Electronic Supplementary Material (ESI) for Chemical Communications

Supporting Information

Coordination driven axial chirality in a microporous solid assembled from an achiral linker *via in situ* C-N coupling

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Experimental Section:

Materials: All the reagents and solvents employed were commercially available and used as supplied without further purification. $Zn(NO_3)_2 \cdot 6H_2O$, $Cd(NO_3)_2 \cdot 6H_2O$ and *trans*-glutaconic acid were obtained from Aldrich Chemical Co. 4,4′-azobipyridine has been synthesised following literature procedure.[1]

Synthesis of {Zn(*Z*-dhpe)·3H$_2$O·EtOH}$_n$ (1) and {Cd$_2$(*Z*-dhpe)$_2$·7H$_2$O·2EtOH}$_n$ (2): An aqueous solution (50 mL) of disodium *trans*-glutaconate (Na_2tga) (1mmol, 0.174 g) was mixed with ethanolic solution (50 mL) of 4,4′-azobipyridine (azpy) (0.5 mmol, 0.078 g) and the resulting solution was stirred for 20 min. to mix well. $Zn(NO_3)_2 \cdot 6H_2O$ (1mmol, 0.297 g) was dissolved in 100 mL water and 2 mL of this Zn(II) solution was slowly and carefully layered with the above mixed ligand solution using 1 mL buffer (1:2 of water and EtOH) solution. Good quality orange colour block shaped crystals were isolated after 45 days. The crystals were separated and washed with EtOH/water (1:1) mixture and air dried. (Yield 53 %). Anal. calcd. for $C_{17}H_{24}ZnN_4O_8$: C, 42.74; H, 5.06; N, 11.73. Found: C, 42.31; H, 4.61; N, 11.02 %. FT-IR (KBr pellet, 4000-400 cm^{-1}): 3430(s), 3244(s), 1612(s), 1445(m), 1114(m). Crystals of **2** were prepared by similar procedure.

Physical Measurements:

Elemental analysis was carried out using a Thermo Scientific Flash 2000 CHN analyzer. IR spectrum was recorded on a Bruker IFS 66v/S spectrophotometer using the KBr pellets in the region 4000-400 cm^{-1}. Thermogravimetric analysis (TGA) was carried out on a METTLER TOLEDO TGA850 instrument in the temperature range of 30 - 600 °C under nitrogen atmosphere (flow rate of 50 mL min^{-1}) at a heating rate of 5 °C min^{-1}. Powder X-ray diffraction (PXRD) pattern in different state of the samples were recorded on a Bruker D8 Discover instrument using Cu-Kα radiation. ^{1}H and ^{13}C NMR were recorded on a Bruker AV-400 spectrometer (in DCl/[D$_6$]-DMSO, TMS as internal standard). Mass spectrum was recorded on a Bruker Ultraflex II MALDI/TOF spectrometer. The adsorption isotherms for N_2 (at 77 K) and CO_2, N_2, H_2, Ar, O_2 (at 195 K) gases were measured in a QUANTACHROME QUADRASORB *SI* analyzer. A known weight (100-125 mg) of the as-synthesized sample was placed in the sample cell, then, prior to measurements, the sample was dried under high vacuum at 373 K for 16 h to remove the guest molecules. The adsorbate was charged into the sample tube, and then the change of the pressure was monitored and the degree of adsorption was determined by the decrease in pressure at the equilibrium state. All operations were computer-controlled and automatic.

Single crystal X-ray diffraction: X-ray single crystal structural data were collected on a Bruker Smart-CCD diffractometer equipped with a normal focus, 2.4 kW sealed tube X-ray source with graphite monochromated Mo-Kα radiation (λ = 0.71073 Å) operating at 50 kV and 30 mA. The programme SAINT[2] was used for integration of diffraction profiles and absorption correction was made with SADABS[3] programme. The structures were solved by SIR 92[4] and refined by full matrix least square method using SHELXL-97[5]. All the hydrogen atoms were fixed by HFIX and placed in ideal positions. Potential solvent accessible area or void space was calculated using the PLATON[6] multipurpose crystallographic software. All calculations were carried out using SHELXL-97[5], PLATON[6] and WinGX[7] system, Ver 1.70.01.

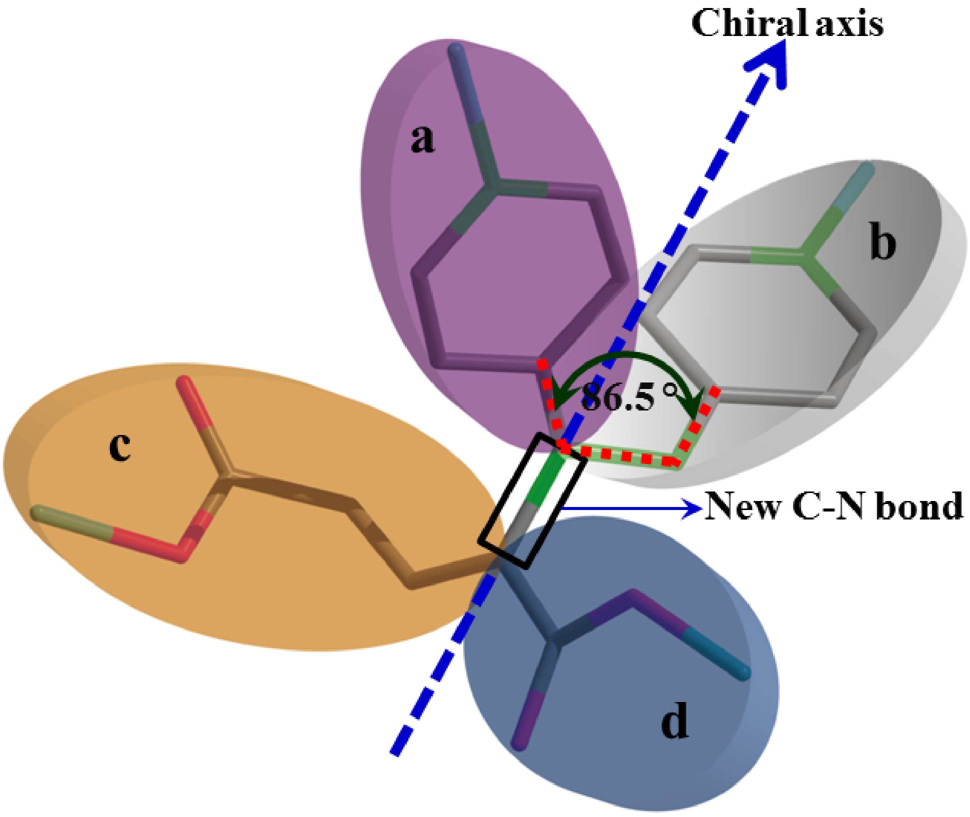


Fig. S1 The loss of molecular symmetry of azpy because of the change in hybridization of two nitrogen atoms N2 and N3 from sp^2 to sp^3 via C-N coupling provides the sufficient angle (~86.5 °) to the pyridyl rings '***a***' and '***b***' to bent away from each other, which gives rise to a distorted tetrahedral geometry of the ***Z*-dhpe** ligand. Coordination of four different groups (a-d) to four tetrahedral Zn(II) atoms fridges the ligand and gives rise to chirality in the framework. We propose that the chiral axis passes through the newly formed C-N bond (in black rectangle).

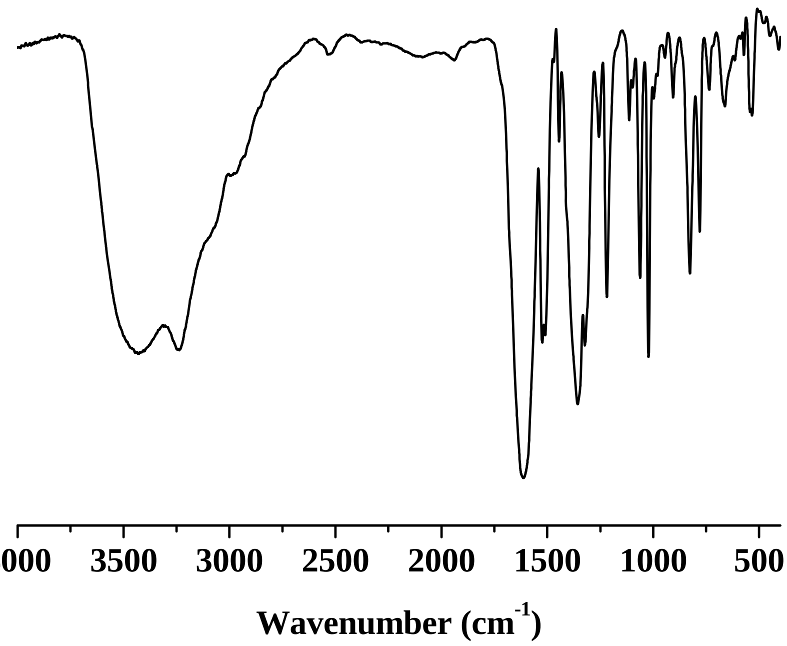


Fig. S2 IR spectrum of compound **1**.

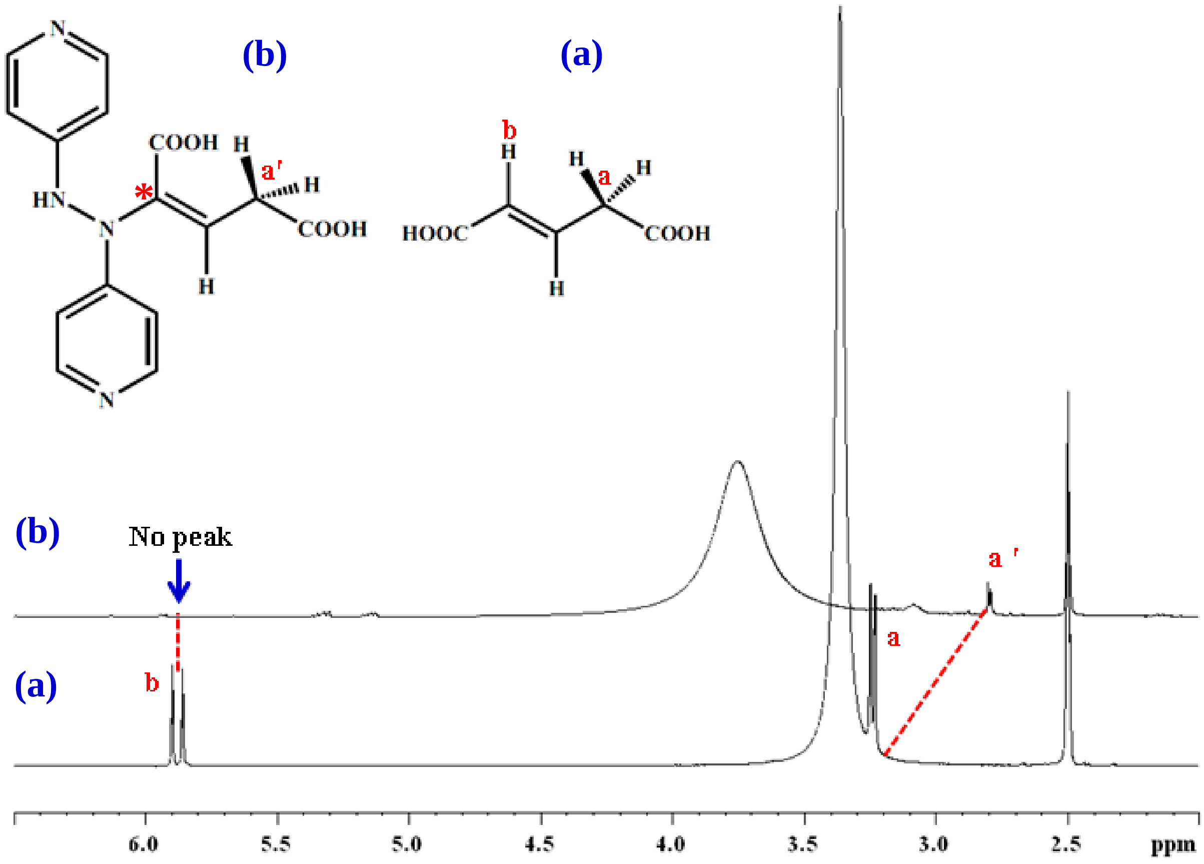


Fig. S3 ^{1}H NMR spectra of digested compound **1** (DCl/[D$_6$]-DMSO). Absence of proton in *marked carbon atom and chemical shift of a protons to a′ confirm the C-N coupling. Dotted lines represent correlation of the peaks.

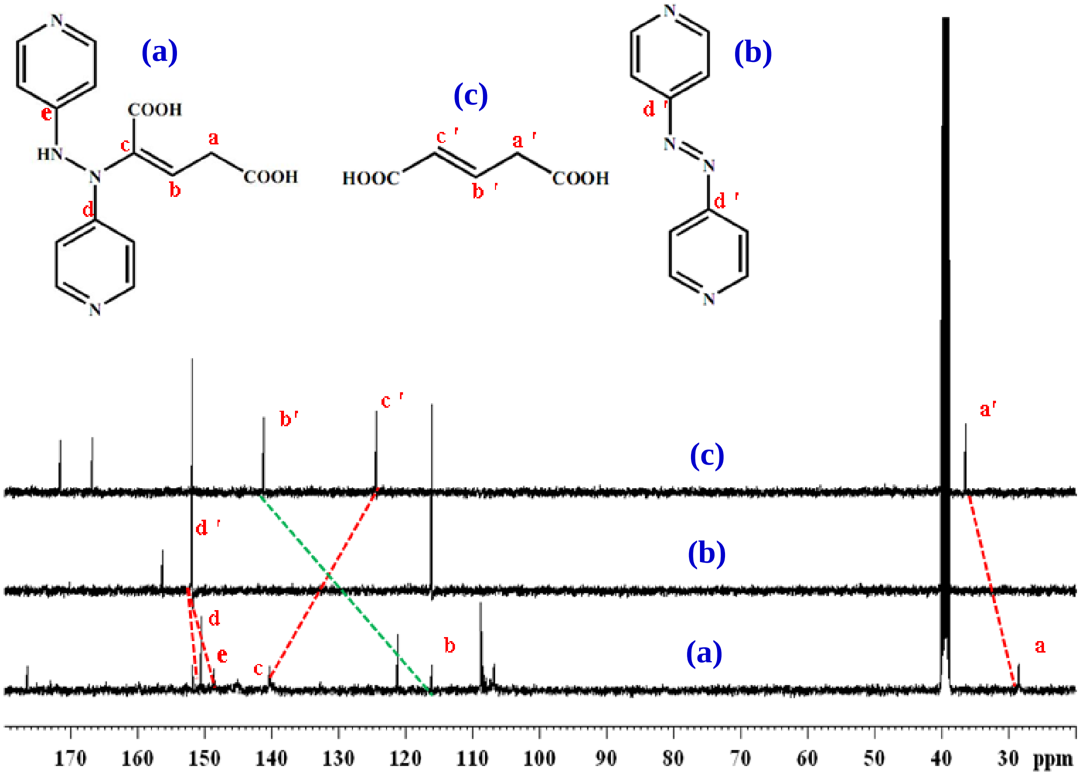


Fig. S4 ^{13}C NMR spectra of digested compound **1** (DCl/D_6-DMSO).Chemical shifts of a, b, c and d carbons and appearance of a new peak e confirm the formation of ***Z*-dhpe** via C-N coupling.

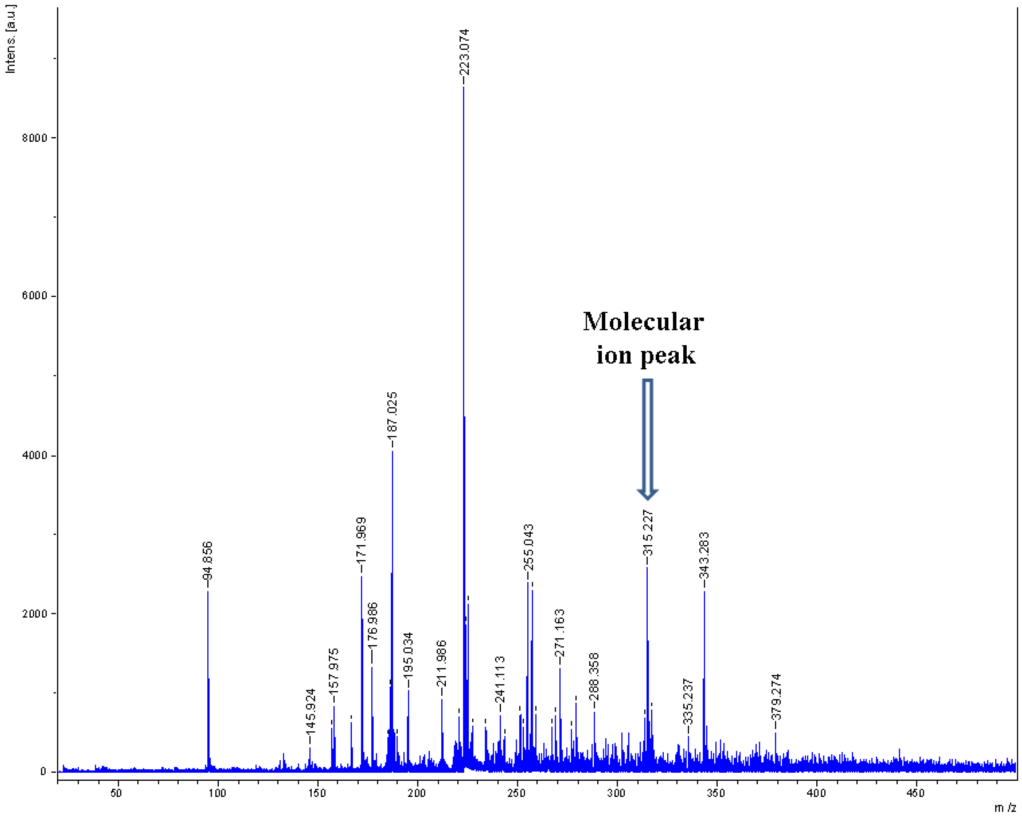
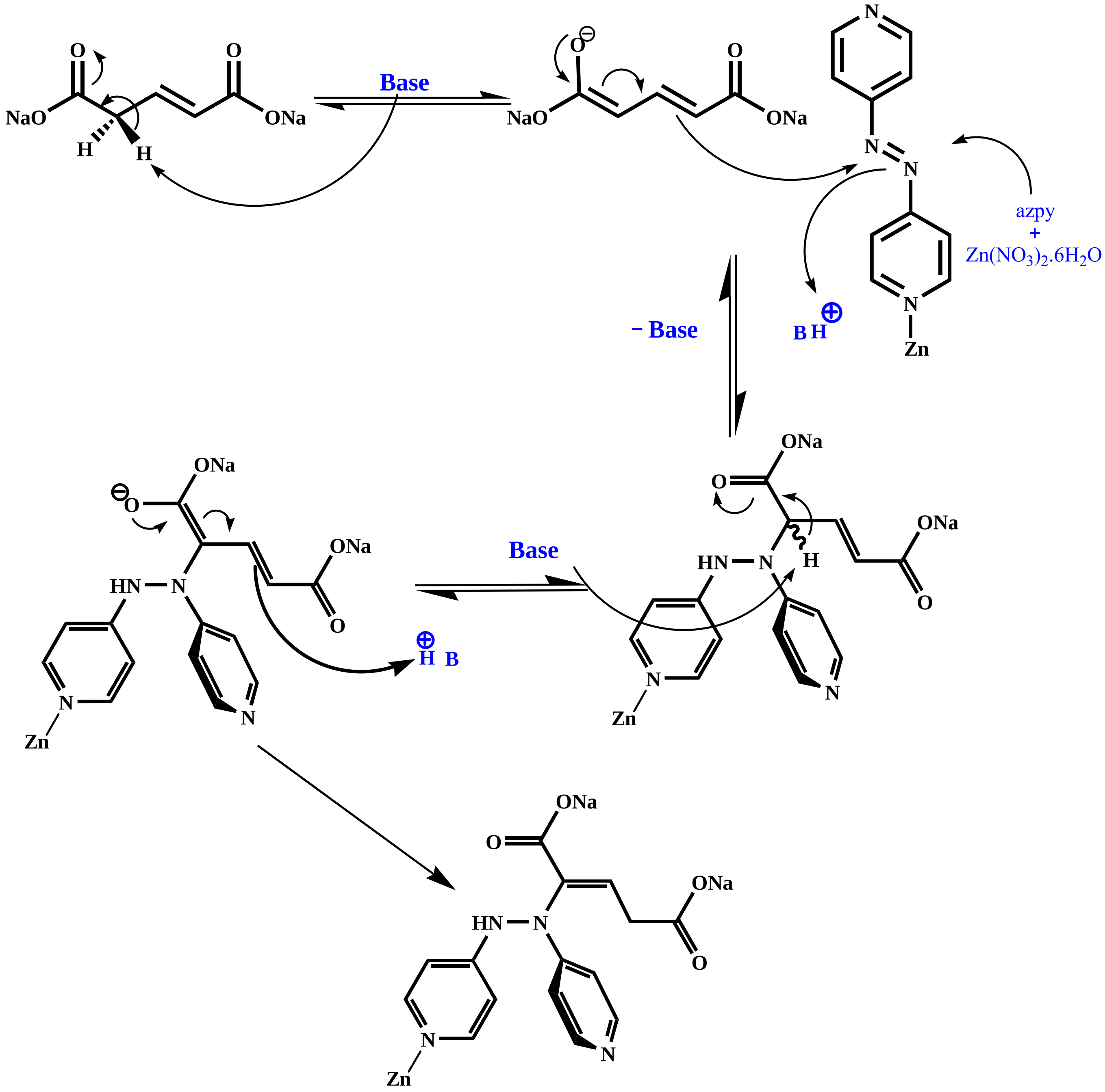


Fig. S5 ESI-MS analysis of digested compound **1**.



Scheme S1 Proposed mechanism for the formation of the ligand ***Z*-dhpe**.

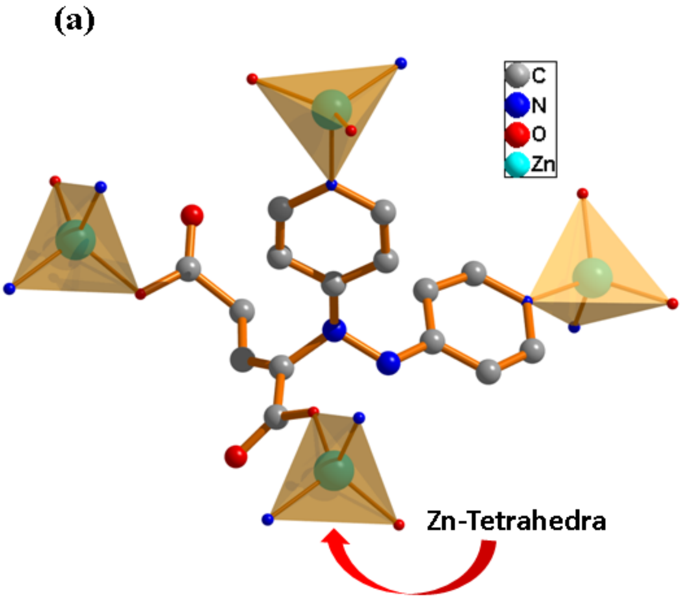


Fig. S6 Different coordination modes of the bi-functional ligand ***Z*-dhpe**: (a) Tetrahedral with Zn(II) in **1** and (b) Octahedral with Cd(II) in **2**.

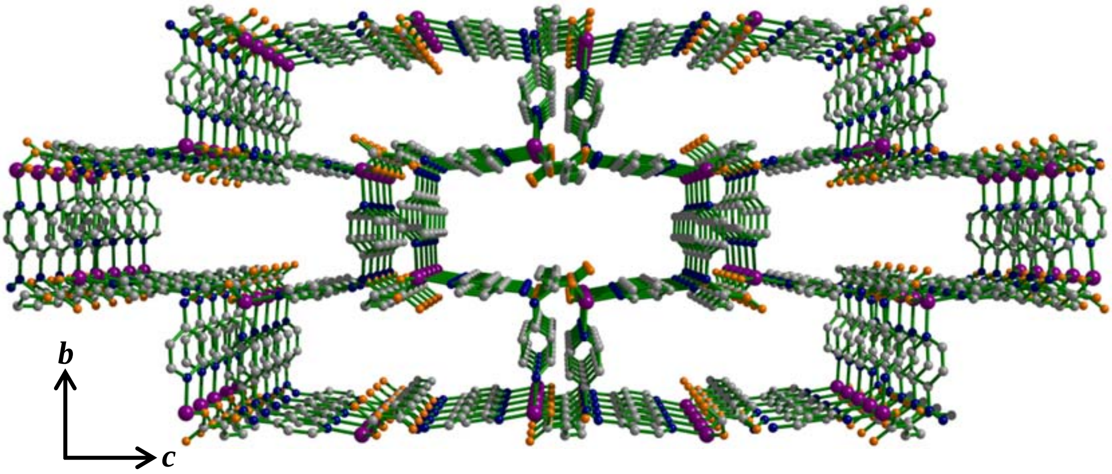


Fig. S7 Perspective view of the guest excluded 3D framework of **1** shows large 1D channels along crystallographic *a* direction.

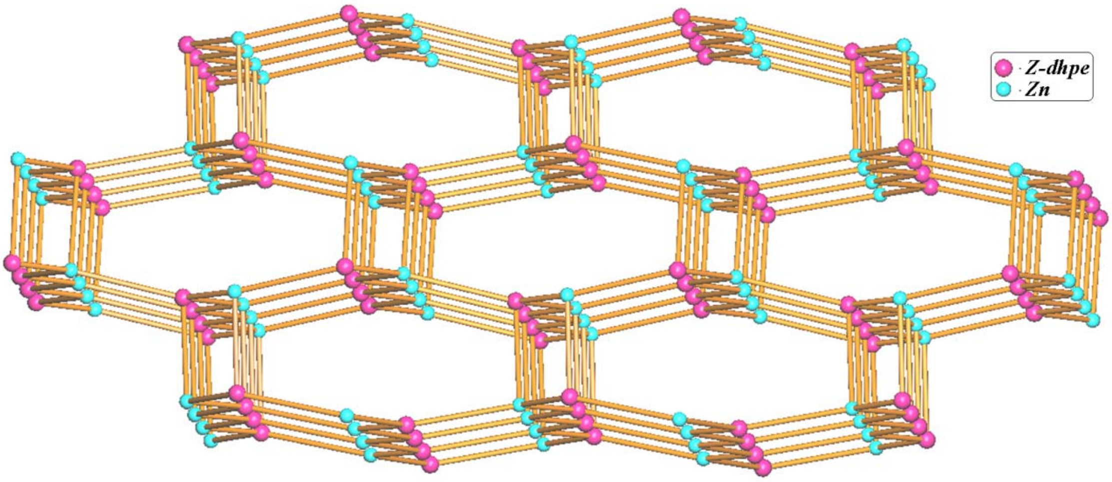


Fig. S8 Topological view of 4-connected uninodal net in **1**.

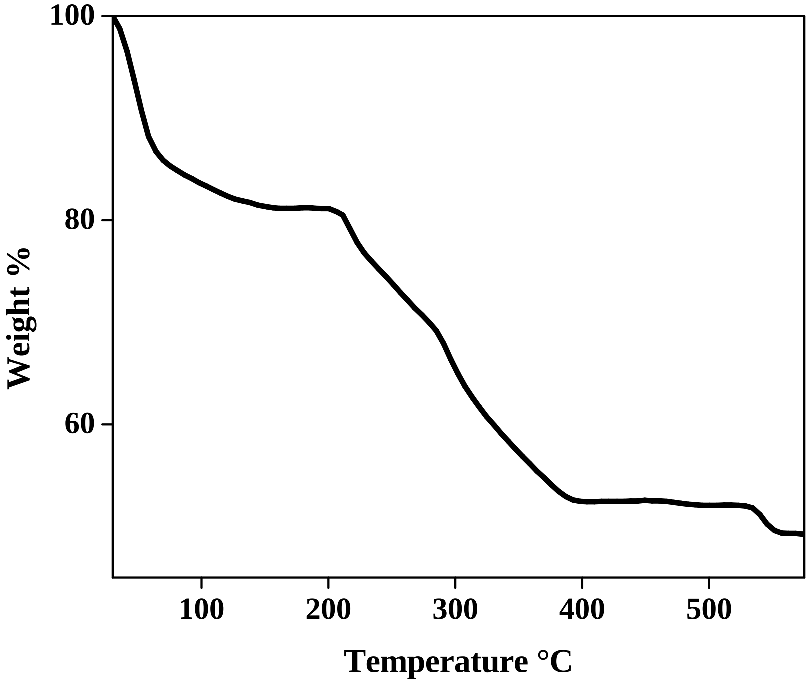


Fig. S9 Thermogravimetric analysis curve of **1** recorded in the 30 – 600 °C temperature range under nitrogen flow.

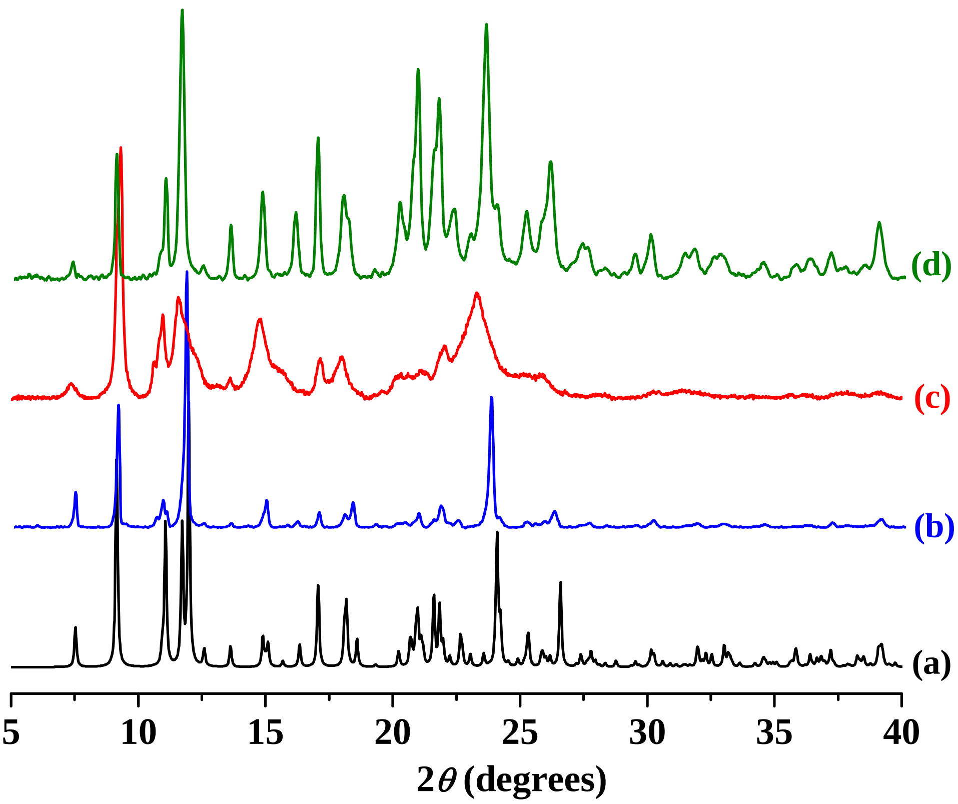


Fig. S10 PXRD pattern of the framework **1**: (a) simulated; (b) assynthesized; (c) heated at 100 ºC and (d) resolvated. The very well correspondence between simulated and assynthesized pattern indicates the high purity of the synthesized sample.

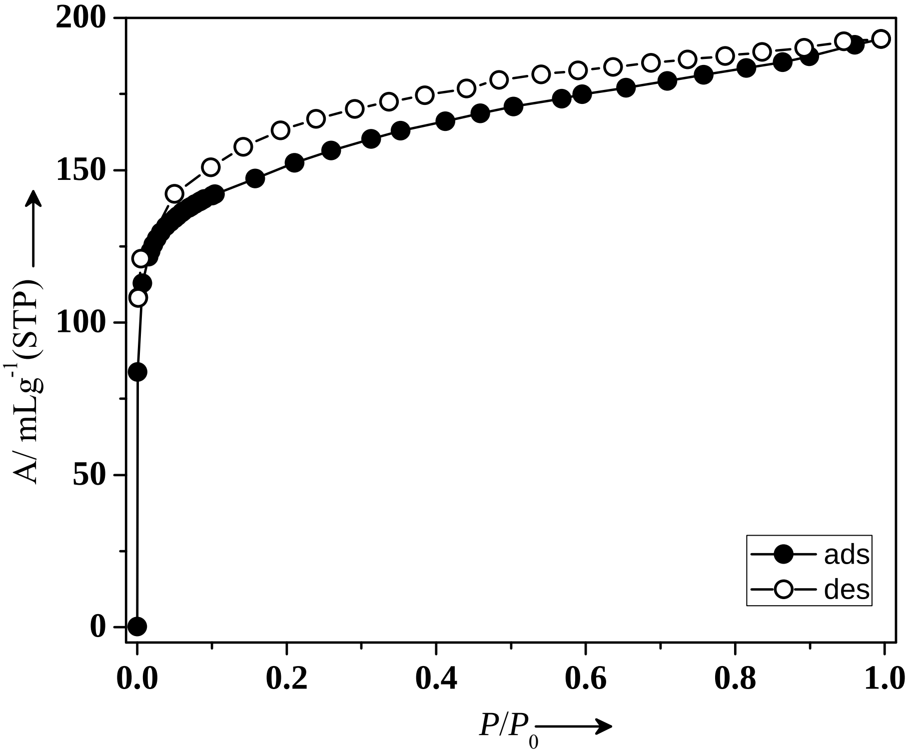


Fig. S11 N_2 adsorption-desorption isotherm at 77 K. Adsorption and desorption data are represented by open and filled symbols, respectively.

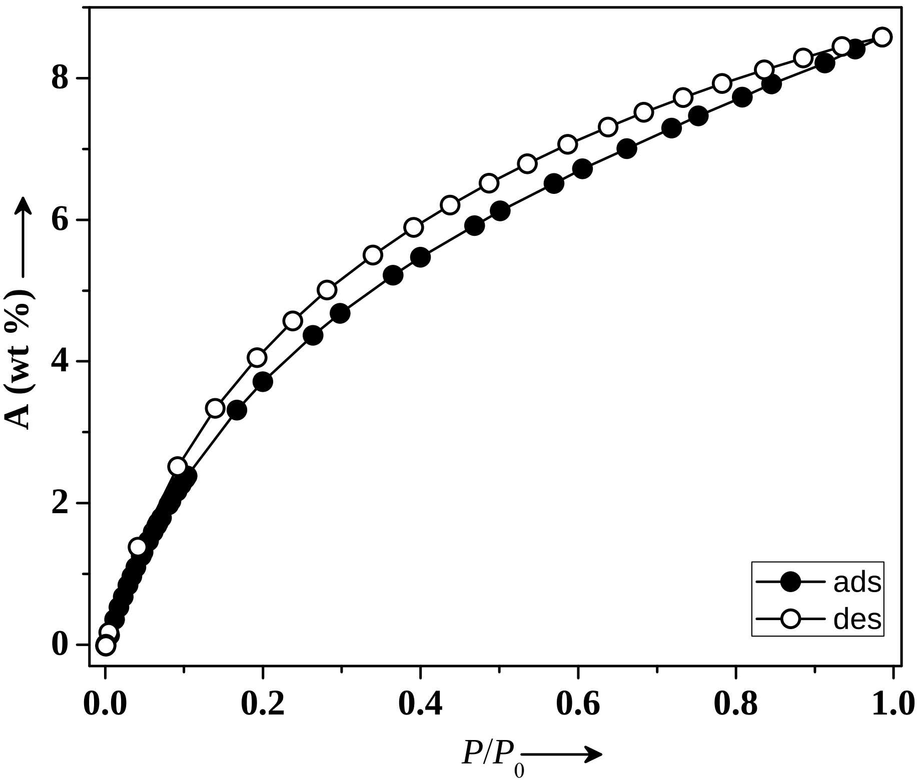


Fig. S12 CO_2 adsorption-desorption isotherm at 298 K. Adsorption and desorption data are represented by open and filled symbols, respectively.

Table S1. Reported *in situ* reactions in MOFs and their properties along with the one observed in this work.

Entry	*In situ* ligand/ coupling type	Reaction Condition	BET surface area (m^2 g^{-1})	CO_2 uptake cc g^{-1}	Other properties	Ref.
1	Tetrazolate ligand	Hydrothermal	---	---	---	4a (main text)
2	C-C and C-N coupling	Hydrothermal	---	---	---	4b (main text)
3	2-methylimidazolate-4-amide-5-imidate	Solvothermal	802	48 at 298 K	---	8a
4	Tetrazolate ligand	Solvothermal	---	---	Photoluminescence	8b
5	5-methyl-1H-tetrazole	Hydrothermal	Negligible	---	Anion sensing	8c
6	Oxidation of trimethyl pyridine	Hydrothermal	---	---	Magnetism	8d
7	2+2 cycloaddition, C-C bond	RT	---	---	---	8e
8	*Z*-dhpe	RT	870	44 at 298 K and 223 at 195 K	Selective CO_2 uptake at 195K and Chirality	This Work

Table S2. Summary of crystal data and refinement results.

Samples	Space group	*a* (Å)	*b* (Å)	*c* (Å)	*R*	R_w	Flack parameter
Crystal 1	$P2_12_12_1$	8.741(5)	14.796(5)	19.340(5)	0.086	0.2689	0.00(3)
Crystal 1a	$P2_12_12_1$	8.7423(6)	14.7183(11)	19.3742(15)	0.0843	0.2300	0.01(6)
Crystal 1b	$P2_12_12_1$	8.7726(4)	14.7582(9)	19.3159(10)	0.0797	0.2428	0.02(4)
Crystal 1c*	$P2_12_12_1$	8.7611(8)	14.7839(16)	19.353(2)	0.0811	0.2286	0.05(5)
Crystal 1d*	$P2_12_12_1$	8.7562(6)	14.8244(11)	19.3329(14)	0.0798	0.2285	-0.01(5)

Crystals with and without *mark have opposite handedness.

References:

1 (*a*) E. V. Brown, G. R. Granneman, *J. Am. Chem. Soc.*, 1975, **97,** 621; (*b*) O. Theilmann, W. Saak, D. Haase, R. Beckhaus, *Organometallics*, 2009**, 28**, 2799.

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