

## Supporting Information

# Supramolecular Design for Two-Component Hydrogels with Intrinsic Emission in the Visible Region

P. Rajamalli, Supriya Atta, Sandeepan Maity and Edamana Prasad\*

*Received (in XXX, XXX) Xth XXXXXXXXXX 20XX, Accepted Xth XXXXXXXXXX 20XX*

DOI: 10.1039/b000000x

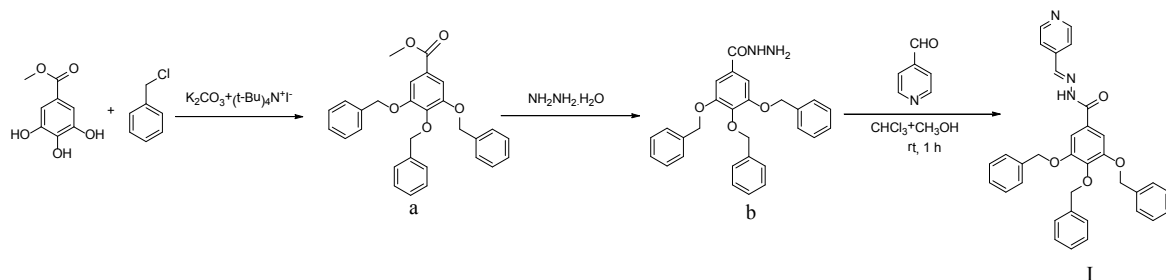
Contents	Page Number
1. General information	02
2. Synthesis procedure and characterizations of dendrons	02
3. SEM image of spherical aggregates	10
4. Dynamic light scattering data	10
5. AFM image spherical aggregate	11
6. FT-IR spectrum of gel	11
7. Critical gel concentration table	12
8. <sup>1</sup> H-NMR spectra of solution and partial gel phase	12
9. Powder X-ray diffraction pattern	12
10. Job plot of gel	13
11. Schematic representation of lamellar arrangement	14
12. SEM image of xerogel	14
13. AFM image of xerogel	15
14. TEM image of xerogel	15
15. Steady state fluorescence spectra	16
16. Fluorescence decay profiles	17

## 1. General information

The poly(aryl ether) dendron derivatives have been synthesized according to reported procedures.<sup>1</sup> All the starting materials were obtained from Aldrich or s.d. fine-chem. Pvt. Ltd. India. The used organic solvents were dried according to standard procedures. <sup>1</sup>H and <sup>13</sup>C NMR data were collected on a Bruker 400 MHz and 500 MHz spectrometer (<sup>1</sup>H: 400 MHz; <sup>1</sup>H: 500 MHz; <sup>13</sup>C: 100 MHz). IR spectrum was recorded using Jasco FT/IR-4100 spectrometer. Luminescence experiments were carried out on a Horiba JobinYvon Fluoromax-4 fluorescence spectrophotometer. The UV-Vis spectroscopic studies were carried Jasco V-660 Spectrophotometer. The scanning electron microscopic studies were carried out using a FEI-Quanta Microscope. AFM samples were prepared by spin-coating method on silicon wafer and images were recorded using Park-system XE-100 in the non-contact mode regime. Powder-XRD patterns were recorded on a Bruker D8 Advance X-ray diffractometer using Cu- K $\alpha$  radiation ( $\lambda = 1.54178 \text{ \AA}$ ). Dynamic light scattering (DLS) experiments were carried out with Malvern Zetasizer nano series 25 °C, with a path length of 1 cm. The wavelength of the laser used was 632.8 nm and the scattering angle was kept as 90. The fluorescence decay measurements were carried out by the time correlated single-photon counting technique (TCSPC) with a microchannel plate photomultiplier tube (MCP-PMT) as detector and picosecond laser as excitation source (model 5000 U, IBH, UK).

## 2. Synthetic procedures and characterization of dendrons

### Synthetic procedure for compound I



### Synthesis of (AB)<sub>3</sub>G<sub>1</sub>-COOCH<sub>3</sub> (a)

Methyl-3, 4, 5-trihydroxybenzoate (9 g, 0.045 mole) and potassium carbonate (24.84 g, 0.18 mole) were taken in 130 mL of 1,4-dioxane in a 250 mL round bottom flask. Benzyl chloride (33 mL, 0.135 mole) was added to the above reaction mixture, followed by the addition of a catalytic amount of tetra butyl ammonium iodide (1.4 g, 0.0045 mole). The solution was heated to

refluxing condition along with stirring for 24 hours. The solvent was then removed under reduced pressure using a rotary evaporator, affording an oily substance, which turned into a solid upon standing. The solid was recrystallized from methanol to yield the product Compound **a** (18.5 g, 90.5%);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$ : 3.8 (s,  $\text{COOCH}_3$ , 3H), 4.9 (s,  $\text{ArCH}_2\text{O}$ , 2H), 5.01 (s,  $\text{ArCH}_2\text{O}$ , 4H), 7.1-7.3 (m,  $\text{ArH}$  &  $\text{PhH}$ , 17H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$ : 52.25, 71.27, 75.15, 109.13, 125.26, 127.57, 127.96, 128.04, 128.21, 128.56, 136.69, 137.48, 142.46, 152.59, 166.66; IR (KBr)  $\nu$  = 3064, 3031, 2947, 2878, 1715, 1589, 1499, 1453, 1110 and 754  $\text{cm}^{-1}$ .

### Synthesis of $\text{G}_1\text{TNHNH}_2$ (**b**)

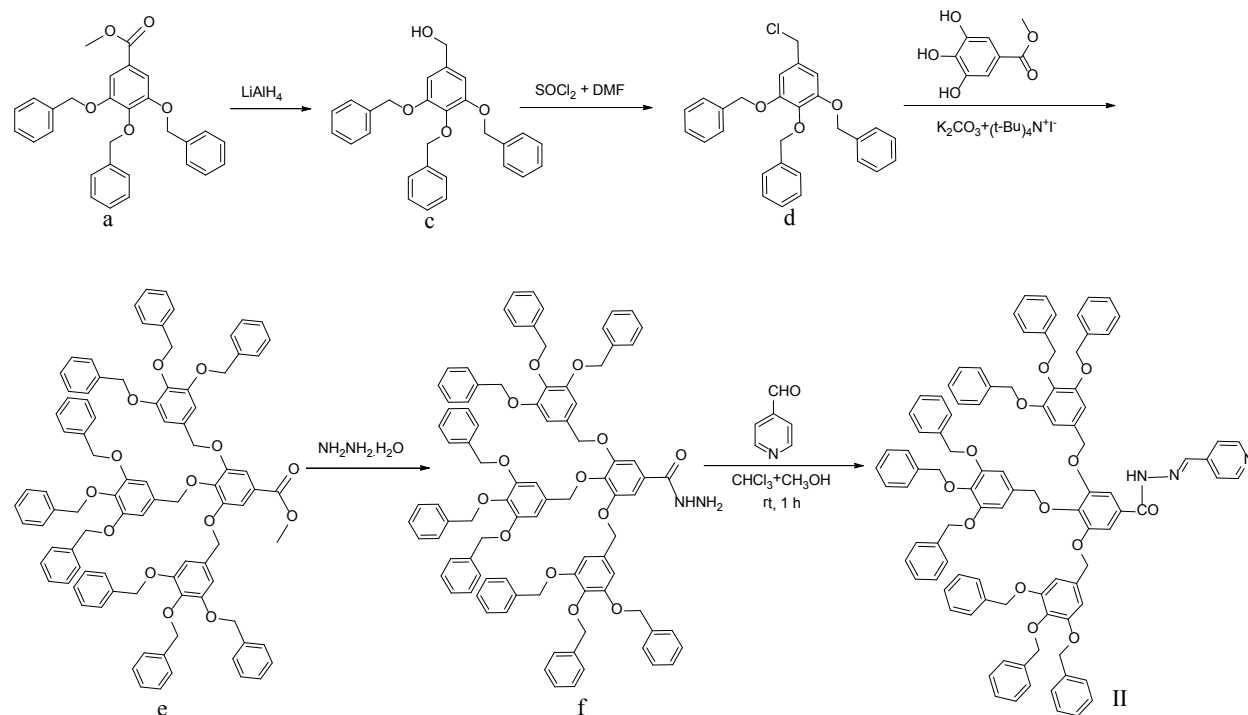
Compound **a** (4 g, 0.0088 mole) and hydrazine monohydrate (22 mL, 0.44 mole) were dissolved in MeOH (30 mL) and THF (15 mL). The reaction mixture was stirred at 70°C for 12 hours. After the heating was stopped, the reaction mixture was allowed to cool to room temperature, and the volatiles were removed under reduced pressure. The residue was dissolved in  $\text{CH}_2\text{Cl}_2$  and washed with  $\text{H}_2\text{O}$ . The organic layer was then dried over anhydrous  $\text{Na}_2\text{SO}_4$ , and the solvent was evaporated to get crude product, which was purified by column chromatography using silica gel as the stationary phase and 5% MeOH in  $\text{CH}_2\text{Cl}_2$  as the eluent to get the pure product as a white powder (3.75 g, 93 %);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$ : 5.03 (s,  $\text{ArCH}_2\text{O}$ , 6H), 6.96 (s,  $\text{ArH}$ , 2H), 7.18-7.30 (m,  $\text{PhH}$ , 15H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$ : 71.54, 75.31, 106.96, 127.60, 128.09, 128.19, 128.32, 128.69, 136.70, 137.52, 141.72, 142.57, 153.03, 168.44; IR (KBr)  $\nu$  = 3282, 3195, 3110, 3089, 3063, 3030, 3007, 2940, 2870, 1631, 1583, 1518, 1498, 1455, 1423, 1153 and 779  $\text{cm}^{-1}$ ; HRMS (ES<sup>+</sup>):  $m/z$  Calcd for  $\text{C}_{24}\text{H}_{26}\text{N}_2\text{O}_4$ : 454.1893, found: 455.1964 [ $\text{M}+\text{H}$ ]<sup>+</sup>; m.p. 122 °C.

### Synthesis of compound **I**

A solution of 4-pyridine carboxaldehyde (0.497 mL, 5.28 mmole) in methanol was added drop wise to a  $\text{CHCl}_3$  solution of compound **b** (2 g, 4.40 mmole). The mixture was stirred for 1 hour and the resulting gel was dried under vacuum to yield **I** (2.368 g, 99 %).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$ : 4.97 (s,  $\text{ArCH}_2\text{O}$ , 4H), 5.01 (s,  $\text{ArCH}_2\text{O}$ , 2H), 7.06 (s,  $\text{ArH}$ , 2H), 7.16-7.27 (m,  $\text{PhH}$ , 15H), 7.43 (s,  $\text{PyH}$ , 2H), 8.14 (s,  $\text{CONH}$ , 1H), 8.54 (s,  $\text{PyH}$ , 2H), 10.01 (s,  $\text{CH}=\text{N}$ , 1H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ - $\text{DMSO}-d_6$ )  $\delta$ : 71.26, 75.02, 107.04, 121.22, 127.51, 127.90, 128.00, 128.12, 128.35, 128.40, 128.42, 128.47, 128.50, 128.52, 128.57, 136.51, 137.31, 141.64, 145.58,

150.14, 152.53, 164.18; **HRMS (ES<sup>+</sup>):** *m/z* Calcd for C<sub>34</sub>H<sub>29</sub>N<sub>3</sub>O<sub>4</sub>: 543.2158, found: 544.2215 [M+H]<sup>+</sup>.

### Synthetic procedure for compound II



### Synthesis of (AB)<sub>3</sub>G<sub>1</sub>-CH<sub>2</sub>OH (c)

Lithium aluminum hydride (0.809 g, 0.0213 mole) was suspended in 40 mL of freshly distilled THF in a dry three-neck round-bottom flask under nitrogen atm. Compound **a** (9 g, 0.0198 mole) was dissolved in 50 mL of freshly distilled THF and added drop wise to the lithium aluminum hydride solution. The reaction mixture was refluxed with stirring for 2 h. The THF solution was cooled to room temperature and transferred to a beaker. Water was added drop wise to the vigorously stirred THF solution until the gray color of the lithium aluminum hydride was disappeared and a white solid was formed which is filtered and washed with THF. Excess solvent was removed under reduced pressure and the crude product was recrystallized from 95% methanol/water mixture to get the pure product Compound **c** (7.6 g, 90%); **<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)**  $\delta$ : 4.6 (s, CH<sub>2</sub>OH, 2H), 5.09 (s, ArCH<sub>2</sub>O, 2H), 5.15 (s, ArCH<sub>2</sub>O, 4H), 6.72 (s, ArH, 2H), 7.30-7.48 (m, PhH, 15H); **<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)**  $\delta$ : 65.42, 71.22, 75.26, 106.46, 127.45, 127.83, 127.90, 128.18, 128.52, 128.62, 136.66, 137.13, 137.81, 137.87, 153.02.

### Synthesis of[(AB)<sub>3</sub>G<sub>1</sub>-Cl] (d)

To a solution of compound **c** (5 g, 0.0117 mole) in dichloromethane (40 mL) was added a catalytic amount of DMF (3 mL) followed by SOCl<sub>2</sub> (1.6 mL, 0.014 mole) with stirring. The reaction mixture was stirred at room temperature for 2 hours. The solvent and excess SOCl<sub>2</sub> were distilled out under reduced pressure. The resulting yellow solid was dissolved in diethyl ether and washed with water and the organic layer was dried over Na<sub>2</sub>SO<sub>4</sub>. The solvent was removed under reduced pressure and directly used for further step.

### Synthesis of (AB)<sub>3</sub>G<sub>2</sub>-COOCH<sub>3</sub>dendron (e)

Methyl-3, 4, 5- trihydroxy benzoate (0.61 g, 0.0034 mole) and K<sub>2</sub>CO<sub>3</sub> (3.31 g, 0.0204 mole) in 35 mL dry acetone were taken in a 100 mL round bottom flask. Compound **d** (4.5 g, 0.010 mole) was added followed by the addition of a catalytic amount of tetra butyl ammonium iodide (0.365 g, 0.001 mole). The solution was heated to reflux with stirring for 24 hours. After completion of reaction, the reaction mixture was cooled to room temperature and filtered. The filtered salts were further washed twice with dichloromethane. The solvent was then removed under reduced pressure using a rotary evaporator, yielding an oily substance that turned into a solid upon standing. The solid was recrystallized from hexane: toluene mixture (70:30). The yield of the product Compound **e** was 4.2 g (89.3%); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ: 3.82 (s, COOCH<sub>3</sub>, 3H), 4.75-4.93 (s, ArCH<sub>2</sub>O, 24H), 6.66 (s, ArH, 2H) 6.68 (s, ArH, 4H), 7.10-7.29 (m, ArH&PhH, 47H); <sup>13</sup>C NMR(100 MHz, CDCl<sub>3</sub>) δ: 52.31, 71.03, 71.25, 71.49, 75.10, 75.21, 107.03, 107.65, 109.71, 125.44, 127.45, 127.49, 127.67, 127.77, 127.88, 128.10, 128.16, 128.40, 128.49, 132.29, 133.06, 136.99, 137.03, 137.92, 138.30, 142.43, 152.51, 152.83, 153.11, 166.51; IR(KBr) ν = 3088, 3062, 3030, 2934, 2864, 1719, 1591, 1504, 1454, 1435, 1112 and 733 cm<sup>-1</sup>.

### Synthesis of G<sub>2</sub>TNHNH<sub>2</sub> (f)

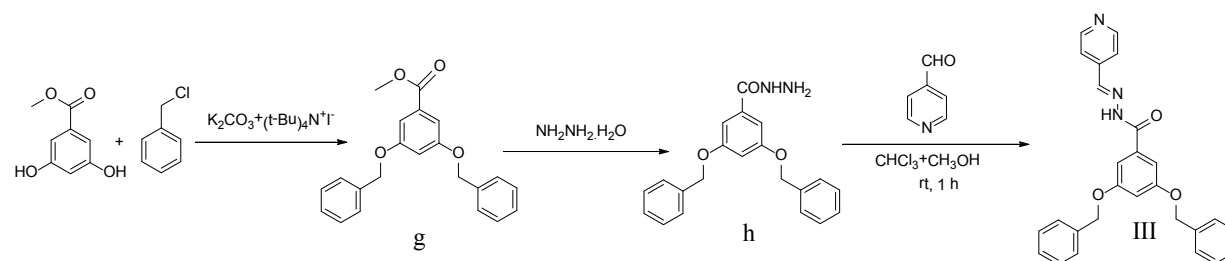
Compound **e** (3 g, 0.0021 mole) and hydrazine monohydrate (5.3 mL, 0.11 mole) were placed in a round bottomed flask and dissolved in MeOH (20 mL) and THF (20 mL). The reaction mixture was stirred at 70°C for 12 hours. The heating was stopped, the reaction mixture was allowed to cool to room temperature, the volatiles were removed under reduced pressure, and the product was dissolved in CH<sub>2</sub>Cl<sub>2</sub> and washed with H<sub>2</sub>O. The organic layer was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, and the solvent was evaporated to get crude product, which was purified by column chromatography by using silica gel as the stationary phase and 5% MeOH in CH<sub>2</sub>Cl<sub>2</sub> as the

eluent to get the pure product as a white powder ( 2.71 g, 93.3 %); **<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)**  $\delta$ : 4.73-4.89 (m, ArCH<sub>2</sub>O, 24H), 6.63-6.65 (m, ArH, 6H), 6.94 (s, ArH, 2H), 7.13-7.32 (m, PhH, 45H); **<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)**  $\delta$ : 71.05, 71.25, 71.63, 75.19, 75.26, 106.91, 107.28, 107.61, 127.51, 127.73, 127.83, 127.94, 128.16, 128.21, 128.45, 128.55, 132.24, 133.08, 136.98, 137.03, 137.91, 138.31, 141.53, 152.90, 153.15, 168.13; **IR(KBr)**  $\nu$ =3286, 3109, 3088, 3062, 3030, 2932, 2865, 1637, 1590, 1505, 1454, 1435, 1121 and 733 cm<sup>-1</sup>; **HRMS (ES+)**:  $m/z$  Calcd for C<sub>91</sub>H<sub>80</sub>N<sub>2</sub>O<sub>13</sub>: 1408.5660, found: 1410.5817; m.p. 120 °C.

### Synthesis of compound II

A solution 4-pyridine carboxaldehyde (0.16 ml, 1.703 mmole) in methanol was added drop wise to a CHCl<sub>3</sub> solution of compound **f** (2 g, 1.418 mmole) under nitrogen atmosphere. The mixture was stirred for 1 hour and the resulting gel was dried under vacuum to yield **II** (1.998 g, 94 %); **<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)**  $\delta$ : 5.19 (s, ArCH<sub>2</sub>O, 4H), 6.95 (s, ArH, 1H), 7.26-7.49 (m, ArH&PhH, 12H), 8.06 (dd,  $J$ =8.0 Hz,  $J$ =3.6 Hz, PyH, 2H), 8.49 (s, PyH, H), 8.93 (d,  $J$ =6.0 Hz, PyH, 2H), 9.39 (s, CH=N, 1H); **<sup>13</sup>C NMR (100 MHz, DMSO-d<sub>6</sub>)**  $\delta$ : 70.61, 70.82, 71.16, 74.88, 74.93, 106.98, 107.57, 107.61, 108.74, 127.15, 127.55, 127.74, 128.13, 128.31, 128.46, 128.63, 128.88, 128.95, 128.98, 130.24, 130.78, 131.12, 131.30, 131.77, 131.89, 133.84, 133.98, 134.80, 134.93, 137.25, 137.41, 148.36, 151.90, 152.54, 168.29; **MS (MALDI-TOF)**:  $m/z$  Calcd for C<sub>97</sub>H<sub>83</sub>N<sub>3</sub>O<sub>13</sub>: 1497.5926; found: 1520.6752 [M+Na]<sup>+</sup>.

### Synthetic procedure for compound III



### Synthesis of (AB)<sub>2</sub>G<sub>1</sub>-COOCH<sub>3</sub> (**g**)

Methyl-3, 5-dihydroxybenzoate (8 g, 0.0476 mole) and potassium carbonate (13.2 g, 0.0952 mole) were taken in 130 mL of 1,4-dioxane in a 250 mL round bottom flask. Benzyl chloride (10.95 mL, 0.0952 mole) was added followed by the addition of a catalytic amount of tetra butyl ammonium iodide (1.5 g, 0.0047 mole). The solution was heated to reflux with stirring for 24 hours. The solvent was then removed under reduced pressure using a rotary evaporator to get an

oily substance that turned into a solid upon standing. The solid was crystallized from methanol to get Compound **g** (15 g, 90.9%); **<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)**  $\delta$ : 3.80 (s, COOCH<sub>3</sub>, 3H), 4.97 (s, ArCH<sub>2</sub>O, 4H), 6.71 (s, ArH, 1H), 7.23-7.34 (m, ArH&PhH, 12H); **<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)**  $\delta$ : 52.29, 70.34, 107.32, 108.46, 127.60, 128.15, 128.50, 128.67, 132.12, 136.54, 159.86, 166.80; IR(KBr)  $\nu$  = 3095, 3062, 3027, 2949, 2905, 2862, 1714, 1596, 1499, 1472, 1439, 1106 and 761.

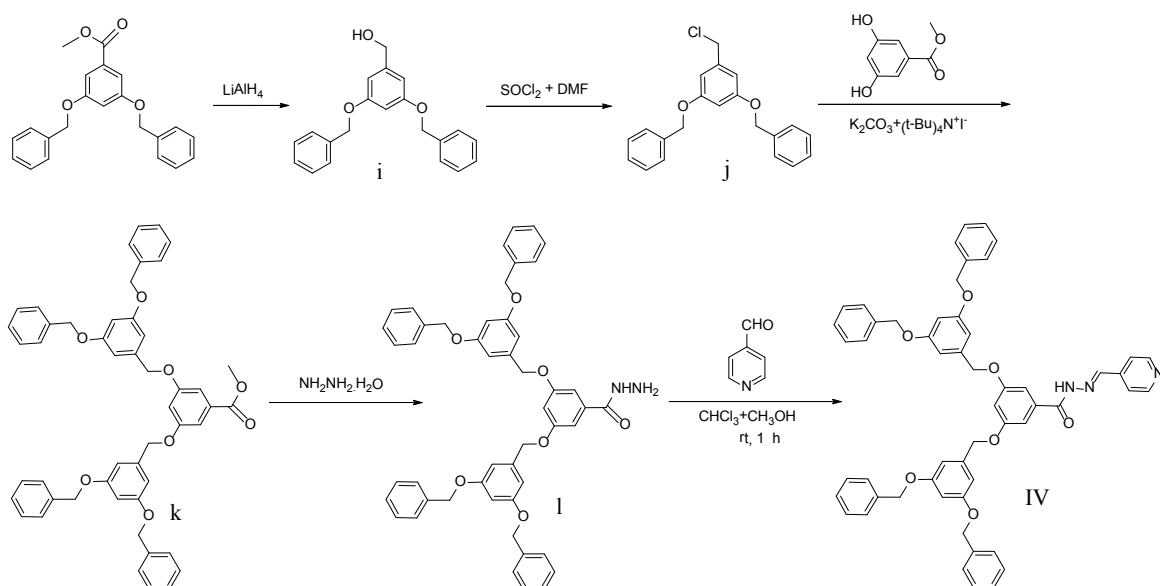
### Synthesis of G<sub>1</sub> DNHNH<sub>2</sub> (**h**)

Compound **g** (4 g, 0.011 mole) and hydrazine monohydrate (27.5 mL, 0.55 mole) were dissolved in MeOH (30 mL) and THF (15 mL). The reaction mixture was stirred at 70°C for 12 hours. After the heating was stopped, the reaction mixture was allowed to cool to room temperature, and the volatiles were removed under reduced pressure. The residue was dissolved in CH<sub>2</sub>Cl<sub>2</sub> and washed with H<sub>2</sub>O. The organic layer was then dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, and the solvent was evaporated to get crude product, which was purified by column chromatography using silica gel as the stationary phase and 5% MeOH in CH<sub>2</sub>Cl<sub>2</sub> as the eluent to get the pure product as a white powder (3.8 g, 95%); **<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)**  $\delta$ : 4.87 (s, ArCH<sub>2</sub>O, 4H), 6.63 (s, ArH, 1H), 6.90 (s, ArH, 2H), 7.09-7.27 (m, PhH, 10H); **<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)**  $\delta$ : 70.40, 105.77, 106.14, 127.32, 127.63, 128.25, 128.73, 134.86, 136.49, 160.19, 168.49; IR(KBr)  $\nu$  = 3287, 3088, 3062, 3030, 2923, 2858, 1637, 1591, 1514, 1497, 1453, 1436, 1112 and 795 cm<sup>-1</sup>; **HRMS (ES<sup>+</sup>):**  $m/z$  Calcd for C<sub>21</sub>H<sub>20</sub>N<sub>2</sub>O<sub>3</sub>: 348.1474, found: 349.1562[M+H]<sup>+</sup>.

### Synthesis of compound III

A solution of 4-pyridine carboxaldehyde (0.648, 6.88 mmole) in methanol was added drop wise to a CHCl<sub>3</sub> solution of compound **h** (2 g, 5.74 mmole). The mixture was stirred for 1 hour and the resulting gel was dried under vacuum to yield **III** (2.486 g, 99 %); **<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)**  $\delta$ : 4.97(s, ArCH<sub>2</sub>O, 4H), 6.70 (s, ArH, 1H), 7.01 (s, ArH, 2H), 7.27-7.32 (m, PhH, 10H), 7.51 (s, PyH, 2H), 8.23 (s, CONH, 1H), 8.56 (s, PyH, 2H), 9.71(s, CH=N, 1H); **<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>.DMSO-d<sub>6</sub>)**  $\delta$ : 70.10, 105.35, 107.04, 121.23, 127.52, 128.04, 128.48, 135.15, 136.26, 141.60, 145.73, 150.03, 159.74, 164.12; **HRMS (ES<sup>+</sup>):**  $m/z$  Calcd for C<sub>27</sub>H<sub>23</sub>N<sub>3</sub>O<sub>3</sub>: 437.1739 found: 438.1820 [M+H]<sup>+</sup>.

## Synthetic procedure for compound IV



### Synthesis of (AB)<sub>2</sub>G<sub>1</sub>-CH<sub>2</sub>-OH (i)

Lithium aluminum hydride (1.54 g, 0.0405 mole) was suspended into 50 mL of freshly distilled THF in a dry three-neck round-bottom flask under nitrogen atm. Compound **g** (13.1 g, 0.0376 mole) was dissolved in 60 mL of freshly distilled THF and added drop wise to the lithium aluminum hydride solution. The reaction mixture was heated to reflux with stirring for 2 hours. The THF solution was cooled to room temperature and transferred to a beaker. Water was added drop wise to the vigorously stirred THF solution until the gray color of the lithium aluminum hydride was disappeared and a white solid was formed which is filtered and washed with THF, Excess solvent was removed under reduced pressure and the crude product was recrystallized from 95% methanol/water mixture to get the alcohol Compound **i** with yield 10.9 g (90.6%); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ: 4.54 (s, CH<sub>2</sub>OH, 2H), 4.95 (s, ArCH<sub>2</sub>O, 4H), 6.47-6.54 (s, ArH, 3H), 7.17-7.34 (m, PhH, 10H); <sup>13</sup>CNMR (100 MHz, CDCl<sub>3</sub>) δ : 65.34, 70.13, 101.39, 105.82, 127.54, 128.03, 128.62, 136.89, 143.47, 160.22.

### Synthesis of (AB)<sub>2</sub>G<sub>1</sub>-CH<sub>2</sub>Cl (j)

To a solution of Compound **i** (7 g, 0.0218 mole) in dichloromethane (40 mL), a catalytic amount of DMF and SOCl<sub>2</sub> (1.95 mL, 0.026 mole) were added with stirring. It was stirred at room



temperature for 2 hours. The solvent and excess  $\text{SOCl}_2$  were distilled out under reduced pressure. The resulting yellow solid was dissolved in diethyl ether, washed with water and the organic layer was dried over  $\text{Na}_2\text{SO}_4$ . The solvent was removed under reduced pressure and directly used to further step.

### Synthesis of $(\text{AB})_2\text{G}_2\text{-COOCH}_3$ dendron (**k**)

Methyl-3, 5-dihydroxy benzoate (1.9 g, 0.0118 mole) and  $\text{K}_2\text{CO}_3$  (3.9 g, 0.0283 mole) in 35 mL dry acetone were taken in a 250 mL round bottom flask. Compound **j** (8 g, 0.0236 mole) was added followed by the addition of a catalytic amount of tetra butyl ammonium iodide (0.358 g, 0.001 mole). The solution was heated to reflux for 24 hours. After completion of reaction, the reaction mixture was cooled to room temperature and filtered. The filtered salts were further washed twice with dichloromethane. The solvent was then removed under reduced pressure to afford an oil that turned into a solid upon standing. The solid was recrystallized from hexane : toluene mixture (70:30) with a yield of 7.9 g (89.4%);  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$ : 3.96 (s,  $\text{COOCH}_3$ , 3H), 5.06-5.09 (s,  $\text{ArCH}_2\text{O}$ , 12H), 6.63-6.82 (s,  $\text{ArH}$ , 7H), 7.30-7.47 (m,  $\text{ArH}$  &  $\text{PhH}$ , 22H);  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$ : 52.39, 70.27, 101.85, 106.54, 07.33, 108.54, 127.67, 128.14, 128.72, 132.21, 136.90, 139.02, 159.83, 160.33, 166.85; IR (KBr)  $\nu$  = 3089, 3061, 3029, 3006, 2948, 2910, 2871, 1712, 1520, 1497, 1438, 1110 and  $769\text{ cm}^{-1}$ .

### Synthesis of $\text{G}_2\text{DNHNH}_2$ (**l**)

Compound **k** (3.5 g, 0.0045 mole) and hydrazine monohydrate (11.3 mL, 0.22 mole) were placed in a round bottomed flask and dissolved in MeOH (20 mL) and THF (20 mL). The reaction mixture was stirred at  $70^\circ\text{C}$  for 12 hours. The heating was stopped, the reaction mixture was allowed to cool to room temperature, the volatiles were removed under reduced pressure, and the product was dissolved in  $\text{CH}_2\text{Cl}_2$  and washed with  $\text{H}_2\text{O}$ . The organic layer was dried over anhydrous  $\text{Na}_2\text{SO}_4$ , and the solvent was evaporated to get crude product, which was purified by column chromatography using silica gel as the stationary phase and 5% MeOH in  $\text{CH}_2\text{Cl}_2$  as the eluent to get the pure product as a white powder (3.2 g, 91.4 %);  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$ : 4.83-4.93 (s,  $\text{ArCH}_2\text{O}$ , 12H), 6.48-6.85 (s,  $\text{ArH}$ , 9H), 7.16-7.32 (m,  $\text{PhH}$ , 20H);  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$ : 70.16, 101.67, 105.62, 106.00, 106.39, 127.19, 127.61, 128.08, 128.25, 128.48, 128.64, 134.78, 136.73, 138.79, 160.02, 160.23, 168.44; IR (KBr)  $\nu$  = 3332, 3088, 3060, 3030, 2909, 2866, 1654, 1596, 1519, 1497, 1446, 1156 and 732; HRMS (ES+):  $m/z$  Calcd for  $\text{C}_{49}\text{H}_{44}\text{N}_2\text{O}_7$ : 772.3149, found: 773.3215 $[\text{M}+\text{H}]^+$ ; m.p.  $110^\circ\text{C}$ .

### Synthesis of compound IV

A solution of Pyridine 4- carboxaldehyde (0.292ml, 3.105 mmole) in methanol was added drop wise to a  $\text{CHCl}_3$  solution of compound **I** (2 g, 2.587 mmole). The mixture was stirred for 1 hour and the resulting gel was dried under vacuum to yield **IV** (2.096 g, 94 %);  **$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )**  $\delta$ : 4.92 (s,  $\text{ArCH}_2\text{O}$ , 4H), 4.99 (s,  $\text{ArCH}_2\text{O}$ , 8H), 6.55 (s,  $\text{ArH}$ , 6H), 6.56 (s,  $\text{ArH}$ , 1H), 6.62 (s,  $\text{ArH}$ , 2H), 7.29-7.39 (m,  $\text{PhH}$ , 22H), 8.19 (s,  $\text{CONH}$ , 1H), 8.59 (s,  $\text{PyH}$ , 2H), 9.86(s,  $\text{CH}=\text{N}$ , 1H);  **$^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ .DMSO- $d_6$ )**  $\delta$ : 70.23, 76.89, 101.66, 106.09, 106.51, 127.72, 127.74, 127.76, 128.19, 128.68, 128.70, 128.75, 128.78, 136.74, 138.83, 141.05, 150.43, 159.5, 160.30, 165.32; **HRMS (ES+)**:  $m/z$  Calcd for  $\text{C}_{55}\text{H}_{47}\text{N}_3\text{O}_7$ : 861.3414, found: 860.3352  $[\text{M}+\text{H}]^+$ .

### 3. SEM image of spherical aggregates

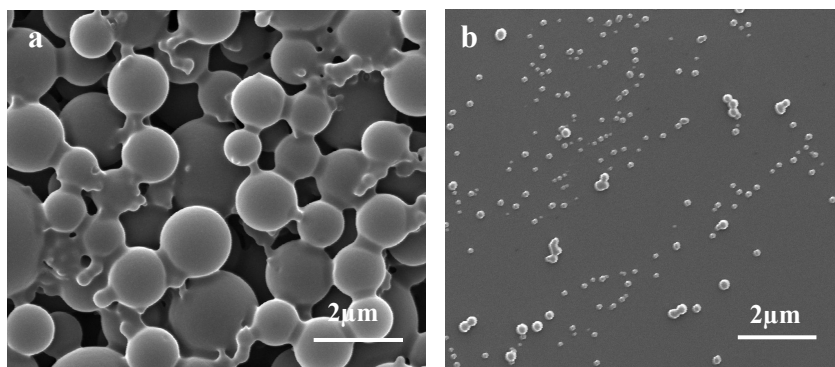


Fig. S1 SEM image of a) **II** in THF-water b) **III** in THF-water

### 4. Dynamic light scattering data

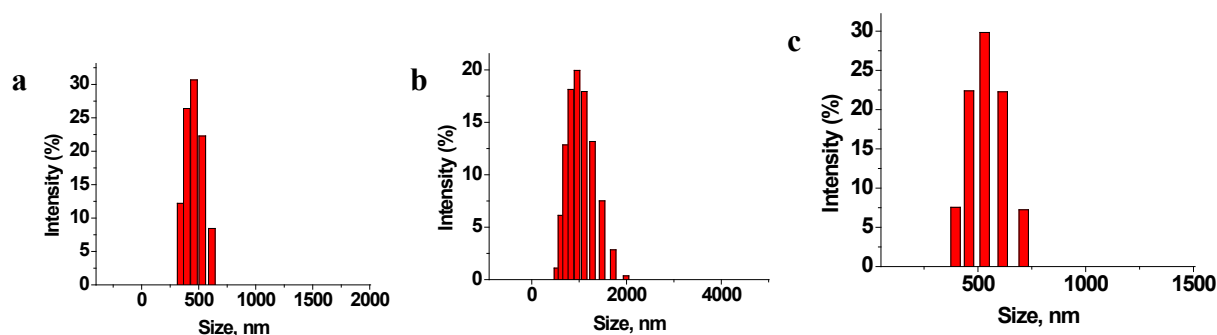
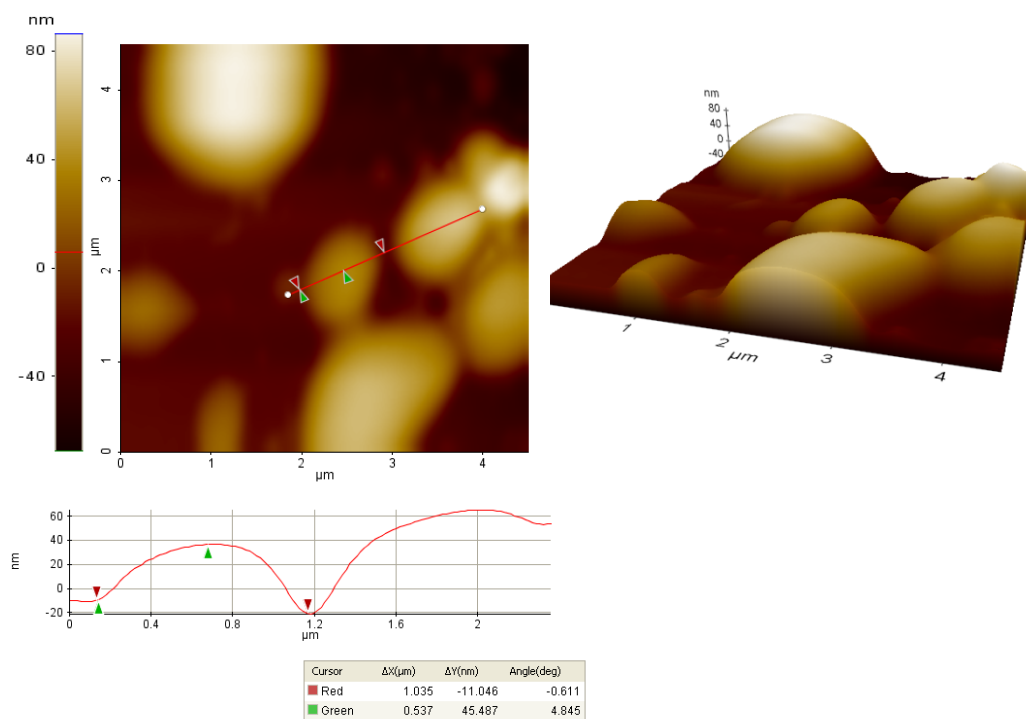


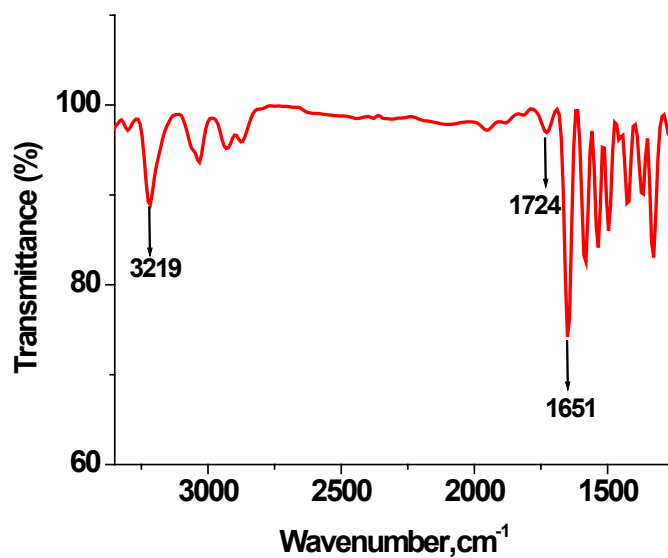
Fig. S2 DLS of compound (a) **I**, (b) **II** and (c) **III** in THF-water

## 5. AFM image spherical aggregate



**Fig. S3** AFM image of compound IV/TA in THF-water (left) and 3D view (right)

## 6. FT-IR spectrum of gel

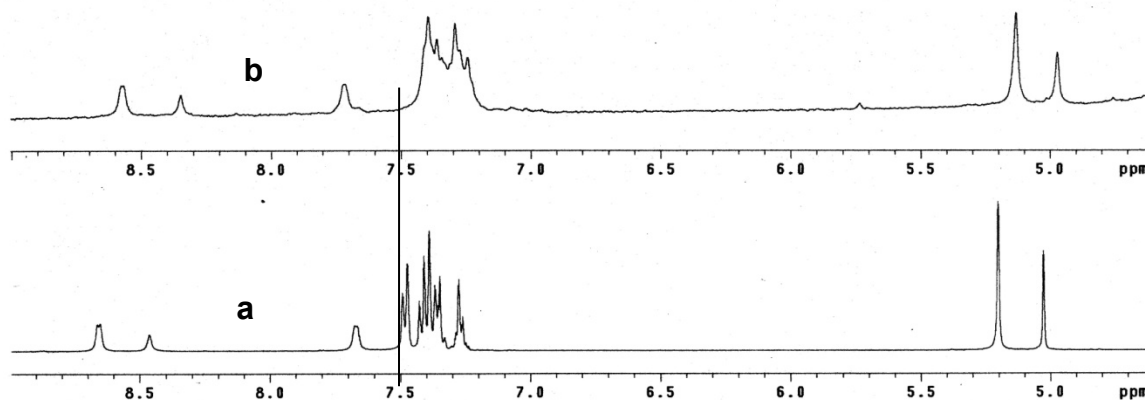


**Fig. S4** FT-IR spectrum of the xerogel formed from compound I/TA in THF-water

**7. Table S1: Gelation properties and critical gel concentration (CGCs) of dendrons with tartaric acid in THF-water.**

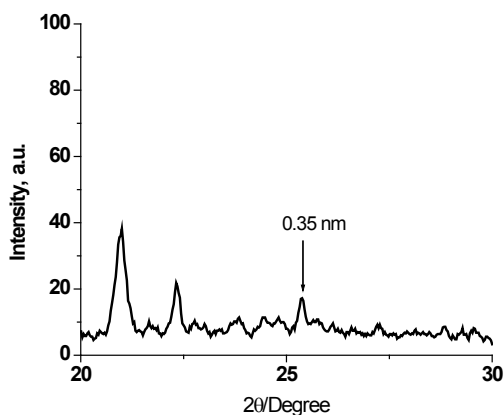
Acids	I	II	III	IV
L-Tartaric acid (THF-water)	G(2.5 mg/mL)	G(4 mg/mL)	G (8 mg/mL)	G(6 mg/mL)

**8.  $^1\text{H}$ -NMR spectra of solution and partial gel phase**



**Fig. S5**  $^1\text{H}$ NMR spectrum compound **I** in a) solution and b) partialgel state (**I**:TA; 2:1 ratio)

**9. Powder X-ray diffraction pattern**



**Fig. S6** Powder XRD pattern of xerogel formed from a) compound **IV**/TA in THF-water

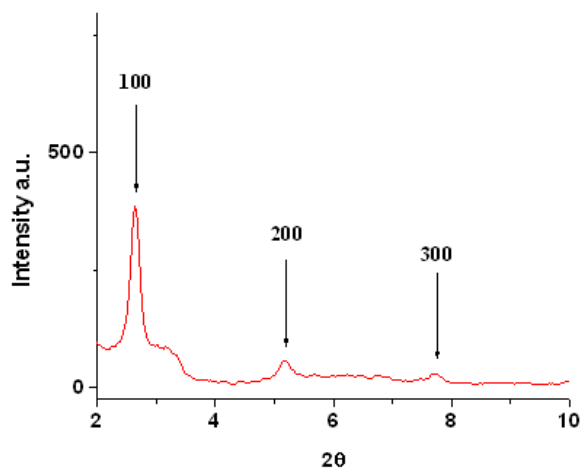


Fig. S7 Powder XRD pattern of compound **I** + tartaric acid (2:1) from THF: water (1:1 v/v)

## 10. Job plot

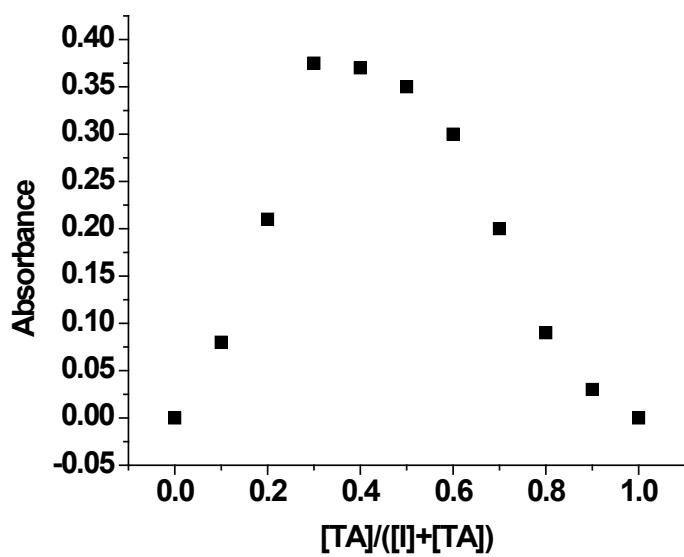


Fig. S8 Job plots showing the 2:1 stoichiometry of the complex between **I** and TA

## 11. Schematic representation of lamellar arrangement

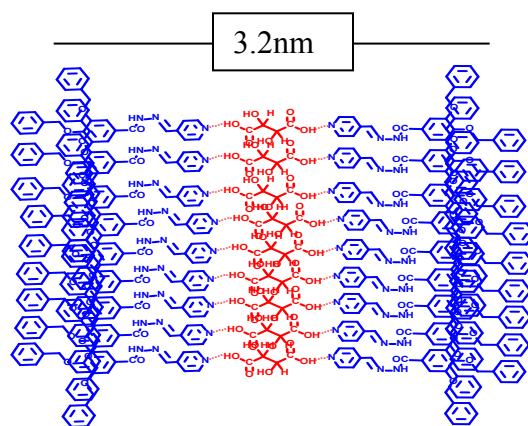


Fig. S9 Schematic representation of lamellar arrangement

## 12. SEM of xerogel

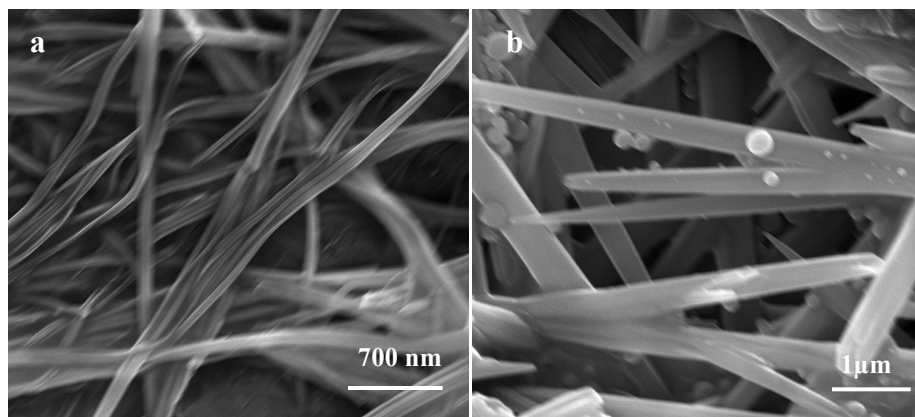
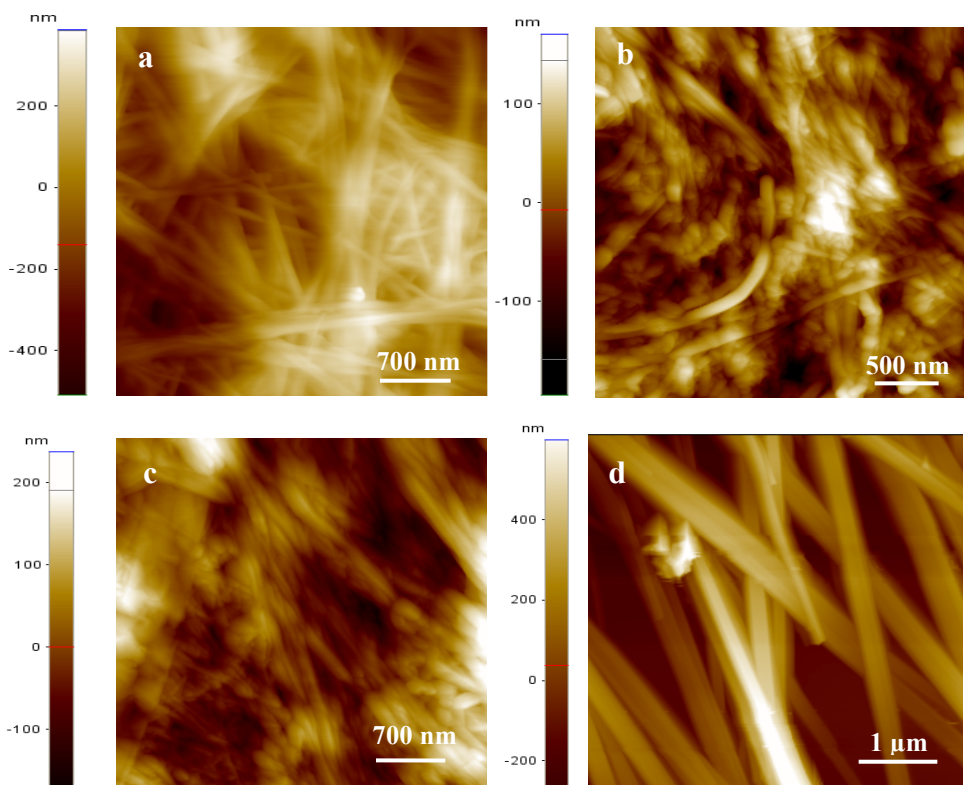


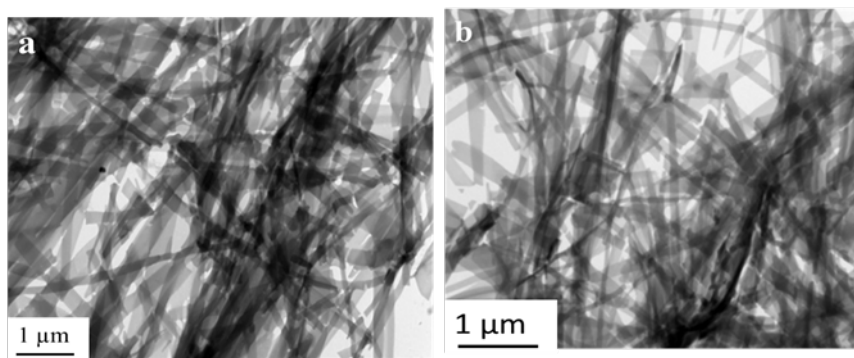
Fig. S10 SEM image of a) compound II/TA (2:1), b) compound IV/TA (2:1) in THF-water

### 13. AFM image of xerogel



**Fig. S11** AFM image of xerogel formed from a) compound **I**/TA, b) compound **II**/TA, c) compound **III**/TA d) compound **IV**/TA in THF-water

### 14. TEM image of xerogel



**Fig. 12** TEM image of (a) compound **I** +tartaric acid (2:1) from THF: water (1:1 v/v), (b) compound **III** +tartaric acid (2:1) from THF: water (1:1 v/v)

## 15. Steady state fluorescence spectra

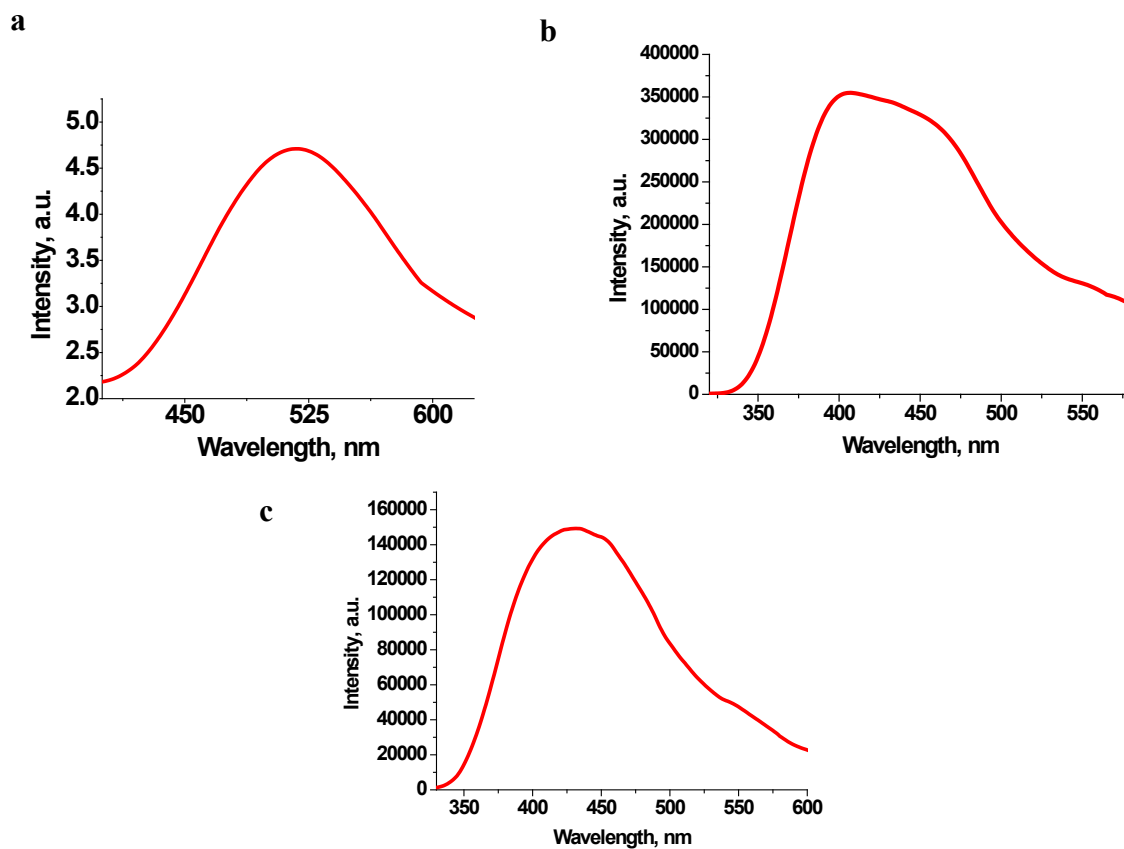
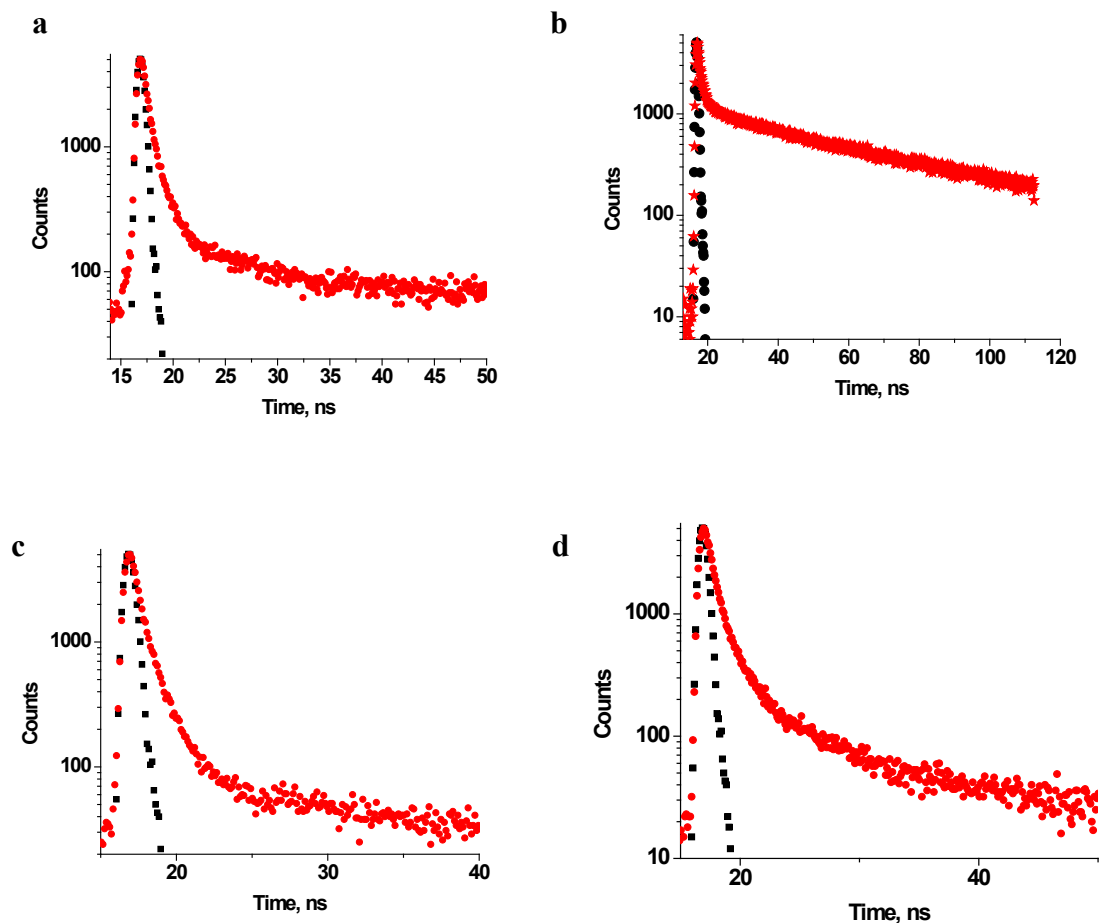


Fig. S13 Emission spectra of (a) compound **I**/TA, (b) compound **III**/TA, (c) compound **IV**/TA in THF-water



## 16. Fluorescence decay of compounds



**Fig. S14** Fluorescence decay of gel formed from compound a) **I**/TA b) **II**/TA, c) **III**/TA, d) **IV**/TA in THF-water (Decay-red; black -lamp profile)

## Reference

1. P. Rajamalli and E. Prasad, *Org. Lett.*, 2011. **13**, 3714.