## Supporting Information for A Generalized Supramolecular Strategy for Self-sorted Assembly between Donor and Acceptor Gelators

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**Materials and Methods:** Methyl 3,4,5-trihydroxybenzoate, and 1,4,5,8-napthalenetetracarboxylic bis-anhydride were purchased from Aldrich Chemical Co. The solvents and the reagents were purchased from commercial source and purified by standard methods.<sup>1</sup> For UV-vis studies, spectroscopic grade solvents were used and spectra were recorded in a Perkin Elmer Lambda 25 spectrometer. <sup>1</sup>H NMR spectra were recorded in a Bruker DPX-300 MHz NMR spectrometer and calibrated against TMS. Transmission Electron Microscopy (TEM) was performed in JEOL-2010EX machine operating at an accelerating voltage of 200KV. FTIR spectra were obtained in a Perkin Elmer Spectrum 100 FT-IR Spectrometer.

## Synthesis and Characterization

**NDI-1** was synthesized using the synthetic protocol as outlined in Scheme S1. New compounds have been characterized by <sup>1</sup>H NMR, UV-visible, melting point (if solid) and HRMS (ESI). Synthesis of **ND1-2**<sup>2</sup> and **DAN-1**<sup>3</sup> have been described by us elsewhere.



a) aq KOH / dioxane, 90 °C, 48 h, yield = 75%, b) DMF, 140 °C,12 h, yield = 27 %, c) 25 % TFA / DCM, RT,12 h, yield = 98 %, d) NEt<sub>3</sub> / DCM, 0 °C - RT, 12 h, yield = 60 %, e) aq LiOH / THF, 0 °C - RT, 18 h, yield = 99 %, f) DCC, HOBT, DMAP, 0 °C - RT, 12 h, yield = 43 %

Scheme S1: Synthetic route for NDI-1

**Compound 1:** Synthesis of this compound is reported by us elsewhere.<sup>4</sup>

**3,4,5-tris(octyloxy)benzenamine (2):** To 100 mL aqueous solution of KOH (17.8 g, 317.6 mmol), a solution of **1** (1g, 1.98 mmol) in 25 mL dry dioxane was added dropwise and the reaction mixture was stirred at 90 °C for 12 h. The reaction was stopped, cooled to room temperature and transferred to a separating funnel. The chocolate brown organic layer (floating on the top of the separating funnel) was collected, diluted with 15 mL CH<sub>2</sub>Cl<sub>2</sub> and washed with water H<sub>2</sub>O (3 x 30 mL). Excess CH<sub>2</sub>Cl<sub>2</sub> was evaporated to get the crude product which was further dissolved in 25 mL dioxane, added to 50 mL aq NaOH (5 g) and refluxed for 48 h. The reaction was stopped, cooled to room temperature, and excess dioxane was evaporated. The product was extracted with 15 mL CH<sub>2</sub>Cl<sub>2</sub> and washed with water (2 x 30 mL) and brine (1 x 30 mL) and passed through anhydrous Na<sub>2</sub>SO<sub>4</sub> and then CH<sub>2</sub>Cl<sub>2</sub> was evaporated to get the crude product as chocolate brown solid (712 mg, 75 %). As the product was found to be pure from TLC and <sup>1</sup>H NMR, it was carried to the next step as such. M.P. 119 ° C – 125 ° C; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz):  $\delta$  (ppm) = 5.91 (s, 2H), 3.91 (t, *J* = 6.5 Hz, 4H), 3.84 (t, *J* = 6.6 Hz, 2H), 3.49 (bs, 2H), 1.84 – 1.66 (m, 6H), 1.52 – 1.39 (m, 6H), 1.38 – 1.21 (m, 24H), 0.94 – 0.82 (m, 9H); UV-visible (CHCl<sub>3</sub>):  $\lambda_{max}$  ( $\varepsilon$ ) = 261 (7257 M<sup>-1</sup> cm<sup>-1</sup>); HRMS (ESI): *m*/*z* calcd for C<sub>30</sub>H<sub>35</sub>NO<sub>3</sub>H [*M* + H]<sup>+</sup>: 478.4262; found: 478.4269.

**Compound (5):** Compound **2** (507 mg, 1.06 mmol), **3**<sup>2</sup> (170 mg, 1.06 mmol) and 1,4,5,8naphthalenetetracarboxylic bis-anhydride (290 mg, 1.06 mmol) were taken together in a flask with dry DMF (15 mL) and the reaction mixture was stirred at 140 °C for 12 h under N<sub>2</sub> atmosphere. The solution was allowed to cool to RT and placed in the refrigerator for 1h. The orange precipitate obtained was filtered and collected. The filtrate was added with MeOH (10 mL) to get more orange precipitate which was mixed with the first crop and the solid was purified by column chromatography using silica gel as stationary phase and 0.5 % MeOH in CH<sub>2</sub>Cl<sub>2</sub> as eluent to obtain the desired product as orange crystalline solid (245 mg, 27 %); M.P. = 168 °C -171 °C; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz):  $\delta$  (ppm) = 8.80 (s, 4H), 6.49 (s, 2H), 4.87 (bs, 1H), 4.40 (t, *J* = 5.5, 2H), 4.04 (t, *J* = 6.6, 2H), 3.95 (t, *J* = 6.5, 4H), 3.65 – 3.49 (m, 2H), 1.87 – 1.72 (m, 6H), 1.54 – 1.15 (m, 39H), 0.94 – 0.83 (m, 9H); UV-visible (CHCl<sub>3</sub>):  $\lambda_{max}$  ( $\varepsilon$ ) = 380 (23223), 359 (19127), 341 (11576 M<sup>-1</sup> cm<sup>-1</sup>); HRMS (ESI): *m*/*z* calcd for C<sub>51</sub>H<sub>71</sub>N<sub>3</sub>O<sub>9</sub>H [*M* + H]<sup>+</sup>: 870.5272; found: 870.5273.

**Compound (6):** Compound **5** (516 mg, 0.59 mmol) was dissolved in 25% TFA/ CH<sub>2</sub>Cl<sub>2</sub> (10 mL) and stirred for 12 h at RT under N<sub>2</sub> atmosphere. Excess CH<sub>2</sub>Cl<sub>2</sub> and TFA were removed under vacuum. The crude product was added with CH<sub>2</sub>Cl<sub>2</sub> (5 mL) and anhydrous K<sub>2</sub>CO<sub>3</sub> (50 mg) and stirred for 30 min at RT. The solution was filtered and the solvent was evaporated to obtain the desired product as orange solid (450 mg, 98 %). As the product was found to be pure from TLC and <sup>1</sup>H NMR, it was carried to the next step as such. M.P. 170 ° C – 173 ° C; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz):  $\delta$  (ppm) = 8.80 (s, 4H), 6.49 (s, 2H), 4.33 (t, *J* = 6.5, 2H), 4.04 (t, *J* = 6.6, 2H), 3.95 (t, *J* = 6.5, 2H)

4H), 3.13 (t, J = 6.5, 2H), 1.86 – 1.73 (m, 6H), 1.55 – 1.17 (m, 30H), 0.97 – 0.82 (m, 9H); UVvisible (CHCl<sub>3</sub>):  $\lambda_{max}$  ( $\varepsilon$ ) = 380 (26578), 358 (22563), 340 (13683 M<sup>-1</sup> cm<sup>-1</sup>); HRMS (ESI): m / z calcd for C<sub>46</sub>H<sub>63</sub>N<sub>3</sub>O<sub>7</sub>H [M + H]<sup>+</sup>: 770.4746; found: 770.4739.

**Compound 8:** It was made following a literature procedure.<sup>5</sup>

Methyl 3-(3,4,5-tris(octyloxy)benzamido)propanoate (9): A solution of freshly prepared compound  $7^2$  (1.46 g, 2.77 mmol) in 12 ml dry CH<sub>2</sub>Cl<sub>2</sub> was added dropwise to an ice-cold solution of compound 8 (520 mg, 5.0 mmol) and Et<sub>3</sub>N (1.5 ml, 11.1 mmol) in dry CH<sub>2</sub>Cl<sub>2</sub> (5 mL). The reaction mixture was stirred in the ice-bath for another 1h and then at RT for 12 h. The mixture was diluted with CH<sub>2</sub>Cl<sub>2</sub> (15 mL) and washed with H<sub>2</sub>O (2 x 30 mL) and brine (1 x 30 mL). The organic layer was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and the solvent was evaporated to get the crude product which was purified by column chromatography with silica gel as the stationary phase and CH<sub>2</sub>Cl<sub>2</sub> as the eluent to get the pure product as light yellow oil (977 mg, 60 %).<sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz):  $\delta$  6.95 (s, 2H), 6.69 (t, J = 5.4, 1H), 4.02 – 3.96 (m, 6H), 3.71 (s, 3H), 3.74 – 3.66 (m, 2H), 2.65 (t, J = 5.8, 2H), 1.87 – 1.67 (m, 6H), 1.54 – 1.41 (m, 6H), 1.39 – 1.18 (m, 24H), 0.96 – 0.80 (m, 9H); UV-visible (CHCl<sub>3</sub>):  $\lambda_{max}$  ( $\varepsilon$ ) = 262 (8790 M<sup>-1</sup> cm<sup>-1</sup>); HRMS (ESI): m / z calcd for C<sub>35</sub>H<sub>61</sub>NO<sub>6</sub>Na [M + Na]<sup>+</sup>: 614.4397; found: 614.4396.

**3-(3,4,5-tris(octyloxy)benzamido)propanoic acid (10) :** 20 mL aqueous solution of LiOH (2.13 g , 88.6 mmol) was stirred at 0 °C for 15 min. To the above solution, a solution of **9** (874 mg, 1.48 mmol) in THF (25 ml) was added and the mixture was stirred at 0 °C for 1h and then at RT for 18 h. Excess THF was evaporated and the solution was diluted with water (15 mL) and acidified by adding dilute HCl (2N) dropwise. White precipitate obtained was filtered at the pump and dried under vacuum to get the crude product as white powder (847 mg, 99 %). The product obtained was found to be pure from TLC and <sup>1</sup>H NMR, and carried to the next step as such. M.P. 148 °C- 152 °C; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz):  $\delta$  6.97 (s, 2H), 6.97 (bs, 1H), 4.02 – 3.87 (m, 6H), 3.69 – 3.55 (m, 2H), 2.66 – 2.52 (m, 2H), 1.84 – 1.65 (m, 6H), 1.50 – 1.37 (m, 6H), 1.37 – 1.20 (m, 24H), 0.94 – 0.79 (m, 9H); UV-visible (CHCl<sub>3</sub>):  $\lambda_{max}$  ( $\varepsilon$ ) = 263 (8170 M<sup>-1</sup> cm<sup>-1</sup>); HRMS (ESI): m/z calcd for C<sub>34</sub>H<sub>59</sub>NO<sub>6</sub>H [M + H]<sup>+</sup>: 578.4422; found: 578.4423.

**Compound 11<sup>6</sup> :** Compound **6** (400 mg, 0.52 mmol), **10** (330 mg, 0.57 mmol), HOBT (77 mg, 0.57 mmol) and DMAP (70 mg, 0.57 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 DCC (118 mg, 0.57 mmol) was added and the reaction mixture was stirred at 0 °C for another 2 h and then at RT for 12 h. The solution was allowed to cool to RT and placed in the refrigerator for 3 h to give a white precipitate which was filtered and the filtrate was diluted with  $CH_2Cl_2$  and washed with 1N HCl, saturated  $Na_2CO_3$  followed by brine. Then  $CH_2Cl_2$  was evaporated and the crude product was purified by column chromatography using silica gel as stationary phase and 1% MeOH in  $CH_2Cl_2$  as eluent to obtain the desired product as orange solid (300 mg, 43 %). M.P.  $163^{\circ}$  C  $-166^{\circ}$  C; <sup>1</sup>H NMR

(CDCl<sub>3</sub>, 300 MHz):  $\delta$  8.71 (s, 4H), 6.89 (bs, 1H), 6.76 (s, 2H), 6.53 (s, 2H), 6.24 (bs,1H), 4.54 – 4.34 (m, 2H), 4.15 – 3.81 (m, 12H), 3.81 – 3.69 (m, 2H), 3.67 – 3.52 (m, 2H), 2.53 – 2.37 (m, 2H), 1.96 – 1.72 (m, 12H), 1.72 – 1.50 (m, 12H), 1.47 – 1.13 (m, 48H), 1.06 – 0.74 (m, 18H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 500 MHz): 158.91, 131.15, 120.72, 107.00, 105.77,104.95, 73.52, 69.16, 40.35, 39.09, 36.25, 35.65, 31.90, 30.31,29.60, 26.11, 22.67, 14.09; UV-visible (CHCl<sub>3</sub>):  $\lambda_{max}$  ( $\varepsilon$ ) = 380 (18528), 359 (16477), 341 (10129 M<sup>-1</sup> cm<sup>-1</sup>); HRMS (ESI): *m* / *z* calcd for C<sub>18</sub>H<sub>22</sub>Br<sub>2</sub>O<sub>2</sub>Na [*M* + Na]<sup>+</sup>: 1329.8983; found: 1329.8984

**Gelation test**: The gelation ability of **NDI-1** and the (1:1) mixtures of **NDI-1** and structurally related **DAN** molecules were checked in MCH. Stock solution of the gelators were 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. In all cases gelation was noticed within 5 min which was tested by the " the stable-to-inversion of a vial " method. For the mixed gels, solutions of individual components in  $CHCl_3$  were mixed together and then similar procedure was followed as described above.

For determination of critical gelation concentration of **NDI-1**, the gel was made at relatively higher concentration and gradually diluted with measured amount of the same solvent. Each time after adding the solvent, the sample was heated to get the homogeneous solution and allowed to cool to RT before the gelation was tested. Beyond certain concentration, gelation was not observed even after waiting for few hours and that concentration is reported as the critical gelation concentration. Gelation of **DAN-1** and **NDI-2** in MCH is reported elsewhere.<sup>3</sup>

**UV-visible studies**: For the solvent variable experiment, stock solution of **NDI-1** was made in CHCl<sub>3</sub> at 2.0 mM concentration. 0.1 mL stock was diluted with 1.9 mL MCH to adjust the final concentration to 0.1 mM and solvent composition to MCH / CHCl<sub>3</sub> (95 : 5). The solution was allowed to equilibrate at RT for 1 h before spectral measurements. The experiment was done in 1cm pathlength cuvette. For **DAN-1**, no appreciable spectral changes were observed at 0.1 mM concentration in MCH / CHCl<sub>3</sub> (95 : 5). Therefore the absorption was recorded at higher concentration (2.5 mM) in MCH where it formed gel. The experiment was done in 0.1cm path-length cuvette. For the mixture, 50  $\mu$ L each of **DAN-1** and **NDI-1** in CHCl<sub>3</sub> (0.4 mM) were mixed together in a vial and diluted with MCH (1.9 mL) to adjust the final concentration to 0.2 mM.

For studying the effect of stoichiometric imbalance of **NDI-1** and **DAN-1** on their self-assembly in the mixture, the two chromophores were mixed at different molar ratios in MCH / CHCl<sub>3</sub> (95 : 5) with a fixed total concentration of 0.2 mM. To find the spectral contribution of **DAN-1** in the mixture following equation was used. For details see ref: 2

 $\mathbf{S}_{\text{DAN-1}} = \mathbf{S}_{\text{mixed}} - (\alpha_{\text{NDI-1}} \times \mathbf{S}_{\text{NDI-1}})$ (1)

Where  $S_{DAN-1}$ ,  $S_{mixed}$ ,  $S_{NDI-1}$  and  $\alpha_{NDI-1}$  are the modified **DAN-1** spectrum, original spectrum of the mixture, spectrum of **NDI-1** alone and mole fraction of **NDI-1** in the mixture, respectively.

**FT-IR spectroscopy:** NH-stretching frequency of the individual gels (2.5 mM) and the mixture **NDI-1** + **DAN-1** (1:1) at 5 mM concentration in MCH were recorded in the ATR mode.

<sup>1</sup>**H NMR spectroscopy:** Individual gels and the mixture **NDI-1+ DAN-1** (1:1) were made in TCE at 5.0 and 10 mM concentration respectively. 10 %  $C_6D_6$  in TCE was added for locking the signal. For the temperature variable experiment, sample solutions were heated from 25 °C to higher temperature 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, 9 scans were taken with 1 sec delay time.

**TEM measurements**: Stock solutions of **NDI-1** and **DAN-1** were made in  $CHCl_3$  at 4.0 mM concentration. 0.1 mL stock was diluted with 1.9 mL MCH to adjust the final concentration to 0.2 mM and solvent composition to MCH /  $CHCl_3$  (95: 5). The above solutions were drop casted on copper grid and the samples were left open to the atmosphere for 24 h (to allow MCH to evaporate) prior to imaging.

## **Additional figures:**



**Fig S1:** TEM pictures of **NDI-1** (a) **DAN-1** (b). Concentration of the chromophore = 0.2 mM and solvent composition = MCH / CHCl<sub>3</sub> (95: 5). Average diameter of the fibers were (8 - 10) nm and (10 -12) for **NDI-1** and **DAN-1** respectively.



**Fig S2:** Normalized absorption and fluorescence spectra of **DAN-1** in monomeric (CHCl<sub>3</sub>) and aggregated (MCH) form; Concentration = 2.5 mM, T= 25°C,  $\lambda_{ex}$  =295 nm. Relatively less (~18 nm) fluorescence stoke shift was observed in MCH compared to CHCl<sub>3</sub> (~20 nm). During normalization, the intensities of the most prominent peaks for absorption and fluorescence in both the solvents were matched. In this process the ratio of emission intensities in CHCl<sub>3</sub> and MCH remains unaltered. However, that for the absorption intensities (as appeared here) does not indicate the observed change. For actual change in the absorption intensities due to aggregation see **Fig.** 2b in the main text.



**Fig S3:** UV-vis spectra of **NDI-1** + **DAN-1** (1:1) and mathematical sum of the spectrum of individual chromophores in the CT-region; Total concentration of the chromophores = 0.2 mM and solvent composition = MCH / CHCl<sub>3</sub> (95: 5).



**Fig S4:** UV/Vis absorption spectra of **NDI-1** + **DAN-1** at various ratios in MCH / CHCl<sub>3</sub> (95 : 5) (a), the subtracted spectra for **DAN-1** as obtained by using equation -1 (b) and the plot of absorbance as a function of the mole fraction of **DAN-1** (c); Total chromophore concentration = 0.2 mM.



**Fig S5:** IR-spectra of **NDI-1** (a), **DAN-1** (b) and **NDI-1** + **DAN-1** (1:1) (c) in  $CHCl_3$ . Total concentration = 2.5 mM for **NDI-1** and **DAN-1** and 5 mM for the mixture.



**Fig S6**: Solvent and temperature-dependent proton NMR spectra (selected region) of **DAN-1** gel. In case of TCE, 10 %  $C_6D_6$  was used for locking the signal. Concentration of **DAN-1** = 5 mM. Amide protons appear at 6.15 ppm in CDCl<sub>3</sub>. In TCE, due to H-bonding, the amide protons are downfield shifted. With increase in temperature, H-bonding breaks and up-field shift of the amide protons occurred. However, at 70 ° C the chemical shift is even lower than that in CDCl<sub>3</sub>. This can be due to difference in polarity of the two solvent.



**Fig S7:** Structurally similar DAN-molecules with varying number of methylene units between the DAN-chromophore and the two amide groups (a), Gel pictures of **NDI-1 + DAN-2** (b) and **NDI-1 + DAN-3** (c); Total chromophore concentration = 10 mM. Synthesis and characterization of **DAN-2**<sup>2</sup> and **DAN-3**<sup>4</sup> is reported by us elsewhere.



**Fig S8:** Pictures of the gels derived from **NDI-1** + **DAN-1** (1:1) mixture in various solvents (a-cyclohexane, b- benzene, c- toluene, d- o-xylene, e- tetrachloroethylene, f- carbon tetrachloride). Total gelator concentration = 10 mM in each case.

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