Supporting Information

A Supramolecular Strategy for Tuning the Energy Level of Naphthalenediimide: Promoted Formation of Radical Anions with Extraordinary Stability

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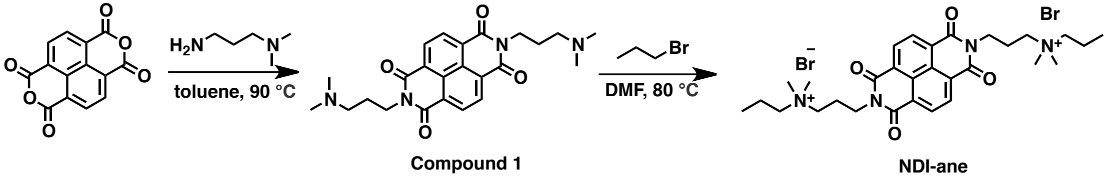
1. Materials & Methods

Materials were obtained from commercial suppliers and were used without further purification. ^{1}H NMR and ^{13}C NMR spectra were recorded on a JOEL JNM-ECA400 apparatus. EPR (Electron Paramagnetic Resonance) experiments were performed at room temperature on a JEOL JES-FA200 apparatus. ITC (Isothermal Titration Calorimetry) experiments were carried out with a Microcal VP-ITC apparatus at 298.15 K. UV/vis spectra were obtained using a HITACHI U-3010 spectrophotometer (path length: 0.5 mm). Fluorescence spectra were measured using a HITACHI F-7000 apparatus (path length: 10 mm, excitation wavelength: 262 nm). The UV irradiation process was carried out with a high-pressure mercury lamp (RW-UVA, China, 900 mW/cm^2). Time-resolved fluorescence measurements were performed on a homemade time-correlated single photon counting (TCSPC) apparatus. Briefly, the output of an optical parametric amplifier (OPA) pumped by a Spectra Physics 1 kHz amplified Ti:Sapphire laser was used as the excitation light (345 nm,150 fs). The emission was collected and sent into a Princeton Instruments SP2358 monochromator and detected with a Hamamatsu R3809U-50 MCP-PMT. The output of the R3809U-50 MCP-PMT and the output of a fast TDA 200 photodiode were respectively connected to a Becher & Hickl GmbH SPC-130 module as the start and stop pulses. Magic angle detection was used to get rid of the molecular reorientation effect. The instrumental response function of this setup was about 75 ps. Cyclic voltammograms tests were conducted on an electrochemical workstation (CHI 760D, China) under computer control.

2. Experimental section

(1) Synthesis of **NDI-ane**



Scheme S1 Synthetic route of **NDI-ane**

Compound **1**:

1,4,5,8-naphthalenetetracarboxylic dianhydride (540 mg, 2 mmol) was dissolved in 100 mL toluene and heated to 90 °C, and N,N-dimethyl-1,3-propanediamine (1.5 mL, 12 mmol) was added dropwise over 10 min. The reaction mixture was heated at 120 °C for 24 h. The crude mixture was concentrated on a rotary evaporator, and the yellow crystalline Compound **1** was purified by recrystallizing from ethanol (510 mg, 58%).

^{1}H NMR (400 MHz, CHLOROFORM-D): δ (ppm) 8.76 (s, 4H), 4.27 (t, 4H), 2.46 (t, 4H), 2.25 (s, 12H), 1.94 (m, 4H).

^{13}C NMR (100 MHz, CHLOROFORM-D): δ (ppm) 163.01, 131.06, 126.82, 112.75, 57.33, 45.45, 39.48, 26.06.

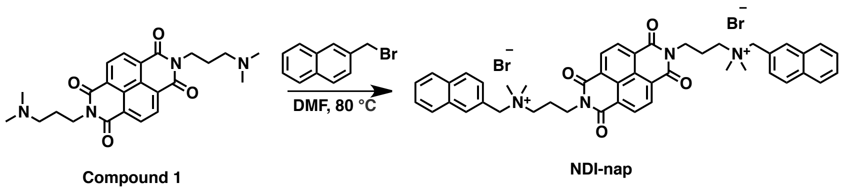
NDI-ane:

Compound **1** (200 mg, 0.46 mmol) was first dissolved in 10 mL DMF and then 1-bromopropane (0.4 mL, 4.4 mmol) was added. The mixture was heated at 80 °C for 12 h. After precipitated in toluene, the pale yellow product **NDI-ane** was collected by filtration and dried under vacuum (260 mg, 83%).

^{1}H NMR (400 MHz, D_2O): δ (ppm) 8.62 (s, 4H), 4.26 (t, 4H), 3.54 (m, 4H), 3.32 (m, 4H), 2.75 (s, 12H), 2.29 (m, 4H), 1.84 (m, 4H), 1.00 (t, 6H).

^{13}C NMR (100 MHz, D_2O): δ (ppm) 164.10, 131.13, 126.08, 112.25, 65.91, 61.58, 50.64, 37.84, 21.06, 15.74, 9.87.

(2) Synthesis of **NDI-nap**



Scheme S2 Synthetic route of **NDI-nap**

NDI-nap:

Compound **1** (200 mg, 0.46 mmol) was first dissolved in 10 mL DMF and then 2-(bromomethyl)naphthalene (400 mg, 1.8 mmol) was added. The mixture was heated at 80 °C for 6 h. After precipitated in toluene, the light yellow product **NDI-nap** was collected by filtration and dried under vacuum (260 mg, 83%).

^{1}H NMR (400 MHz, D_2O): δ (ppm) 8.44 (s, 4H), 7.90 (s, 2H), 7.53 (d, 2H), 7.46 (q, 4H), 7.31 (d, 2H), 7.22 (t, 2H), 7.15 (t, 2H), 4.69 (s, 4H), 4.28 (t, 4H), 3.28 (m, 4H), 3.24 (s, 12H), 2.40 (m, 4H).

^{13}C NMR (100 MHz, D_2O): δ (ppm) 163.89, 133.10, 132.75, 132.18, 131.22, 128.75, 128.34, 127.98, 127.49, 127.24, 126.80, 125.49, 124.67, 68.45, 60.15, 50.96, 37.56, 21.48.

(3) Cyclic voltammetry experiment

Conditions: 1 mM in H_2O (solutions for both NDI and supramolecular complex); reference electrode, Hg/Hg_2Cl_2; working electrode, glassy carbon; auxiliary electrode, Pt; degassed with nitrogen for 15 min before measurement; 298 K; scan rate, 100 mV/s.

3. ITC study of the complexation of NDI and CB[7]

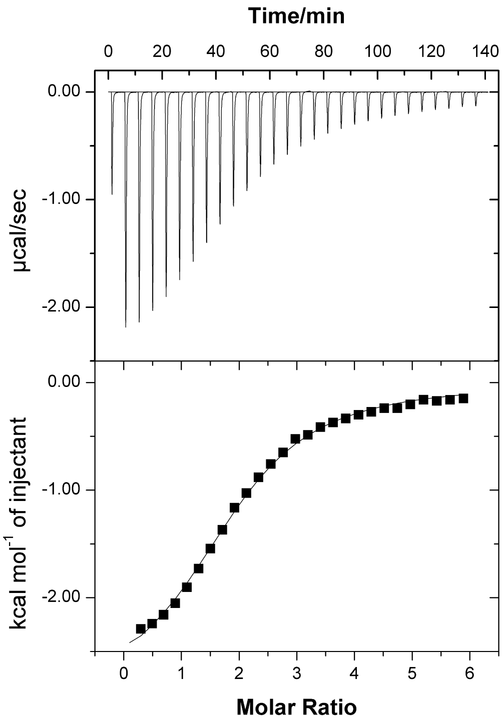


Figure S1 ITC data for titration of NDI (0.08 mM) with CB[7] (2 mM) in 50 mM HAc/NaAc (pH=4.75) at 25 °C. Fitting data using one set of the binding site model gave a binding constant of 2.4×10^4 M^{-1} with binding ratio of 2:1.

4. EPR experiment of NDI/CB[7]

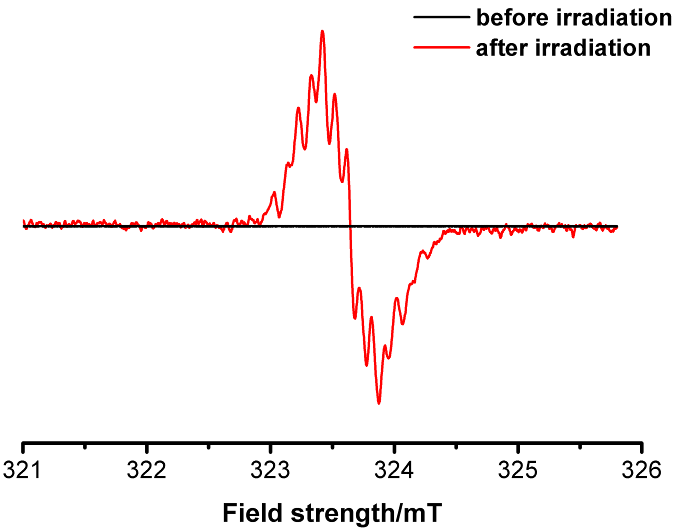


Figure S2 EPR spectra of NDI/CB[7] before (black line) and after (red line) UV irradiation.

5. ^{1}H NMR of NDI/CB[7] before and after UV irradiation

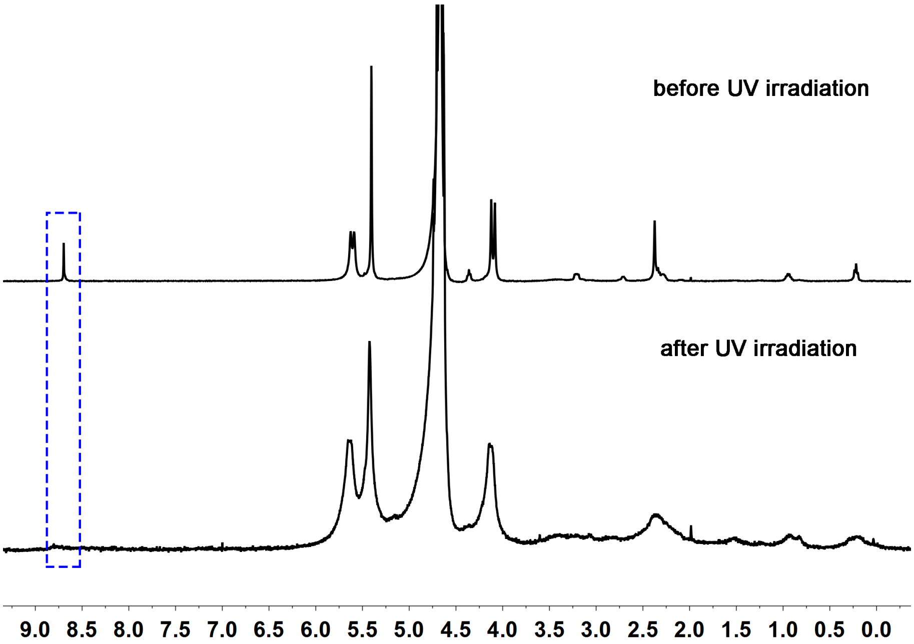


Figure S3 ^{1}H NMR of NDI/CB[7] before and after UV irradiation. Peak at 8.44 ppm vanished after UV irradiation, indicating the formation of NDI radical anions. (400 MHz, D_2O, [NDI] = 1 mM)

6. Fluorescence spectra

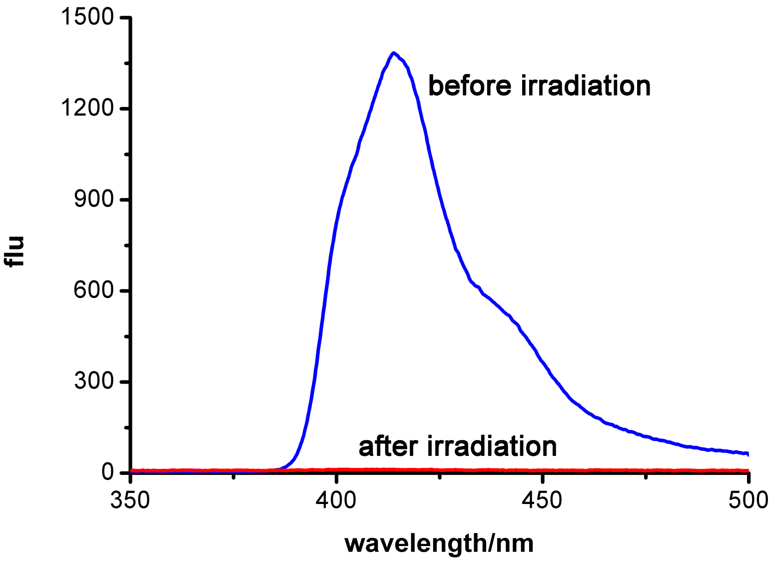


Figure S4 Fluorescence spectra of NDI/CB[7] before and after UV irradiation. After UV irradiation, the fluorescence was fully quenched, demonstrating the formation of NDI radical anions. (EX: 262 nm, [NDI] = 0.2 mM)

7. ^{1}H NMR of NDI/CB[7] before and after adding ADA.

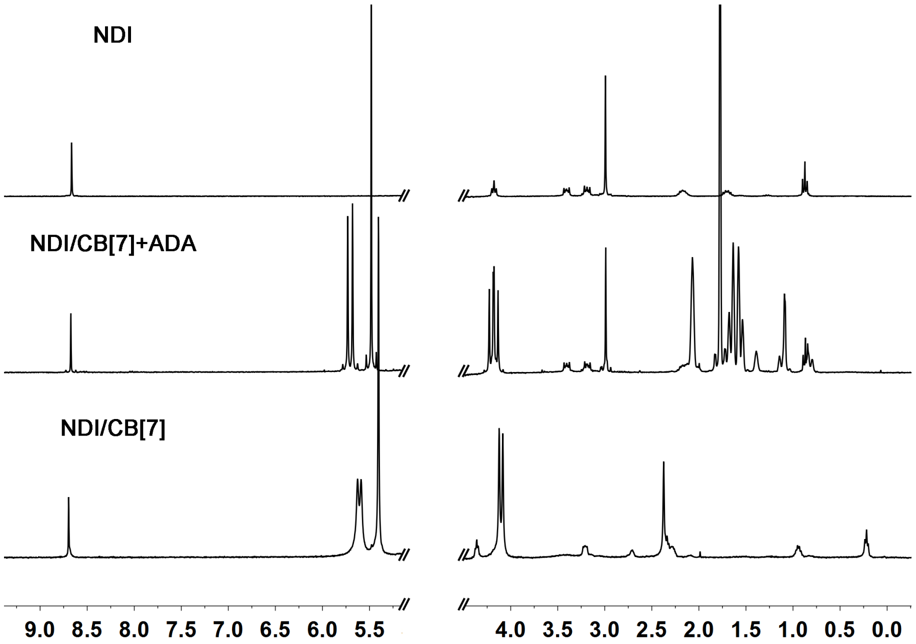


Figure S5 ^{1}H NMR of NDI/CB[7] before and after adding ADA as well as NDI. After adding ADA, peaks belonging to NDI shifted back, indicating the supramolecular complexation of NDI and CB[7] was destroyed by ADA. (400 MHz, D_2O, [NDI] = 1 mM, [ADA] = 10 mM)

8. UV/vis spectra of NDI/CB[7] before and after adding ADA under UV irradiation.

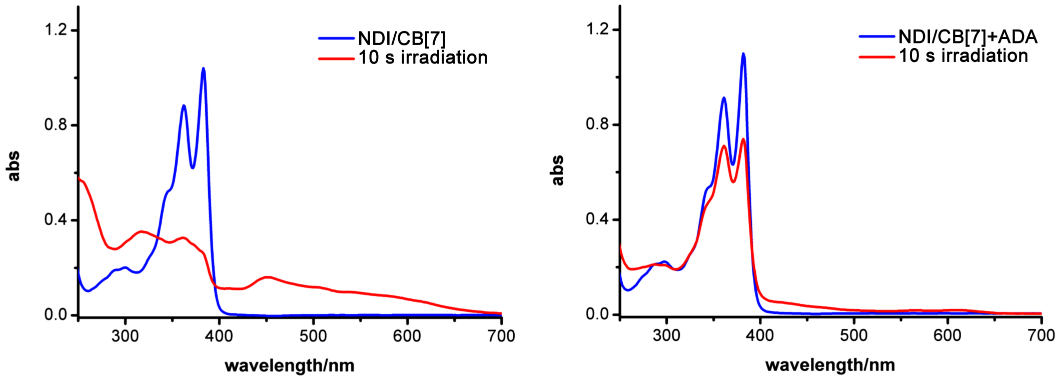


Figure S6 UV/vis spectra of the supramolecular complex of NDI/CB[7] before and after adding ADA under 10 s UV irradiation.

9. Photo-reduction of cytochrome *c* at the existence of NDI or NDI/CB[7]

$NDI^{\cdot}$+cyt *c* (Fe^{3+}) → NDI+cyt *c* (Fe^{2+})

Conditions: [cytochrome *c*]=10 mg/mL, [NDI]=0.2 mM, [CB[7]]=1 mM

10. Complexation of NDI-nap and CB[7]

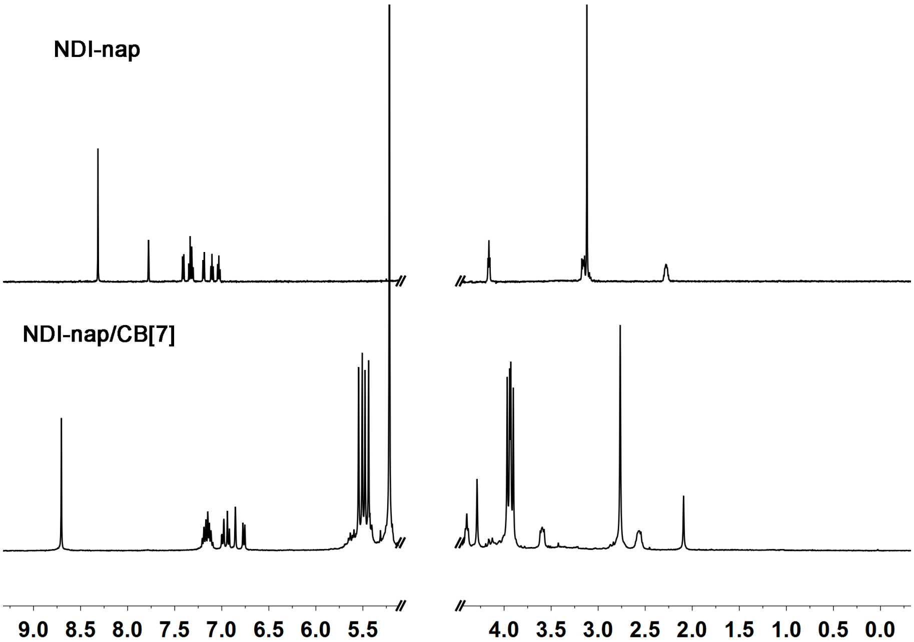


Figure S7 ^{1}H NMR of NDI-nap before and after the supramolecular complexation with CB[7]. (400 MHz, D_2O, [NDI-nap] = 1 mM)

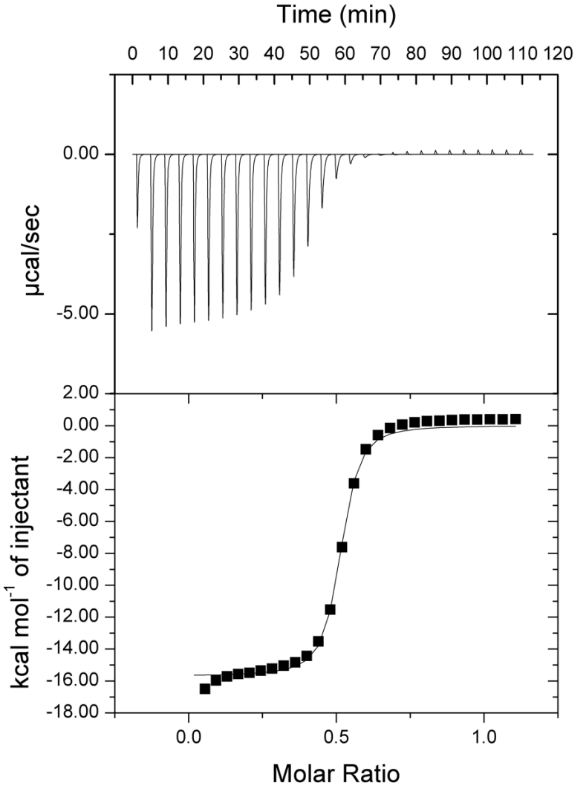


Figure S8 ITC data for titration of CB[7] (0.2 mM) with NDI-nap (1 mM) in 50 mM HAc/NaAc (pH=4.75) at 25 °C. Fitting data using one set of the binding site model gave a binding constant of 2.8×10^6 M^{-1} with binding ratio of 1:2.

11. LUMO of NDI-nap and NDI-nap/CB[7]

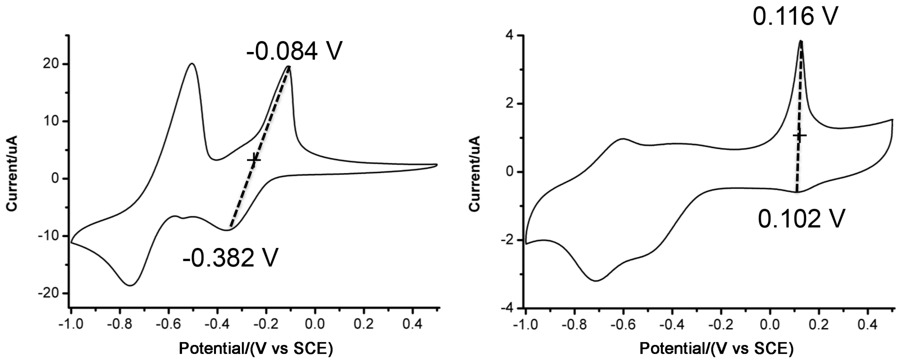


Figure S9 Cyclic voltammograms of NDI-nap and NDI-nap/CB[7].

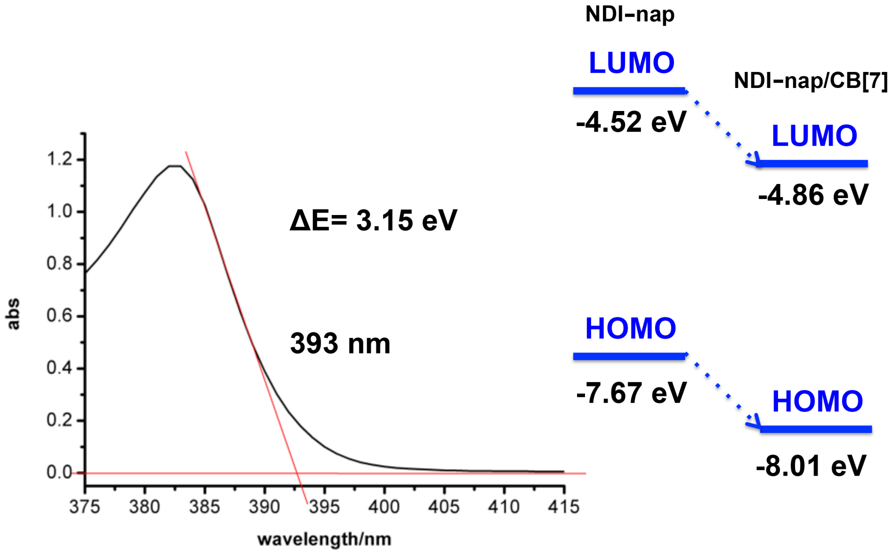


Figure S10 Calculation of band gap between HOMO and LUMO of NDI-nap and NDI-nap/CB[7] (left); LUMO and HOMO energy of NDI-nap and NDI-nap/CB[7] (right).

12. COSY of NDI-ane

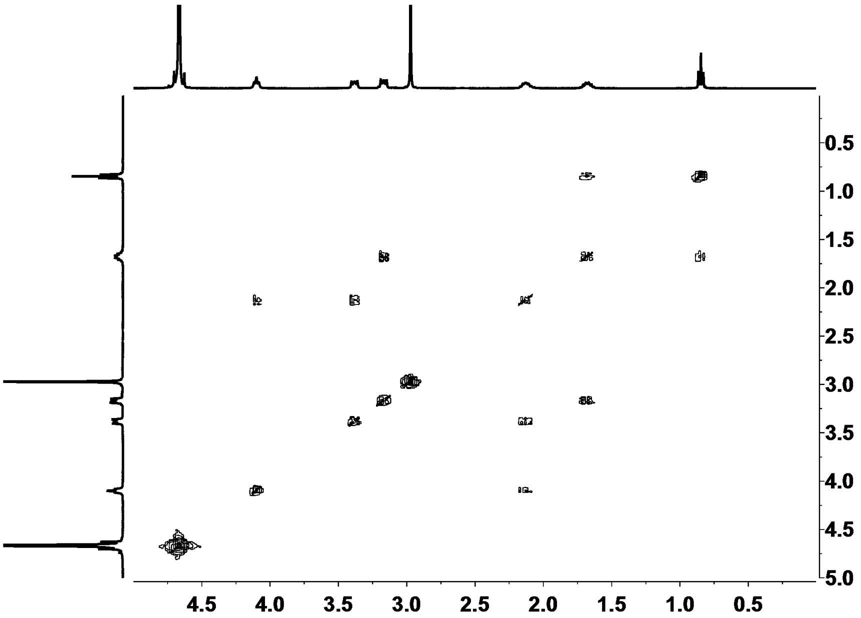


Figure S11 COSY spectrum of NDI-ane. (400 MHz, D_2O)