Electronic supplementary Information

The effect of *meta* versus *para* substitution on the aggregation of bis-cholesteryl appended 2,6-disubstituted pyridine-based gelators

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Synthesis of 2a

Compound **2a** was prepared by the following reported procedure.[1]First, *p*-phenylenediamine (17.28 g, 160 mmol) and triethylamine (1.16 ml, 4 mmol) were dissolved in THF (150 ml). To this solution, 80 ml of THF solution of cholesterylchloroformate**1** (3.6 g, 4 mmol) was added dropwisewhile stirring in an ice bath. After addition, the mixture was allowed to stir at room temperature for 18 h. Then, the mixture was filtered and the filtrate was concentrated in vacuum. The thus-obtained residues were dissolved in dichloromethane and washed with water followed by a brine solution. Then, the organic phase was separated, dried over anhydrous magnesium sulfate, and concentrated in vacuum. The crude solid that was obtained was recrystallized twice from methanol, and the product **2a** was obtained as a yellow powder, with a 38% yield. A similar procedure was adopted for the synthesis of **2b** in which *m*-phenylenediamine was used instead of *p*-phenylenediamine, which yielded **2b** as white powder with a 35% yield

2a: Yield = 38%, FTIR (KBr, ν_{max}/cm^{-1}):3332 (NH), 2950 (CH, aromatic), 1730 (C=O), 1595 (N-H bending), 1207 (-C-O). ^{1}H-NMR ($CDCl_3$, δ= ppm): δ 7.14-7.15 (d, 2H, benzene), 6.63-6.65 (d, 2H, benzene), 6.34 (s, 1H, CONH), 5.39 (s, 1H, alkenyl), 3.55 (s, 2H, $-NH_2$), 0.94-2.44 (m, 43H, cholesteryl protons). ^{13}C NMR (125.7 MHz, $CDCl_3$, δ in ppm): δ= 162.3, 150.3, 147.64, 139.70, 136.20, 129.85, 124.90, 111.40, 110.87, 106.33.

2b: Yield = 35%, FTIR (KBr, ν_{max}/cm^{-1}): 3402 (NH), 2937 (CH, aromatic), 1726 (C=O), 1620 (N-H bending), 1219 (-C-O). ^{1}H-NMR ($CDCl_3$, δ= ppm): δ 7.03-7.26 (t, 1H, benzene), 6.97 (s, 1H, CONH), 6.56-6.58 (d, 1H, benzene), 6.45 (s, 1H, benzene), 6.37-

6.38 (d, 1H, benzene), 5.40 (s, 1H, alkenyl), 4.56-4.61 (m, 1H, oxy-cyclohexyl), 3.68 (s, 2H, -NH_2), 0.68-2.44 (m, 43H, cholesteryl protons). ^{13}C NMR (125.7 MHz, $CDCl_3$, δ in ppm): δ= 162.46, 159.20, 144.64, 139.70, 127.85, 122.90, 122.40, 116.87.

Synthesis of PyPC and **PyMC**

Thionyl chloride (15 g, 126 mmol) was added dropwise to the mixture of 2,6-pyridine dicarboxylic acid (**3)** (3 g, 17.95 mmol), and 5 drops of dimethylformamide in dry CH_2Cl_2 (100 ml) and was refluxed for 4 h. The excess thionyl chloride was removed under reduced pressure to give 2,6-pyridine dicarbonyl chloride (**4)** as a yellow liquid. Compound **2a** (1.04 g, 2 mmol) and triethylamine (0.29 ml, 2 mmol) were dissolved in 100 ml of THF, and the mixture was stirred in an ice-water bath. To this mixture, the solution of **4** (0.204 g, 1 mmol) in THF (40 ml) was added dropwise with vigorous stirring. After addition, the mixture was allowed to stir for 18 h at room temperature. Then, the reaction mixture was filtered, and the filtrate was evaporated. The resulting solid was washed five times with acetone and then dried under vacuum to give the desired product as a yellow powder with a 29% yield. A similar procedure was adopted for the synthesis of **PyMC,** in which compound **2b** was used instead of **2a** in the above procedure to give **PyMC** as white powder with a 28% yield.

PyPC: Yield = 29%, $[\alpha]_D^{25}$ = -24.44, FTIR (KBr, ν_{max}/cm^{-1}): 3327 (NH), 2954 (CH, aromatic), 1712, 1684 (C=O, -NH), 1554 (NH, bending), 1219 (-C-O). ^{1}H-NMR ($CDCl_3$, 500 MHz, δ= ppm): δ 9.50 (s, 2H, CONH), 8.48-8.49 (d, 2H, pyridine), 8.13 (t, 1H, pyridine), 7.70-7.72 (d, 4H, benzene), 7.43-7.44 (d, 4H, benzene), 6.61 (s, 2H, CONH), 5.41 (s, 2H, alkenyl), 4.62 (s, 2H, oxy-cyclohexyl), 0.92-2.96 (m, 86H, cholesteryl protons).^{13}C NMR (125.7 MHz, $CDCl_3$, δ in ppm): δ= 162, 153.3, 149.44, 140.70, 139.20,

133.61, 124.85, 122.40, 72.1, 56.70, 50.06, 42.33, 40.49, 39.75, 39.70, 38.53, 37.11, 36.63, 36.13, 35.83, 31.81, 28.29, 28.15, 27.76, 23.81, 21.17, 18.46, 14.30, 12.03.

PyMC: Yield = 28%, $[\alpha]_D^{25}$ = -9.53, FTIR (KBr, ν_{max}/cm^{-1}): 3346 (NH), 2952 (CH, aromatic), 1701 (C=O), 1545 (N-H bending), 1223 (-C-O). ^{1}H-NMR (Pyridine-d5, 500 MHz δ= ppm): δ 11.454 (s, 2H, CONH), 10.517 (s, 2H, CONH), 8.739 (s, 2H, benzene), 8.477-8.491 (d, 2H, benzene), 7.992-8.018 (t, 1H, pyridine), 7.932-7.947 (d, 2H, pyridine), 7.787-7.801 (d, 2H, benzene), 7.349-7.377 (t, 2H, benzene), 4.785 (s, 2H, alkenyl), 1.066-2.547 (m, 86H, cholesteryl protons). ^{13}C NMR (125.7 MHz, Pyridine-d_5, δ in ppm): δ= 162.93, 154.69, 149.61, 140.63, 139.96, 139.85, 130.08, 126.16, 116.10, 112.40, 75.06, 57.30, 56.87, 50.76, 43.00, 40.45, 40.25, 39.55, 37.77, 37.31, 36.99, 36.53, 32.66, 32.56, 30.94, 29.09, 28.72, 23.41, 21.78, 19.86, 12.50.

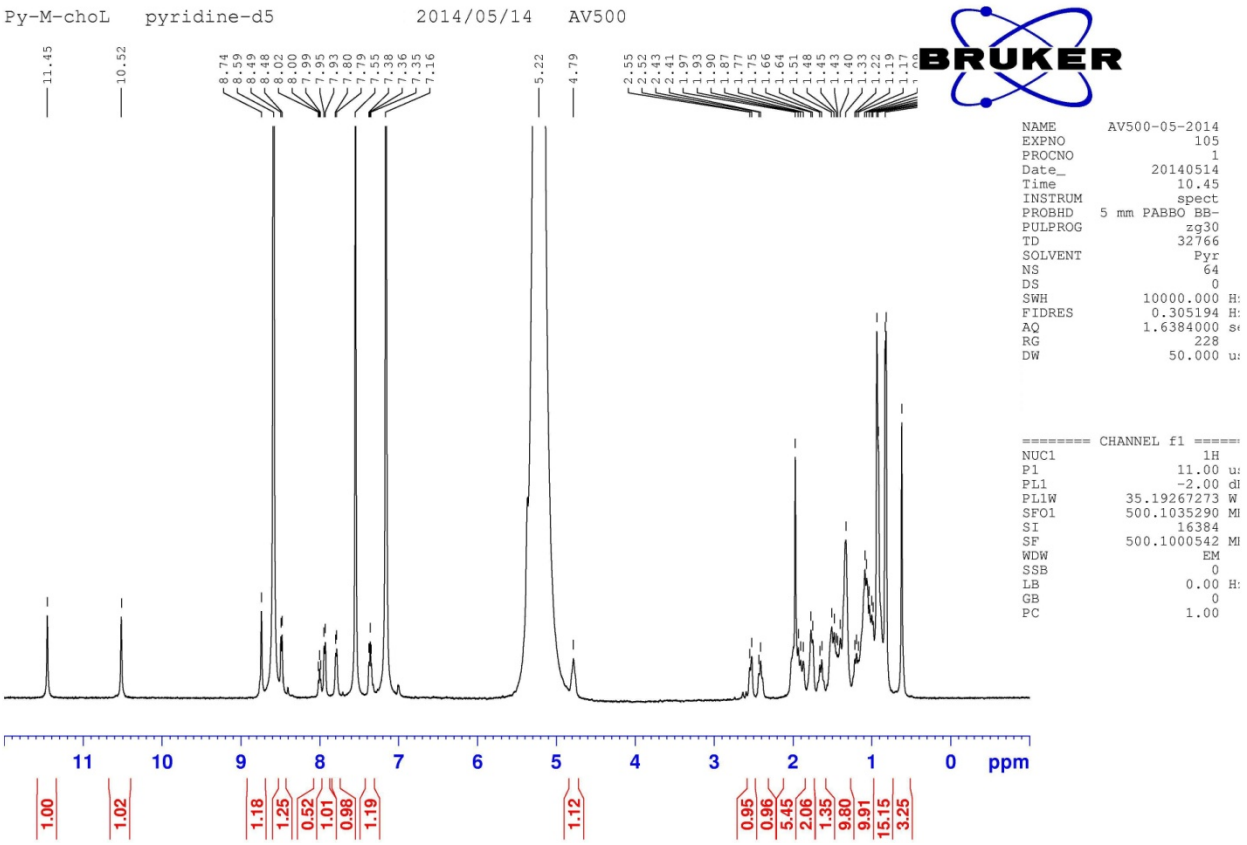

Fig. S1. ^{1}H-NMR spectrum of **PyMC** in pyridine-d_5

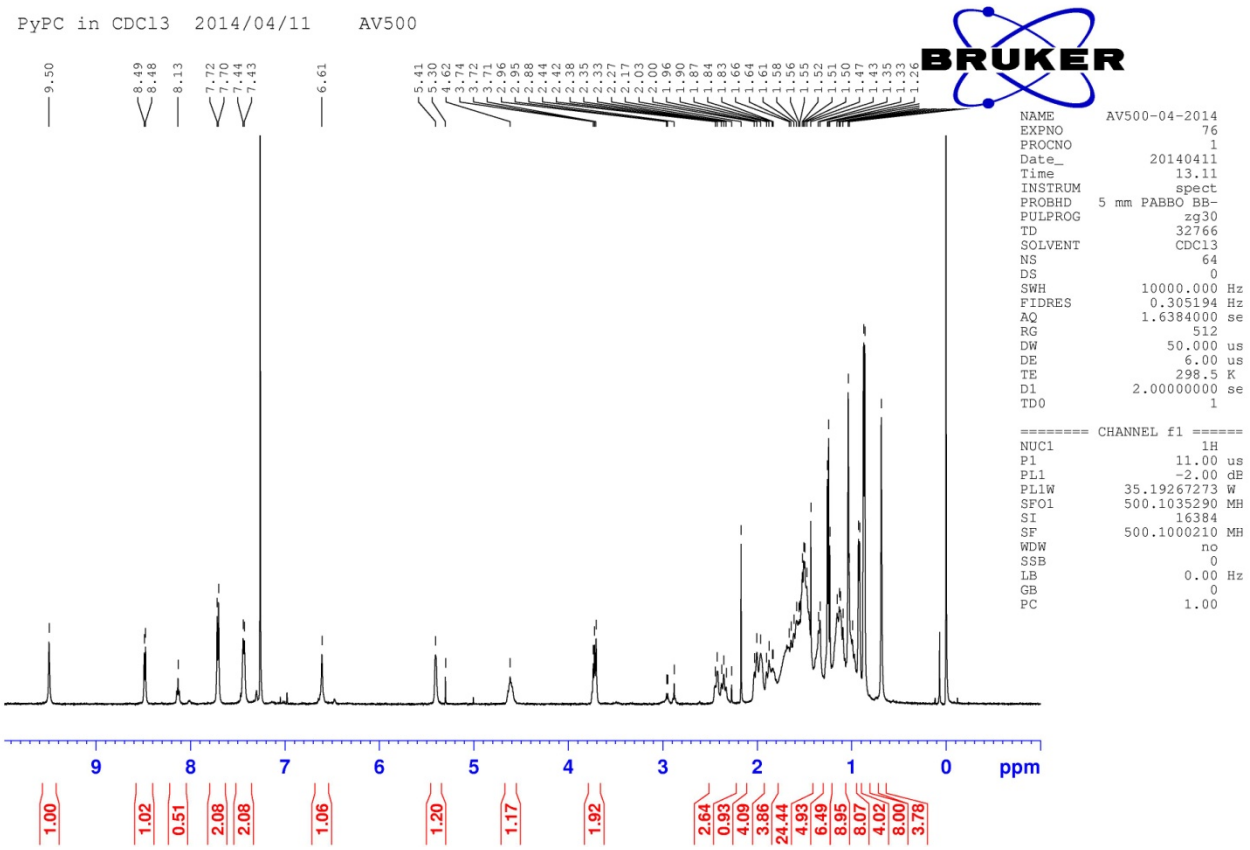

Fig. S2. ^{1}H-NMR spectrum of **PyPC** in $CDCl_3$

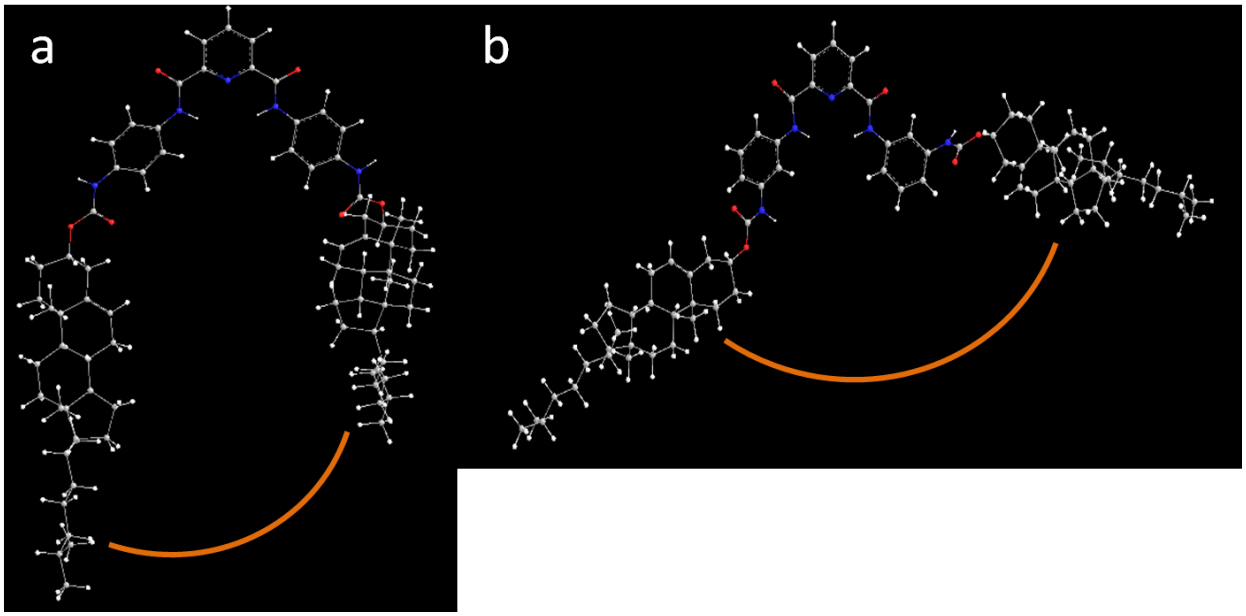

Fig. S3. Simulated molecular model of (a) PyPC and (b) PyMC at minimized energy state via PC Spartan Plus

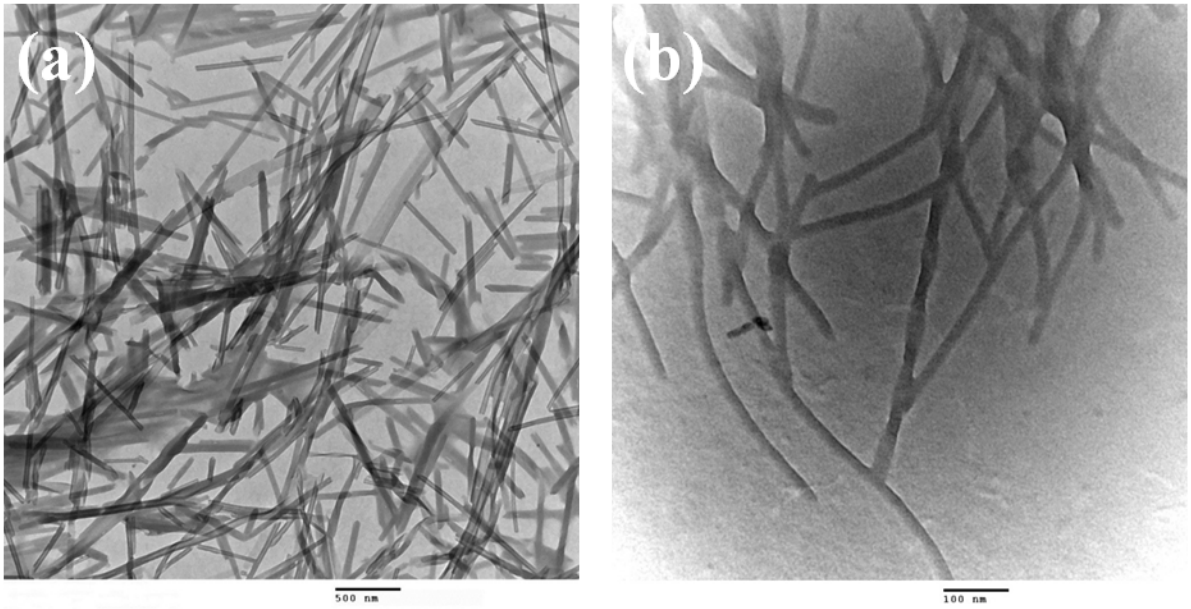

Fig. S4. TEM images of the xerogel of PyPC in (a) dodecanol and (b) octanol (Scale: a is 500 nm and b is 100 nm)

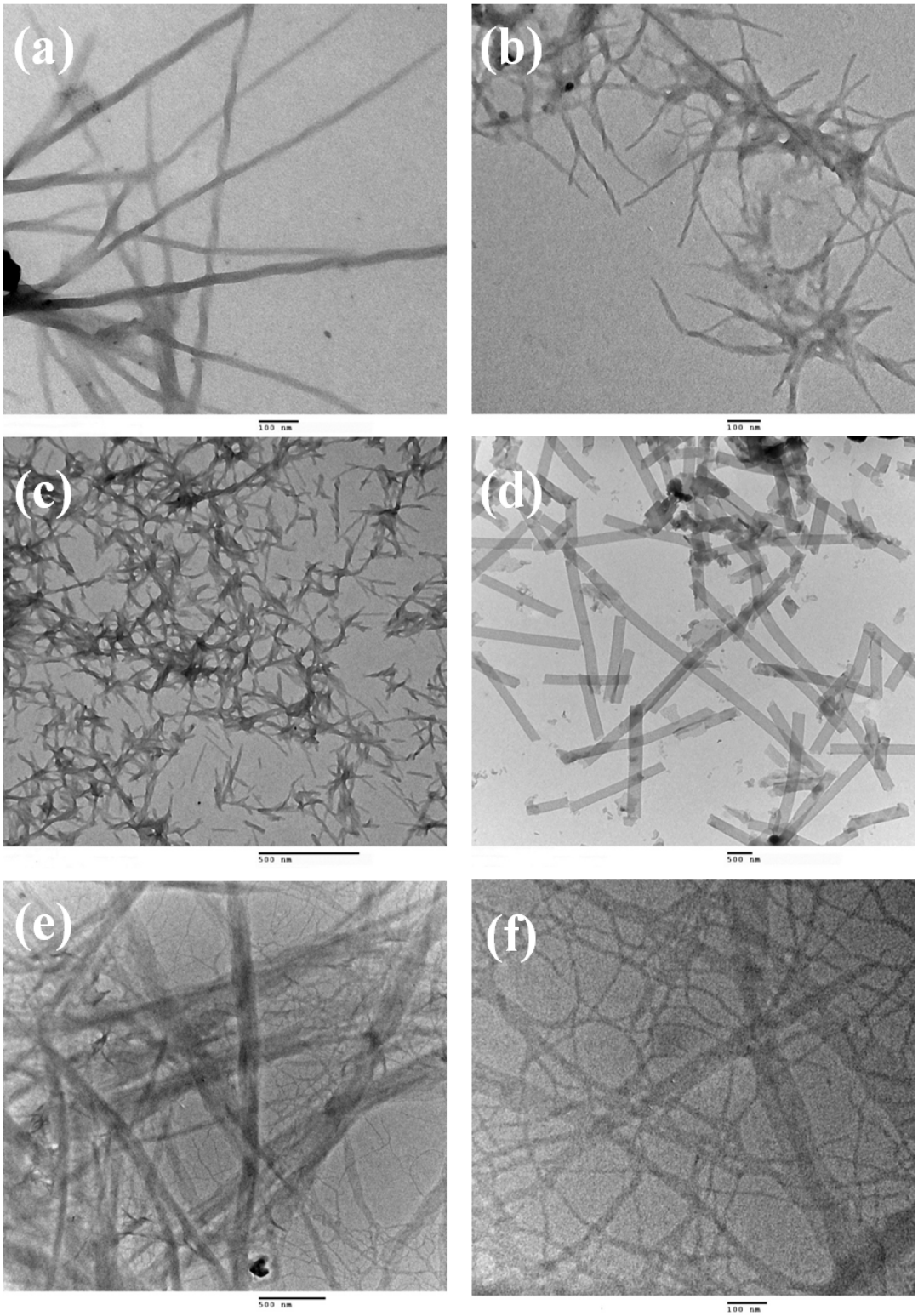

Fig. S5. TEM images of the xerogel of PyMC in (a) hexanol , (b) diphenyl ether, c) dodecanol, d) DMSO, e and f) xylene (Scale: a,b and f is 100nm; c,d,e is 500 nm)

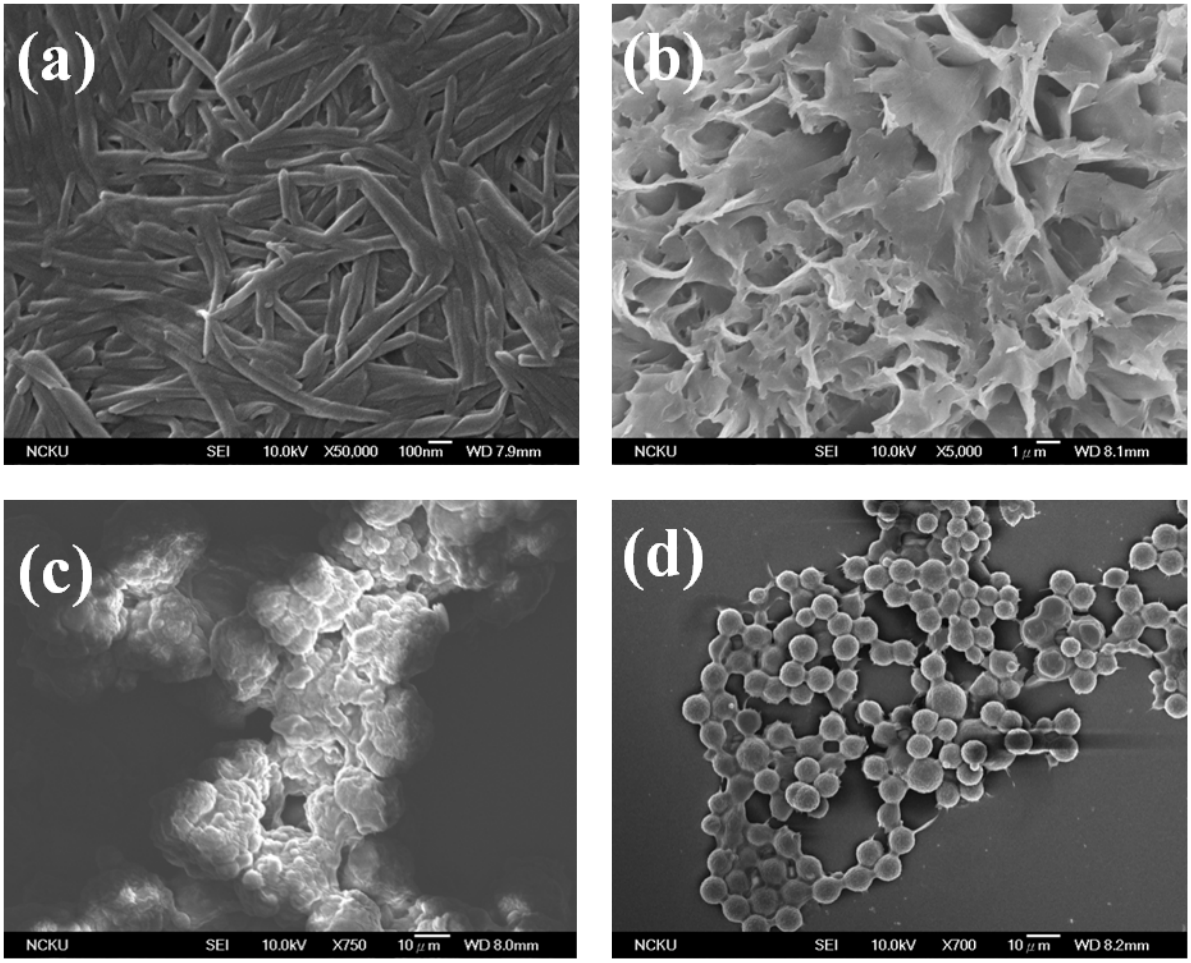

Fig. S6. SEM images of the xerogel of (a) PyPC in dodecanol , (b) PyMC in DMSO, (c) PyMC in diphenyl ether and (d) PyMC in xylene (Scale: a is 100nm; b is 1μm; c and d is 10μm).

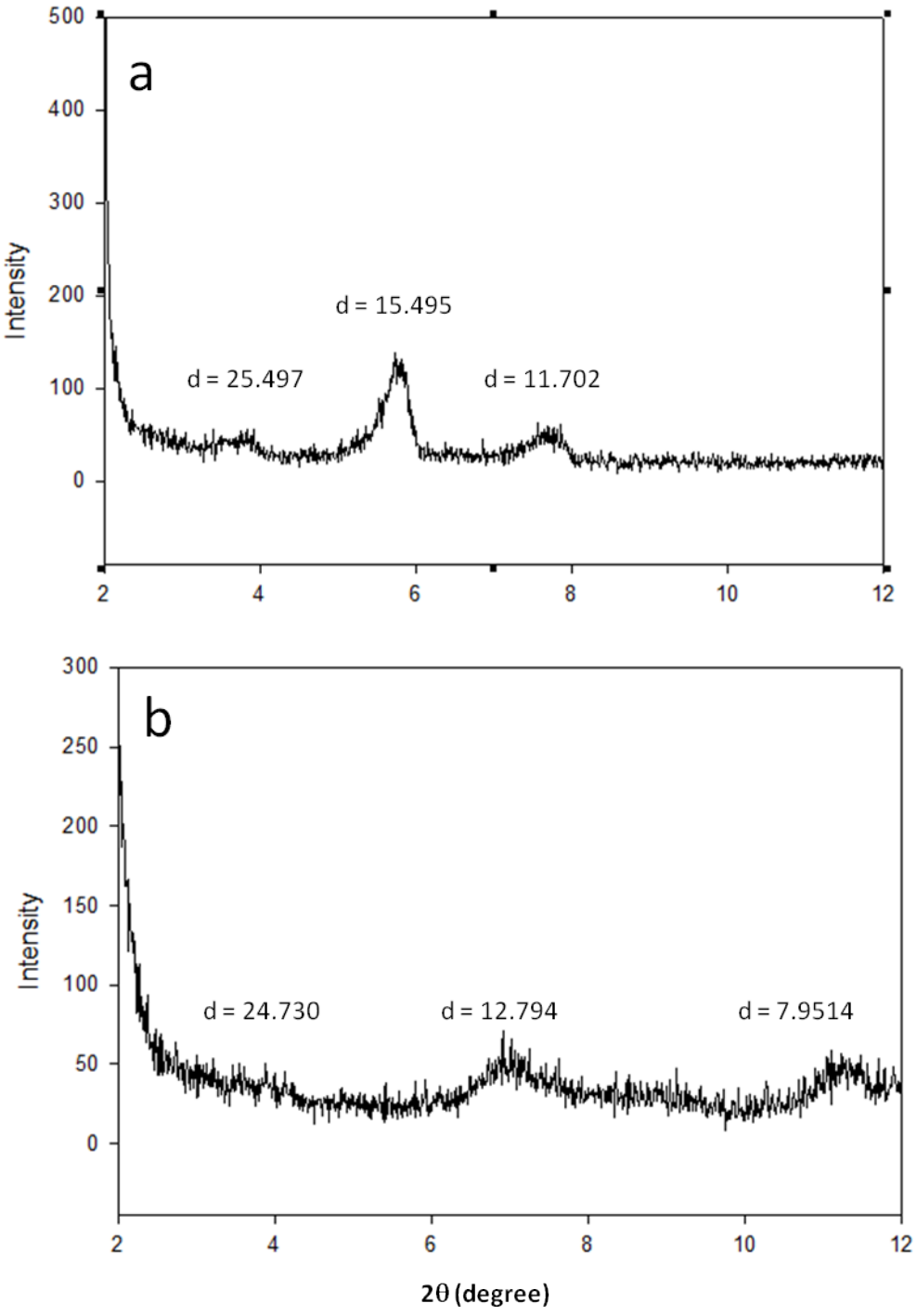

Fig. S7. XRD diffraction pattern of the xerogel (a) PyPC and (b) PyMC in 1-dodecanol.

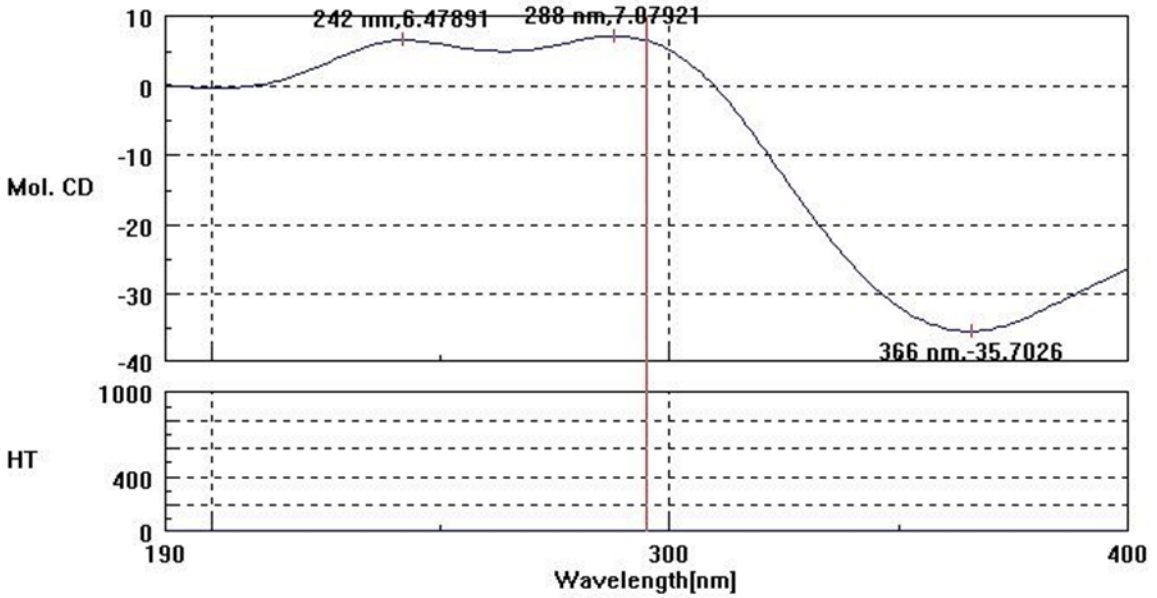

Fig. S8. CD spectra of PyPC in 1-dodecanol (0.001 M) at room temperature