SUPPORTING INFORMATION for

Highly Porous Interpenetrated MOF-5 Type Network
Based on Bipyrazolate Linkers

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Materials and methods

All the reagents and solvents employed were commercially available and used as received. Thermogravimetric analyses (TGA) were performed, under either nitrogen or a reactive air atmosphere, on a Shimadzu-TGA-50H equipment, at a heating rate of 20 °C min^{-1}. Except for the structural analysis, all the X-ray powder diffraction data were acquired on a D2 PHASER Bruker AXS diffractometer using CuK$_\alpha$ radiation (λ = 1.5418 Å). N$_2$ and CO$_2$ adsorption isotherms were measured, at 77 K and 273 K respectively, on a Micromeritics Tristar 3000 volumetric instrument. Prior to measurement, the samples were heated at 200 °C for 12 h and outgassed to 10^{-5} bar.

Synthesis of 4,4'-buta-1,3-diyne-1,4-diylbis(1-Boc-3,5-dimethyl-pyrazole) (Boc$_2$L)

The first intermediate, 1-Boc-3,5-dimethyl-4-iodopyrazole, was obtained as reported in Reference 1 and recovered quantitatively as yellow needle crystals.

1-Boc-3,5-dimethyl-4-iodopyrazole (1.52 g, 6.86 mmol), dichlorobis(triphenylphosphine)palladium(II) (0.39 g, 0.58 mmol) and copper(I) iodide (0.13 g, 0.68 mmol) were stirred in a deoxygenated mixture of Et$_3$N (40 mL) and dry THF (80 mL) under an Ar atmosphere for 15 min at 0 °C. Subsequently, tetra-*n*-butylammonium fluoride trihydrate (1.03 g, 3.92 mmol) was added to the stirred

solution. 1,4-bis(trimethylsilyl)butadiynetrimethyl[4-(trimethylsilyl)-1,3-butadiynyl]silane (0.67 g, 3.43 mmol) was slowly added and the mixture was stirred further for 6 h. The solvent was removed and the residue was dissolved in ethylacetate (25 mL) and washed with a saturated solution of ammonium chloride (15 × 3 mL). The organic phase was dried over anhydrous Na_2SO_4 and the solvent was removed. The residue was purified by column chromatography (silica gel, hexane/ethylacetate 8:2) to afford pure Boc_2L in the form of polycrystalline powders (934 mg, yield 64 %). IR (KBr) 2987(m), 2937(m), 2154(m), 1739(vs), 1572(s), 1496(m), 1414(s), 1381(s), 1356(vs), 1311(vs), 1259(m), 1227(w), 1163(vs), 1086(vs), 850(m), 771(m), 660(w), 619(w), 546(w) cm^{-1}. ^1H NMR ($CDCl_3$) δ: 1.62 (s, 18H), 2.32 (s, $2CH_3$), 2.57 (s, $2CH_3$). ^{13}C NMR ($CDCl_3$) (DEPT) δ: 12.9 (CH_3), 14.0 (CH_3), 27.8 (CH_3), 72.7 (C), 78.72 (C), 86.6 (C), 105.9 (C), 147.9 (C), 148.6 (C), 153.7 (C).

Synthesis of $[Co_4O(L)_3 \cdot solv]_n$

In a typical synthesis, $Co(AcO)_2 \cdot 4H_2O$ (50 mg, 0.20 mmol) and Boc_2L (60 mg, 0.15 mmol) were dissolved in DMF (50 mL) until the solution became limpid and pink. The mixture was then heated in a Teflon liner at 125 ºC for 70 h. The bright blue microcrystalline solid deposited on the walls of the liner was filtered, washed with fresh DMF and dried in air (41 mg, 67% yield). Anal. calc. for $[Co_4O(C_{14}N_4H_{12})_3](C_3H_7NO)_8(H_2O)_5$ (1635.37 g mol^{-1}) C, 48.47; H, 2.29; N, 17.13; found C, 48.92; H, 7.09; N, 16.82.

X-ray powder diffraction structural analysis

A sample of $Co_4O(L)_3$ was ground in an agate mortar, then deposited in the hollow of an aluminium-framed sample holder equipped with a quartz zero-background plate. The diffraction data were collected by means of an overnight scan in the 2θ range of 5-95°, with 0.02° steps, on a Bruker AXS D8 Advance diffractometer, equipped with Ni-filtered CuK_α radiation (λ = 1.5418 Å) and with a Lynxeye linear position-sensitive detector, and mounting the following optics: primary beam Soller slits (2.3°), fixed divergence slit (0.3°), receiving slit (8 mm). The generator was set at 40 kV and 40 mA. A standard peak search below 30° was followed by indexing through the singular value decomposition method[2] implemented in TOPAS-R,[3] which allowed the determination of the lattice parameters. Systematic absences permitted to individuate the most probable space group. The model here proposed, in *I-43m*, has the advantage of easier

interpretation and graphical rendering. Prior to structure solution, a Le Bail refinement was carried out to confirm the unit cell and space group. Worthy of note, the similar agreement factors and residual plots in the final Rietveld refinements for a disordered *Im-3m* model and an ordered *I-43m* one suggested the existence of local (twofold) disorder of the Co_4O tetrahedra and of the ligands, the orientations of which are spatially uncorrelated. A preliminary structural model was determined *ab-initio* by the simulated annealing approach implemented in TOPAS-R. An idealized rigid model was used to describe the crystallographically independent portion of the ligand. [4] The difference Fourier map calculated with the structure factors of the framework alone revealed that the solvent is highly disordered. Its electronic density was modelled by locating, within the cavities, the number of oxygen atoms whose refined site occupation factors, combined with the site multiplicity, represent the total electron density of the solvent, as estimated from the elemental and TG analyses. Structure refinements were carried out by means of the Rietveld method[5] with TOPAS-R. The peak shapes were described with the fundamental parameters approach.[6] The background was modeled by a Chebyshev polynomial function. The thermal effect was simulated by using a single isotropic parameter for the metal ion, augmented by 2.0 Å^2 for lighter atoms. The final Rietveld refinement plot is supplied in Figure S1. Fractional atomic coordinates are provided as CIF file. Crystallographic data in CIF format have been deposited at the Cambridge Crystallographic Data Center as supplementary publication no. 949078. Copies of the data can be obtained free of charge on application to the Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: +44-1223-335033; e-mail: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

Crystal data for **$Co_4O(L)_3$**, $[Co_4O(C_{14}N_4H_{12})_3](C_3H_7NO)_8(H_2O)_5$, Mr = 1635.37; cubic, *I-43m*, a = 16.6103(7) Å, V = 4582.8(5) Å^3, Z = 2, $F(000)$ = 2508, $\mu(CuK\alpha)$ = 60.8 cm^{-1}, ρ = 1.18 g cm^{-3}, R_p = 0.006, R_{wp} = 0.012, R_{Bragg} = 0.831 for 4426 datapoints and 41 parameters. Please note that the very low figures of merit are due to the very pronounced background affected by the fluorescence of cobalt, which cannot be eliminated in our instrumental set-up.
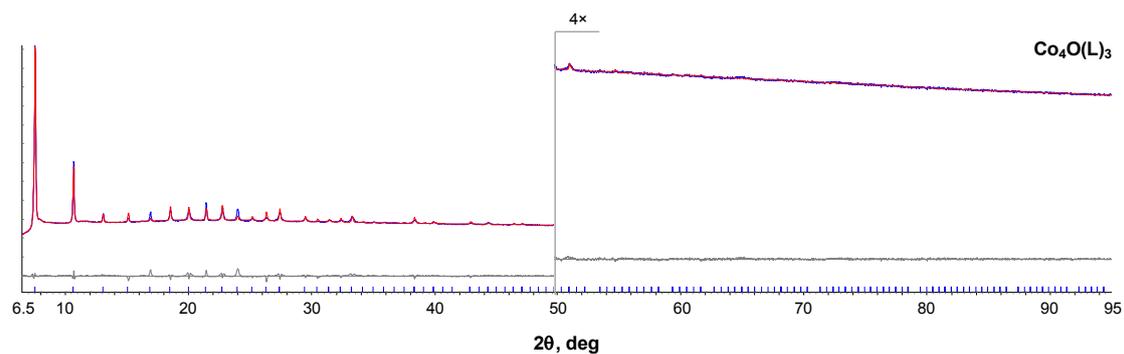
Fig. S1 Final Rietveld refinement plot for the **$Co_4O(L)_3$**, in terms of experimental (blue), calculated (red), and difference (grey) traces. The Bragg peak markers are reported at the bottom. Horizontal axis, 2θ (deg); vertical axis, intensity (counts). The high-angle region of the diffractogram is shown at a magnified scale ($2\times$).
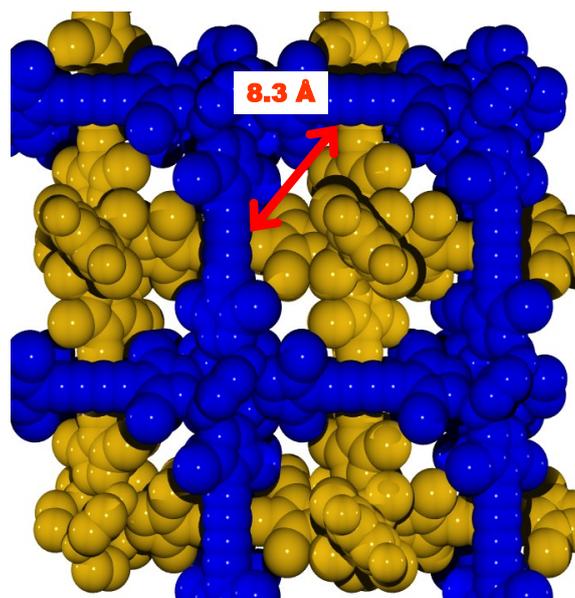
Fig. S2 Space filling view of the structure of **$Co_4O(L)_3$** along the [100] direction. The size of the pores windows is highlighted. The two frameworks are depicted in blue and orange for the sake of clarity.
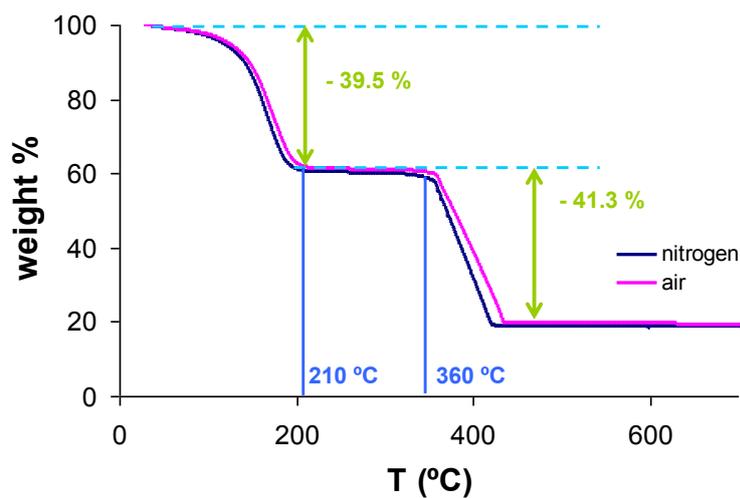
Fig. S3 TGA traces for **Co₄O(L)₃** in air (purple trace) and N₂ (blue trace) atmosphere.
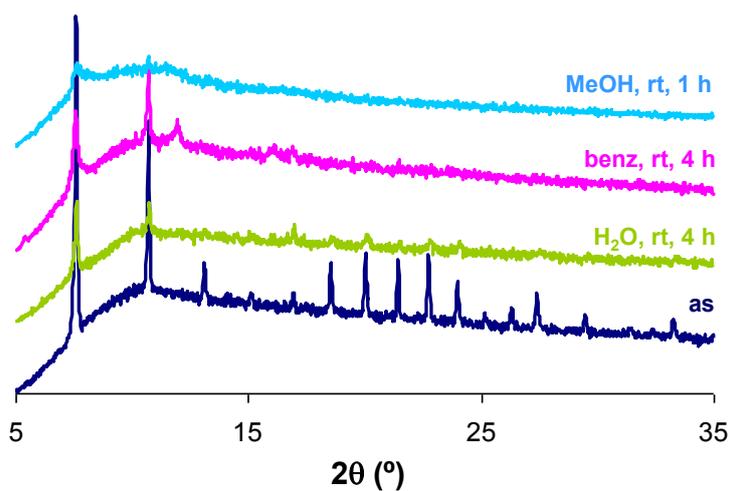
Fig. S4 X-ray powder diffraction patterns acquired on **Co₄O(L)₃** as synthesized (as) and after suspension in methanol (1 h), benzene (4 h) and water (4 h) at room temperature.

References

1   M. I. Rodríguez-Franco, I. Dorronsoro, A. I. Hernández-Higueras, G. Antequera, *Tetrahedron Letters*, 2001, **42**, 863.

2   A. A. Coelho, *J. Appl. Cryst.,* 2003, **36**, 86.

3   TOPAS Version 3.0, Bruker AXS 2005, Karlsruhe, Germany.

4   The z-matrix formalism was used to describe the crystallographically independent portion of the ligand. Idealized bond distances and angles were adopted as follows: C-C, C-N, N-N of the five-membered ring 1.36 Å; Å C-C single bonds 1.50 Å; C-C triple bonds 1.24 Å; C-H 0.95 Å; five-membered ring internal bond angles 108°.

5   R. A. Young, *The Rietveld Method*, *IUCr Monograph N. 5,* Oxford University Press, New York, 1981.

6   R. W. Cheary, A. A. Coelho, *J. Appl. Cryst.*, 1992, **25**, 109.