Materials and methods: Solvents and reagents were purchased from Merck-India sources and further purified following standard procedures before using. Naphthalene di-anhydride, 1,3 dibromo-5,5-dimethylhydantoin, n-Octylamine, 4-(aminomethyl) piperidine and S-Citronellyl bromide were purchased from Sigma Aldrich. Spectroscopic grade solvents were used for physical studies. 1HNMR experiments were performed on a Bruker DPX-500 MHz, 400 MHz and 300 MHz NMR instrument and the peaks were calibrated against TMS. FT-IR spectra were recorded in a Perkin Elmer Spectrum 100FT-IR spectrometer. For determination of mass of the synthesized compound, electron spray ionization (ESI) technique Q-tof-micro quadruple mass spectrometer was used. UV/Vis spectra were performed in a Perkin Elmer Lambda 25 spectrometer. Atomic force microscopy (AFM) images were taken in an Innova instrument from Bruker. Circular dichroism spectra were recorded in a Jasco J815 Spectropolarimeter. Viscosity measurements were performed by using Brookfield instrument. Multicell DSC from TA instrument was used to examine the thermodynamic properties.

Experimental Section

Synthesis:

Scheme S1: Synthetic scheme of cNDI-1.

Synthesis of cNDI-1: cNDI-1 was prepared by coupling reaction of compound A and B which were reported earlier. 2 In a 50 ml round bottom flask, 50 mg of compound A, 2.0 mole equivalent of B and 0.3 equivalent of DMAP were taken and dissolved in dry DCM (5.0 ml) and stirred at 0 °C under nitrogen atmosphere for 15 min. To this cold solution, EDC solution in DCM (2 mole equivalent, 5 ml solvent) was added drop wise and stirred for 48 h. Subsequently the reaction was stopped, and the solution was washed with 0.1 N aqueous HCl (10 ml) and then with distilled water (2 x 10 ml). The organic layer was passed through anhydrous Na₂SO₄ and then solvent was evaporated producing a blue pasty mass as the crude product. It was then purified by column chromatography using DCM/MeOH (98/2) mixture as eluent to get the desired product as blue waxy material. Yield = 80%. 1HNMR (CDCl₃, 400 MHz, TMS): δ (ppm) = 8.44 (2H, s), 6.98 (4H, s), 6.2 (2H, broad) 4.16 (4H, t, J = 7 Hz), 4.08-4.01
(12H, m), 3.64 (4H, d, J = 10 Hz), 3.45 (4H, t, J = 6 Hz), 3.23 (4H, t, J = 12 Hz), 1.96-1.83 (20H, m), 1.7-1.61 (36H, m), 1.35-1.16 (38H, m), 0.93-0.86 (60H, m). $^{13}$C NMR (CDCl$_3$) $\delta$ (ppm) = 168.4, 167.7, 163.1, 161.2, 153.2, 129.6, 105.8, 71.8, 67.8, 39.4, 39.3, 37.6, 37.4, 36.5, 31.9, 29.9, 29.7, 29.3, 28.1, 27.3, 24.4, 22.8, 22.7, 19.7, 14.2. HRMS (ESI): m/z calc. for C$_{118}$H$_{190}$N$_8$O$_{12}$ [M + H]$^+$: 1860.4522; found: 1860.4506.

**Gelation test:** To check the gelation properties of cNDI-1, measured volume of the stock solution (4.0 mM in CHCl$_3$) was transferred to a screw capped vial and solvent was evaporated by heating to make a thin film. To this, a desired volume of apolar solvent (decane/ MCH) was added and then heated in closed condition with hot air gun until the entire compound was dissolved. The hot solution was allowed to settle at room temperature for 1h and then tilted to confirm gel formation. Concentrated gel was diluted gradually by adding the same solvent to measure the critical gelation concentration (CGC). After each addition, the mixture was heated to make a homogeneous solution and allowed to stand at room temperature and gelation was checked by tilting the vial after 30 min. CGC was noted at that concentration below which gelation was not occurred.

**Preparation of seed:** 100 µl of a stock solution of cNDI-1 or cNDI-2 (C = 1 mM) was taken in a vial and solvent was evaporated by heating with hot air gun to make a thin film and then 2000 µl of decane was added to it and heated to make clear solution (C = 5 X 10$^{-5}$ M). The solution was allowed to stand at rt for 10 min and then subjected to sonication for 20 min which was then examined by AFM and UV/Vis and used as the seed solution.

**UV-Vis and CD studies:** Solutions of cNDI-1 or cNDI-2 were prepared (1.0 mM) either in decane or MCH by following the procedure explained in the gelation test section. Solutions of different concentrations were prepared by required dilution of the 1.0 mM solution with decane/ MCH. For solvent dependent UV/ Vis studies quartz cuvettes were used with path length of 1.0 cm. For variable temperature UV/Vis studies, hot solution was gradually cooled using a peltier with a cooling rate of 1.0 K/ min. CD spectra were recorded using a quartz cuvette of path length of 1.0 cm with scan speed = 50 nm/ min and a response time of 2s. In variable temperature experiment, hot solution was cooled with a peltier with cooling rate of 1.0 K/ min

**Analysis of variable temperature UV/Vis and CD data:** The mechanistic pathways of supramolecular polymerization were analyzed from the experimental data obtained from cooling curves in UV/Vis and CD spectra by fitting with the nucleation-elongation model by using following equations.$^3$

$$\alpha_{agg} = \alpha_{const} \left[ 1 - \exp\left(-\frac{h_e}{RT_e} (T - T_e)\right) \right] \quad \text{(E1)}$$

$$\alpha_{agg} = \alpha_{const} \left[ \sqrt{K_a} \exp\left(\frac{2}{3} \sqrt{K_a} - 1\right) - \frac{h_e}{RT_e} (T - T_e) \right] \quad \text{(E2)}$$

$$<N_a> = \frac{1}{\sqrt{K_a}} \frac{1 - \exp\left(-\frac{h_e}{RT_e} (T - T_e)\right)}{\exp\left(-\frac{h_e}{RT_e} (T - T_e)\right)} \quad \text{(E3)}$$

Where $T_e$ is the elongation temperature that separates nucleation and elongation regimes, $K_a$ is the dimensionless equilibrium constant, $h_e$ serves as enthalpy released during non-covalent interaction, $\alpha_{agg}$ is the mole fraction of aggregate, $\alpha_{const}$ is a constant that secures the ratio of $\alpha_{agg}$ to $\alpha_{const}$ does not exceed unity, $N_a$ is the degree of polymerization in the elongation regime, T is the absolute temperature and R is the universal gas constant. $\alpha_{agg}$ at each temperature could be estimated using the following equation.
\[ \alpha_{agg} = \frac{A_T - A_M}{A_{agg} - A_M} \]  

(E4)

Where \( A_T \), \( A_M \), and \( A_{agg} \) represent absorption intensity at a given temperature, at the monomeric state (highest temperature) and in aggregated state (lowest temperature). Thermodynamic parameters obtained from this analysis are shown in Table S1. Both UV/Vis and the CD data indicate highly cooperative supramolecular polymerization in decane. Difference in the thermodynamic parameters obtained from the UV/Vis and CD data are attributed to the difference in sensitivity of these two techniques to nucleation and elongation process.

**Microscopy studies:** For atomic force microscopy (AFM) studies, a solution of a given sample solution was placed on mica surface and spin coated at 1000 rpm. The films were allowed to stand at room temperature for overnight before capturing the images.

**Viscosity Measurement:** Solutions of cNDI-1 in MCH (\( C = 1 \) mM) in the presence or absence of the seed were placed at rt and 500 \( \mu l \) of aliquot was transferred to the sample chamber after a specific time interval viscosity was measured at 20 °C in a Brookfield DV2T instrument at 10 r.p.m. Specific viscosity was calculated by the following equation where \( \eta \) and \( \eta_o \) are the viscosity of the solution and solvent respectively.

\[ \eta_{sp} = \frac{\eta - \eta_o}{\eta_o} \]  

(E5)

**Micro-DSC Measurement:** Differential scanning calorimetric measurements were performed by placing a solution of cNDI-1 (\( C = 4 \) mM) in MCH (in the absence or presence of seed) in the sample cell at a fixed temperature, 20 °C as a function of time in the isothermal mode. Respective solvents are used as reference in the reference cell. The heat changes were recorded in 1 s interval.
Additional figures:

Fig. S1: Fitted data of cooling curve of cNDI-1 in decane obtained from a) UV/Vis ($C = 5 \times 10^{-5}$ M) and b) CD ($C = 1 \times 10^{-4}$ M) spectroscopy. Cooling curves were measured by monitoring the absorption band at 383 nm for UV/Vis and 610 nm for CD. The elongation temperatures ($T_e$) obtained from UV/Vis and CD are 337 and 341 K respectively. MATLAB Software was used for fitting these data.

Table S1: Thermodynamic parameters of cNDI-1 in decane obtained from UV/Vis and CD spectroscopy.

<table>
<thead>
<tr>
<th>Spectroscopy</th>
<th>C X $10^{-5}$ /M</th>
<th>$\alpha_{\text{const}}$</th>
<th>$T_e$ /K</th>
<th>$h_e$/KJ mol$^{-1}$</th>
<th>$K_a$ $\times 10^{-3}$</th>
<th>$N_a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>UV/Vis</td>
<td>1.0</td>
<td>1.00</td>
<td>337.2</td>
<td>-80.5</td>
<td>3.5</td>
<td>6</td>
</tr>
<tr>
<td>CD</td>
<td>10.0</td>
<td>1.00</td>
<td>341.5</td>
<td>-128</td>
<td>0.1</td>
<td>21</td>
</tr>
</tbody>
</table>

Fig. S2: UV/Vis spectra of cNDI-1 in decane before (black line) and after (red line) sonication. ($C = 5 \times 10^{-5}$ M; $l = 1.0$ cm)
Fig. S3. Time dependent variation of specific viscosity of cNDI-1 solution in MCH (red- 1.0 mM, green-2.0 mM) after addition of 20 % seed

Fig. S4. AFM image of cNDI-1 in MCH: after 30 min aging a) on its own or b) after addition of 20% decane. (C = 5 \times 10^{-5} \text{ M})

Fig. S5. AFM image of seed in decane prepared by sonication for 20 min (C = 2.5 \times 10^{-6} \text{ M}). The average length of the seed is 280 nm.
Fig. S6. a) CD spectra of cNDI-2 + cNDI-1 (numbers inside the figure indicate mole % of cNDI-1 in the mixture) in decane ($C = 1 \times 10^{-4}$ M); b) Variation of molar ellipticity (band intensity at 590 nm was used for this calculation) as a function of % of sergeant (cNDI-1) in the mixture. The trend shows a bi-phasic behavior which indicates at higher content (> 30 %) of the sergeant the soldiers and sergeant principle may not be operative. Furthermore, the band maxima also shows shift beyond 30 % sergeant and appears more similar to the pure cNDI-1 spectrum. These indicate complex co-assembly behavior\textsuperscript{[4-5]} depending on the ratio of the chiral and achiral components which will be studied in detail in the future. c) AFM image of cNDI-2/cNDI-1 (80/20) mixture ($C = 5 \times 10^{-5}$ M). Stock solutions of cNDI-2 and cNDI-1 in good solvent CHCl$_3$ were mixed in a good solvent CHCl$_3$ (4:1), transferred to a vial, dried by removing the solvent and then decane was added and the mixed aggregated solution was prepared by heating. Spectra were recorded after 1.0 h equilibration time.
Fig S7. AFM images of cNDI-1 in various linear and cyclic hydrocarbon solvents. $C = 2.5 \times 10^{-5}$ M

Fig S8. AFM images of cNDI-1 in MCH/Decane solvent mixtures showing pronounced fibrillar assembly with more amount of decane in the mixture. $C = 2.5 \times 10^{-5}$ M

References

