Electronic Supplementary Material (ESI) for Nanoscale.

Supporting Information for

J-aggregation, impact on excited state dynamics and unique solvent effects on macroscopic assembly of a core-substituted naphthalenediimide

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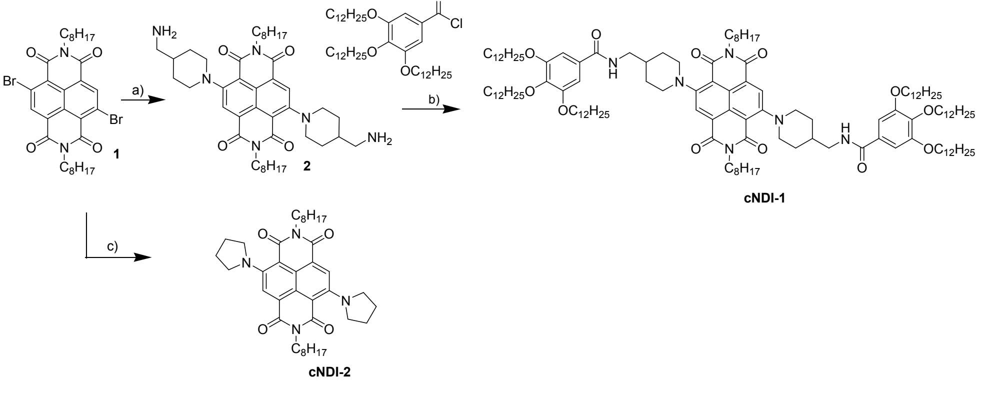
Materials and methods: Reagents and chemicals were purchased from Sigma Aldrich Chemical Co. and used without further purification. Solvents were purchased from commercial sources and purified by reported protocol.[1] Spectroscopic graded solvents were used for physical measurements. NMR data were recorded either on a Bruker DPX-300 MHz or 500 MHz NMR machine and all the data were calibrated against TMS. UV/vis spectroscopic experiments were performed in a Perkin-Elmer Lambda 25 spectrometer. Photoluminescence studies were performed in a Horiba Fluoromax-3 spectrophotometer. Mass spectrometric data were acquired by an electron spray ionization (ESI) technique on a Q-tof-micro quadruple mass spectrometer (Micro mass). MALDI-TOF MS data were recorded using Bruker Daltonics flex Analyzer. Transmission electron microscopy (TEM) was done in a JEOL-2010EX machine operating at an accelerating voltage of 200 kV. Atomic force microscopy (AFM) was done in an Innova instrument from Bruker in tapping mode. Rheological studies were performed with an AR 2000 advanced Rheometer (TA instruments) by cone and plate method. FT-IR spectra were recorded in a Perkin Elmer Spectrum 100FT-IR spectrometer. Circular Dichroism (CD) experiments were carried out in a JASCO CD spectrometer (model-J815).

Scheme S1: Synthesis of **cNDI-1** and **cNDI-2**



Reagents and conditions : a) 4-(aminomethyl) piperidine, toluene, rt, 12h, 94% b) $CHCl_3$, Et_3N, ice cold to rt, 12h, 60% c) pyrrolidine, DCM, rt, 12h, 80%

Synthesis

Compound 2: Dibromo-substituted NDI-derivative (**1**) was prepared following a literature reported procedure.[2] To a solution of compound **1** (0.40 g, 0.61mmol) in toluene (15 ml), 4-(aminomethyl)-piperidine (4.17 g, 36.6 mmol) was added dropwise and stirred at rt for 12 h under N_2 atmosphere. Then the solvent was removed under reduced pressure to get a bluish liquid which was dissolved in chloroform (20 ml) and washed with distilled water (2 x 20 ml). The organic layer was separated and passed through anhydrous Na_2SO_4 and the solvent was removed to get the crude product as a blue semisolid in 94% yield which was taken to the next step without further purification as the characterization data showed absence of any significant impurity. ^{1}HNMR ($CDCl_3$, 500 MHz, TMS): δ (ppm) = 8.43 (2H, s), 4.16 (4H, t, $J = 5$ Hz), 3.63 (4H, d, $J = 10$ Hz), 3.17 (4H, d, $J = 10$ Hz), 2.69 (4H, d, $J = 5$ Hz), 1.90 (4H, d, $J = 10$ Hz), 1.71-1.67(4H, m), 1.60 (6H, m), 1.40-1.26 (20H, m), 0.85(6H, t, $J = 5$Hz); HRMS (ESI): m/z calc for $C_{42}H_{62}N_6O_4$ $[M + H]^+$: 715.4911; found: 715.4906.

cNDI-1: A solution of O-alkylated galic-acid chloride [3] (1.14g, 1.65 mmol) in chloroform (10 ml) was added drop-wise over a period of 30 min to an ice-cold mixture of compound **2** (0.40 g, 0.55 mmol) and triethyl amine (0.3 ml, 1.65mmol) in chloroform (10ml) under N_2 atmosphere. After the addition was over the reaction mixture was stirred at rt for 14h.Then the reaction mixture was diluted with another 20 ml chloroform and washed with brine solution (2 x 20 ml). Organic layer was separated and passed through anhydrous Na_2SO_4 and the solvent was evaporated to get the crude product as a bluish oil which was purified by column chromatography using basic alumina as stationary phase and 10% petroleum ether in $CHCl_3$ as eluent to get the desired product as a blue waxy material. Obtained Yield = 0.67 gm (60%) .^{1}HNMR ($CDCl_3$, 400 MHz, TMS): δ (ppm) = 8.47 (2H, s), 6.98 (4H, s), 6.22 (2H, broad) 4.16 (4H, t, $J = 5$ Hz), 4.04-3.97 (12H, m), 3.68 (4H, d, $J = 10$ Hz), 3.44 (4H, d, J=10 Hz), 3.23 (4H, d, J=5 Hz), 1.98-1.96 (6H, m), 1.85-1.70 (56H, m), 1.49-1.26 (92H, m), 0.86 (24H, t, J=5Hz). ^{13}C NMR ($CDCl_3$) δ (ppm) =167.5, 163.5, 162.2, 153.3, 148.2, 147.5, 142.3, 139.5, 138.2, 129.5, 124.6, 123.1, 122.2, 119.1, 114.3, 106.1, 73.7, 37.2, 35.0, 34.6, 32.0, 31.9, 31.5, 30.4, 30.3, 30.1, 29.8, 29.7, 29.6, 29.5, 29.3, 29.1, 27.3, 27.2, 26.2, 22.8, 22.7, 19.8, 14.2. MALDI-TOF: m/z calc for $C_{128}H_{214}N_6O_{12}$ $[M + H]^+$: 2028.638, obtained = 2029.170.

cNDI-2: A solution of compound **1** (0.5 gm, 0.73 mmol) in dichloromethane (8 ml) was mixed with pyrrolidine (1.27 ml, 15.4 mmol) and stirred at room temp for 12h under argon atmosphere. Subsequently the solution was poured into water (25 ml) and extracted with DCM (20ml). Organic layer was passed through anhydrous sodium sulphate and excess solvent was evaporated to get the desired cNDI-2 in adequately pure form as indicated by TLC and ^{1}H NMR. Yield: 80% ; ^{1}HNMR ($CDCl_3$, 400 MHz, TMS): δ (ppm) = 8.40 (2H, s), 4.18 (4H, t, J=7Hz), 3.52 (8H, s), 2.08 (8H, s), 1.71(4H,m), 1.40-1.26

(20H, m), 0.86 (6H, m). MALDI-TOF: m/z calc for $C_{38}H_{52}N_4O_4$ $[M + 2H]^+$: 630.412, obtained = 630.743. M.P. 150± 3 °C.

Additional Figures

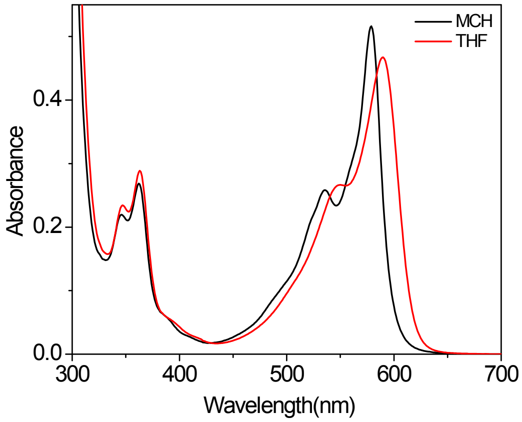


Fig S1. Solvent dependent UV/vis spectra of **cNDI-2**; *l* = 1.0 mm; *C* = 0.2 mM; *T* = 25 °C

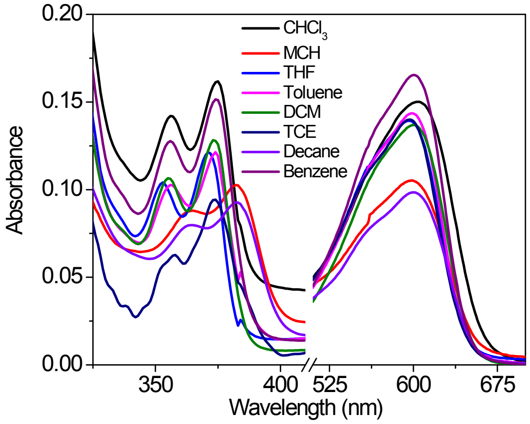


Fig S2. Solvent dependent UV/vis spectra of **cNDI-1**; *l* = 1.0 mm; *C* = 0.1 mM; *T* = 25 °C

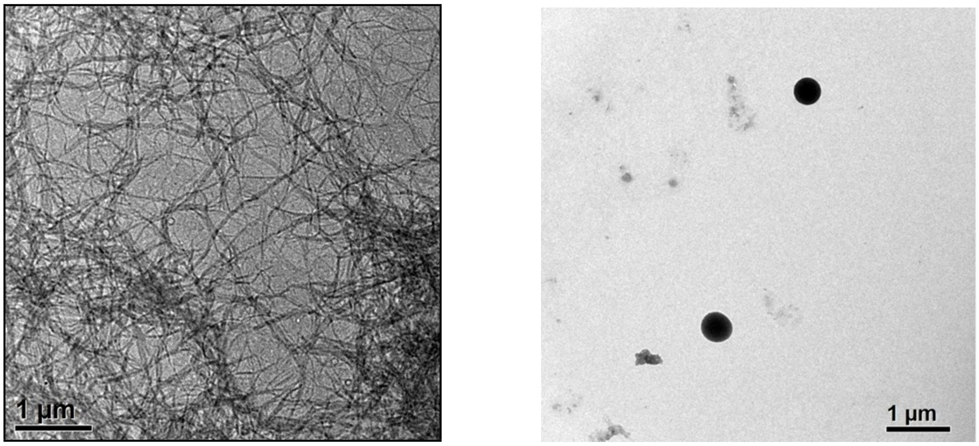


Fig S3. TEM images of samples prepared from **cNDI-1** in decane (left) and MCH (right); $C = 0.2$ mM

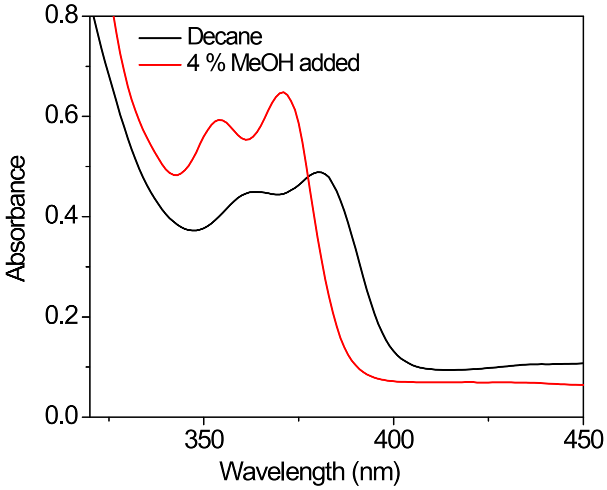


Fig S4. UV/vis absorption spectra of **cNDI-1** in decane gel before (black) and after (red) MeOH addition showing disassembly in presence of trace amount of protic solvent

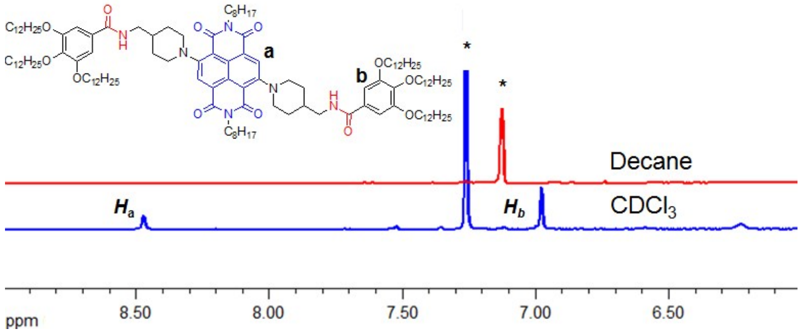


Fig S5. ^{1}H NMR spectra (selected region) of **cNDI-1** in monomeric ($CDCl_3$, blue) and aggregated (n-decane gel, red) state. $C = 4.0$ mM; 10% C_6D_6 was added in decane for signal locking purpose. * indicates peaks coming from solvents. Possibly due to very long relaxation time in aggregated state no aromatic signals (H_a and H_b) appear in decane gel state

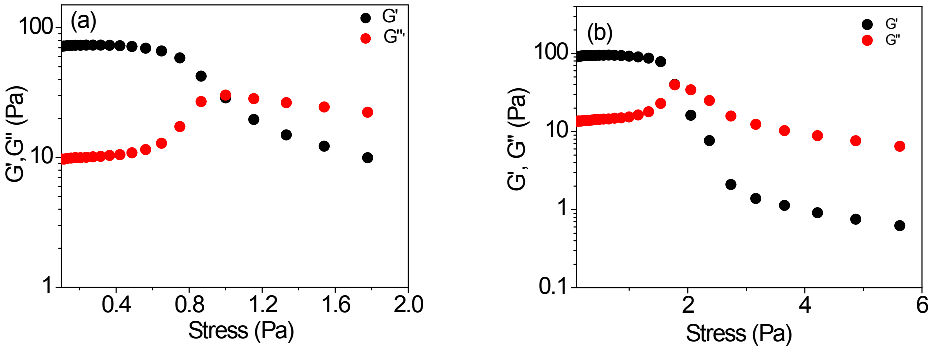


Fig S6. Stress amplitude sweep measurements results for **cNDI-1** gel ($c = 10$ mM) in (a) *n*-octane and (b) *n*-decane.

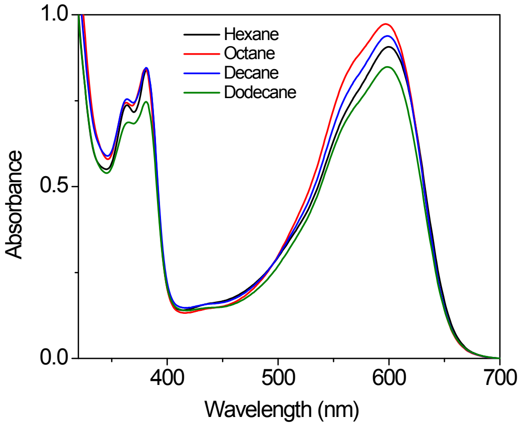


Fig S7. UV/ vis spectra of **cNDI-1** in different linear hydrocarbon solvents at (*c*=1.5 mM, *l*= 1 mm) showing identical nature of self-assembly.

Table S1. Gelation test (*c* = 4.0 mM) results of **cNDI-1** in different solvents

Solvent	**Observation**	**Solvent**	**Observation**
THF	Solution	*n*-dodecane	Gel
TCE	Solution	*n*-Decane	Gel
Cyclohexane	Solution	*n*-Octane	Gel
Methyl Cyclohexane	Solution	*n*-hexane	Gel
CCl_4	Solution	Benzene	Solution
t-Butanol	Precipitate	Toluene	Solution
Acetone	Precipitate	$CHCl_3$	solution

Calculation of Oscillator strength:

To determine oscillator strength, we first de-convolute S_0-S_1 transition band from THF (fig-1a) and MCH spectra (fig1b). From there we have estimated ν_{max} and Einstein coefficient (B_{12}). Finally using equation-1 we have determined oscillator strength

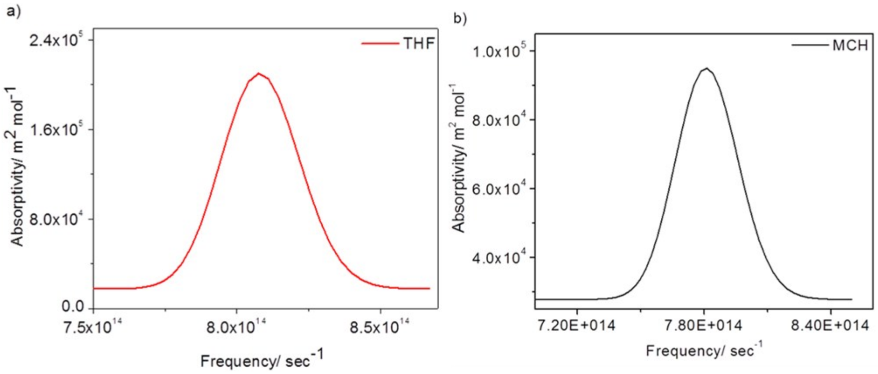


Fig S8: De convoluted S_0-S_1 transition band of **cNDI-1** in a) THF b) MCH at c= 0.2 mM , *l*= 0.1 cm

$$f = \frac{4\varepsilon_0 m_e h\nu}{e^2} B_{12} \tag{1}$$

Where f= oscillator strength, ε_0 = vacuum permittivity, me= mass of the electron, h= plank constant, ν= frequency, e=charge of the electron, B_{12}= Einstein coefficient. Calculation is done in SI unit

Solvent	ν (s^{-1})	B_{12} ($J^{-1}M^3s^{-2}$)	f
THF	8.07 x10^{14}	2.09 x10^{22}	14.1
MCH	7.80 x10^{14}	1.58 x 10^{22}	10.3

Calculation of Quantum yield:

Fluorescence quantum yield was determined at excited wavelength (λex= 350 nm) using quinine sulphate in sulphuric acid (0.1M) aqueous solution (Φ_{ST}= 0.54) as a standard.

$$\phi_X = \phi_{ST}\left(\frac{Grad_X}{Grad_{ST}}\right)\left(\frac{\eta_X^2}{\eta_{ST}^2}\right) \tag{2}$$

ST and X represents standard and test respectively, η is refractive index. Grad is the gradient from the plot of integrated fluorescence intensity vs absorbance.

Compound	QY(MCH)	QY(THF)
cNDI-1	0.153	0.077
cNDI-2	0.091	0.075

Table S2. Literature reported [6] solubility parameters of few aliphatic hydrocarbon solvents

Solvent	δ[a], cal ½ cm$^{-3/2}$					δ, Mpa$^{1/2}$				
	δ	δ_0	δ_d	δ_p	δ_h	δ	δ_0	δ_d	δ_p	δ_h
n-Hexane	7.3	7.3	7.3	0.0	0.0	14.9	14.9	14.9	0.0	0.0
n-Octane	7.6	7.6	7.6	0.0	0.0	15.5	15.5	15.5	0.0	0.0
n-Dodecane	7.9	7.8	7.8	0.0	0.0	16.2	16.0	16.0	0.0	0.0
Methyl Cyclohexane	7.8	7.8	7.8	0.0	0.5	16.0	16.0	16.0	0.0	1.0

[a] δ is solubility parameter which consists of dispersive (δ_d), polar (δ_p), hydrogen bonding (δ_h) and total (δ_0) solubility parameters at 25˚C.

References

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