

## Supporting Information

### **Solvophobic control aggregation-induced emission of tetraphenylethene-substituted naphthalene diimide *via* intramolecular charge transfer**

**Anushri Rananaware, La Duc Dong, Sheshanath V. Bhosale\***

School of Applied Sciences, RMIT University, GPO Box 2476, Melbourne, VIC-3001, Australia

Corresponding E-mail: sheshanath.bhosale@rmit.edu.au

**General Methods & Materials:** All reagents were purchased either from Sigma Aldrich Chemical Co. or Merck and used as such without any further purification. All the solvents were received from commercial sources and purified by standard methods. Naphthalene tetracarboxy dianhydride, octyl amine, 3-ethyl-hexylamine, chloroform, methanol, dichloromethane, tetrahydrofuran and hexane were purchased from Aldrich and used without purification, unless otherwise specified. The UV-vis absorption spectra were recorded on a Perkin Elmer Lambda 40p spectrometer. <sup>1</sup>H NMR, <sup>13</sup>C-NMR spectra were recorded on a Bruker spectrometer using chloroform-d as solvent and tetramethylsilane as an internal standard. The solvents for spectroscopic studies were of spectroscopic grade and used as received. Mass spectra (MS) were obtained by using Bruker AutoFlex Matrix Assisted Laser Desorption/Ionisation (MALDI) Time of Flight (TOF)- Mass Spectrometer (MALDI-TOF-MS). The X-ray diffraction (XRD) pattern spectra were performed on a Bruker D8 FOCUS diffractometer using a Cu target radiation source ( $\lambda = 0.15418$  nm).

**UV-vis absorption spectroscopy:** A 0.2 mL aliquot of the stock solution of 2-TPEcNDI or 2,6-DTPEcNDI (conc. =  $10^{-3}$  M) was transferred to various ratios of CHCl<sub>3</sub>/hexane, CHCl<sub>3</sub>/MeOH and THF/water in different volumetric flasks, and made up to 2 mL volume. The solutions were allowed to equilibrate for 2 h prior to the spectroscopic measurements.

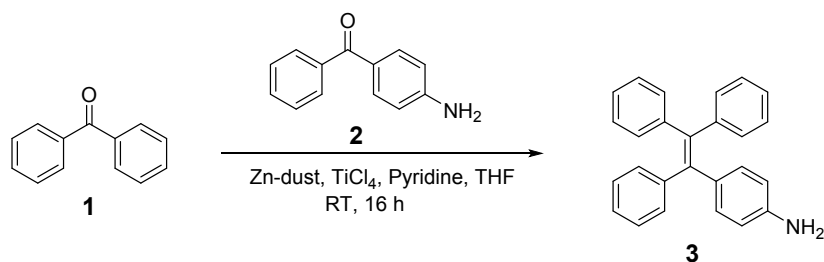
**Fluorescence Spectroscopy:** Fluorescence emission spectra were recorded on a Horiba Jobin Yvon FluoroMax®-4-Spectrofluorometer. All experiments were performed in a quartz cell with a 1 cm path length with 365 nm excitation wavelength. All the solutions were prepared in a similar manner to that in the UV-Vis study.

**Sample preparation:** A 0.2 mL aliquot of the stock solution of each one was transferred separately to four different volumetric flasks of (i) THF/water (1:4, v/v), (ii) CHCl<sub>3</sub>/MeOH (1:7, v/v), (iii) CHCl<sub>3</sub>/hexane (1:9, v/v) and made up to 2 mL volume with respective solvents. The solutions were allowed to equilibrate for 2 h prior to the Scanning Electron Microscopy (SEM) measurements.

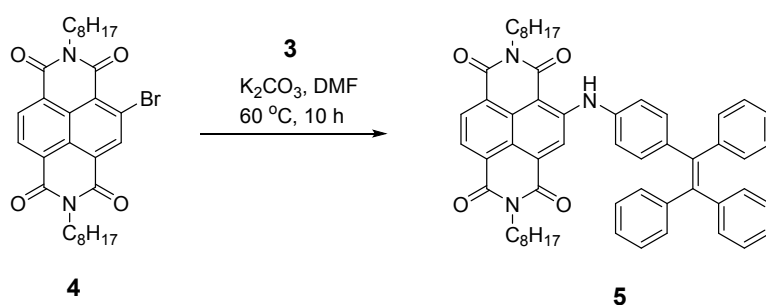
**Scanning Electron Microscopy (SEM):** SEM measurements were performed on a FEI Nova NanoSEM (Hillsboro, USA) operating at high vacuum and SEM and images were collected. Freshly prepared 0.5 μL of TPEcNDI or 2,6-DTPEcNDI samples were sputter coated with gold for 10 s at 0.016 mA Ar plasma (SPI, West Chester, USA) after drop-casting the solutions on glass coverslip and solvent

evaporation.

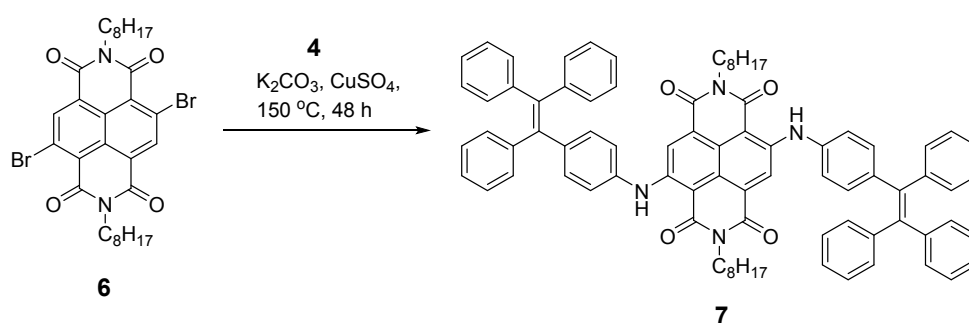
**A**



**B**



**C**



**Scheme S1.** Synthesis of (A) 4-(1,2,2-triphenylvinyl) aniline (**3**), (B) 2,7-dioctyl-4-((4-(1,2,2-triphenylvinyl) phenyl)amino)benzo[*lmn*] [3,8]phenanthroline-1,3,6,8(2H,7H)-tetraone (**5**) and (C) 2,7-dioctyl-4,9-bis((4-(1,2,2-triphenylvinyl)phenyl)amino)benzo[*lmn*] [3,8]phenanthroline-1,3,6,8(2H,7H)-tetraone (**7**).

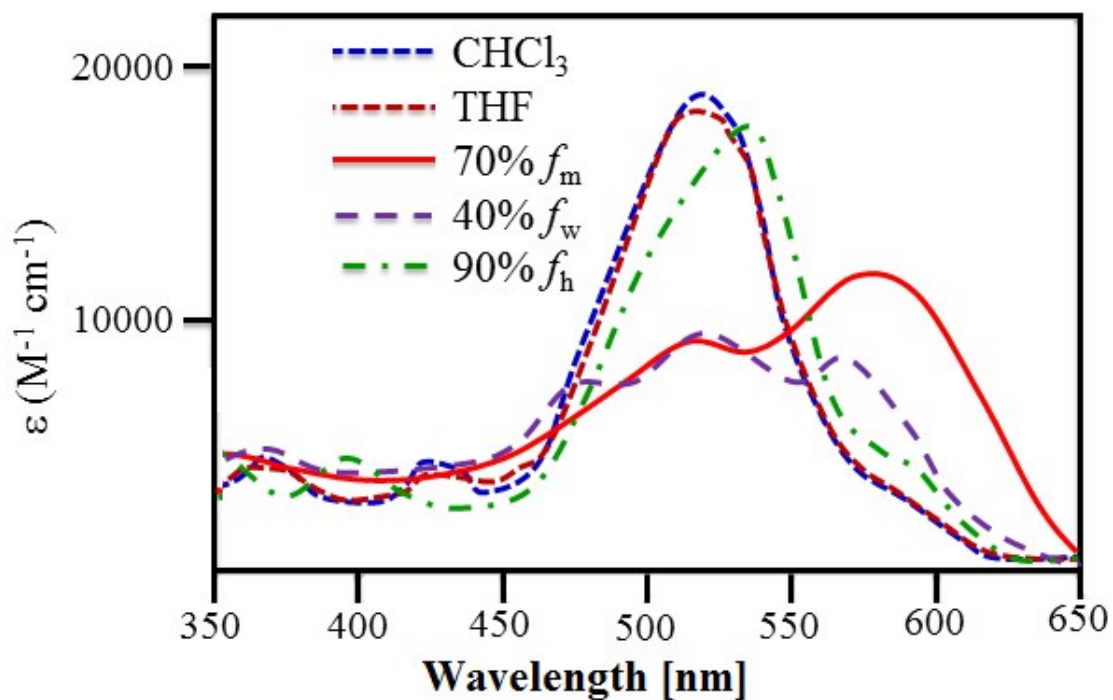
(A): In a 2-necked round bottom flask was charged with Zn powder (8.04 g, 123.37 mmol) and dry THF (460 mL) was added under an argon atmosphere. The mixture was cooled to -5 °C and TiCl<sub>4</sub> (6.72 mL, 61.68 mmol) was added slowly by syringe with the temperature maintained under 10 °C. The suspended mixture was warmed to r.t. and stirred for 0.5 h, then heated to reflux for 2.5 h. The mixture was again cooled to -5 °C then pyridine (4 mL) was added and reaction mixture was stirred for 10 min. The solution of **1** (4.0 g, 21.95 mmol) and **2** (3.5 g, 17.78 mmol) mixed in THF (60 mL) separately and was added slowly over above reaction mixture. After completion

of addition the mixture was heated to reflux for 16 h. The progress and completion of the reaction was checked by TLC analysis. Upon completion, reaction was quenched by addition of 10% aq  $K_2CO_3$  and mixture was extracted with DCM (3x100 mL). Organic layer was dried over sodium sulphate and evaporated under reduced pressure and obtained crude compound which was purified by flash chromatography to afford pure compound **3** as a Yellow solid. (5 g, yield 65 %).  $^1H$  NMR (300 MHz,  $CDCl_3$ )  $\delta$  7.19–6.98 (m, 15H), 6.86–6.77 (m, 2H), 6.48–6.40 (m, 2H), 3.59 (s, 2H,  $NH_2$ ).  $^{13}C$  NMR (75 MHz,  $CDCl_3$ )  $\delta$  144.8, 144.4, 144.2, 144.1, 140.9, 139.3, 134.0, 132.5, 131.5, 131.4, 131.3, 127.7, 127.6, 127.5, 126.2, 126.1, 114.3. HRMS (MALDI-TOF, m/z):  $[M^+]$  calcd for  $C_{26}H_{21}N$ : 347.17, obtained: 347.16.

**(B)**: To a stirred solution of 4-bromo-2, 7-dioctylbenzo [lmn] [3, 8] phenanthroline-1, 3, 6, 8(2*H*, 7*H*)-tetraone **4** (0.1 g, 0.175 mmol) in dry DMF (5 mL) then **3** (0.061 g, 0.175 mmol) was added followed by anhydrous  $K_2CO_3$  (0.024 g, 0.175 mmol) and resultant reaction mixture was heated at 60 °C for 10 h. Reaction completion was checked by TLC analysis. After completion, reaction mixture was quenched with water and extracted with DCM (3x20 mL). Organic layer was dried over sodium sulphate and evaporated to give crude compound which was purified by column chromatography to afford pure compound **5** as a red solid (0.09 g, 61%).  $^1H$  NMR (300 MHz,  $CDCl_3$ )  $\delta$  11.62 (s, 1H), 8.61 (d,  $J = 7.9$  Hz, 1H), 8.40 (s, 1H), 8.33 (d,  $J = 7.8$  Hz, 1H), 7.16 – 6.94 (m, 19H), 4.20–4.00 (m, 4H), 1.78–1.55 (s, 4H), 1.45–1.10 (m, 20H), 0.89–0.71 (m, 6H);  $^{13}C$  NMR (75 MHz,  $CDCl_3$ )  $\delta$  162.8, 144.2, 144.2, 144.1, 140.8, 139.4, 134.6, 132.9, 132.5, 131.4, 131.4, 131.3, 130.9, 127.9, 127.8, 127.6, 127.5, 126.6, 126.2, 126.1, 123.5, 114.7, 41.0, 31.8, 29.2, 28.1, 27.1, 22.6, 14.1; MALDI-TOF, m/z:  $[M^+]$  calcd for  $C_{56}H_{57}N_3O_4$ : 835.43, found: 835.54.

**(C)** A mixture of dibromo-NDI **6** (0.1g, 0.154 mmol), **5** (0.107 g, 0.308 mmol), anhydrous  $K_2CO_3$  (0.084 g, 0.617 mmol) and  $CuSO_4$  (0.0 20 g) was grinded properly for 10 min and then resultant mixture was heated at 150 °C for 2 days. Reaction completion was checked by TLC analysis. After completion resultant residue was dissolved in water and extracted with DCM (3x20 mL). Organic layer was separated, dried over sodium sulphate and evaporated under reduced pressure and obtained crude residue was further purified by silica gel flash column chromatography to give **7** as a

blue solid. (0.1 g, yield 54.7%).  $^1\text{H}$  NMR (300 MHz,  $\text{CD}_2\text{Cl}_2$ )  $\delta$  10.98 (s, 2H), 8.38 (s, 2H), 7.27–6.81 (m, 38H), 4.14–3.85 (m, 4H), 1.82 (m, 2H), 1.38–1.07 (m, 20H), 0.82 (m, 6H);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CD}_2\text{Cl}_2$ )  $\delta$  167.0, 147.1, 143.98, 141.4, 137.6, 133.0, 131.7, 131.6, 128.3, 128.1, 128.0, 126.9, 123.1, 120.9, 38.3, 31.2, 29.1, 24.5, 23.5, 14.1, 10.8; HRMS (MALDI-TOF, m/z):  $[\text{M}^+]$  calcd for  $\text{C}_{82}\text{H}_{76}\text{N}_4\text{O}_4$ : 1180.59, found: 1180.61.

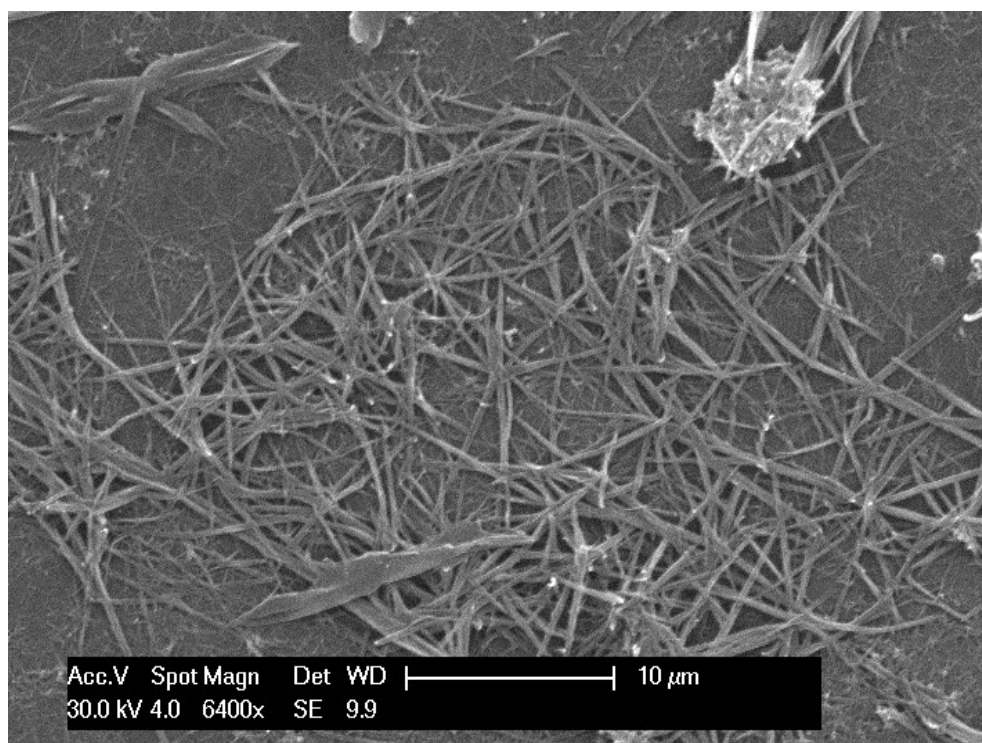


**Fig. S1** The UV-vis absorption of 2-TPEcNDI in solvent mixes.

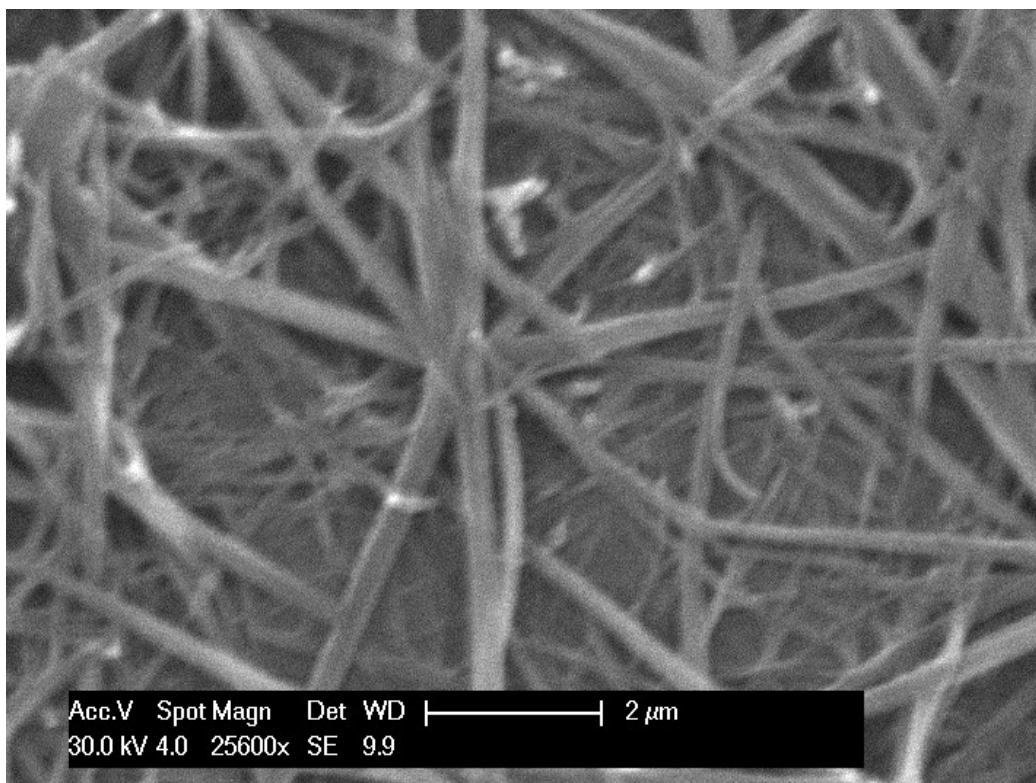
Table S1. Optical properties<sup>a</sup>

|                     | Solvent      | UV-vis ( $\lambda_{\max}$ ) | PL ( $\lambda_{\max}$ ) | $\Phi_F$ (%) |
|---------------------|--------------|-----------------------------|-------------------------|--------------|
| <b>2-TPEcNDI</b>    |              |                             |                         |              |
|                     | Chloroform   | 519                         | 569                     | 1.9          |
|                     | DCM          | 518                         | 568                     | 0.98         |
|                     | Toluene      | 511                         | 571                     | 8.32         |
|                     | n-hexane     | 506                         | 567                     | 8.39         |
|                     | THF          | 503                         | 575                     | 0.90         |
|                     | DMF          | 503                         | 579                     | 7.81         |
|                     | Ethanol      | 500                         | 618                     | 10.01        |
|                     | Acetonitrile | 501                         | 512                     | 2.01         |
| <b>2,6-DTPEcNDI</b> |              |                             |                         |              |
|                     | Chloroform   | 629                         | 675                     | 0.09         |
|                     | DCM          | 627                         | 671                     | 0.05         |
|                     | Toluene      | 623                         | 678                     | 17.32        |
|                     | n-hexane     | 616                         | 678                     | 22.71        |
|                     | THF          | 614                         | 687                     | 0.09         |
|                     | DMF          | 615                         | 693                     | 14.31        |
|                     | Ethanol      | 610                         | 705                     | 19.71        |
|                     | Acetonitrile | 612                         | 702                     | 2.01         |

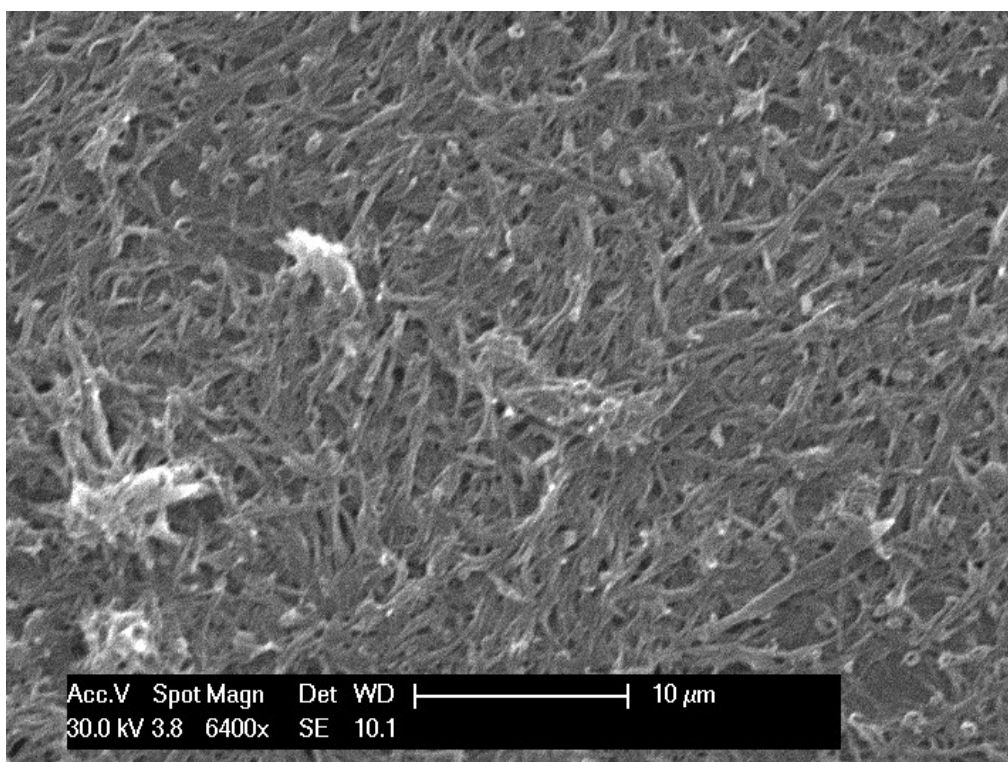
$\lambda_a$  = UV-vis absorption peaks at concentration =  $10^{-5}$  M and PL  $\lambda_{\max}$  was measured at  $\lambda_{\text{ex}}$  for 2-TPEcNDI at 501 and for 2,6-DTPEcNDI at 610 nm, respectively. The fluorescence quantum efficiency ( $\Phi_F$ ) of the samples with absorption (intensity  $\sim 0.05$ ) was estimated using fluorescein in ethanol ( $\Phi_F = 70\%$ ) as standard solution



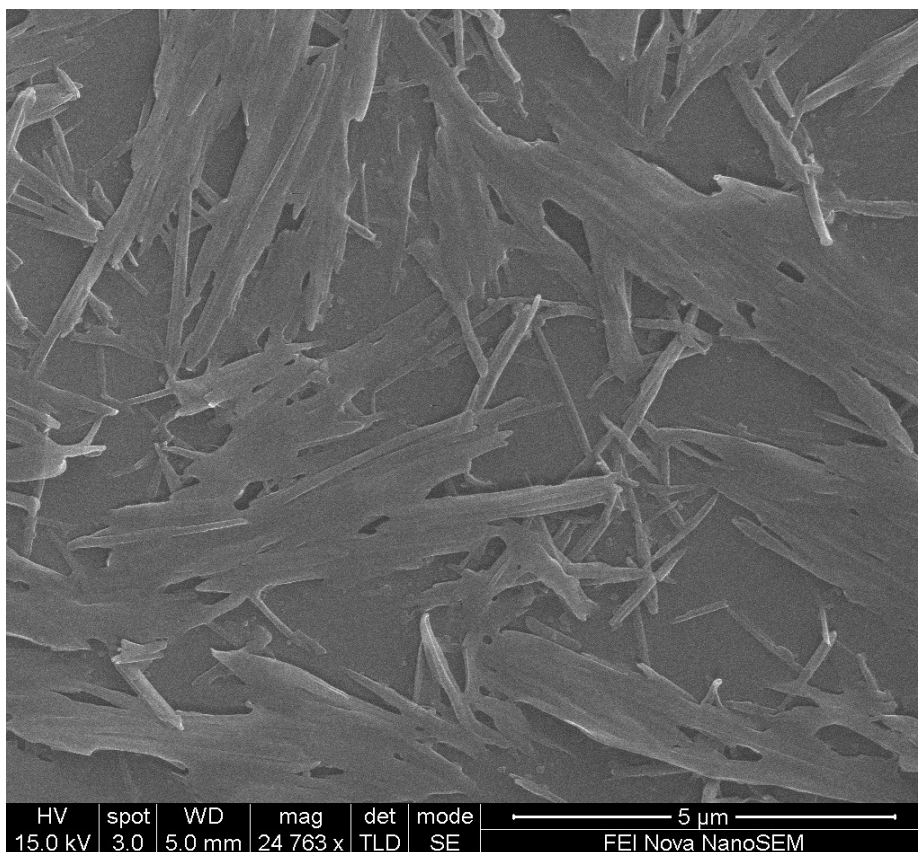
**Fig. S2** SEM images of the self-assembled aggregates formed by 2,6-DTPEcNDI and methanol/ $\text{CHCl}_3$  mixture with a methanol fraction ( $f_m = 40\%$ ).



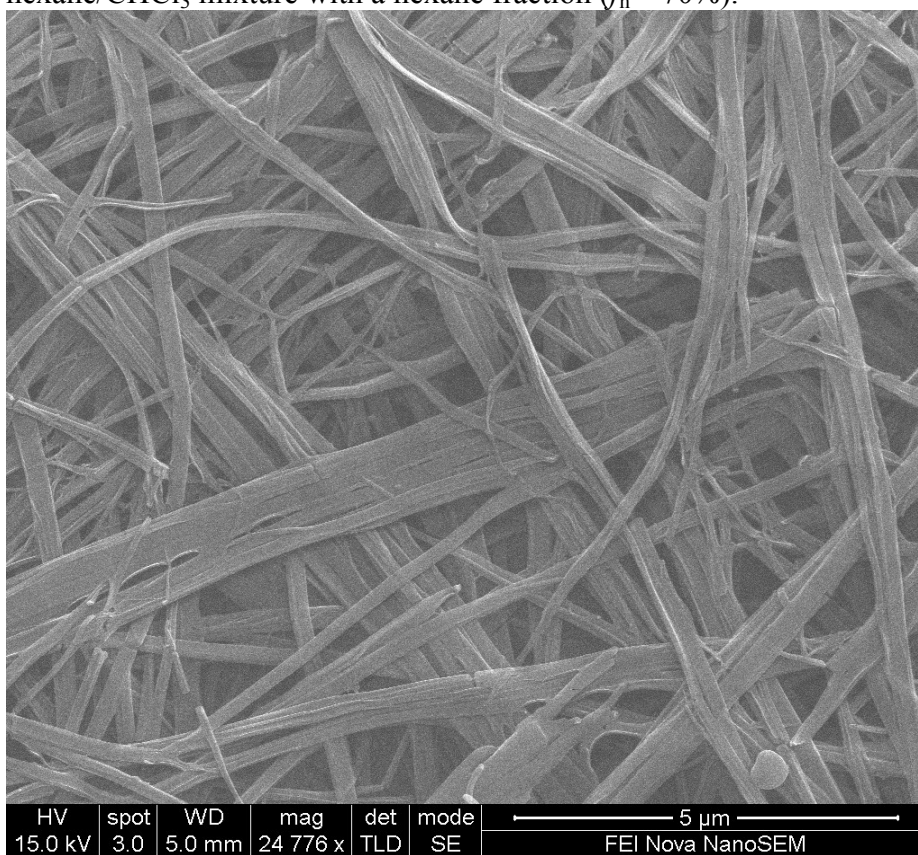
**Fig. S3** SEM images of the self-assembled aggregates formed by 2,6-DTPEcNDI and methanol/ $\text{CHCl}_3$  mixture with a methanol fraction ( $f_m = 70\%$ ).



**Fig. S4** SEM images of the self-assembled aggregates formed by 2,6-DTPEcNDI and hexane/ $\text{CHCl}_3$  mixture with a hexane fraction ( $f_h = 50\%$ ).



**Fig. S5** SEM images of the self-assembled aggregates formed by 2,6-DTPEcNDI and hexane/CHCl<sub>3</sub> mixture with a hexane fraction ( $f_h = 70\%$ ).

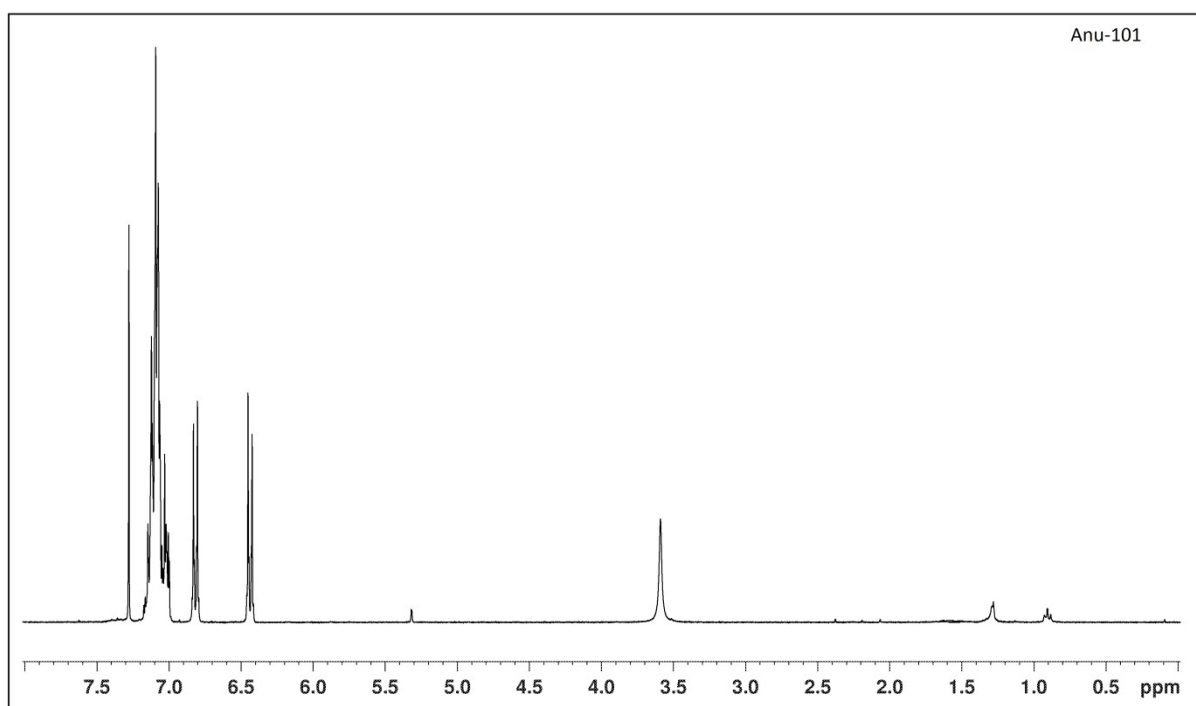


**Fig. S6** SEM images of the self-assembled aggregates formed by 2,6-DTPEcNDI in THF/water mixture with a water fraction ( $f_w = 80\%$ ).

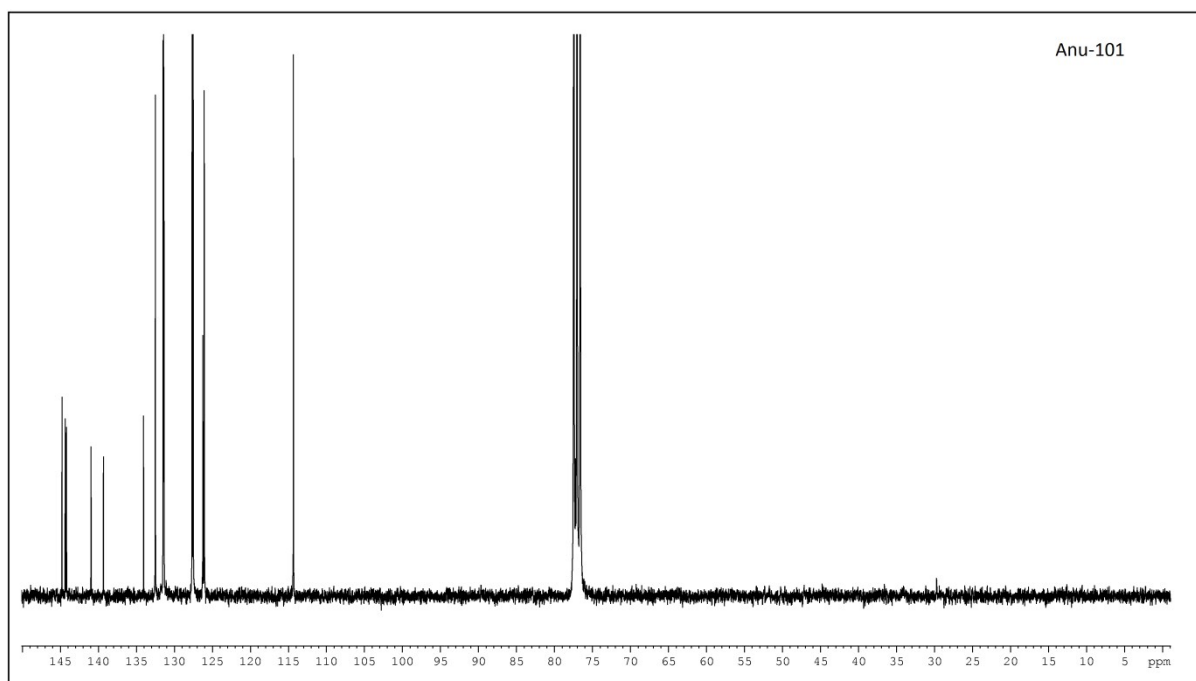


$^1\text{H}$  NMR,  $^{13}\text{C}$  NMR and Maldi mass spectrums

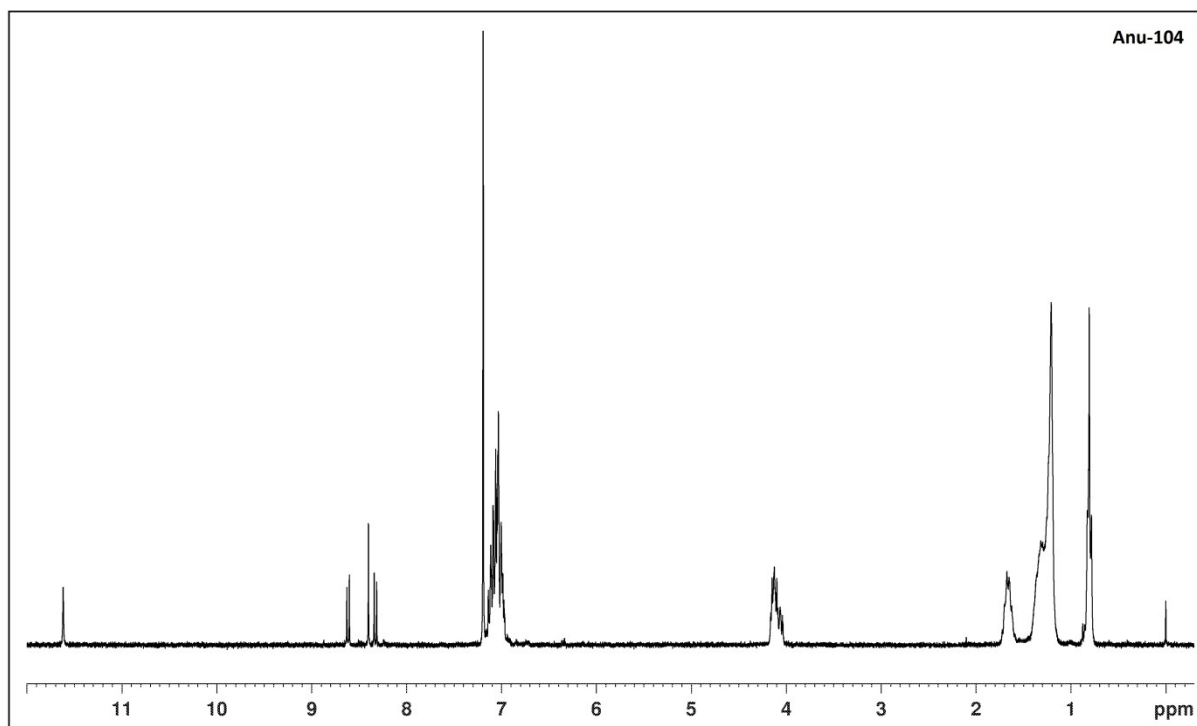
$^1\text{H}$ NMR of **3**



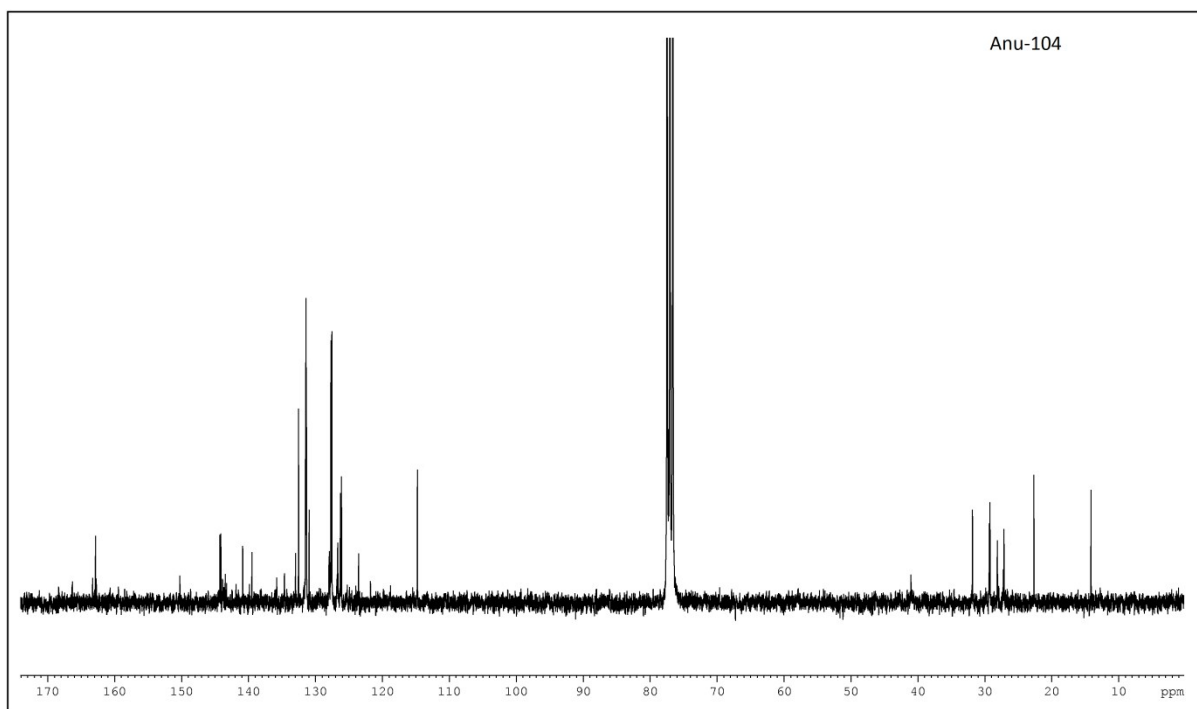
$^{13}\text{C}$ NMR of **3**



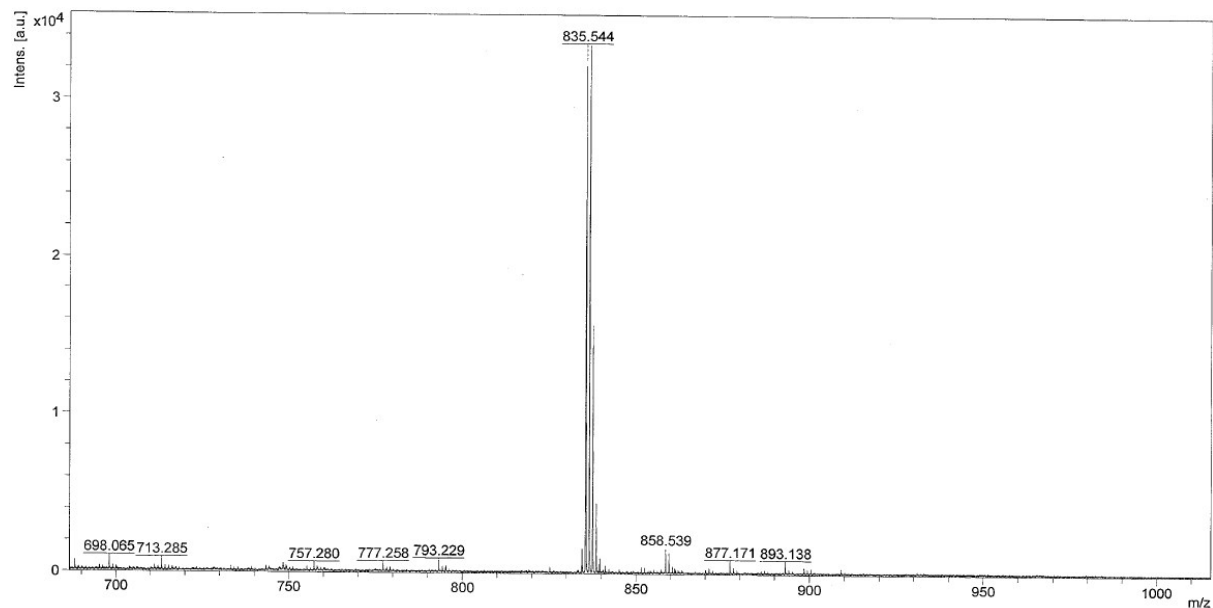
$^1\text{H}$ NMR of **5**



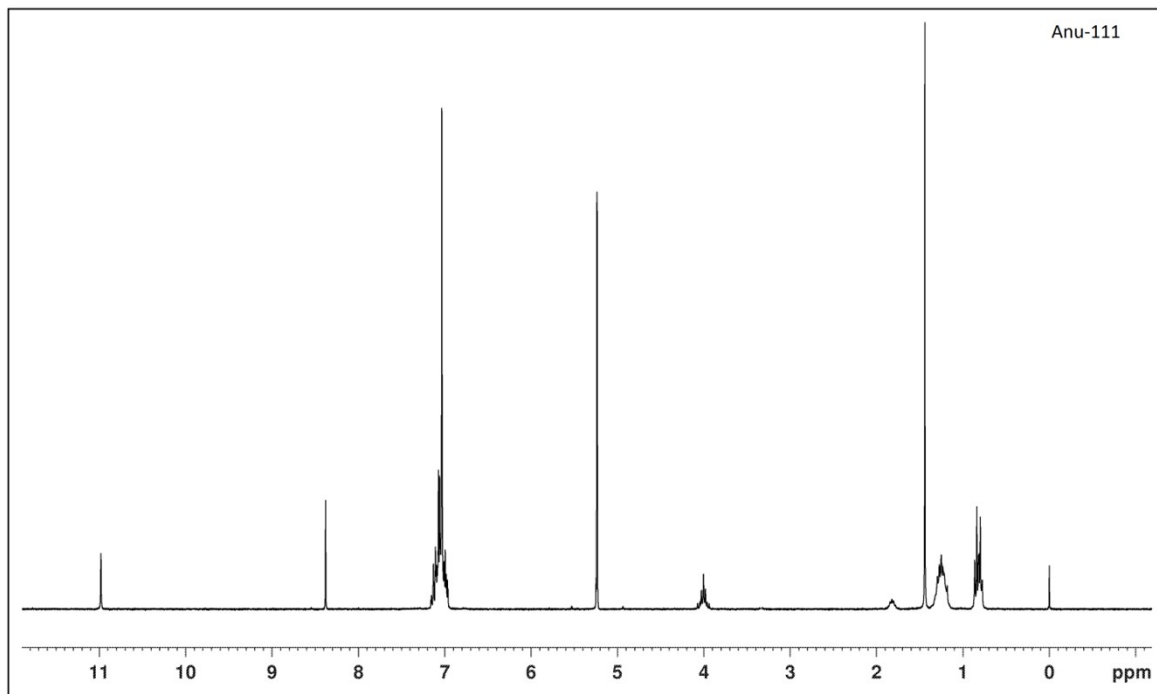
$^{13}\text{C}$ NMR of **5**



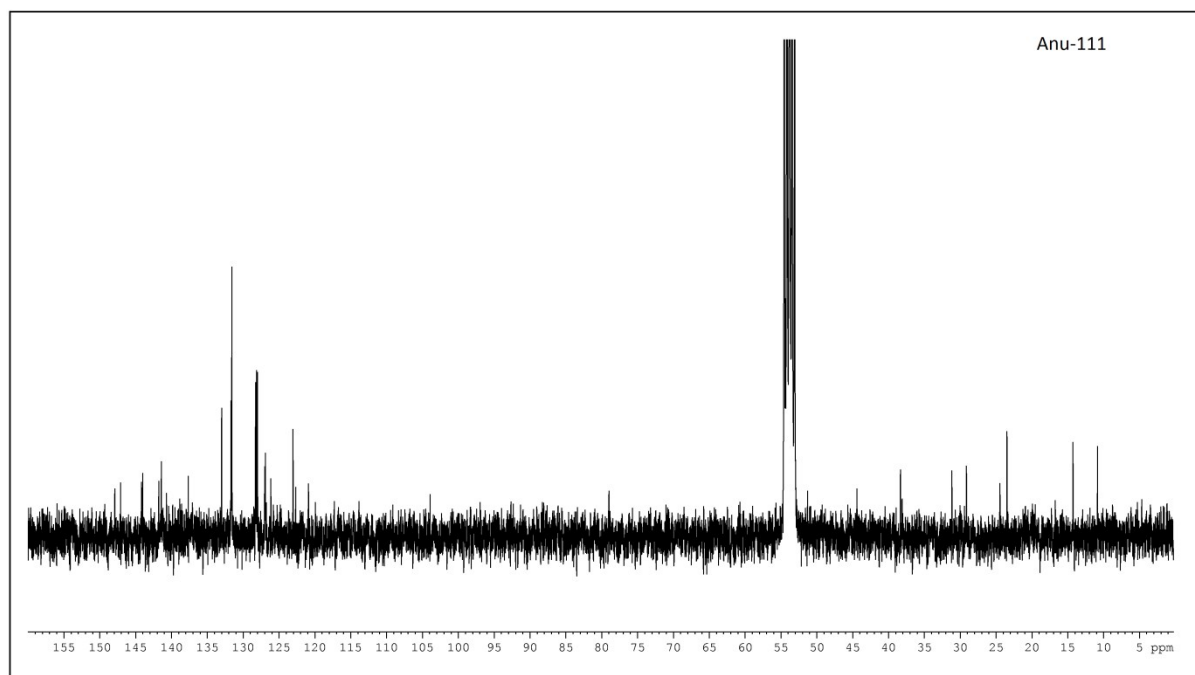
Maldi-TOF mass spectrum of **5**



<sup>1</sup>H NMR of **7**



$^{13}\text{C}$ NMR of 7



Maldi-TOF mass spectrum of 7

