

Supporting Information for

## Three Component Assembly by Orthogonal H-Bonding and Donor-Acceptor Charge-Transfer Interaction

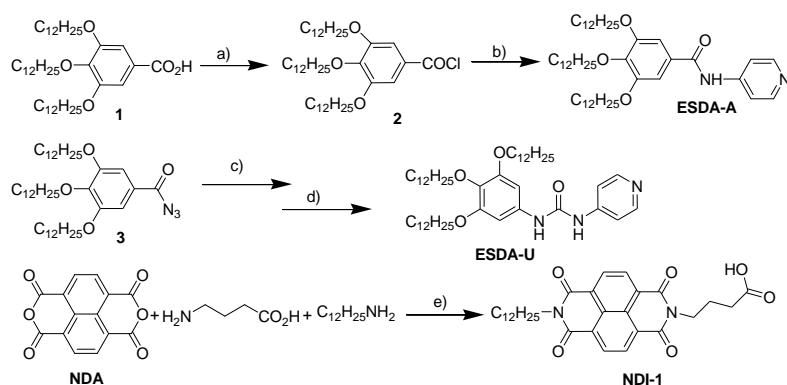
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**Materials and methods:** All the reagents were received from Sigma Aldrich Chemical Co. and used without further purification. Solvents were purchased from commercial sources and purified by reported protocol.<sup>1</sup> Spectroscopic grade solvents were used for physical studies. Thin layer chromatography was carried out on silica gel aluminum plates (specification: 60 F<sub>254</sub> from Merck, Germany). <sup>1</sup>H NMR and <sup>13</sup>C NMR experiments were done on a Bruker DPX-300 MHz and 500 MHz NMR machine and all the data were calibrated against TMS. UV / vis absorption experiments were performed in a Perkin-Elmer Lambda 25 spectrometer. Mass spectrometric data were acquired by an electron spray ionization (ESI) technique on a Q-tof-micro quadrupole mass spectrometer (Micro mass). Transmission electron microscopy (TEM) was done in a JEOL-2010EX machine operating at an accelerating voltage of 200 kV. Rheological studies were performed with an AR 2000 advanced Rheometer (TA instruments) by cone and plate method. Dynamic Light Scattering (DLS) measurement was performed in a Malvern instrument. FT-IR spectra were recorded in a Perkin Elmer Spectrum 100FT-IR spectrometer. XRD data was recorded on a Seifert XRD3000P diffractometer having a Cu K $\alpha$  radiation source ( $\alpha = 0.15406$  nm) operating at a voltage and current of 40 kV and 30 mA, respectively.

### Synthesis:



**Scheme S1:** Synthesis of various compounds studied in this work.

**ESDA-A:** Freshly distilled thionyl chloride (5.36 ml, 74 mmol) was added drop wise to a solution of **1** (2.5 g, 3.70 mmol) in dry  $\text{CHCl}_3$  and after the additions was over the reaction mixture was stirred for 12 h at rt under nitrogen atmosphere. After that excess thionyl chloride was removed by distillation and the residue was dried in a vacuum pump for 6 h to get the crude product (**2**) as light brown semi-solid materials (yield = 90%). A solution of crude compound **2** (2.40 g, 3.46 mmol) in chloroform (10 ml) was added slowly to a ice cold solution of 4-amino pyridine (0.65 g, 6.92 mmol) in chloroform (8 ml) in presence of triethyl amine (1 ml, 6.92 mmol) under  $\text{N}_2$  atmosphere. Then reaction mixture was stirred at rt for 10h and then the solution was diluted with chloroform (60 ml) and washed with water (2 x 30 ml). Organic layer was passed through anhydrous  $\text{Na}_2\text{SO}_4$  and the solvent was removed to get the crude product as an oily liquid. It was purified by column chromatography using silica gel (100-200 mesh) as stationary phase and 30% EtOAc in petroleum ether as eluent to get the desired product ( $R_f = 0.28$ ) as white solid. Yield = 65%.  $^1\text{H}$ NMR ( $\text{CDCl}_3$ , 500 MHz, TMS):  $\delta$  (ppm) = 8.80 (1H, s, broad), 8.45 (2H, d,  $J = 4.5$  Hz), 7.89 (2H, d,  $J = 4.5$  Hz), 7.15 (2H, s), 4.05 – 4.00 (6H, m), 2.08-2.04 (6H, m), 1.83-1.36(6H, m), 1.32-1.25(48H, m), 0.92-0.86 (9H,m);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  (ppm) = 166.72, 153.22, 150.14, 146.19, 141.90, 128.89, 114.34, 106.19, 69.41, 32.02, 30.43, 29.84, 29.81, 29.79, 29.75, 29.68, 29.52, 29.43, 26.17, 22.78, 14.18; HRMS (ESI):  $m/z$  calc for  $\text{C}_{48}\text{H}_{83}\text{N}_2\text{O}_4^+$  [ $\text{M} + \text{H}$ ] $^+$ : 751.6353; found: 751.6328;  $\text{C}_{48}\text{H}_{84}\text{N}_2\text{O}_4^{2+}$  [ $\text{M} + 2\text{H}$ ] $^{2+}$ : 752. 6432; found 752.6674; FTIR (KBr,  $\text{cm}^{-1}$ ), 3293 (N-H stretching), 1655 (amide carbonyl symmetric stretching), 1636 (amide carbonyl asymmetric stretching); M.P. 65 °C.

**ESDA-U:** A solution of compound **3**<sup>2</sup> (0.76 g, 1.08 mmol) in dioxane (12 ml) was refluxed for 1h and then the reaction mixture was allowed to come 80 °C and to this solution 4 - amino pyridine (0.15 gm, 1.66 mmol) was added and stirred for 30 min at 80 °C. By this time a yellow solution was obtained from which solvents were removed under reduced pressure to get the crude product as yellow oil. This was dissolved in chloroform (40 ml) and the solution washed with water (2 x 20 ml). The organic layer was passed through anhydrous sodium sulphate and the solvent was removed to obtain the product as white waxy material which was purified by column chromatography using silica gel (100-200 mesh) as stationary phase and methanol/ chloroform (3%) as eluent to get the desired product ( $R_f = 0.30$ ) as a white sticky compound (yield = 63 %).  $^1\text{H}$ NMR ( $\text{CDCl}_3$ , 300 MHz, TMS):  $\delta$  (ppm) = 9.49 (1H, s, broad), 8.20 (3H, d,  $J = 6.3$  Hz), 7.66 (2H, d,  $J = 6$  Hz), 6.69 (2H, s), 3.92 – 3.88 (6H, m), 2.08-2.04 (6H, m), 1.83-1.36(6H, m), 1.32-1.25(48H, m), 0.92-0.86 (9H,m);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  (ppm) = 154.75, 153.56, 152.25, 146.64, 134.99, 133.60, 113.39, 99.82, 73.93, 69.45, 32.10, 30.52, 30.42, 29.92, 29.89, 29.68, 29.84, 29.53, 26.33, 22.84, 14.22 HRMS (ESI):  $m/z$  calc for  $\text{C}_{48}\text{H}_{84}\text{N}_3\text{O}_4^+$  [ $\text{M} + \text{H}$ ] $^+$ : 766.6453; found: 766.6453.

$C_{48}H_{85}N_3O_4^{2+}$  [M + 2H]<sup>+</sup>: 767.6532; found: 767.6583. FTIR (KBr, cm<sup>-1</sup>), 3250 (N-H stretching), 1622 (carbonyl of urea group) .

**NDI-1:** NDA (0.42 g, 1.56 mmol), 3-amino butyric acid (0.16 g, 1.56 mmol), dodecyl amine (0.29 g, 1.56 mmol) were dissolved in dry DMF (10 ml) and refluxed at 130 °C for 12 h under N<sub>2</sub> atmosphere. Then the reaction mixture was allowed to come to rt and placed in a refrigerator for 2h. A light brown precipitate was obtained which was filtered and washed with methanol for several times and purified by column chromatography using silica gel (100-200 mesh) as stationary phase and 2% methanol in chloroform as eluent to get a off white solid (yield 40 %) as the pure product (R<sub>f</sub> = 0.21). <sup>1</sup>HNMR (CDCl<sub>3</sub>, 300 MHz, TMS): δ (ppm) = 8.76 (4H, s), 4.29 (2H, t, J = 6.9 Hz), 4.18 (2H, t, J = 7.8 Hz), 2.50 (2H, t, J = 7.5 Hz), 2.11 (2H, t, J = 7.2 Hz), 1.75 - 1.68 (18H, m), 1.18 (4H, m). <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ (ppm) = 175.66, 163.04, 131.20, 126.81, 40.99, 40.07, 32.02, 30.01, 29.28, 28.36, 27.08, 23.42, 22.51, 14.27 UV-visible (CHCl<sub>3</sub>): λ<sub>max</sub> (ε) = 360 nm (14,000), 380 nm (17,100 M<sup>-1</sup>cm<sup>-1</sup>). HRMS (ESI): m/z calc for C<sub>30</sub>H<sub>36</sub>N<sub>2</sub>O<sub>6</sub>Na<sup>+</sup> [M + Na]<sup>+</sup>: 543.2471; found : 543.2471; C<sub>30</sub>H<sub>39</sub>N<sub>2</sub>O<sub>6</sub>Na<sup>5+</sup> [M + Na+ 4H]<sup>+</sup>: 570.2687; found: 570.2858. M.P- 215 °C.

**Gelation Test:** Stock solutions of NDI-1 (10 mM), Py-1 (10 mM) and a given ESDA (10 mM) were prepared in chloroform. 50 μl of NDI-1 and Py-1 and 100 μl of ESDA were mixed in a screw cap vial and chloroform was removed by gentle heating to obtain a red film. To this vial, measured amount of a non-polar solvent like MCH / CHCl<sub>3</sub> (90: 10) was added and the contents were heated in closed condition with a hot air gun until the entire solid dissolved. The solution was allowed to stand at rt for ~ 30 minutes before gelation ability was checked by standard “stable-to-inversion of a vial” method. Likewise we checked gelation of various other combinations as stated in the manuscript.

**Rheological Measurement :** Stress-amplitude sweep measurement was carried out with 12 mM three component gel (measurements were done 6 h after the gel was prepared) in 90 : 10 MCH / CHCl<sub>3</sub> using an Advanced Rheometer AR 2000 (TA Instrument) with the cone diameter, cone angle and truncation of 40 mm, 4° 0' 22" and 121 μM, respectively. The runs were conducted at a constant oscillation frequency of 1.0 Hz and at 25 °C.

**XRD:** In a typical XRD experiment, the three component gel (concentration = 13 mM) consisting of NDI-1, Py-1 and ESDA-A was transferred on a glass slide and allowed to air drying for 12h. Data was recorded with this sample from 1° to 30 ° with sampling interval of 0.02 Å per state.

**TEM:** Morphology of three component supramolecular assembly was checked by Transmission Electron Microscope (TEM). The CT-gel/ sol were prepared at 10 mM concentration and diluted to 4 mM by 90:10

MCH / CHCl<sub>3</sub>. Then the sample was drop casted and allowed to stand at ambient temperature for 18 h before taking the images.

**UV/ vis studies:**

a) Solvent dependent experiments: Stock solutions of NDI-1, Py-1 and ESDA-A were prepared in chloroform (10 mM) and measured amount of these solutions (100 µl for NDI-1 and Py-1; 200 µl for ESDA-A) were mixed in a vial, solvent was removed and the solid mixture was added with 360 µl MCH and 40 µl CHCl<sub>3</sub> to adjust MCH / CHCl<sub>3</sub> (90: 10) solvent composition. In the same way a series of sample solution were prepared by varying MCH / CHCl<sub>3</sub> ratio so that the concentration remained same in all samples but the solvent composition was different. The solutions were allowed to equilibrate at rt for 1h before spectral measurements.

b) Variable Temp UV/ vis experiments: The three component gel or sol (NDI-1 = 2.5 mM, Py-1= 2.5 mM, ESDA-A/ ESDA-U = 5.0 mM) in MCH / CHCl<sub>3</sub> (90: 10) was placed in a quartz cuvette (*l* = 1 mm) and spectra were recorded at different temperature (5 °C interval) using an attached peltier system. 10 min equilibrium time was allowed after a desired temperature was reached. From this data  $\alpha_{agg}$  values were estimated by equation 1.

$$\alpha_{(agg)} = \frac{A(T) - A(\min)}{A(\max) - A(\min)} \dots\dots\dots 1$$

Where A (max), A (min) and A (T) stand for charge transfer band intensity maximum, minimum and recording temp.

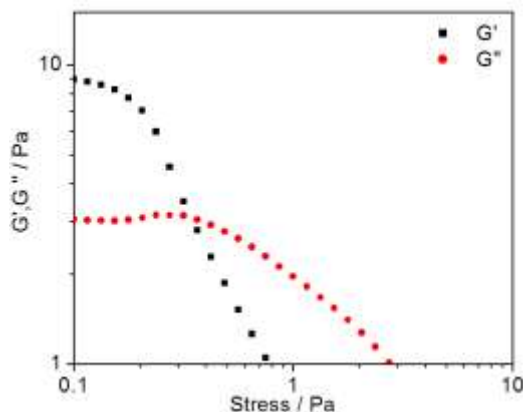
c) Dilution experiment: Similar to variable temp experiments, gel and charge transfer solution were prepared in MCH / CHCl<sub>3</sub> (90 : 10) . Then gel and sol was diluted with measured amount solvent mixture individually and the spectrum was recorded. Each of the solution was allowed to settle for 10 min prior to spectra was taken.

**Determination of Association constant:**<sup>3</sup> A series of three component sol/ gels at different concentrations were prepared maintaining the same solvent composition and for this concentration dependent absorbance data association constant (K) was determined using equation 2.

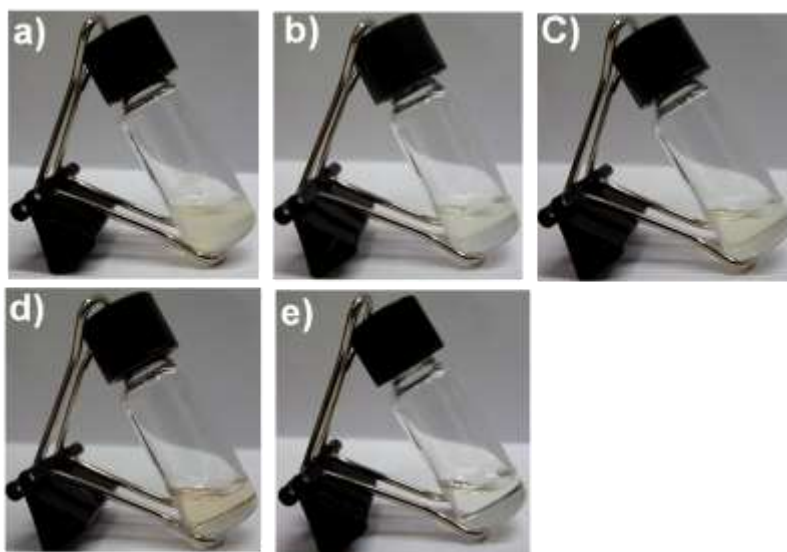
$$C / A = \frac{1}{\sqrt{K \epsilon l}} \times \frac{1}{\sqrt{A}} + \frac{1}{\epsilon l} \dots\dots\dots 2$$

Where as C, A, K,  $\epsilon$ , *l* represent concentration, absorbance of charge transfer band, association constant, extinction coefficient, path length of cuvette respectively.

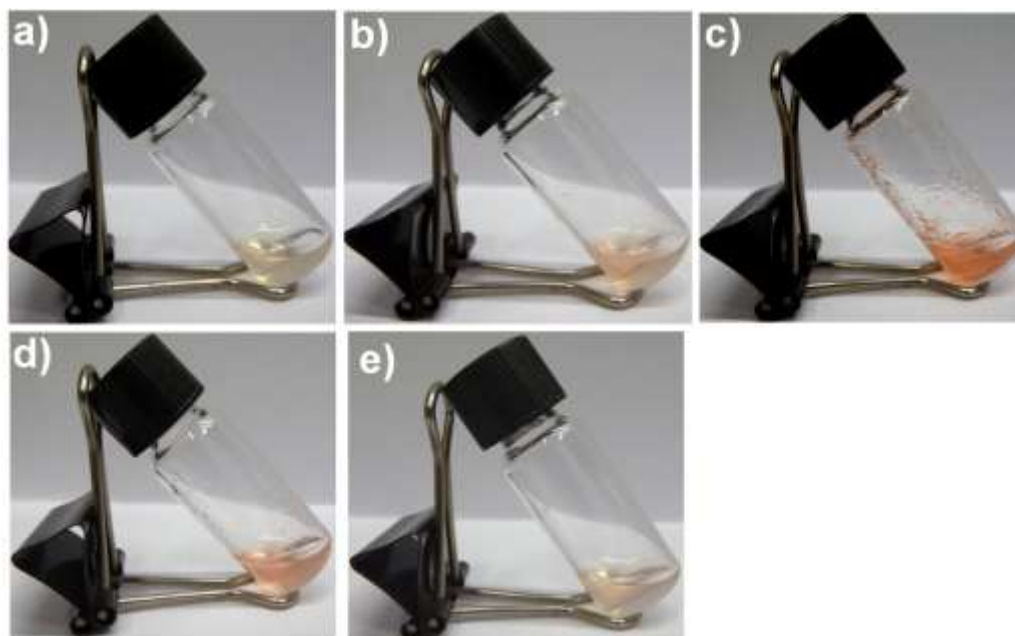
**Additional Figure:**



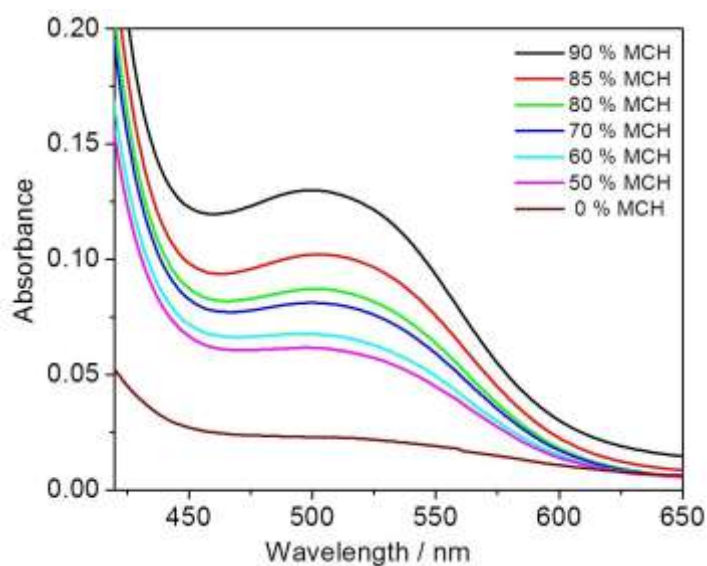
**Fig S1:** Variation of the elastic modulus ( $G'$ ) and the viscous modulus ( $G''$ ) as a function of applied stress for the three component gel consisting of NDI-1 (3 mM) + Py-1 (3 mM) + ESDA-A (6 mM) in 90: 10 MCH/  $\text{CHCl}_3$ ) at 25°C.



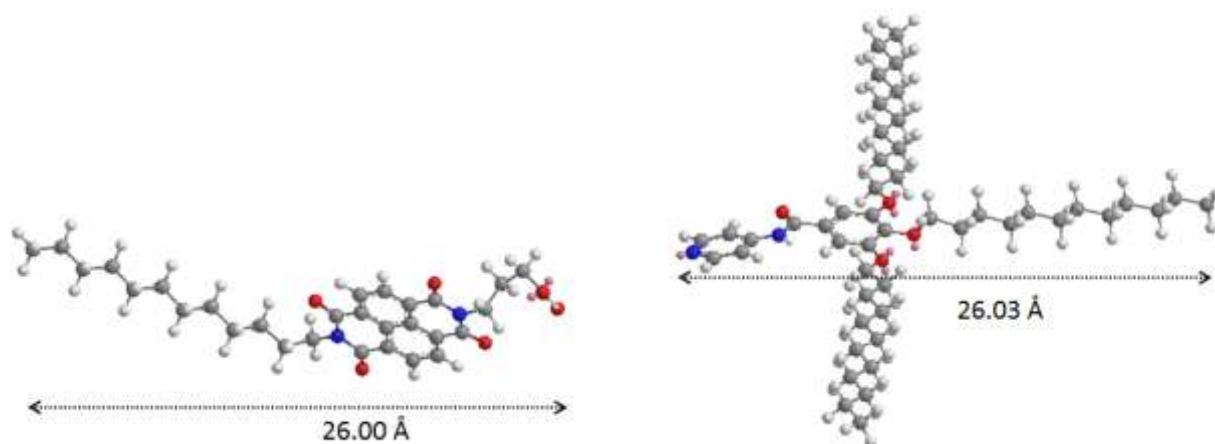
**Fig S2:** Images of samples in MCH /  $\text{CHCl}_3$  (90: 10) solvent with various compositions such as a) NDI-1 + ESDA-A; b) NDI-1 + Py + ESDA-A; c) NDI-2 + Py + ESDA-A; d) NDI-2 + Py-1 + ESDA-A and e) Py-1 + ESDA-A. In all cases concentration of donor = 2.5 mM, acceptor = 2.5 mM and ESDA = 5.0 mM. Stock solutions of individual components were prepared in chloroform, mixed in appropriate ratio and solvent was removed. Then the solid obtained was added with mixed solvent MCH/  $\text{CHCl}_3$  (90: 10), heated to get a clear solution and allowed to stand at rt for 1 h before the images were captured.



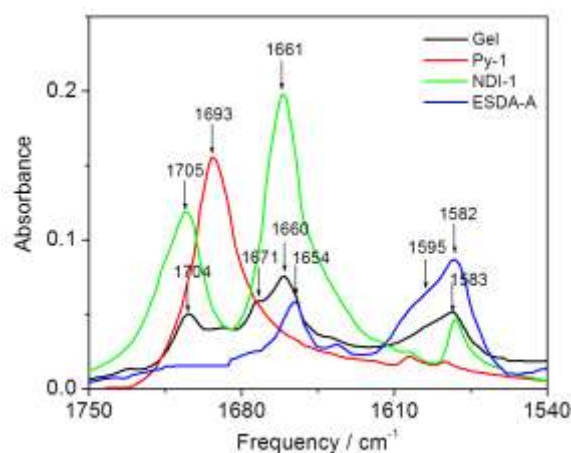
**Fig S3:** Images of NDI-1 (2.5 mM ) + Py-1 (2.5 mM )+ ESDA-A (5 mM ) in various solvents like a) benzene; b) CCl<sub>4</sub>; c) dodecane; d) s-limonene and e) TCE.



**Fig S4:** Solvent dependent UV/ vis spectra of NDI-1(2.5 mM) + Py-1(2.5 mM) + ESDA-A (5 mM).

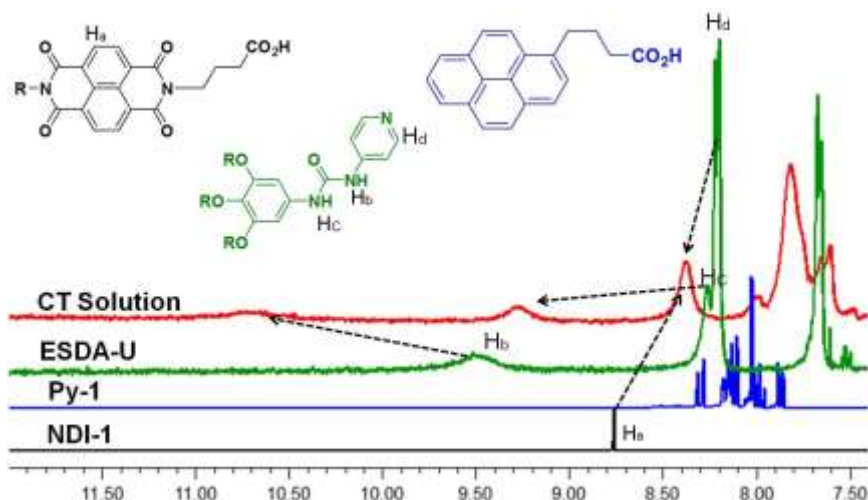


**Fig S5:** Energy minimized structure of the **NDI-1** (left) and **ESDA-A** (right). Molecular modeling was done in Chem3D Ultra 8.0 using MM2 for energy minimization. The summation of the length of the two units = 52.03Å which closely matches with the *d* spacing observed (46.6 Å) for the three component supramolecular assembly and thus supports the proposed model for gelation (Scheme 1).

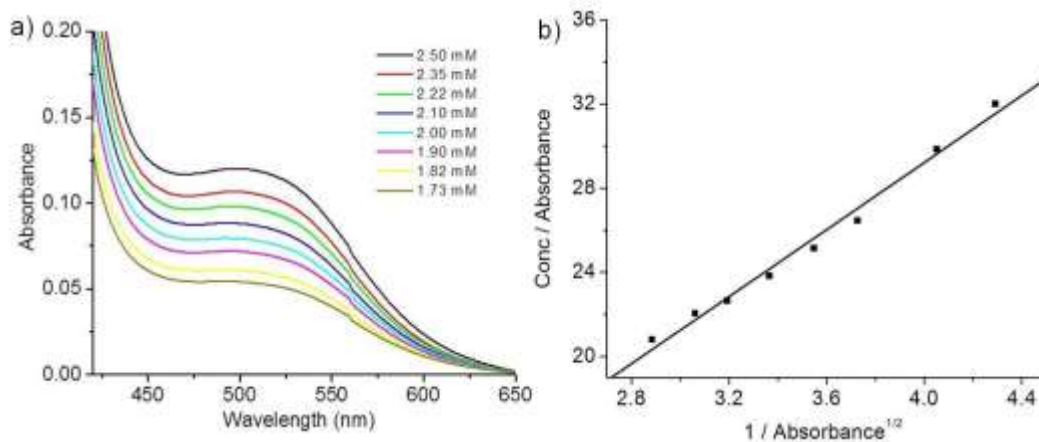


**Fig S6:** FT-IR spectra of the three component gel (NDI-1 + Py-1 + ESDA-A, total concentration = 10 mM) and individual components; Blue spectrum- peaks at 1595 cm<sup>-1</sup> and 1582 cm<sup>-1</sup> are attributed to the amide-2 and C=N of pyridine ring of ESDA-A which together appears as a broad peak (black spectrum) at 1583 cm<sup>-1</sup> in gel state indicating H-bonding induced shift of the C=N peak; Green spectrum- Peaks at 1661 cm<sup>-1</sup> and 1705 cm<sup>-1</sup> correspond to the imide and carboxylic acid carbonyl groups, respectively; Red spectrum- The peak at 1693 cm<sup>-1</sup> corresponds to the carbonyl group of carboxylic acid; In gel state (black) the carbonyl peaks of NDI-1 and Py-1 appear at lower frequencies indicating H-bonding.



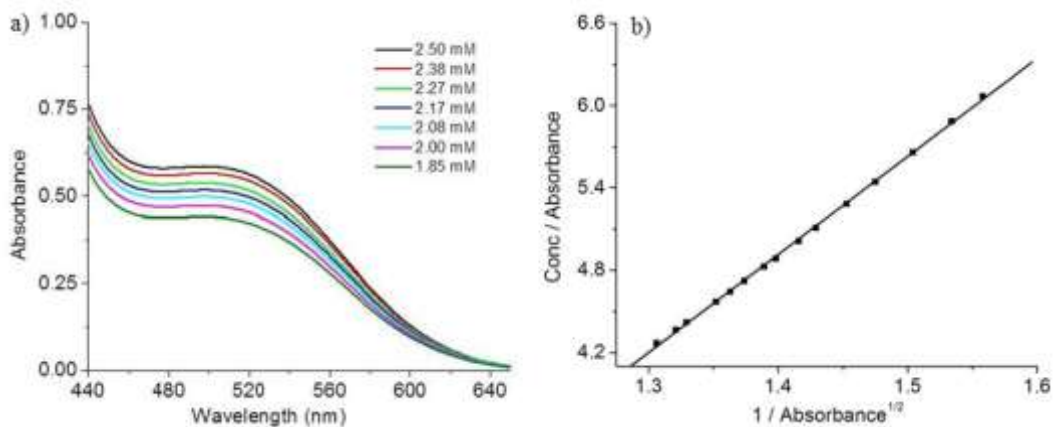


**Fig S7:**  $^1\text{H}$ NMR spectra (selected region) of charge-transfer (CT) solution (NDI-1 + Py-1 + ESDA-U) in  $\text{CDCl}_3/\text{MCH} = 10: 90$ ) and the individual components (in  $\text{CDCl}_3$ ). Notably the urea proton ( $\text{H}_b$ ) of the ESDA-U (green spectrum) is downfield shifted in the mixture (red line) by  $\sim 1.0$  ppm suggesting it is involved in H-bonding. The  $\text{H}_d$  proton (green spectrum) that is adjacent to the nitrogen atom of the pyridine ring is downfield shifted (red spectrum) possibly due to the generation of  $\delta^+$  charge on the N atom in the H-bonded state. The NDI ring protons ( $\text{H}_a$ ) of NDI-1 (black spectrum) experienced prominent upfield shift in presence of ESDA-U (red spectrum) as a result of shielding effect in the alternate D-A stacking. Same is also true for the pyrene ring protons although to a lesser extent which is consistent with previous reports on alternate D-A stacking.



**Fig S8:** a) Concentration dependent UV/vis absorption spectra of (NDI-1 + Py-1 + ESDA-A) in  $\text{MCH}/\text{CHCl}_3$  (90:10) at  $25^\circ\text{C}$ ,  $l = 1$  mm; b) Analysis of the data according to equation 2.

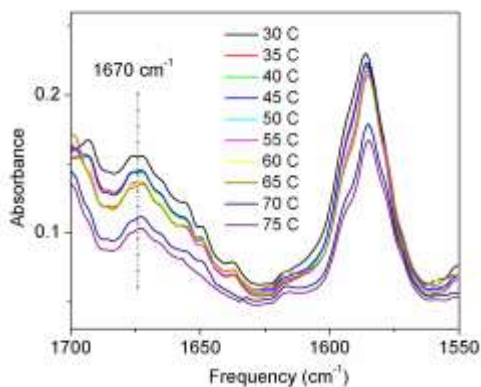




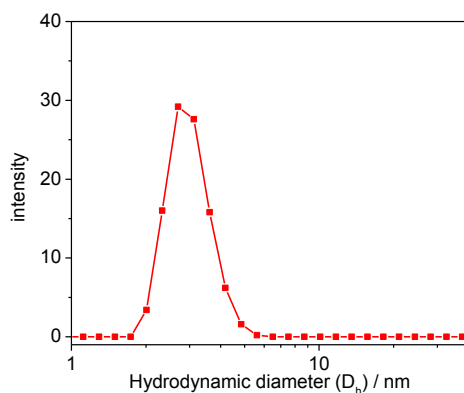
**Fig S9:** a) Concentration dependent UV/vis absorption spectra of (NDI-1 + Py-1 + ESDA-U) in MCH/ $\text{CHCl}_3$  (90:10) at 25 °C,  $l = 5$  mm; b) Analysis of the data according to equation 2.



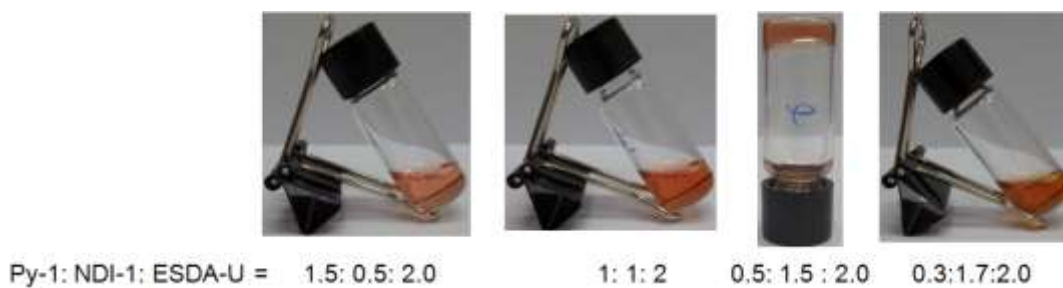
**Fig S10:** Image of a solution at 45 °C produced by cooling a hot mixture of {NDI-1 (2.5 mM) + Py-1 (2.5 mM) + ESDA-A (5.0 mM) in MCH/ $\text{CHCl}_3$  (90: 10).



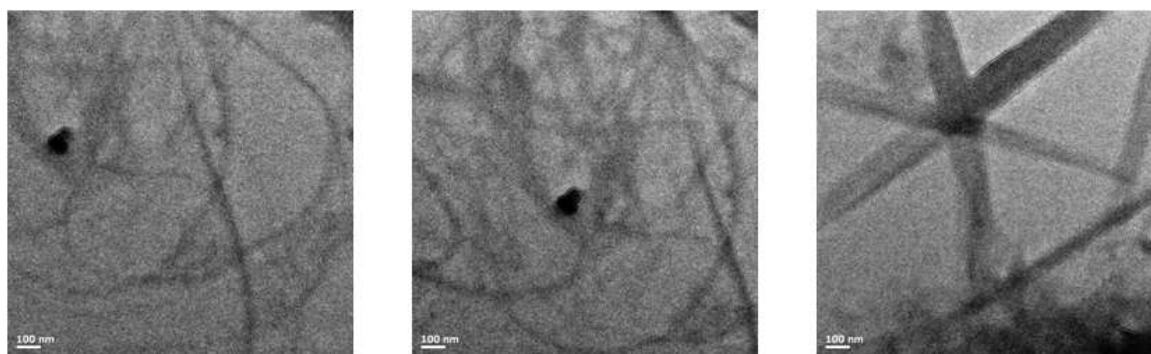
**Fig S11:** Variable temperature FT-IR spectra (selected region) of ESDA-A in MCH/ $\text{CHCl}_3$  (90: 10).  $C = 5.0$  mM



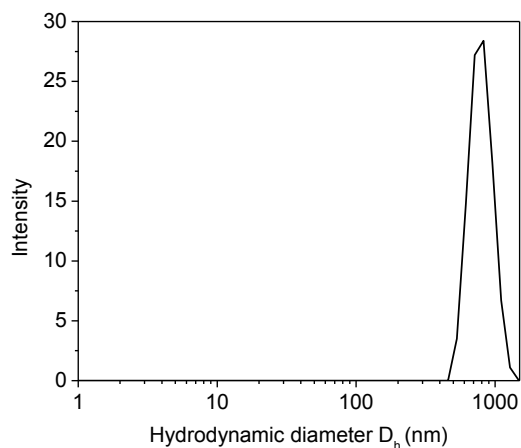
**Fig S12:** Dynamic light scattering data of NDI-1 + Py-1 + ESDA-U (1:1:2) in MCH/ CHCl<sub>3</sub> (90: 10).



**Fig S13:** Images of solution/ gel at 25 °C produced by cooling a hot mixture of NDI-1 + Py-1 + ESDA-U (Total concentration = 10.0 mM) in MCH/ CHCl<sub>3</sub> (90: 10). D: A ratio was varied as indicated in the figure.



**Fig S14:** TEM images of diluted gel from NDI-1 + Py-1 + ESDA-U (1.5:0.5: 2.0) in MCH/ CHCl<sub>3</sub> (90: 10).



**Fig S15:** Dynamic light scattering data of NDI-1 + Py-1 + ESDA-U (1.5:0.5:2) in MCH/ CHCl<sub>3</sub> (90: 10).

#### References:

1. D. Perrin, W. L. F. Armarego and D. R. Perrin, *Purification of Laboratory Chemicals*, 2<sup>nd</sup> ed., Pergamon, Oxford, 1980.
2. H. Kar, M. R. Molla and S. Ghosh, *Chem commun.*, 2013, **49**, 4220.
3. M. B. Nielsen, J. O. Jeppesen, J. Lau, C. Lomholt, D. Damgaard, J. P. Jacobsen, J. Becher and J. F. Stoddart, *J. Org. Chem.*, 2001, **66**, 3559.