Supporting information

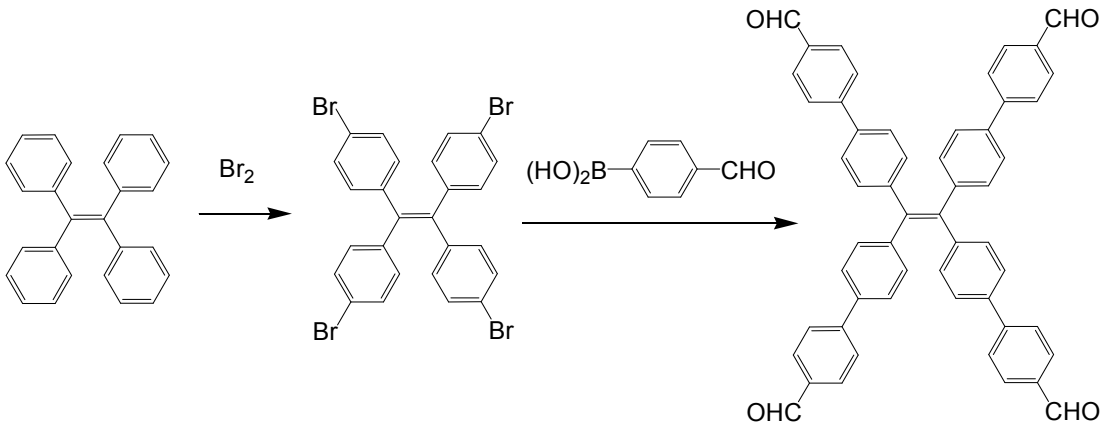
Experimental

Materials and methods

Chemicals and solvents were obtained from commercial sources and used as received. Tetrakis(4-aminophenyl)-methane was prepared according to the literature method.[1] Mass spectra were recorded on a Bluker UltrafleXtreme MALDI TOF/TOF Mass Spectrometer. Scanning electron micrographs were recorded on a JSM-6330F emission environmental scanning electron microscope. Samples were prepared by dispersing in EtOH upon sonication and placing on top of aluminum foil. Transmission electron micrographs were conducted on a JEOL JEM-2010HR microscope. Samples for TEM observations were prepared by dispersing the gels in ethanol by sonication and then immersing a carbon-coated copper grid. IR spectra were recorded on a Bruker Nicolet 205 FT-IR spectrometer with KBr pellets in the range 4000-400 cm^{-1}. Adsorption measurements were performed using a Quantachrome Autosorb-iQ_2 or Autosorb-iQ analyzer. Prior to analysis, the DCG-1 aerogel was degassed at 373^{o}C for 12 h to remove the solvated molecules. The photoluminescence spectra were measured on EDINBURGH FLSP920 combined fluorescence life time and stead states spectrometer.

Synthesis of 1,1,2,2-tetrakis(4-formyl-(1,1'-biphenyl))ethene (B4). The synthetic route is shown in Scheme S1. Tetrakis(4-bromophenyl)ethylene was prepared according to the published procedure.[2] Tetrakis(4-bromophenyl)ethylene (684 mg, 1 mmol) and 4-formylphenylboronic acid (900 mg，6 mmol) was dissolved in toluene (80 mL), and then an aqueous solution of K_2CO_3 (1.66 g, 12 mmol) in water (15 mL) and tetrabutyl ammonium chloride (1 mL) were added. Then $Pd(PPh_3)_4$ catalyst (10 mg) was added and the reaction mixture was stirred at 85^{o}C for 1 d. After cooling to room temperature, the reaction mixture was mixed with water and the organic layer was precipitated by CH_3OH to get crude product. Recrystallization with $CHCl_3$ and diethyl ether to obtain yellowish green solid (535 mg, 71%). ^{1}H NMR (DMSO-d_6 400

Hz): δ (ppm) = 10.03 (s, 4H), 7.96 (d, J = 8.3 Hz, 8H), 7.90 (d, J = 8.3 Hz, 8H), 7.69 (d, J = 8.3 Hz, 8H), 7.24 (d, J = 8.3 Hz, 8H). MS (MALDI-TOF): *m/z* calcd for $C_{54}H_{36}O_4$ $[M]^+$ 748.261, found 748.294.



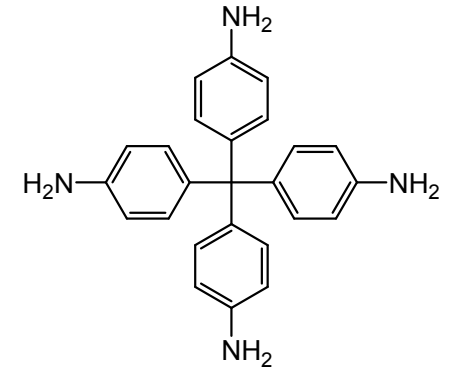
Scheme S1. Synthetic route for 1,1,2,2-tetrakis(4-formyl-(1,1'-biphenyl))ethane (B4).

Preparation of DCG-1. A4 (5.7 mg, 0.020 mmol) was dissolved in DMSO (0.5 mL) and B4 (11.2 mg, 0.020 mmol) in DMSO (0.5 mL). The solutions were mixed and one drop of acetic acid (3 mol/L, in DMSO) was added. The reaction mixture was heated at 80^{o}C for 1 d to obtain a yellow opaque gel. The wet gel was subsequently dried by subcritical CO_2(l) to get the corresponding aerogel (17 mg, >99%).

Detection of picric acid (PA). The DCG-1 gel was dispersed in water with the aid of sonication to give a 10 mL gel (0.13 mmol L^{-1}). Fluorescence quenching titrations were carried out by gradually adding aqueous solution of PA (1.0×10^{-2} mol L^{-1}) into 3.00 mL of the gel dispersed medium in an incremental fashion. The corresponding fluorescence emission spectra and the PL intensity of the mixture were recorded excited at 469 nm.

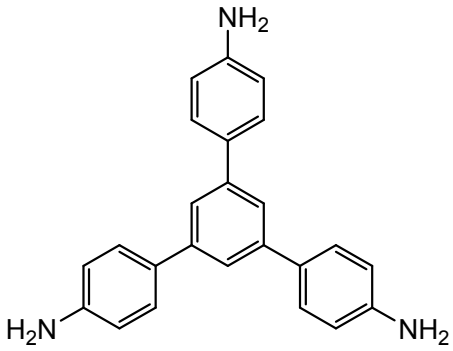
1 P. Ganesan , X. Yang , J. Loos , T. J. Savenije, R. D. Abellon , H. Zuilhof and E. J. R. Sudhölter, *J. Am. Chem. Soc.*, 2005, **127**, 14530–14531.

2 V. S. Vyas, M. Banerjee and R. Rathore, *Tetrahedron Lett.*, 2009, **50**, 6159–6162.

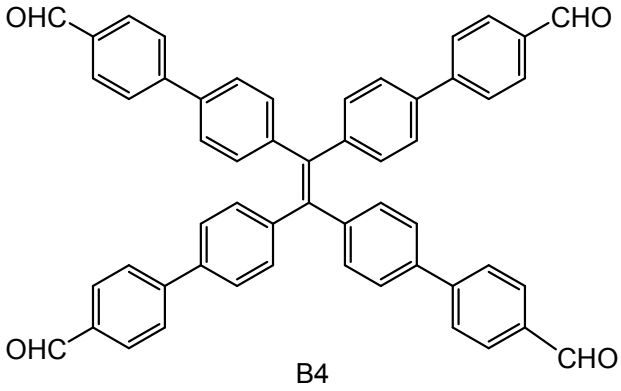


A4

A2



A3



B4

Scheme S2. Molecular structures of building units for DCGs, tetrakis-(4-aminophenyl)methane (A4), 1,4-diaminobenzene (A2), 1,3,5-tris(4-aminophenyl)benzene (A3) and 1,1,2,2-tetrakis(4-formyl-(1,1'-biphenyl))ethene (B4).

Table S1. Gelation tests of B4 and various bridging amines as shown in Scheme S2.

Entry	Precursors and solvent[a]	Temperature	Results
1	B4 (7.5 mg, 0.01 mmol), A4 (3.8 mg, 0.01 mmol), DMSO (1.0 mL), cat.	80°C	Partial weak yellow gel
2	B4 (11.2 mg, 0.015 mmol), A4 (5.7 mg, 0.015 mmol), DMSO (1.0 mL), cat.	80°C	Yellow opaque gel
3	B4 (15.0 mg, 0.02 mmol), A4 (7.6 mg, 0.02 mmol), DMSO (1.0 mL), cat.	80°C	Yellow opaque gel (DCG-1
4	B4 (7.5 mg, 0.01 mmol), A2 (2.2 mg, 0.02 mmol), DMSO (1.0 mL), cat.	80°C	Precipitate
5	B4 (11.2 mg, 0.015 mmol), A2 (3.2 mg, 0.03 mmol) , DMSO (1.0 mL), cat.	80°C	Precipitate
6	B4 (15.0 mg, 0.02 mmol), A2 (4.3 mg, 0.04 mmol), DMSO (1.0 mL), cat.	80°C	Precipitate
7	B4 (15.0 mg, 0.02 mmol), A2 (4.3 mg, 0.04 mmol), DMF (2.0 mL), cat.	80°C	Precipitate
8	B4 (22.4 mg, 0.03 mmol), A2 (6.5 mg, 0.06 mmol), DMF (2.0 mL)	80°C	Precipitate
9	B4 (29.9 mg, 0.04 mmol), A2 (8.6 mg, 0.08 mmol) , DMF (2.0 mL)	80°C	Precipitate
10	B4 (11.2 mg, 0.015 mmol), B3 (7.0 mg, 0.015 mmol), DMSO (1.0 mL), cat.	80°C	Precipitate

[a] cat, one drop of acetic acid (3 mol/L, in DMSO) was added as catalyst.

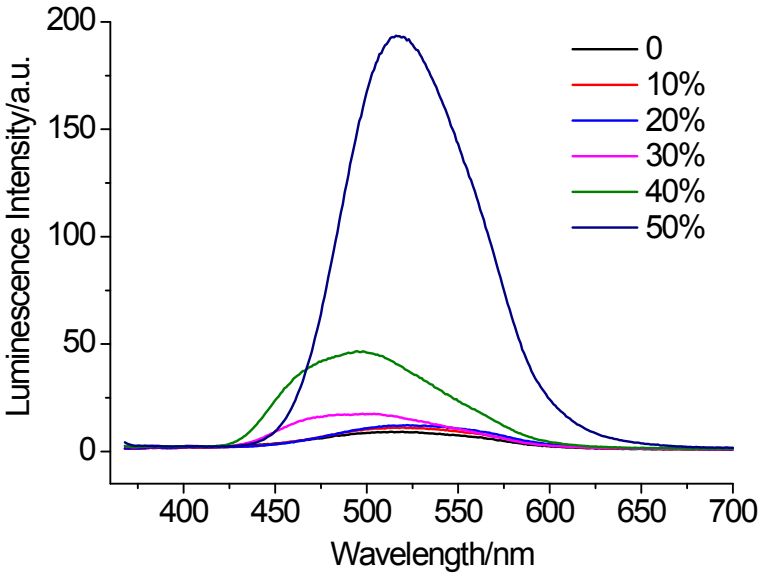


Figure S1. Fluorescence emission spectra of B4 in DMSO-H_2O mixtures with the volume fractions of water varying in the range of 0-50% (1.0×10^{-5} mol L^{-1}, λ_{ex} = 358 nm).

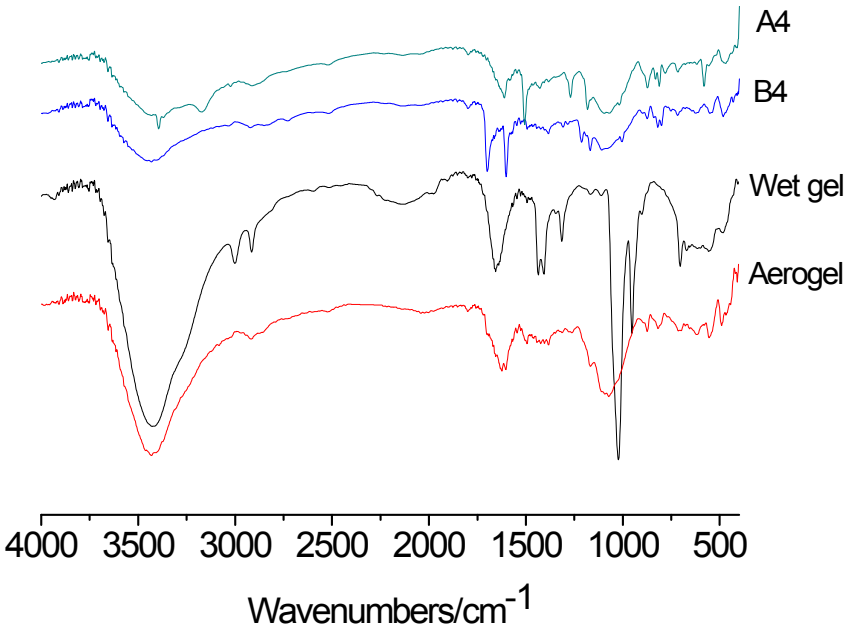


Figure S2. FT-IR spectra of A4, B4, DCG-1 wet gel and aerogel.

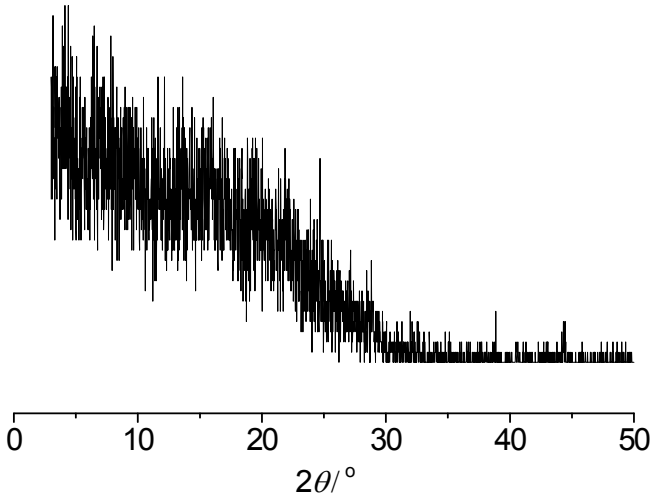


Figure S3. Powder X-ray diffraction pattern of DCG-1.

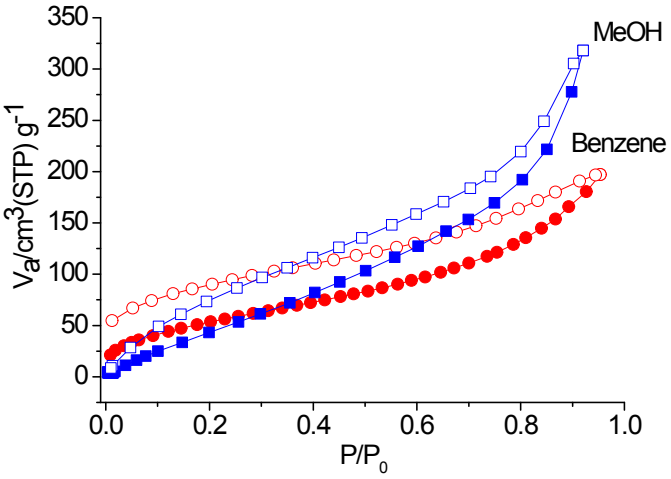


Figure S4. Methanol and benzene vapour adsorption (solid symbols) and desorption (open symbols) isotherms at 298 K.

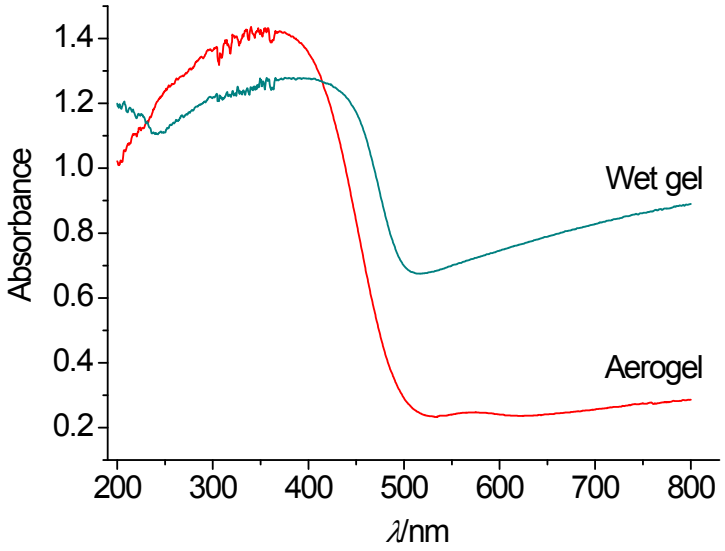


Figure S5. UV-vis absorption spectra of DCG-1 wet gel and aerogel.

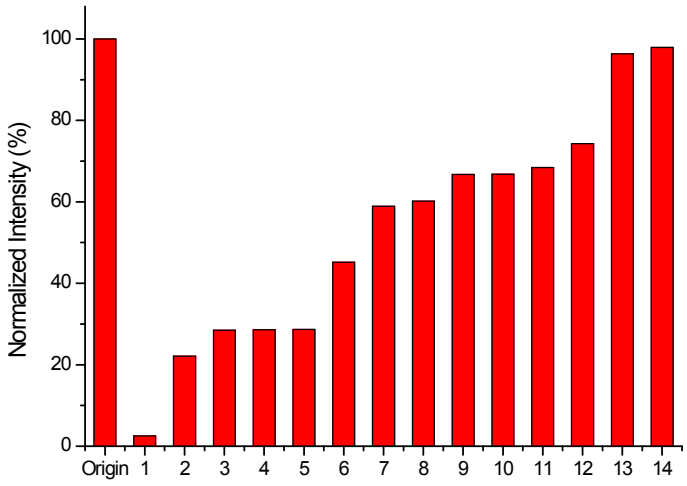


Figure S6. Reduction in the fluorescence intensity upon addition of various quenchers (1, PA; 2, 2,4,6-trinitrotoluene; 3, 2,4-dinitrotoluene; 4, 4-nitrobenzaldehyde; 5, 3,5-dinitrosalicylic acid; 6, 2,6-dinitrotoluene; 7, 5-nitro-1,3-benzenedicarboxylic acid; 8, 2-bromo-nitrobenzene; 9, 4-fluoro-nitrobenzene; 10, 4-cholo-nitrobenzene; 11, 2,5-dibromo-nitrobenzene; 12, water; 13, benzoic acid; 14, 2-nitro-1,4-benzenedicarboxylic acid).

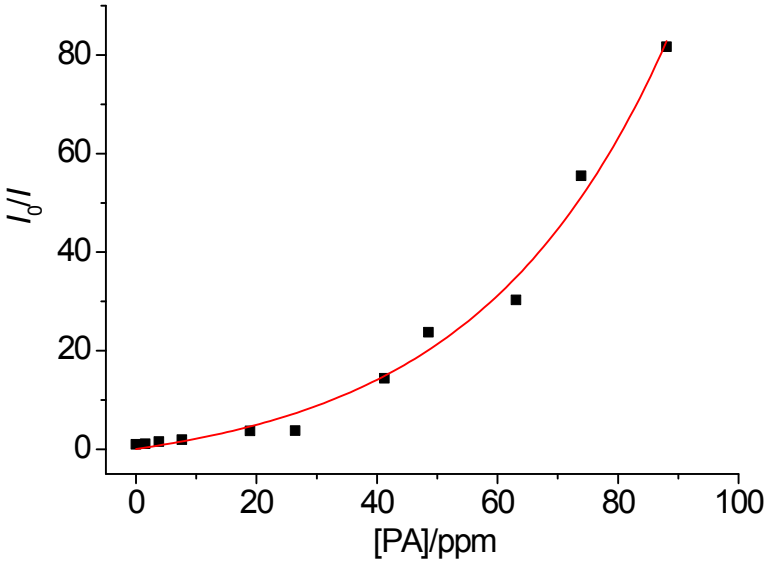


Figure S7. Stern-Volmer plot of the relative fluorescence intensity vs. PA concentration in aqueous solution.