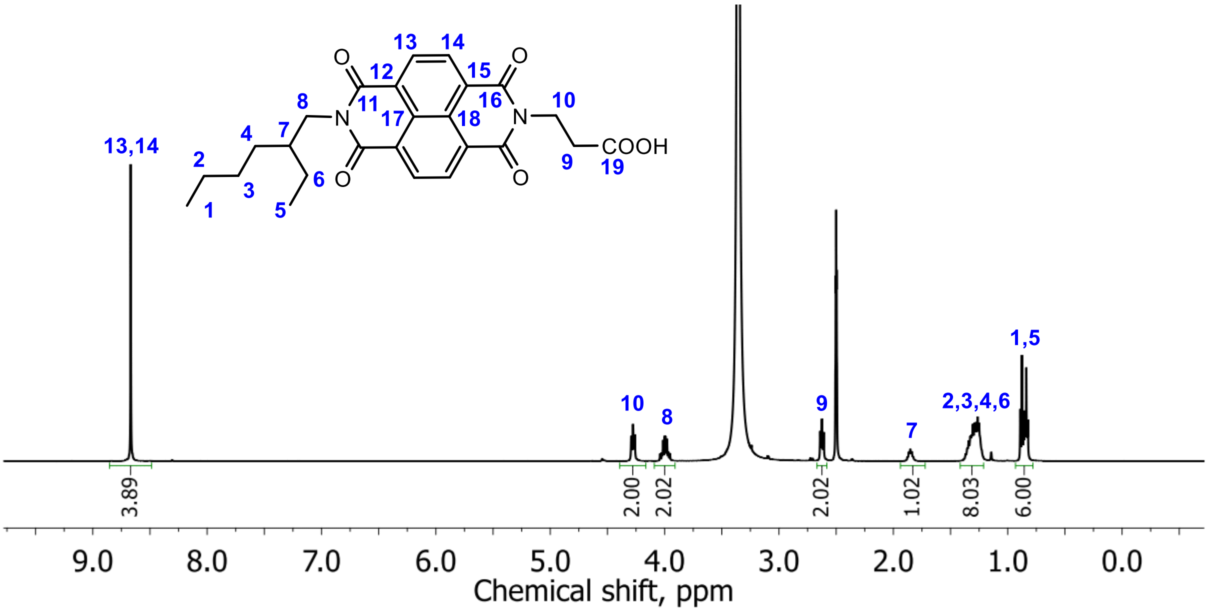

Figure S1. ^{1}H NMR spectrum of compound **1**.

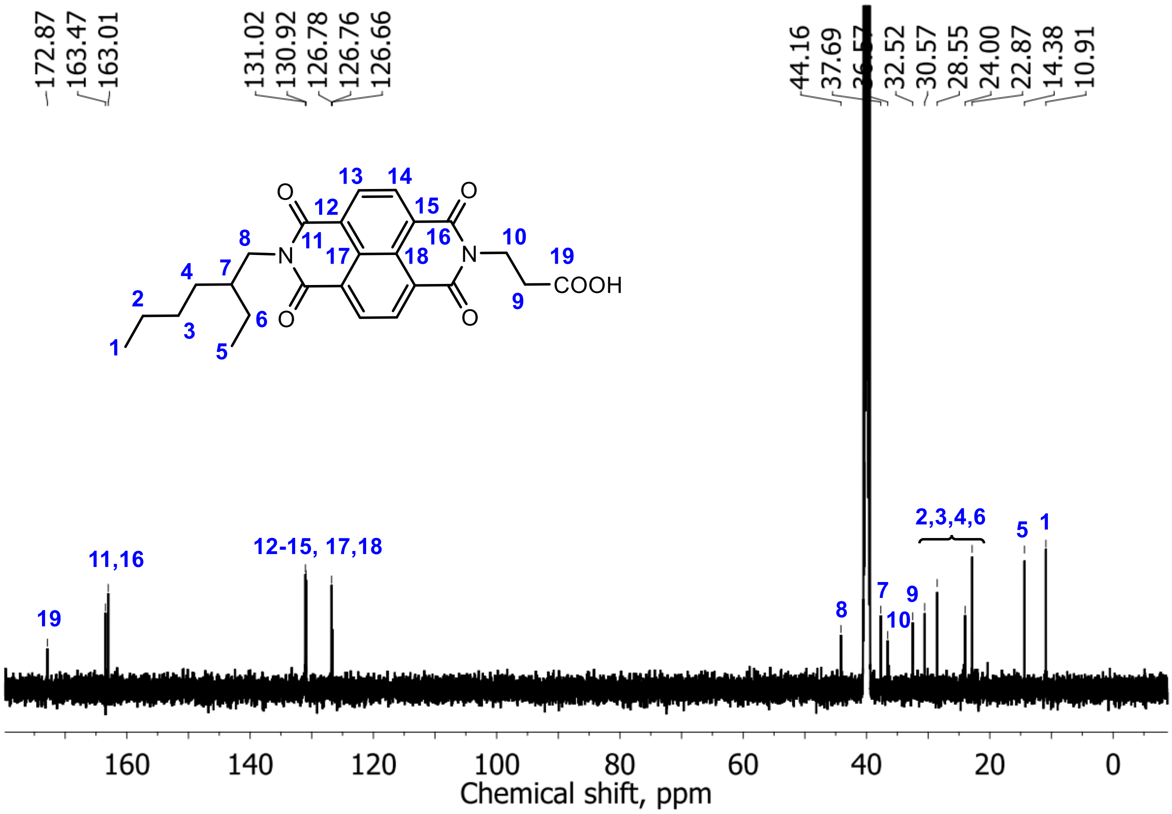

Figure S2. ^{13}C NMR spectrum of compound **1**.

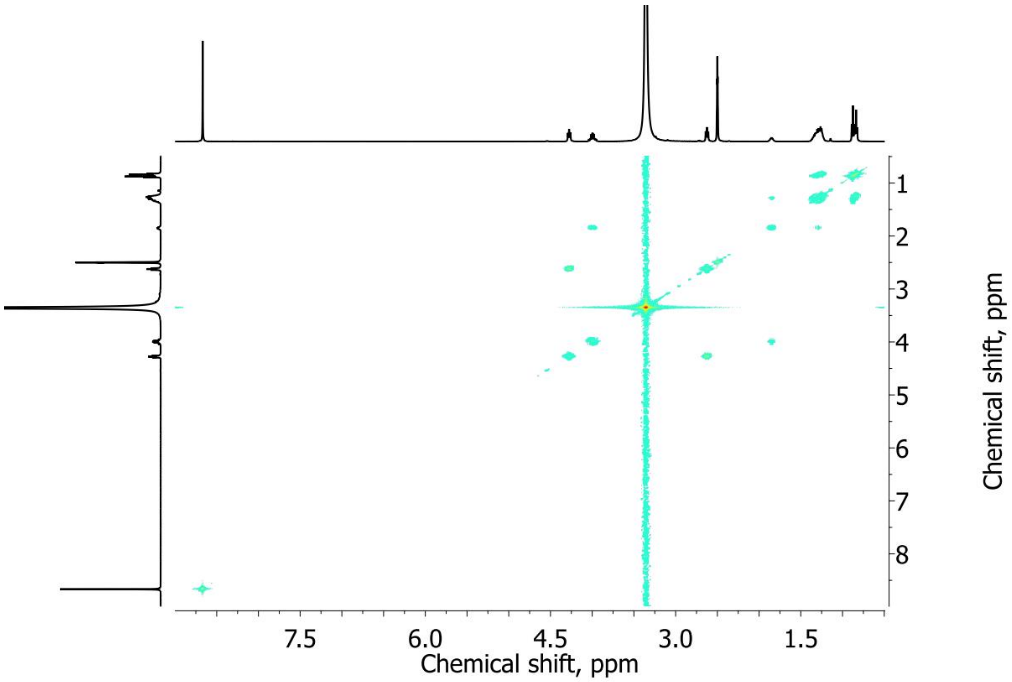

Figure S3. ^1H-^1H COSY NMR spectrum of compound **1**.

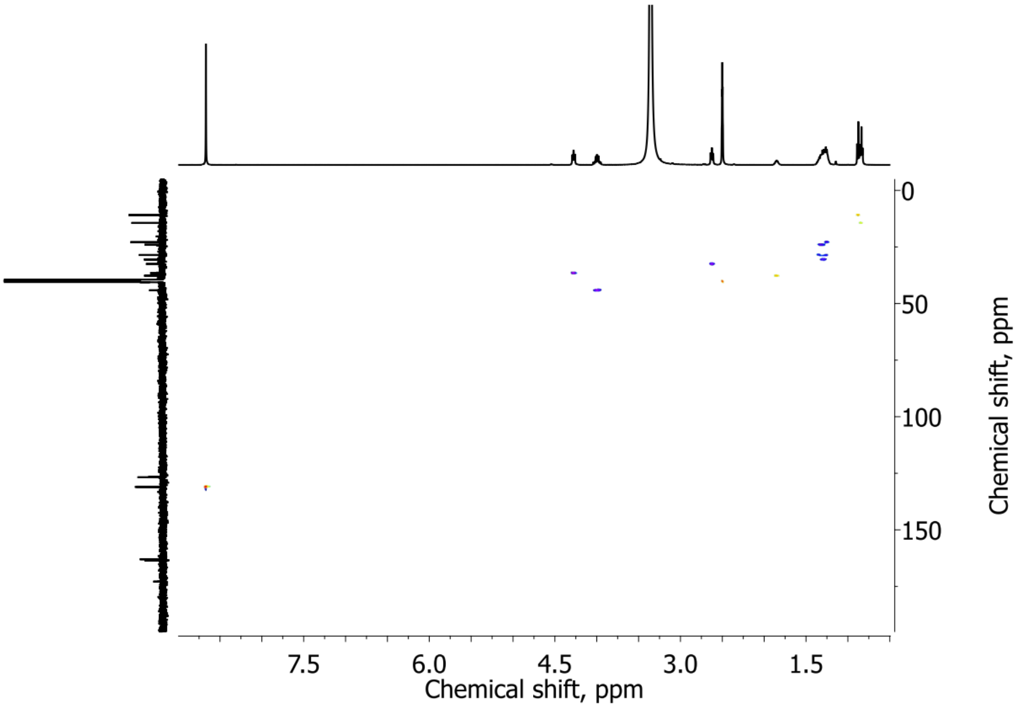

Figure S4. ^1H-^{13}C HSQC NMR spectrum of compound **1**.

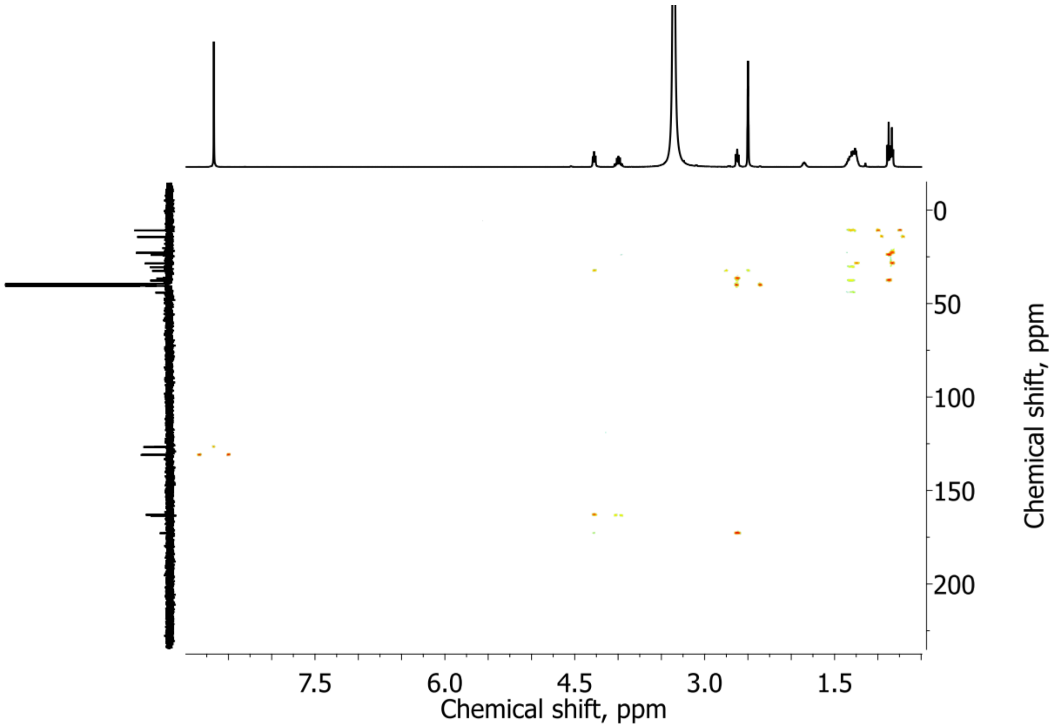

Figure S5. ^{1}H-^{13}C HMBC NMR spectrum of compound **1**.

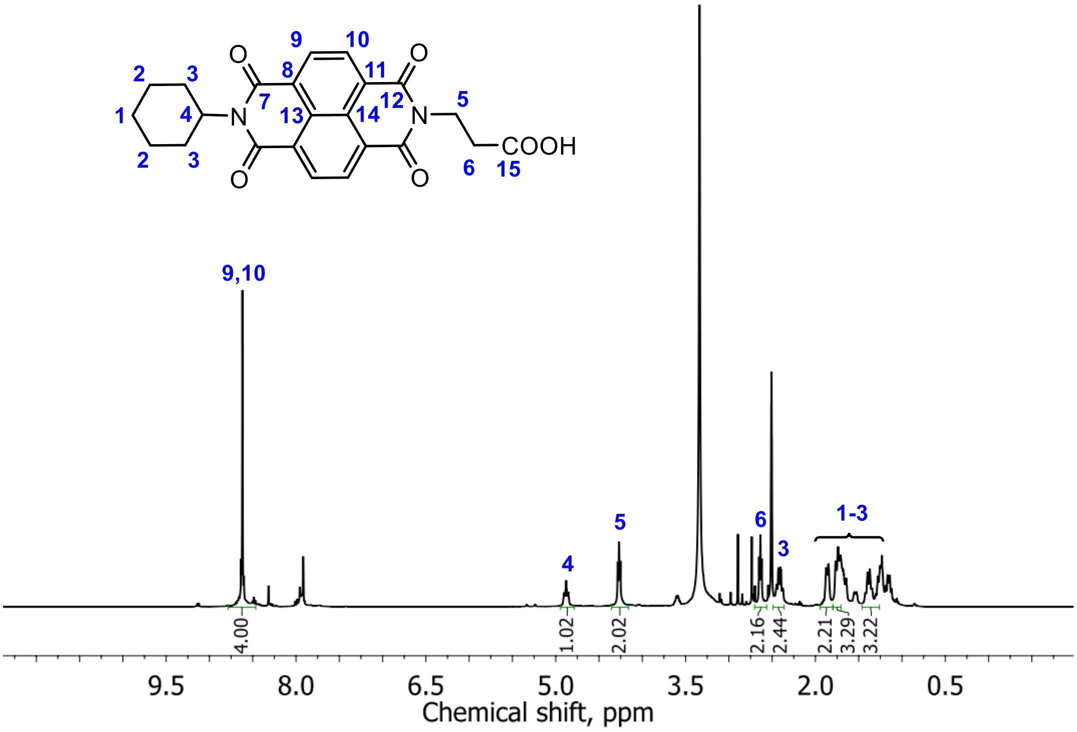

Figure S6. ^{1}H NMR spectrum of compound **2**.

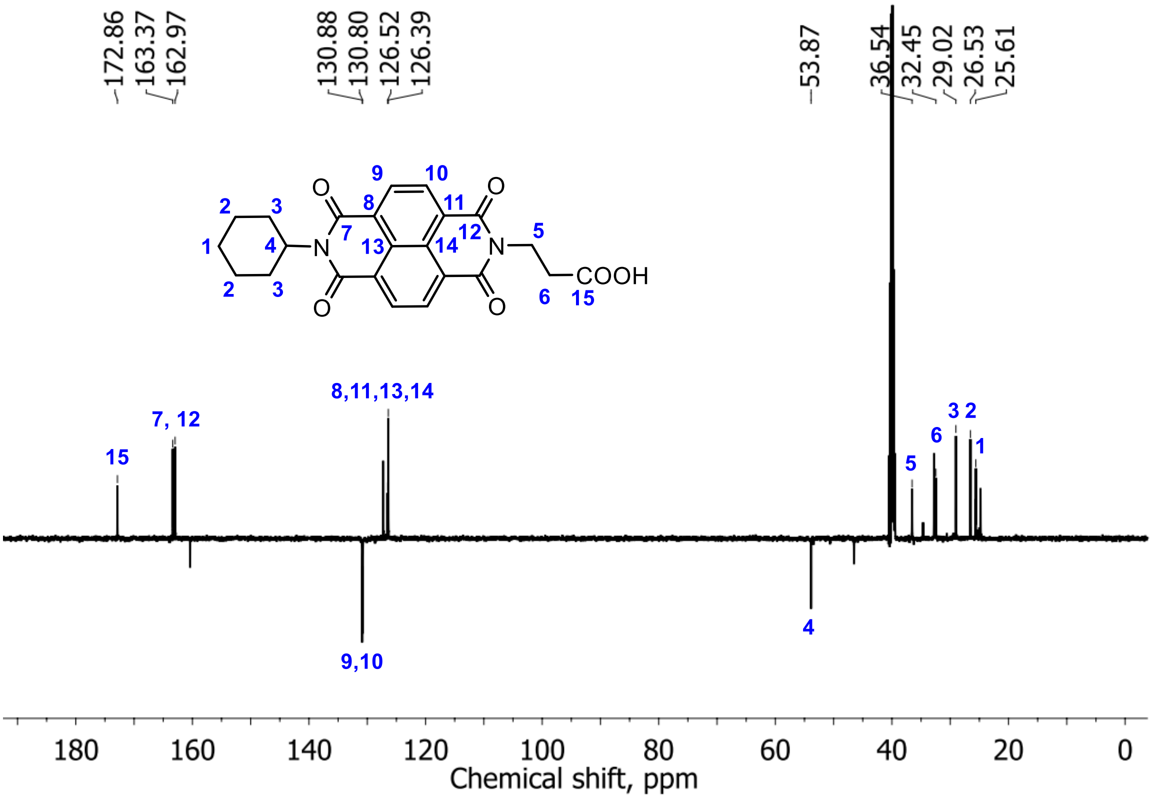

Figure S7. *J*-modulated spin-echo ^{13}C NMR spectrum of compound **2**.

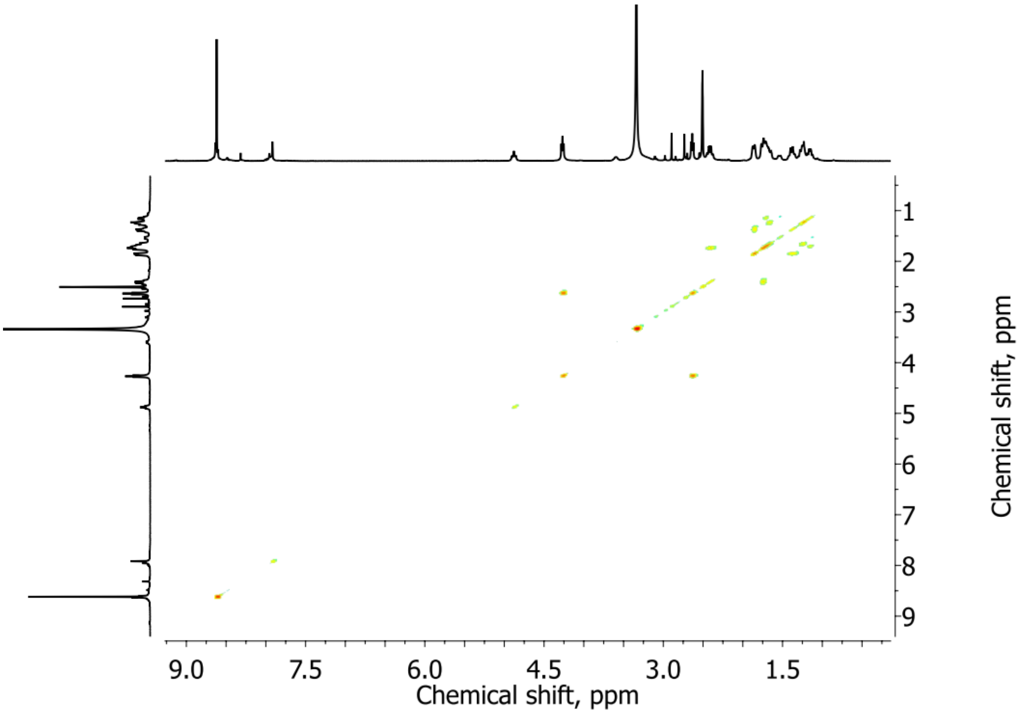

Figure S8. ^{1}H-^{1}H COSY NMR spectrum of compound **2**.

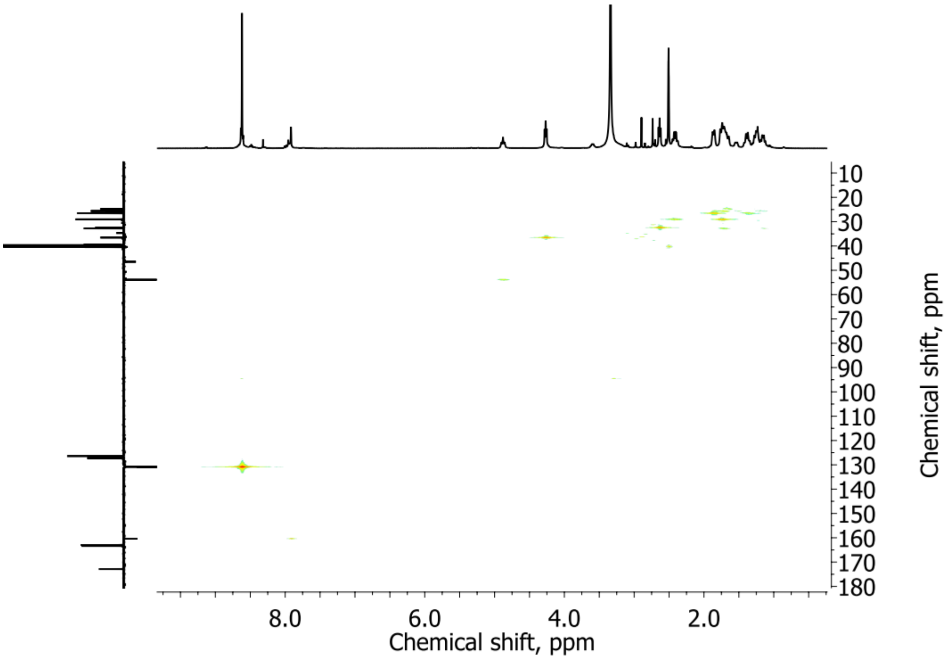

Figure S9. ^{1}H-^{13}C HSQC NMR spectrum of compound **2**.

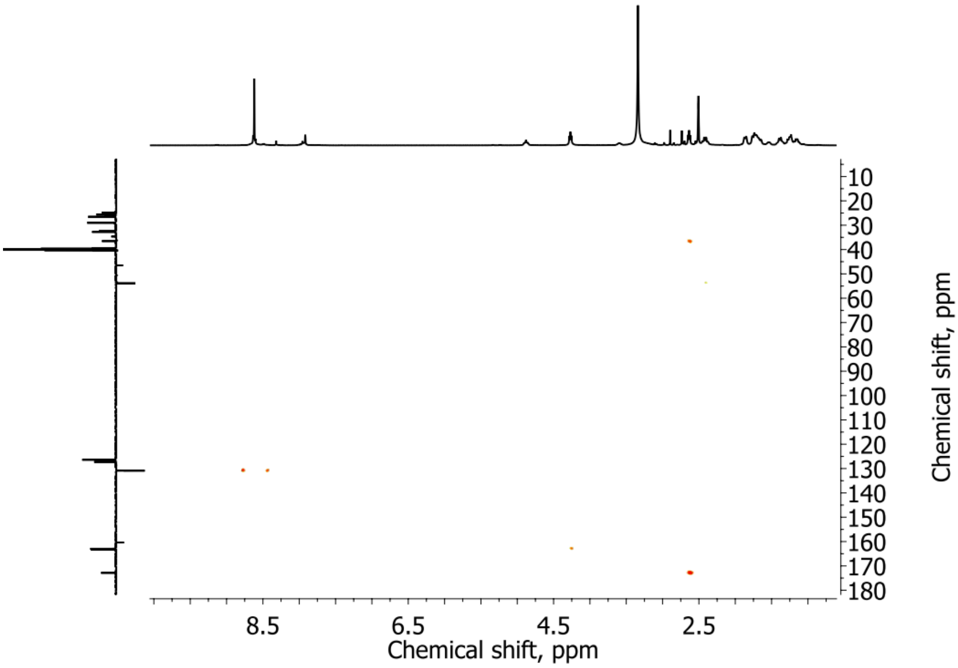

Figure S10. ^{1}H-^{13}C HMBC NMR spectrum of compound **2**.

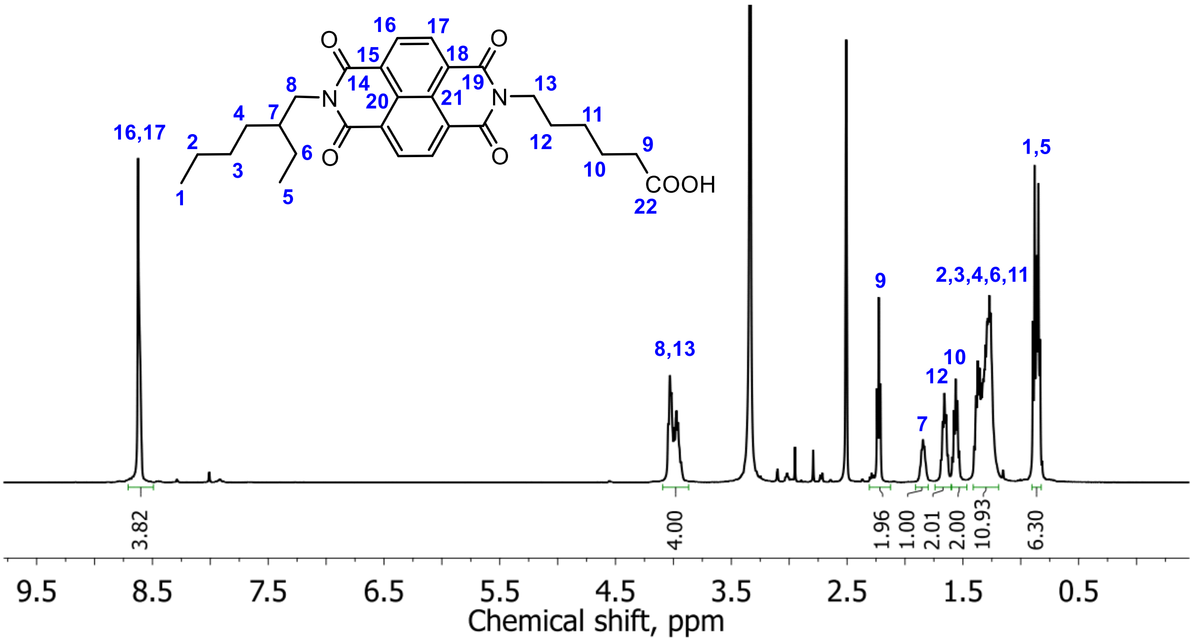

Figure S11. ^{1}H NMR spectrum of compound **3**.

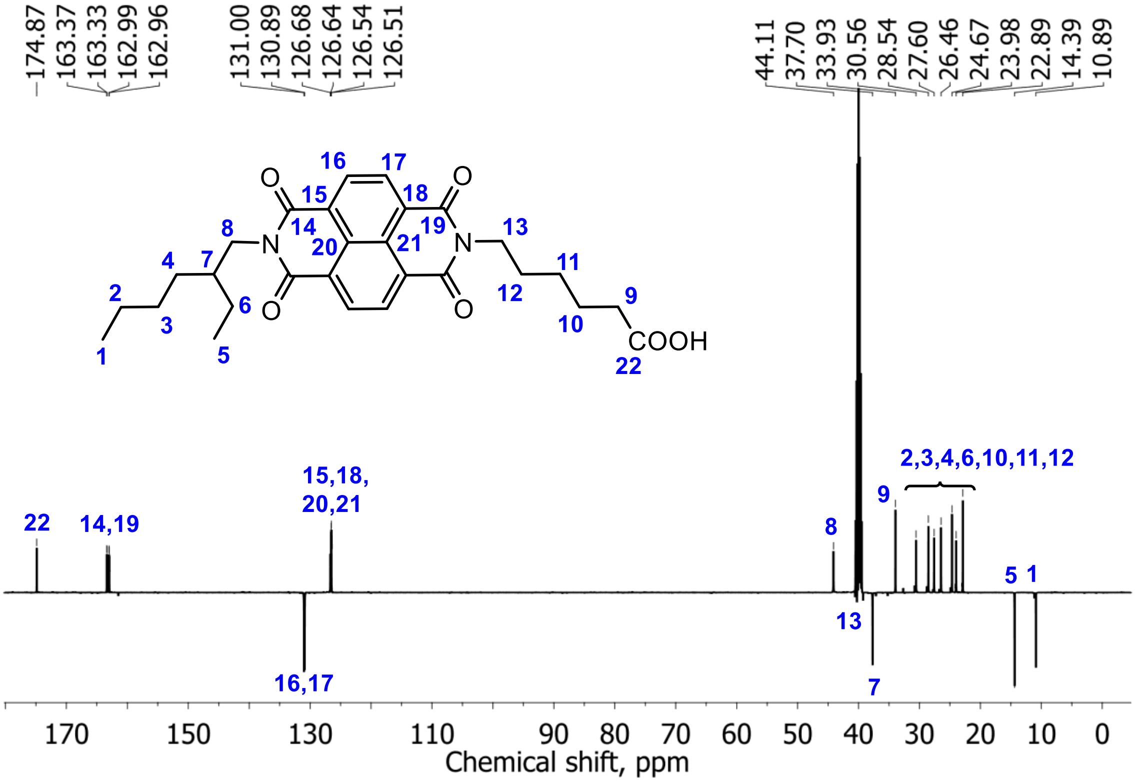

Figure S12. *J*-modulated spin-echo ^{13}C NMR spectrum of compound **3**.

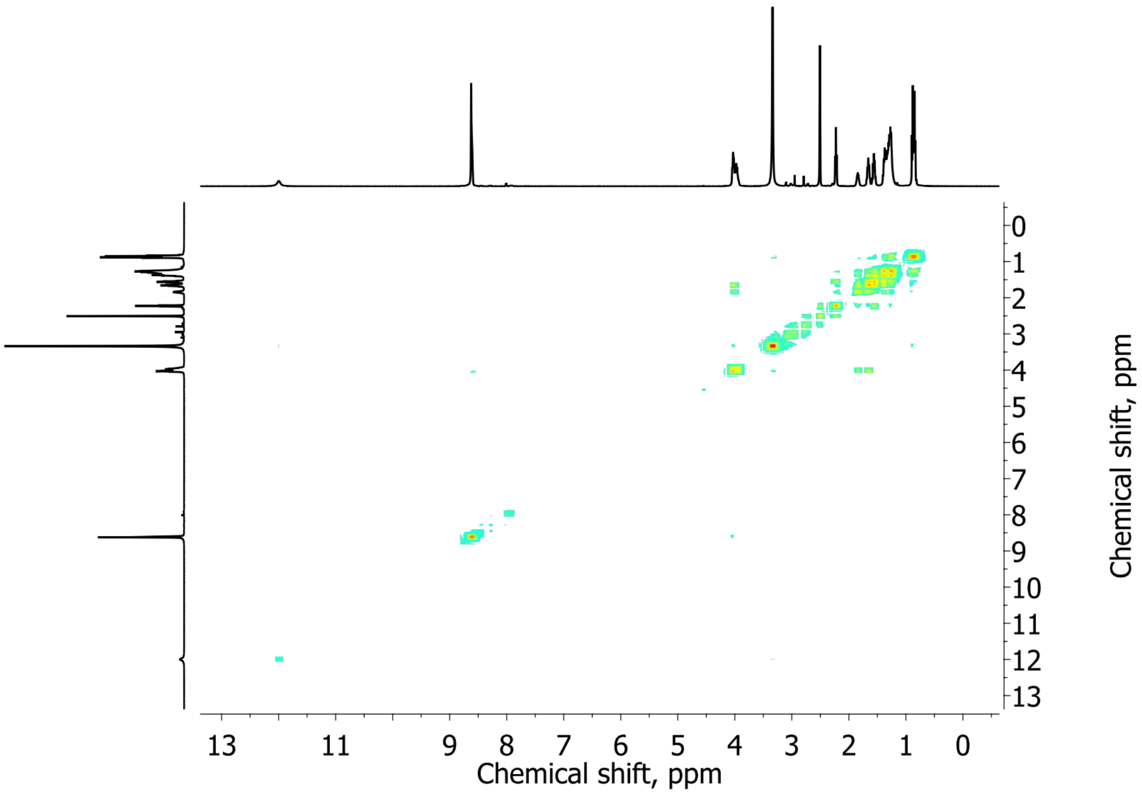

Figure S13. ^{1}H-^{1}H COSY NMR spectrum of compound **3**.

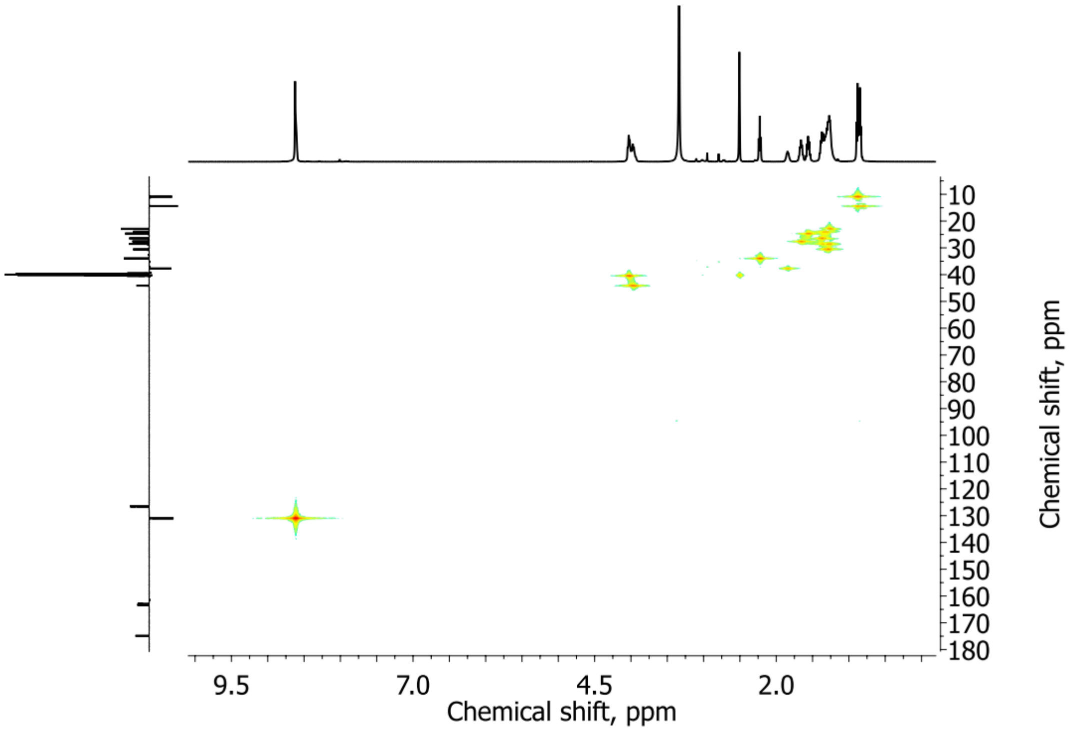

Figure S14. ^{1}H-^{13}C HSQC NMR spectrum of compound **3**.

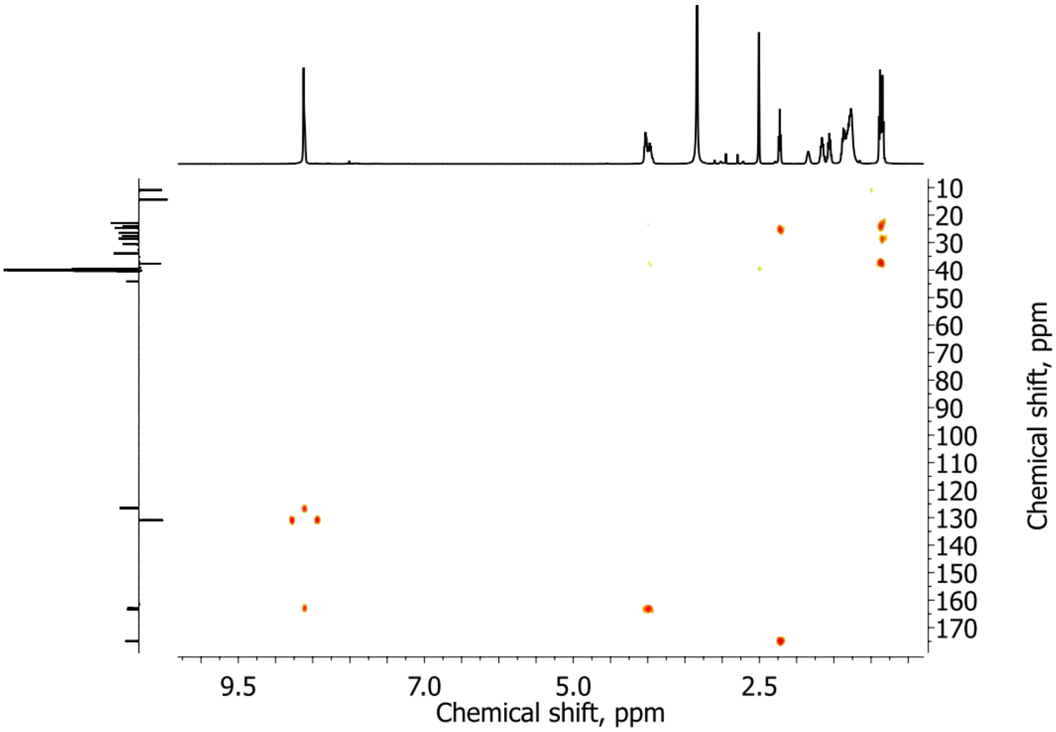

Figure S15. ^{1}H-^{13}C HMBC NMR spectrum of compound **3**.

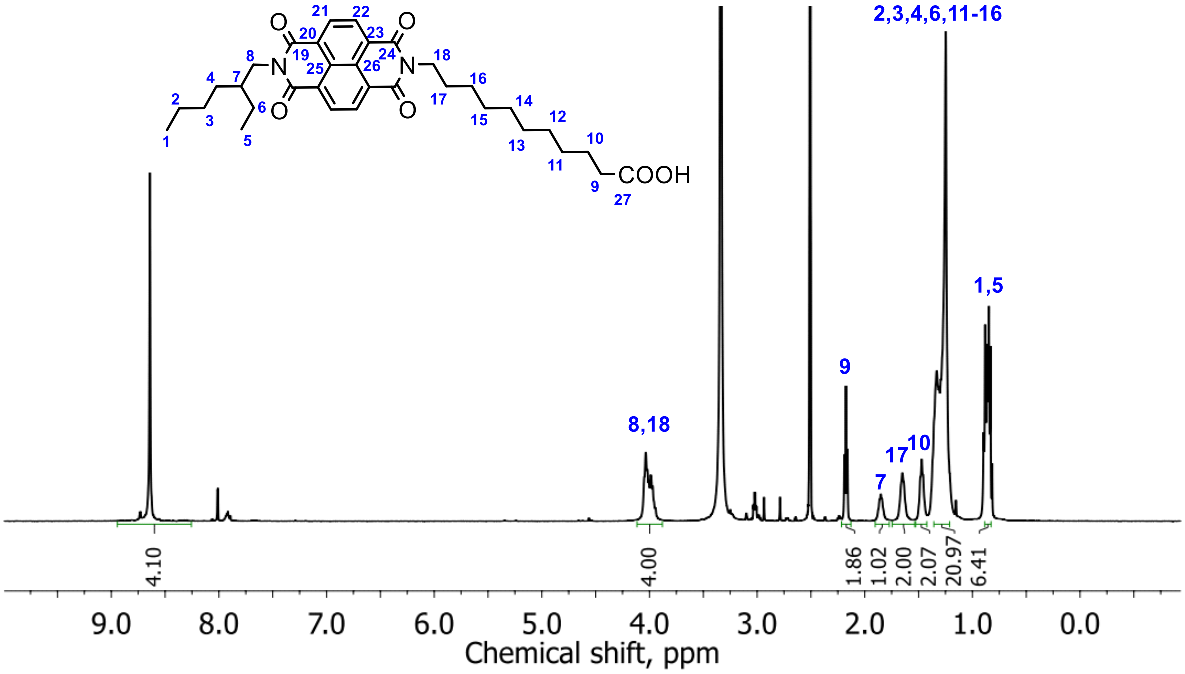

Figure S16. ^{1}H NMR spectrum of compound **4**.

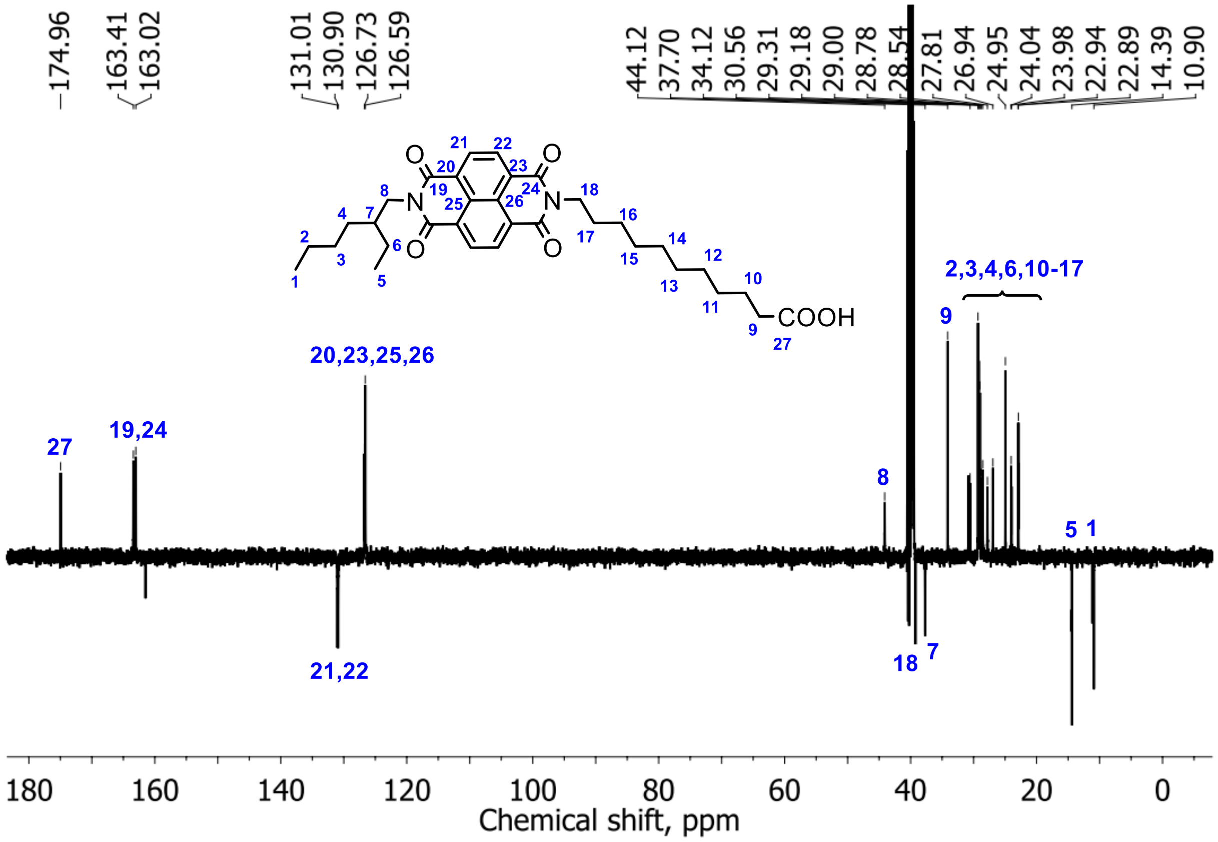

Figure S17. *J*-modulated spin-echo ^{13}C NMR spectrum of compound **4**.

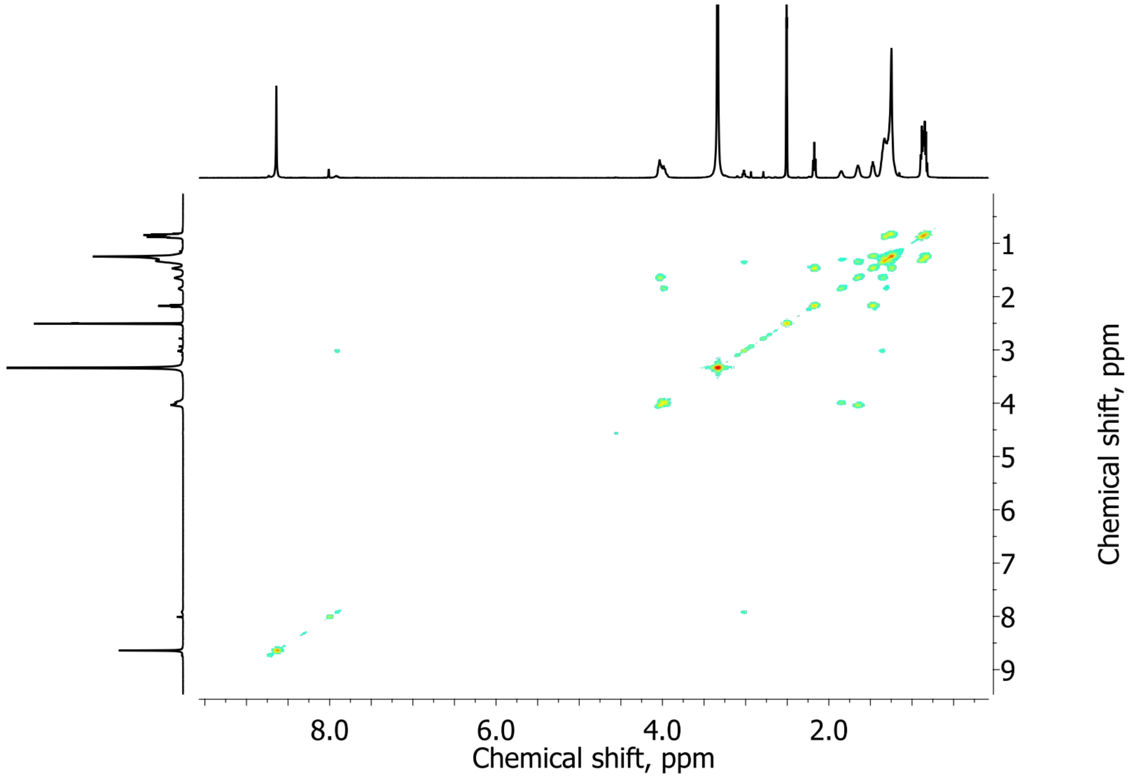

Figure S18. ^{1}H-^{1}H COSY NMR spectrum of compound **4**.

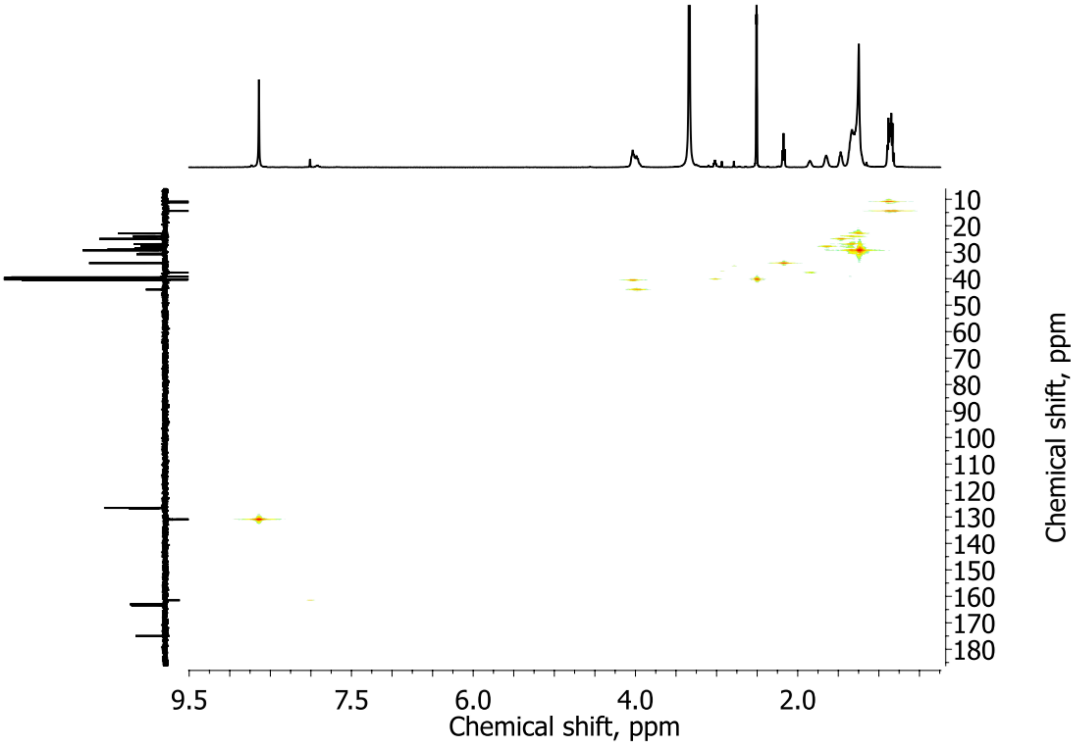

Figure S19. ^{1}H-^{13}C HSQC NMR spectrum of compound **4**.

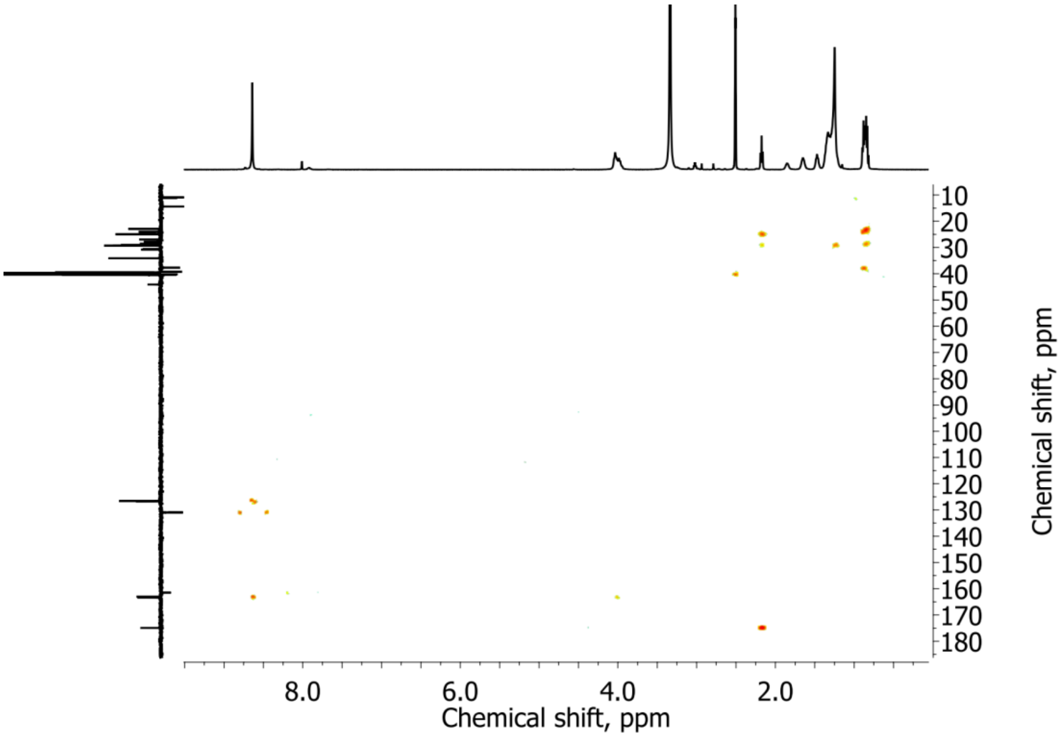

Figure S20. ^{1}H-^{13}C HMBC NMR spectrum of compound **4**.

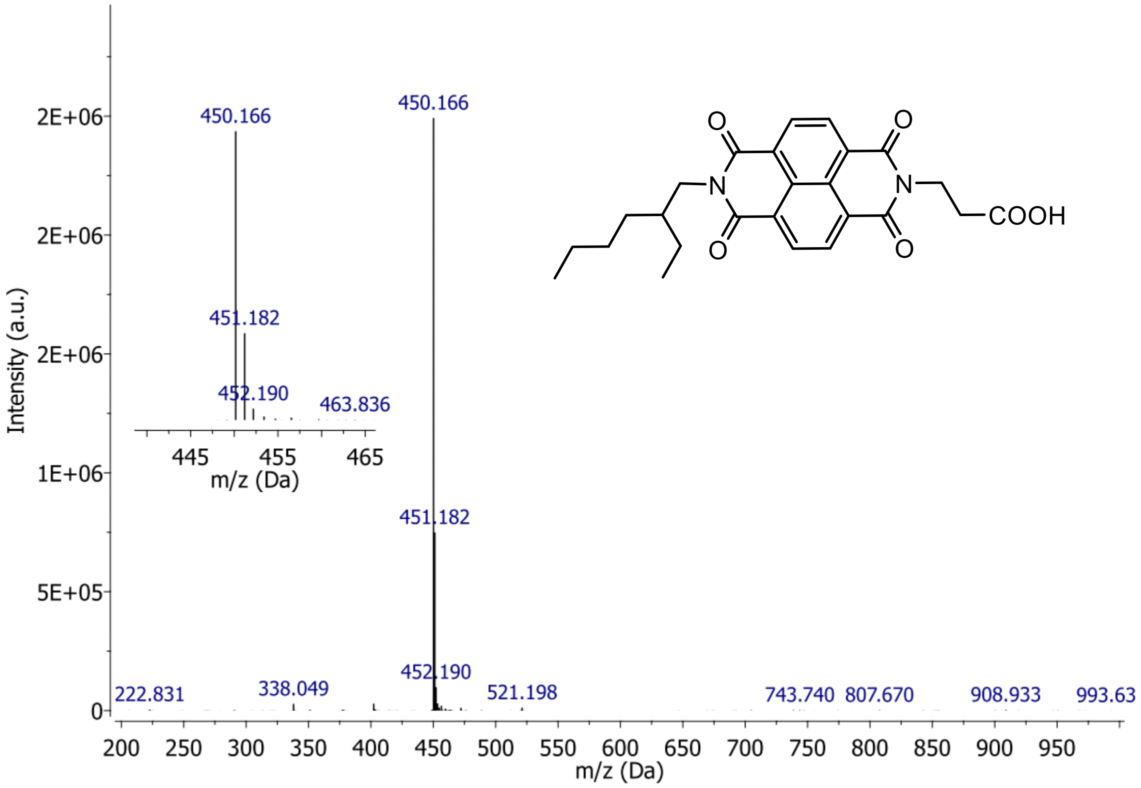

Figure S21. LDI mass spectrum of compound **1**.

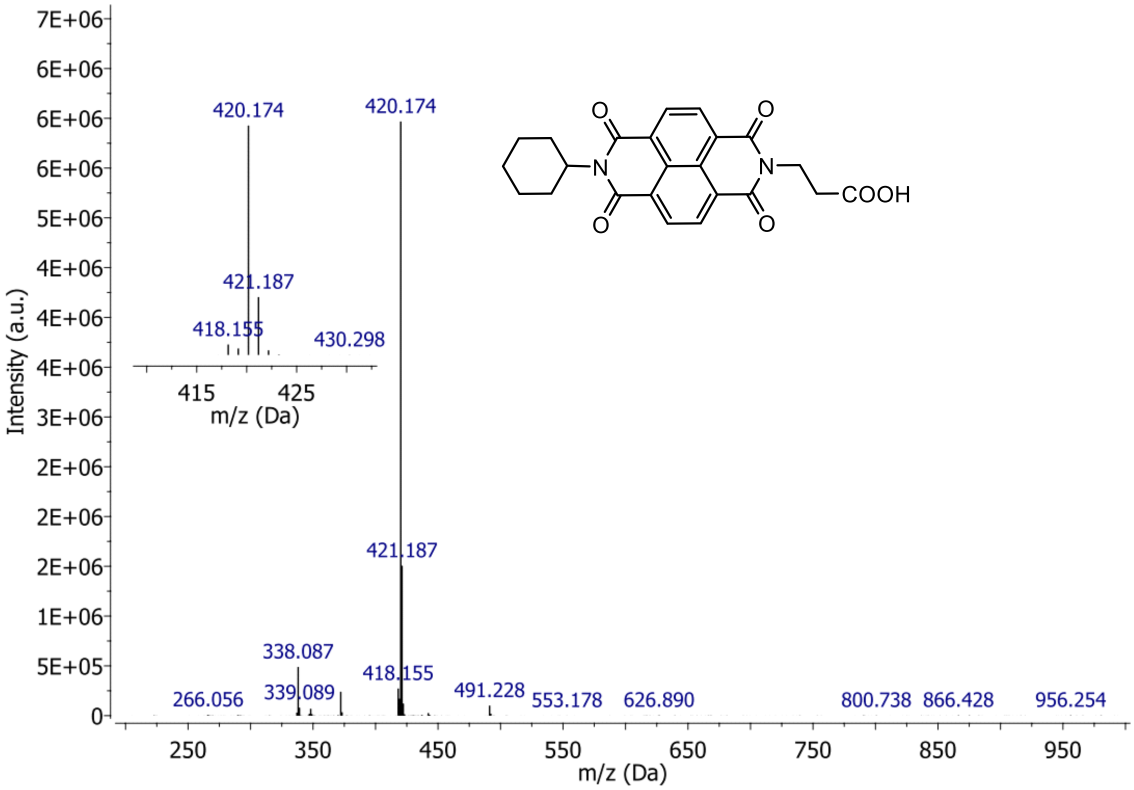

Figure S22. LDI mass spectrum of compound **2**.

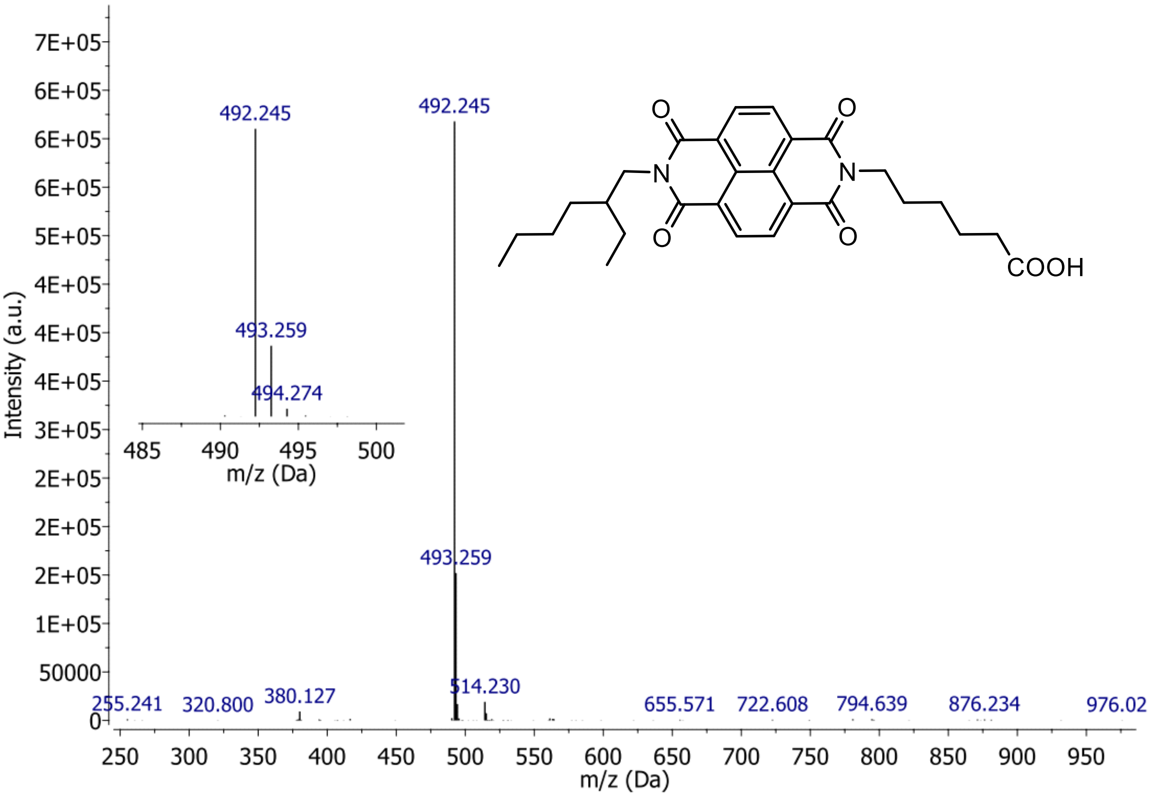

Figure S23. LDI mass spectrum of compound **3**.

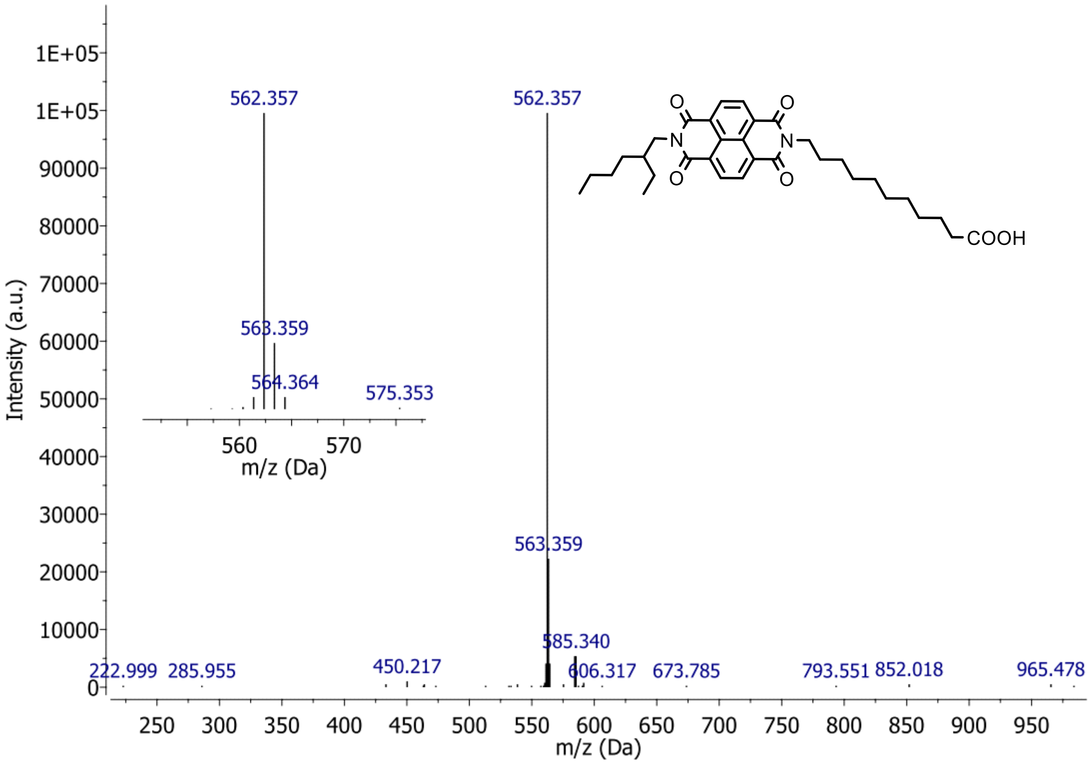

Figure S24. LDI mass spectrum of compound **4**.

Table S1. Surface properties of bare SnO_2 films and modified with NDIs **1-4.**

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/**1** (s)	*77.9*	*54.2*	*57.8*	*38.0*	*31.9*	*6.1*
SnO_2/**1** (c, 3000 rpm)	73.1	54.1	30.7	40.3	31.9	8.3
SnO_2/**2** (s)	*90.6*	*44.8*	*48.3*	*38.3*	*37.1*	*1.1*
SnO_2/**2** (c, 3000 rpm)	22.9	29.8	32.4	73.9	44.3	29.6
SnO_2/**3** (s)	*60.9*	*45.8*	*49.5*	*49.7*	*36.6*	*13.1*
SnO_2/**3** (c, 3000 rpm)	25.3	32.9	31.5	72.3	43	29.4
SnO_2/**4** (s)	*89.1*	*54.9*	*59.6*	*33.8*	*31.5*	*2.3*
SnO_2/**4** (c, 3000 rpm)	46.3	37.9	47.2	60.5	40.6	19.8

* “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).

Table S2. The performance characteristics of n-i-p PSCs assembled using different ETL materials extracted from reverse-scan *J-V* characteristics.

ETL	Method	V_{OC}, mV	J_{SC}, mA cm^{-2}	J_{SC}^{EQE}, mA cm^{-2}	FF, %	PCE, %
SnO_2/1	Spin-coating	953.1 (946.5±8.5)	22.6 (22.2±0.4)	22.4	71.7 (70.5±1.2)	15.5 (14.8±0.7)
	Soaking	826.2 (747.9±38.7)	22.1 (21.2±0.5)	21.7	65.1 (62.5±4.1)	11.9 (9.9±1.2)
SnO_2/2	Spin-coating	980.6 (960.9±18.4)	21.0 (20.7±1.0)	20.8	73.4 (70.6±2.3)	15.2 (14.0±1.0)
	Soaking	750.6 (732.2±18.7)	15.0 (14.7±0.8)	14.9	50.1 (45.6±2.5)	5.6 (4.9±0.4)
SnO_2/4	Spin-coating	989.8 (956.6±33.2)	23.1 (22.3±0.8)	22.9	72.2 (70.7±1.8)	16.5 (15.1±1.4)
	Soaking	891.2 (826.4±35.4)	22.0 (21.7±0.6)	21.5	66.7 (64.6±3.0)	13.1 (11.6±0.9)
SnO_2/PCBA	Spin-coating	1044.1 (1033.2±10.8)	22.3 (22.1±0.4)	22.2	75.7 (73.4±2.9)	17.6 (16.7±0.9)
	Soaking	1026.9 (1018.8±6.2)	22.3 (21.5±0.7)	22.1	75.9 (75.1±1.0)	17.4 (16.5±0.6)
SnO_2	-	986.5 (906.4±80.1)	19.7 (18.7±1.1)	19.5	45.4 (37.2±8.2)	7.9 (6.3±1.6)