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Novel versatile cobalt azobenzene-based metal–organic framework as hydrogen adsorbent

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Abstract:	<p>A novel URJC-3 material based on cobalt and 5,5'-(diazene-1,2-diyl)diisophthalate ligand, containing Lewis acid and basic sites, has been synthesized under solvothermal conditions. Compound URJC-3, with polyhedral morphology, crystallizes in the tetragonal and P43212 space group, exhibiting a three-dimensional structure with small channels along a and b axes. This material was fully characterized and its hydrogen adsorption properties were estimated for a wide range of temperatures (77-298 K) and pressures (1-170 bar). The hydrogen storage capacity of URJC-3 is quite high according to its moderate surface area, which is probably due to the confinement effect of hydrogen molecules inside its reduced pores of 6 Å, near the ionic radii of hydrogen molecules. The storage capacity of this material is not only higher than that of active carbon and purified single-walled carbon nanotubes, but also surpasses the gravimetric hydrogen uptake reached by most MOF materials.</p>
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	<p>FRAMEWORK AS HYDROGEN ADSORBENT” Authors: Helena Montes-Andrés, Pedro Leo, Gisela Orcajo, Antonio Rodríguez-Diéguez, Duane Choquesillo-Lazarte, Carmen Martos, Juan Ángel Botas, Guillermo Calleja Corresponding author: Gisela Orcajo, Department of Chemical, Energy and Mechanical Technology, ESCET, Universidad Rey Juan Carlos, C/ Tulipán s/n, 28933 Móstoles, Madrid, Spain. E-mail: gisela.orcajo@urjc.es Manuscript type: Article</p> <p>that we would like to submit for its publication in the Special Issue “Hydrogen Energy” of ChemPhysChem.</p> <p>Metal-organic frameworks are very versatile materials that could serve as an ideal platform for the development of next generation adsorbents owing to their high crystallinity and porosities and their extraordinary structural and chemical variety. After the previous works in our research group related to the synthesis of novel MOF materials, such as ITF-1, constituted by In³⁺ ions and the non-commercial 1H-imidazol-4,5-tetrazole ligand (Gisela Orcajo, Guillermo Calleja, Juan A. Botas, Lukasz Wojtas, Mohamed H. Alkordi, Manuel Sánchez-Sánchez, Cryst. Growth Des. 2014, 14, 739–746), and URJC-1 material, formed by Cu²⁺ metal ions and the same interesting organic ligand (Pedro Leo, Fernando Martínez, Guillermo Calleja, David Briones, Lukasz Wojtas and Gisela Orcajo, Polymers 2016, 8, 44), this work is focused on the obtaining of the new URJC-3 material containing Co²⁺ metal ions and the 5,5'-(diazene-1,2-diyl)diisophthalic acid organic ligand. The experimental results reported in this manuscript confirm that URJC-3 material appears as a very promising porous MOF material with dual Lewis acid and basic properties, suitable for hydrogen adsorption, due to the co-existence of cobalt sites and non-coordinated nitrogen atoms of the ligand, respectively. Its hydrogen adsorption properties were evaluated at different conditions of temperature and pressure, observing an interesting confinement effect of the H₂ molecules inside the reduced cavities of the framework, which reflects in higher excess hydrogen storage capacities at 77 K and 298 K than expected, considering its moderate surface area. Thus, we think it could be a good scientific contribution to be published as an article in ChemPhysChem Journal.</p> <p>Looking forward to hearing from you. Sincerely yours,</p> <p>Gisela Orcajo Department of Chemical, Energy and Mechanical Technology ESCET, Rey Juan Carlos University. C/Tulipán s/n, E-28933 Móstoles, Madrid, Spain Tel: 34 91 488 76 01, Fax: 34 91 488 70 68, e-mail: gisela.orcajo@urjc.es</p>
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Novel versatile cobalt azobenzene-based metal-organic framework as hydrogen adsorbent

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Abstract: A novel URJC-3 material based on cobalt and 5,5'-(diazene-1,2-diyl)diisophthalate ligand, containing Lewis acid and basic sites, has been synthesized under solvothermal conditions. Compound URJC-3, with polyhedral morphology, crystallizes in the tetragonal and $P4_32_12$ space group, exhibiting a three-dimensional structure with small channels along *a* and *b* axes. This material was fully characterized and its hydrogen adsorption properties were estimated for a wide range of temperatures (77-298 K) and pressures (1-170 bar). The hydrogen storage capacity of URJC-3 is quite high according to its moderate surface area, which is probably due to the confinement effect of hydrogen molecules inside its reduced pores of 6 Å, near the ionic radii of hydrogen molecules. The storage capacity of this material is not only higher than that of active carbon and purified single-walled carbon nanotubes, but also surpasses the gravimetric hydrogen uptake reached by most MOF materials.

Introduction

Metal-organic framework materials (MOFs) have attracted increasing attention during the last years, particularly due to their interesting variety of architectures and topologies, which are defined by the abundant organic ligands, metals and crystallization conditions.^[1-4] Because of the high customize ability of these porous structures, they have been considered as potential candidates for a wide range of applications such as gas storage, heterogeneous catalysis, drug delivery and sensing, among others.^[5,6] Considering the high demand for efficient use of clean and renewable energy, and being hydrogen an attractive fossil fuel alternative owing to its high gravimetric energy density, the development of hydrogen storage materials has been strongly promoted.^[7-10] Among them, MOF materials are able to store hydrogen through physisorption mechanism, which presents many advantages in comparison with chemisorption in chemical hydrides, such as total reversibility and fast adsorption-desorption kinetics.^[11-13] Inspired by these premises, a wide range of MOF materials has been rationally designed for hydrogen storage applications.^[14-20]

It is well known that the chemical nature of both, metal clusters and organic linkers, have a huge influence in the interactions between H₂ molecules and MOF structure.^[21,22] In our and other previous studies, it has been observed that cobalt-based MOFs show high affinity to hydrogen molecules, reaching higher isosteric heat of adsorption values than other isostructural frameworks based on different metals, maybe since cobalt could act as a Lewis acid site.^[23-28] Moreover, numerous works report that MOFs constructed by aromatic ligands use to show high internal surface areas, displaying significant hydrogen uptakes.^[7,21,29] Particularly, carboxylic linkers, which are easily deprotonated, are able to form MOF materials with different geometries constituted by multiple strong metal-oxygen coordination bonds that provide good thermal stability and rigidity to the framework.

In this regard, the synthesis of new cobalt-based materials using the multifunctional ligand, 5,5'-(diazene-1,2-diyl)diisophthalic acid (H₄ABTC) has been explored over the last years.^[30-37] The coordination chemistry of H₄ABTC is interesting since its four carboxylate groups can be partially or completely deprotonated in order to generate H₂ABTC²⁻, HABTC³⁻, and ABTC⁴⁻ anions under different synthesis conditions that can coordinate with metal ions in multiple ways. Besides, the azo functionality is well-known as photochromic group that could reverse its geometrical isomerization between *cis* and *trans* states upon irradiation and other conditions, leading to the possibility of forming a series of MOF materials with interesting topologies and properties.^[38-40] In addition, the presence of azobenzene group from the ligand could contribute in improving the H₂-MOF interaction as a result of the lone pair of electrons on the nitrogen atoms that could perform as Lewis base.^[41]

In this context, herein we report the solvothermal synthesis of a novel cobalt azobenzene-based metal-organic framework, named URJC-3. Moreover, the new structure has been elucidated and the bulk sample was characterized by different physico-chemical techniques. Finally, its hydrogen adsorption properties, as well as the affinity of the material to H₂ molecules has been estimated by means of the adsorption-desorption isotherms at different temperatures and pressures.

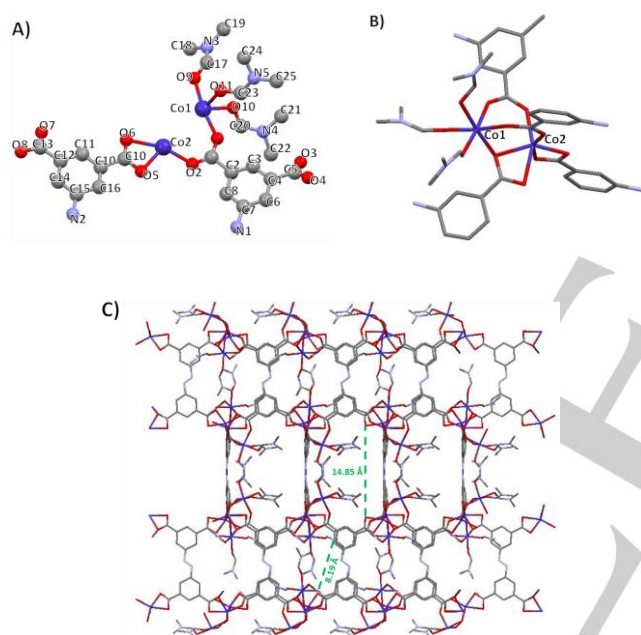
Results and Discussion

The crystalline structure of the new material was solved by the single crystal X-ray diffraction technique. Compound URJC-3 crystallizes in the tetragonal and $P4_32_12$ space group. Despite the fact that its chemical formula is simplified as C_{29.5}H_{37.5}Co₂N_{6.5}O_{12.5}, the asymmetric unit is comprised of two cobalt ions, three coordinated DMF molecules and one independent 5,5'-(diazene-1,2-diyl)diisophthalate ion ligand (Figure 1A). Co1 atom exhibits an almost ideal octahedral environment established by three O donor atoms set from three carboxylate groups pertaining to three different ligand molecules, and three coordinated DMF molecules. Co2 atom shows a

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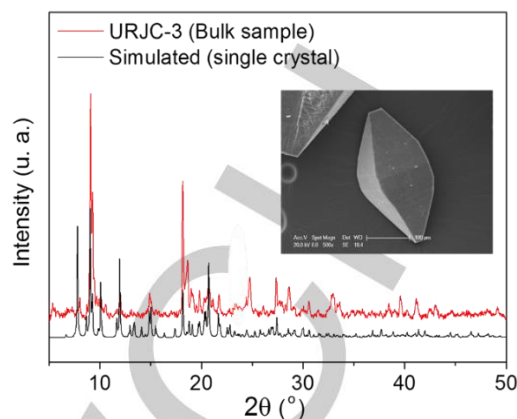
Supporting information for this article is given via a link at the end of the document.

1 distorted octahedral geometry due to the presence of two small
 2 bond angles O-Co-O with values of 60.51(14)° and 61.21(15)°,
 3 where cobalt is coordinated twice to two oxygens from the same
 4 carboxylate group and twice to one oxygen from other
 5 carboxylate (Figure 1B). In according to the coordination modes
 6 of the organic linker ABTC⁴⁻, one of them is coordinated with
 7 eight cobalt ions exhibiting a bridging bis-bidentate coordination
 8 mode, and the other organic linker connects six cobalt ions, for
 9 which four carboxylate groups are in chelating bidentate mode
 10 while the other four show a tridentate chelating bridging mode
 11 with cobalt atoms. Such building units are repeated to form a
 12 three-dimensional (3-D) network, containing Lewis acid sites
 13 from Co ions and Lewis basic sites from azobenzene groups
 14 from the ligand, suitable not only for hydrogen adsorption but
 15 also for catalysis purposes. It also has coordinated DMF
 16 molecules pointing towards the interior of the cavities (Figure
 17 1C), differentiating two different cavities of around 8.19 and
 18 14.85 Å, without extracting carbon and oxygen radii.



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43 **Figure 1.** (A) Asymmetric unit of URJC-3, (B) Coordination environment of
 44 Co²⁺ ions and (C) 3D view of URJC-3 MOF. Hydrogen atoms have been
 45 omitted for clarity.

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48 In order to confirm the purity of the crystalline phase of the
 49 material, experimental powder X-ray diffraction pattern was
 50 compared to the simulated pattern from the crystallographic data
 51 (Figure 2). Thus, it was observed that both diffractograms match
 52 very well in most of the reflections, confirming the exclusive
 53 presence of URJC-3 crystalline phase. Moreover, by scanning
 54 electron microscopy (Figure 2-Insert), the morphology and size of
 55 the crystals were determined, observing that it is constituted by
 56 only polyhedral crystals with average size of 100 μm (Figure S3
 57 of the Supplementary Information).



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65 **Figure 2.** XRD patterns of powder URJC-3 sample and simulated from its
 single-crystal data.

The thermal stability of the material was studied by TG/DTG
 analysis (Figure S4). Two main weight loss steps were found,
 the first occurs in the temperature range of 40–150 °C that could
 correspond to the loss of water and possible DMF molecules
 filling the pores and some of them coordinated to the structure.
 The second weight loss is detected from roughly 275 °C, which
 was associated to the decomposition of the organic ligand,
 leading to the subsequent structure collapse.

The textural properties of URJC-3 were measured by Ar
 adsorption-desorption analysis at 87 K (Figure S5A). The
 isotherm revealed the microporosity of the new material since
 the sharp adsorption at very low relative pressure. However, the
 typical plateau after the edged adsorption at low pressure
 described for Type I isotherms is not observed in this case,
 having a progressive slope that indicates possible desorption
 species such as coordinated DMF. The resulting BET specific
 surface area was 171 m²g⁻¹, and a pore volume of 0.076 cm³g⁻¹.
 Besides, the pore size distribution (PSD) was also estimated
 using non-local DFT method, obtaining a bimodal narrow
 distribution at around 6 and 11 Å (Figure S5B), which matches
 with the before mentioned crystallographic information of this
 structure. The crystalline density of the new material was 1.51
 g·cm⁻³ (Table 1), regarding the results of the He pycnometry
 analysis.

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65 **Table 1.** Textural properties of URJC-3.

Surface Area (m ² g ⁻¹)	Pore volume (cm ³ g ⁻¹)	Skeletal density (g·cm ⁻³)	Crystal density (g·cm ⁻³)
171	0.076	1.7	1.51

Hydrogen adsorption measurements, at different conditions of
 pressure and temperature were carried out in order to determine
 the hydrogen adsorption properties of the novel MOF. For this
 purpose, URJC-3 sample was activated under high vacuum at
 1·10⁻⁵ mbar and 120 °C during 6 h. First, the hydrogen uptake at
 77 K and up to 16 bar was recorded (Figure 3). There, a type I

profile regarding the IUPAC was identified, which is roughly saturated at 16 bar with a gravimetric hydrogen excess uptake of about 3.50 wt %, which corresponds to a total H₂ storage capacity of 3.63 wt % (Table 2).

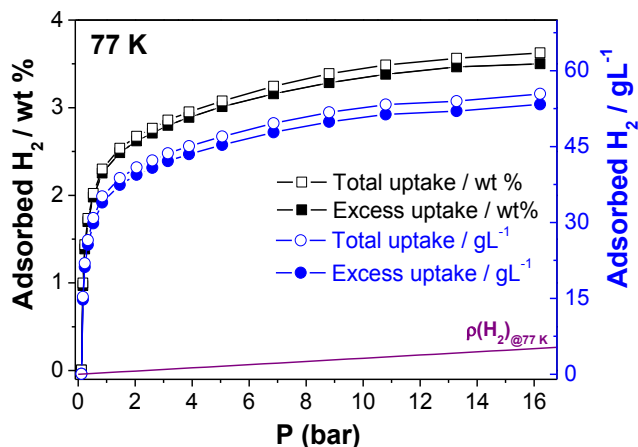


Figure 3. Hydrogen adsorption isotherms at 77 K. Left: gravimetric units, right: volumetric units.

Table 2. Excess and total gravimetric and volumetric H₂ adsorption capacity at 77 K and 18 bar of URJC-3

Excess gravimetric H ₂ adsorption capacity (wt %)	Total gravimetric H ₂ adsorption capacity (wt %)	Excess volumetric H ₂ adsorption capacity (gL ⁻¹)	Total volumetric H ₂ adsorption capacity (gL ⁻¹)
3.50	3.63	53.35	55.40

The hydrogen storage capacity of URJC-3 is quite high according to its low surface area, as rationalized by Chahine on a variety of microporous materials.^[42] This drifting from the tendency of the rule could be related to the higher interaction due to the confinement effect of hydrogen molecules inside the pores of the MOF structure when is endowed with small sized pores in the range near ionic radii of hydrogen molecules, which is the case of the 6 Å pores of URJC-3. The storage capacity of this material is not only higher than that of active carbon and purified single-walled carbon nanotubes,^[43] but also surpasses the gravimetric hydrogen uptake reached by other MOF materials such as ZIF-8, MIL-100(Fe) and MOF-74(Zn, Mg).^[44-47] In terms of volumetric units, which are more significant for H₂ storage applications in light-duty vehicles, URJC-3 displays an excess uptake of 53.35 gL⁻¹, which is a value far higher than the volumetric hydrogen storage capacity of a compressed-tank at the same conditions of pressure and temperature, about 5.4 gL⁻¹. This high volumetric value is probably related to the low pore volume and high crystal density of the material compared to other opener structures.^[7] This result has been also observed for other MOF materials with reduced pore volume that have been used for small molecules recognition and separation.^[48]

Additionally, H₂ adsorption-desorption isotherms at room temperature (298 K) and high pressure (170 bar) have been collected for URJC-3, whose data can be shown in Figure 4 and Table 3. In this case the difference between the excess and total adsorption capacity of the material is more marked than at 77 K, for which case the saturation is near to be reached.

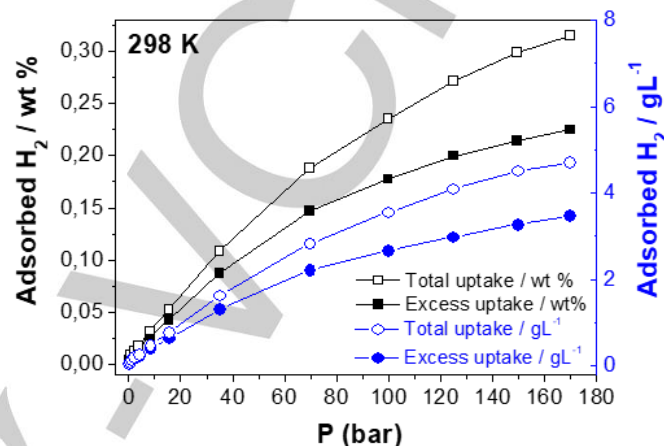


Figure 4. Hydrogen adsorption isotherms at 298 K. Left: gravimetric units, right: volumetric units.

Table 3. Excess and total gravimetric and volumetric H₂ adsorption capacity at 298 K and 170 bar of URJC-3.

Excess gravimetric H ₂ adsorption capacity (wt %)	Total gravimetric H ₂ adsorption capacity (wt %)	Excess volumetric H ₂ adsorption capacity (gL ⁻¹)	Total volumetric H ₂ adsorption capacity (gL ⁻¹)
0.23	0.32	3.47	4.7

These results were also compared with the experimental excess hydrogen adsorption uptake at room temperature of the well-known MOF-5 and PCN-5 materials with BET surface areas of 2296 and 2095 m²g⁻¹, for which were reached 0.25 and 0.19 wt %, respectively, at high pressure,^[7] similar than the 0.23 wt % reached by URJC-3. Considering the low surface area displayed by the new material, these results confirm that the hydrogen storage capacity at ambient temperature does not depends directly on the surface area, but on the pore size and chemical nature of the MOF scaffold, which promote the interaction with the H₂ molecules.

Finally, with the purpose of studying the strength of H₂-MOF interactions, the isosteric heat of adsorption profile for URJC-3 was estimated (Figure 5), using the Clausius-Clapeyron equation applied to the hydrogen adsorption data at near room temperature. There, it can be shown that the isosteric heat of adsorption at low hydrogen loadings is around 8.4 kJmol⁻¹, which is a good value among the average for MOF materials.

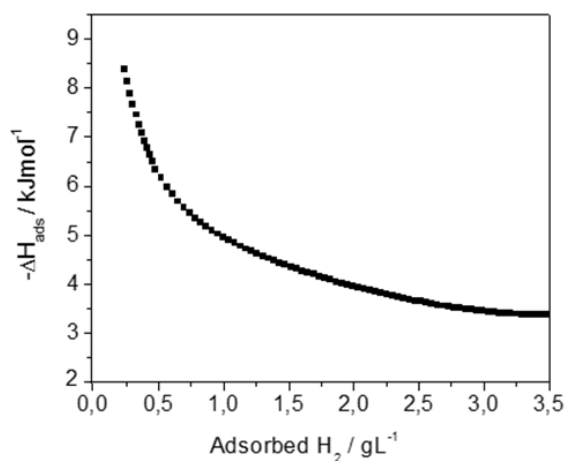


Figure 5. Heat of adsorption plotted as a function of the volumetric amount of H₂ adsorbed at near room temperature.

Conclusions

A novel versatile cobalt and azobenzene metal-organic framework, called URJC-3, containing Lewis acid and basic sites, has been synthesized and properly characterized by single and powder crystal X-ray diffraction, SEM, Ar adsorption at 87 K, TGA, and FT-IR. Compound URJC-3, with polyhedral morphology, crystallizes in the tetragonal and $P4_32_1$ space group, exhibiting a three-dimensional structure with small channels along a and b axes. The reduced pore volume together with the nature of the metallic centers make this microporous material especially interesting for the recognition and adsorption of hydrogen molecules. Thus, the hydrogen storage capacity of URJC-3 was studied at different conditions of pressure and temperature, observing an interesting confinement effect of the H₂ molecules inside the cavities of the framework of around 6 and 11 Å. The excess hydrogen storage capacity of the novel MOF in gravimetric terms was 3.5 wt.% at 77 K and 20 bar, and 0.23 wt.% at 298 K and 170 bar, which are higher than the expected values, considering its low surface area. Thus, in order to design the next generation of materials for on-board hydrogen storage at near room temperature, it is imperative to still improve the density of stored H₂, maximizing the interactions of H₂ molecules with the MOF material.

Experimental Section

Synthesis of H₄ABTC. The organic ligand 3,3',5,5'-azobenzene tetracarboxylic acid was prepared in according with the synthetic procedure described by Dhakshinamoorthy and colleagues,^[49] slightly modified by a further purification of the product by means of recrystallization in DMF (Detailed synthesis procedure is in section S2 of the Supporting Information).

Synthesis of URJC-3: A mixture of 5,5'-(diazene-1,2-diyl)diisophthalic acid (0.01 mmol) and cobalt(II) nitrate hexahydrate (0.01 mmol) was dissolved in a mixture of N,N-dimethylformamide (5 mL) and some drops of nitric acid. The solution was then added to a 20 mL scintillation vial and placed in a preheated oven at 100 °C for 72 hours. After cooling down to room temperature, high quality crystals for single X-ray diffraction were obtained. Red crystals were isolated by decanting the mother liquid and washed with DMF. The resulting crystals were finally immersed in fresh DMF. Yield ca. 55% (based on linker). IR = 1656 (m), 1616 (s), 1552 (s), 1441 (s), 1377 (m), 1243 (m), 1105 (s), 920 (s), 776 (s) 715 (s) 681 (s) 514 (m) cm⁻¹. Anal. Calc. for C_{29.5}H_{37.5}Co₂N_{6.5}O_{12.5} (1): C, 40.58; H, 4.33; N, 10.23. Found: C, 44.23; H, 4.68; N, 11.37.

Materials and methods: X-ray data collection of suitable single crystals of compound URJC-3 was performed at 100(2) K on a Bruker VENTURE area detector equipped with graphite monochromated Mo-K α radiation ($\lambda = 0.71073$ Å) by applying the ω -scan method. The data reduction was performed with the APEX2^[50] software and corrected for absorption using SADABS.^[51] Crystal structure was solved by direct methods using the SIR97 program^[52] and refined by full-matrix least-squares on F2 including all reflections using anisotropic displacement parameters by means of the WINGX crystallographic package.^[53] All hydrogen atoms were included as fixed contributions riding on attached atoms with isotropic thermal displacement parameters 1.2 times or 1.5 times those of their parent atoms for the organic ligands. During the structure refinement, regions of electron density were identified as highly disordered DMF molecules. Attempts to model these electron densities as DMF were not successful due to the extent of the disorder. In the final structure model, the contribution of the electron density from 1.5 DMF molecules has been removed from the intensity data using the solvent mask tool in Olex2.^[54] The contribution from the 1.5 DMF molecule has been included in the empirical formula to give the correct calculated density, absorption coefficient and molecular weight. Details of the structure determination and refinement of compound is summarized in Table S1. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC 1884280. Copies of the data can be obtained free of charge on application to the Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, U.K. (Fax: +44-1223-335033; e-mail: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk). Powder X-ray Diffraction (XRD) analysis were carried out with a Philips X'PERT MPD equipment using Cu-K α monochromatic radiation (1.542 Å) with a 0.01 step, 10 s of accumulation time between steps and a non-proportional detector Xcelerator. Ar adsorption-desorption measurements at 87 K were made in an AutoSorb equipment (Quantachrome Instruments). Specific surface area was calculated by the Brunauer-Emmett-Teller (BET) equation,^[55] while micropore volume and pore size distribution of materials were estimated by

1 Non-Local Density Functional Theory (NL-DFT).^[56] Fourier
2 Transform Infrared Spectra (FT-IR) were recorded in a FT-IR
3 Varian Excalibur Series 3100 e UMA 600 spectrophotometer
4 with a resolution up to 4 cm⁻¹. Thermogravimetric Analysis (TGA)
5 was performed in a Mettler-Toledo DSC-TGA Star System
6 device in air atmosphere, by heating samples at a rate of
7 1 °C/min. Skeletal density was determined through He
8 pycnometry in an AccuPyc II 1340 apparatus. H₂ adsorption
9 isotherms (99.999%) at 77 and 87 K were obtained on a Hiden
10 Analytical Intelligent Gravimetric Analyser (IGA-003) equipped
11 with an ultra-high vacuum system. The buoyancy correction was
12 achieved after collecting He (99.99999%) adsorption-isotherms
13 at 273 K. For H₂ adsorption-desorption isotherms at high
14 pressure and RT conditions, a volumetric Quantachrome
15 iSorbHP1 equipment was used, with an operation range of 0.06–
16 200 bar. According to the National Institute of Standards and
17 Technology reference values [NIST. Isothermal properties for
18 hydrogen n.d.: <http://webbook.nist.gov/>], H₂ density was
19 calculated by Helmholtz real-gas EOS.^[57] The adsorption
20 isotherm model used for fitting the experimental adsorption data
21 was the Virial 2 equation.^[54] The isosteric heat of hydrogen
22 adsorption for material was calculated by the Clausius-
23 Clapeyron equation^[58] using data of H₂ adsorption isotherms at
24 273, 298 and 323 K (up to 170 bar).

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33
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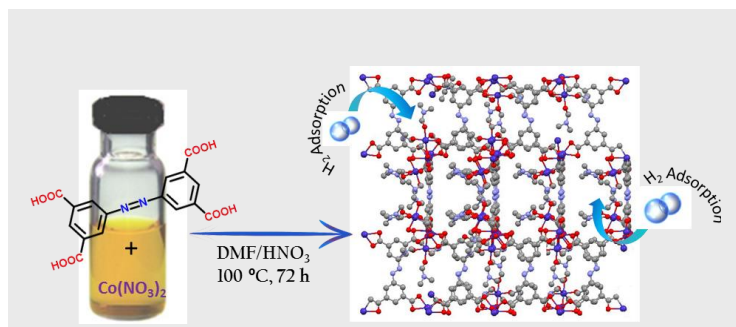
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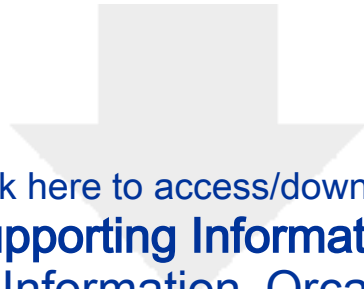
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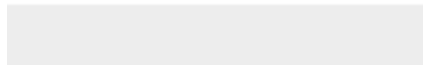
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