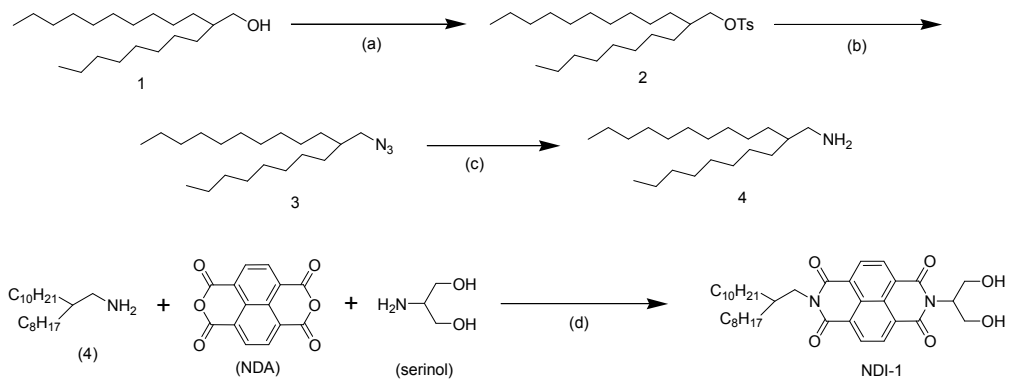
Supporting information for

Extended supramolecular organization of π-systems using yet unexplored simultaneous intra- and inter-molecular H-bonding motif of 1,3-dihydroxy derivatives

Tathagata Mondal, Dipankar Basak, Abdelaziz Al-Ouahabi, Marc Schmutz, Philippe Mésini* and Suhrit Ghosh*

Materials and method: Solvents and reagents were purchased from commercials sources and purified by standard protocols.[1] Serinol, 2-octyl dodecanol, naphthalene di-anhydride and pyromellitic dianhydride were obtained from Sigma. ^{1}H NMR spectras were recorded in a Bruker DPX-500 MHz spectrometer and peaks were calibrated using TMS as the internal standard. Perkin Elmer Spectrum 100FT-IR spectrometer was used to record the FT-IR spectra. Electron spray ionization (ESI) technique Q-tof-micro quadruple mass spectrometer (Micro mass) was used for determination of mass of the synthesized compounds. Spectroscopic grade solvents were used for all spectroscopic studies. UV-Vis spectra were recorded in a Perkin Elmer Lambda 25 spectrometer. Fluorescence emission spectral studies were conducted in a FluoroMax-3 spectrophotometer from HORIBA Jobin. Transmission electron microscopy images were captured in a JEOL-2010EX machine operating at an accelerating voltage of 200 kV. AFM images were taken in an Innova instrument from Bruker in tapping mode. SEM pictures were taken from a JEOL-6700F microscope. X-ray diffraction (XRD) was measured on a Seifert XRD3000P diffractometer with Cu Kα radiation (a = 0.154 06 nm) and a voltage and a current of 40 kV and 30 mA, respectively. A Nikon Coolpix camera was used for capturing the images.



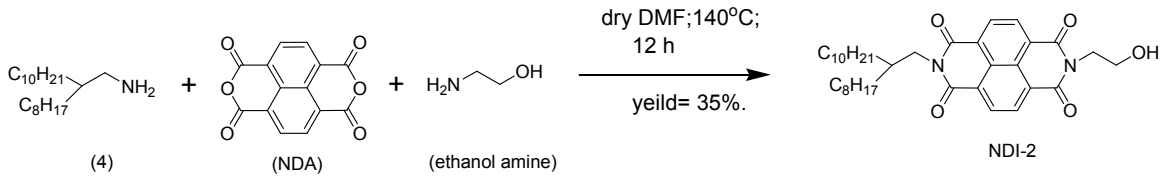
Reagents: (a) Ts-Cl; Pyridine; dry DCM; 0°C-5°C; 48 h, yeild=80%. (b) NaN_3; dry DMF; 90°C; 12 h; yeild=92% (c) H_2; Pd/C; EtOAc; 50 psi; 12 h. (d) dry DMF;140°C; 12 h; yeild=40%.

Scheme S1. Synthesis of **NDI-1**

Compound **2**: A solution of *p*-toluene sulfonylchloride (TsCl) (0.7g, 3.68 mmol) in 10.0 mL dry dichloromethane (DCM) was added drop-wise to an ice-cold solution of compound **1** (1.0 g, 3.34 mmol) and pyridine (2.65g, 33.4 mmol) in 10 mL dry DCM. Subsequently the reaction mixture was allowed to stir at rt for 48 h. The stirring was stopped, solvent was evaporated and the contents were dissolved in chloroform (70 mL) and washed with 2N aqueous HCl solution (2 x 30 mL) and brine (2 x 30mL). The organic layer was dried over anhydrous Na_2SO_4 and concentrated to get the crude product as light yellow oil which was purified by column chromatography using silica gel (100-200 mesh) as a stationary phase and petroleum ether/ ethyl-acetate (50: 1) mixture as eluent. The desired product was isolated as colorless oil. Yield = 80 %. ^{1}H NMR ($CDCl_3$, 400 MHz, TMS): δ (ppm) = 7.79 (2H, d); 7.32 (2H, d); 3.91 (2H, d); 2.44 (3H, s); 1.57 and 1.23 (33H, multiplate); 0.88 (6H, t).

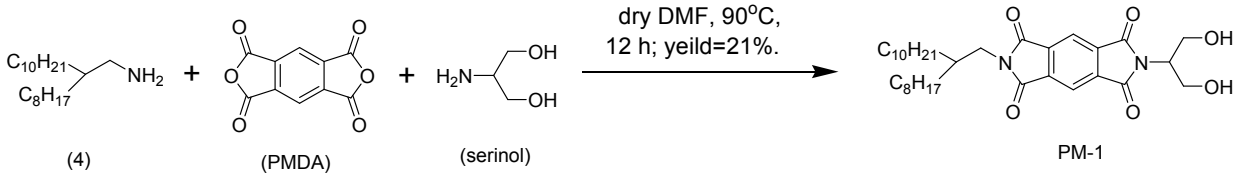
Compound **3**: Sodium azide (0.47g, 7.2 mmol) and compound **2** (1.1 g, 2.4 mmol) were mixed in 20 mL dry N,N'-dimethyl formamide (DMF) and was stirred for 12 h at 90 ^{o}C. Then the reaction was stopped cooled to rt and solution was poured to 100 mL water. The product was extracted with diethyl ether (70 mL) and the organic solution was then washed with brine (3 x 30 mL); dried over anhydrous Na_2SO_4 and concentrated to get the crude product as light yellow oil. Yield = 92%. ^{1}H NMR ($CDCl_3$, 400 MHz, TMS): δ (ppm) = 3.22 (2H, d); 1.54 (1H, broad); 1.27 (32H, multiplate); 0.88 (6H, t).

NDI-1: A solution of compound **3** (700 mg) in ethyl acetate (15 mL) was mixed with 10 % Pd/C (70 mg) and was stirred at rt in a closed high pressure reaction vessel under 55 psi pressure of H_2 gas for 12 h. Then the solution was passed through celite to remove the catalyst concentrated to get the branched amine (**4**) which was used for the next step without any purification. Serinol (184 mg, 2.01 mmol), naphthalene dianhydride (NDA) (540 mg, 2.01 mmol) and the branched amine **4** (600 mg, 2.01 mmol) were dissolved in dry DMF (20 mL) and the reaction mixture was heated at 140 ^{o}C for 12 h under inert atmosphere. The heating was stopped and the reaction mixture was allowed to stand at rt while solid precipitate came out (possibly the diimide product having alkyl chains in both sides) which was removed by filtration and the supernatant was added with 20 mL ice cold water while another batch of precipitate came out which was collected and dissolved in 20 mL $CHCl_3$ and was dried over Na_2SO_4 and concentrated to get the crude product as light brown solid. It was purified by column chromatography (1% MeOH/$CHCl_3$) using silica gel (100-200 mesh) as a stationary phase and the desired product **NDI-1** was collected as a pale yellow solid. Yield = 40%. ^{1}H NMR ($CDCl_3$, 500 MHz, TMS) δ (ppm): 8.7 (4H, s); 5.52 (1H, t); 4.18 (4H, dd); 4.13 (2H, d); 1.98 (1H); 1.3 (32H, aliphatic protons); 0.86 (6H, t); ^{13}C NMR ($CDCl_3$) δ (ppm): 164.27, 163.11, 131.56, 131.13, 126.93, 126.84, 126.66, 126.46, 61.32, 57.23, 45.16, 36.72, 32.02, 31.99, 31.78, 30.11, 29.74, 29.66, 29.44, 29.40, 26.54, 22.79, 14.22; HRMS (ESI): m/z calc for $C_{37}H_{52}N_2O_6Na^+$ [M + Na] $^+$: 643.3723; found: 643.3726.



Scheme S2. Synthesis of **NDI-2**

NDI-2: Compound **4** (800 mg, 2.68 mmol), NDA (721 mg, 2.68 mmol) and ethanol amine (164 mg, 2.68 mmol) were taken in 20 mL dry DMF and the solution was stirred for 12 h at 140 °C under inert atmosphere. The heating was stopped and the reaction mixture was allowed to stand at rt while solid precipitate came out (possibly the diimide product having alkyl chains in both sides) which was removed by filtration and the supernatant was added with 20 mL ice cold water while another batch of precipitate came out which was collected and dissolved in 20 mL $CHCl_3$ and was dried over Na_2SO_4 and concentrated to get the crude product as light brown solid. It was purified by column chromatography (1% MeOH/$CHCl_3$) using silica gel (100-200 mesh) as a stationary phase and the desired product **NDI-2** was collected as a yellow solid in 35 % yield. ^{1}HNMR ($CDCl_3$, 500 MHz, TMS): δ (ppm) = 8.77 (4H, s); 4.48 (2H, t); 4.1 (2H, d); 4.0 (2H, t); 1.99 (1H); 1.27 (32H, aliphatic protons); 0.85 (6H, t). ^{13}C NMR (CDCl3) δ (ppm): 163.65, 163.15, 131.29, 131.09, 126.90, 126.80, 126.76, 126.36, 61.19, 45.13, 43.1, 36.72, 32.02, 31.97, 31.77, 30.1, 29.72, 29.65, 29.43, 29.38, 26.52, 22.77, 14.20. HRMS (ESI): m/z calc for $C_{36}H_{50}N_2O_5Na^+$ $[M + Na]^+$: 613.3618; found : 613.3616.



Scheme S3: Synthesis of **PM-1**

PM-1: A mixture of **4** (0.37 g, 1.68 mmol), PMDA (0.5 g, 1.68 mmol) and serinol (0.15 g, 1.68 mmol) in 15 mL dry DMF was stirred at 90 °C for 12 h under inert atmosphere. Subsequently DMF was removed under reduced pressure and to the pasty mass 100 mL water was added and the product was extracted with $CHCl_3$ (3 x 30 mL); washed with water (2 x 30 mL), brine (2 x 30 mL) and then dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The crude product was purified by column

chromatography (2% MeOH/$CHCl_3$) to afford yellowish sticky solid which upon washing with hexanes produced white solid of **PM-1** (0.12 g, 21%). ^{1}H NMR ($CDCl_3$, 500 MHz) δ (ppm) : 8.29 (s, 2H), 4.51 (m, 1H), 4.15-4.05 (m, 4H), 3.64 (d, J = 7 Hz), 1.90 (bs, 1H), 1.29-1.24 (m, 32H), 0.87 (m, 6H); ^{13}C NMR ($CDCl_3$) δ (ppm): 167.37, 166.54, 137.63, 136.94, 118.59, 61.60, 55.73, 43.19, 37.13, 32.05, 32.01, 31.63, 30.06, 29.75, 29.70, 29.65, 29.47, 29.41, 26.38, 22.80; HRMS (ESI) calcd. for $C_{33}H_{50}N_2O_6$ H^+, $[M+H]^+$: 571.3747; found: 571.3383.

Gelation studies: A stock solution of a particular building block (**NDI-1** or **NDI-2** or **PM-1**) in chloroform was prepared at 20.0 mM concentration. Measured volume of the stock was transferred to a gelation vial and chloroform was evaporated to get a thin film which was added with measured amount of a apolar solvent (for example MCH) and warmed with a hot air gun under closed cap condition while a clear solution was obtained. The vial was gently placed on the table and allowed settle at rt. After approximately and hour gelation was examined by tilting the vial and the observation are noted in Table S1. For CT-gelation, same procedure was followed except in the stock solution appropriate amount of pyrene was added so that **NDI-1**: pyrene = 1: 1 and concentration of each component is 20 mM. For estimating the T_g, a given gel at 10.0 mM concentration was placed in a water bath and the temperature was increased by 2 ^{o}C interval. At each point the survival of the gel phase was examined by titling the vial and the temperature at which the gel flowed to the bottom of the vial was noted as the T_g. For CGC determination a given gel at 10.0 mM concentration was gradually added with the same solvent and after each addition the gel was melted by heating and allowed to stand at rt for 1 h. Gelation was then examined by tilting the vial. The concentration at which the gel was destroyed was noted as the CGC.

Pyrene diffusion in NDI-1 gel: A gel of **NDI-1** in MCH (550 μL, 25.45 mM) was prepared in a tube. A solution of pyrene in benzene (93.3 mM, 150 μL) (so that finally in the mixture each component should be 20.0 mM) was gently placed on the top of the organogel while the yellow gel gradually turned red due to diffusion of pyrene to the gel and intercalation between NDIs by CT-interaction.

UV-Vis, PL and FT-IR studies: For spectroscopic experiments, solutions were prepared following same procedure as mentioned for gelation studies but at much lower concentrations. UV-Vis spectra were recorded at different concentration (1.0 to 0.05 mM) in 1.0 mm quartz cuvette. These solutions were also used to record the emission spectra. For temperature dependent study, **NDI-1** in MCH (1.0 mM) was used and the temperature was gradually increased from lower to higher values by 5 ^{o}C interval. After a desired temperature was reached, an equilibrium time of 10 min was allowed. The FTIR of **NDI-1** in MCH, $CHCl_3$ and of **NDI-2** in MCH (C = 20 mM in all cases) were recorded against the air background. Each spectrum was manually corrected by the corresponding solvent spectrum. For **NDI-1**, solid state spectrum was recorded in a KBr pellet form against air background.

Microscopic studies: For HRTEM studies, a solution of the gelator (2.0 mM) was drop-casted on a carbon coated copper grid and dried in air for overnight before the images were captured. For SEM and AFM studies, similarly samples were prepared on mica surface. For freeze fracture TEM, small pieces were cut from the gels (typically 2 x 2 x 2 mm) and placed between two copper holders and rapidly frozen in liquid N_2. The samples were kept frozen while transferred in a home-made freeze-fracture apparatus (developed by J.-C. Homo) where the holders were split opened to fracture the gels. Pt (2 nm) was evaporated on the samples under a 45° angle, then a reinforcing carbon layer (20 nm) under a 90° angle respectively to the surface. The sample was warmed up to room temperature and the replica were carefully washed with chloroform and picked up onto 400 mesh grids. The grids were observed with a Philipps CM12 operating at 120 kV with a SIS Megaview III camera or a FEI Tecnai G2 at 200 kV with a FEI eagle 2k ssCCD camera. Distances were measured on a statistically relevant numbers of objects with the AnalySIS software from Olympus.

X-Ray diffraction studies: A gel in MCH (10 mM) was drop casted over a glass slide to make a thick film and dried in air for overnight. The powder XRD data was recorded from 1° to 30° with 0.02 Å intervals per state.

SAXS studies: Small angle scattering experiments have been performed on an Elexience diffractometer equipped with a Rigaku microfocus rotating anode generator (Micromax™-007 HF) operating at 40 kV and 30 mA and using the CuK□ radiation (λ=1.54 Å). The X-ray beam was monochromatized and focused using a confocal Max-Flux Optics™ developed by Osmics, Inc. together with a three pinholes collimation system. Scattered intensity was measured with a 2D multiwire detector located at 0.7 m from the sample. This configuration allowed investigation of q vectors in the range 0.01 $Å^{-1} < q < 0.3$ $Å^{-1}$. (q is defined as $(4\pi/\lambda \sin(\theta/2))$ where λ is the wavelength of the incoming beam and □ is the scattering angle). Gels of NDI-1 in MCH (2 wt. %) were placed in cells with walls made of calibrated mica sheets, one millimetre apart. Scattering patterns were treated according to the usual procedures for isotropic small angle scattering. Data were radially integrated, and corrected for electronic background, detector efficiency, empty cell scattering, sample transmission and sample thickness. Scattering from the pure solvent was measured separately and was corrected and subtracted from the sample solution according to its corresponding volume fraction. Intensity was converted into absolute scale using calibrated Lupolen as a standard. The corrected intensity was normalized to the Porod invariant as defined by:

$$Q = \frac{1}{2\pi^2} \int_0^\infty q^2 \, d\Sigma/d\Omega(q) dq$$

The normalized intensities were not fitted with model form and structure factors.

Additional figures

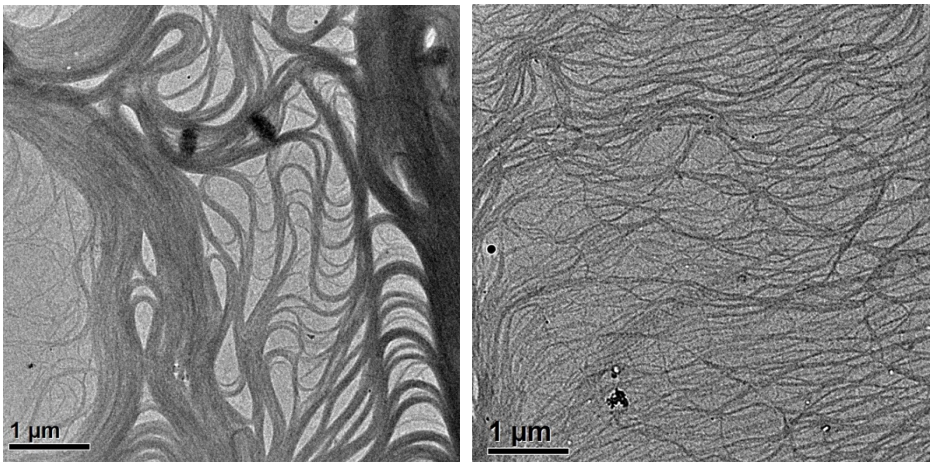


Fig S1. HRTEM image of **NDI-1** in MCH

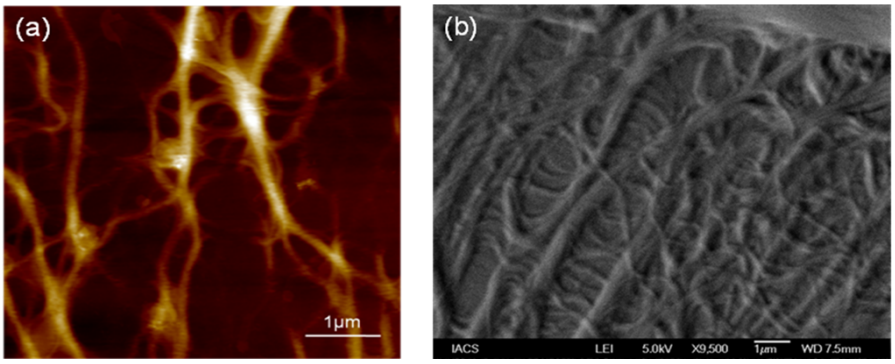


Fig S2. (a) AFM and (b) SEM images of **NDI-1** in MCH

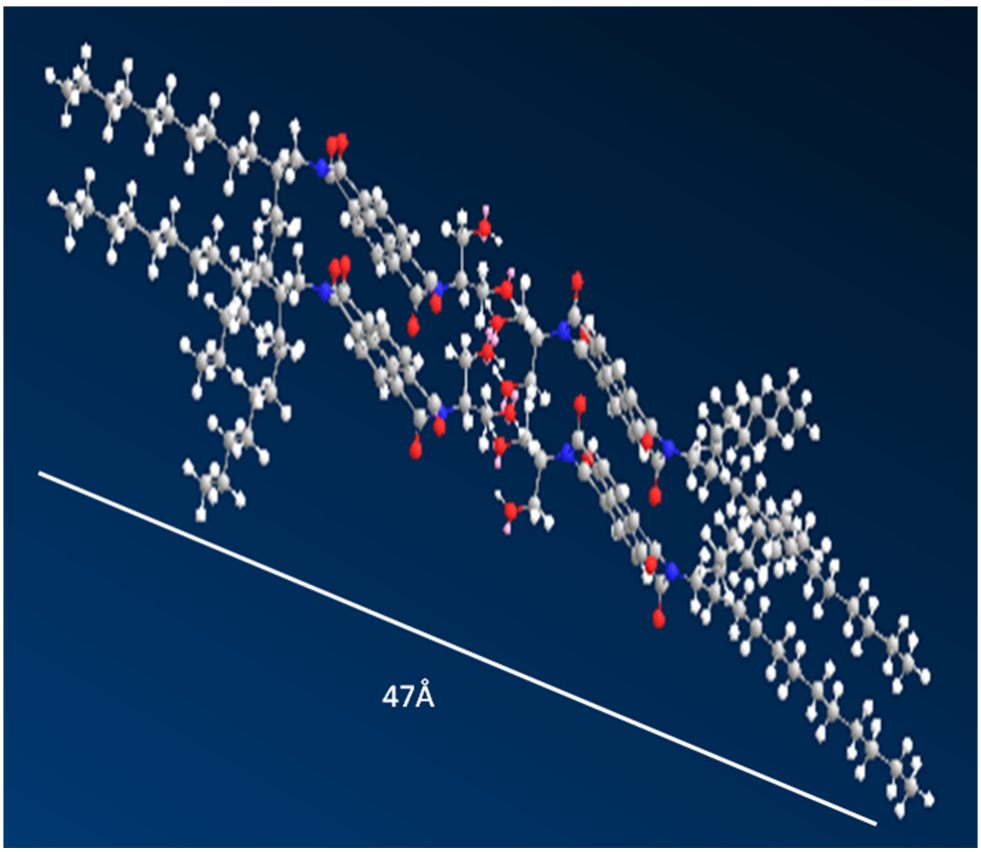


Fig S3. Energy minimized structure of self-assembled **NDI-1** with four units. Molecular modeling was done in Chem3D Ultra 8.0 software using MM2 for energy minimization. As per this structure the distance for intra- and inter-molecular H-bonding among the OH groups are 1.8 Å and 2.0 Å, respectively. The centre to centre distance among the NDI rings is ~ 4.0 Å which, though not most ideal, is still within the allowed distance for π-π interaction as per literature precedence.[2]

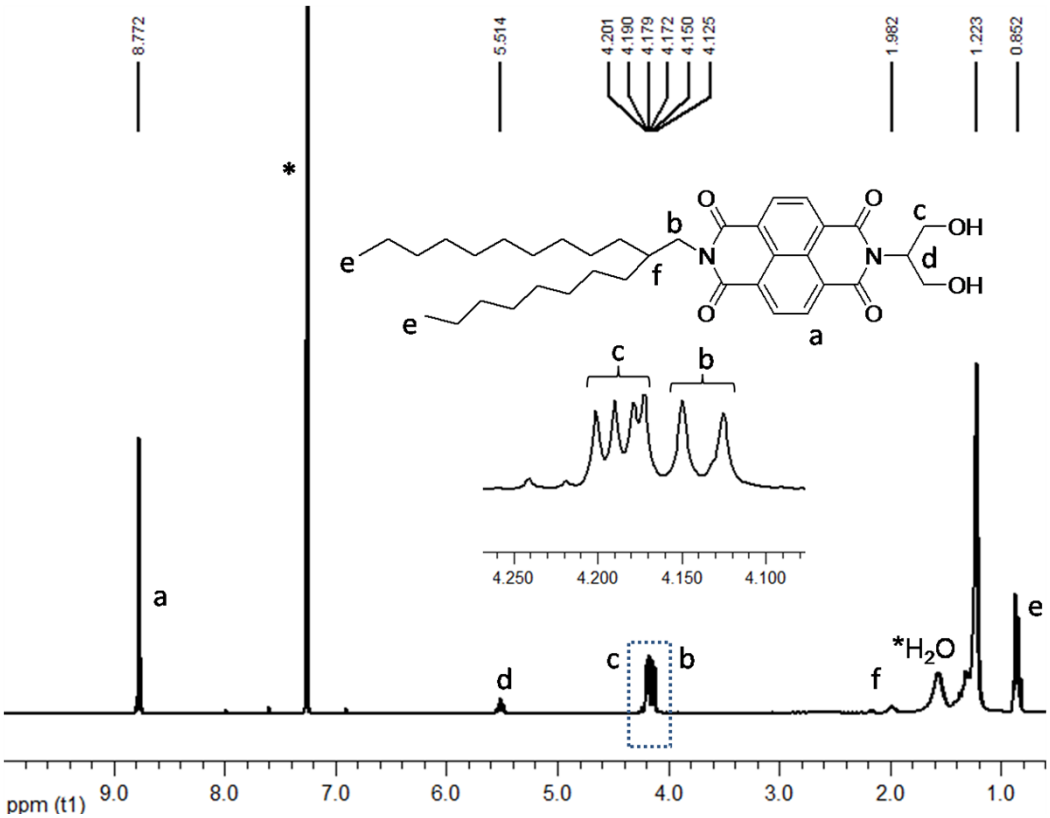


Fig S4. ^{1}H NMR of **NDI-1** in $CDCl_3$. * indicates solvent peaks

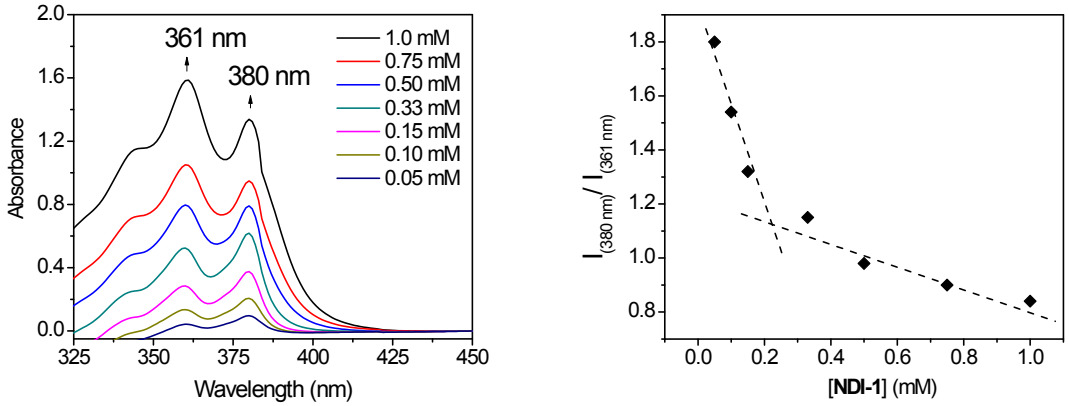


Fig S5. *Left*- Concentration dependent UV-Vis spectra (l = 1.0 mm) of **NDI-1** in MCH; *Right*- Variation of the intensity ratio of the two peaks (380 and 361 nm) as a function of concentration.

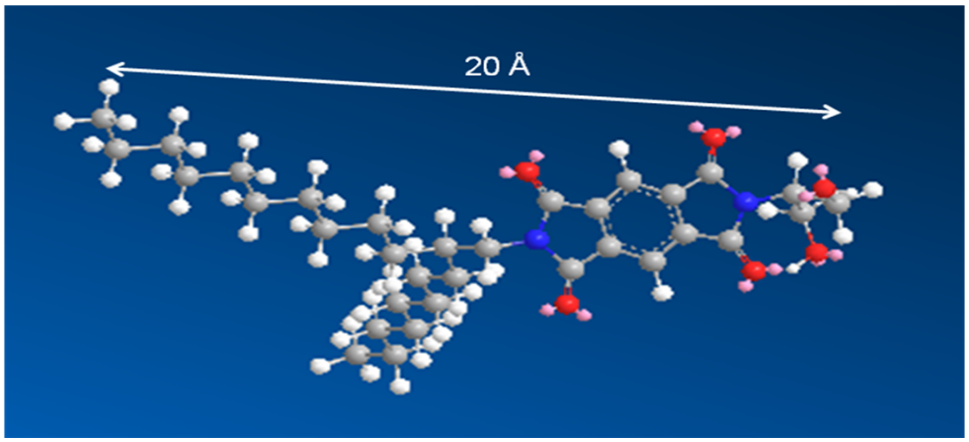


Fig S6. Energy minimized structure of **PM-1**

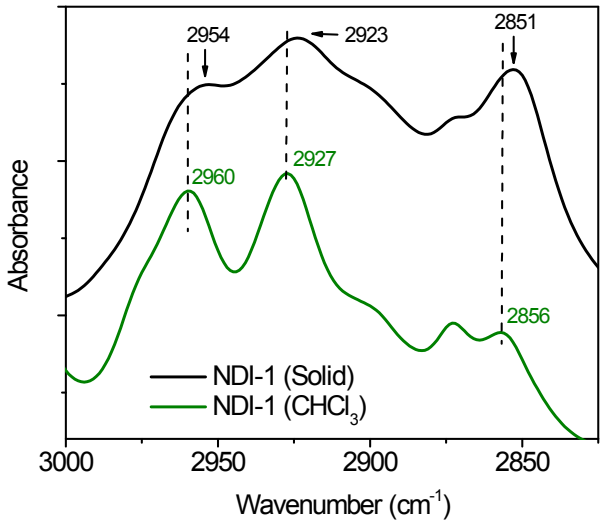


Fig S7: Selected region of FT-IR spectra of **NDI-1** in Chloroform (monomeric state) and solid state. Going from chloroform to solid, C-H asymmetric stretching of methyl group, C-H asymmetric stretching of methylene group and C-H symmetric stretching of methylene group exhibits notable shift (2960 cm^{-1} to 2954 cm^{-1}; 2927 cm^{-1} to 2923 cm^{-1} and 2856 cm^{-1} to 2851 cm^{-1}, respectively) indicating ordering among the alkyl chains in solid state.[3] In MCH, as the solvent peaks appear around the same region, no conclusive data could be gathered regarding the shift of the above mentioned CH stretching frequencies.

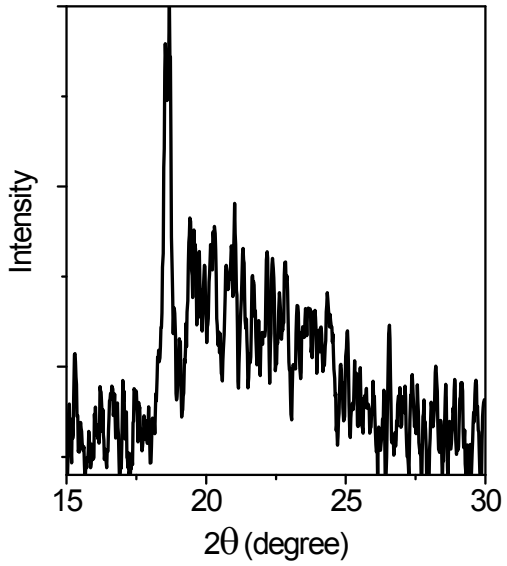


Fig S8: Wide angle XRD of **NDI-1** showing a broad peak at 2θ = 22.24 that corresponds to d= 3.9Å possibly due to π-π interaction.

Table S1. Gelation tests in different solvents

Solvent/ System	**NDI-1**[a]	**NDI-1**+ Pyrene [b]	**PM-1**[a]
MCH	Gel	Gel	Gel
$CHCl_3$	Solution	Solution	Solution
TCE	Solution	Solution	Solution
THF	Solution	Solution	Solution
trans-Decalin	Gel	Gel	Gel
Toluene	Solution	Solution	Solution
Cyclohexane	Viscous Solution	Viscous Solution	Viscous Solution
n-Heptane	Precipitate	Precipitate	Precipitate
Benzene	Solution	Solution	Solution

[a] C = 10 mM; [b] [**NDI-1**] = 10 mM, [pyrene] = 10.0 mM

Reference

1. D. Perrin, W. L. F. Armarego, D. R. Perrin, Purification of Laboratory Chemicals, 2nd ed., Pergamon, Oxford, 1980.

2. S. K. Burley, G. A. Petsko, *Science*, 1985, **229**, 23.

3. J. Mandal, S. K. Prasad, D. S. S. Rao, S. Ramakrishnan, *J. Am. Chem. Soc.*, 2014, **136**, 2538.