Electronic Supplementary Information

Assembly of Amino Acid containing Naphthalene Diimide-based Molecules: The Role of Intervening Amide Groups in Self-assembly, Gelation, Optical and Semiconducting Properties

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Experimental section:

NMR: All NMR studies were carried out on a Brüker DPX 500 MHz spectrometer at 300 K. Concentrations were in the range of 5–10 mmol in $CDCl_3$, $(CD_3)_2SO$ and toluene-d_8 (C_7D_8). The concentration of **P1** and **P2** were the same (3 mM) in C_7D_8. Solvent dependent titration have been carried out by gradually adding small amount of $(CD_3)_2SO$ into C_7D_8 solution of the compounds.

Mass spectrometry: Mass spectra were recorded on a Q-Tof microTM (Waters Corporation) mass spectrometer by positive mode electro spray ionization process.

MALDI-TOF MS: MALDI-TOF MS analysis has been performed by using Applied Biosystems MALDI TOF/TOF Analyzer in dithranol as a matrix.

Field Emission Scanning Electron Microscopy (FE-SEM) study: FE-SEM experiments were performed by placing a small portion of gel sample on a microscope cover glass. Then,

these samples were dried first in air and then in vacuum and coated with platinum for 90 seconds at 10 kV voltages and 10 μA current. The average thickness of the coating layer of platinum was 3 to 4 nm. After that micrographs were taken by using a Jeol Scanning Microscope JSM-6700F.

FT-IR: All FT-IR spectra were recorded by using the KBr pellet technique in a Nicolet 380 FT-IR spectrophotometer (Thermo Scientific).

XRD: X-ray diffraction studies of the dried gels were carried out by placing the samples on a glass plates. Experiments were carried out by using an X-ray diffractometer (Bruker AXS, Model No. D8 Advance). The instrument was operated at a 40 kV voltages and 40 mA current using Ni-filtered CuK_{α} radiation and the instrument was calibrated with a standard Al_2O_3 (corundum) sample before use. For scan 5°-28°, the Lynx Eye super speed detector was used with scan speed 0.3s and step size 0.02°.

UV/Vis spectroscopy: UV/Vis absorption spectra were recorded on a hewlett-packard (model 8453) UV/Vis spectrophotometer (varian carry 50.bio).

PL spectroscopy: Fluorescence studies of the samples were carried out in a Perkin Elmer LS55 Fluorescence Spectrometer instrument using the front face geometry. The samples were excited at 340 nm wavelength and emission scans were recorded from 350 to 750 nm.

Rheology study: The rheological measurement of the organogels were studied under dynamic and steady shear measurement at room temperature (25 °C) on parallel-plate geometry (25 mm diameter, 1 mm gap). Rheological experiment was carried out using and SDT Q Series Advanced Rheometer AR 2000. Visco-elastic measurement of the organogel was performed at room temperature using parallel-plate geometry (PP-25 mm, gap 0.5 mm).

Time-Correlated Single Photon Counting (TCSPC) study: TCSPC measurements were performed by Horiba JobinYvon IBH instrument having MCP PMT Hamamatsu R3809 detector.

Quantum Yield Measurement: For the compounds the quantum yield (Φ) has been calculated using Quinine Sulphate as a standard reference dye.[1]

I-V Measurement: The electrical conductivity of the xerogels (obtained from organogels) prepared were measured using the two-probe method. The gel materials were placed on indium-tin oxide (ITO) conducting strips and allowed to dry in air for 2 days, and then under

vacuum for another 2 days to make xerogels. The areas of the sample thin films were 0.8 cm^2, and the average thicknesses of the samples were 250 nm. The conductivity of the samples were measured by an electrometer (Keithley, model 2401) at 30 ^{0}C under inert atmosphere (Argon atmosphere). Current-voltage (I-V) studies were performed by varying the voltage from -5 to +5 V and measuring the current at each applied voltage.

Synthesis of the molecules

Synthesis of molecule P1:

Synthesis of Boc-Acp-Phe-C_{12}: The synthetic procedure has been described in *Biomacromolecules*, **2017**, 18, 3621–3629.

Synthesis of H_2N-Acp-Phe-C_{12}: The synthetic procedure has been described in *Biomacromolecules*, **2017**, 18, 3621–3629.

Synthesis of C_{12}-Phe-Acp-NDI-Acp-Phe-C_{12} (P1): H_2N-Acp-Phe-C_{12} (557 mg, 1.25 mmol) and naphthalene dianhydride (NDA) (134 mg, 0.5 mmol) were taken in a 100 ml round bottom flask. 10 ml dry DMF was added and the reaction mixture was stirred for 12 h at 130°C under N_2 atmosphere. After that reaction mixture was cooled down to room temperature and 30 ml ethyl acetate was gradually added. A precipitate was appeared and filtered by Buchner funnel. The solid product was purified by column chromatography by 1%methanol in chloroform as an eluent. **Yield:** 280 mg (0.25 mmol, 50%).

^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ 8.73 (4H, s, NDI), 7.05-7.47 (10H, m, CH of Phe), 6.22 (2H, br s, NH), 5.74 (2H, br s, NH), 4.53 (2H, m, α-CH of Phe), 4.19-4.16 (4H, t, J= 7.5Hz, $^{\alpha}CH_2$), 3.13-2.89 (8H, m, $^{\beta}CH_2$ of Phe and C_{11}-H of dodecyl amine), 2.12 (4H, m, -CH_2CO), 1.75-1.21 (52H, m, $^{\beta}CH_2$, $^{\gamma}CH_2$, $^{\delta}CH_2$ and chain CH_2s), 0.89-0.86 (6H, t, CH_3). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 170.69, 163.66, 162.96, 155.16, 137.04, 131.11, 129.40, 128.84, 127.17, 126.88, 126.81, 93.84, 54.93, 40.76, 39.70, 38.98, 36.43, 32.07, 29.78, 29.73, 29.64, 29.49, 29.43, 29.36, 27.81, 26.92, 26.63, 25.25, 22.83, 14.23. **MALDI-TOF MS:** 1145.741 $[M+Na]^+$.

Synthesis of molecule P2:

Synthesis of C_{12}-Phe-OMe: Dodecanoic acid (2 g, 10 mmol) was dissolved in 10 ml DMF in a 250 ml round bottom flask in an ice water bath. 1.48 g (11 mmol) HOBt was added to it. H-

Phe-OMe was obtained by neutralization with saturated Na_2CO_3 from its hydrochloride salt and subsequent extraction with ethyl acetate. The ethyl acetate solution was then concentrated to 10 mL and added to the DMF solution followed by 2.47 g (12 mmol) of N,N-dicylohexylcarbodiimide (DCC). The reaction mixture was diluted with ethyl acetate and filtered to separate N, N- dicyclohexyl urea (DCU). The organic layer was washed with 1(N) HCl (3 × 30 ml), brine (1 × 30 ml), saturated sodium carbonate (3 × 30 ml) and brine (2 × 30 ml), dried over anhydrous Na_2SO_4 and evaporated in vacuum. A white material was obtained. **Yield:** 2.59 g (7.2 mmol, 70%)

^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ 7.31-7.08 (5H, m, CH of Phe), 5.86-5.84 (1H, d, NH), 4.93-4.88 (1H, m, $^{\alpha}$CH of Phe), 3.73 (3H, s, OMe), 3.18-3.06 (2H, m, $^{\beta}CH_2$ of Phe), 2.18-2.14 (2H, t, J= 8 Hz, $^{\alpha}CH_2$), 1.60-1.25 (18H, m, chain CH_2s), 0.89-0.86 (3H, t, J= 7.2 Hz). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 172.80, 172.35, 136.07, 129.41, 128.70, 127.26, 53.05, 52.42, 38.11, 36.73, 32.06, 29.75, 29.61, 29.47, 29.36, 25.70, 22.82, 14.24. **HRMS (m/z)**: 362.2993 $[M+H]^+$, 384.2798 $[M+Na]^+$.

Synthesis of C_{12}-Phe-OH: 2.16 g (6 mmol) of C_{12}-Phe-OMe was taken in a roundbottomed flask and it was dissolved in 50 mL methanol. 13 mL of 1 (N) NaOH was added to it and kept under stirring for 6 hours. The progress of hydrolysis was monitored by thin layer chromatography (TLC). After the completion of the reaction, as indicated by TLC, the methanol was removed in vacuum. The aqueous was acidified with 1 (N) HCl and extracted with ethyl acetate (3 x 40 mL). The ethyl acetate extract was dried over anhydrous sodium sulfate and evaporated in vacuum to obtain a white sticky product. **Yield:** 1.91 g (5.5 mmol, 91.66 %).

^{1}H NMR (500 MHz, DMSO-d_6, 25 °C): δ 8.08-8.07 (1H, d, NH), 7.26-7.16 (5H, m, CH of Phe), 4.44-4.39 (1H, m, $^{\alpha}$CH of Phe), 3.06-3.02 (2H, dd, *J*= 4.5 Hz, $^{\beta}CH_2$ of Phe), 2.03-2.00 (2H, t, *J*= 7.5 Hz, $^{\alpha}CH_2$), 1.39-1.08 (18H, m, chain CH_2s), 0.86-0.83 (3H, t, J= 7 Hz, CH_3). **^{13}C NMR** (125MHz, DMSO-d_6): δ 173.11, 172.30, 137.74, 129.01, 128.06, 126.30, 53.22, 36.80, 35.11, 31.25, 28.96, 28.86, 28.74, 28.64, 28.42, 25.15, 22.05, 13.88. **HRMS (m/z)**: 370.1092 $[M+Na]^+$.

Synthesis of mono-Boc protected hexamethylenediamine: Hexamethylenediamine (6.96 g, 60 mmol) was taken in a 250 ml round bottom flask and it was dissolved in 100ml

dichloromethane. 2.18 g (10 mmol) di-tertbutyl dicarbonate was dissolve in 50 ml dichloroform and it was take in dropping funnel. Di-tertbutyl dicarbonate solution was added dropwise over a period of 3 h at 0°C and it was stirred at room temperature for 24 h. Upon completion of thereaction, water was added to the reaction mixture and the organic layer was separated, washed with brine, dried over anhydrous Na_2SO_4, and evaporated in vacuum. **Yield:** 1.73 g (8 mmol, 80 %).

Synthesis of Boc-C_6-Phe-C_{12}: C_{12}-Phe-OH (1.76 g, 5 mmol) was dissolved in 10 ml DMF in a 250 ml round bottom flask in an ice water bath 675 mg (5 mmol) HOBt was added to it. Then monoboc protected hexamethylenediamine (1.29 g, 6 mmol) followed by DCC (1.236 g, 6 mmol) was added to the reaction mixture. The reaction mixture was allowed to come to room temperature and stirred for 48 h. The reaction mixture was diluted with ethyl acetate and filtered to separate N, N- dicyclohexyl urea (DCU). The organic layer was washed with 1(N) HCl (3 × 30 ml), brine (1 × 30 ml), saturated sodium carbonate (3 × 30 ml) and brine (2 × 30 ml), dried over anhydrous Na_2SO_4 and evaporated in vacuum. A white material was obtained. **Yield:** 1.91 g (3.5 mmol, 70%).

^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ 7.30-7.20 (5H, m, CH of Phe), 6.27 (1H, brs, NH), 5.87 (1H, brs, NH), 4.61-4.57 (2H, m, $^{\alpha}$CH of Phe and NH), 3.15-2.97 (4H, m, $^{\beta}CH_2$ of Phe), 2.17-2.14 (2H, t, J= 7.5 Hz, $^{\alpha}CH_2$), 1.56-1.15 (26H, m, chain CH_2s), 0.89-0.86 (3H, t, J= 7 Hz). **^{13}C NMR** (125 MHz, $CDCl_3$): δ 173.26, 170.95, 156.20, 137.07, 129.41, 128.76, 127.08, 54.75, 40.43, 39.32, 38.75, 36.75, 32.05, 30.04, 29.75, 29.60, 29.47, 29.33, 29.25, 28.59, 26.28, 26.23, 25.73, 22.81, 14.23. **HRMS(m/z)**: 568.2355 $[M+Na]^+$.

Synthesis of H_2N-C_6-Phe-C_{12} ($C_{27}H_{47}N_3O_2$): To 1.63 g (3 mmol) of Boc-C_6-Phe-C_{12}, 5 ml of 98% formic acid was added and the removal of the Boc group was monitored by TLC. After 6 h, formic acid was removed under a vacuum. The residue was taken in water (8 ml) and pH of the aqueous solution was then adjusted to 8.0 with 30% aqueous NH_3. The aqueous portion was evaporated in a vacuum. A white material was obtained, purified using basic alumina in chloroform and methanol (9:1) as eluent. **Yield:** 1.11 g (2.5 mmol, 83%)

^{1}H NMR (500 MHz, DMSO-d_6, 25 °C): δ 7.96-7.95 (1H, d, NH), 7.86 (1H, br, NH), 7.24-7.16 (5H, m, CH of Phe), 4.44-4.43 (1H, m, $^{\alpha}$CH of Phe), 3.03-2.90 (4H, m, $^{\beta}CH_2$ of Phe and

$^{\alpha}CH_2$), 2.02-1.99 (2H, t, J= 7.5Hz, $^{\alpha}CH_2$), 1.38-1.06 (26H, m, chain CH_2s), 0.86-0.83 (3H, t, J= 7 Hz, CH_3). **^{13}C NMR** (125MHz, DMSO-d_6): δ 172.19, 171.08, 169.19, 138.03, 129.15, 128.00, 126.20, 53.98, 37.92, 35.27, 31.33, 29.10, 29.04, 28.93, 28.82, 28.73, 28.48, 26.17, 26.08, 26.02, 25.92, 25.23, 22.62, 22.13, 13.98. **HRMS(m/z)**: 446.5065 $[M+Na]^+$.

Synthesis of C_{12}-Phe-C_6-NDI-C_6-Phe-C_{12} (P2): H_2N-C_6-Phe-C_{12} (890 mg, 2 mmol) and naphthalene dianhydride (NDA) (238 mg, 0.89 mmol) were taken in a 100 ml round bottom flask. 15 ml dry DMF was added and the reaction mixture stirred for 12 h at 130°C under N_2 atmosphere. After that reaction mixture was cooled down to room temperature and 30 ml ethyl acetate added. A precipitate was appeared and filtered by Buchner funnel. The solid product was purified by column chromatography by 1% methanol in chloroform as an eluent. **Yield**: 617 mg (0.55 mmol, 61.7%).

^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ 8.77-8.76 (4H, d, NDI, J= 8 Hz), 7.30-7.20 (10H, m, CH of Phe), 6.15-6.13 (2H, d, NH), 5.70-5.67 (2H, t, J= 5.6 Hz, NH), 4.61-4.56 (2H, m, $^{\alpha}$CH of Phe), 4.18-4.14 (4H, t, J= 7.6 Hz, $^{\alpha}CH_2$), 3.75-3.69 (4H, m, $^{\alpha}CH_2$), 3.19-2.94 (4H, m, $^{\beta}CH_2$ of Phe), 2.18-2.14 (4H, t, J= 8 Hz, $^{\beta}CH_2$), 1.41-1.22 (52H, m, chain CH_2s), 0.89-0.86 (3H, t, J= 7.2 Hz, CH_3). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 173.19, 171.02, 162.83, 137.09, 131.19, 129.42, 128.83, 127.14, 58.64, 54.99, 39.20, 36.80, 32.06, 29.85, 29.76, 29.61, 29.48, 29.34, 25.73, 22.83, 18.60, 14.25. **MALDI-TOF MS:** 1146.161 $[M+H+Na]^+$.

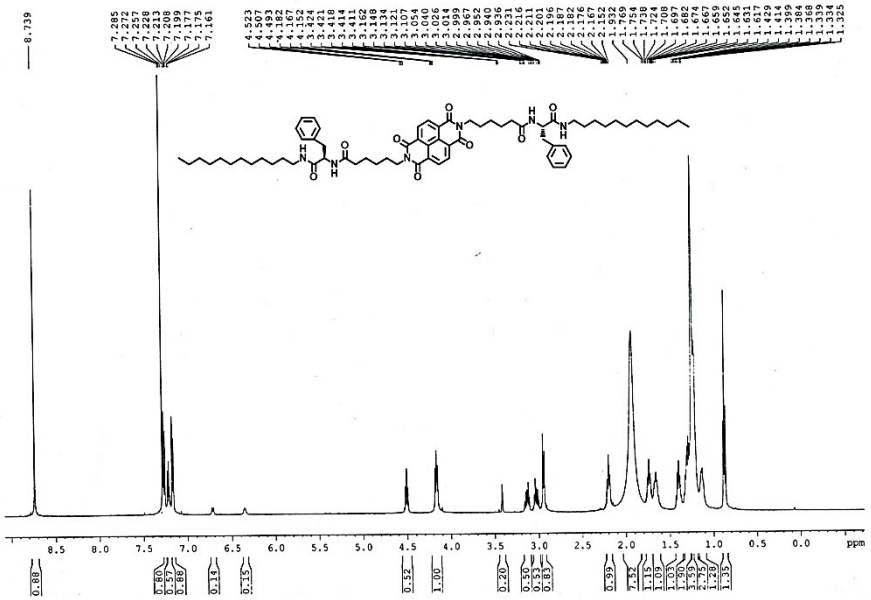

Fig.S1** [1]H-NMR spectrum of **P1.

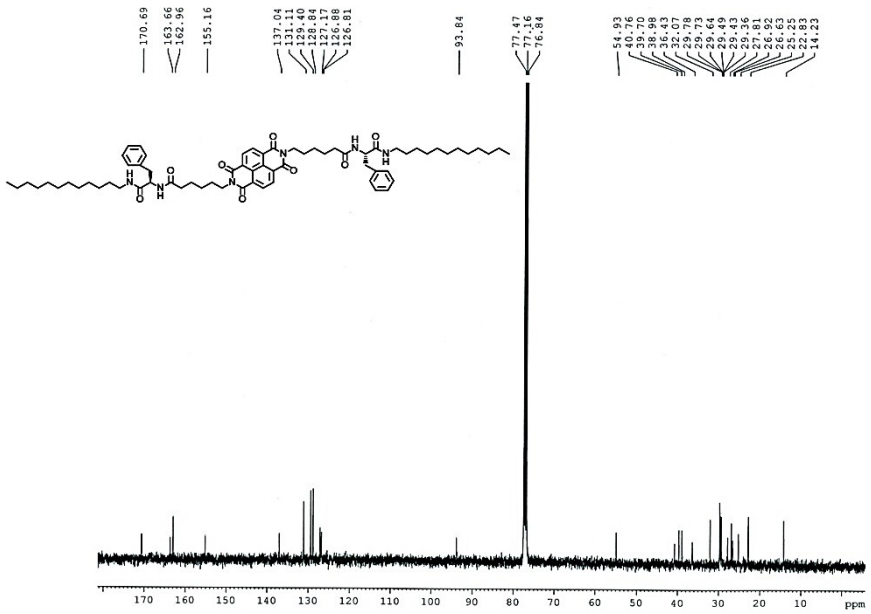

Fig. S2*[13]C-NMR spectrum of* ***P1.***

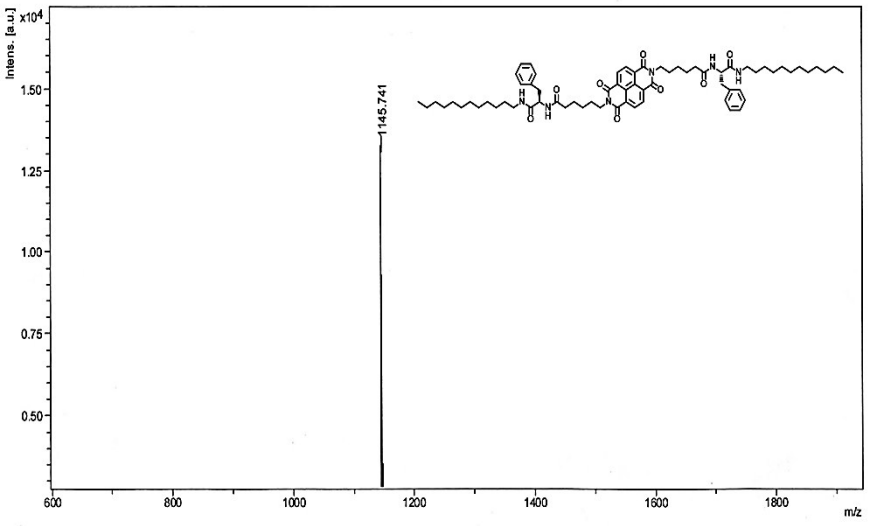

Fig. S3*MALDI-TOF MS spectrum of* ***P1.***

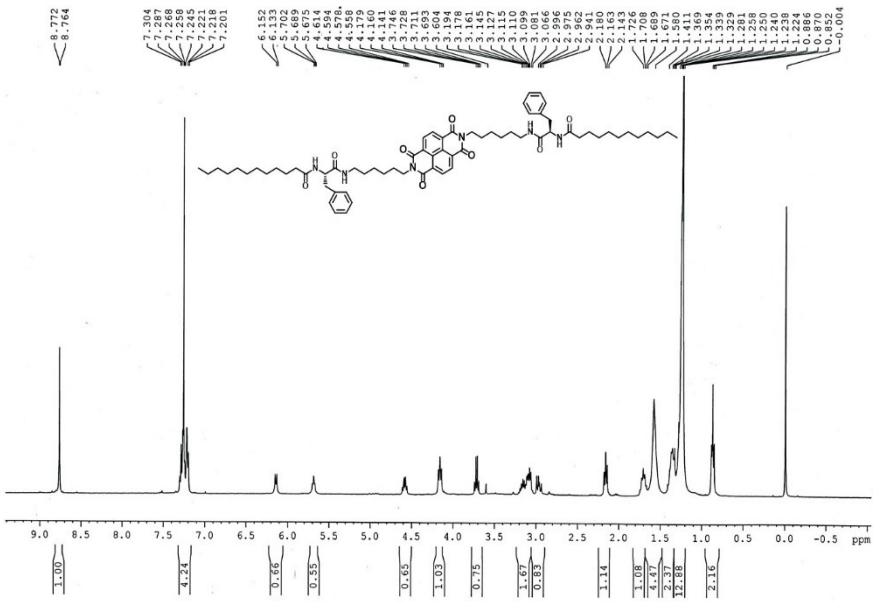

Fig. S4 *[1]H-NMR spectrum of* ***P2.***

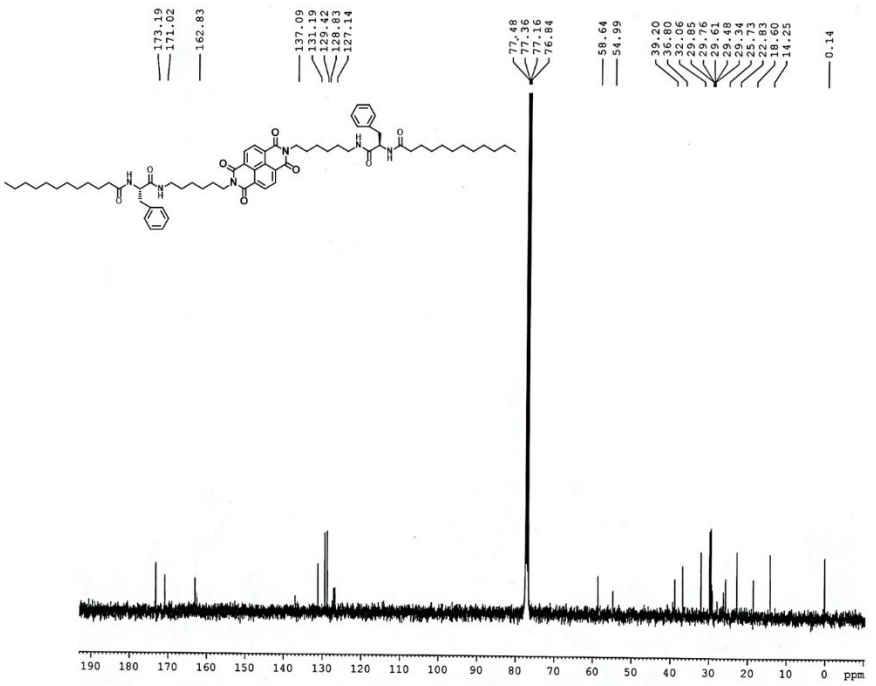

Fig. S5 [13]C-NMR spectrum of **P2.**

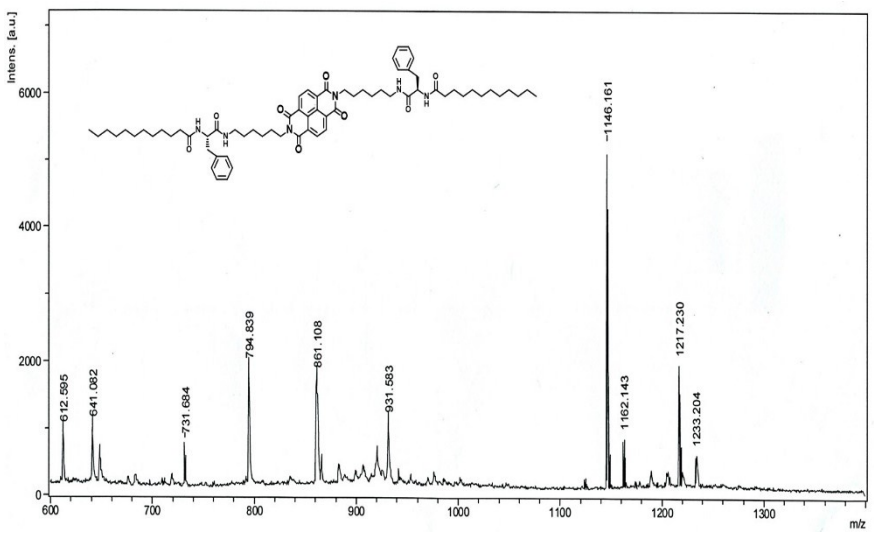

Fig.S6 MALDI-TOF MS spectrum of **P2.**

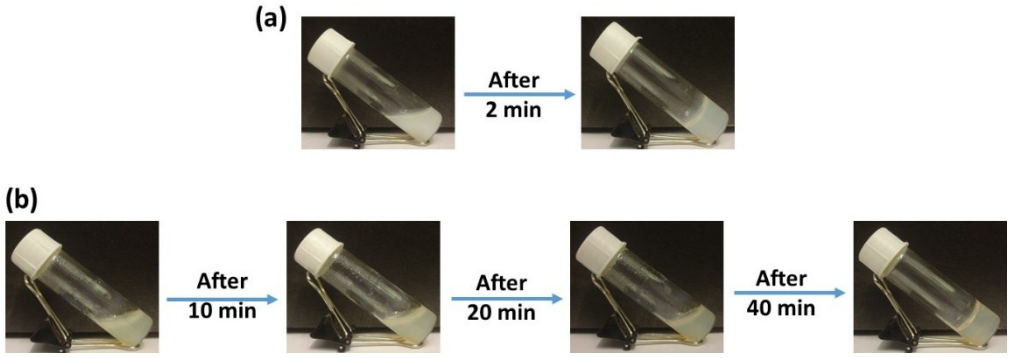

Fig. S7 Photographs of the gels formed with time demonstrating the gel formation kinetics of (a) P1 and (b) P2 compounds.

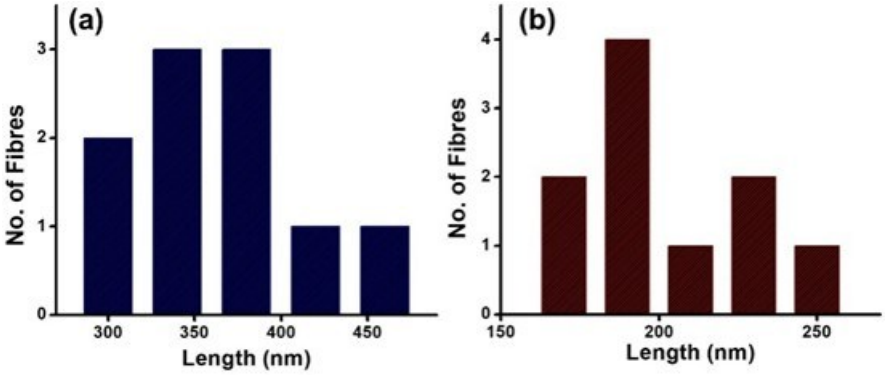

Fig. S8 Size distribution curve by calculating the widths of the nanofibers from the FE-SEM images of (a) **P1** and (b) **P2** xerogels.

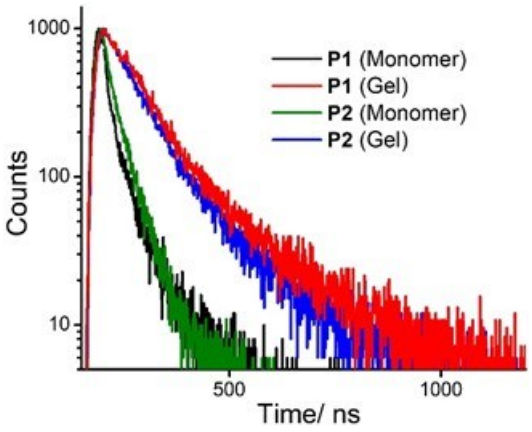

Fig. S9 TCSPC decay profiles of **P1** and **P2** in their monomeric (monitored = 410 nm) and gel ($CHCl_3$-MCH: 5:95) conditions (monitored = 540 nm) at 0.5 mM concentration.

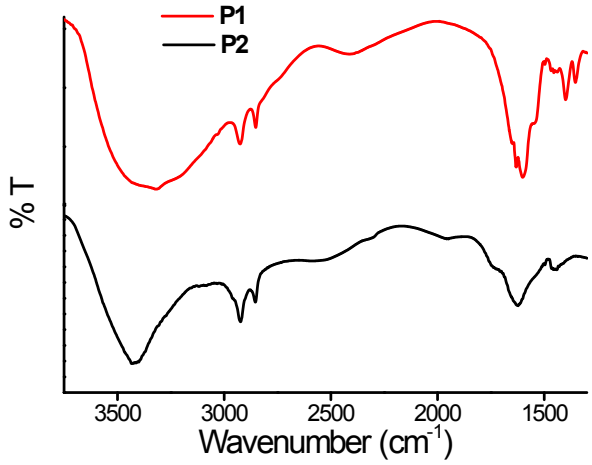

Fig. S10 Extended FTIR spectra of xerogels **P1** and **P2** gels prepared from $CHCl_3$-MCH (5:95 v/v) mixture.

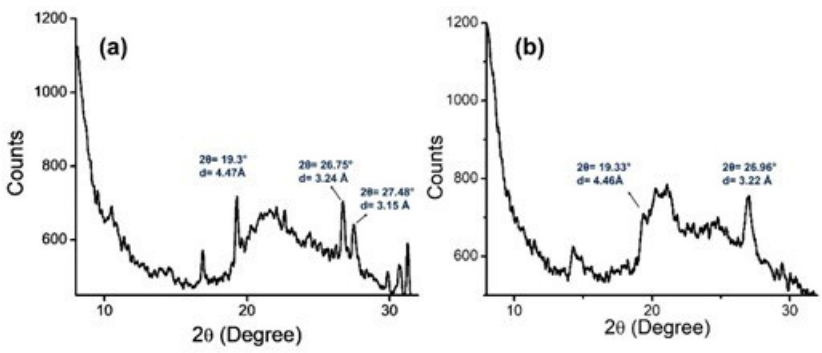

Fig. S11 Powder X-ray diffraction pattern obtained from (a) **P1** and (b) **P2** xerogels prepared in gelling solvent ($CHCl_3$: MCH= 5:95 v/v).

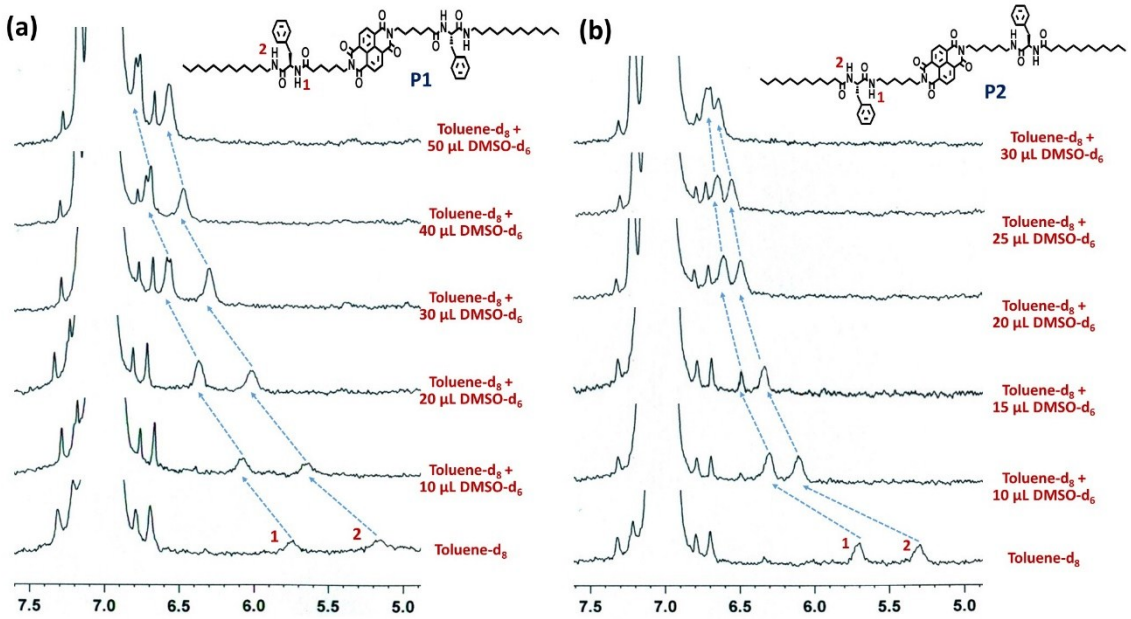

Fig S12. ^1H NMR spectrum of (a) **P1** and (b) **P2** (in tolune-d_8) upon gradual addition of DMSO-d_6 (at 85 ^0C).

Table S1. Chemical shift values (in ppm) for NH(1) and NH(2) for (a) **P1** and (b) **P2** in pure toluene-d_8 and in various composition of toluene-d_8+DMSO-d_6 mixture (at 85 ^0C).

(a)

Added DMSO-D_6 (µL)	NH(1) peak position	NH(2) peak position
0	5.744	5.170
10	6.100	5.654
20	6.351	6.006
30	6.592	6.302
40	6.690	6.475
50	6.785	6.593

(b)

Added DMSO-D_6 (µL)	NH (1)peak position	NH(2) peak position
0	5.697	5.294
10	6.303	6.112
15	6.553	6.352
20	6.592	6.476
25	6.652	6.556
30	6.695	6.642