

Supplementary Material (ESI) for Chemical Communications
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**A mesoporous hydrogen-bonded organic-inorganic framework bearing the
isopolymolybdate $[\text{Mo}_{36}\text{O}_{112}(\text{OH})_{16}]^{8-}$**

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Experimental details

All reagents were obtained from commercial sources and used without further purification. The elemental analyses were performed (C, H, N) on a model EA1108 Fisons elemental analyzer. The FT-IR spectrum was recorded from KBr disc, using a Nicolet Magna-IR 560 spectrophotometer (Fig. S4). Thermogravimetric Analyses were performed in a TGA/SDTA851^c Mettler Toledo under a dynamic nitrogen atmosphere (17 ml/min) (Figs S5 and S6). XRPD patterns were recorded on a Siemens D5005 Diffractometer with Cu(K α) (1.5418 Å) radiation, with a scan speed of 2 deg/min. BET measurements were measured on Micromeritics ASAP 2010. A full adsorption isotherm was obtained using N₂ as adsorbate. This sample was prepared by overnight dehydration at room temperature under high vacuum. Data were processed to calculate porosity distribution using density functional theory method (DFT)

Crystal structure determination. Intensity data were recorded on a Rigaku AFC-7S diffractometer equipped with a graphite monochromator and Mo(K α) radiation ($\lambda = 0.71073$ Å) at room temperature. Three reflections were re-measured every 150 reflections to monitor instrument and crystal stability. Data were corrected for Lp effects and absorption.^[1] The first model was solved by direct methods^[2] and Fourier techniques. The refinement was carried out by full-matrix least-squares on F^2 with anisotropic displacement parameters for non-H atoms. H-atoms on nitrogen were included in their found positions, whereas those on carbon were calculated in ideal positions. Both were refined with isotropic displacement parameters set to $1.2 \times U_{eq}$ of the attached atom. H-atoms on crystallization and coordinated water molecules were not found. Several water molecules of crystallization were found disordered and were modelled including two positions for each O atoms with partial occupancy factors. Most of the cases, these partial occupancies were refined to value very close to 0.5 so this last value was fixed for the next refinements. The occupancy factor of the O22w was refined to a value of 0.65 (x) as the O23w a complementary value (1-x) was included as a restriction. Likewise, one of the cations H₂bipy²⁺ is disordered in two set of positions, which were included by constraining the pyridine rings to be a regular hexagon. H-atoms for this cation were not considered. Data reduction were performed using teXsan^[1] crystallographic software package, whereas refinement calculations were made using SHELXTL-PLUS V5.^[2] Crystallographic data have been deposited with the Cambridge Crystallographic Data Center with the following deposition number 249299.

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1. Molecular Structure Corporation. teXsan. Version 1.10. MSC, 9009 New Trails Drive, The Woodlands, TX 77381-5209, USA. 1999.
2. Crystallographic software package SHELXL-NT V5.1. PC version, Bruker Analytical X-Ray Systems. Madison, WI, USA 1998

Full description of the crystal structure. The crystal structure consists of an open framework built up from the hydrogen bonded assembly of centrosymmetric anionic building block $[\text{Mo}_{36}\text{O}_{128}(\text{OH}_2)_{16}]^{8-}$ (Fig S1a) and cationic entities $(\text{H}_2\text{bipy})^{2+}$. The $\{\text{Mo}\}_{36}$ cluster is located in a special position $2a$ in the unit cell and displays approximately C_{2h} symmetry.

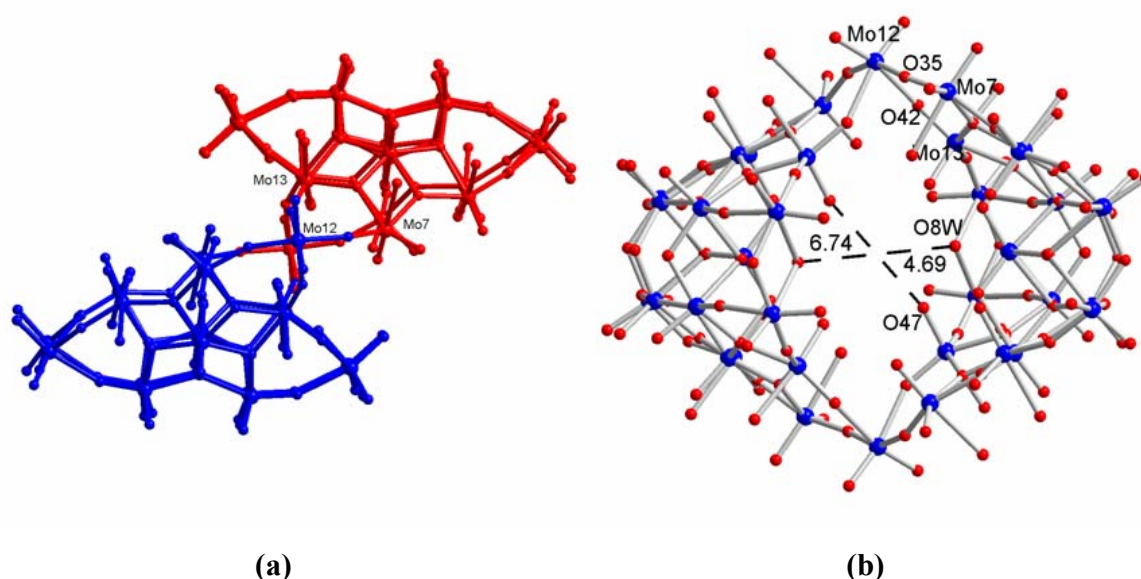


Fig. S1. Different views of the structure of the anion of **1**

This moiety is integrated by two $\{\text{Mo}\}_{18}$ (Fig. 1a in the paper) subunits, in which each one is constructed from the combination of sixteen $\{\text{MoO}_6\}$ pseudo-octahedra and two $\{\text{MoO}_7\}$ distorted pentagonal bipyramids. The structure of the fragment $[\text{Mo}_{18}\text{O}_{56}(\text{OH}_2)_8]^{4-}$ can also be described as one central group of polyhedra built up by a couple of chains where each one contains four $\{\text{MoO}_6\}$ octahedra (Mo1, Mo4, Mo14, Mo17 and Mo2, Mo5, Mo15, Mo18, respectively). These $\{\text{Mo}\}_4$ -chains are linked by corner sharing along its axis and by edge sharing from each other. A remaining $\{\text{MoO}_6\}$ octahedron (Mo9) is located below both chains joined by edge sharing to the central $\{\text{MoO}_6\}$ octahedra (Mo4, Mo14, Mo5, and Mo15). This central group is then assembled to two $\{\text{Mo}\}_4$ tetrameric subunits to form a $\{\text{Mo}\}_{17}$ substructures. These $\{\text{Mo}\}_4$ entities are constituted by corner sharing of three $\{\text{MoO}_6\}$ octahedra (Mo3, Mo7, Mo13), which are linked by edge sharing to a central $\{\text{MoO}_7\}$ pentagonal bipyramid (Mo8). The final $\{\text{Mo}\}_{18}$ moiety is, thus, reached by the junction of the $\{\text{Mo}\}_{17}$

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units through corner sharing with one $\{\text{MoO}_6\}$ octahedra (Mo12). The self-assembly from two of these $\{\text{Mo}\}_{18}$ moieties, *via* corner sharing Mo12—O35—Mo7ⁱ and Mo12—O42—Mo13ⁱ ($i = -x, -y, -z$), lead to the final cyclic $[\text{Mo}_{36}\text{O}_{112}(\text{OH}_2)_{16}]^{8-}$ anion, which shows an internal cavity of approximately 0.7 x 0.5 nm (Fig. S1b).

The crystal packing seem to be defined for the size and the pseudo-spherical shape of the anion. Thus, they adopt a close packing arrangement with an $\cdots\text{ABAB}\cdots$ sequence in the b -direction (Fig. S2). This packing allows large voids between the anions where $(\text{H}_2\text{bipy})^{2+}$ units are located. One of the cation maintains its (N \cdots N)-axis with a roughly parallel orientation to the b -axis, as the other one is more tilted. In the b -direction, however, remains very large channels (Fig. S3) where water of crystallization are accommodated. Comparing Fig. S3 and Fig. 2a included in the paper, it is possible to observe that the channels and the internal cavities of the anion are interconnected between them.

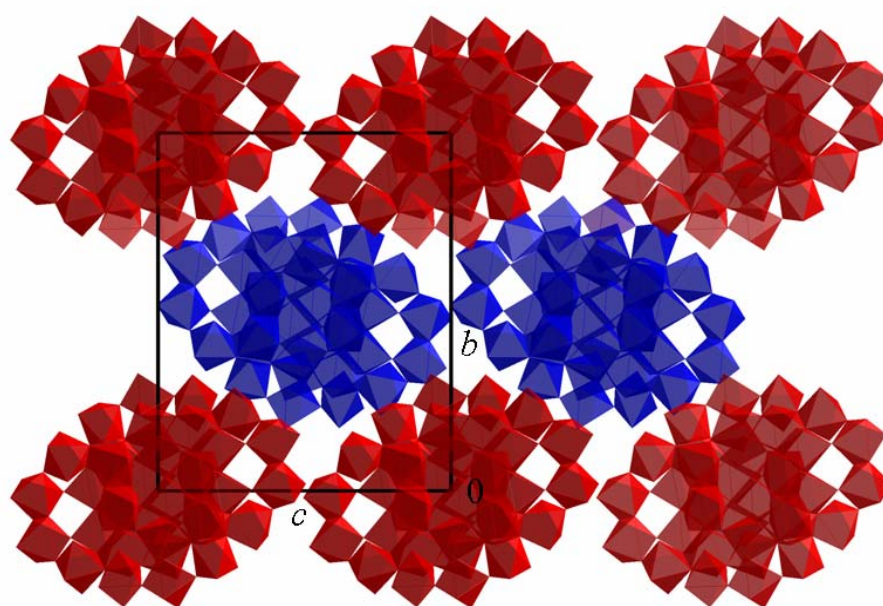


Fig. S2. Close packing arrangement with an $\cdots\text{ABAB}\cdots$ sequence in the b -direction observed in the crystal packing of **1**. Water molecules of crystallization and cations were omitted.

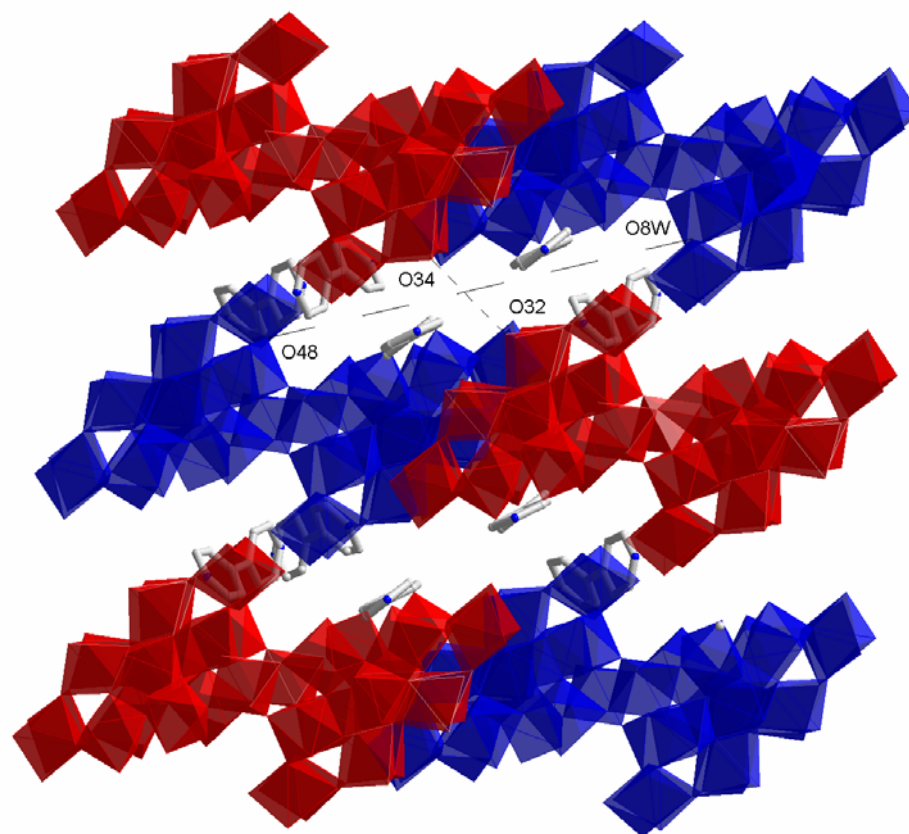


Fig. S3. View of the large channels observed along the *b*-direction. Distance O34...O32= 4.87 Å and O8w...O48= 19.36 Å. Water molecules of crystallization were omitted.

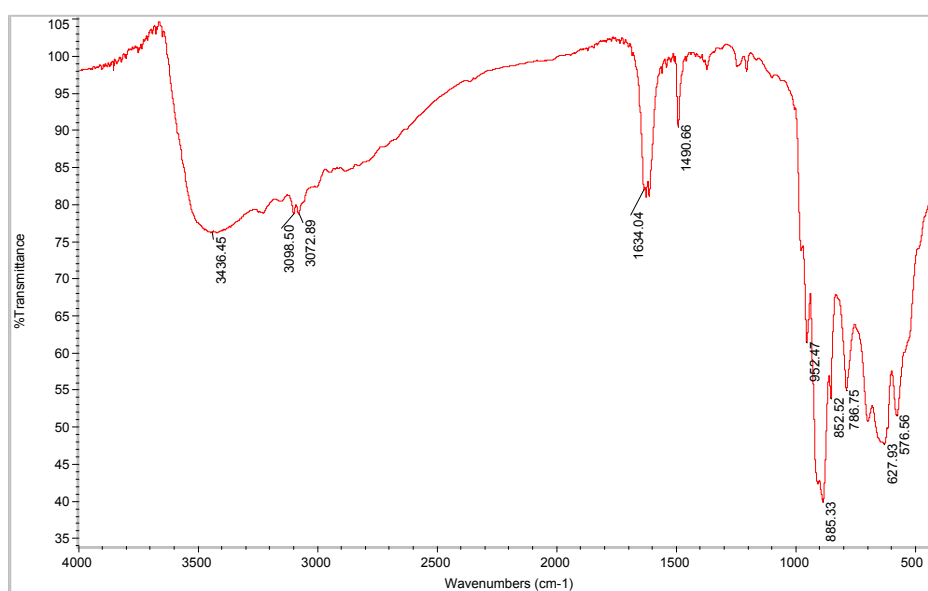


Fig. S4 Infrared spectrum of **1**.

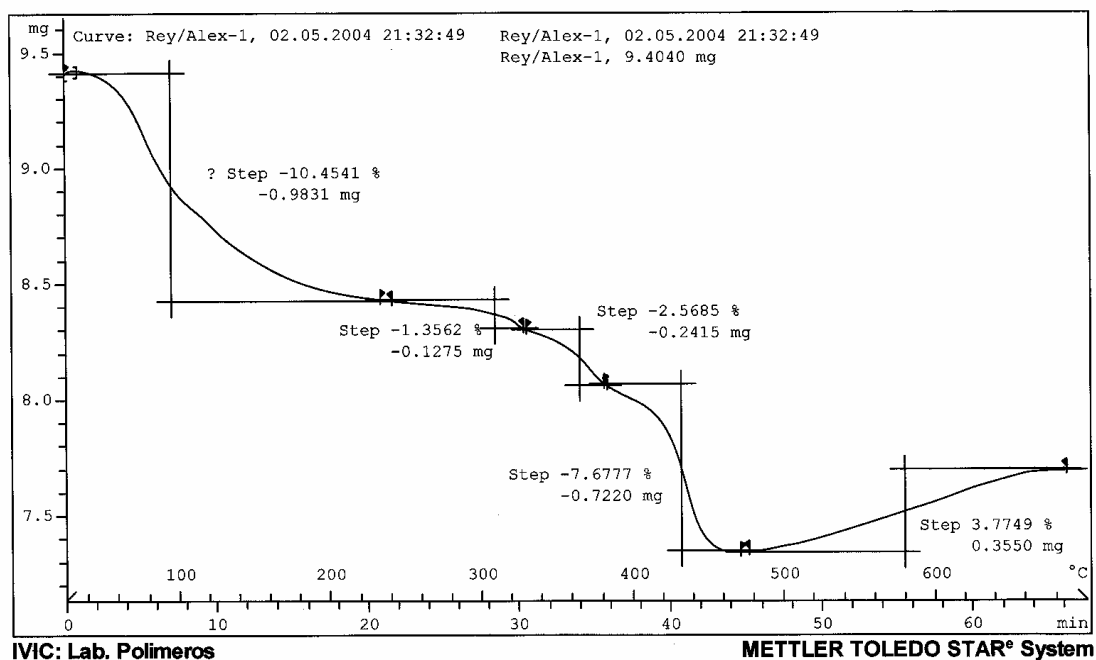


Fig. S5 TG analysis for 1.

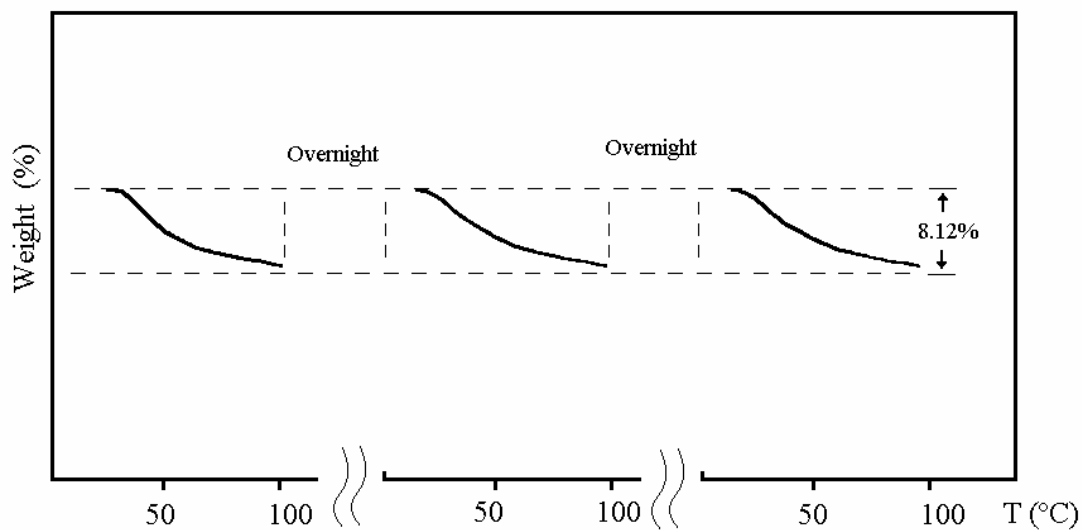


Fig S6. TG analyses for 1 during subsequent dehydration and hydration cycles.

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Micromeritics Instrument Corporation
DFT Plus(TM) V1.02 (2010) Unit 1 Page 1
Sample: Mo36
Operator: ML
Submitter: Reinaldo
File: C:\DFTPLUS\DATA\000-519.SMP
Started: 07/09/04 17:06:12 Analysis Adsorptive: N2
Completed: 07/09/04 22:25:07 Analysis Bath: 77.35 K
Report Time: 07/21/04 14:57:25 Thermal Correction: No
Sample Weight: 0.0387 g Equil. Interval: 10 secs
Warm Freespace: 26.9795 cm³ Cold Freespace: 87.4344 cm³
Porosity Distribution by Original Density Functional Theory
Model: N2 @ 77K on Carbon, Slit Pores
Method: Non-negative Regularization; No Smoothing
Volume in Pores < 25.20 A : 0.00000 cm³/g
Total Volume in Pores <= 4003.09 A : 0.00773 cm³/g
Total Area in Pores >= 25.20 A : 2.648 m²/g

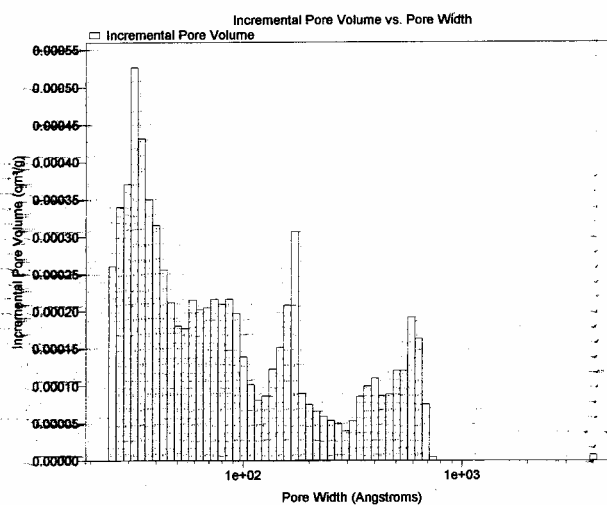


Fig. S7 Pore size distribution for 1.