

Supporting Information

Structural variation in Zn(II) coordination polymers built with a semi-rigid tetracarboxylate and different pyridine linkers: synthesis and selective CO₂ adsorption studies

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General Methods

Reagent grade 3,3',5,5'-tetracarboxydiphenylmethane (**L₆H₄**), 4-cyanopyridin, hydrazine hydrate and Zn(NO₃)₂·6H₂O were acquired from Aldrich Chemical Company (USA) and used as received. All the solvents were acquired from S.D. Fine Chemicals (India), which were freshly purified before use following standard procedure [1]. Confirmation of the ligands **L₂** and **L₃** were obtained by ¹H NMR and ¹³C NMR spectroscopy on a JEOL JNM-LA500 FT instrument (500 MHz) in DMSO-d₆ with TMS as the internal standard. The following abbreviations were utilized to describe peak patterns: s = singlet, d = doublet, t = triplet, dd = doublet of doublet, br = broad and m = multiplet. Melting points were recorded on an electrical melting point apparatus by PERFIT India and are uncorrected. Infrared spectra were recorded on a (KBr disk, 400–4000 cm⁻¹) Perkin-Elmer Model 1320 spectrometer. Powder X-Ray diffraction (PXRD) patterns were recorded with a Bruker D8 Advance diffractometer equipped with nickel filtered Cu-K_α radiation. The tube voltage and current were 40 kV and 40 mA, respectively. Microanalyses for the compounds were obtained using a CE-440 elemental analyzer (Exeter Analytical Inc.). Thermogravimetric analysis (TGA) (5 degree/min heating rate under nitrogen atmosphere) was

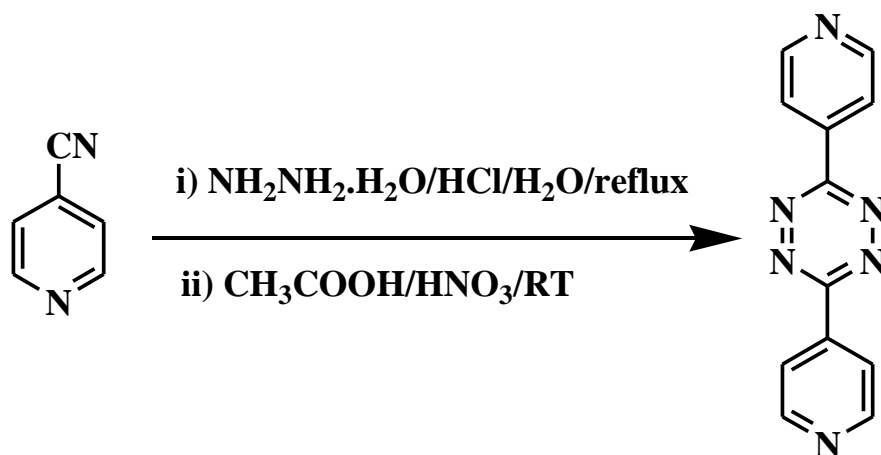
performed with a Mettler Toledo Star System. Elemental analyses were obtained from the Central Drug Research Institute, Lucknow, India.

Gas Adsorption Experiments:

Gas adsorption measurements were performed using automatic volumetric BELSORP-MINI-II adsorption equipment. Prior to BET adsorption measurements, compound **1** was immersed in ethanol solvent for 3 days at room temperature to replace lattice guest molecules and after that, the complex was heated to 120 °C for 12 h under vacuum to produce the guest-free framework (**1'**).

Synthesis of 3,6-dipyridin-4-yl-[1,2,4,5]tetrazine (L**₂)**

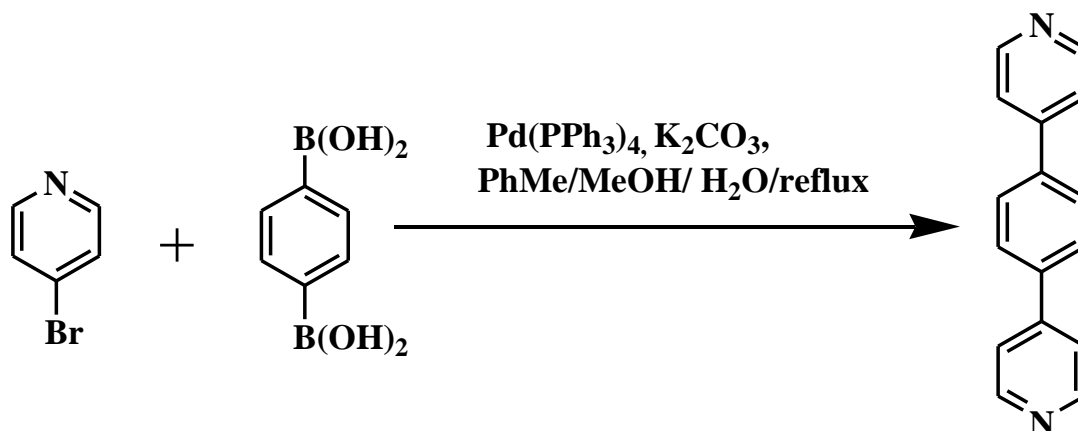
4-Cyanopyridine (5.5 g), hydrazine monohydrate (25 mL), concentrated HCl (5 mL), and deionized water (5 mL) were refluxed together for 2 h. The reaction was allowed to cool to room temperature. The precipitate (orange solid) was filtered and added to 200 mL of glacial acetic acid with stirring. A 35 mL of 30% HNO₃ was added dropwise to the brown solution. The pink solid was collected by filtration and recrystallized from pyridine to yield a purple solid. Melting point: 256 °C. ESI-MS, *m/z* (%): 237 (100) [HL₂⁺] (Fig. S3). ¹H- NMR (500 MHz, DMSO-*d*₆), TMS, 25 °C): δ (ppm) 8.94 (d, 4H, Ar-H), 8.42 (d, 4H, Ar-H). IR (KBr, cm⁻¹, selected peaks): 1389 vs, 1060 s, 920 s, 834 s, 716 s, 598 s, (Fig. S4). Anal. calcd. for C₁₂H₈N₆ : C, 61.01; H, 3.41; N, 35.58 %. Found: C, 61.65; H, 3.72; N, 34.83%.



Scheme S1. Synthetic scheme for ligand **L₂**

Synthesis of 4,4'-(1,4-phenylene)bispyridine [**L₃**].

The bispyridyl compound was prepared using a modified literature procedure [2]. 4-Bromopyridyl hydrochloride (2.4 g, 17.8 mmol), 1,4-phenyldiboronic acid (1.40 g, 5.92 mmol), and K_2CO_3 (11.6 g, 35.5 mmol) were added to a 2:1:1 mixture of dry PhMe/EtOH/ H_2O (300 mL), which had been degassed with argon for 15 min. Next, $Pd(PPh_3)_4$ (0.68 g, 0.59 mmol) was added to the reaction mixture and the solution heated to 120 °C under argon for 48 h. Then, the reaction mixture was cooled to room temperature and the palladium catalyst filtered off using Celite. The organic phase was concentrated under vacuum and then dissolved in CH_2Cl_2 followed by washing with H_2O three times. The organic layer was made acidic (pH 2–3) by adding concentrated HCl drop wise, which caused the desired product to precipitate from solution. The precipitate was collected by filtration and then dissolved in H_2O . Finally, aq. NaOH (10 M) was added drop-wise to the water layer until the pH was ~8–9, which resulted in precipitation of pure product as a white solid. Yield: 65%; mp 193° C; 1H -NMR (500 MHz, $DMSO-d_6$, 25 °C, TMS, δ): 8.68(d, 4H, ArH), 7.76(s, 4H, ArH), 7.54(d, 2H, ArH); ESI-MS (m/z): 233 (100%) [HL_3] $^+$. Anal. calcd. for $C_{16}H_{12}N_2$: C, 82.73; H, 5.21; N, 12.06 %. Found: C, 82.86; H, 5.52; N, 11.83%.



Scheme S2. Synthetic route for **L**₃

Characterization of Ligand **L**₂:

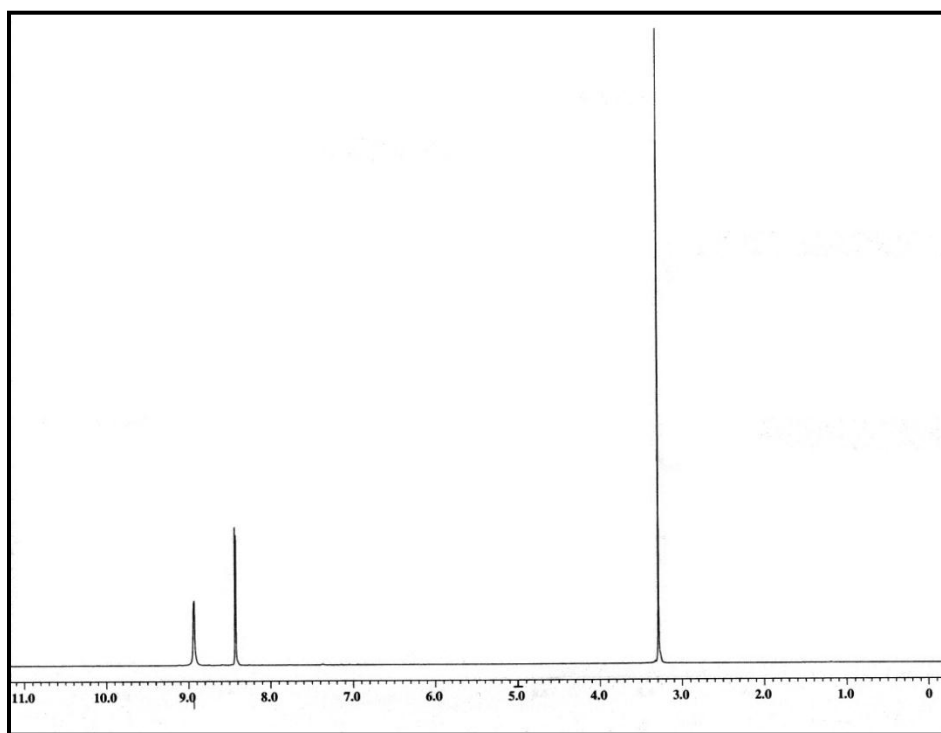


Fig. S1 500 MHz ¹H-NMR spectrum of **L**₂

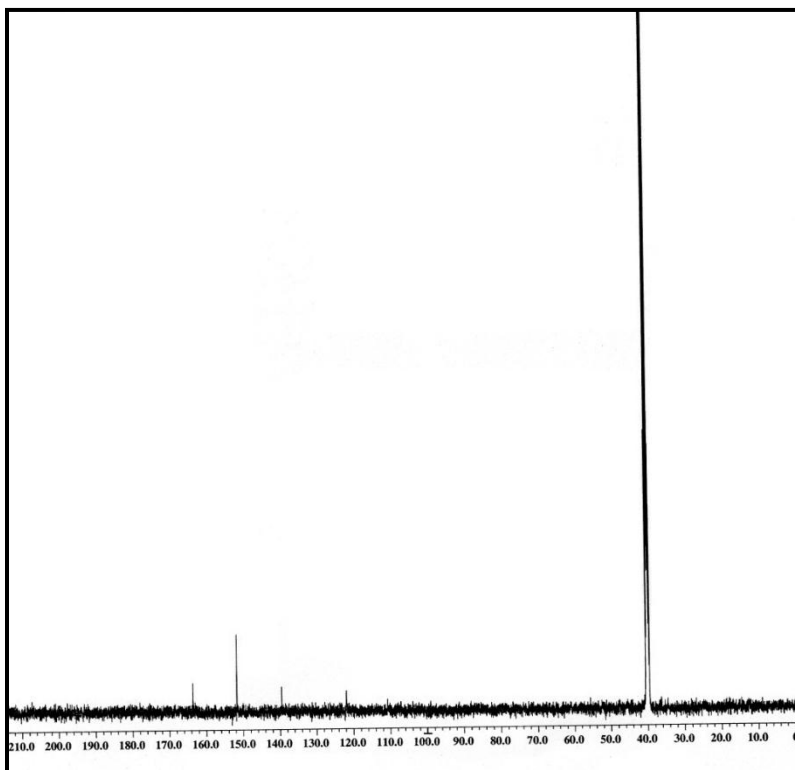


Fig. S2 500 MHz ¹³C-NMR spectrum of L₂

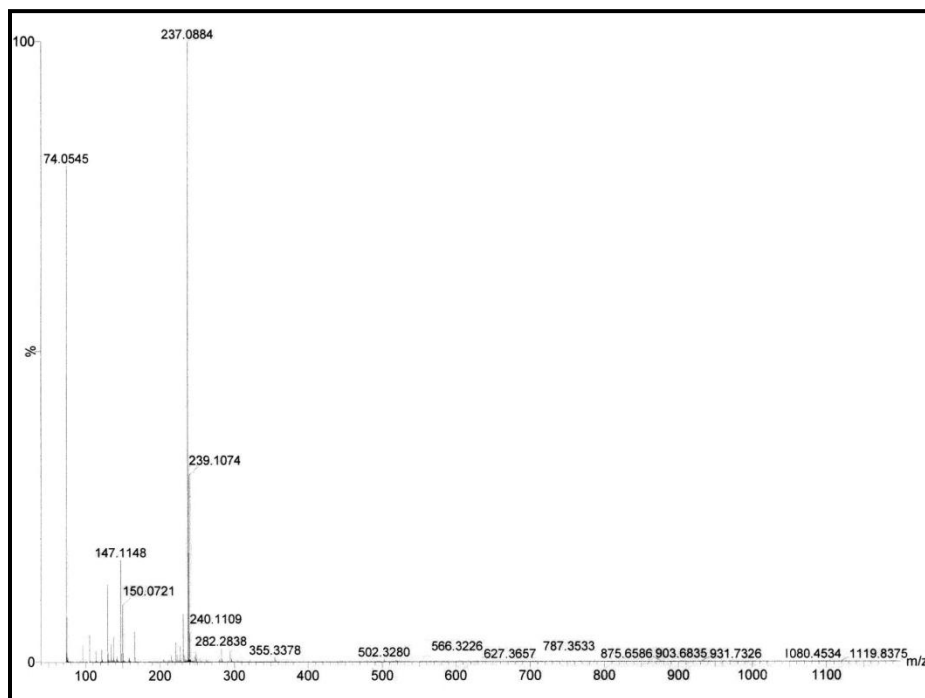


Fig. S3 ESI-MS spectra of L₂

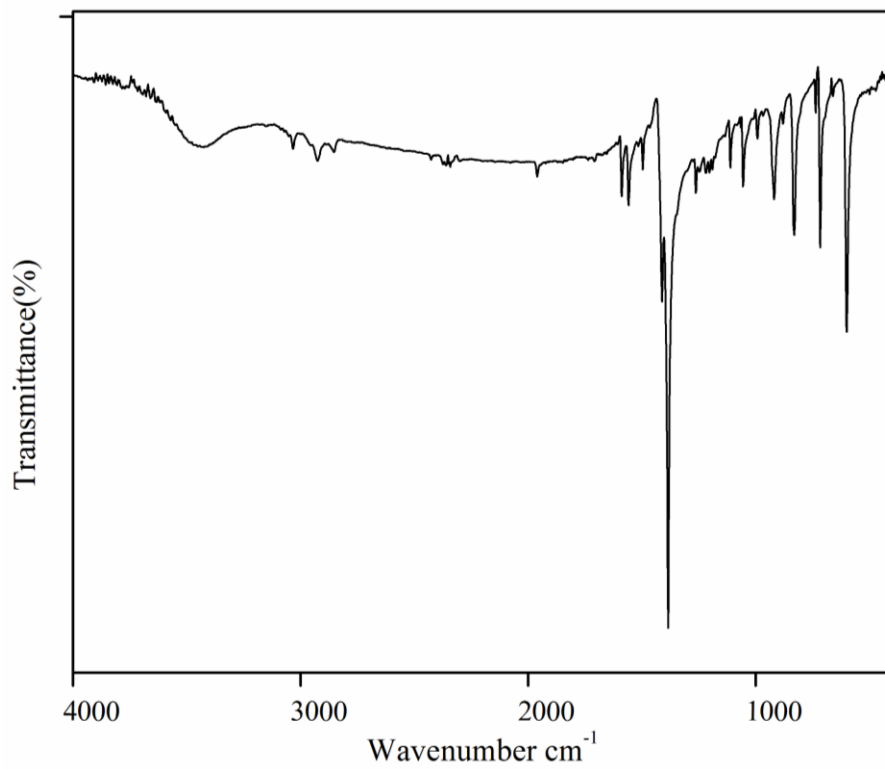


Fig. S4 FTIR spectrum of **L**₂

Characterization of Ligand **L₃:**

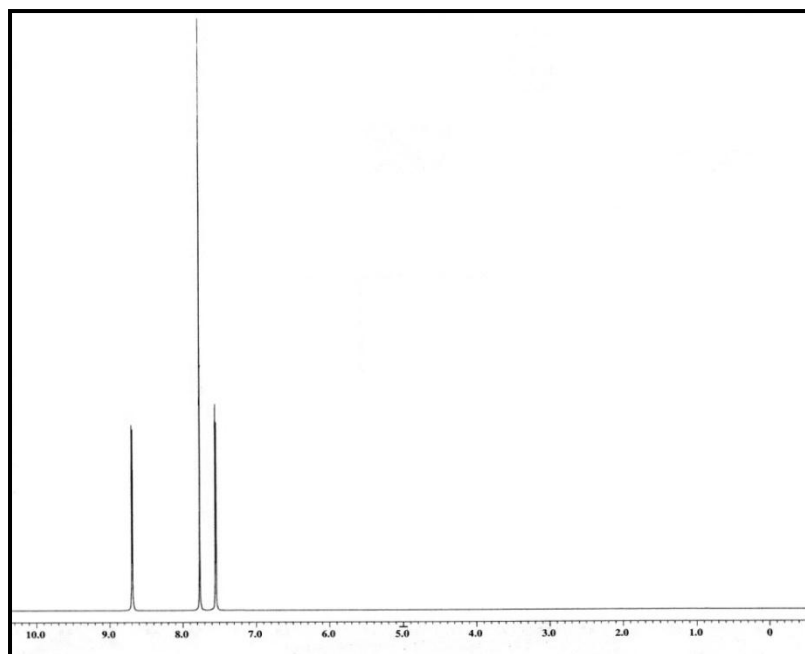


Fig. S5 500 MHz ¹H-NMR spectrum of **L**₃

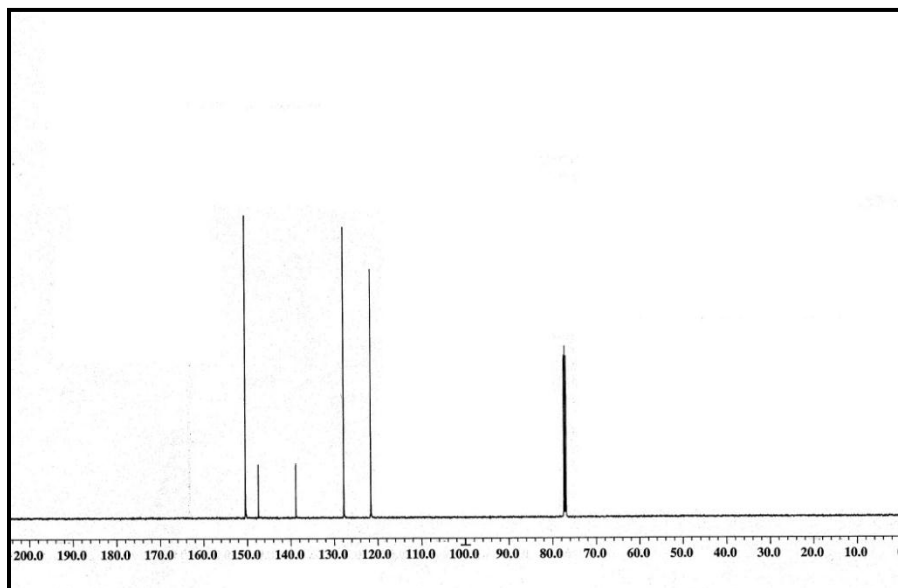


Fig. S6 500 MHz ¹³C-NMR spectrum of L₃

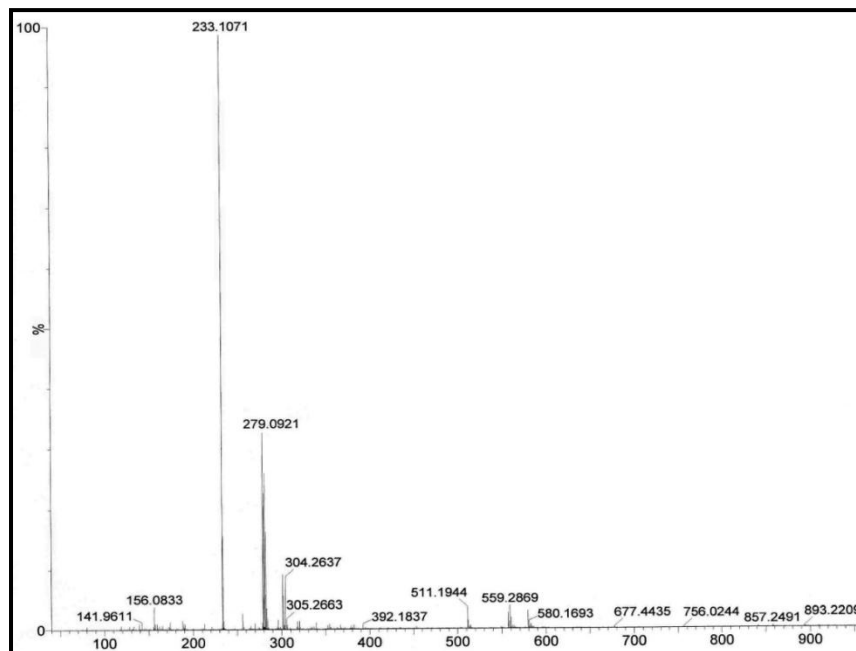


Fig. S7 ESI-MS Mass spectrum of L₃

Characterization of **1**:

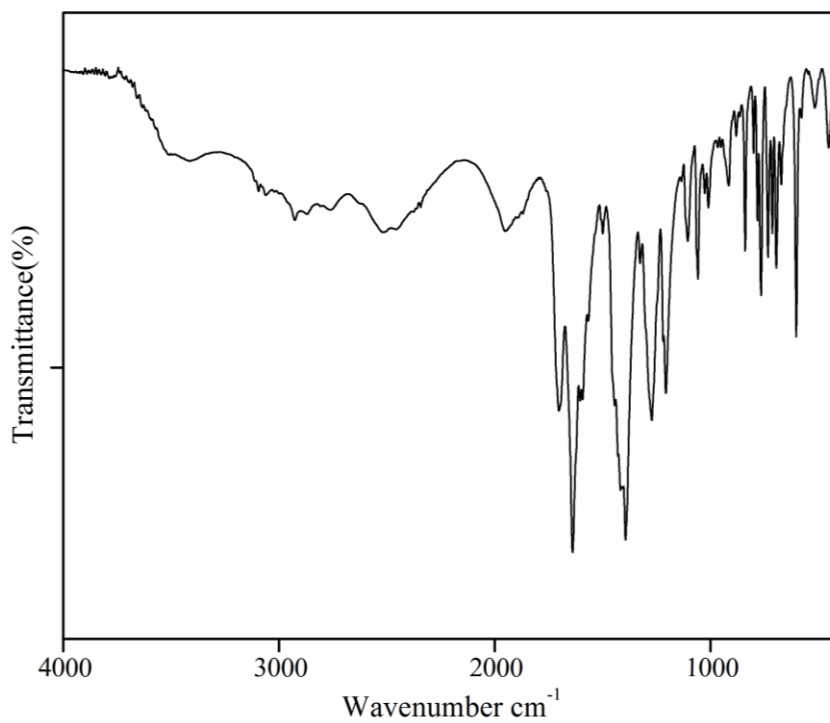


Fig. S8 FTIR spectrum of **1**

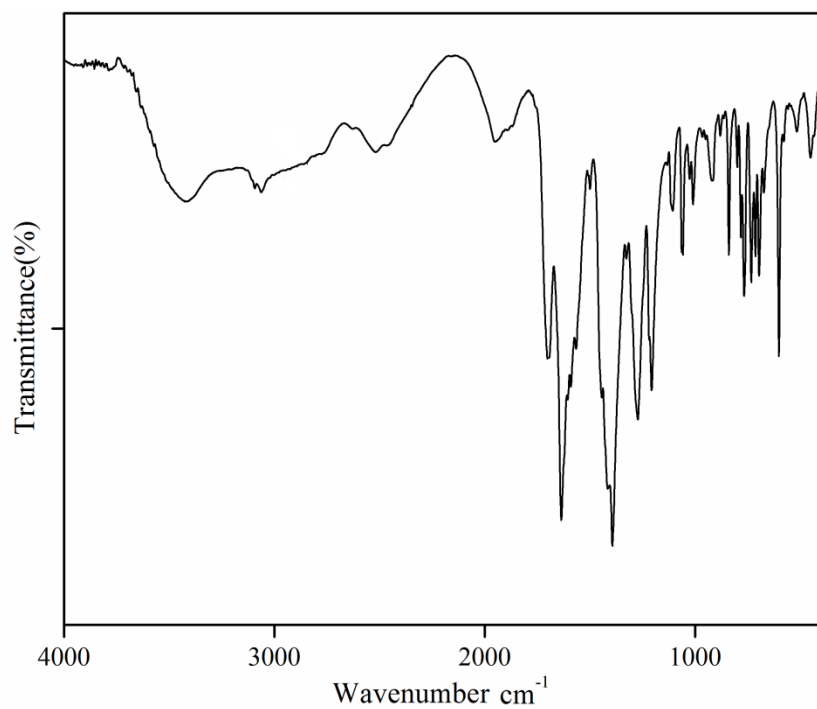


Fig. S9 FTIR spectrum of **1'**

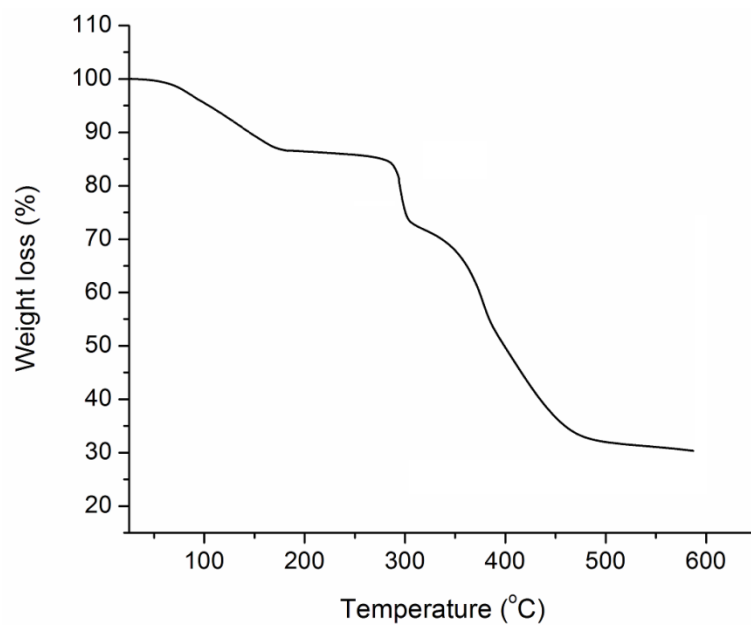


Fig. S10 TGA curve of **1**

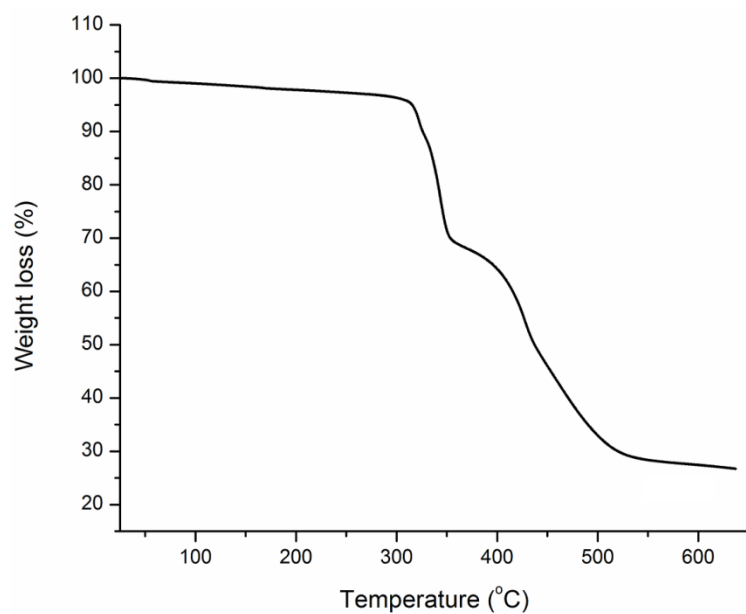


Fig. S11 TGA data after complete removal of guest DMF and H₂O from **1**

Characterization of 2:

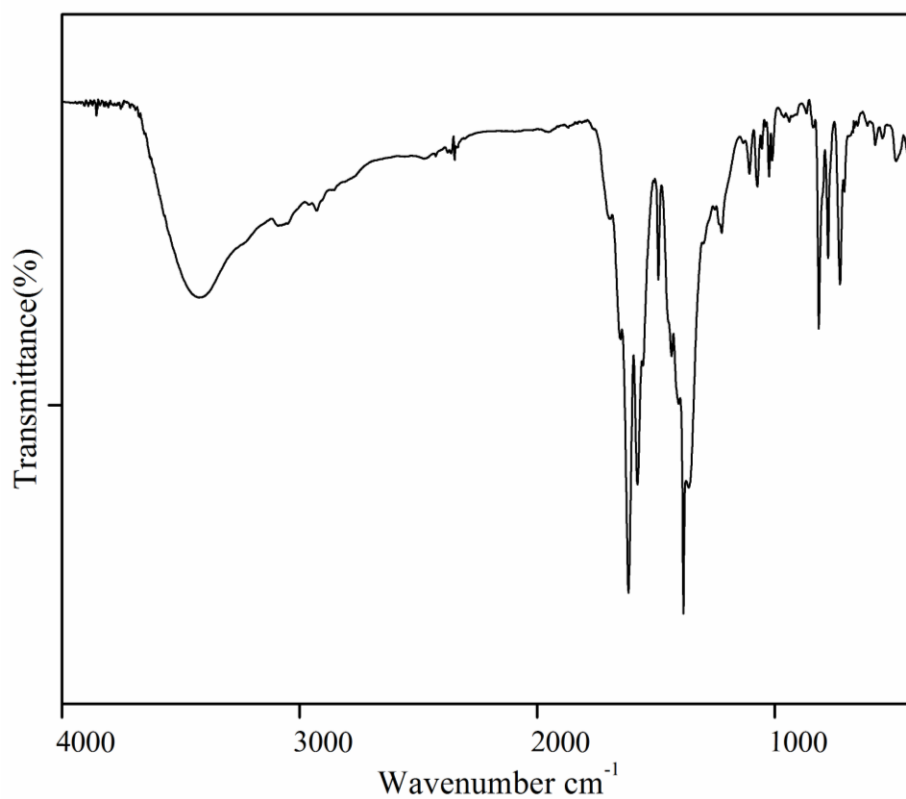


Fig. S12 FTIR spectrum of **2**

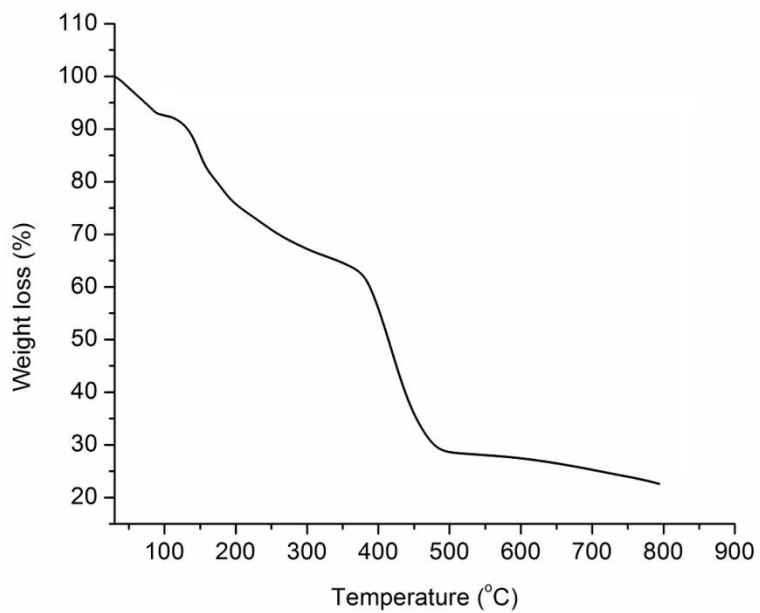


Fig. S13 TGA curve of **2**

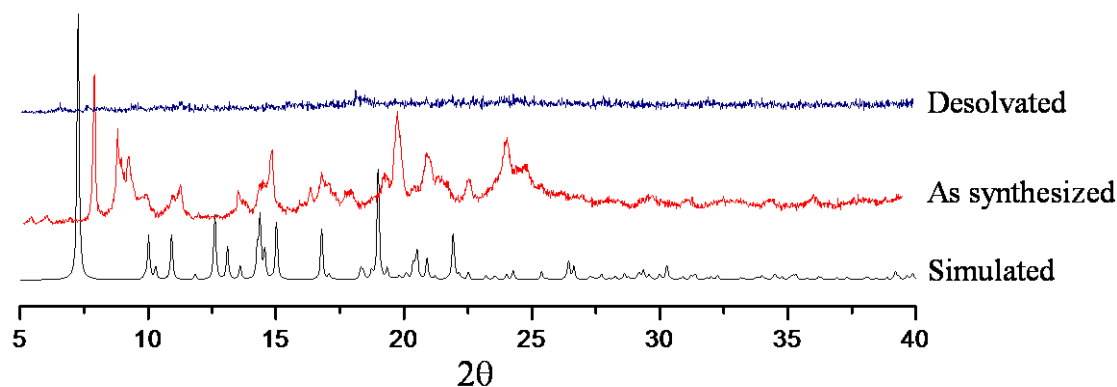


Fig. S14 Powder X-ray diffraction curves for **2**, together with the simulated and desolvated samples, showing complete collapse of the framework after solvent removal.

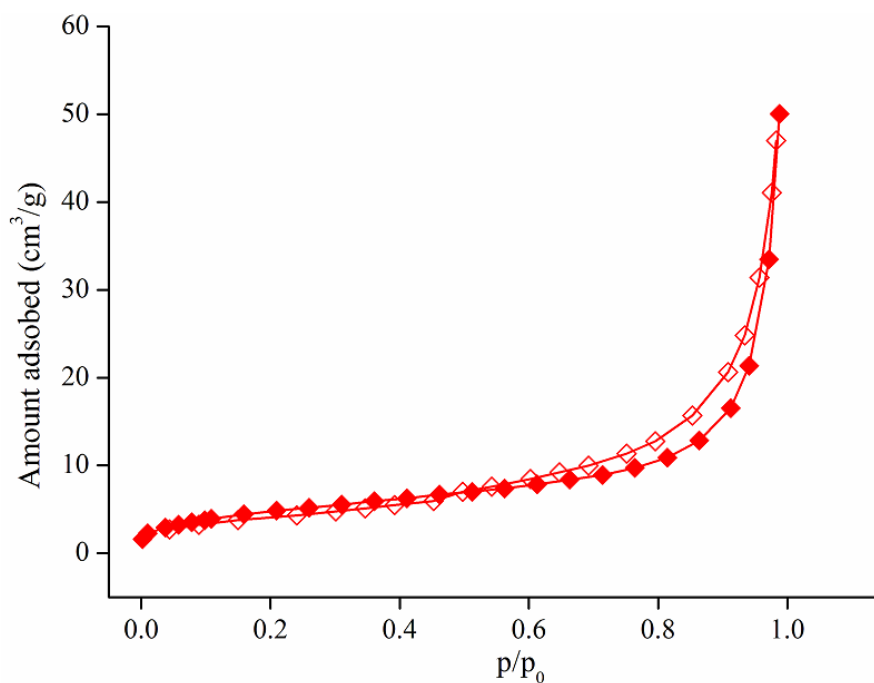


Fig. S15 N₂ gas sorption isotherm of **1'** at 77 K.

1 (a) D. D. Perrin and W. L. F. Armarego, *Purification of Laboratory Chemicals*; Pergamon Press: New York, 1980 and reference cited therein. (b) B. S. Furniss, A. J. Hannaford, P. W. G. Smith and A. R. Tatchel, *Vogel's textbook of Practical Organic Chemistry*, 5th ed.; Pearson: Harlow, 1989 and reference cited therein

2 A. J. Amoroso, A. M. W. Cargill Thompson, J. P. Maher, J. A. McClevery and M. D. Ward, *Inorg. Chem.* 1995, **34**, 4828.