

Supporting Information for
**Slothful Gelation of a Dipolar Building Block by “Top-Down” Morphology
Transition from Microparticle to Nanofibre**

*Anindita Das,^a Bholanath Maity^b Debasis Koley^{*b} and Suhrit Ghosh^{*a}*

^a Polymer Science Unit, Indian Association for the Cultivation of Science,
2A & 2B Raja S.C. Mullick Road, Jadavpur, Kolkata - 700 032, India;

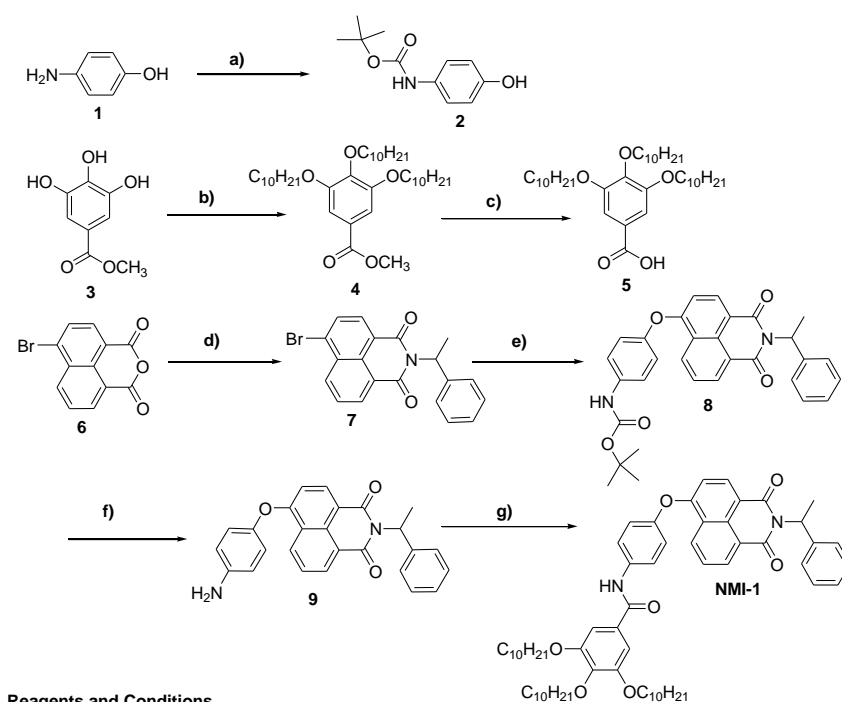
^b Chemical Science Division, Indian Institute of Science Education and Research,
Kolkata, India-741252

*Corresponding author: Email: psusg2@iacs.res.in

Materials and Methods: Methyl 3,4,5-trihydroxybenzoate and 4-bromo-1,8-naphthalic anhydride were purchased from Aldrich Chemical Co. All solvents and reagents were purchased from local commercial sources and purified by following standard protocols.¹ For UV-vis and ¹H NMR studies, spectroscopic grade solvents were used. ¹H NMR spectra were recorded on a Bruker DPX-300 MHz NMR spectrometer and calibrated against TMS. Mass spectrometric data were obtained by an electron spray ionization (ESI) technique on a Q-tof-micro quadrupole mass spectrometer (Micro mass). UV-vis spectra were recorded in a Perkin Elmer Lambda 25 spectrometer equipped with temperature variable experimental setup. Fluorescence spectra were recorded in a Fluorolog spectrophotometer, from Horiba Jobin Yvon. Transmission Electron Microscopy (TEM) was performed in JEOL-2010EX machine with an accelerating voltage of 200KV. Fluorescence microscopic images were taken in an Olympus (1x2-KSP, 6M 24413) machine, Japan. XRD data was recorded on a Seifert XRD3000P diffractometer with Cu K α radiation (λ = 0.15406 nm) and a voltage and a current of 40 kV and 30 mA, respectively. Circular Dichroism (CD) and Linear Dichroism (LD) experiments were carried out in a JASCO CD spectrometer (model-J815) equipped with a peltier for temperature variation experiments.

Synthesis and Characterization

Synthesis of the compound **NMI-1** was done using the synthetic protocol shown in Scheme S1. The compound was characterized by ¹H NMR, UV-visible, melting point and HRMS (ESI). Synthesis of Compound **2** and **5** has been done following standard procedure.^{2, 3}



a) Boc_2O , THF, 0 °C, 12 h, yield = quantitative; b) $\text{C}_{10}\text{H}_{21}\text{Br}$, K_2CO_3 , DMF, 75 °C, 48h, yield = 54%,
c) hydrolysis, aq KOH/EtOH, 7h, 100 °C, Yield = 97%; d) (S)-(-)- α -Methylbenzylamine, Toluene, 110 °C, 12h, yield = 54%;
e) 2, K_2CO_3 , DMF, 110 °C, 12h, yield = 98%; f) 40% THF/DCM, rt, 7h, yield = quantitative;
g) 5, EDC, HOBT, diisopropylethylamine, DCM, 0°C-rt, yield = 50%

Scheme S1: Synthesis of NMI-1

Synthesis and Characterization:

tert-butyl 4-hydroxyphenylcarbamate (2)²: Boc_2O (4.4 g, 2.0 mmol) was taken with 20 mL THF at 0 °C. To this, **1** (2.0 g, 1.833 mmol) was added and the reaction mixture was stirred at 0 °C for 12 h. Excess THF was evaporated under reduced pressure and the solid mass was dissolved in CH_2Cl_2 (20 mL) and washed with water (2 x 20 mL). The organic layer was passed through Na_2SO_4 and the solvent was evaporated to obtain a light brown solid (4.0 g, quantitative yield) which was carried to the next step without further purification. ^1H NMR (300 MHz, DMSO-d_6 , TMS): δ (ppm) = 8.95 (brs, 1H), 7.20 (d, J = 8.2 Hz, 2H), 6.62 (d, J = 8.6 Hz, 2H), 1.45 (s, 9H).

Methyl 3,4,5-tris(decyloxy)benzoate (4)³: Compound **3** (2.0 g, 10.8 mmol), anhydrous K_2CO_3 (7.5 g, 54.3 mmol), n-decyl bromide (7.21 g, 32.6 mmol) and 40 mL dry DMF were taken together in a round bottom flask and stirred at 75 °C for 48 h under N_2 atmosphere. The reaction mixture was cooled to room temperature and poured into 200 mL ice-cold water and extracted with diethyl ether (3 x 50 mL). The organic layer was washed with brine (2 x 50 mL) and dried over anhydrous Na_2SO_4 . The solvent was evaporated under reduced pressure to get the crude product as light brown color oil. It was purified by column chromatography using basic alumina as stationary phase and petroleum ether as eluent to obtain

pure product as colorless oil (3.58 g, 54 %). ^1H NMR (300 MHz, CDCl_3 , TMS): δ (ppm) = 7.27 (s, 2H), 4.04-3.99 (m, 6H), 3.89 (s, 3H), 1.84-1.72 (m, 6H), 1.50-1.43 (m, 6H), 1.42-1.28 (m, 36H), 0.89 (t, J = 6.2 Hz, 9H).

3,4,5-Tris(decyloxy)benzoic acid (5)³: A solution of compound **4** (3.3 g, 5.45 mmol) was taken with 15 mL ethanol in a round bottom flask and mixed with aqueous KOH solution (1.90 g, 33.9 mmol in 15 mL water) and the reaction mixture was stirred at 100 °C for 7 h. The reaction was stopped and cooled to room temperature and then poured into a solution of concentrated HCl (5 mL) in ice cold water (125 mL). The white precipitate obtained was filtered and washed with distilled water and dried under vacuum to get the crude product as a white powder (3.12 g, 97 %) which was used for the next step without further purification. ^1H NMR (300 MHz, CDCl_3 , TMS): δ (ppm) = 6.99 (s, 2H), 3.86 - 3.74 (m, 6H), 1.69-1.56 (m, 6H), 1.42-1.24 (m, 42 H), 0.87 (m, J = 6.2 Hz, 9H).

Compound 7: (S)-(-)- α -Methylbenzylamine (0.29 mg, 2.38 mmol) and **6** (0.6g, 2.16 mmol) were taken together in 15 mL toluene and the reaction mixture was stirred at 110 °C for 12 h. The reaction was cooled to room temperature and the solvent was removed under reduced pressure to obtain a yellow crude which was purified by column chromatography using silica gel (100-200 mesh) as stationary phase and 1:1 CH_2Cl_2 / petroleum ether as eluent to obtain pure product as a cream colored solid (446 mg, 54%). M.P. = 139 °C- 141 °C ; ^1H NMR (300 MHz, CDCl_3 , TMS): δ (ppm) = 8.62 (d, J = 7.2 Hz, 1H), 8.55 (d, J = 8.5 Hz, 1H), 8.37 (d, J = 7.7 Hz, 1H), 8.02 (d, J = 7.8 Hz, 1H), 7.83 (t, J = 7.6 Hz, 1H), 7.49 (d, J = 7.5 Hz, 1H), 7.35-7.21 (m, 3H), 6.52 (q, J = 7.0 Hz, 1H), 1.98 (d, J = 7.1 Hz, 3H); HRMS (ESI): m/z calcd for $\text{C}_{20}\text{H}_{14}\text{BrNO}_2\text{Na}$ [$\text{M} + \text{Na}$]⁺: 402.0106; found : 402.0106; UV-visible (CHCl_3): $\lambda_{\text{max}}(\epsilon)$ = 360 (17,100), 344 nm (19,800), 246 (20,700) $\text{M}^{-1}\text{cm}^{-1}$.

Compound 8: Compound **2** (440 mg, 2.1 mmol) and **7** (380 mg, 1.0 mmol) were taken together with K_2CO_3 (276 mg, 2.0 mmol) in dry DMF (15 mL) and stirred at 110 °C for 12 h. The reaction was cooled to room temperature and DMF was removed under reduced pressure. The crude obtained was dissolved in CH_2Cl_2 (20 mL) and washed with water (2x 20 mL) which was purified by column chromatography using silica gel (100-200 mesh) as stationary phase and CH_2Cl_2 as eluent to obtain pure product as yellow solid (500 mg, 98%). M.P. = 132 °C- 134 °C ; ^1H NMR (500 MHz, CDCl_3 , TMS): δ (ppm) = 8.68 (d, J = 8.5, 1H), 8.61 (d, J = 7.5, 1H), 8.40 (d, J = 8.0, 1H), 7.75 (t, J = 7.5, 1H), 7.50-7.46 (m, 4H), 7.32-7.22 (m, 3H), 7.11 (d, J = 8.5, 1H), 6.85 (d, J = 8.0, 1H); 6.55 (q, J = 7.0, 1H), 1.98 (d, J = 7.0, 3H); HRMS (ESI): m/z calcd for $\text{C}_{31}\text{H}_{28}\text{N}_2\text{O}_5\text{Na}$ [$\text{M} + \text{Na}$]⁺: 531.1896; found : 531.1896; UV-visible; (CHCl_3): $\lambda_{\text{max}}(\epsilon)$ = 366 (11,800), 249 nm (29,700 $\text{M}^{-1}\text{cm}^{-1}$).

Compound 9: Compound **8** (300 mg, 0.59 mmol) was taken with 40% TFA/ CH_2Cl_2 (10 mL) and stirred at room temperature for 6 h. Excess TFA was removed under reduced pressure and the solid mass was taken with K_2CO_3 (50 mg) in CH_2Cl_2 (4 mL) and stirred at rt for another 1 h and passed through Na_2SO_4 . The solvent was evaporated to obtain yellow solid as pure product (277 mg, quantitative yield) which was used for the next step as such. M.P. = 195 °C- 200 °C; ^1H NMR (300 MHz, CDCl_3 , TMS): δ (ppm) = 8.70 (d, J = 8.0 Hz, 1H), 8.60 (d, J = 7.2 Hz, 1H), 8.39 (d, J = 8.3 Hz, 1H), 7.75 (t, J = 7.7 Hz, 1H), 7.49 (d, J

= 7.6 Hz, 1H), 7.33-7.21 (m, 3H), 6.97 (d, J = 8.6 Hz, 1H), 6.83 (d, J = 8.3 Hz, 1H); 6.76 (d, J = 8.7 Hz, 1H) 6.55 (q, J = 7.1, 1H), 3.72 (br, 2H), 1.97 (d, J = 7.1, 3H); HRMS (ESI): m/z calcd for $C_{26}H_{21}N_2O_3$ $[M + H]^+$: 409.1552; found: 409.1574; UV-visible; ($CHCl_3$): $\lambda_{max}(\epsilon)$ = 366 (11,900), 246 (27,800) $M^{-1}cm^{-1}$).

Compound NMI-1: Compound **9** (100 mg, 0.245 mmol), **5** (217 mg, 0.367 mmol), HOBT (50 mg, 0.367 mmol) and DIEA (79 mg, 0.612 mmol) were taken together in a round bottom flask along with 20 mL dry CH_2Cl_2 and stirred at 0 °C for 15 min under N_2 atmosphere. To the above solution EDC (71 mg, 0.367 mmol) was added and the reaction mixture was stirred at 0 °C for another 2 h and then at rt for 12 h. The organic layer was washed with water (3 x 20 mL) and dried over Na_2SO_4 . The crude was purified by column chromatography using silica gel (100-200 mesh) as stationary phase and 0.25% EtOAc in CH_2Cl_2 as eluent to obtain the desired product as cream colored gummy solid (120 mg, 50%). 1H NMR (500 MHz, $CDCl_3$, TMS): δ (ppm) = 8.68 (d, J = 8.5 Hz, 1H), 8.62 (d, J = 7.0 Hz, 1H), 8.42 (d, J = 8.5 Hz, 1H), 7.81-7.72 (m, 4H), 7.49 (d, J = 8.0 Hz, 1H), 7.32-7.17 (m, 5H), 7.07 (s, 2H), 6.91 (d, J = 8.0 Hz, 1H); 6.54 (q, J = 7.0 Hz, 1H), 4.04 (m, 6H), 1.98 (d, J = 7, 3H), 1.84-1.73 (m, 6H), 1.62-1.47 (m, 18H), 1.32-1.20 (m, 24H), 0.892-0.842 (m, 9H); ^{13}C NMR ($CDCl_3$): δ (ppm) = 165.88, 164.00, 163.9, 160.09, 153.50, 151.24, 141.12, 135.68, 133.13, 132.22, 129.95, 128.40, 127.12, 126.68, 123.92, 122.34, 121.58, 117.09, 110.62, 106.14, 73.77, 69.74, 50.16, 32.07, 29.79, 26.24, 22.84, 16.44, 14.26; HRMS (ESI): m/z calcd for $C_{63}H_{84}N_2O_7K$ $[M + K]^+$: 1019.5916; found: 1019.5916; UV-visible; ($CHCl_3$): $\lambda_{max}(\epsilon)$ = 366 (12,700), 275 nm (17,800), 249 (21,800 $M^{-1}cm^{-1}$).

Experimental Section:

Gelation test: The gelation ability of **NMI-1** was checked in MCH. Stock solution of the gelator was made in a good solvent like $CHCl_3$ at a fixed concentration. Measured volume of the stock was taken in a screw capped sample vial and the solvent was evaporated by heating. To this solid film, known volume of MCH was added and the mixture was heated until all the solid dissolved completely and was allowed to cool to room temperature. A clear solution was noticed on cooling which slowly turned into gel in ~ 80 h which was tested by the “the stable-to-inversion of a vial”.

UV-visible studies: Stock solution of **NMI-1** was made in $CHCl_3$ at 2.5 mM concentration. 0.1 ml stock was taken in a vial and the solvent was evaporated to obtain a thin film which was diluted with 0.1 ml MCH to adjust the final concentration to 1.25 mM. The solution was allowed to equilibrate at RT for 1 h before spectral measurements. The experiment was done in 0.1 cm path-length cuvette. The same solution was kept in the cuvette for ~ 80 h to allow it to turn gel before taking the absorption spectrum in the gel state.

For temperature variable UV-studies, the gel in the cuvette was heated from 25 °C to higher temperature with the help of an external temperature controller and the spectral measurements were carried out at different temperatures. On reaching the desired temperature, 10 min equilibrium time was provided before each measurement.

Photoluminescence (PL) studies: A solution of **NMI-1** (1.25 mM) in CHCl_3 and MCH gel were recorded in a PL cuvette with path length 0.1 cm. The gel was prepared in the similar method discussed above.

^1H NMR studies: Solution of **NMI-1** in MCH was made at 5.0 mM concentration and transferred into an NMR tube. 10 % C_6D_6 in MCH was added for locking the signal. Sample was allowed to equilibrate for 1 h before taking the spectrum of in the solution state. For recording the ^1H NMR in the gel state, same solution was kept in the NMR tube for ~80 h and allowed to turn gel before taking the spectrum.

For the temperature variable experiment, gel prepared in the NMR tube was heated from 30 -80 °C with an external temperature controller and the spectral measurements were carried out at different temperatures. On reaching the desired temperature, 10 min equilibrium time was provided before each measurement. The NMR experiment was performed in 300 MHz spectrometer. For each reading, 16 scans were taken with 1 sec delay time.

Transmission Electron Microscopic studies: A solution of **NMI-1** in MCH (2.0 mM) was drop casted on the copper grid with carbon after 1 h, 40 h and 80 h of sample preparation to record the TEM images of the sample in sol, gel and intermediate states respectively. All samples were left open to the atmosphere for 30 min (to allow MCH to evaporate) prior to imaging.

Fluorescence Microscopic studies: A solution of **NMI-1** in MCH (2.0 mM) in both sol and gel state were placed between two clean glass slips and images were captured on a fluorescence microscope (OLIMPUS BX-61) at 40X magnification.

Circular Dichroism (CD) and Linear Dichroism (LD) studies: In a typical experiment, stock solution of **NMI-1** was made in CHCl_3 (2.5 mM). An aliquot (0.1 ml) was taken in a vial and the solvent was evaporated to obtain a thin film. To this, 0.2 ml MCH was added to adjust the final concentration to 1.25 mM. The solution was transferred to a quartz cuvette (path length = 0.1 cm) and equilibrate for 1 h before taking the spectra (CD or LD) in the sol state. For recording the spectrum in the gel state, the same solution was kept undisturbed in the cuvette for ~80 h to allow gel formation.

For temperature variable **CD**, the gel was heated from 25 °C to higher temperature and the CD spectra were recorded at different temperatures. For each measurement, 10 min equilibrium time was provided after reaching the desired temperature.

Powder X-Ray diffraction studies: A solution of **NMI-1** in MCH (0.5 ml) in sol and gel state were drop-casted repeatedly on two separate glass slides to make a thick film and were then air dried for 24 h. Data were recorded for these two samples from 0.3° to 30 ° with sampling interval of 0.02 ° per state.

Computational Details: All calculations were performed in Gaussian09 quantum code.⁴ To expedite the calculation we have truncated the $\text{C}_{10}\text{H}_{21}\text{O}$ alkoxy chains in **NMI-1** with CH_3O — and labelled this model as **1_m**. The geometry is optimized with the generalized approximation (GGA) to DFT by using the exchange functional of the Becke⁵ in addition with the Grimme's functional⁶ including a long-range dispersion (B97D). The split valence 6-31G(d,p) (double- ζ) type basis set was used for all atoms. The resolution-of-the-identity (RI) approximation (also called “density fitting”) for the two electron integrals was employed.⁷ Geometry is fully optimized normally without symmetry constraints. The TD-DFT

singlet excitation energies⁴ of the monomer in gas-phase were calculated. In the calculation of the optical spectra, the 50 lowest spin-allowed singlet-singlet transitions were taken into account. Transition energies and oscillator strengths were interpolated by a Gaussian convolution with a width of 0.2 eV. All the frontier molecular orbitals are drawn in Chemcraft visualization software.⁸

Additional Figures:

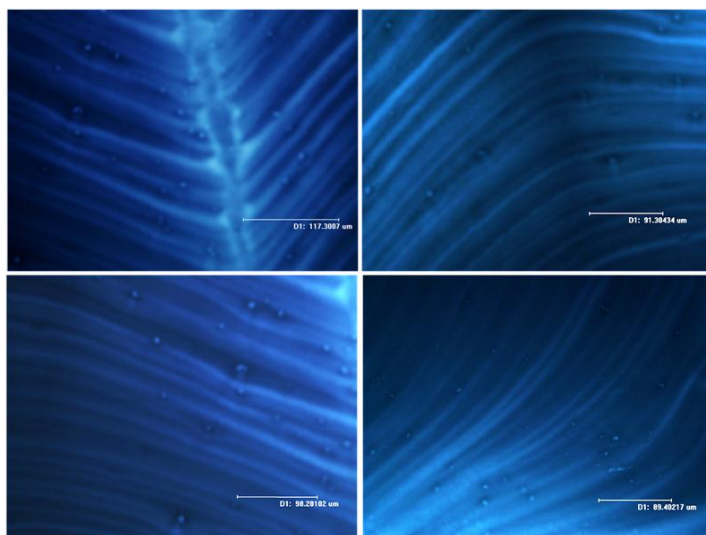


Figure S1: Florescence microscopic images of the blue emitting gel fibres in MCH. Concentration = 2.0 mM.

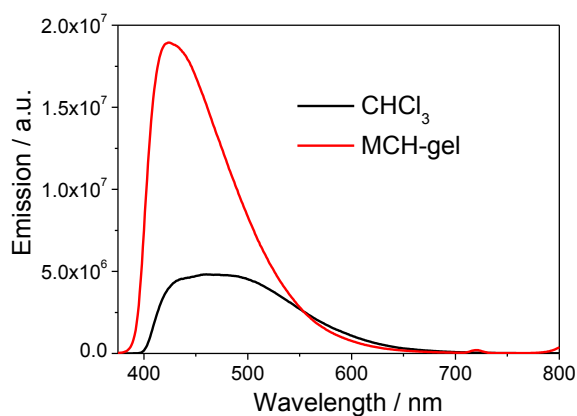
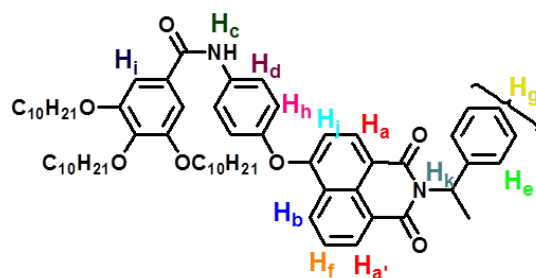


Figure S2: Solvent-dependent PL spectra of **NMI-1**. Concentration = 1.25 mM; $\lambda_{\text{ex}} = 360$ nm



| Protons | H _a | H _{a'} | H _b | H _c | H _d | H _e | H _f | H _g | H _h | H _i | H _j | H _k |
|------------------------------|----------------|-----------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|
| δ in CHCl ₃ (ppm) | 8.62 | 8.69 | 8.43 | 7.81 | 7.72 | 7.49 | 7.78 | 7.32-7.20 | 7.17 | 7.07 | 6.91 | 6.53 |
| δ in MCH gel (30 °C) (ppm) | 8.31 | 8.31 | 8.08 | 8.46 | 7.56 | 7.39 | 7.32 | 7.08-6.97 | 6.79 | 6.87 | 6.49 | 6.43 |

Table S1: Chemical shift values of assigned protons of **NMI-1** in CHCl₃ and MCH (in gel state, 75 h after solution prepared)

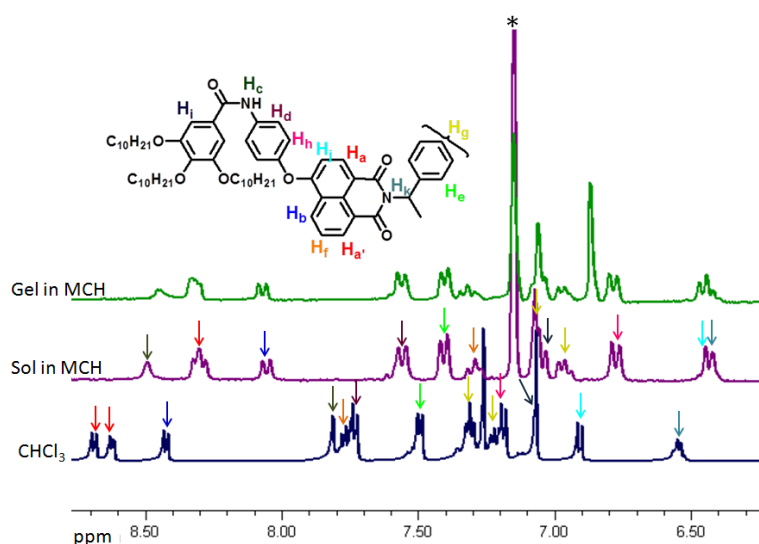


Figure S3: Selected region of ¹H NMR spectra of a freshly prepared solution of **NMI-1** in CHCl₃, MCH and in the gel state; Concentration = 5.0 mM, 10 % (v/v) C₆D₆ was added in MCH for locking.

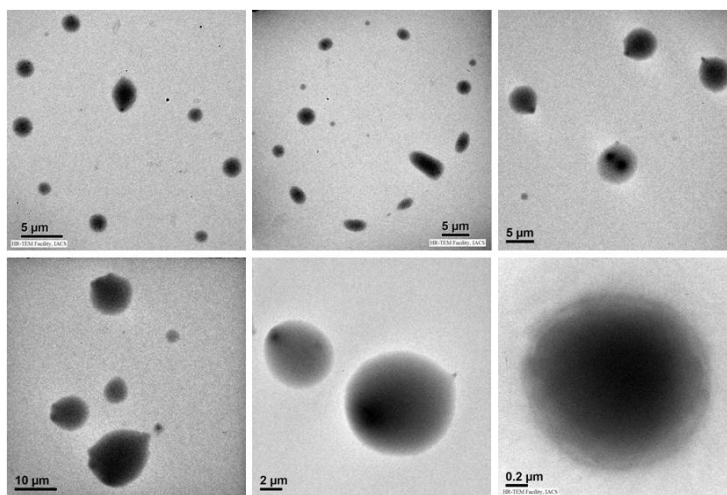


Figure S4: TEM images of freshly prepared solution of **NMI-1** in MCH; Concentration = 2.0 mM

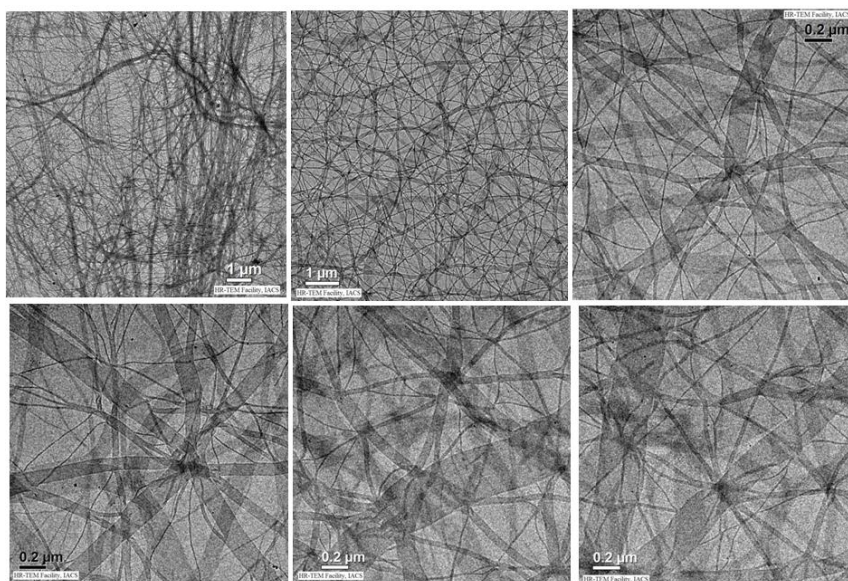


Figure S5: TEM images of **NMI-1** in MCH in the gel state; Concentration = 2.0 mM

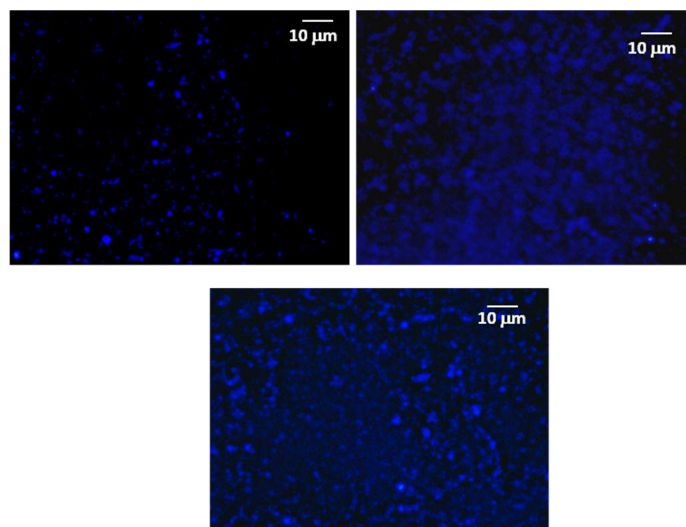


Figure S6: Fluorescence microscopic images of the blue emitting spherical particle obtained from freshly prepared solution of **NMI-1** in MCH. Concentration = 2.0 mM

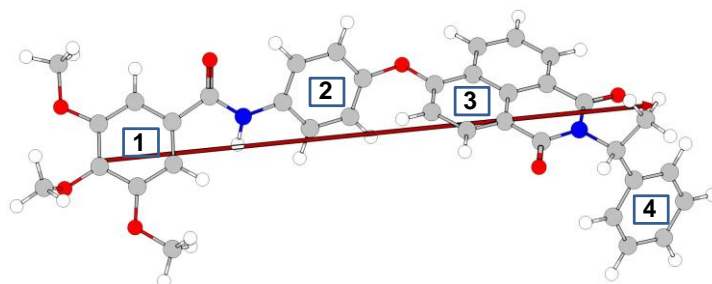


Figure S7: B97D/6-31G(p,d) gas-phase optimized structure of **1_m**. The arrow represents the ground state dipole moment of the molecule. The numbers (1 to 4) within the rectangles are designated to the π -planes. There is a significant out-of-planar orientation observed in the donor- π -acceptor framework. The torsion angle (Φ) between planes 3 and 2 is highest, ($\Phi_{3,2} = 66^\circ$) while 3 and 4 being lowest ($\Phi_{3,4} = 26^\circ$) with an intermediate value ($\Phi_{1,2} = 32^\circ$) for 1 and 2 respectively. The finite dipole moment (5.7 D) of **1_m** clearly indicates the electron rich and deficient regions of the molecule that can be better visualized from the frontier molecular orbitals sketched in Figure S8.

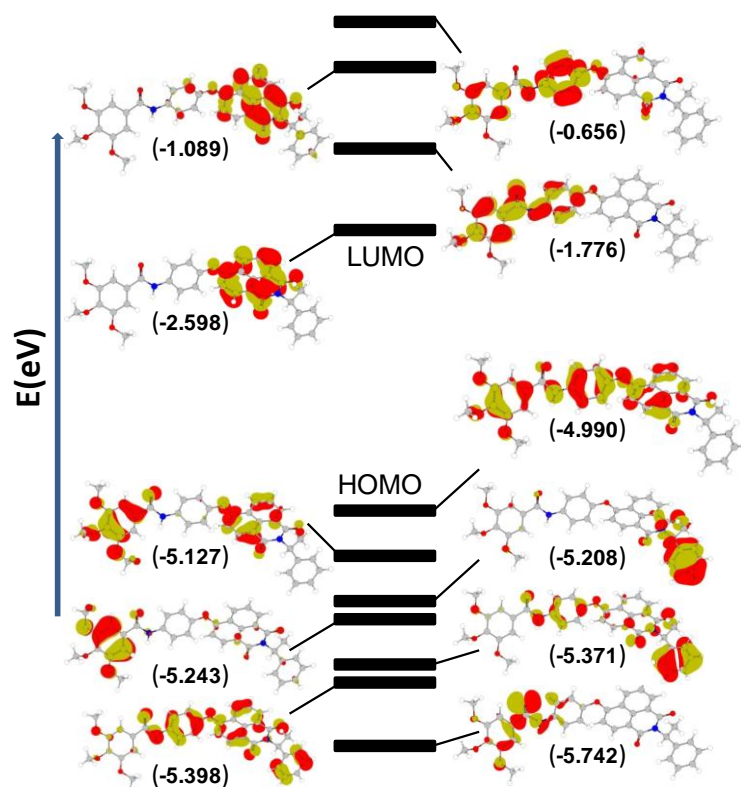


Figure S8: KS-Molecular orbitals of **1_m** in the order H-7, H-5, H-4, H-3, H-2, H-1, H, L, L+1, L+3 and L+5. The HOMO and LUMO are abbreviated as H and L. The Figure is not drawn to scale

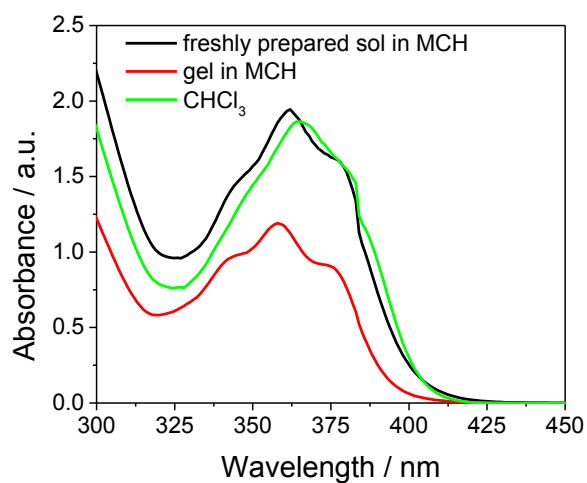


Figure S9: UV/vis spectra of **NMI-1** in freshly prepared MCH solution, gel state and in CHCl_3 ; Concentration = 1.25 mM; Pathlength = 0.1 cm

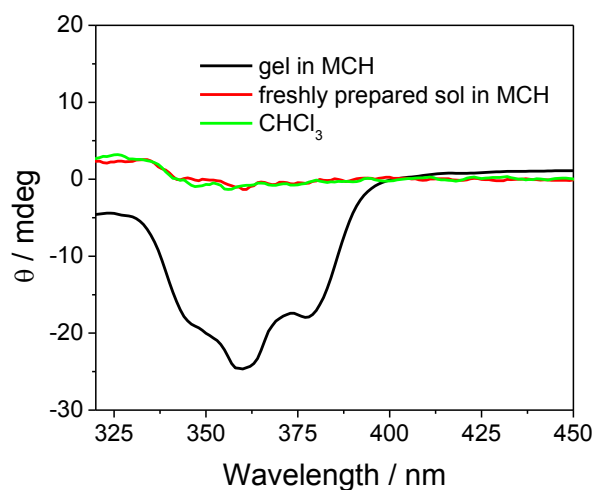


Figure S10: CD spectra of **NMI-1** in freshly prepared MCH solution, gel state and in CHCl_3 ; Concentration = 1.25 mM; Pathlength = 0.1 cm

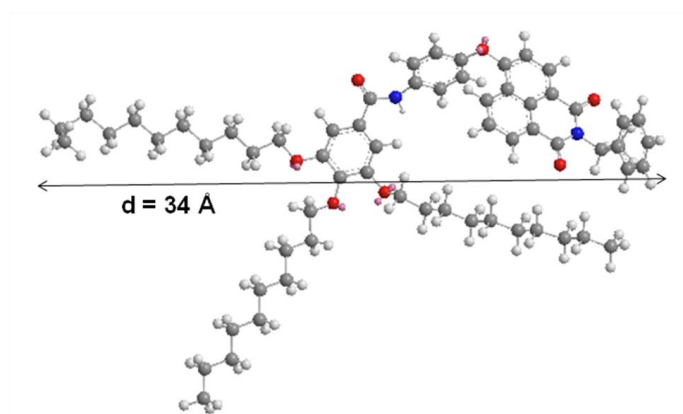


Figure S11: Energy minimized structure of **NMI-1** obtained from Chem 3D Ultra 8.0; Length of the molecule = 34 Å

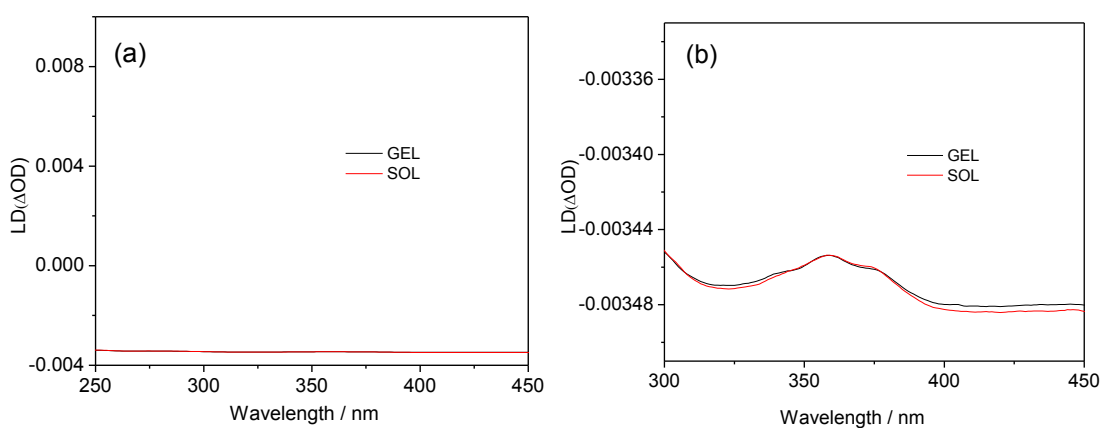


Figure S12: (a) LD spectra of **NMI-1** in freshly prepared MCH solution and in gel state. Concentration = 1.25 mM; Path length = 0.1 cm; (b) Selected region of spectra shown in Fig S12a in an expanded Y-axis scale.

Table S2: Details of the vertical excitation for the DFT optimized monomer species **1_m**.

| λ (nm) ¹ | f^2 | ΔE_x (eV) ³ | Transition electric μ (D) ⁴ | Orbitals (percentage contribution) ⁵ |
|-----------------------------|--------|-----------------------------------|---|---|
| 506.5 | 0.0283 | 2.447 | 1.200 | H-1→L(26%); H→L(73%) |
| 473.6 | 0.0213 | 2.617 | 0.845 | H-3→L(48%); H-1→L(29%); H-2→L(14%) |
| 460.1 | 0.0429 | 2.694 | 1.651 | H-3→L(37%); H-5→L(24%); H-1→L(20%); H-4→L(12%) |
| 317.4 | 0.0802 | 3.906 | 2.130 | H-5→L+1(49%); H-4→L+1(20%) |
| 337.8 | 0.3557 | 3.669 | 10.058 | H-1→L+1(51%); H→L+1(30%) |
| 386.9 | 0.1884 | 3.205 | 6.098 | H-7→L(35%); H-5→L(23%); H-1→L(11%) |
| 397.6 | 0.0833 | 3.118 | 2.773 | H-7→L(64%); H-5→L(15%) |

[1] Wavelength of the transition. [2] The oscillator strength of the transition. [3] Excitation energies for each transition. [4] For each transition from the ground to the higher excited state. [5] Molecular orbitals involved in the transitions; H = HOMO, L = LUMO. The respective contributions are in parentheses.

Table S3. Cartesian coordinates (in Å) of the optimized structure **1_m**.

| | | | | |
|-------------|---|--------------|--------------|--------------|
| Monomer (1) | 6 | 3.138758000 | -0.988353000 | -0.281907000 |
| | 6 | 2.190308000 | -0.318408000 | -1.089769000 |
| | 6 | 2.725703000 | -2.095332000 | 0.492496000 |
| | 6 | 0.858902000 | -0.738054000 | -1.131750000 |
| | 1 | 2.504287000 | 0.535966000 | -1.695660000 |
| | 6 | 1.387340000 | -2.508340000 | 0.454656000 |
| | 1 | 3.450737000 | -2.618703000 | 1.107611000 |
| | 6 | 0.464603000 | -1.834867000 | -0.351947000 |
| | 1 | 0.129104000 | -0.223765000 | -1.757514000 |
| | 1 | 1.055178000 | -3.360042000 | 1.049213000 |
| | 8 | -0.843365000 | -2.327534000 | -0.420441000 |
| | 6 | -1.887414000 | -1.543529000 | 0.005985000 |
| | 6 | -3.194634000 | -2.004857000 | -0.368403000 |
| | 6 | -1.726739000 | -0.391290000 | 0.776977000 |
| | 6 | -3.410664000 | -3.168740000 | -1.156367000 |
| | 6 | -4.328948000 | -1.242399000 | 0.076707000 |
| | 6 | -2.856589000 | 0.340235000 | 1.193688000 |
| | 1 | -0.727507000 | -0.062554000 | 1.058134000 |
| | 6 | -4.702013000 | -3.563703000 | -1.488663000 |
| | 1 | -2.549850000 | -3.744405000 | -1.495961000 |
| | 6 | -5.639605000 | -1.669738000 | -0.275919000 |
| | 6 | -4.148023000 | -0.065519000 | 0.856350000 |
| | 1 | -2.735177000 | 1.240910000 | 1.796141000 |
| | 6 | -5.818023000 | -2.816561000 | -1.048699000 |
| | 1 | -4.856678000 | -4.457962000 | -2.094917000 |
| | 1 | -6.834681000 | -3.117695000 | -1.303156000 |
| | 6 | -5.309117000 | 0.737512000 | 1.306857000 |
| | 8 | -5.173801000 | 1.787716000 | 1.942273000 |
| | 7 | -6.600304000 | 0.239523000 | 0.973920000 |
| | 6 | -6.837037000 | -0.903777000 | 0.176696000 |
| | 8 | -7.980560000 | -1.250724000 | -0.122730000 |
| | 6 | -7.782943000 | 1.054696000 | 1.428790000 |
| | 6 | -8.445509000 | 1.741237000 | 0.236089000 |

| | | | |
|---|---------------|--------------|--------------|
| 6 | -9.673957000 | 1.326584000 | -0.305397000 |
| 6 | -7.785894000 | 2.848095000 | -0.334861000 |
| 6 | -10.235313000 | 2.009045000 | -1.395749000 |
| 1 | -10.184560000 | 0.460962000 | 0.114532000 |
| 6 | -8.340446000 | 3.526276000 | -1.428999000 |
| 1 | -6.832979000 | 3.171052000 | 0.091857000 |
| 6 | -9.570980000 | 3.108129000 | -1.962009000 |
| 1 | -11.190624000 | 1.675769000 | -1.807887000 |
| 1 | -7.818345000 | 4.384132000 | -1.859315000 |
| 1 | -10.009542000 | 3.636490000 | -2.811765000 |
| 6 | -8.706117000 | 0.249391000 | 2.357831000 |
| 1 | -9.480238000 | 0.923898000 | 2.756064000 |
| 1 | -9.190123000 | -0.587096000 | 1.841852000 |
| 1 | -8.119227000 | -0.144320000 | 3.201764000 |
| 1 | -7.321663000 | 1.843262000 | 2.033506000 |
| 7 | 4.456631000 | -0.489180000 | -0.288802000 |
| 1 | 4.607304000 | 0.300430000 | -0.908872000 |
| 6 | 5.604486000 | -1.016268000 | 0.302070000 |
| 8 | 5.622118000 | -2.080842000 | 0.924248000 |
| 6 | 6.842509000 | -0.182560000 | 0.099381000 |
| 6 | 6.799674000 | 1.215717000 | -0.077104000 |
| 6 | 8.072228000 | -0.862266000 | 0.122354000 |
| 6 | 7.998123000 | 1.935371000 | -0.246864000 |
| 1 | 5.851876000 | 1.747396000 | -0.005322000 |
| 6 | 9.268942000 | -0.149783000 | -0.063976000 |
| 1 | 8.062462000 | -1.937346000 | 0.286724000 |
| 6 | 9.239561000 | 1.253750000 | -0.263271000 |
| 8 | 10.515549000 | -0.713658000 | -0.074212000 |
| 8 | 10.393050000 | 1.957436000 | -0.504172000 |
| 8 | 8.076962000 | 3.294414000 | -0.388080000 |
| 6 | 11.152158000 | 2.243320000 | 0.686762000 |
| 1 | 12.041578000 | 2.794358000 | 0.350954000 |
| 1 | 10.564171000 | 2.871539000 | 1.378869000 |
| 1 | 11.457990000 | 1.311821000 | 1.191173000 |
| 6 | 6.849492000 | 4.024222000 | -0.384286000 |
| 1 | 7.129597000 | 5.075457000 | -0.528062000 |
| 1 | 6.188189000 | 3.697404000 | -1.207526000 |
| 1 | 6.315887000 | 3.906478000 | 0.576382000 |
| 6 | 10.594390000 | -2.126062000 | 0.146938000 |
| 1 | 10.178231000 | -2.398617000 | 1.132651000 |
| 1 | 10.053811000 | -2.680723000 | -0.639809000 |
| 1 | 11.663595000 | -2.370016000 | 0.109314000 |

References:

1. D. D. Perrin, W. L. F. Armarego, D. R. Perrin, *Purification of Laboratory Chemicals*, 2nd Ed. Pergamon, Oxford, **1980**
2. T. Tahtouh, J. M. Elkins, P. Filippakopoulos, M. Soundararajan, G. Burgy, E. Durieu, C. Cochet, R. S. Schmid, D. C. Lo, F. Delhommel, A. E. Oberholzer, L. H. Pearl, F. Carreaux, J.-P. Bazureau, S. Knapp and L. Meijer, *J. Med. Chem.* 2012, **55**, 9312.
3. S. H.-Ainsa, J. Barbera, M. Marcos, and J. L. Serrano, *Chem. Mater.* 2010, **22**, 4762.
4. Gaussian 09, Revision **C.01**, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, G. H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, Jr. J. A. Montgomery, J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N.

- Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, D. J. Fox, Gaussian, Inc., Wallingford CT, 2010.
5. A. D. Becke, *Phys. Rev. A* 1988, **38**, 3098.
 6. S. Grimme, *J Comp. Chem.*, 2006, **27**, 1787.
 7. B. I. Dunlap, *J. Chem. Phys.*, 1983, **78**, 3140–3142; B. I. Dunlap, *J. Mol. Struct. (Theochem)*, 2000, **529**, 37.
 8. <http://www.chemcraftprog.com>