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An indirect generation of 1D M^{II}-2,5-dihydroxybenzoquinone coordination polymers, their structural rearrangments and generation of materials with a high affinity for H_2, CO_2 and CH_4†

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Abstract

A series of solid-state structural transformations are found to accompany desolvation of relatively simple coordination polymers to yield materials that exhibit unexpected gas sorbing properties. Reaction of 1,2,4,5-tetrahydroxybenzene with M^{II} salts (M = Mg, or Zn) in an alcohol/water solution in the presence of air affords *cis*-$M^{II}(C_6H_2O_4^{-II})(H_2O)_2\cdot 2H_2O\cdot x$ROH, (M = Mg, or Zn), crankshaft-like chains in which the absolute configurations of the chiral metal centres follow the pattern ···Δ Δ Λ Λ Δ Δ Λ Λ···, and are hydrogen bonded together to generate spacious channels. When crystals of the crankshaft chain are air dried the crystals undergo a single crystal-to-powder rearrangement to form linear *trans*-$M^{II}(C_6H_2O_4^{-II})(H_2O)_2$ chains. Further dehydration yields microporous solids that reversibly sorb H_2, CH_4 and CO_2 with high sorption enthalpies.

The field of coordination polymers has undergone immense growth in the last 25 years and is currently an area of intense worldwide interest.[1-3] Early work provided an indication of the scope of the type materials that may be produced and focussed on development of synthetic approaches, the characterization of the materials and the use of topological representations to describe the connectivity of networks.[4,5] Building on these foundations, later work was directed towards applications spanning diverse areas such as electronics, catalysis, luminescence, drug delivery and separation.[6-10] One of the most intensely investigated areas includes the generation of porous coordination polymers for storage of gaseous fuels or the capture of environmentally harmful gases.[11-14] Research in this area has demonstrated that coordination polymers possessing nano-scale cavities are capable of sorbing considerable quantities of gas, especially under cryogenic conditions and high pressures.[15-17] These systems commonly rely upon van der Waals-type interactions between the gas molecules (H_2, CO_2, CH_4 etc.) and the internal pore surfaces of the framework materials. As a result of the relatively weak interactions between host and guest, the gas uptake of these materials under conditions involving more moderate pressures and ambient temperatures can be significantly lower. Nevertheless, work in this area is progressing towards the development of materials with pore shapes[18-23] and surfaces[24-28] that enhance framework – gas molecule interactions allowing for optimal uptake, storage and release of gas under practical conditions.

Upon deprotonation, dihydroxybenzoquinone, H_2dhbq, is able to act as a bridge between a variety of metal centres within discrete and polymeric systems. In regards to the formation of coordination polymers our interest in this readily available ligand stems from the fact that as a charged ligand capable of chelation, it is able to bind strongly to metal centres and thus has the potential to provide robust coordination polymers. Furthermore, the redox activity of the dianion, (dhbq^{2-} is capable of undergoing reduction to both a radical trianion and a tetranion) offers the prospect of forming redox-active porous coordination polymers that may possess interesting and perhaps useful magnetic and electronic properties.[29,30] Intermittently since the early 1990's we have been exploring procedures for obtaining transition metal derivatives of H_2dhbq in the form of single crystals suitable for X-ray diffraction study, but until recently our results had been uniformly disappointing. Given the great potential interest of dhbq-based coordination polymers, we consider it very likely that other groups have had similar discouraging experiences that have gone unreported. We suspect this is the reason why structural data on very simple dhbq-based derivatives such as *trans*-$M^{II}(dhbq)(H_2O)_2.yH_2O$ (M = Mg, Mn, Fe, Co, Ni and Zn) (Fig. 1) were first reported as recently as 2009[31,32] and even then, mainly on the basis of powder data. In our recent work with H_2dhbq and its derivatives however, we have discovered that the indirect generation of the H_2dhbq through the *in-situ* aerial oxidation of the starting material 1,2,4,5-tetrahydroxybenzene (H_4thb) has been a productive avenue for the formation of nicely crystalline metal-$dhbq^{2-}$ polymers, which could not be obtained when employing H_2dhbq as the starting material.[33,34]

In this work we present the synthesis, structures‡ and gas sorption properties of two new polymers of $dhbq^{2-}$, in which crystals suitable for X-ray analysis were not obtained directly from H_2dhbq itself but by *in-situ* oxidation of the H_4thb precursor when combined with M^{2+} cations in an alcoholic reaction mixture. The products, of composition *cis*-$M^{II}(dhbq)(H_2O)_2\cdot 2H_2O\cdot x$ROH (M = Mg, or Zn) (R = Me for the Mg derivative or Et for Zn), have closely related compositions to the compounds, *trans*-$M^{II}(dhbq)(H_2O)_2\cdot yH_2O$, (M = Mg, Mn, Co, Ni, Zn), described by H. Kitagawa *et al*,[31,32] but have a structure significantly different to the strip-like *trans*-$M^{II}(dhbq)(H_2O)_2$ polymer which is depicted in Fig. 1. The structures of *cis*-$M(dhbq)(H_2O)_2\cdot 2H_2O\cdot x$ROH (M = Mg, or Zn) contain almost identical crankshaft-like $M^{II}(dhbq)(H_2O)_2$ 1D polymeric chains, an example of which (the Mg derivative) is shown in Fig. 2a. Two types of $dhbq^{2-}$ ligand are present. One type, type A in Fig. 2a, bridges two metal centres, the line between which is oriented roughly parallel to the general direction in which the infinite chain extends, whilst the type B ligands are very significantly inclined to that direction. The metal centres are essentially octahedral, being attached to one chelated ligand A, one chelated ligand B and two *cis*-aqua ligands. The metal centres are thus individually chiral, and their absolute configurations alternate in the fashion ··Λ Λ Δ Δ Λ Λ Δ Δ·· along the length of the chain. Crankshaft chains are linked together by hydrogen bonds between the coordinated aqua ligands and $dhbq^{2-}$

oxygen centres, as shown in Fig. 2b. Every chain is linked in this way along its entire length to four others, whereby a 3D hydrogen bonded network that contains channels (see Fig. 2c) occupied by non-coordinated water and methanol molecules (in the case of the magnesium derivative) or water/ethanol (present in the zinc derivative) is formed. Two well-defined, non-coordinated water molecules form hydrogen bonds to $dhbq^{2-}$ oxygen centres, whereas the alcohol molecules are disordered over a number of sites.

Elemental analysis of air-dried crystals of the *cis*-$Mg(dhbq)(H_2O)_2 \cdot 2H_2O \cdot 2.5MeOH$ crankshaft chains (ESI, S.1) indicates that upon removal of the sample from its mother liquor, practically all the channel solvent molecules are lost. Powder X-ray diffraction measurements performed on a sample of air-dried *cis*-$Mg(dhbq)(H_2O)_2 \cdot 2H_2O \cdot 2.5MeOH$ reveals the powder pattern no longer resembles the pattern expected for the crankshaft chains, but instead matches the diffraction pattern of the *trans*-$Mg(dhbq)(H_2O)_2$ strip-like chains observed by H. Kitagawa *et al* and shown above in Fig. 1. Following this insight, an experiment was conducted in which powder X-ray data were initially collected on a bulk slurry of *cis*-$Mg(dhbq)(H_2O)_2 \cdot 2H_2O \cdot 2.5MeOH$, the solid was then isolated from its mother liquor and air dried for further powder X-ray data measurements. The resulting X-ray powder patterns (shown in ESI S.2) provide resounding evidence that, quite remarkably, by simply exposing the *cis*-$Mg(dhbq)(H_2O)_2 \cdot 2H_2O \cdot 2.5MeOH$ crankshaft-like chains to air, the non-coordinated solvent molecules are lost and the chains undergo a single crystal-to-powder structural rearrangement to the planar strip-like chains (ESI Fig. S4). Similar experiments conducted on *cis*-$Zn(dhbq)(H_2O)_2 \cdot 2H_2O \cdot 1.5EtOH$ indicate the same structural rearrangement occurs for the Zn derivative. A further experiment in which a sample of the *trans*-$Mg(dhbq)(H_2O)_2$ strips were immersed in a methanolic solution and subsequently analysed with powder X-ray diffraction indicated that the transformation from the *cis*-$Mg(dhbq)(H_2O)_2$ crankshaft chains to *trans*-$Mg(dhbq)(H_2O)_2$ strips is not reversible (ESI Fig. S5).

Given the propensity of the *cis*-$M^{II}(dhbq)(H_2O)_2 \cdot 2H_2O \cdot x$ROH crankshaft chains to undergo a structural rearrangement to the strip-like *trans*-$M(dhbq)(H_2O)_2$ chains upon the loss of alcohol, we also performed synthetic investigations in which we set out to deliberately prepare the *trans*-$M(dhbq)(H_2O)_2$ strips ($M = Mg^{2+}$ or Zn^{2+}), in a nicely crystalline form, using H_4thb as a starting material in combination with the appropriate M^{II} salt in an aqueous reaction mixture that is free of methanol or ethanol. The motivation behind such investigations were to a) determine if the crankshaft chain formation was dependent on the presence of alcohol and b) investigate whether following the synthetic approach of the *in-situ* oxidation of H_4thb would permit the formation of *trans*-$M^{II}(dhbq)(H_2O)_2$ as high quality single crystals; H. Kitagawa *et al* reported the single crystal structure of only the manganese derivative, the structures of the remaining compounds were determined using powder X-ray diffraction. The combination of H_4thb with Mg^{2+} and Zn^{2+} in water, did indeed lead to nicely crystalline samples of *trans*-$M(dhbq)(H_2O)_2$.‡ These results suggest that the short-chain alcohols (MeOH and EtOH) play a templating role in the synthesis of *cis*-$M^{II}(dhbq)(H_2O)_2 \cdot 2H_2O \cdot x$ROH crankshaft-type chains. A summary of the synthetic routes to the formation of both *cis*-, and *trans*-$M^{II}(dhbq)(H_2O)_2$ and the structural rearrangements they undergo upon various levels of desolvation is provided in Scheme 1.

Thermogravimetric analysis (ESI, S.3) indicates the two molecules of water bound to the metal centres of *trans*-$Mg(dhbq)(H_2O)_2$ are lost in the range 125-180°C. Perhaps not surprisingly, the removal of the bound water molecules results in a loss of single crystal character thus preventing structural characterization of the completely desolvated material. X-ray powder diffraction indicates that the solvent-free Mg(dhbq) compound is microcrystalline (ESI, Fig. S6) although the diffraction peaks are rather broad making unambiguous determination of cell dimensions difficult. Nevertheless it is possible to make a tentative unit cell assignment as primitive tetragonal with cell dimensions a = 9.284, c = 12.680 Å.

The completely desolvated material shows reversible sorption of H_2, CH_4 and CO_2. The gas uptake results pertaining to the Mg(dhbq) sample are presented here whilst the sorption data for Zn(dhbq), which is similar to that found for Mg(dhbq), is provided in the ESI. The hydrogen uptake on a sample of Mg(dhbq) was measured at 77 K. The isotherm, presented in Fig. 3a, shows the sorption path rises steeply with an uptake of 80 cm^3(STP)/g at ~1 kPa. The uptake of the gas continues to increase to approximately 100 kPa, when the uptake is of the order of one H_2 molecule per metal centre. Whilst the total H_2 uptake reported here falls below that of a number of coordination polymers that possess very large pore volumes,[15-17] the high H_2 uptake at very low pressures is suggestive of the gas binding favourably to the internal surfaces of the desolvated compound. A second H_2 isotherm collected at 87 K allowed a calculation of the isosteric enthalpies of sorption (see ESI S.5). At low H_2 loading, the isosteric enthalpy of sorption is 9.5 kJ mol^{-1}. As further H_2 is introduced to the solid, the value declines to 7 kJ mol^{-1} and beyond this point the sorbent material is saturated. A review of the literature reveals that porous metal-ligand systems typically have hydrogen isosteric enthalpy of sorption values in the range 4 to 7 kJ mol^{-1}.[11,35-37] In cases where metal-ligand systems have sorption enthalpies comparable to those reported here, the favourable interactions have been attributed to either the presence of unsaturated metal centres throughout the sorbent material,[38-41] or materials with pores of optimal shape and size that allow for the maximum interaction of a gas molecule with the internal surfaces of the framework.[20,42,43] Carbon dioxide and methane uptake measurements also indicate a high affinity for carbon dioxide and methane at low pressures (Fig. 3b). The isosteric enthalpy of sorption values for CO_2 and CH_4, of 37 kJ mol^{-1} and 26 kJ mol^{-1} respectively, are higher than those commonly encountered with porous coordination networks; the methane isosteric sorption enthalpy at low loading in particular is amongst the highest recorded.[13,14,18,44]

The interesting sorption properties of the desolvated Mg(dhbq) and Zn(dhbq) compounds provides an opportunity to speculate on the structural nature of the material that is responsible for the gas sorption. In the case of the 1D polymers, Mg(dhbq)(H_2O)$_2$ and Zn(dhbq)(H_2O)$_2$ (either as the *cis*-crankshaft or *trans* strip structures) the octahedral metal centres are bound by a pair of $dhbq^{2-}$ dianions that each adopt the commonly observed bridging-chelating coordination mode. Upon loss of the coordinated water molecules the coordination number of the metal centre would drop from six to four unless each dhbq^{2-} has a coordination mode in which it links to more than two metal centres. Such a change may lead to an increase in dimensionality of the structure from 1D to 2D or even 3D. In the compound Mg-MOF74 (also known as CPO-27-Mg)[45,46] Mg^{2+} centres are linked by the ligand, 2,5-dioxido-1,4-benzene dicarboxylate (dobdc^{4-}) which shares some structural similarities with dhbq^{2-}. Single O donors, bound directly to the aromatic ring of dodbc^{4-}, provide links between pairs of Mg^{2+} centres, which leads to the generation of a porous 3D network that exhibits excellent gas sorption properties. If single oxygen atoms in Mg(dhbq) or Zn(dhbq) are able to bind pairs of metal centres in a similar manner then it is conceivable that a porous network would be generated.

In the case of Mg-MOF74 the Mg^{2+} centres are coordinately unsaturated, a feature that is responsible for the reported relatively high magnitude for the CO_2 isosteric enthalpy of sorption (39 to 47 kJ mol^{-1}),[13,47-49] values close to that obtained for Mg(dhbq). Similarly, in the case of H_2, our value of 9.5 kJ mol^{-1} for Mg(dhbq) is comparable to the value of 10.3 kJ mol^{-1} found for Mg-MOF74 which was based upon isotherm data (a value of 12 kJ mol^{-1} was found for Mg-MOF74, determined from an IR spectroscopic analysis).[41] The similarity of these results raises the prospect of the Mg^{2+} centres in Mg(dhbq) being coordinately unsaturated and that the high binding enthalpies reflects a direct interaction between the metal centres and the guest molecules. On the other hand, as indicated above, small pore size can lead to elevated sorption enthalpies because the guest molecules can make multiple contacts with the internal pore surface. As a consequence it is possible that the relatively high sorption enthalpies reflect the presence of small pores within the host network.

In summary, this work provides further examples of an indirect approach to the generation of M^{2+}-dhbq^{2-} coordination polymers, based on the *in-situ* aerial oxidation of 1,2,4,5-tetrahydroxybenzene, as a means to obtain crystalline products suitable for X-ray diffraction studies. We recently reported a family of compounds, in a form suitable for single crystal structure determination, of composition $(NBu_4)_2[M^{II}_2(dhbq^{-II})_3]$ (M = Mn, Fe, Co, Ni, Zn and Cd) in which the $[M^{II}_2(dhbq^{-II})_3{}^{2-}]$ coordination framework possessed the (10,3)-a topology;[33] the $dhbq^{2-}$ component in these cases was generated, again not directly from H_2dhbq itself, but by *in*-*situ* hydrolysis of 2,5-diaminobenzoquinone. These results, together with those reported above, afford encouragement that indirect routes involving the *in situ* generation of $dhbq^{2-}$ may provide access to new classes of potentially interesting $dhbq^{2-}$-based coordination polymers in a form suitable for single crystal X-ray structure determination, thereby surmounting a major and long-standing impediment to progress in this area. Moreover, the products above afford, upon dehydration, microporous materials with surfaces that are suited for the uptake of significant quantities of H_2, CO_2 and CH_4 at low pressures. The sorption enthalpies reported here are consistent with materials that possess either surfaces lined with coordinately unsaturated metal sites or have pore structures that are of a shape and size that allow for gas molecules to be in simultaneous contact with multiple surfaces.

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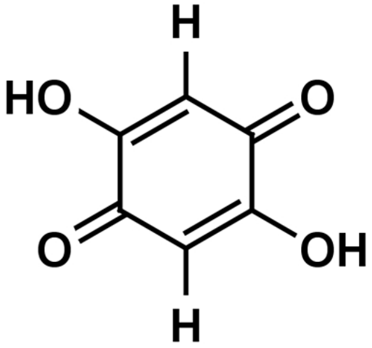
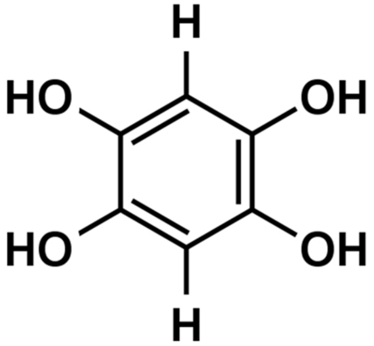


H_2dhbq



H_4thb

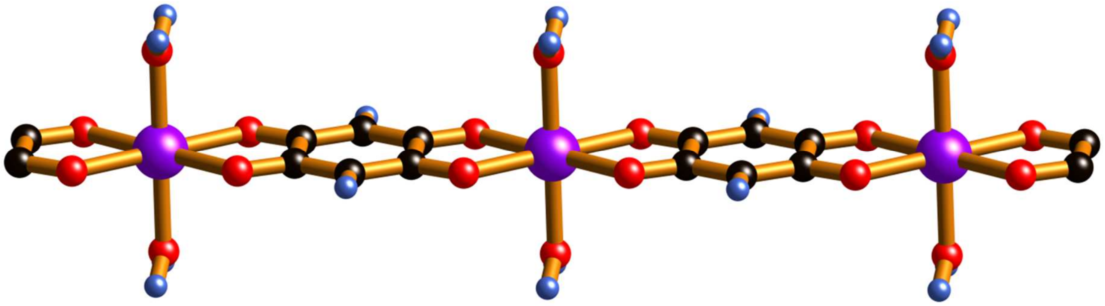
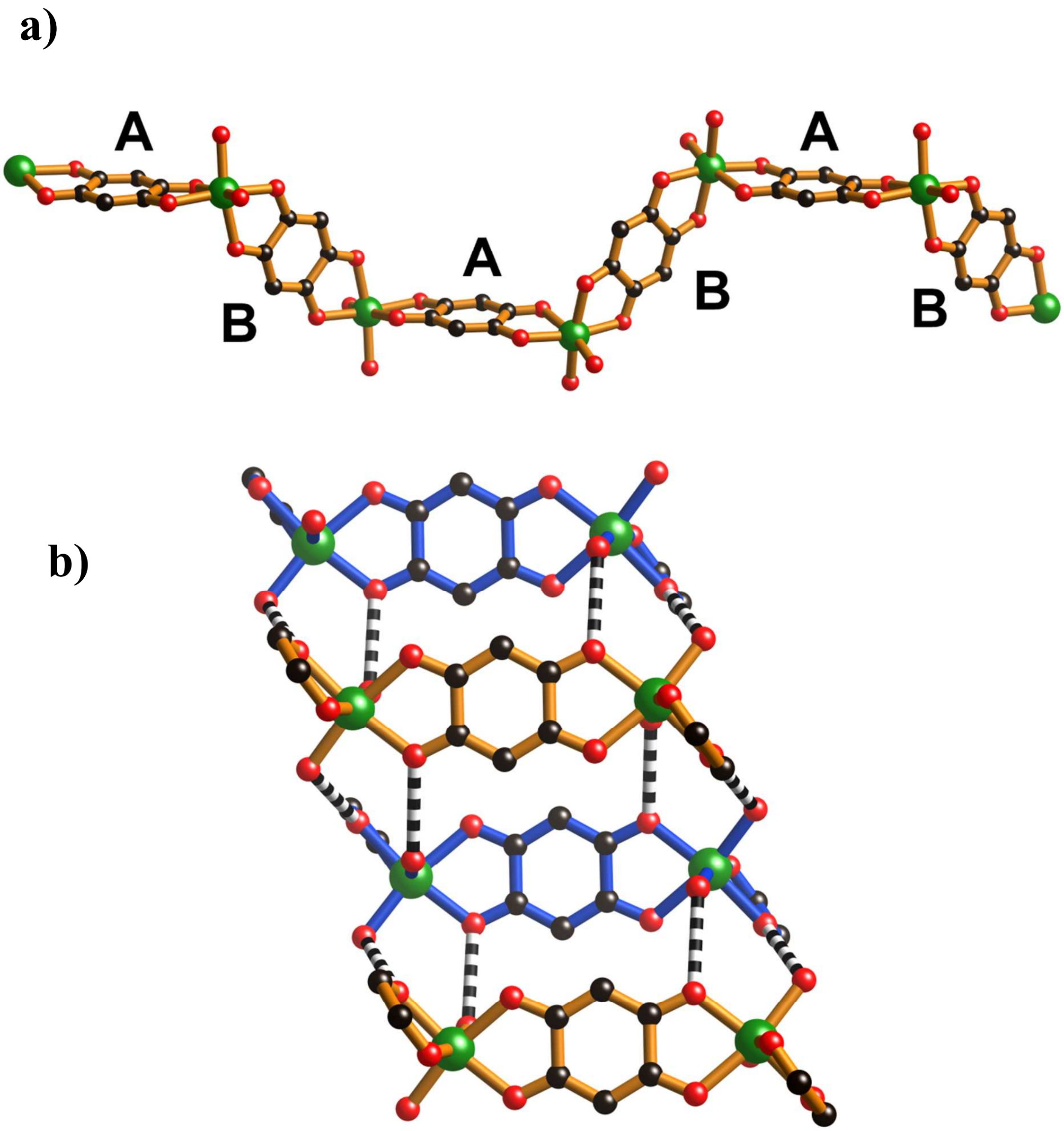


Fig. 1: The planar strip-like *trans*-M(dhbq)(H_2O)$_2$ chain reported by H. Kitagawa *et al.*[3]


a)
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b)

c)

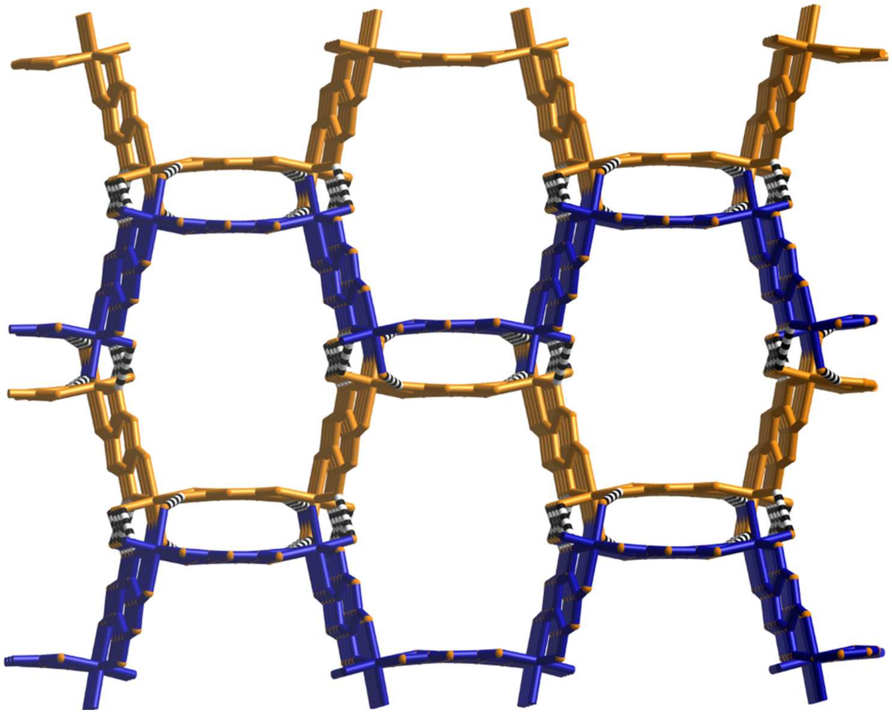
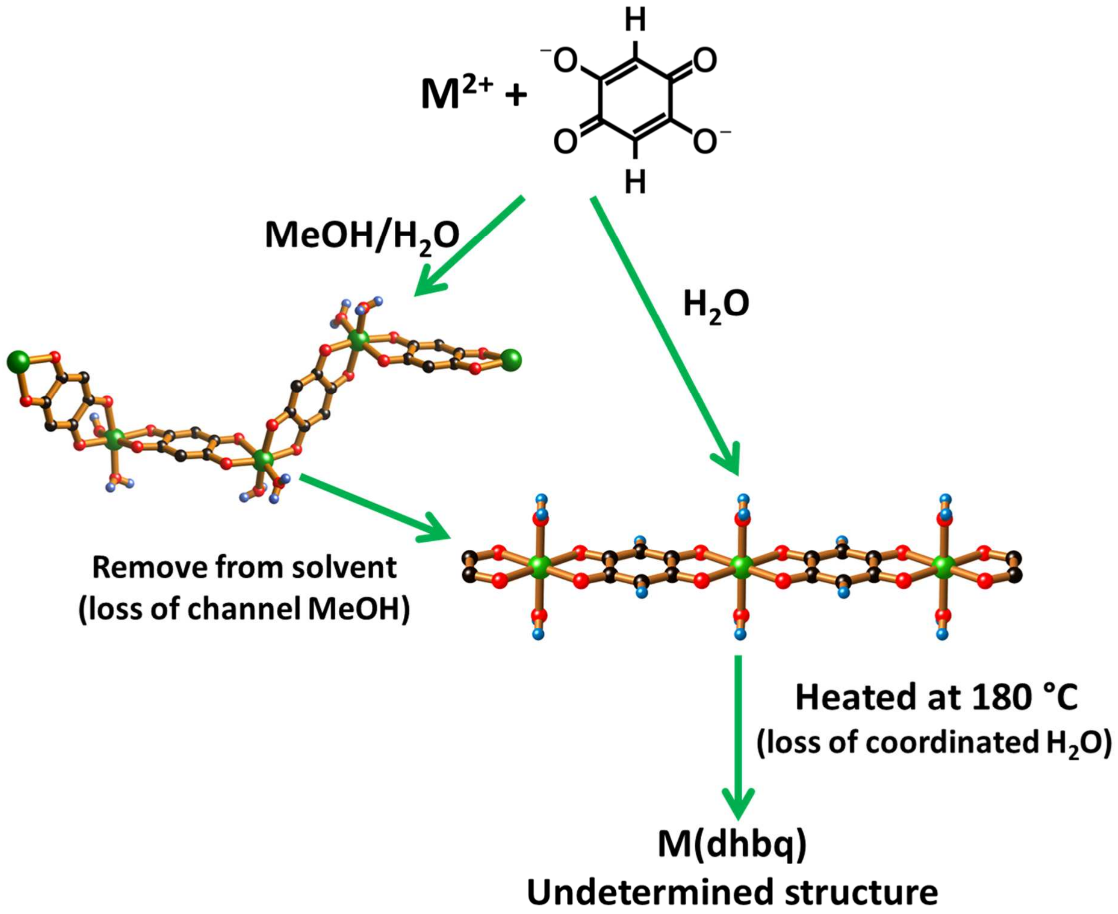


Fig. 2: a) One *cis*-Mg(dhbq)(H_2O)$_2$ crankshaft-like coordination polymer. Ligands of types A and B are indicated. b) The hydrogen bonding pattern linking *cis*-Mg(dhbq)(H_2O)$_2$ crankshaft-like chains together. O-H···O bonds are represented by black and white banded connections. Four type A ligands are shown face-on. For clarity only a fraction of each of the type B ligands (the O-C-C-O system) is shown. c) The extended 3D hydrogen bonded network containing spacious channels.



Scheme 1: A summary of the synthetic routes for both *cis*-, and *trans*-M^{II}(dhbq)(H$_2$O)$_2$ and the structural rearrangements they undergo upon various levels of desolvation.

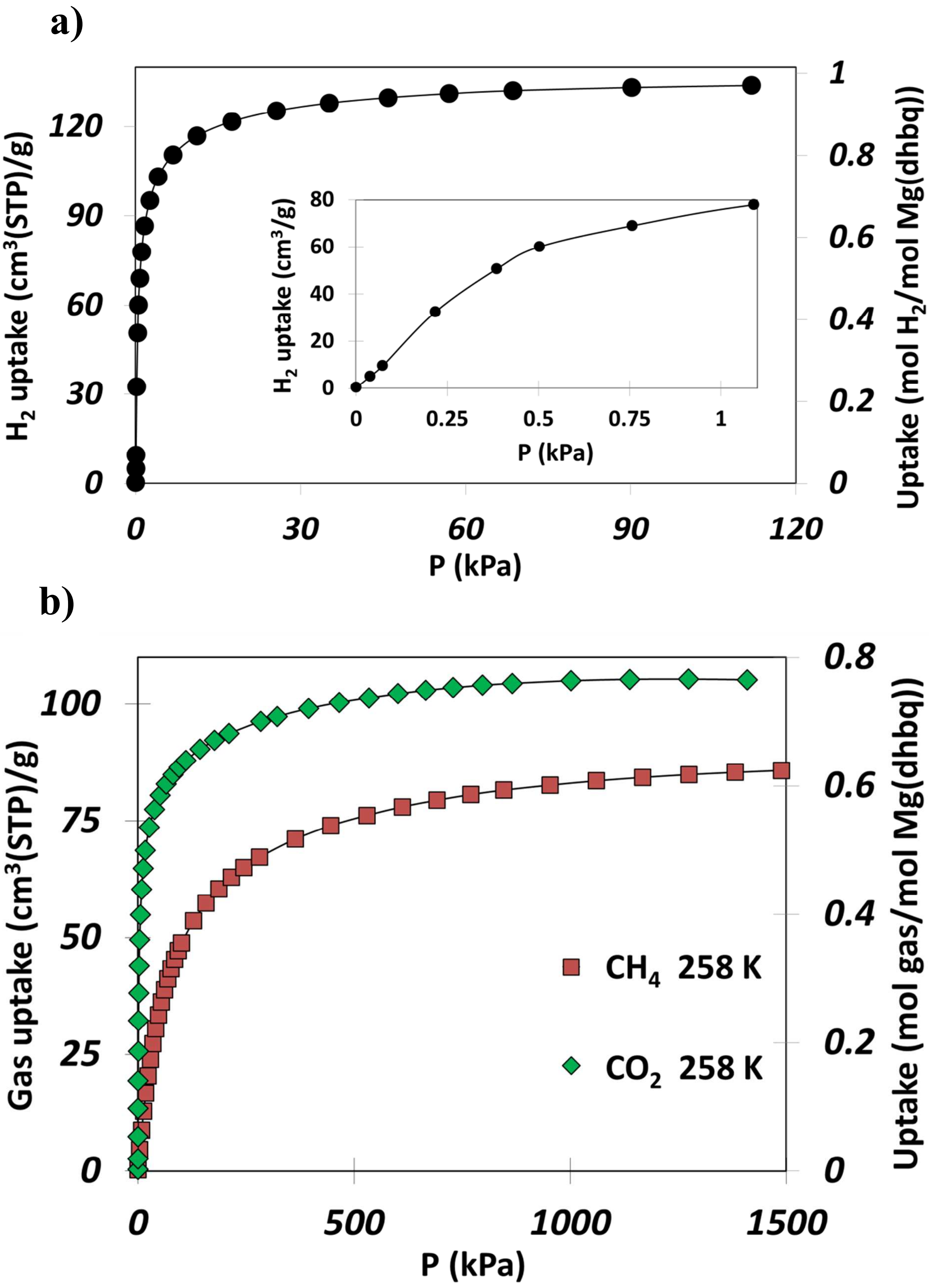


Fig. 3: a) A H_2 sorption isotherm measured on a sample of Mg(dhbq) at 77 K. Inset: H_2 uptake at pressures up to 1 kPa. b) CO_2 (green diamonds) and CH_4 (red squares) sorption isotherms measured on Mg(dhbq) at 258 K.

Notes and References

‡ Crystal data for *cis*-Mg(dhbq)$(H_2O)_2$·$2H_2O$·2MeOH: $[C_{8.5}H_{20}MgO_{10.5}]$ monoclinic, $C2/c$, a = 21.0769(13) Å, b = 15.6680(8) Å, c = 9.2192(4) Å, β = 103.261(12)°, V = 2963.3(3) Å^3, Z = 8, λ = 1.54184 Å, T = 130 K, reflections collected 4769, 2818 unique (R_{int} = 0.0428). R_1 0.0571 ($I > 2\sigma(I)$), $wR2$ 0.1562 (all data), GOF = 0.996. Crystal data for *cis*-Zn(dhbq)$(H_2O)_2$·$2H_2O$·1.5EtOH: $[C_9H_{19}O_{9.5}Zn]$, monoclinic, $C2/c$, a = 21.4589(10) Å, b = 15.5785(6) Å, c = 9.2643(3) Å, β = 102.941(4)°, V = 3018.4(2) Å^3, Z = 8, λ = 1.54184 Å, T = 130 K, reflections collected 4348, 2303 unique (R_{int} = 0.0329). R_1 0.0427 ($I > 2\sigma(I)$), $wR2$ 0.1180 (all data), GOF = 0.922. Crystal data for *trans*-Mg(dhbq)$(H_2O)_2$:$[C_6H_6MgO_6]$, monoclinic, $C2/m$, a = 6.8276(7) Å, b = 7.6461(7) Å, c = 7.8635(7) Å, β = 112.777(12)°, V = 378.50(7) Å^3, Z = 2, λ = 1.54184 Å, T = 130 K, reflections collected 745, 379 unique (R_{int} = 0.0303). R_1 0.0424 ($I > 2\sigma(I)$), $wR2$ 0.1169 (all data), GOF = 1.090. Crystal data for *trans*-Zn(dhbq)$(H_2O)_2$:$[C_6H_6O_6Zn]$, monoclinic, $C2/m$, a = 6.715(2) Å, b = 7.7544(13) Å, c = 7.842(2) Å, β = 113.45(3)°, V = 374.6(1) Å^3, Z = 2, λ = 1.54184 Å, T = 130 K, reflections collected 757, 381 unique (R_{int} = 0.0257). R_1 0.0340 ($I > 2\sigma(I)$), $wR2$ 0.0893 (all data), GOF = 1.128.

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Table of contents entry

Zinc and magnesium dihydroxybenzoquinone coordination polymers transform from crankshaft-type chains to strips and finally to sorbent materials upon desolvation.