Electronic Supplementary Information

Aggregation Induced Emission Switching and Electrical Properties of Chain Length dependent π-Gels of Phenylenedivinylene bis-Pyridinium Salts in Alcohol-Water Mixtures

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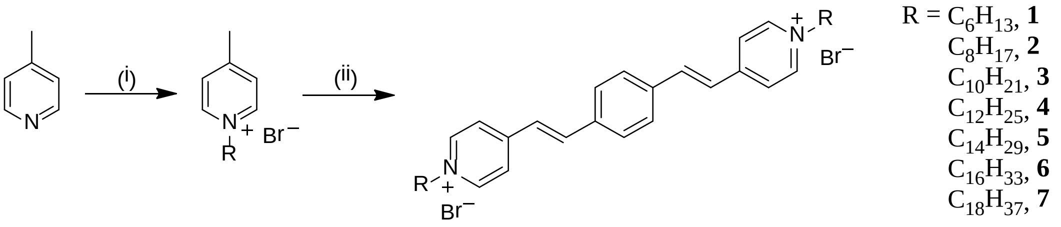
(a) Synthetic Schemes and Characterization



Scheme S1. *Reagents, conditions, and yields:* (i) R-Br, EtOH, reflux, 12 h; (ii) Terephthaldehyde, K_2CO_3 or NaOH, EtOH/H_2O, 0 °C, 2 h, 26-52 %.

General procedure for the Synthesis of 1-7. Compounds **1-4** were synthesized upon modification of reported literature procedures [S1] and [S2]. A mixture of each alkyl bromide ($C_nH_{2n+1}Br$, *n* = 6, 8, 10 and 12) and 4-picoline (1:2, mole) was individually refluxed in ethanol for 12 h to obtain the corresponding 4-picolinium salts. Then the reaction mixture was cooled and excess 4-picoline was removed under vacuum followed by repeated washing with hexane giving rise to white solid. Respective 4-picolinium salt as obtained and terephthaldehyde were dissolved in a 2:1 molar ratio in ethanol and the aqueous solution (2 mL) of 2 equivalent of either K_2CO_3 (for **1-3**) or NaOH (for **4**) was added drop-wise into the ethanol solution at ice-cold condition. The mixture was stirred at ice-cold condition for 2 h and then the reaction was quenched by acidification with 3N HCl. Ethanol was removed under vacuum and the precipitate was filtered and washed with ice-cold water. The crude product was dissolved in methanol and precipitated using ethyl acetate and filtered to get yellow solid. This cycle was repeated several times until pure product was obtained as indicated from TLC.

Compound 1 (4,4'-((1E,1'E)-1,4-phenylenebis(ethene-2,1-diyl))bis(1-hexylpyridin-1-ium) bromide): Yield 26%; FT-IR (Neat): υ_{max} = 2926, 2851, 1615, 1522, 1479, 1359, 1209, 1172, 996, 874, 726 cm^{-1}. ^1H NMR (500 MHz, CD_3OD) δ (ppm) 0.91-0.93 (t, 6 H, CH_3), 1.27-1.38 (m, 12 H, CH_2), 2.01 (m, 4 H, N^+-CH_2-CH_2), 4.54 (t, 4 H, N^+-CH_2), 7.53-7.56 (d, J = 16.5, 2 H, vinylic), 7.86 (s, 4 H, aromatic), 7.96-7.99 (d, J = 16.0, 2 H, vinylic), 8.21- 8.22 (d, J = 6.0, 4 H, aromatic), 8.82- 8.83 (d, J = 6.0, 4 H, aromatic). ^{13}C NMR (125 MHz, CD_3OD) δ (ppm) 14.23, 23.46, 26.89, 32.29, 32.32, 62.04, 125.30, 125.59, 128.69, 130.11, 130.83, 138.64, 141.85, 145.35, 155.20. TOF-MS: calcd for $C_{32}H_{42}N_2^{2+}$: 227.1674 (M/Z); found: 227.1676. Anal. Calcd. For $C_{32}H_{42}N_2Br_2$: C, 62.55; H, 6.89; N, 4.56, found: C, 62.63; H, 6.88; N, 4.84.

Compound 2 (4,4'-((1E,1'E)-1,4-phenylenebis(ethene-2,1-diyl))bis(1-octylpyridin-1-ium) bromide): Yield 29%; FT-IR (Neat): υ_{max} = 2920, 2852, 1615, 1519, 1468, 1353, 1328, 1210, 1173, 979, 847, 723 cm^{-1}. ^1H NMR (500 MHz, CD_3OD) δ (ppm) 0.88-0.90 (t, 6 H, CH_3), 1.30-1.39 (m, 20 H, CH_2), 2.01 (m, 4 H, N^+-CH_2-CH_2), 4.54 (t, 4 H, N^+-CH_2), 7.53-7.56 (d, J = 16.0, 2 H, vinylic), 7.86 (s, 4 H, aromatic), 7.96-8.00 (d, J = 16.5, 2 H, vinylic), 8.21- 8.22 (d, J = 6.5, 4 H, aromatic), 8.82- 8.83 (d, J = 6.5, 4 H, aromatic). ^{13}C NMR (125 MHz, CD_3OD) δ (ppm) 14.38, 23.65, 27.22, 30.09, 30.18, 32.38, 32.86, 62.03, 125.29, 125.57, 130.11, 138.63, 141.83, 145.35, 155.17. TOF-MS: calcd for $C_{36}H_{50}N_2^{2+}$: 255.1987 (M/Z); found: 255.1985. Anal. Calcd. For $C_{36}H_{50}N_2Br_2.2H_2O$: C, 61.19; H, 7.70; N, 3.96; found: C, 61.35; H, 8.02; N, 4.18.

Compound 3 (4,4'-((1E,1'E)-1,4-phenylenebis(ethene-2,1-diyl))bis(1-decylpyridin-1-ium) bromide): Yield 30%; FT-IR (Neat): υ_{max} = 2919, 2850, 1615, 1469, 1353, 1329, 1211, 1176, 978, 847, 722 cm^{-1}. ^1H NMR (400 MHz, CD_3OD) δ (ppm) 0.86-0.89 (t, 6 H, CH_3), 1.28-1.39 (m, 28 H, CH_2), 1.99-2.02 (m, 4 H, N^+-CH_2-CH_2), 4.52-4.56 (t, 4 H, N^+-CH_2), 7.52-7.56 (d, J = 16.4, 2 H, vinylic), 7.86 (s, 4 H, aromatic), 7.96-8.00 (d, J = 16.0, 2 H, vinylic), 8.21- 8.23 (d, J = 6.8, 4 H, aromatic), 8.82- 8.84 (d, J = 7.2, 4 H, aromatic). ^{13}C NMR (100 MHz, CD_3OD) δ (ppm) 14.40, 23.70, 27.21, 30.11, 30.37, 30.49, 30.56, 32.36, 33.02, 62.05, 125.30, 125.59, 130.11, 130.83, 138.64, 141.86, 145.35, 155.19. TOF-MS: calcd for $C_{40}H_{58}N_2^{2+}$: 283.2300 (M/Z); found: 283.2301. Anal. Calcd. For $C_{40}H_{58}N_2Br_2$: C, 66.11; H, 8.04; N, 3.85. Found: C, 66.10; H, 8.21; N, 3.77.

Compound 4 (4,4'-((1E,1'E)-1,4-phenylenebis(ethene-2,1-diyl))bis(1-dodecylpyridin-1-ium) bromide): Yield 35%; FT-IR (Neat): υ_{max} = 2918, 2849, 1617, 1520, 1467, 1353, 1329, 1211, 1175, 979, 846, 722 cm^{-1}. ^1H NMR (400 MHz, CD_3OD) δ (ppm) 0.86-0.89 (t, 6 H, CH_3), 1.22-1.39 (m, 36 H, CH_2), 1.99-2.02 (m, 4 H, N^+-CH_2-CH_2), 4.52-4.55 (t, 4 H, N^+-CH_2), 7.52-7.56 (d, J = 16.4, 2 H, vinylic), 7.86 (s, 4 H, aromatic), 7.95-7.99 (d, J = 16.0, 2 H, vinylic), 8.20- 8.22 (d, J = 6.8, 4 H, aromatic), 8.81- 8.83 (d, J = 6.8, 4 H, aromatic). ^{13}C NMR (100 MHz, CD_3OD) δ (ppm) 14.41, 23.72, 27.21, 30.11, 30.45, 30.48, 30.60, 30.72, 32.36, 33.06, 62.06, 125.03, 125.31, 125.59, 128.69, 130.12, 130.83, 138.65, 141.86, 145.36, 155.21. TOF-MS: calcd for $C_{44}H_{66}N_2^{2+}$: 311.5041 (M/Z); found: 311.3030. Anal. Calcd. For $C_{44}H_{66}N_2Br_2$: C, 67.51; H, 8.50; N, 3.58; found: C, 67.53; H, 8.77; N, 3.43.

Compound 5 (4,4'-((1E,1'E)-1,4-phenylenebis(ethene-2,1-diyl))bis(1-tetradecylpyridin-1-ium) bromide): Yield 38%; FT-IR (Neat): υ_{max} = 2918, 2848, 1617, 1520, 1467, 1353, 1211, 1176, 979, 846, 722 cm^{-1}. ^1H NMR (400 MHz, CD_3OD) δ (ppm) 0.86-0.89 (t, 6 H, CH_3), 1.26-1.39 (m, 44 H, CH_2), 1.98-2.01 (m, 4 H, N^+-CH_2-CH_2), 4.51-4.55 (t, 4 H, N^+-CH_2), 7.52-7.56 (d, J = 16.0, 2 H, vinylic), 7.86 (s, 4 H, aromatic), 7.95-7.99 (d, J = 16.4, 2 H, vinylic), 8.20-8.22 (d, J = 6.8, 4 H, aromatic), 8.81- 8.83 (d, J = 6.8, 4 H, aromatic). ^{13}C NMR (100 MHz, CD_3OD) δ (ppm) 14.41, 23.72, 27.20, 30.10, 30.46, 30.59, 30.70, 30.75, 32.34, 33.06, 62.07, 125.31, 125.58, 130.11, 138.65, 141.86, 145.36, 155.21. TOF-MS: calcd for $C_{48}H_{74}N_2^{2+}$: 339.5573 (M/Z); found: 339.3012. Anal. Calcd. For $C_{48}H_{74}N_2Br_2$: C, 68.72; H, 8.89; N, 3.34; found: C, 68.69; H, 9.17; N, 3.58.

Compound 6 (4,4'-((1E,1'E)-1,4-phenylenebis(ethene-2,1-diyl))bis(1-hexadecylpyridin-1-ium) bromide): Yield 50%; FT-IR (Neat): υ_{max} = 2918, 2848, 1617, 1520, 1467, 1352, 1211, 1176, 978, 846, 722 cm^{-1}. ^1H NMR (400 MHz, CD_3OD) δ (ppm) 0.86-0.89 (t, 6 H, CH_3), 1.26-1.39 (m, 52 H, CH_2), 2.01 (m, 4 H, N^+-CH_2-CH_2), 4.52-4.55 (t, 4 H, N^+-CH_2), 7.52-7.56 (d, J = 16.0, 2 H, vinylic), 7.86 (s, 4 H, aromatic), 7.95-7.99 (d, J = 16.4, 2 H, vinylic), 8.20-8.22 (d, J = 6.0, 4 H, aromatic), 8.81- 8.83 (d, J = 6.4, 4 H, aromatic). ^{13}C NMR (100 MHz, CD_3OD) δ (ppm) 14.42, 23.72, 27.19, 30.09, 30.46, 30.58, 30.69, 30.77, 32.34, 33.06, 62.07, 125.31, 125.57, 130.11, 145.36. TOF-MS: calcd for $C_{52}H_{82}N_2^{2+}$: 367.6105 (M/Z); found: 367.3281. Anal. Calcd. For $C_{52}H_{82}N_2Br_2$: C, 69.78; H 9.23; N 3.13; found: C, 69.61; H, 9.53; N, 3.06.

Compound 7 (4,4'-((1E,1'E)-1,4-phenylenebis(ethene-2,1-diyl))bis(1-octadecylpyridin-1-ium) bromide): Yield 52%; FT-IR (Neat): υ_{max} = 2918, 2849, 1616, 1519, 1468, 1353, 1210, 1175, 977, 847, 721 cm^{-1}. ^1H NMR (400 MHz, CD_3OD) δ (ppm) 0.89-0.93 (t, 6 H, CH_3), 1.24-1.42 (m, 60 H, CH_2), 2.04 (m, 4 H, N^+-CH_2-CH_2), 4.55-4.58 (t, 4 H, N^+-CH_2), 7.55-7.59 (d, J = 16.4, 2 H, vinylic), 7.89 (s, 4 H, aromatic), 7.98-8.02 (d, J = 16.0, 2 H, vinylic), 8.23-8.25 (d, J = 6.8, 4 H, aromatic), 8.84- 8.86 (d, J = 6.8, 4 H, aromatic). ^{13}C NMR (100 MHz, CD_3OD) δ (ppm) 14.41, 23.72, 27.21, 30.11, 30.48, 30.60, 30.72, 32.36, 33.06, 62.07, 125.31, 125.59, 130.12, 138.66, 141.87, 145.36, 155.22. TOF-MS: calcd for $C_{56}H_{90}N_2^{2+}$:

395.6636 (M/Z); found: 395.3410. Anal. Calcd. For $C_{56}H_{90}N_2Br_2$: C, 70.72; H, 9.54; N, 2.95; found: C, 70.51; H, 9.62; N, 2.83.

Reference

S1. B. Juskowiak, M. Ohba, M. Sato, S. Takenaka, M. Takagi, H. Kondo, *Bull. Chem. Soc. Jpn.* **1999**, *72*, 265–277.

S2. J. Tang, C. Wang, Y. Wang, J. Sunb, B. Yang, *J. Mater. Chem.* **2001**, *11*, 1370-1373.

(b) Supporting Figures

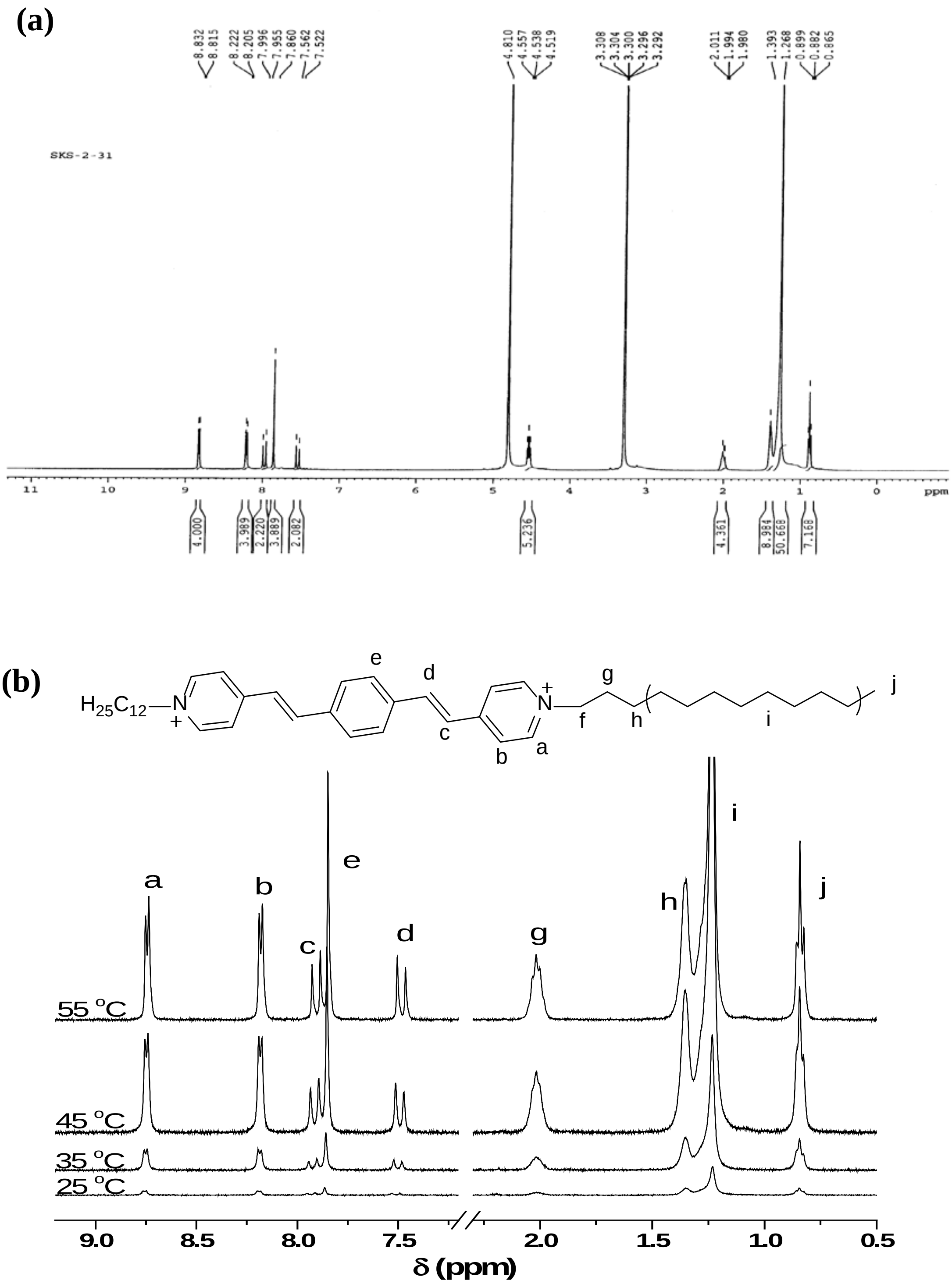


Fig. S1 (a) ^{1}H-NMR spectra of **5** in pure CD_3OD, all trans configuration of the two vinyl moiety was confirmed from the coupling constant values (*J* ≈ 16 Hz). (b) Variable temperature ^{1}H-NMR spectra of **4** (12 mg/mL) in CD_3OD/D_2O (3:2). The peaks were assigned for convenience.

Table S1. Gelation ability of compounds **4-6** in different ratio of EtOH/H_2O mixtures including the MGC values.[a]

Compounds	100 % EtOH	90 % EtOH, 10 % H_2O	80 % EtOH, 20 % H_2O	70 % EtOH, 30 % H_2O	60 % EtOH, 40 % H_2O	50 % EtOH, 50 % H_2O	40 % EtOH, 60 % H_2O
6	S	1.12	0.60	0.53	0.37	0.50	P
5	S	0.87	0.67	0.47	0.35	0.80	P
4	S	1.07	0.8	0.57	0.44	0.76	P

Table S2. Gelation ability of the compounds **1-7** in 60 % EtOH/H_2O mixture.[a]

	7	**6**	**5**	**4**	**3**	**2**	**1**
@ 60% EtOH/H_2O	W	0.37	0.35	0.44	1.36	2.73	S

Table S3. Gelation ability of compounds **4-6** in different solvents.[a]

Compounds	60% MeOH/H_2O	60% EtOH/H_2O	60% ^{n}PrOH/H_2O	60% ^{i}PrOH/H_2O	60% ^{t}BuOH/H_2O	Ethyleneglycol
6	0.67	0.37	0.77	0.61	0.88	0.41
5	0.68	0.35	0.55	0.34	0.77	0.33
4	1.17	0.44	1.06	0.56	0.63	0.76

[a] S = Sol, P = precipitate, W = weak gel. The numerical values indicate the MGC in wt% of the gelator molecules. All the gels were opaque in nature.

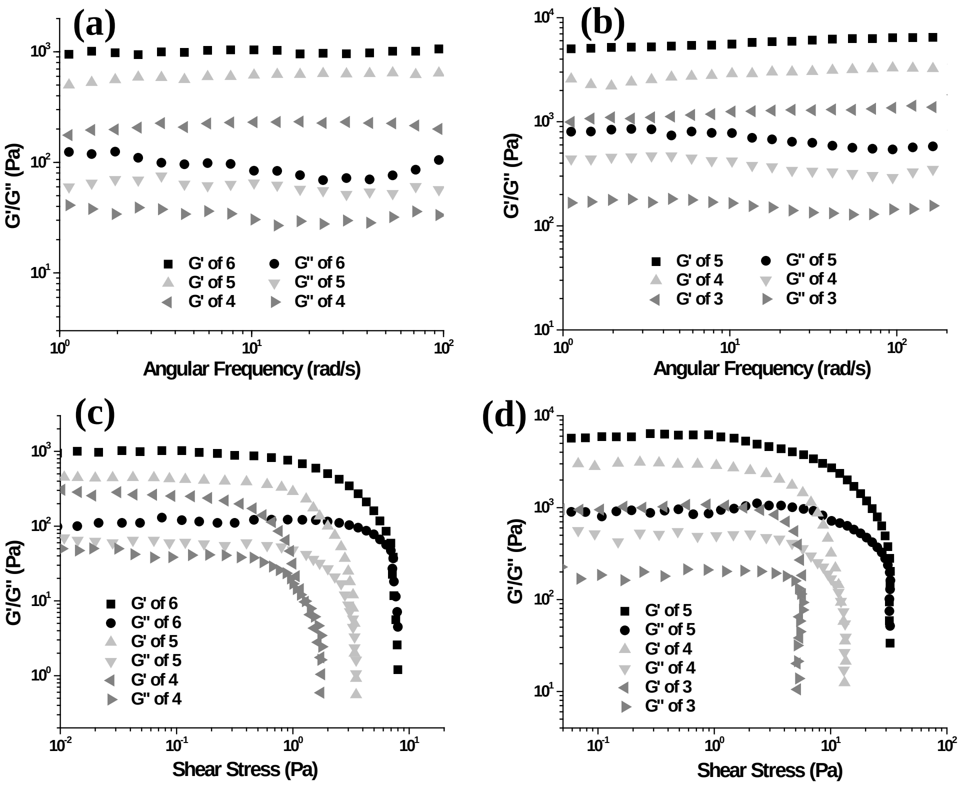


Fig. S2 Rheological experiments show oscillatory frequency sweep experiment of the gels derived from (a) **4, 5** and **6** at 10 mg/mL, (b) **3, 4** and **5** gels at 20 mg/mL; oscillatory amplitude experiment of (c) **4, 5** and **6** gels at 10 mg/mL, (d) **3, 4** and **5** gels at 20 mg/mL. 60% ethanol/water mixture was used in every instance.

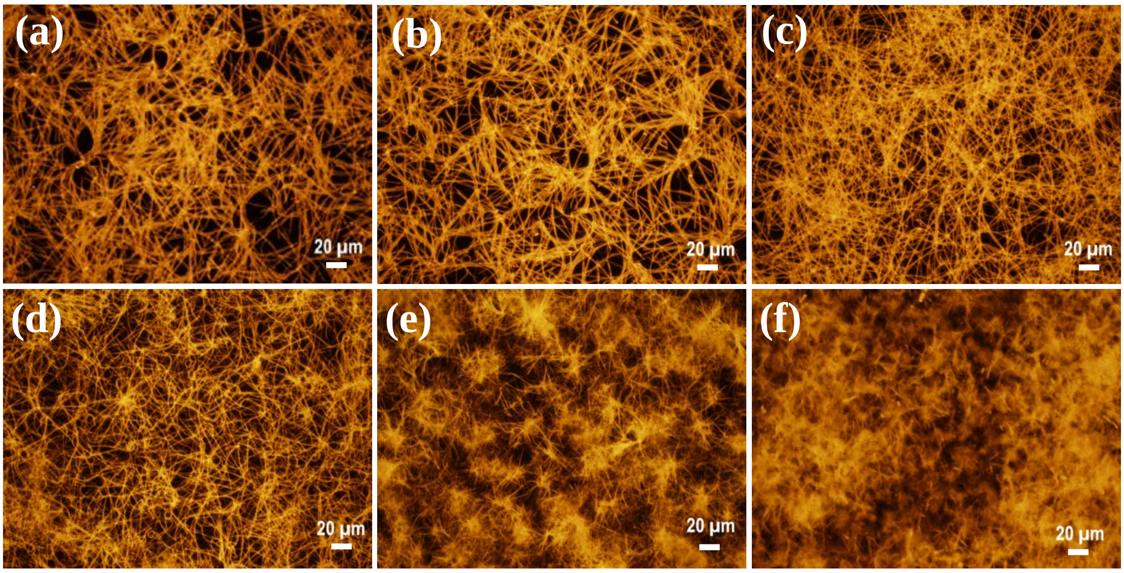


Fig. S3 Fluorescence microscopy images of a thin film of (a) **2**, (b) **3**, (c) **4**, (d) **5**, (e) **6** and (f) **7** when excited at wavelength range of 340-400 nm.

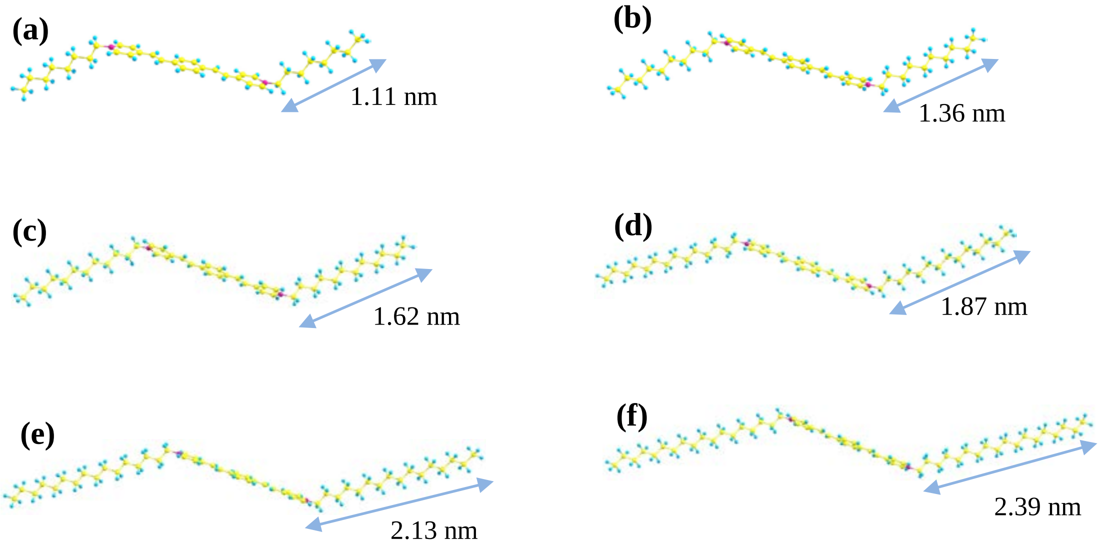


Fig. S4 Snapshots showing the energy minimized structures of (a) **2**, (b) **3**, (c) **4**, (d) **5** (e) **6** and (f) **7** using B3LYP 6-31G* basis set in gas phase. Double-head arrow indicates the length of the alkyl chain upto the pyridinium N^+.

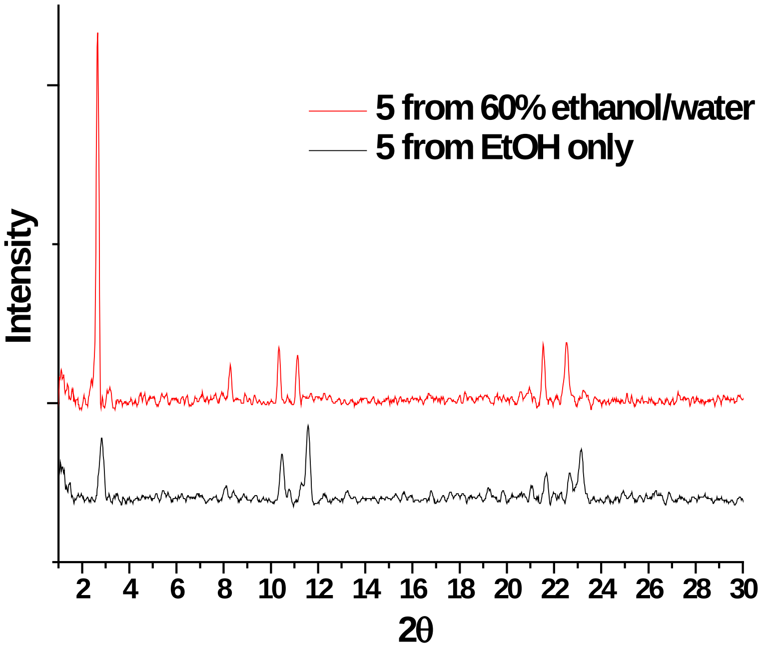


Fig. S5 X-ray diffraction pattern of frozen-dried gels of **5** from 60% ethanol/water and the thin film obtained from ethanol showing the existence of similar supramolecular organization.

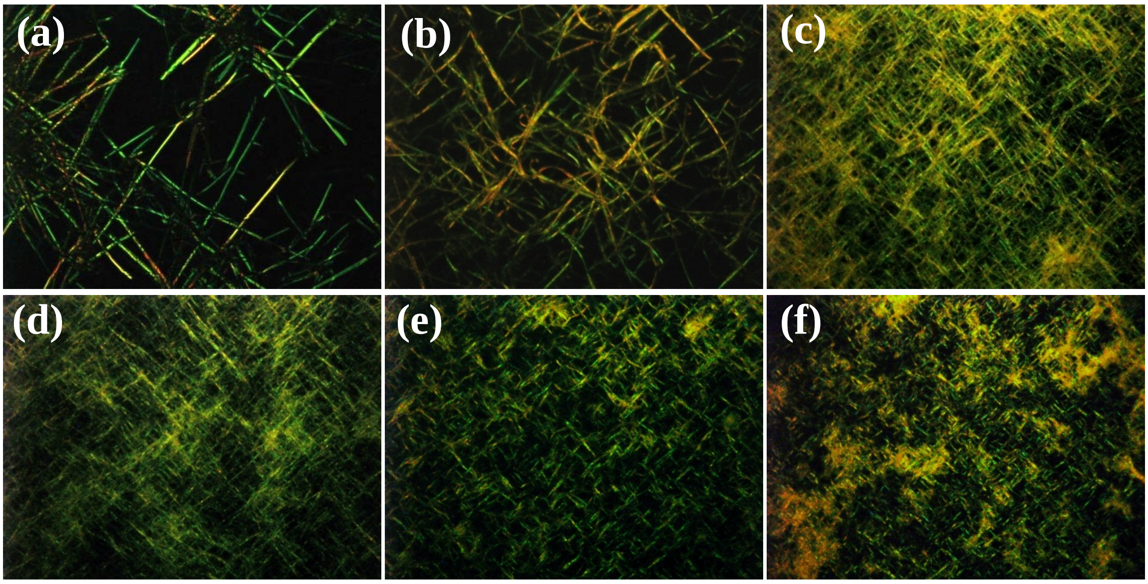


Fig. S6 Polarized optical microscopy images of the films of (a) **2**, (b) **3**, (c) **4**, (d) **5**, (e) **6**, (f) **7** at room temperature (Magnification 50x). [**2**-**7**] = 1 mg/mL in 60% EtOH/H_2O.

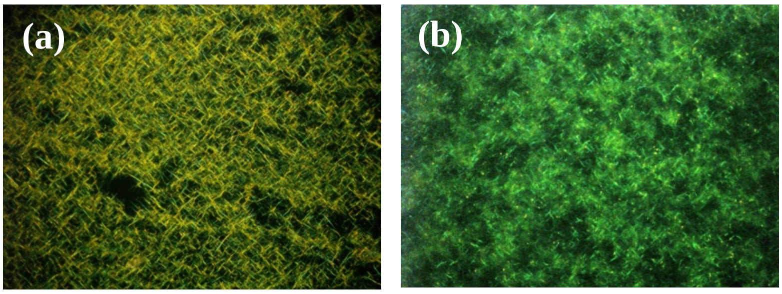


Fig. S7 Polarized optical microscopy images of **5** as a thin film obtained from (a) EtOH and (b) gel in 60% EtOH/H_2O (Magnification 20x).

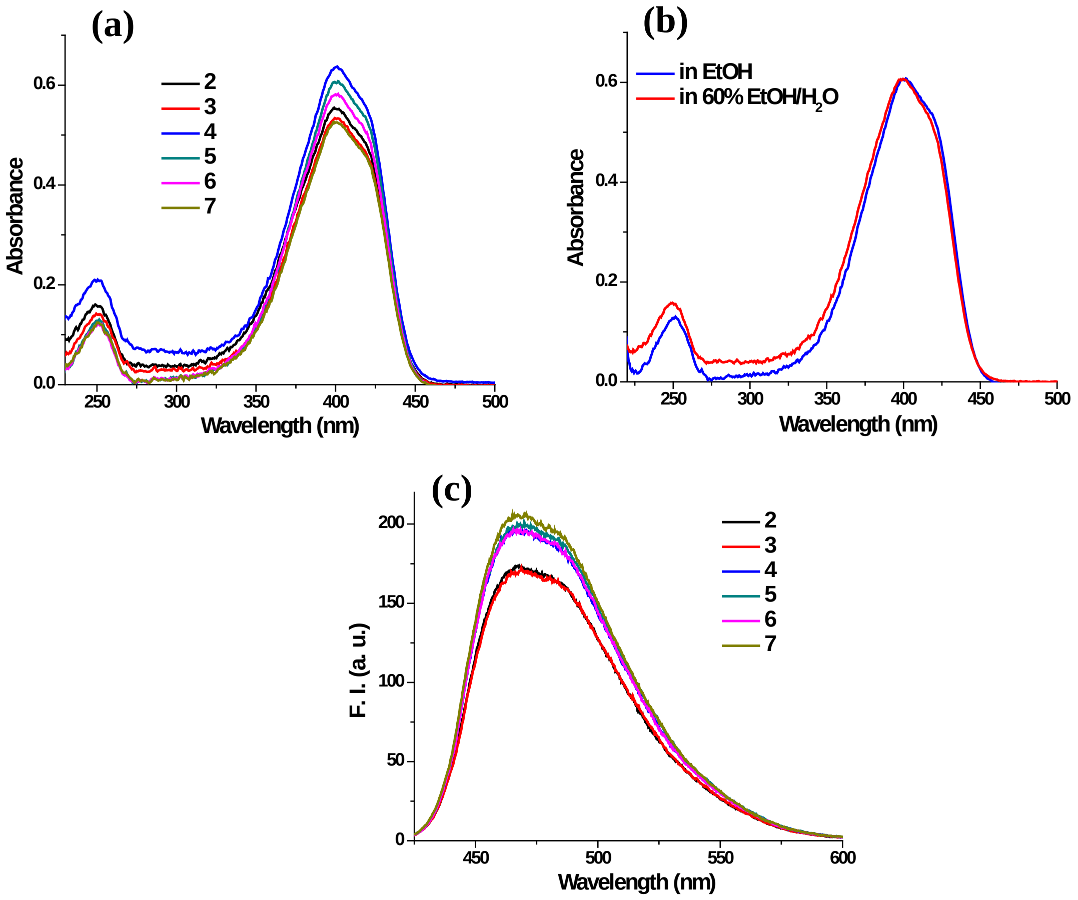


Fig. S8 (a) UV-vis spectra of **2-7** in ethanol at 1x10^{-5} M concentration. (b) UV-vis spectra of **5** in ethanol and in 60% ethanol/water mixture at 1x10^{-5} M concentration. (c) Fluorescence spectra of **2-7** in ethanol at 1x10^{-5} M concentration.

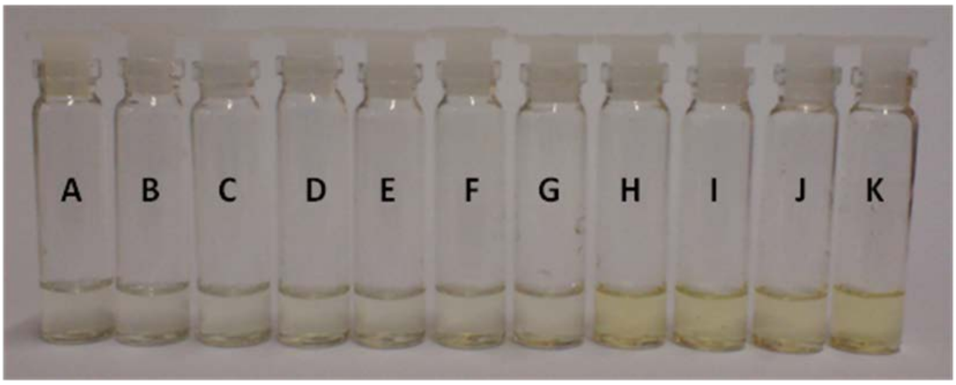


Fig. S9 Solutions of **5** (1x10^{-5} M) in different ethanol/water mixtures (% of EtOH)- (A) 100 %, (B) 90 %, (C) 80 %, (D) 70 %, (E) 60 %, (F) 50 %, (G) 40 %, (H) 30 %, (I) 20 %, (J) 10 %, (K) 0 %.

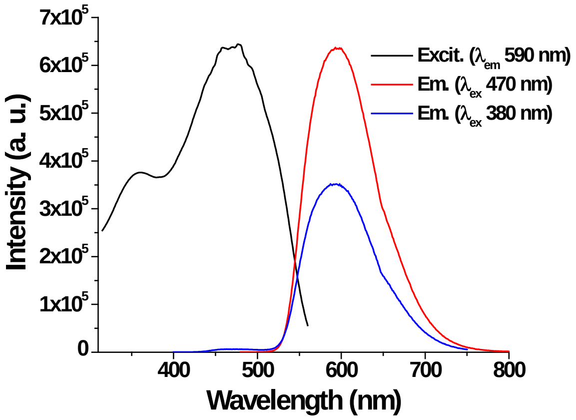


Fig. S10 Excitation and emission spectra of the gel of **5** (7 mg/mL) in 60% ethanol/water mixture recorded under front-face geometry at room temperature.

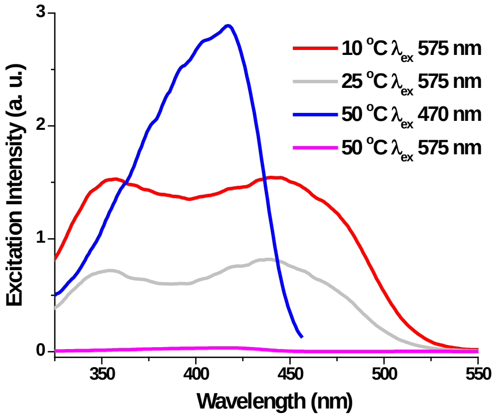


Fig. S11 Excitation spectra of **5** ($2x10^{-5}$ M) in 35% ethanol/water mixture at different temperatures. The spectra at 50 ^{o}C resembled monomeric absorption and thus the spectra showed negligible intensity when recorded at 575 nm.

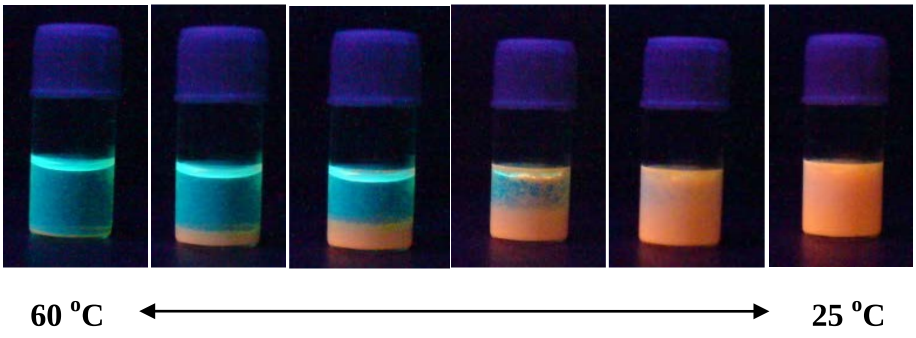


Fig. S12 Gel of **5** (10 mg/mL) in 60% ethanol/water mixture at various temperatures illuminated under 365 nm UV light.

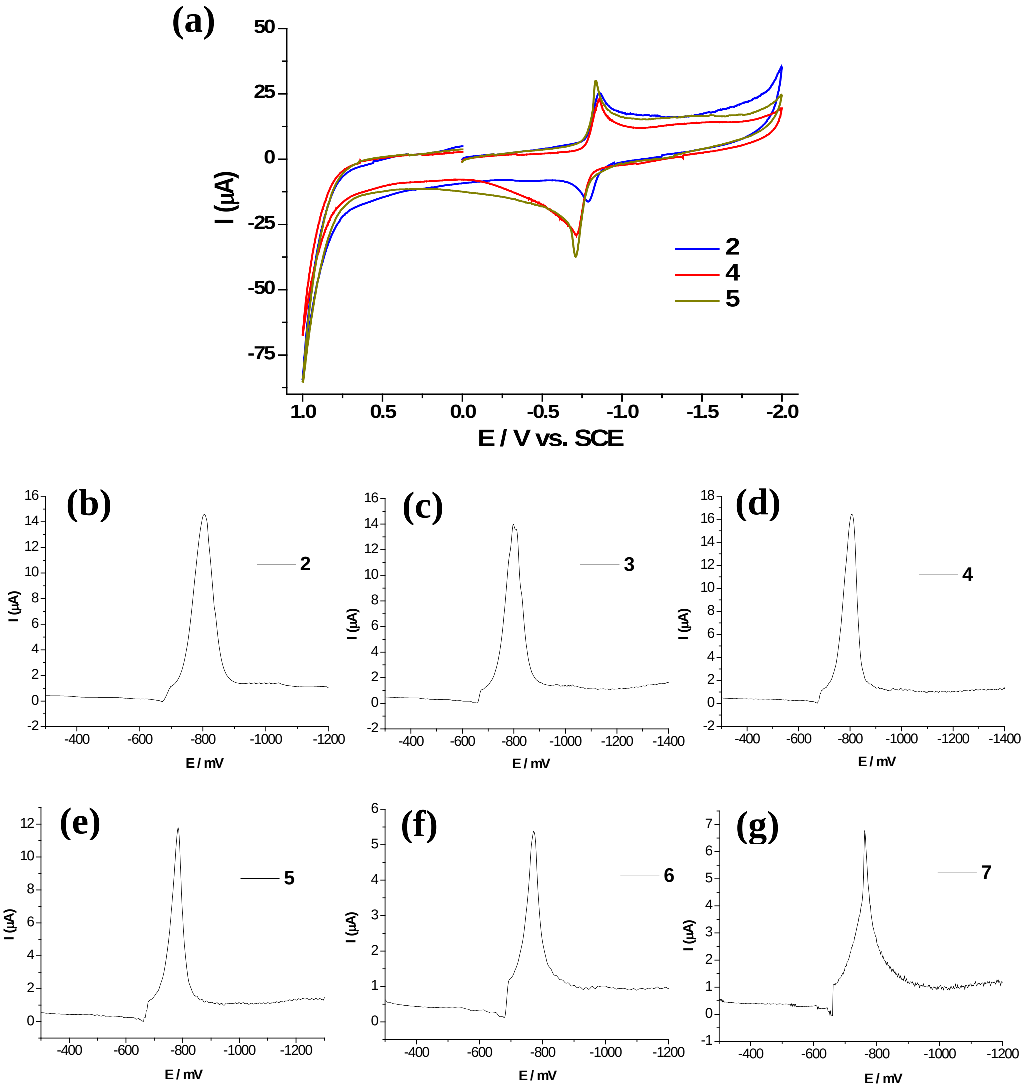


Fig. S13 (a) Cyclic voltammogram of 1 mM solution of each of **2**, **4** and **5** in DMSO at 100 mV/s in the range of (+)1 and (-)2 V showing the presence of only one reduction and oxidation peak. Differential pulse voltammogram of (b) **2**, (c) **3**, (d) **4**, (e) **5**, (f) **6** and (g) **7**. Concentration of individual compounds was 1 mM in DMSO in presence of 100 mM TBAP as the supporting electrolyte, scan rate was fixed at 5 mV/s.

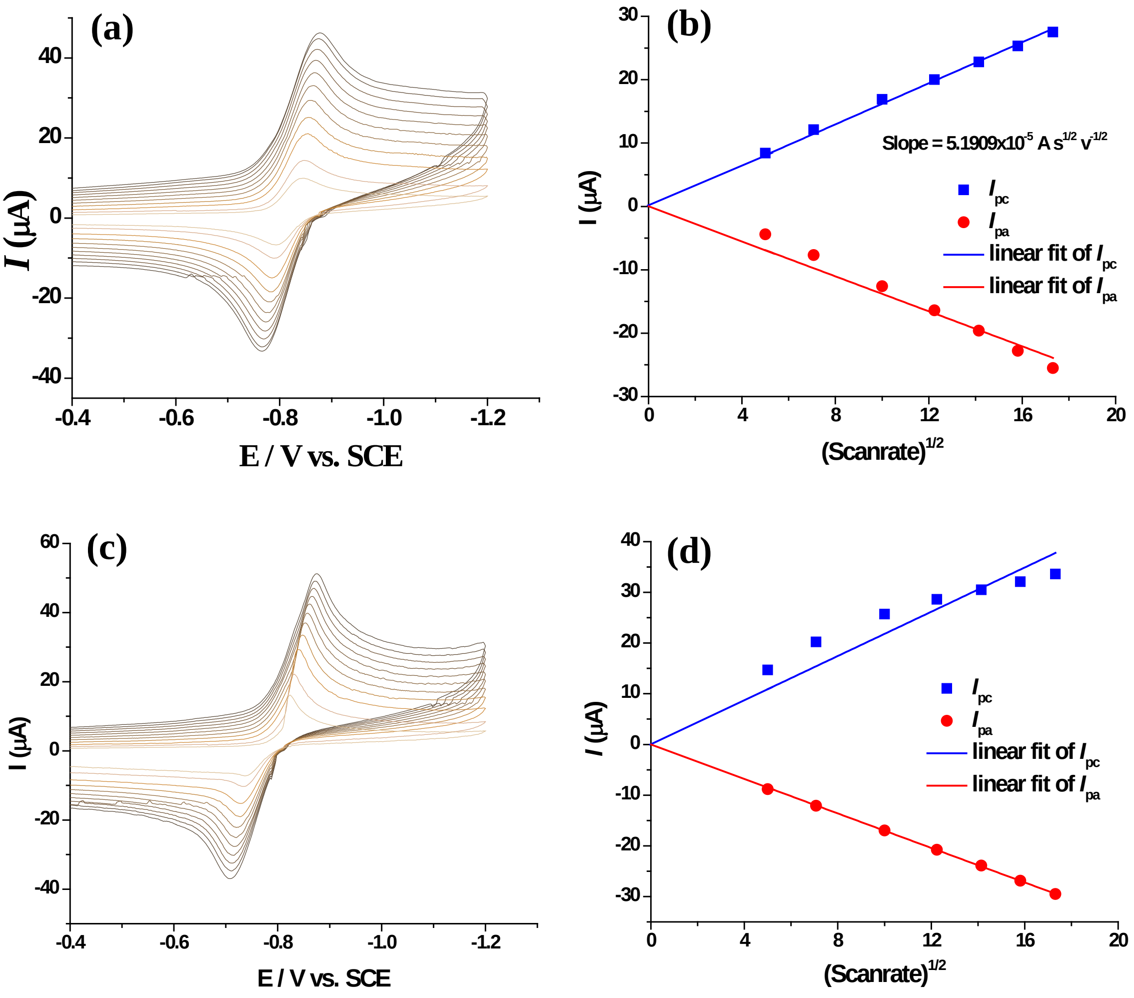


Fig. 14 Cyclic voltammogram of 1 mM solution of (a) **2** and (c) **5** in DMSO at different scan rates (25-500 mV/s). Varation of the cathodic and anodic current for (b) **2** and (d) **5** with the square root of scan rate.

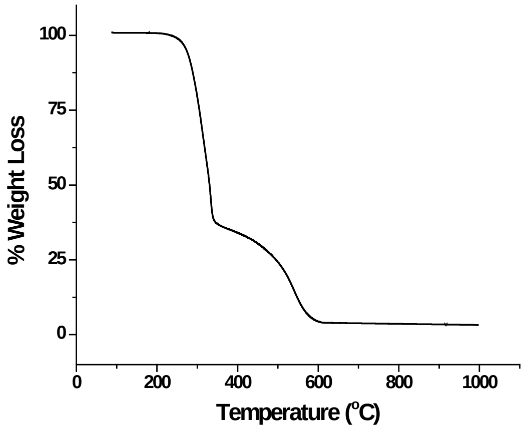


Fig. S15 Typical two-step weight-loss profile for **5** obtained using thermogravimetry analysis.

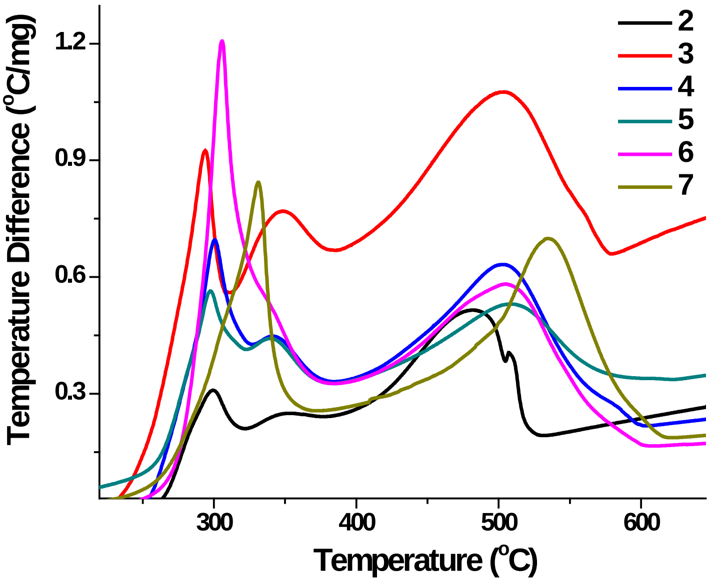


Fig. 16 Differential thermal analysis of **2-7** for the comparison of the peak degradation temperatures.

Table S4. Summary of current at a voltage of 10, 50 and 100 V for the xerogel of **2-7** obtained from the *I-V* curves and the calculated resistance at 10 V.

Entry	I (A) at 10 V	R (Ω) at10 V	I (A) at 50V	I (A) at 100V
2	8.9×10^{-7}	1.1×10^{7}	1.1×10^{-5}	4.9×10^{-5}
3	2.8×10^{-7}	3.5×10^{7}	4.9×10^{-6}	2.4×10^{-5}
4	2.1×10^{-7}	4.7×10^{7}	2.5×10^{-6}	1.4×10^{-5}
5	1.1×10^{-7}	9.1×10^{7}	1.4×10^{-6}	7.6×10^{-6}
6	3.7×10^{-8}	2.7×10^{8}	5.7×10^{-7}	3.2×10^{-6}
7	2.5×10^{-8}	4.0×10^{8}	3.3×10^{-7}	1.4×10^{-6}