

Supporting Information

Helical supramolecular organization of 1,2-diol appended naphthalene diimide organogelator via extended intermolecular H-bonding network

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1. General Methods.

¹H NMR spectra were recorded at 400 MHz, and ¹³C NMR spectra at 101 MHz. All the spectra are calibrated with respect to residual solvent peak. The following abbreviations are used to describe peak patterns where appropriate: b, broad; s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet. Coupling constants are reported in hertz (Hz). High resolution mass spectra (HRMS) were performed either on an electron spray ionization time-of-flight (ESI-TOF). Melting points were measured with a micro melting point apparatus.

2. Instrumentation.

UV-visible and fluorescence spectroscopic measurements: Stock solutions of **1** (1.0 mM) and **2** (1.0 mM) were prepared in spectroscopy grade CHCl_3 . Measured volume of either **1** (1.0 mM) or **2** (1.0 mM) was added to an appropriate volume of methyl cyclohexane (MCH) to set the desired solvent ratio and final concentration of either **1** or **2** to 10 μM .

For investigating effect of MeOH addition on aggregation, a solution of **1** in MCH/ CHCl_3 (95:5) was taken and measured amount of MeOH was added and spectra were recorded.

FESEM, TEM and AFM studies: For recording microscopic images, 10 μL solution of **1** in (95 % MCH in CHCl_3 , $c = 0.1 \text{ mM}$) was placed on a silicon wafer for FESEM, copper grid for TEM, and mica plate for AFM. Subsequently, each sample was allowed to air dry overnight and then vacuum dry for period of 48 h before the images were taken.

Circular Dichroism (CD) Spectroscopy: CD spectra were recorded on a JASCO (J-815) spectrometer under a nitrogen atmosphere. Experiments were carried out at 25 $^\circ\text{C}$ in a quartz cuvette with a 1 mm path length over the range of 190-500 nm. The CD spectra were recorded in CHCl_3 and 95:5 MCH/ CHCl_3 . The concentration of compound used for measurements was 20 μM .

X-Ray diffraction measurements: XRD data was recorded on a Seifert XRD3000P diffractometer, using $\text{Cu-K}\alpha$ radiation ($\lambda = 0.15406 \text{ nm}$) source. In a typical XRD experiment, gel sample prepared from **1** (70% MCH) was placed on a glass slide and air dried. Gel sample was drop casted several times to make a thick film. Data was recorded from 0.5° to 6° and from 6° to 30° with a sampling interval of 0.02° per step with a voltage and current of 40 kV and 30 mA, respectively.

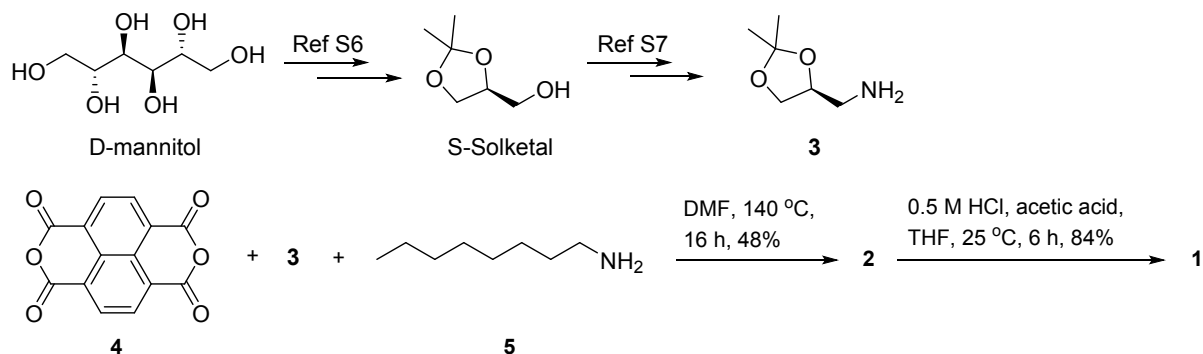
Gelation test: **1** (2.0 mg) in 1.0 mL of the solvent were placed into a capped pyrex tube. The suspension was heated until the compound was dissolved to give clear solution. Then the solution was allowed to cool to room temperature. Gelation was confirmed by the absence of flow of the solvent on inversion of tube. To measure the critical gelation concentration (CGC), 100 μL of solvent was added each time until the concentration was insufficient for forming a stable gel.

Computational details: The monomers and rest of the geometries were built using GAUSSVIEW 5.0 and UCSF CHIMERA software. The calculations were performed using

Gaussian 09^{S1} and MOPAC 2012^{S2} software. Different monomer geometries were tried and structure with most stable energy was chosen to build higher order structures. The octyl chain of each monomer was replaced by an ethyl chain for primary calculations. The interaction energies of monomer (**M**), head-to-head dimer (**M**₂) (Fig. S13) and tetramer (**M**_{2,2}) were calculated at semi-empirical (PM6-DH2)^{S3, S4} and DFT (ω B97X-D)^{S5} levels of theory. The interaction energy was calculated as difference between the energy of either dimer or tetramer assembly and monomer units [$E_{interaction} = E_n - n \times E_1$]; where, E_1 = energy of a monomer unit and $n = 2$ or 4]. The dimer unit was built such that diol groups of monomer units form hydrogen bonds. These dimer units were stacked over each other with stacking distance of 4.68 Å so as to avoid intermolecular steric clashes. The hydrogen bonds were restrained while calculating energies of **M**₂ and **M**_{2,2} units. Each stacked pair was rotated relative to lower adjacent stacked molecule by 1° in the clockwise direction using dihedral shown in Fig. S16A and single point energy was calculated for each conformation. The minima (Fig. S16B) was observed at the -3° angle and hence this angle was chosen to perform calculations on tetramer **1**_{2,2}. This complex was optimized using PM6-DH2 method using MOPAC2012. Interaction energies indicate stabilization of higher order structures. Natural bond orbital (NBO) analysis was performed on the **M**_{2,2} complex at DFT level with ω B97X-D method with 6-31G** basis set using NBO 3.0 program implanted in GAUSSIAN 09. The NBO analysis adequately confirms strong and extended hydrogen bonding interactions of hydroxyl groups.

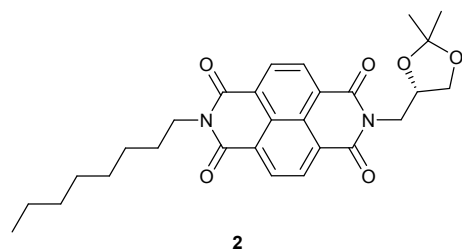
3. Synthesis.

Starting material (*S*)-(2,2-dimethyl-1,3-dioxolan-4-yl)methanamine **3** was prepared from D-mannitol following the reported protocol (Scheme 1).^{S6, S7}



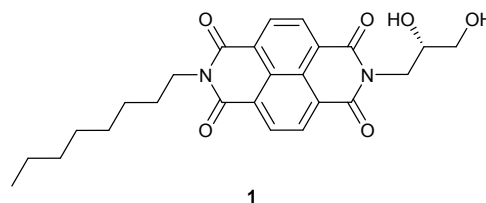
Scheme S1. Synthesis of naphthalenediimide derivatives **1** and **2**.

Synthesis of 2 (C₂₈H₃₂N₂O₆): To a suspension of 1,4,5,8-naphthalene-tetracarboxylic dianhydride **3** (776 mg, 2.90 mmol) and dry DMF (15 mL) placed in a 50 mL round bottomed flask were added and *n*-octylamine **5** (375 mg, 2.90 mmol) and (*S*)-(2,2-dimethyl-1,3-



dioxolan-4-yl)methanamine **3** (380 mg, 290 mmol). The reaction mixture was stirred at 140 °C under N₂ atmosphere for 16 h. The heating was stopped and the solution was allowed to cool to room temperature. The DMF was evaporated under reduced pressure. The resulting residue was dissolved in EtOAc (20 mL) and then washed with water (2 × 5 mL). The organic layer was dried with Na₂SO₄ and concentrated under reduced pressure to obtain brown solid which was further purified by column chromatography over silica gel (*Eluent* : 8% EtOAc in petroleum ether) to furnish **2** as dark pink solid (690 mg, 48%). **M.P.:** 178.0-178.5 °C; **FT IR (neat, ν_{cm⁻¹}):** 3022, 2930, 2859, 1705, 1666, 1581, 1456, 1376, 1336, 1246, 1215, 1181, 1066, 976, 879, 743, 668; **¹H NMR (400 MHz, CDCl₃):** δ 8.77 (d, *J* = 7.6 Hz, 2H), 8.75 (d, *J* = 7.6 Hz, 2H), 4.62 (dd, *J* = 12.4, 7.6 Hz, 1H), 4.58 - 4.54 (m, 1H), 4.21 - 4.13 (m, 4H), 3.92 (dd, *J* = 8.6, 5.0 Hz, 1H), 1.74 (q, *J* = 7.6 Hz, 2H), 1.48 (s, 3H), 1.47 - 1.22 (m, 13H), 0.87 (t, *J* = 6.8 Hz, 3H); **¹³C NMR (100 MHz, CDCl₃):** δ 163.1 (2C), 162.8 (2C), 131.2 (2C), 131.0 (2C), 126.8 (2C), 126.7(2C), 126.5 (2C), 109.1, 73.4, 67.8, 43.5, 41.1, 31.9, 29.4, 29.3, 28.2, 27.2, 26.8, 25.6, 22.7, 14.2; **CHN Analysis:** Calcd. C, 68.28; H, 6.55; N, 5.69 %; Found C, 67.70; H, 5.702; N, 5.52 %.

Synthesis of 1 (C₂₅H₂₈N₂O₆): To a solution of **1** (600 mg, 1.22 mmol) in tetrahydrofuran (10 mL) and acetic acid (10 mL) was added 0.5 M HCl (1 mL) at 0 °C, and mixture was stirred at ambient temperature



for 12 h. The resulting residue was filtered off and residue was washed with pentane and dried under *vacuo* to obtained corresponding diol **2** (463 mg, 84%); **M.P.:** 244.0-245.0 °C; **FT IR (neat, ν cm⁻¹):** 3522, 3346, 3075, 2920, 2852, 1984, 1697, 1645, 1579, 1454, 1334, 1274, 1242, 1171, 1101, 1070, 1046, 972, 898, 850.61, 763, 719; **¹H NMR (400 MHz, CDCl₃):** 8.64 (s, 4H), 4.85 (d, J = 5.1 Hz, 1H), 4.64 (t, J = 5.7 Hz, 1H), 4.24 (dd, 12.9, 8.5 Hz, 1H), 4.06 - 3.98 (m, 3H), 3.92 (ddd, J = 12.7, 10.2, 5.2 Hz, 1H), 3.43 (td, J = 10.6, 5.2 Hz, 2H), 1.65 (q, J = 7.5 Hz, 2H), 1.42 - 1.17 (m, 10H), 0.85 (t, J = 7Hz, 3H); **¹³C NMR (101 MHz, DMSO-*d*₆) δ** 162.77 (2C), 162.52 (2C), 130.38 (2C), 130.34 (2C), 126.32 (2C), 126.09 (2C), 126.02, 125.98, 68.31, 64.49, 43.75, 39.52, 31.26, 28.72, 28.59, 27.36, 26.54, 22.11, 13.97; **HRMS:** (ESI) Calcd. for C₂₅H₂₉N₂O₆ [M + H]⁺ = 453.2026, found 453.2042.

4. NMR Spectra.

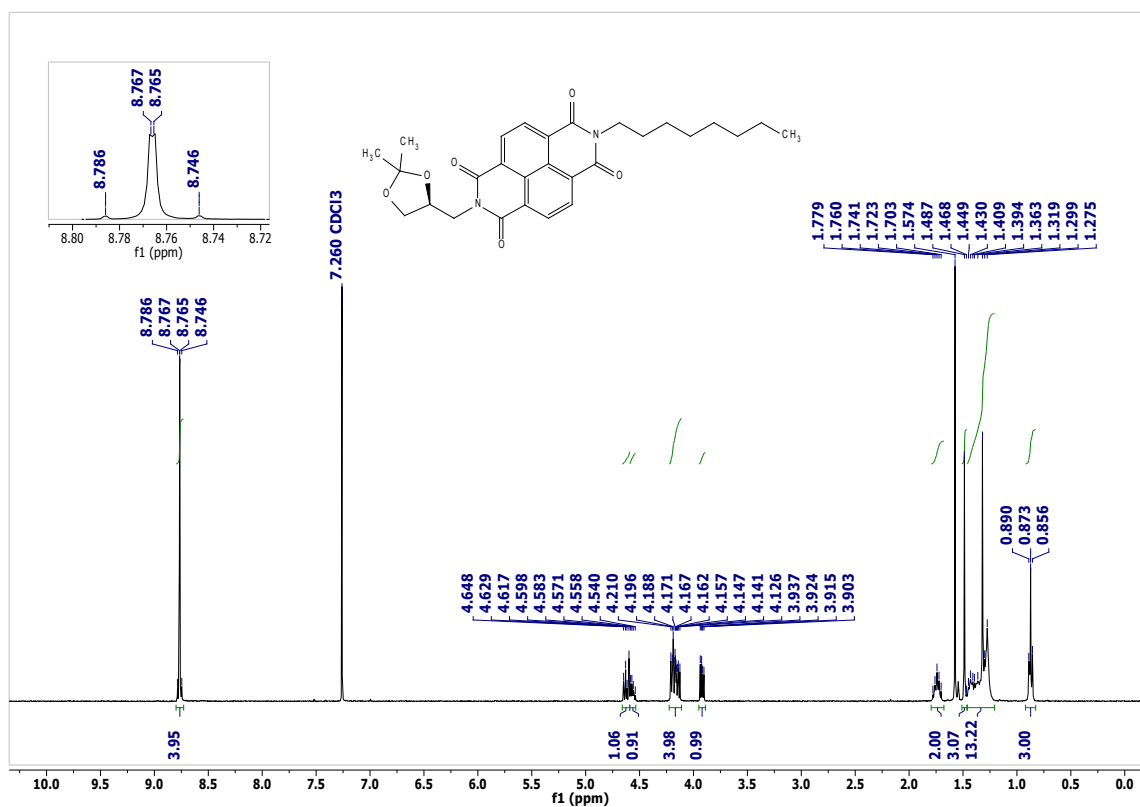


Fig. S1 ¹H NMR spectrum of 2.

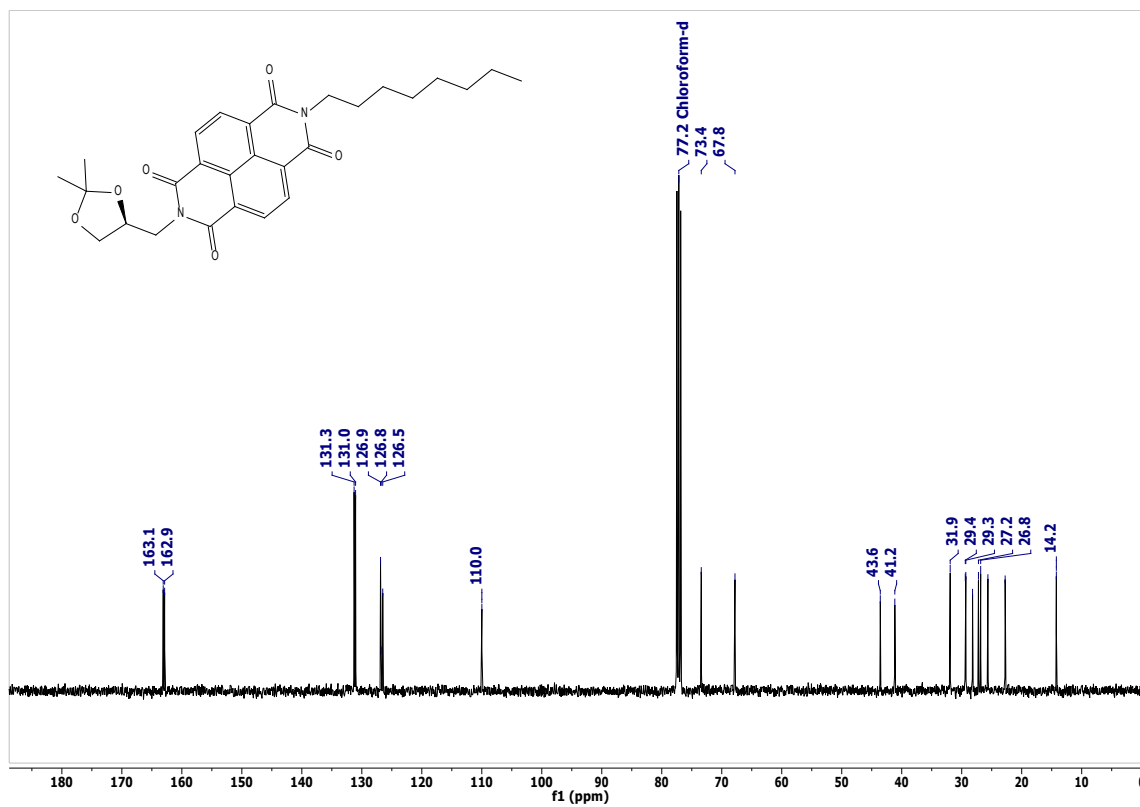


Fig. S2 ¹³C NMR spectrum of 2.

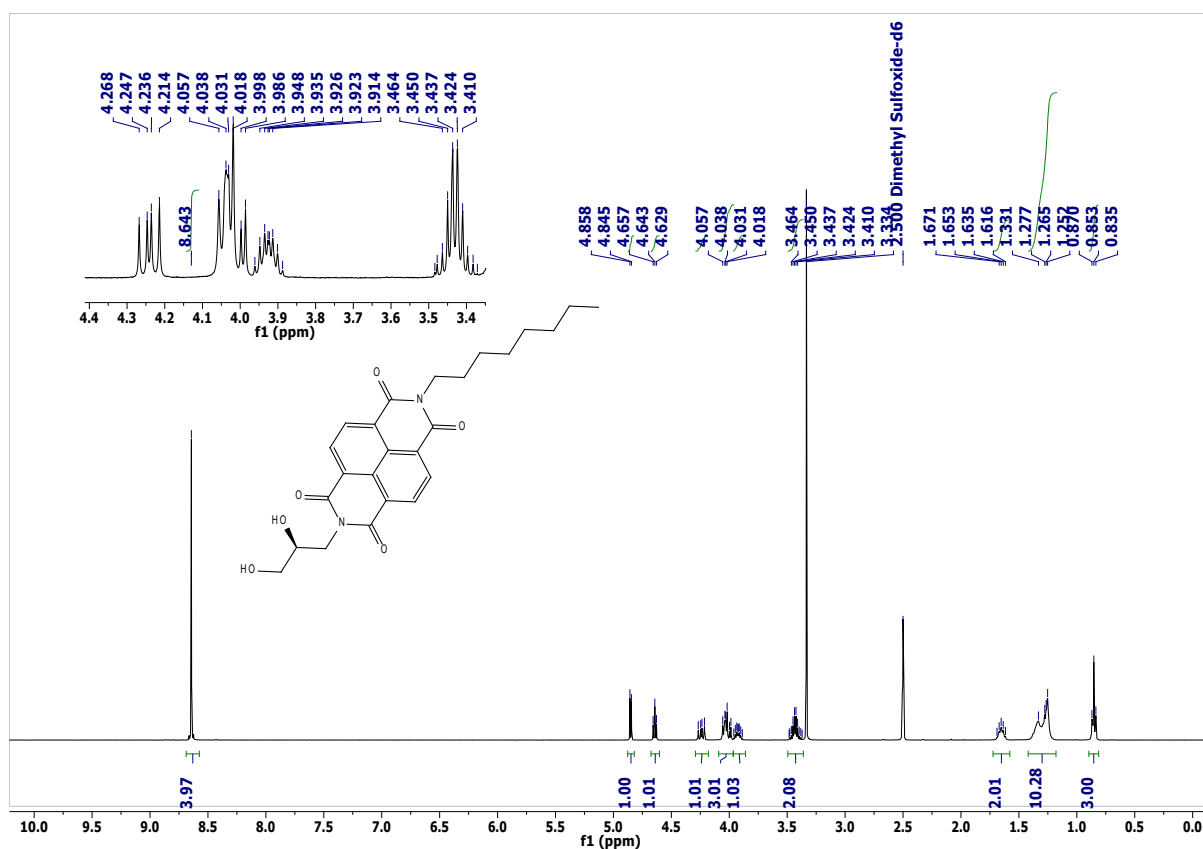


Fig. S3 ¹H NMR spectrum of 1.

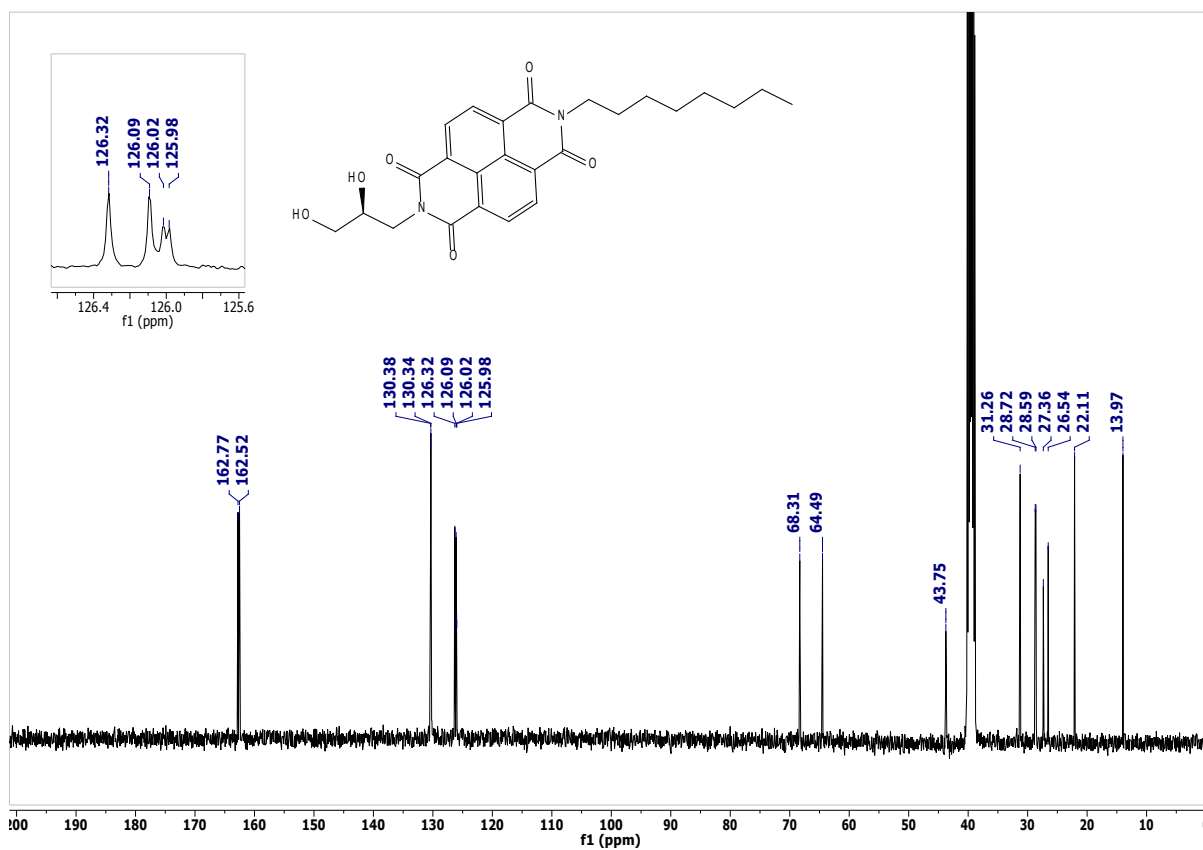


Fig. S4 ¹³C NMR spectrum of 1.

5. Supporting Spectra and Figures.

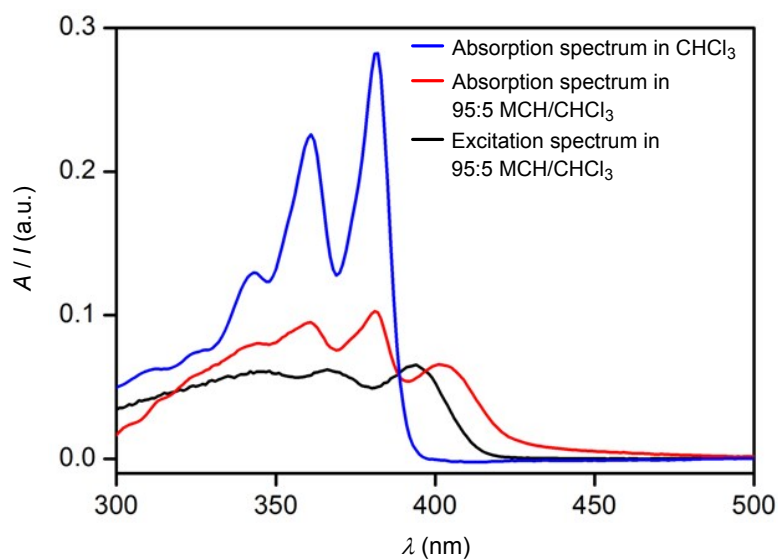


Fig. S5 Absorption spectra of **1** in CHCl_3 (blue line) and 95:5 MCH/ CHCl_3 (red line). Excitation spectrum (black line) in 95:5 MCH/ CHCl_3 recorded at 578 nm (excimer emission).

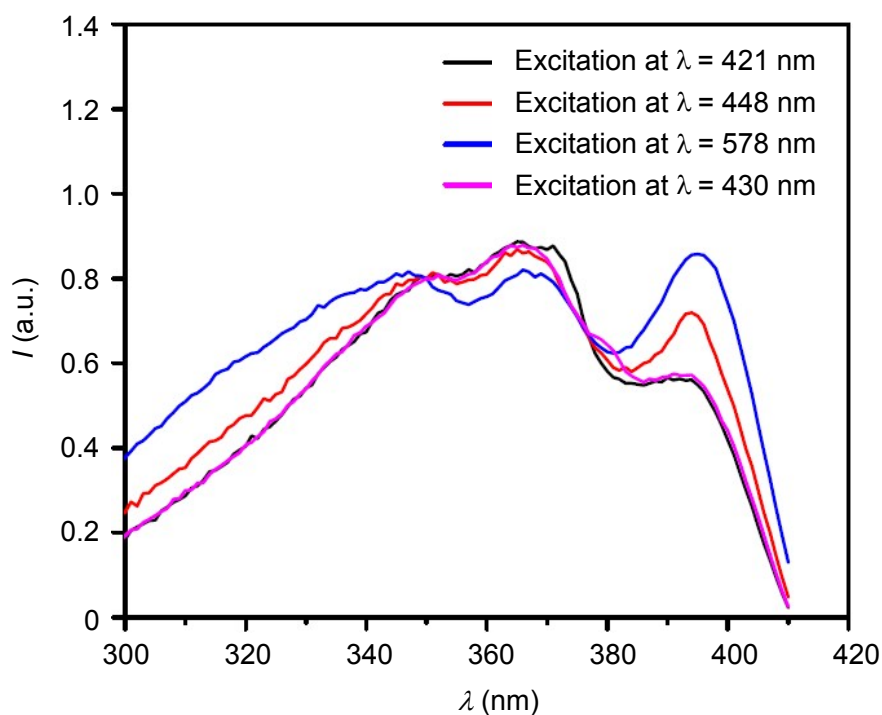


Fig. S6 Excitation spectrum of **1** in 95:5 MCH/ CHCl_3 collected at 421, 448, 578, and 430 nm.

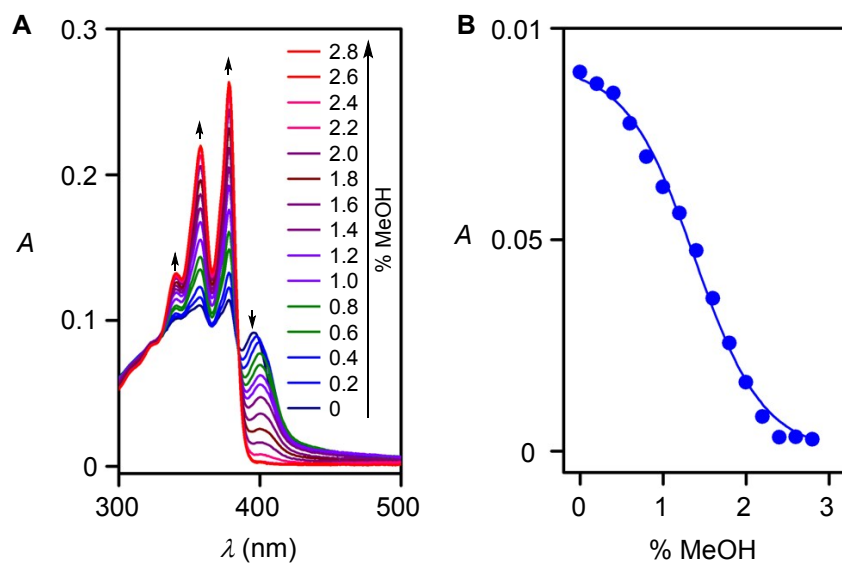


Fig. S7 UV-visible spectra of **1** (1×10^{-5} M) in CHCl₃ with varied percentage of MeOH (A). The plot of absorption maxima (396 - 402 nm region) versus percentage of methanol added (B).

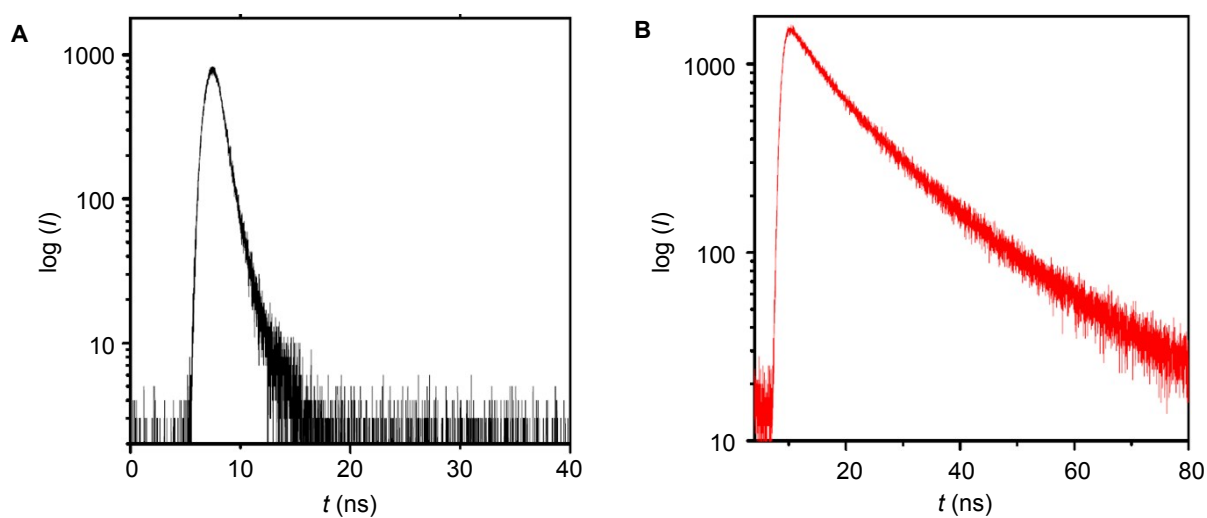


Fig. S8 Time resolved fluorescence decay of **1** ($c = 1 \times 10^{-5}$ M) in MCH. (A) The black line corresponds to the decay collected at 447 nm. (B) The red line corresponds to the decay monitored at 578 nm ($\lambda_{\text{ex}} = 340$ nm).

Table S1. Gelation data for **1** in various solvents (1.5 mg/mL).

Entry	Solvent	Observation
1	1:1 MCH/CHCl ₃	Precipitation
2	3:2 MCH/CHCl ₃	Viscous Solution
3	7:3 MCH/CHCl ₃	Gel
4	4:1 MCH/CHCl ₃	Gel
5	4:1 Toluene/CHCl ₃	Solution
6	Toluene	Solution
7	4:1 Cyclohexane/CHCl ₃	Gel
8	4:1 n-Hexane/CHCl ₃	Insoluble
9	Benzene	Precipitation
10	4:1 n-Heptane/CHCl ₃	Gel

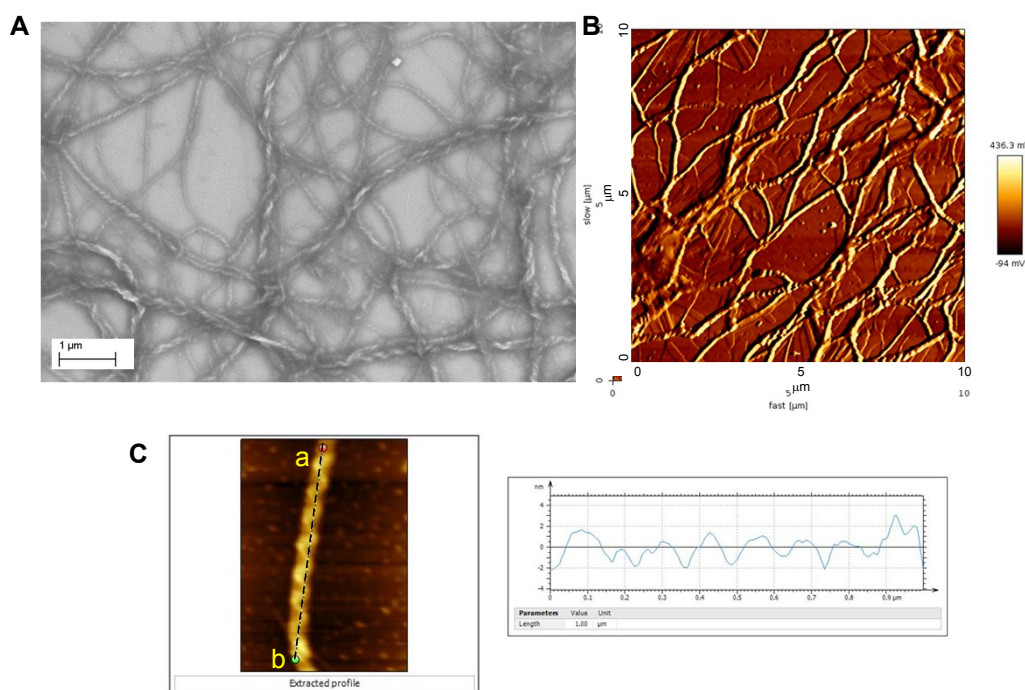


Fig. S9 SEM (A) and AFM (B) images of **1** in MCH. The cross section along *a-b* (C).

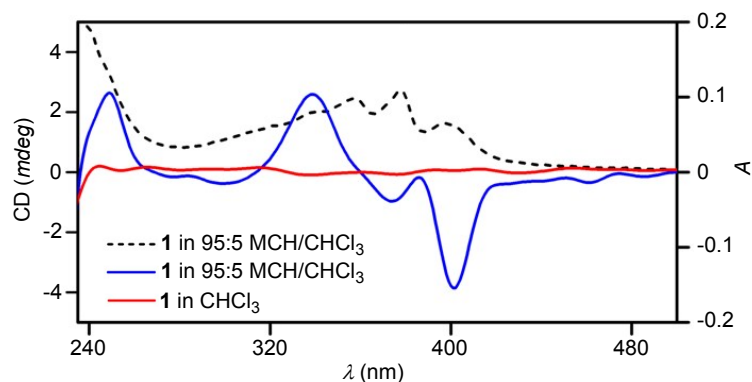


Fig. S10 CD spectra of **1** (1×10^{-5} M) in CHCl_3 and 95:5 MCH/ CHCl_3 . UV-visible spectrum of **1** in 95:5 MCH/ CHCl_3 .

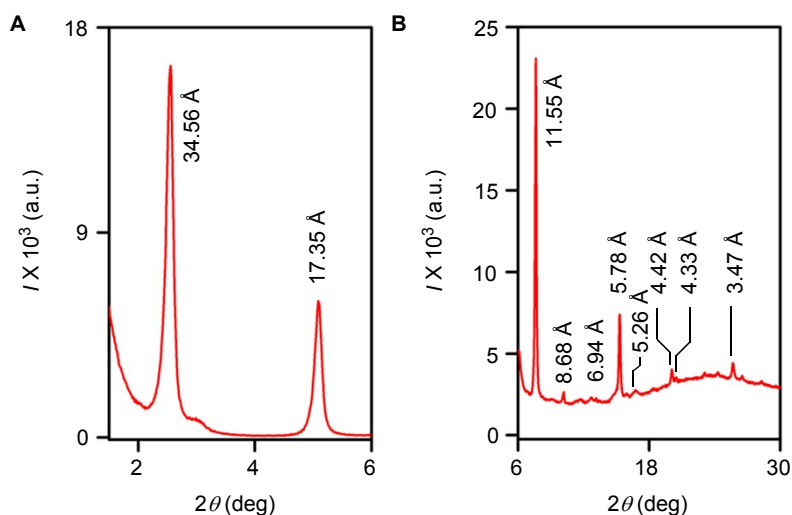


Fig. S11 PXRD pattern of the xerogel prepared from **1** (A and B).

SCLC electron mobility measurement: SCLC electron-only devices were fabricated by following procedure. Bottom aluminum electrode was deposited by thermal evaporation technique with a thickness of 100 nm under vacuum in a glove box. Gel sample (1.5 mg/mL) in 70:30 MCH/ CHCl_3 were drop casted on top of the aluminum electrode. The drop cast films were dried under vacuum at ambient temperature. On top of the active layer aluminum counter electrodes were evaporated through a shadow mask to a thickness of 100 nm in a thermal evaporation chamber. The active device area and thickness was found to be in the range of 0.06 cm^2 and $4.5\text{-}5.2 \text{ }\mu\text{m}$ respectively. The mobility measurements were performed by measuring the current–voltage characteristics with a Keithley 2400 source meter. The average mobility for six devices was $3.64 \times 10^{-8} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$.

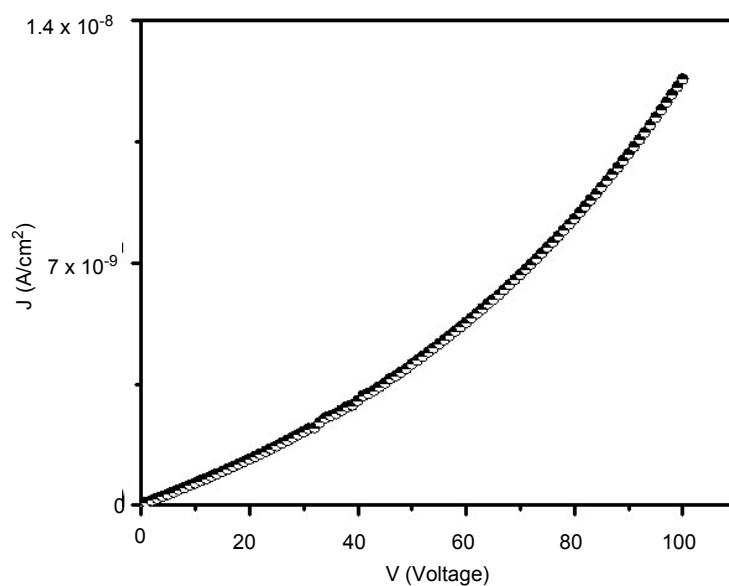


Fig. S12 Plot of the current density (J) versus applied voltage (V) measured for the **NDI-1** gel at room temperature (25°C) in devices with area around 0.06 cm^2 and average thickness of $4.7 \mu\text{M}$.

Theoretical calculations:

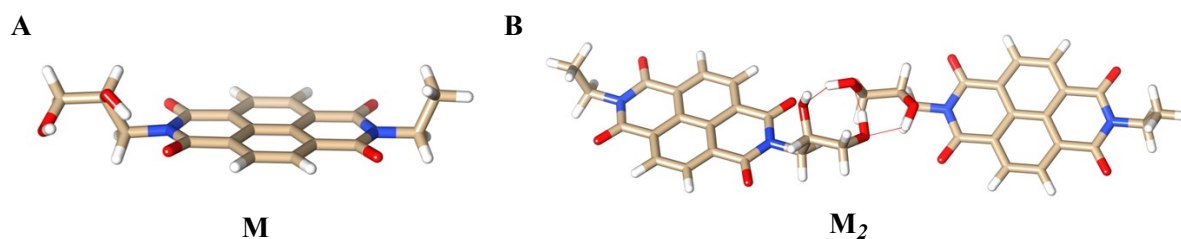


Fig. S13 Optimized geometry of **M** (A) and **M₂** (B).

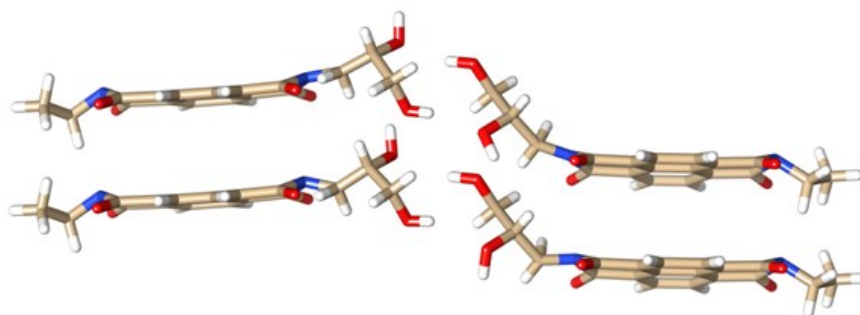


Fig. S14 Initial geometry of **M_{2,2}**.

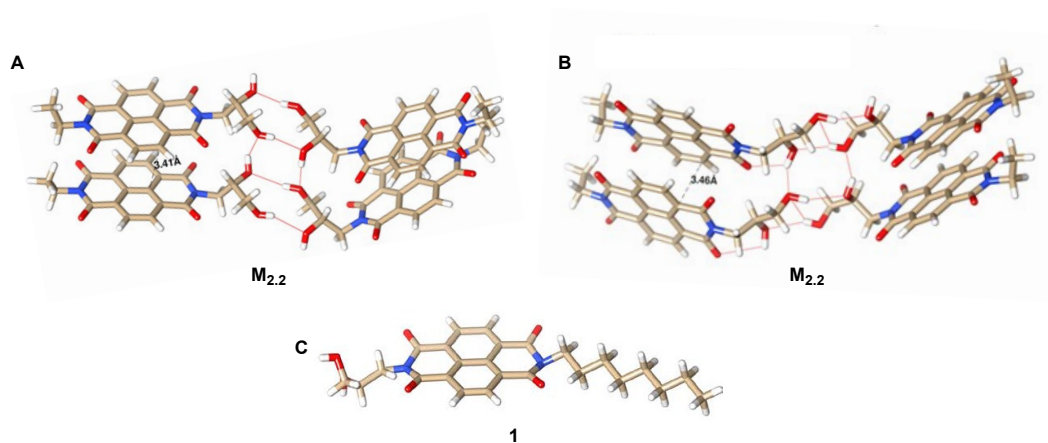


Fig. S15 PM6-DH2 (A) and ω B97X-D (B) optimized geometry of $M_{2.2}$. (C) PM6-DH2 optimized geometry of **1**.

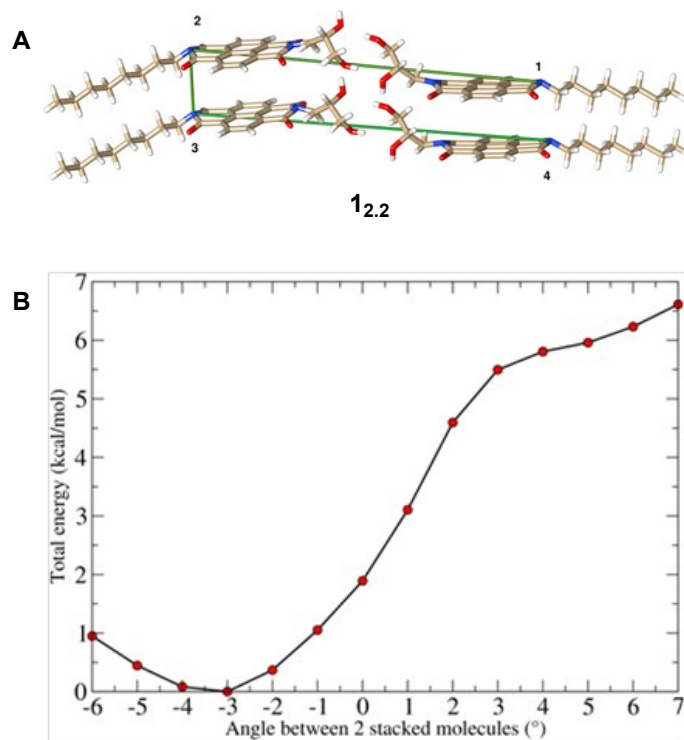


Fig. S16 Dihedral angle of complex **1**_{2.2} (A) and variation of energy along angle (B).

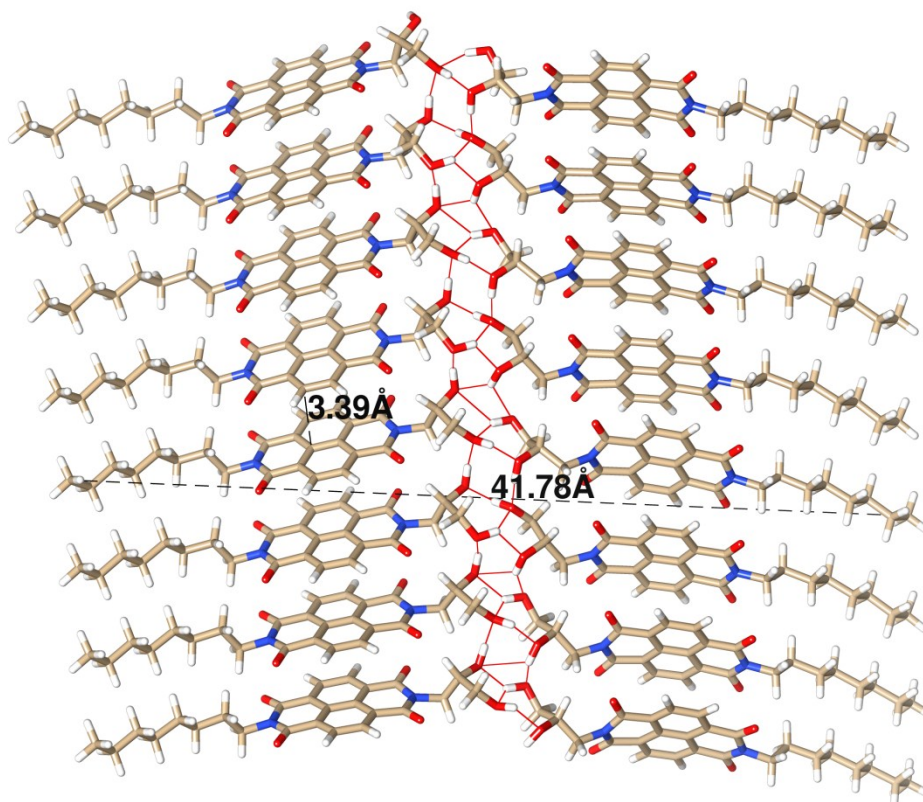


Fig. S17 Side view of optimized structure of **1_{2.8}** complex.

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