Supporting Information

Bimodal self-assembly of an amphiphilic gelator to hydrogel-nanocatalyst and organogel of different morphologies and photophysical properties

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1. Experimental Section.

1.1 Materials and Methods: 1,3,5-tris(bromomethyl)benzene, methyl 4-hydroxybenzoate, 4′-chloro-2,2′:6′,2″-terpyridine, 1,3-diaminopropane, triphenylphosphine (PPh_3), trichloroisocyanuric acid (TCIC) were purchased from Sigma-Aldrich chemical Co. Ltd. Potassium carbonate, potassium iodide, , malononitrile and all solvents were purchased from Spectrochem. For doing catalysis all substrates, benzaldehyde, 4-nitrobenzaldehyde, 4-chlorobenzaldehyde, p-tolualdehyde and p-anisaldehyde, were purchased from Sigma-Aldrich chemical Co. Ltd. All solvents were pre-dried using standard procedures before using. For UV-Vis experiments spectroscopic grade solvents were purchased from Spectrochem. ^{1}H NMR is recorded on a Bruker AV-400 spectrometer with chemical shifts recorded as ppm and all spectra were calibrated against TMS. UV-Vis spectra were recorded in a Perkin-Elmer lamda 900 spectrometer. Fluorescence studies were accomplished using Perkin Elmer Ls 55 Lumeniscence spectrometer. Infrared spectral studies were carried out by making samples with KBr pellets using Bruker FT-IR spectrometer. Powder X-ray diffraction studies were recorded on a Bruker D8 discover instrument using Cu-Kα radiation.

Morphology studies were carried out using Lica-S440I field emission scanning electron microscopy (FESEM) by placing samples on silicon wafer under vacuum with accelerating voltage of 10 kV. Transmission electron microscopy (TEM) analysis was performed using JOEL JEM-3010 with accelerating voltage of 300kV. For this analysis the xerogel was dispersed in ethanol and then drop casted on a carbon coated copper grid.

1.2 Synthesis of 4,4′,4″-[1,3,5-phenyl-tri(methoxy)]-tris-benzoic acid: methyl 4-hydroxybenzoate (1.065 g, 7 mmol), potassium carbonate (2.89 g, 21 mmol), potassium iodide (85 mg, 0.518 mmol) were suspended in dry N, N-dimethylformamide (DMF). The reaction mixture was refluxed at 100 °C for 2 hours maintaining the inert condition. 1,3,5-tris(bromomethyl)benzene (500 mg, 1.4 mmol) was dissolved in 20 ml dry DMF and was dropwise added to the above heated reaction mixture. The mixture was subsequently stirred and heated at 100 °C for 4 hours. After cooling the reaction mixture to room temperature, 100 ml of distilled water was added and the precipitate formed was collected by filtration. The precipitate was washed several times with cold distilled water and air dried. A white solid was obtained with 85% yield. The product was taken in a round bottom flux. 40 ml methanol and 6 g of NaOH in 20 ml of distilled water was added into it. The reaction mixture was refluxed at 50 °C for 12 hours. After cooling to room temperature, the solution was placed in a ice bath and acidified to pH 2 with 3N HCl. The precipitate was then collected, washed several times with distilled water and air dried. A brownish solid was obtained with 98% yield. ^{1}H-NMR (400 MHz, DMSO-d^{6}) δ: 7.89 (d, 6H, ArH), 7.53 (s, 3H, ArH), 7.11 (d, 6H, ArH), 5.22 (s, 6H, CH_2). Selected FTIR data (KBr, cm^{-1}): 3451 (b), 3078-2879 (s), 2673 (s), 2550 (s), 1680 (sh), 1603 (sh), 1510 (m), 1428 (m), 1248 (sh), 1169 (sh), 1009 (m), 940 (s), 846 (m), 771 (m), 695 (s), 648 (s), 609 (s), 564 (s), 504 (s).

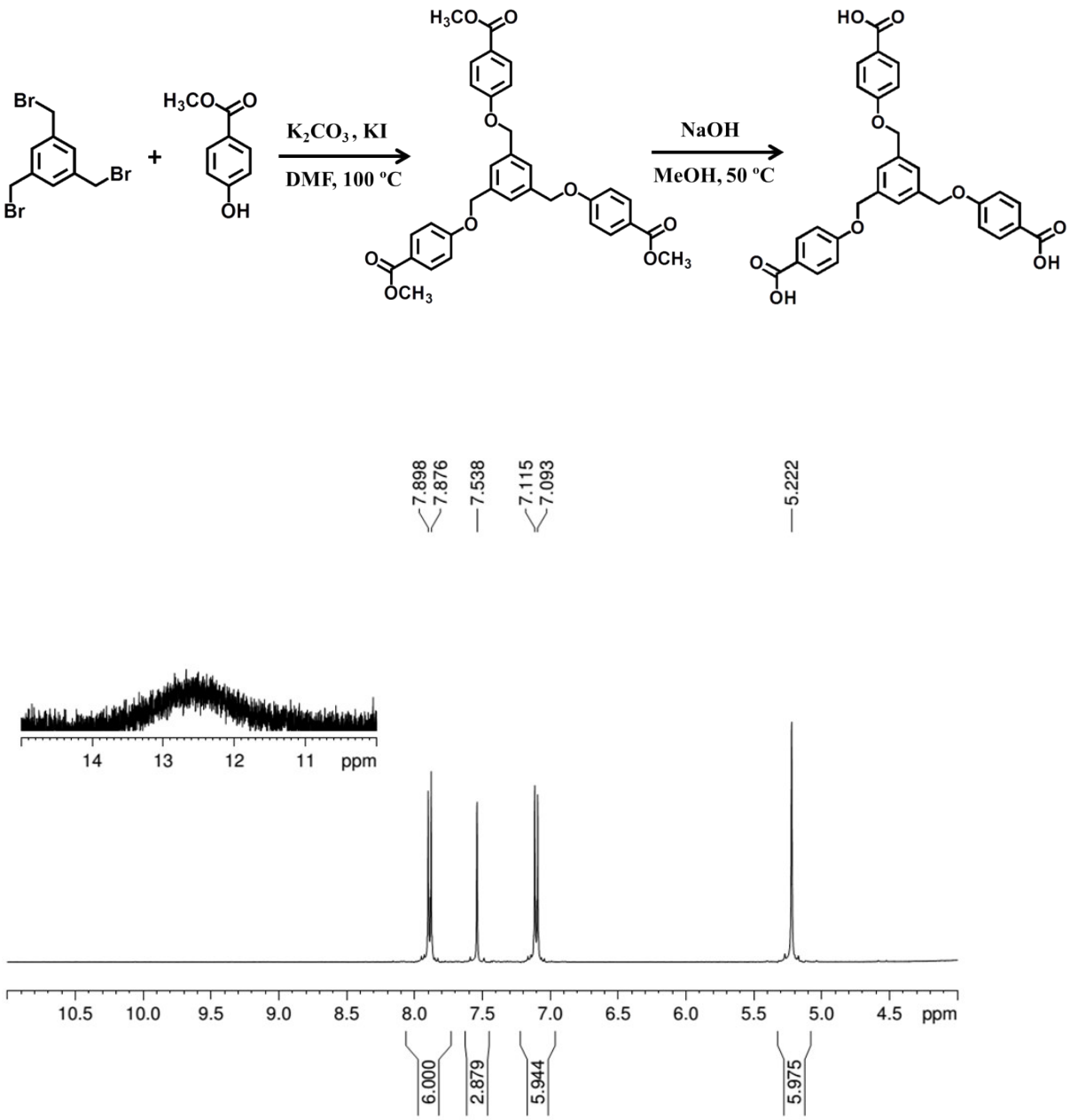


Fig. S1 ^{1}H NMR spectra of 4,4′,4″-[1,3,5-phenyl-tri(methoxy)]-tris-benzoic acid in DMSO-d^6.

1.3 Synthesis of 2,2′;6′,2″-terpyridin-4′-yl-propane-1,3-diamine: 2,2′;6′,2″-terpyridin-4′-yl-propane-1,3-diamine was synthesized by following a reported procedure. 4′-chloro-2,2′:6′,2″-terpyridine, (300 mg, 1.12 mmol) was suspended in 1,3-diamino propane (2.16 ml). The reaction mixture was then refluxed at 120° C for overnight. After cooling to room temperature, H_2O (25 mL) was added. The white precipitate formed was filtered and further

washed with H_2O. The solid was dissolved in dichloromethane and extracted twice with H_2O. The organic layers were combined and dried over Na_2SO_4, filtered and the solvent was removed under reduced pressure to yield a white solid product. Yield: 82%. ^{1}H-NMR (400 MHz, $CDCl_3$): δ: 8.53 (d, 2H, ArH), 8.52 (d, 2H, ArH), 7.76 (t, 2H, ArH), 7.60 (s, 2H, ArH), 7.25 (t, 2H, ArH), 5.16 (t, 1H, NH), 3.41 (m, 2H, $NHCH_2$), 2.84 (m, 2H, CH_2), 1.77 (m, 2H,NH_2CH_2). Selected FTIR data (KBr, cm^{-1}): 3340 (b), 2965 (m), 1610-1560 (s), 1464 (m), 1402 (m), 1261 (m), 1094-981 (s), 791 (s).

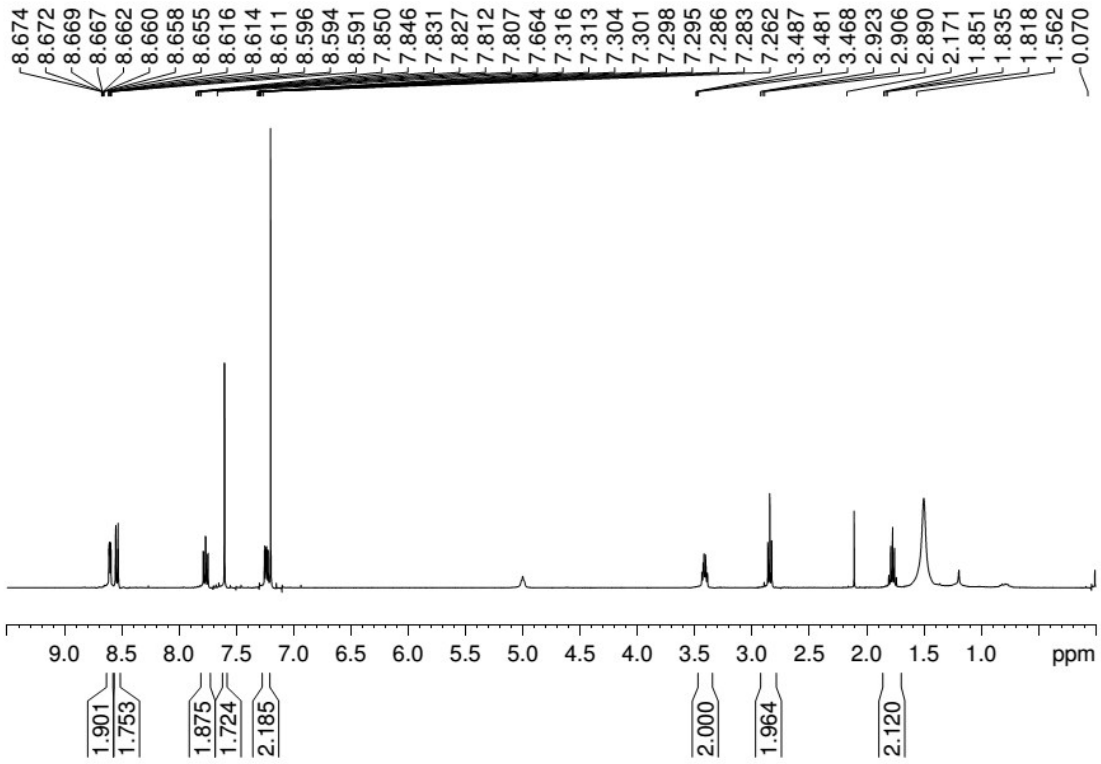
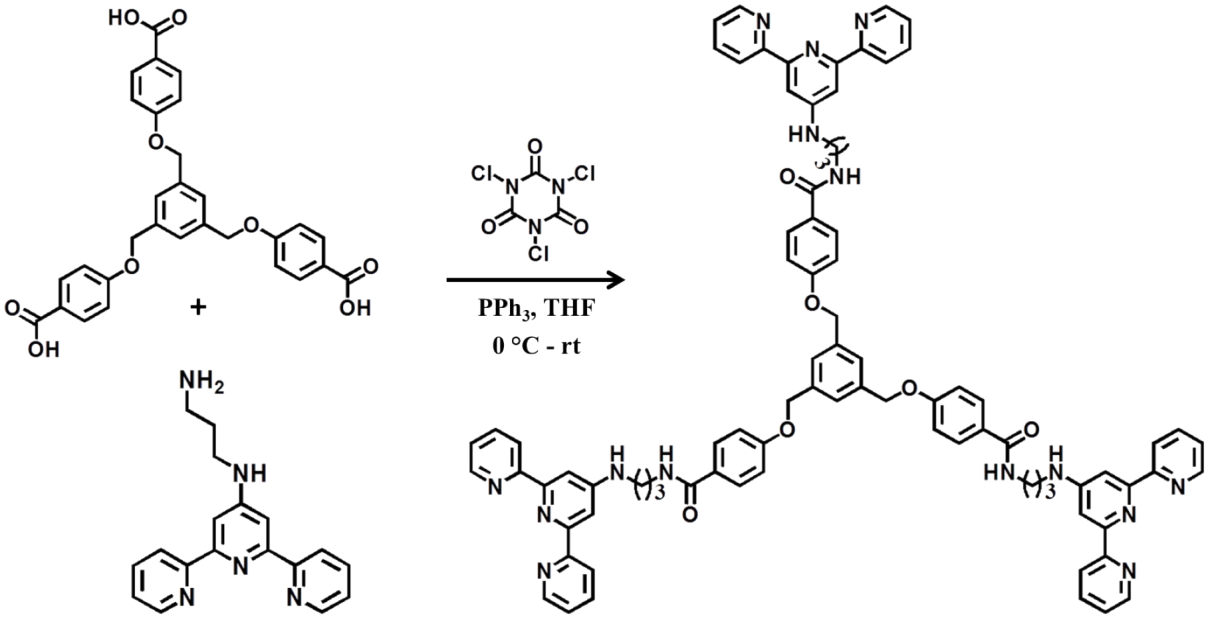


Fig. S2 ^{1}H-NMR spectra of 2,2′;6′,2″-terpyridin-4′-yl-propane-1,3-diamine in $CDCl_3$ solvent.

1.4 Synthesis of 4,4′,4″-[1,3,5-phenyl-tri(methoxy)]-tris-benzene{[3-([2,2′;6′,2″-terpyridin-4′-ylamino)-propyl]-amide}(L): 4,4′,4″-[1,3,5-phenyl-tri(methoxy)]-tris-benzoic acid (280 mg, 0.529 mmol) was dissolved in anhydrous THF (30 mL). TCIC (406 mg, 1.748 mmol) and PPh_3(458 mg, 1.748 mmol) were added into the reaction mixture

and stirred at 0 ºC for 40 min under inert condition. 2,2′;6′,2″-terpyridin-4′-yl-propane-1,3-diamine (532 mg, 1.748 mmol) was dissolved in anhydrous THF (20 ml) and Et_3N (484 µl, 3.496 mmol) was added into it. This reaction mixture was drop-wise added into 4,4′,4″-[1,3,5-phenyl-tri(methoxy)]-tris-benzoic acid / TCIC/ PPh_3 solution at 0 ºC and stirred for 45 minutes. After that the reaction mixture was stirred at room temperature for 3 hrs. Precipitate was collected by filtration and washed several times with $CHCl_3$ and dried under reduced pressure. Yield: 88%. ^{1}H-NMR (400 MHz, DMSO-d^6) δ: 8.65 (d, 2H, ArH), 8.89 (d, 2H, ArH), 8.23 (m, 2H, ArH), 7.90 (s, 2H, ArH), 7.78 (m, 2H, ArH), 7.73 (m, 2H, ArH), 7.53 (s, 1H, ArH), 7.05 (d, 2H, ArH), 5.21 (s, 2H, $ArCH_2OAr$), 3.72 (m, 2H, $CONHCH_2$), 3.02 (m, 2H, CH_2), 2.04 (m, 2H, CH_2NH). Selected FTIR data (KBr, cm^{-1}): 3436 (b), 3039 (b), 2779 (s), 2676 (s), 2493 (s), 1721 (sh), 1695(sh), 1600 (m), 1470 (m), 1399 (m), 1249 (s), 1167 (s), 850 (s), 790 (m), 534 (m).



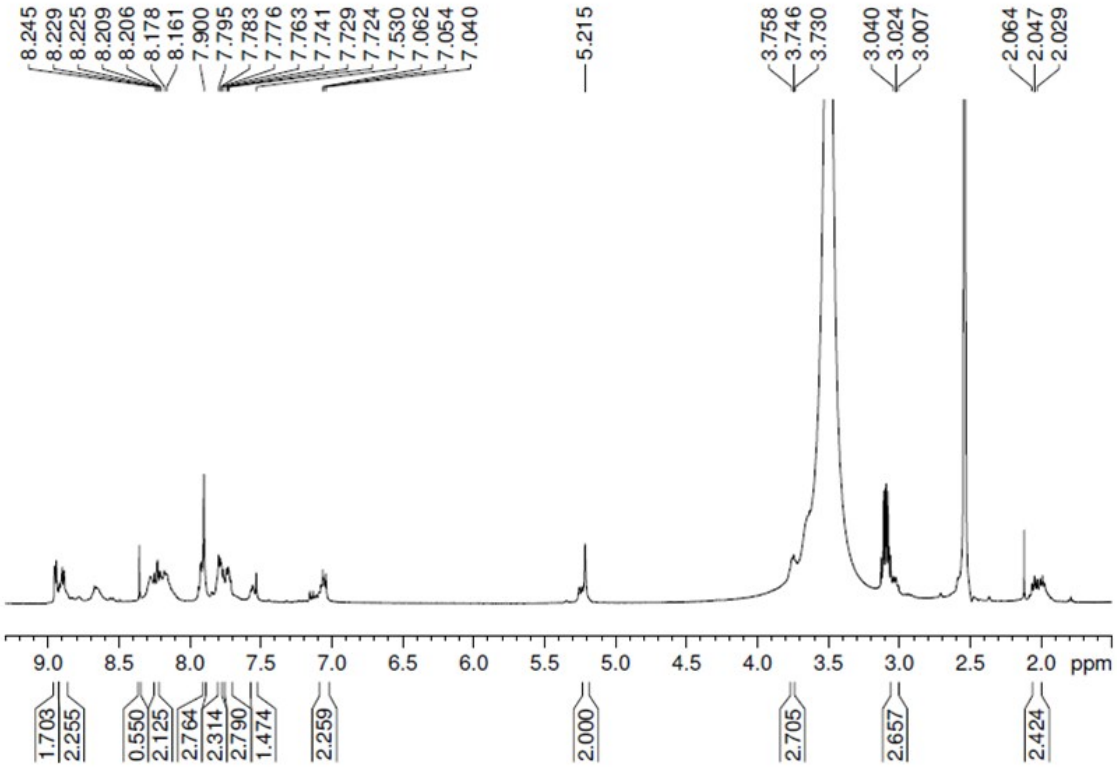


Fig. S3 ^{1}H-NMR spectra of **L** in DMSO-d^{6} solvent.

1.5 Synthesis of HG: 9 mg **L** was dissolved in 600 µl MeOH and 400 µl water was added into the solution during sonication. The mixture was kept at room temperature. After 5-6 min opaque gel was formed. The formation of gel was confirmed by inversion-test method. The **HG** xerogel is prepared by drying the hydrogel in air. Selected IR data of **HG** xerogel (KBr, cm^{-1}): 3436 (b), 3040 (b), 2781 (s), 2679 (s), 2493 (s), 1722 (sh), 1693 (sh), 1594 (m), 1469 (m), 1398 (m), 1248 (s), 1055 (s), 851 (s), 788 (m), 537 (m).

1.6 Synthesis of OG: 8 mg of **L** was dissolved in 800µl $CHCl_3$/THF (v:v= 1:1) mixture was heated at 90^{o} C for few minutes to form a viscous liquid which on cooling resulted in opaque gel. The formation of gel was confirmed by inversion test method. **OG** xerogel is prepared by drying the organogel in air. Selected IR data of OG xerogel (KBr, cm^{-1}): 3420 (b), 3053 (b), 2778 (m), 1716 (sh), 1688(sh), 1465 (m), 1396 (sh), 1052 (m), 771 (s), 534 (sh).

1.7 General procedure for the catalytic reactions: Benzaldehyde derivatives (1 mmol) and melanonitrile (1 mmol) were taken in a Schlenk tube and 15 ml dry THF was added into it under inert atmosphere. The reaction mixture was stirred at room temperature for 5 minutes and **HG** xerogel (1 mol %) was added into it. After that the reaction mixture was refluxed at 40 °C under nitrogen atmosphere. The reaction mixture was cooled down to room temperature and filtered to recover the catalyst. The filtrate was concentrated and analysed using GC-MS analyser and ^{1}H NMR spectroscopy.

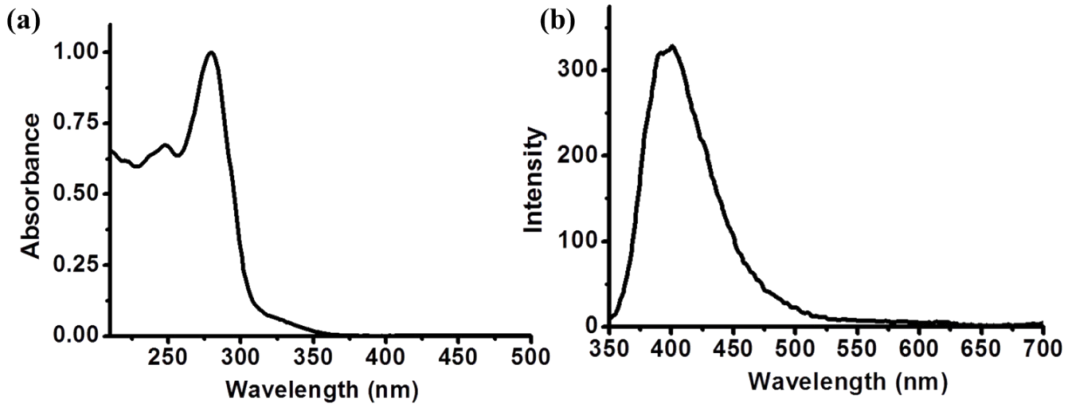


Fig. S4 (a) Absorption spectra of 2,2′;6′,2″-terpyridin-4′-yl-propane-1,3-diamine (1×10^{-4} M) in $CHCl_3$, (b) emission spectra of of 2,2′;6′,2″-terpyridin-4′-yl-propane-1,3-diamine (1×10^{-4} M) in $CHCl_3$.

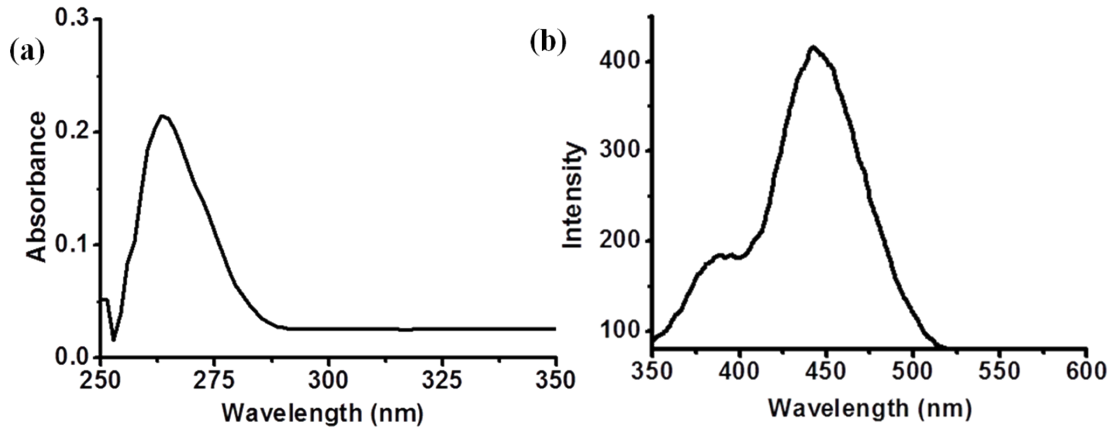


Fig. S5 (a) Absorption spectra of 4,4′,4″-[1,3,5-phenyl-tri(methoxy)]-tris-benzoic acid (1×10^{-4} M) in DMSO, (b) emission spectra of of 4,4′,4″-[1,3,5-phenyl-tri(methoxy)]-tris-benzoic acid (1×10^{-4} M) in DMSO.

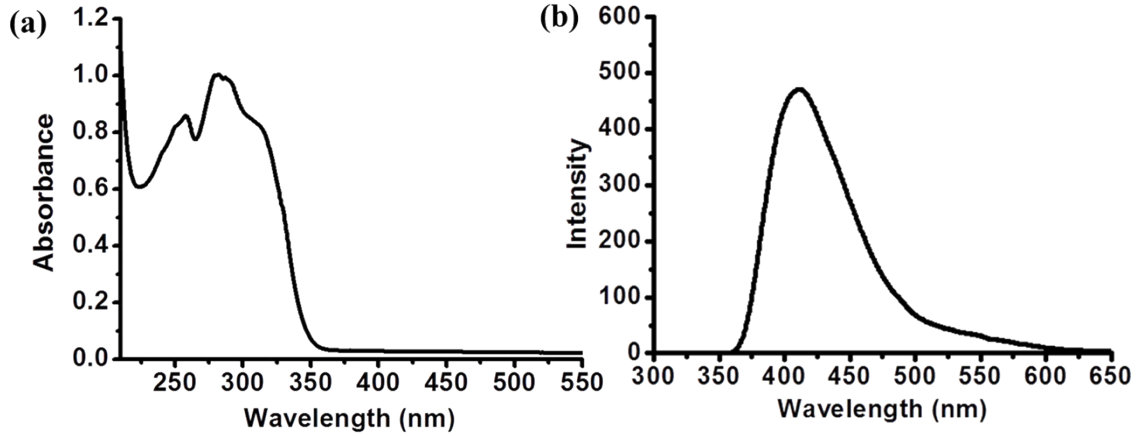


Fig. S6 (a) Absorption spectra of **L** (1×10^{-4} M) in MeOH, (b) emission spectra of **L** (1×10^{-4} M) in MeOH.

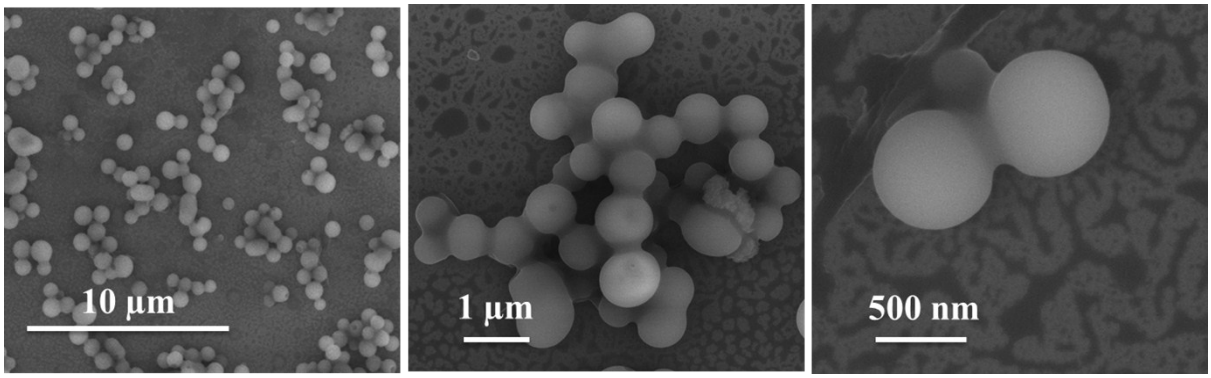


Fig. S7 FESEM images of **HG** xerogel showing formation of nano-sphere.

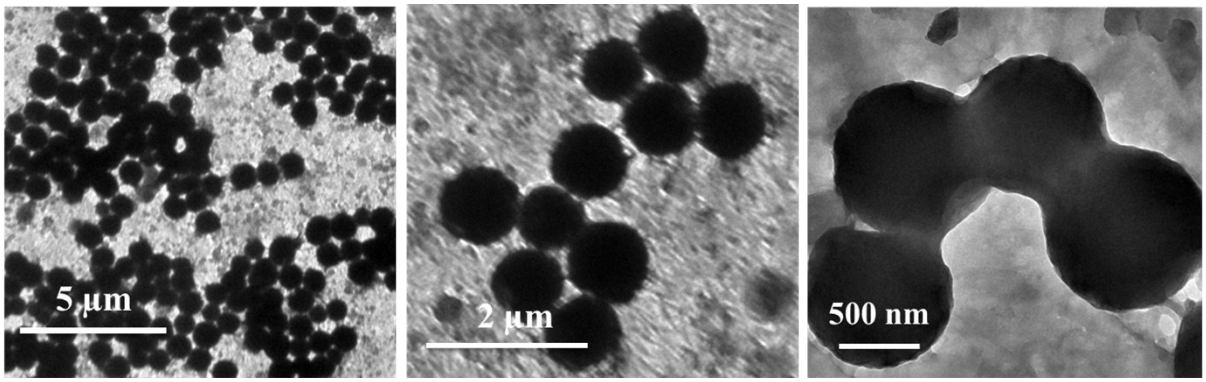


Fig. S8 TEM images of **HG** xerogel showing formation of nano-sphere.

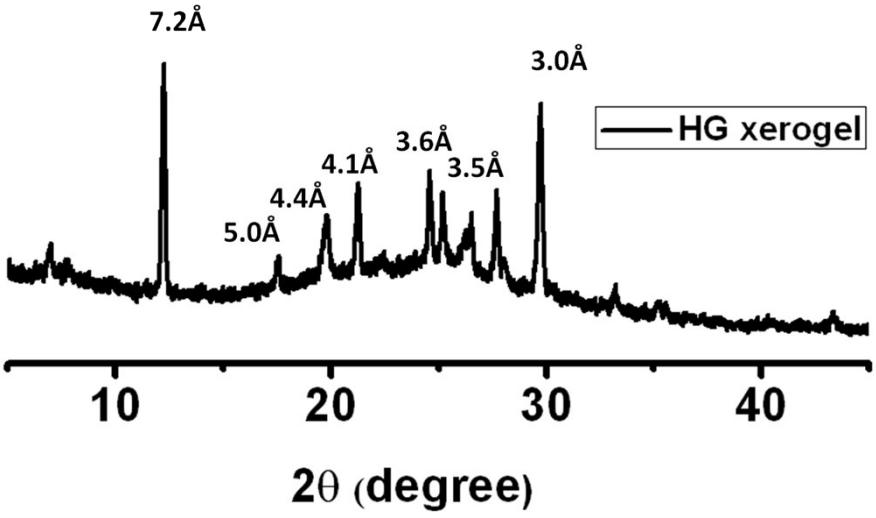


Fig. S9 PXRD of **HG** xerogel. 2θ= 24.5° (d= 3.6 Å) indicates π-π stacking in **HG** xerogel.

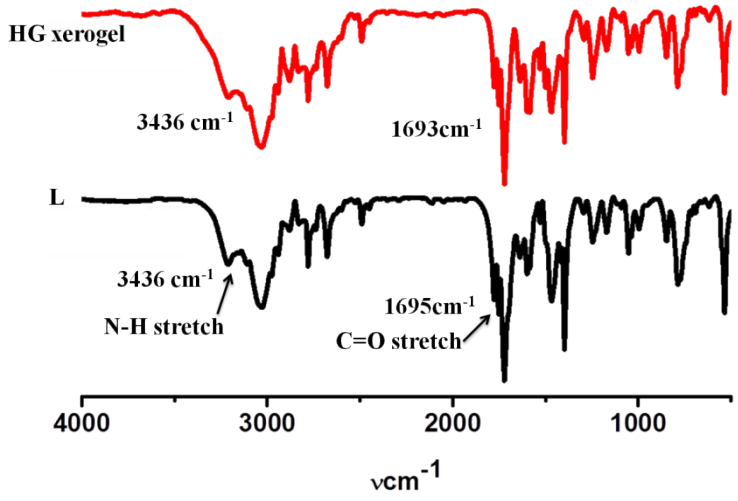


Fig. S10 FTIR spectra of of **L** (black) and **HG** xerogel (red).

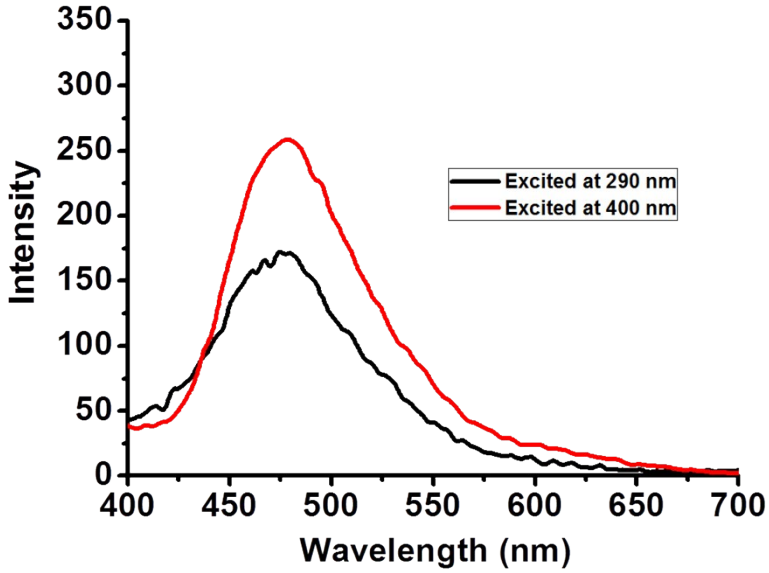


Fig. S11 Emission spectra of **HG** xerogel when excited at 290 nm (black) and 400 nm (red).

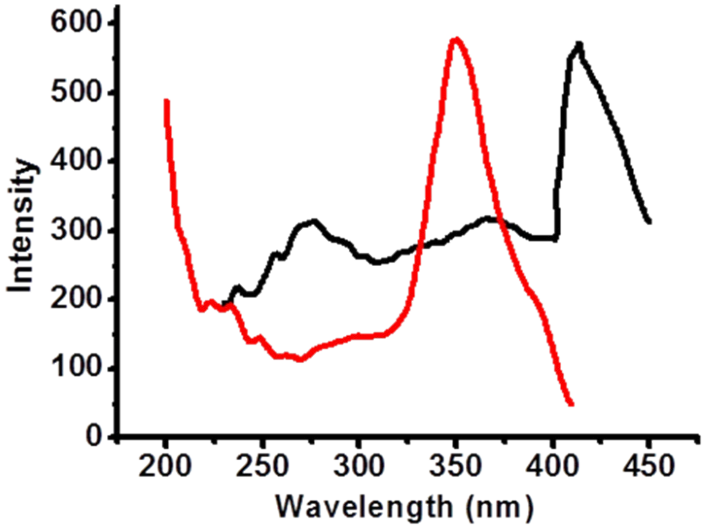


Fig. S12 Comparison of excitation spectra of **L** (red) and **HG** xerogel (black).

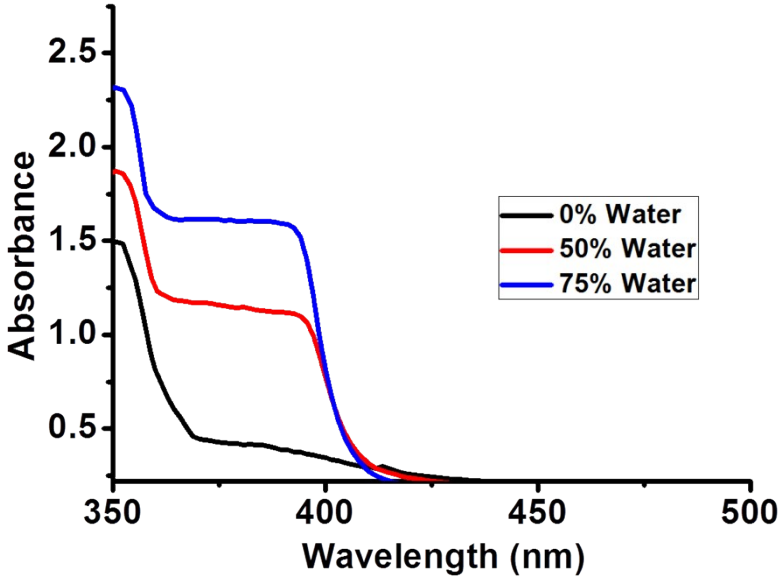


Fig. S13 Change in absorption spectra of methanolic solution of **L** with incremental addition of water.

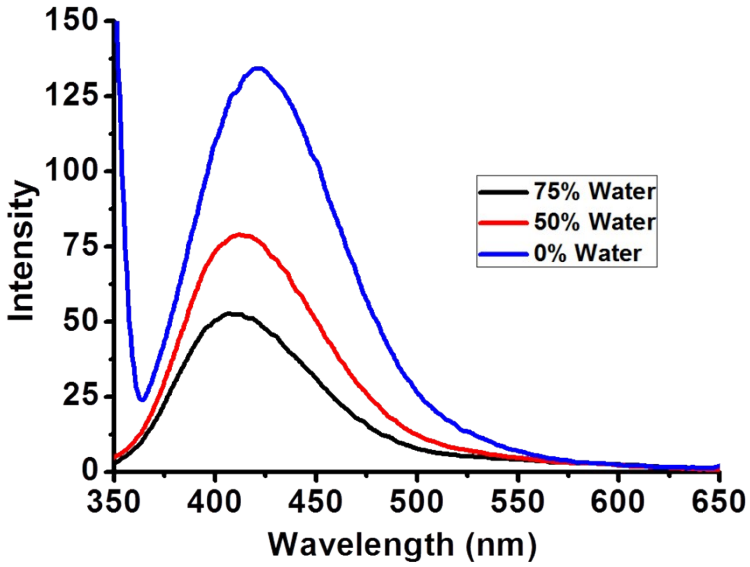


Fig. S14 Change in emission spectra of methanolic solution of **L** with incremental addition of water.

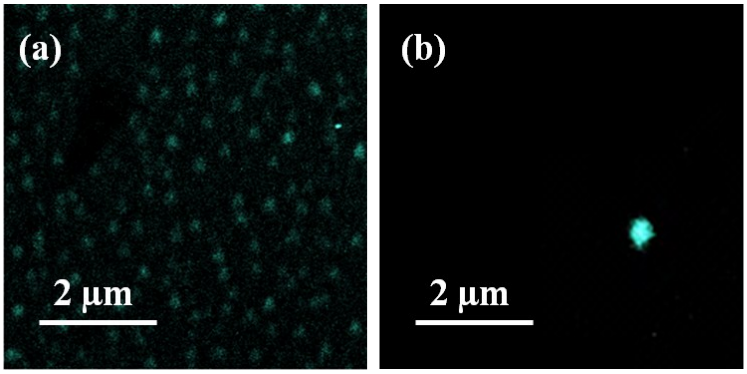


Fig. S15 Confocal fluorescence microscopy images of **HG** xerogel showing presence of cyan emissive nano-spheres.

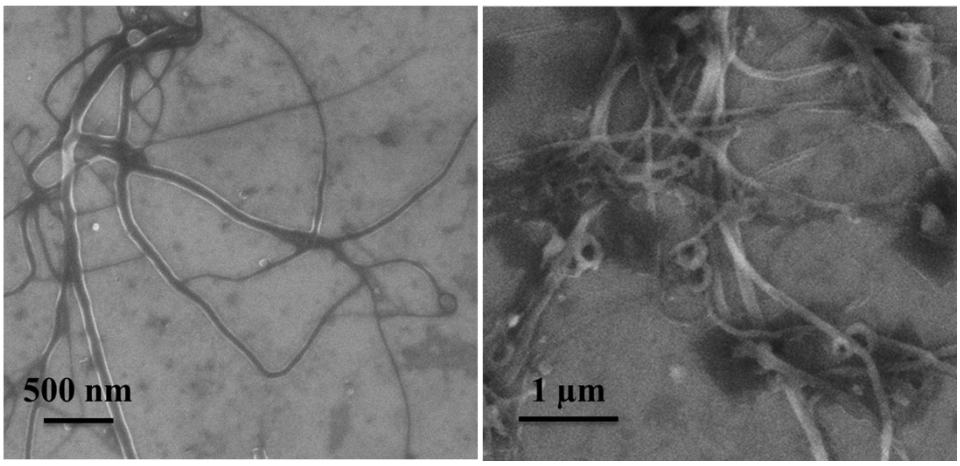


Fig. S16 FESEM images of **OG** xerogel

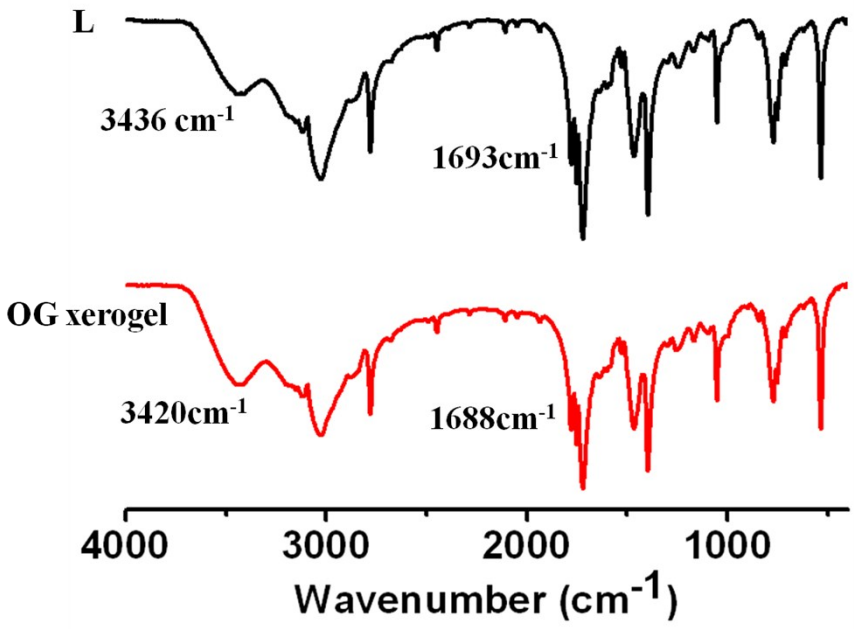


Fig. S17 FTIR spectra of **L** (black) and **OG** xerogel (red).

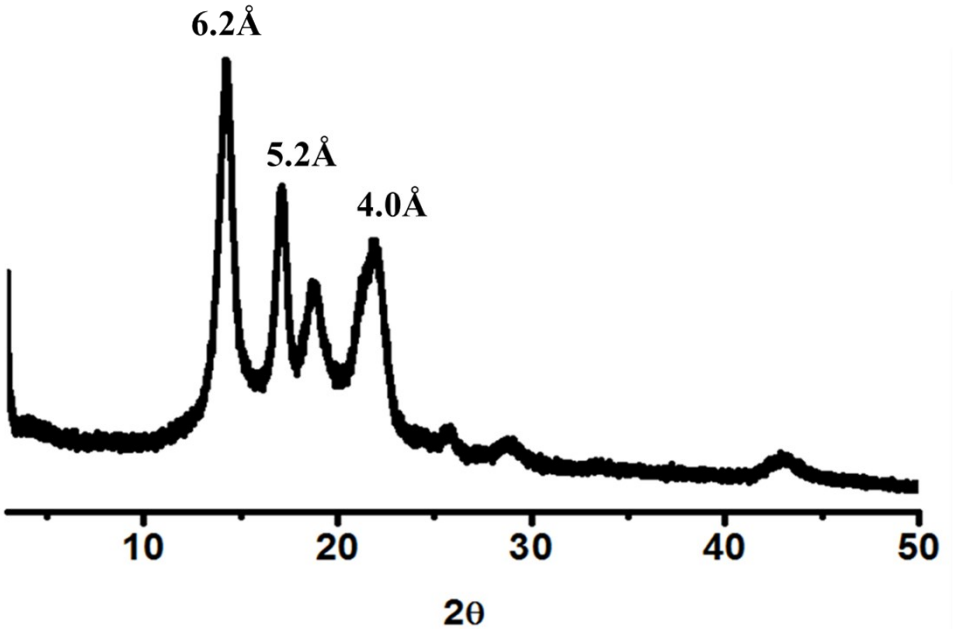


Fig. S18 PXRD of **OG** xerogel.

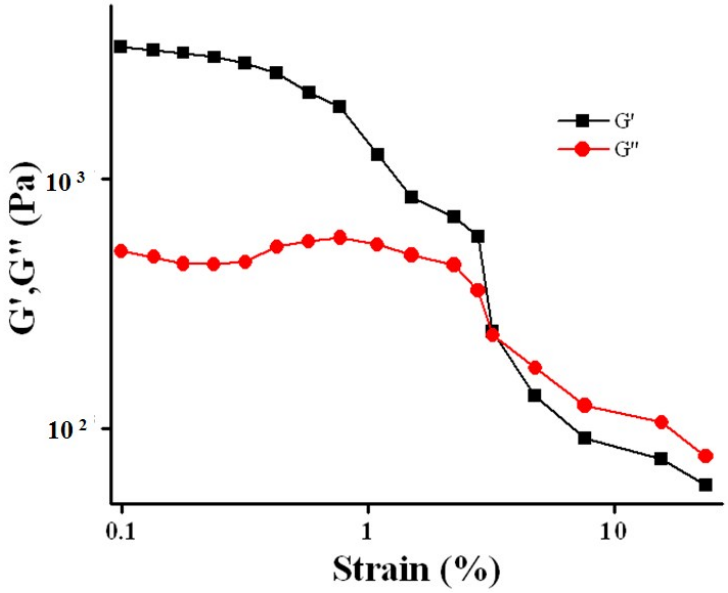


Fig. S19 Oscillatory strain measurements (frequency=1.0 rad/s) of **HG**, the squares (black) and circles (red) indicate storage (G′) and loss modulus (G″) respectively.

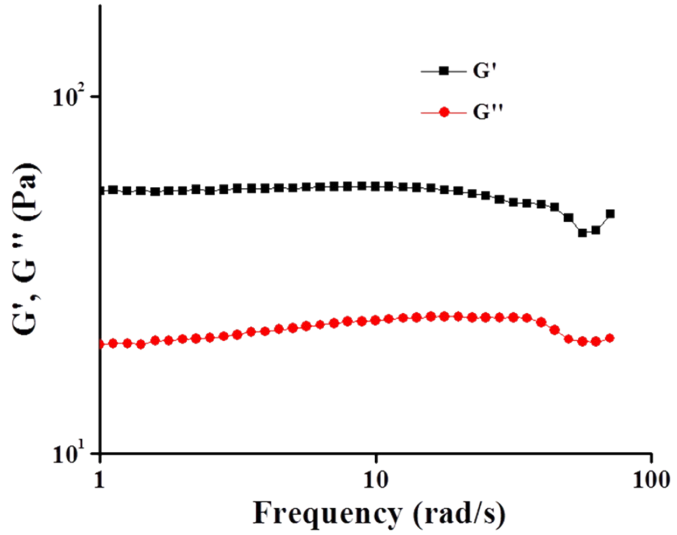


Fig. S20 Oscillatory frequency sweep measurements (strain = 0.01%) of **HG**, the squares (black) and circles (red) indicate storage (G') and loss modulus (G") respectively.

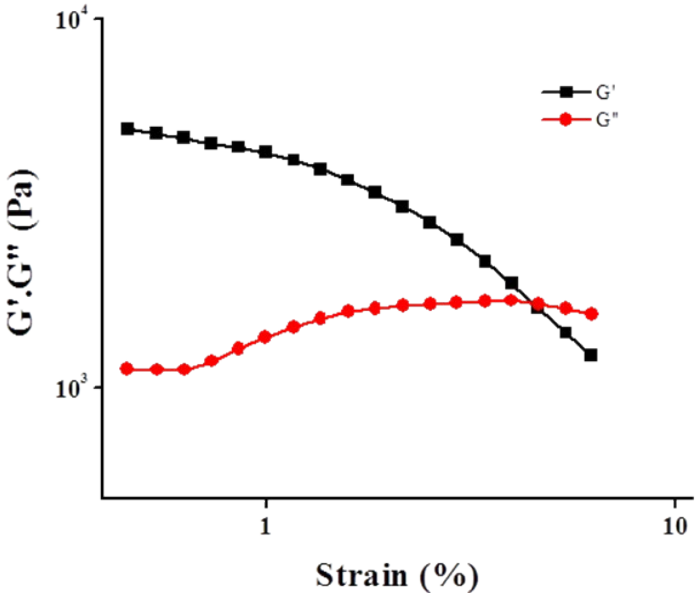


Fig. S21 Oscillatory strain sweep measurements (frequency=1.0 rad/s) of **OG**, the squares (black) and circles (red) indicate storage (G') and loss modulus (G") respectively..

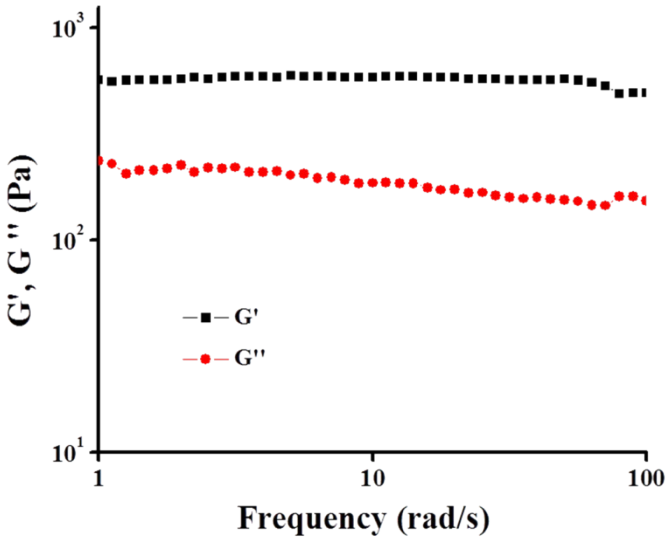


Fig. S22 Oscillatory frequency sweep measurements (strain = 0.01%) of **OG**, the squares (black) and circles (red) indicate storage (G') and loss modulus (G'') respectively.

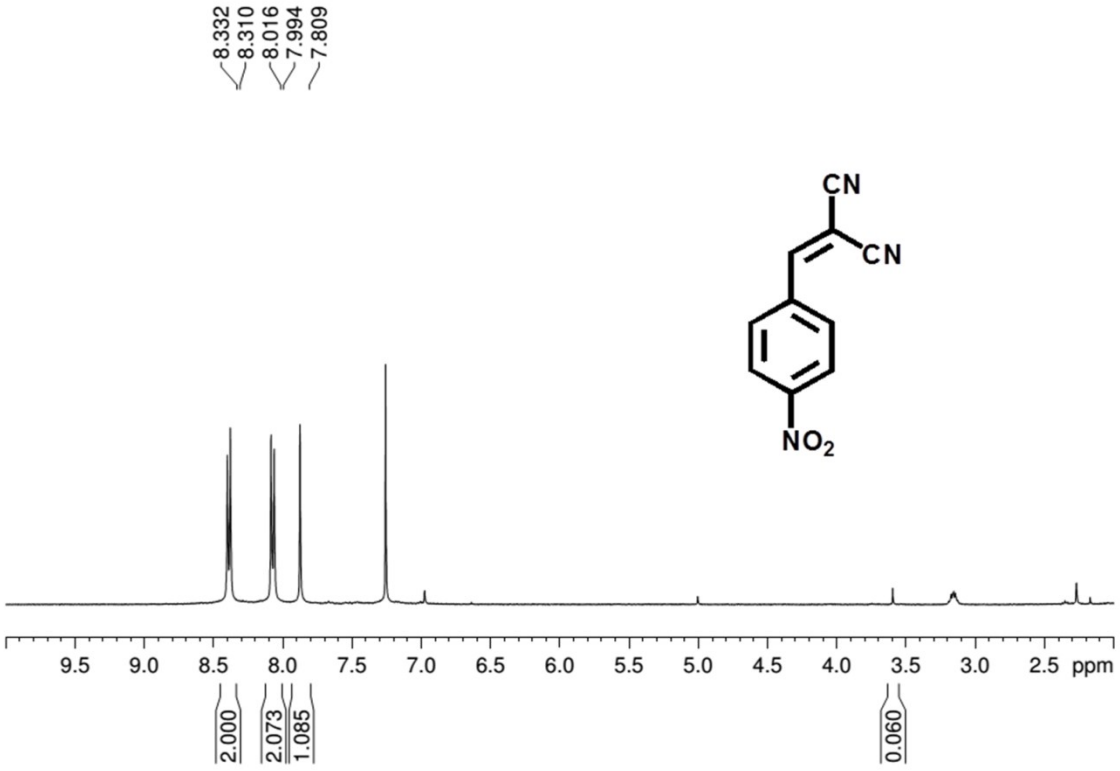
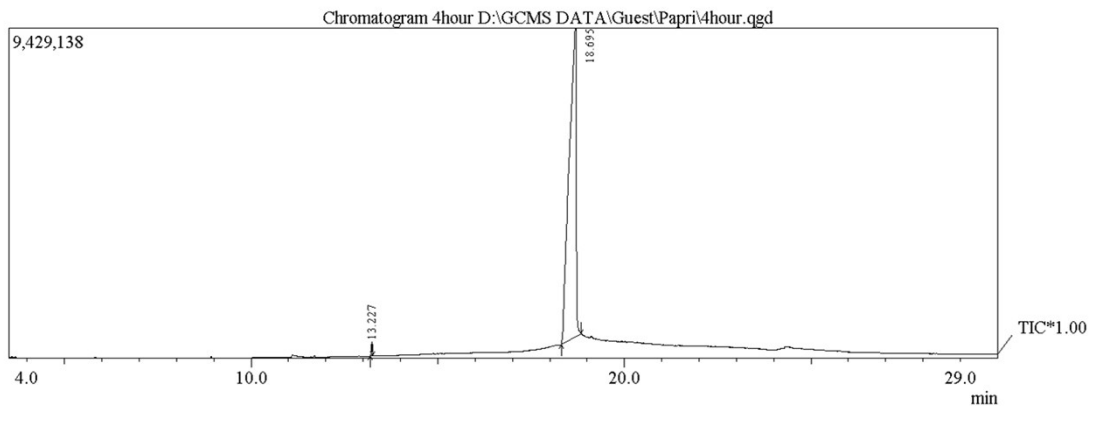


Fig. S23 ^{1}H-NMR spectra (in $CDCl_3$) of 2-(4-nitrobenzylidene)malononitrile formed by the condensation of malononitrile and 4-nitrobenzaldehyde using **HG** xerogel as catalyst.



Spectrum

Peak Report TIC

Peak#	R.Time	I.Time	F.Time	Area	Area%	Height	Height%	A/H	Mark	Name
1	13.227	13.192	13.267	670311	0.57	404748	4.40	1.66		
2	18.695	18.308	18.842	116478428	99.43	8801792	95.60	13.23		
				117148739	100.00	9206540	100.00			

Fig. S24 GC-MS of 2-(4-nitrobenzylidene)malononitrile formed by the condensation of malononitrile and 4-nitrobenzaldehyde after 4 hours using **HG** xerogel as catalyst.

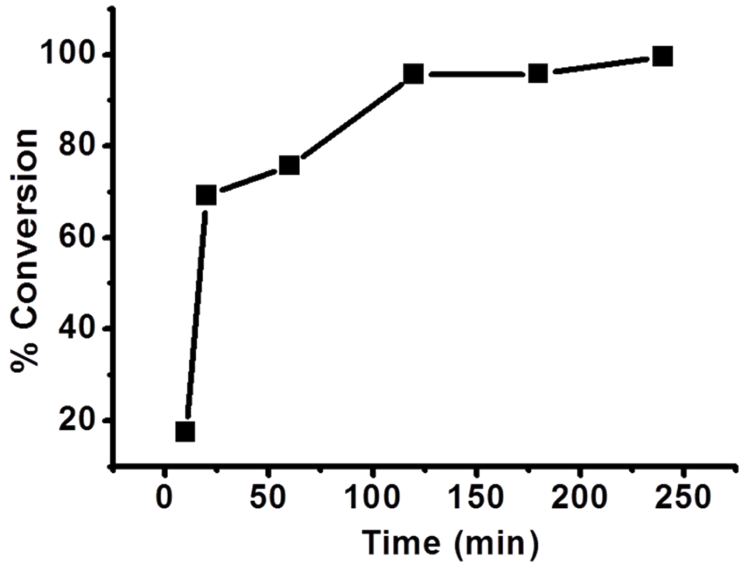


Fig. S25 Conversion [%] versus time [min] for Knoevenagel condensation reaction of 4-nitrobenzaldehyde and malononitrile at 40°C in THF.

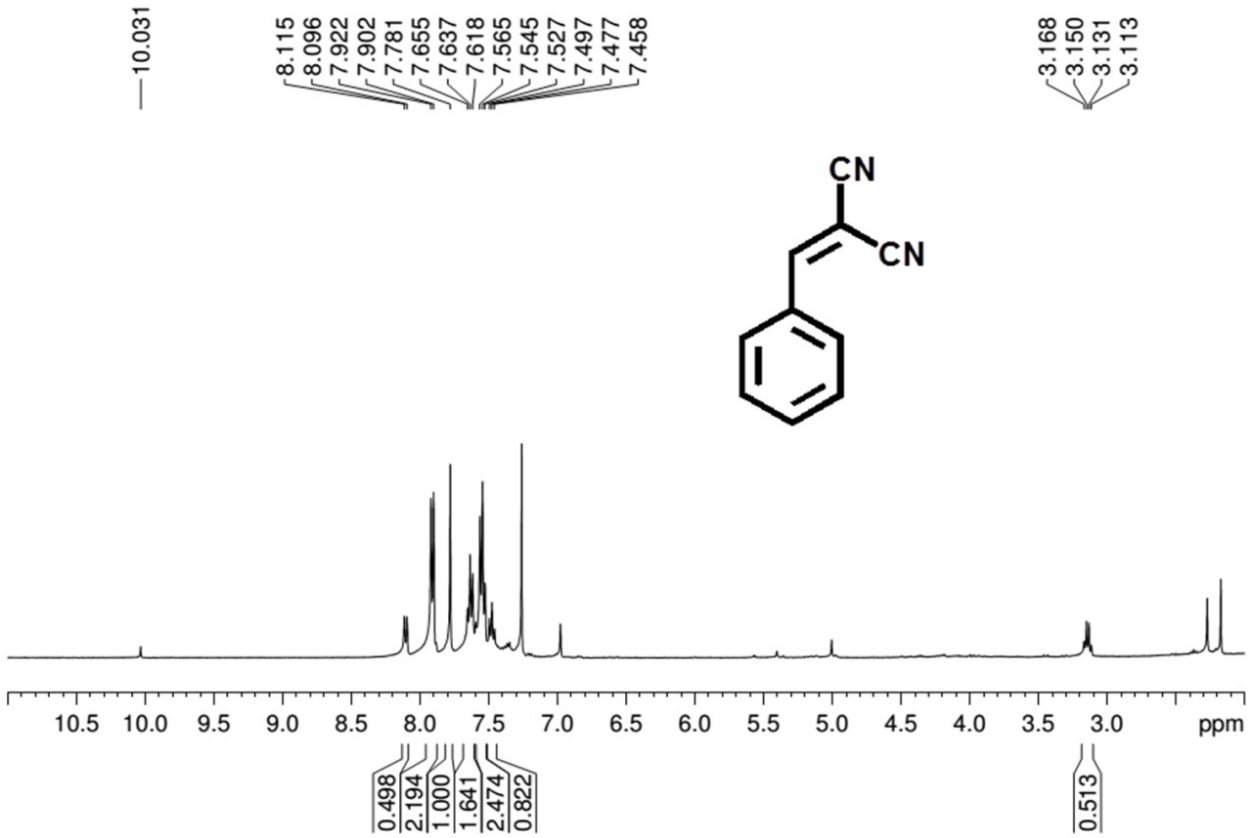


Fig. S26 ^{1}H-NMR spectra (in $CDCl_3$) of 2-benzylidenemalononitrile formed by the condensation of malononitrile and benzaldehyde using **HG** xerogel as catalyst.

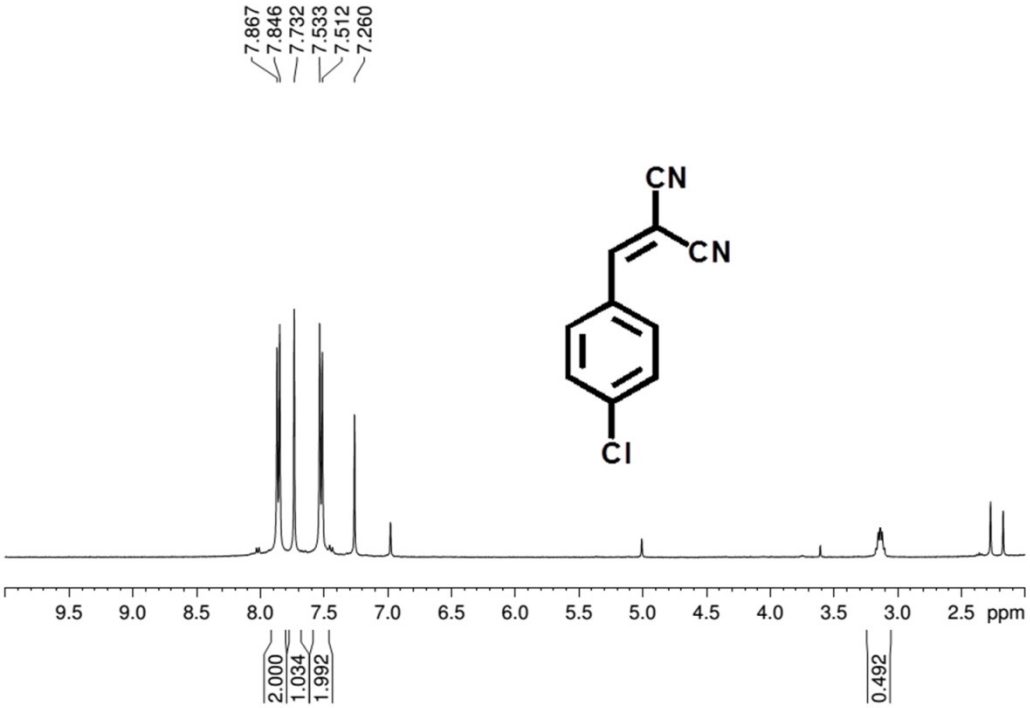


Fig. S27 ^{1}H-NMR spectra (in $CDCl_3$) of 2-(4-chlorobenzylidene)malononitrile formed by the condensation of malononitrile and 4-chlorobenzaldehyde using **HG** xerogel as catalyst.

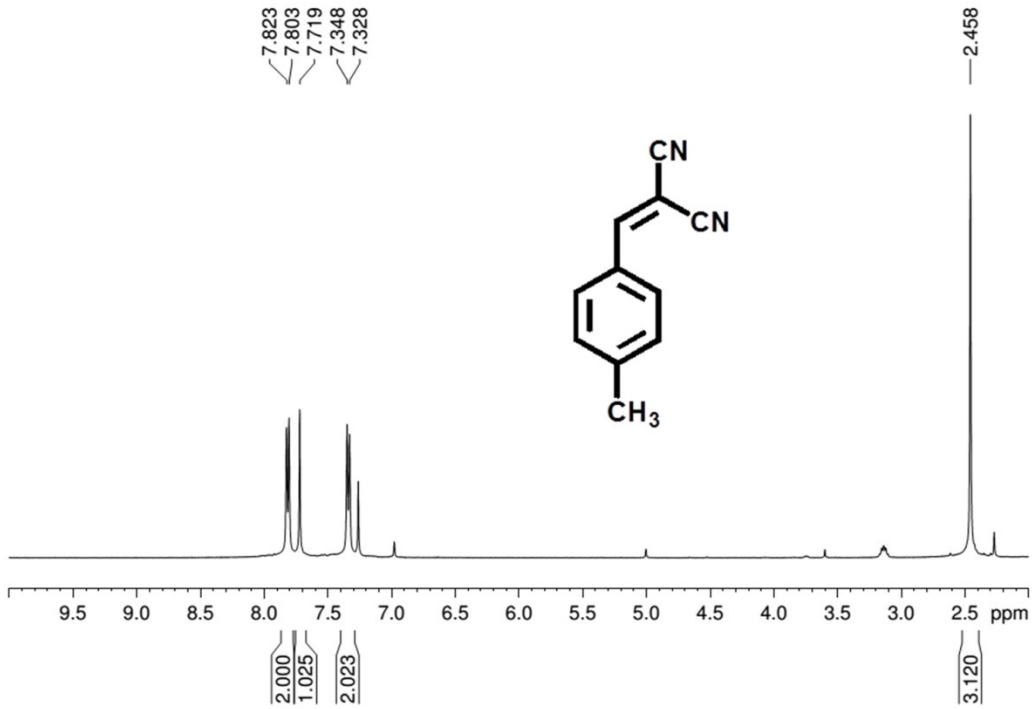


Fig. S28 ^{1}H-NMR spectra (in $CDCl_3$) of 2-(4-methylbenzylidene)malononitrile formed by the condensation of malononitrile and p-tolualdehyde using **HG** xerogel as catalyst.

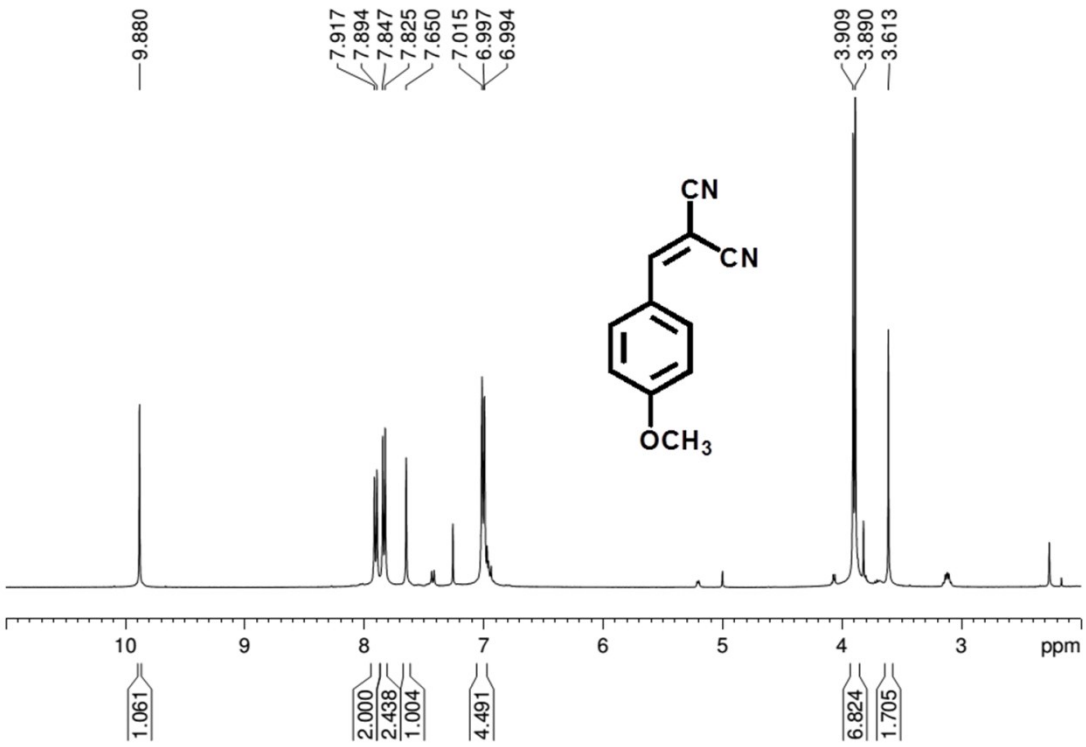


Fig. S29 ^{1}H-NMR spectra (in $CDCl_3$) of 2-(4-methoxybenzylidene)malononitrile formed by the condensation of malononitrile and p-anisaldehyde using **HG** xerogel as catalyst.

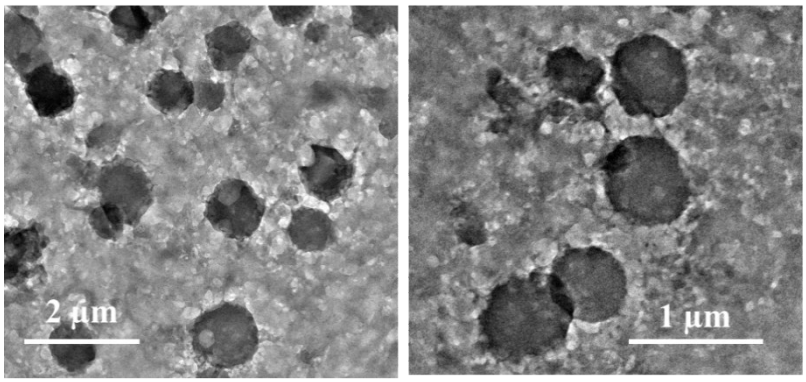


Fig. S30 TEM iamges of **HG** xerogel after 4th cycle of catalytic reaction.

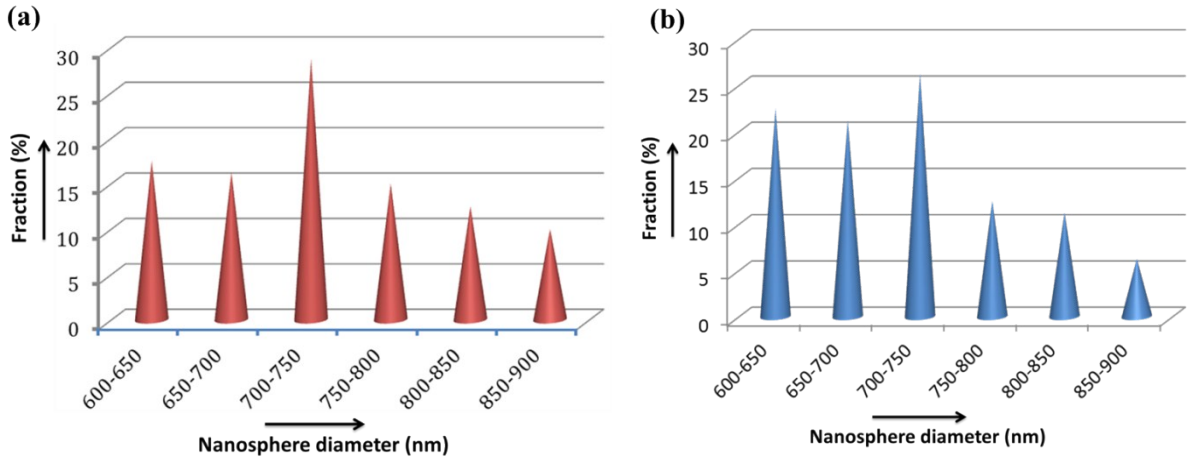


Fig. S31 (a) Size distribution histogram plot of **HG** xerogel before catalytic reaction, (b) Size distribution histogram plot of **HG** xerogel-catalyst, recovered after 4th cycle of catalytic reaction.

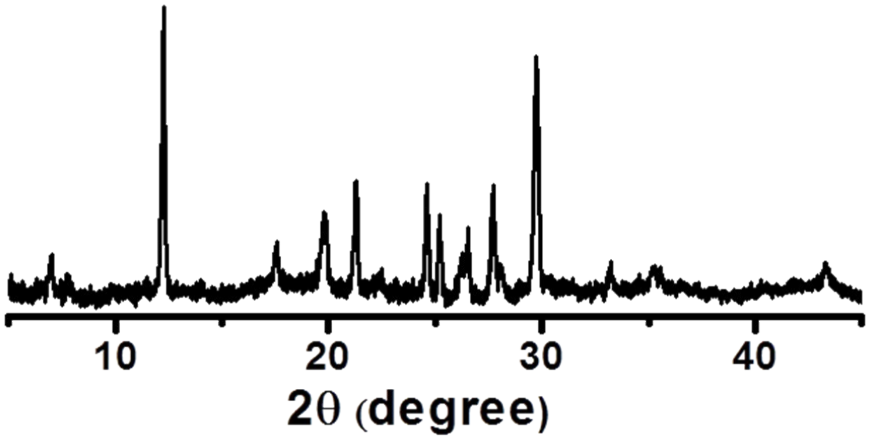


Fig. S32 PXRD pattern of **HG** xerogel (HG@THF) after immersed in THF for 6 hours at 40°C.

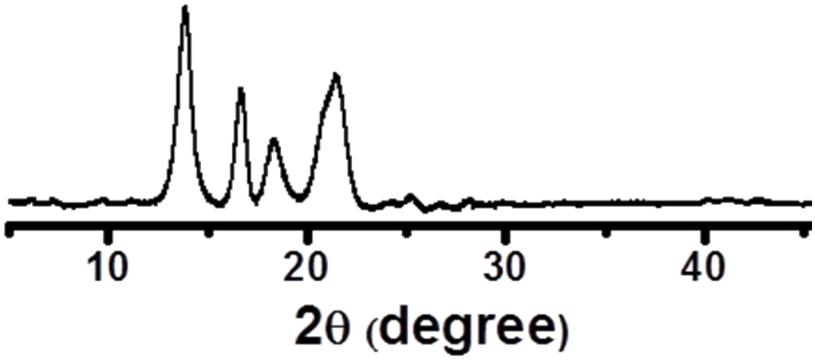


Fig. S33 PXRD pattern of **OG** xerogel (OG@THF) after immersed in THF for 6 hours at 40°C.

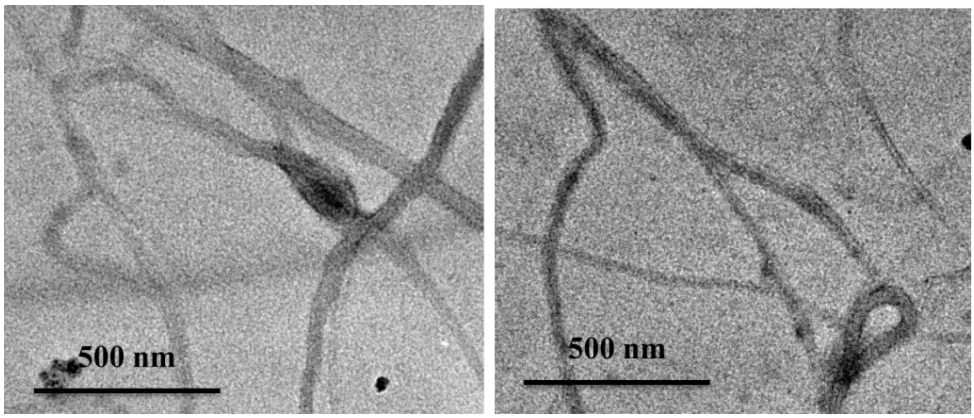


Fig. S34 TEM image of **OG** xerogel after immersed in THF for 6 hours at 40°C.