

## VIEWPOINT

## Demonstration of permanent porosity in flexible and guest-responsive organic zeolite analogs (now called MOFs)

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Christoph Janiak\*

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In the late 1990s rigorous proof of coordination polymer framework or MOF integrity in the absence of guest molecules still needed to be developed. A study by Kepert and Rosseinsky presented X-ray crystal structure refinements as one of the first definitive demonstrations of the retention of structural integrity of a porous coordination polymer framework upon complete desolvation and guest re-adsorption.

In the mid-1990s, the interest grew, or perhaps more appropriately, the race started to advance the hitherto mostly synthetic and structural study of coordination polymers and newly termed metal-organic frameworks to their applications. There was a search for stable microporous organic networks, which exhibited reversible guest exchange. Hopes were running high and potential applications in separation and heterogeneous catalysis appeared to be very promising.<sup>1</sup> It was clear that the key feature was not the incorporation of guest molecules but their reversible exchange and an intact (robust) network in the absence of guest molecules.

In the 1990s porous organic (host-guest) frameworks which exhibited reversible guest removal and stability of the host-framework in the absence of guest molecules were termed organic zeolite analogs.<sup>2</sup> The term “zeolite analogs” in connection with organic frameworks was not meant to imply that the whole functionality of inorganic zeolites (aluminosilicates) should be reproduced, rather it referred to the molecular sieve character of zeolites, the reversible guest removal and the stability of the host-framework in the absence of guest molecules. The property of a microporous host structure to remain intact upon guest removal is characteristic of zeolites. These organic zeolites promised a new range of applications and control in molecular synthesis and sieving through a large variety and the tailoring of the building blocks.<sup>2</sup>

A particularly intriguing strategy for the synthesis of organic zeolite analogs was the use of covalent coordinative bonds and organic or inorganic ligands as linkers between metal ions. Metal ions can differ in their charge, preferred coordination geometries such as octahedral, tetrahedral, square planar and others and together with various organic linkers provide a variety of choices in the construction of coordination networks/metal-organic frameworks.<sup>3</sup> Covalent metal-organic lattices

offered several possible advantages over their purely organic counterparts, including greater mechanical strength and the inherent presence of catalytically active transition metals. An attractive feature of inorganic complexes is the accessibility of 90° joints for the construction of a polymeric framework with macrocyclic boxes<sup>4</sup> together with a potentially interesting interplay of hydrophobic and hydrophilic regions and interactions.<sup>5</sup>

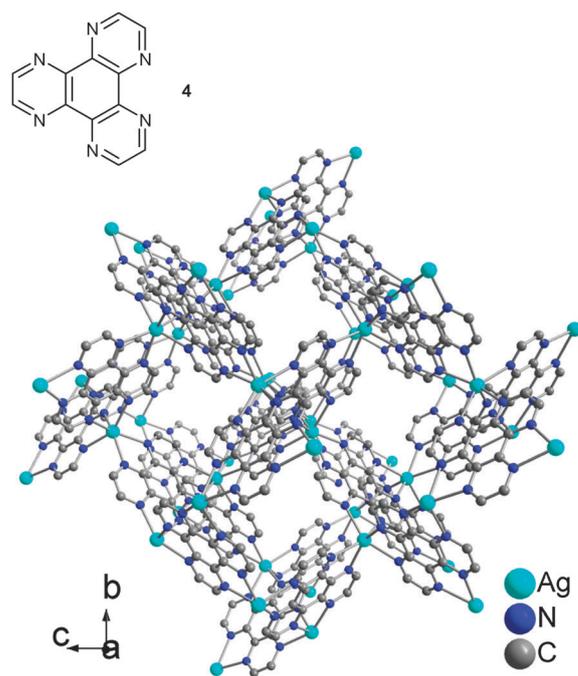
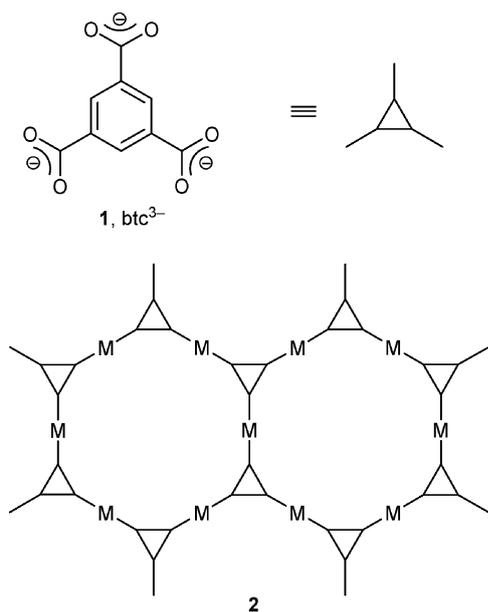
A large number of static metal-ligand frameworks and host-guest structures contrasted with a few known systems where a reversible guest exchange or chemical transformations of the guest inside a coordination polymeric framework had been described.<sup>2,6</sup>

While zeolite analogs made of organic matter<sup>7</sup> promised a new range of applications, *e.g.*, in drug manufacture, molecular sieving, enantiomer separation, chiral synthesis, product-precise catalysis or sensing,<sup>8,9</sup> certain hurdles still needed to be overcome. The basic problem of inclusion crystals based on an organic host lattice was that they mostly tend to lose their crystallinity together with a collapse of the voids upon removal of the (reinforcing) guest molecules from the pores.<sup>10</sup>

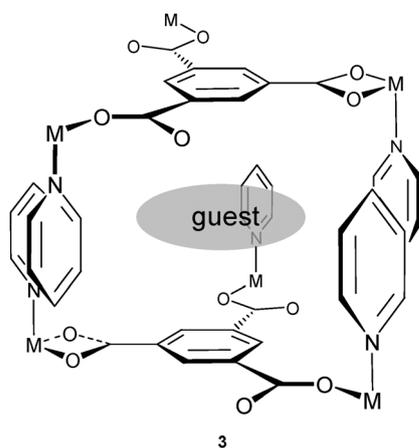
Rigorous proof of framework integrity in the absence of guest molecules still needed to be developed. For example, from the divalent metal ions  $\text{Co}^{2+}$ ,  $\text{Ni}^{2+}$  and  $\text{Zn}^{2+}$  and benzene-1,3,5-tricarboxylate ( $\text{btc}^{3-}$ , **1**) a hydrated solid of formula  $\text{M}_3(\text{btc})_2 \cdot 12\text{H}_2\text{O}$  having a 2D network structure with 1D channels (**2**) was obtained, which reversibly and repeatedly binds water without destruction of the framework.<sup>11</sup> In addition, inclusion of ammonia into the solid was demonstrated while larger molecules and those without a reactive lone pair were disallowed from entering the channels. Retention of the 2D metal-ligand assembly with 1D channels (**2**) was proposed for the porous solid.<sup>11</sup>

The same metal-btc building block but with two additional axial pyridine ligands at the metal center gave a layer structure, with the pyridine ligands functioning as spacer units between the layers (**3**).<sup>12</sup> In the  $\sim 7 \times 10 \text{ \AA}$  rectangular channels, thus formed

*Institut für Anorganische Chemie und Strukturchemie, Universität Düsseldorf, Universitätsstr. 1, D-40225 Düsseldorf, Germany. E-mail: janiak@uni-duesseldorf.de*



aromatic guest molecules were accommodated and could reversibly be removed. The single crystals retained their morphology and crystallinity upon loss of the guests *according to optical microscopy*.<sup>12</sup>



A three-dimensional 10,3-*a* network based on Ag(I) and the planar ligand 1,4,5,8,9,12-hexaazatriphenylene (hat, **4**) proved stable over two nitromethane guest de- and adsorption cycles with the stability evidenced by single-crystal X-ray diffraction over four generations.<sup>13</sup>

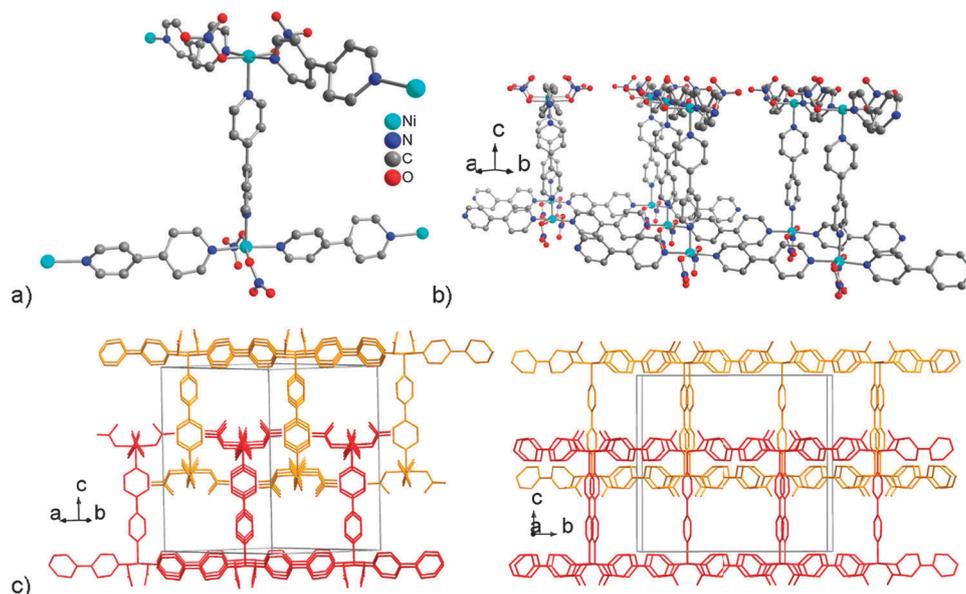
This was pretty much the situation when Kepert and Rosseinsky proved the rigidity of the two-dimensional (2D) coordination polymer network of  $[\text{Ni}_2(4,4'\text{-bipy})_3(\text{NO}_3)_4]$  (bipy = bipyridine) quantitatively by single-crystal X-ray structure analysis of both ethanol-loaded and ethanol-free forms (*cf.* Fig. 2). The structure of  $[\text{Ni}_2(4,4'\text{-bipy})_3(\text{NO}_3)_4]$  is built from single five- to six-coordinated nickel(II) atoms as T-shaped nodes which are connected by neutral 4,4'-bipyridine linkers. Charge-neutrality is achieved through two terminal mono- or bidentate nitrato ligands on each nickel atom (Fig. 1a). The T-shaped metal–ligand units assemble into ‘tongue-and-groove’ bilayers, where infinite chains which are linked by the axial

bipy ligands run nearly perpendicular (Fig. 1b). The bilayers then interdigitate (Fig. 1c and 2).<sup>14</sup>

The crystal structures before and after desolvation were determined (Fig. 2). The structural comparison showed only a small relaxation of the structure upon ethanol guest loss.<sup>14</sup> This work was an *in situ* demonstration of the robustness of the crystal structure at an atomic level.<sup>15</sup> The robustness of a porous coordination network is an important prerequisite for realistic applications, *e.g.*, in gas storage, separation or catalysis.<sup>16</sup> Kepert and Rosseinsky were the first to elucidate single-crystal-to-single-crystal guest removal. By now, many more examples of crystalline-state guest exchange in coordination networks are known<sup>17</sup> as well as the direct observation of gas molecules adsorbed in the nanochannels of porous coordination polymers by *in situ* synchrotron powder diffraction.<sup>18</sup>

The desolvated  $[\text{Ni}_2(4,4'\text{-bipy})_3(\text{NO}_3)_4]$  material was said to contain channels of a cross-section of about  $6 \times 3 \text{ \AA}^2$ .<sup>14</sup> A closer examination of the structure in space-filling mode (Fig. 3) reveals, however, that the  $[\text{Ni}_2(4,4'\text{-bipy})_3(\text{NO}_3)_4]$  network has only very small channels with dimensions of *ca.*  $1.1 \text{ \AA} \times 1.1 \text{ \AA}$ .<sup>21</sup> Therefore, the guest molecules are rather located in cavities (“zero-dimensional closed space”).<sup>21</sup>

In what is now called the “as synthesized” (as) form  $[\text{Ni}_2(4,4'\text{-bipy})_3(\text{NO}_3)_4] \cdot 2\text{EtOH}$ , the cavities formed by the  $\text{Ni}(\text{NO}_3)_2$ -bipy network are occupied by disordered ethanol solvent molecules (Fig. 2a). These ethanol solvent molecules are hydrogen-bonded to the nitrato ligands, are slowly lost at room temperature and can be quickly and fully removed upon heating to  $100 \text{ }^\circ\text{C}$  to give the “activated” form  $[\text{Ni}_2(4,4'\text{-bipy})_3(\text{NO}_3)_4]$ . Ethanol adsorbs again by exposure of the activated network to ethanol vapor. It is suggested that the passage of guest molecules through the small channel windows in and out of the cavities proceeds by a temporary expansion of the window size (*cf.* Fig. 3).  $\text{N}_2$  adsorption measurement on  $[\text{Ni}_2(4,4'\text{-bipy})_3(\text{NO}_3)_4]$



**Fig. 1** (a) Extended building block of the 2D network  $[\text{Ni}_2(4,4'\text{-bipy})_3(\text{NO}_3)_4]$  formed by T-shaped coordination of 4,4'-bipyridine to  $\text{Ni}^{2+}$  with nitrate ligands. A disorder between mono- and bidentate nitrate groups is not shown for clarity. Upper and lower Ni-bipy chains (connected by an axial bipy ligand) run nearly perpendicular. (b) Bilayer with the 'tongue-and-groove' motif. (c) Interdigitation of two adjacent bilayers which are differentiated by color (in wire mode and two different viewing directions).

at 77 K showed that under these conditions  $\text{N}_2$  is not adsorbed. This is presumably because of activated diffusion effects associated with the low thermal energy of the adsorbate relative to the high barrier for diffusion through the small channel windows.<sup>22</sup> In other words, at slow thermal motion at 77 K the  $\text{N}_2$  molecule will statistically only seldom approach the small pore aperture with the correct orientation for penetration, that is, in line with its molecular axis. It is a frequently encountered phenomenon of kinetic hindrance of small pores or pore aperture windows that  $\text{N}_2$  adsorption at 77 K does not occur, while  $\text{H}_2$  at 77 K or  $\text{CO}_2$  at 273 K is adsorbed.

Instead of EtOH, also  $\text{H}_2\text{O}$ , MeOH and  $^i\text{PrOH}$  can be introduced into the porous  $[\text{Ni}_2(4,4'\text{-bipy})_3(\text{NO}_3)_4]$  network.<sup>14</sup> However, later it became apparent that exposure of the Ni-bipy material to methanol vapor causes a guest-driven solid state crystal-to-crystal transformation to a polymorphic form with the same composition  $[\text{Ni}_2(4,4'\text{-bipy})_3(\text{NO}_3)_4]$  but a ladder structure. The transformation from the bilayers to the ladders is suggested to occur with the breaking of at least one of every six or one of every three Ni-bipy bonds and subsequent rotation of the bipy unit.<sup>23</sup>

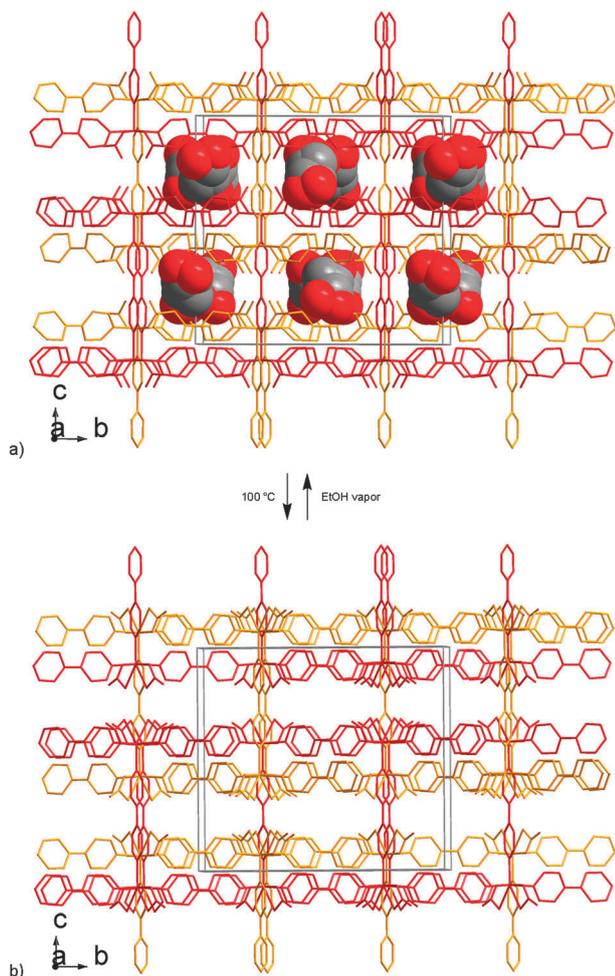
To assess the solvent-filled and solvent-free channel or cavity volume and its disordered contents Kepert and Rosseinsky (already) used the PLATON SQUEEZE option<sup>24</sup> which is now indispensable for the refinement of many MOF structures. The analysis agreed with the  $\sim 20\%$  channel/cavity volume for the ethanol-filled and -empty form. The SQUEEZE routine suggested a cavity population of 24.6 electrons per formula unit (in agreement with 26 electrons for EtOH) for the solvated form. For the solvent-free form the cavity population was only 0.8 electrons per formula unit demonstrating that no electron density was overlooked in the channels upon structure refinement.<sup>14</sup>

The robustness of  $[\text{Ni}_2(4,4'\text{-bipy})_3(\text{NO}_3)_4]$  in the guest-free state is even more remarkable in that this compound is not a

3D framework but "only" a 2D network. However, the framework is constructed as 'tongue-and-groove' bilayers (Fig. 1b). This bilayer motif helps – through the interdigitation of adjacent bilayers (Fig. 1c) with weak but multiple C–H $\cdots$ O interactions – to limit the relative movement of neighboring layers along the  $c$  direction to within 1%. Otherwise an unrestricted movement along  $c$  would unavoidably lead to a collapse of the porosity. The decrease in the unit-cell volume is only 2.4% upon desolvation and the mosaicity of the crystal remains intact. The host structure makes a small scissor-like motion in the  $ab$  plane where the criss-crossed chains of the bilayer adjust their angle within  $2^\circ$ .<sup>14</sup> The Ag-hat framework 4 had a volume change of  $\sim 3\%$  upon de- or resolution.<sup>13</sup>

The hydrate isomorph of  $[\text{Ni}_2(4,4'\text{-bipy})_3(\text{NO}_3)_4]$  had been synthesized before, together with the Co(II) and Zn(II) analogs, and all three anhydrous (activated) isostructural compounds were shown to adsorb  $\text{CH}_4$ ,  $\text{O}_2$  and  $\text{N}_2$ . X-ray powder diffraction patterns confirmed that there was no structural decomposition upon removal of the crystal water.<sup>25</sup> A detailed investigation of the guest sorption thermodynamics and kinetics in  $[\text{Ni}_2(4,4'\text{-bipy})_3(\text{NO}_3)_4]$  has been carried out.<sup>22</sup> The sorption of  $\text{CO}_2$ ,  $\text{N}_2\text{O}$  and methanol vapors in desolvated  $[\text{Ni}_2(4,4'\text{-bipy})_3(\text{NO}_3)_4]$  yielded isotherm steps that are ascribed to structural changes in the host adsorbent, in turn induced by adsorption on different sites. No isotherm steps were seen for ethanol adsorption. This full sorption study was one of the first studies to correlate specific host-guest interactions with structural changes in a flexible porous coordination polymer.<sup>22</sup>

Neutral nitrogen donor linkers, such as 4,4'-bipyridine and other di- to multitopic aromatic or aliphatic amines, had already given a myriad of cationic coordination polymeric network structures with anions in the voids or coordinated to metal atoms and solvent guest molecules. Attempts to remove or exchange solvent

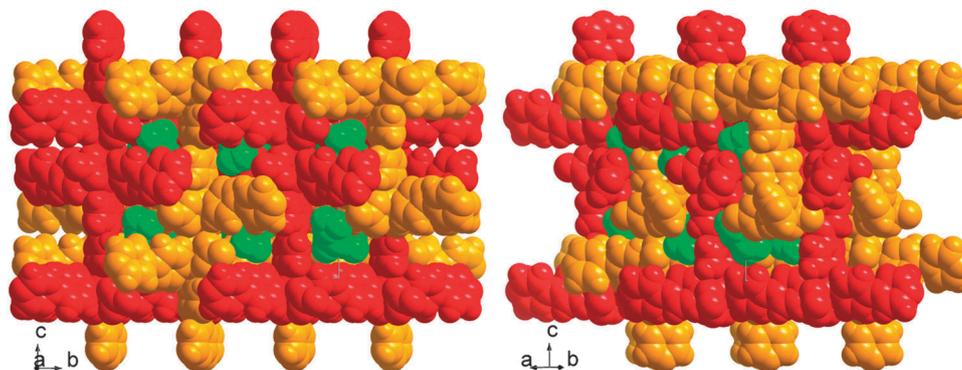


**Fig. 2** Projection of the (a) ethanol-solvated and (b) -emptied form. Channels with cavities run along the crystallographic *a* direction and occupy ~20% of the unit cell volume in both forms. Disordered ethanol molecules in (a) are shown in space-filling mode.<sup>14</sup> Structures are drawn (without H atoms) from deposited cif files as supporting information using the program Diamond (CCDC number 182/1136 or 114887 and 114888).<sup>20</sup>

guest molecules from the pores in these networks resulted in the collapse of the host framework. The work of Kepert and Rosseinsky was among the first exceptions with proven stability

of a metal-bipyridine network on the single crystal level. Following or paralleling their work further studies showed that the integrity of single crystal specimens was maintained during guest desorption.<sup>17</sup> Similarly, the difference in structure refinements then provided convincing proof of the synthesis of a robust open framework.<sup>26</sup> For example, the 2D network of formula  $[\text{Ni}(\text{pyridyl-biphenyl-pyridyl})_2(\text{NO}_3)_2]$  was another metal-bipyridine coordination polymer which was crystallographically shown to be a stable and crystalline solid with  $20 \times 20 \text{ \AA}$  open square-grids even after guest removal.<sup>27</sup> Multitopic pyridyl linkers are still important<sup>21,28</sup> but in the 1990s they favored even more prominently (compared to other linkers) for the construction of coordination networks which usually had single metal atoms as their nodes.<sup>29</sup> The group of Yaghi *et al.* then showed that multi-dentate carboxylate linkers were more favorable for the formation of more rigid frameworks.<sup>3</sup> Such multi-dentate carboxylate linkers like benzene-1,4-dicarboxylate or benzene-1,3,5-tricarboxylate are able to aggregate metal ions into multinuclear oxido-centered metal clusters,<sup>3,30</sup> like tetrahedral  $\{\text{Zn}_4(\mu_4\text{-O})\}$  in IRMOFs<sup>31</sup> or trigonal  $\{\text{M}_3(\mu_3\text{-O})\}$  ( $\text{M} = \text{Cr}, \text{Fe}, \text{Al}$ ) in some MILs.<sup>32</sup> Carboxylate groups then bridge between the metal atoms of these clusters and the multitopic nature of the di- or tri-carboxylate ligand links the clusters to open framework solids.<sup>3,30</sup> In 1999 Yaghi *et al.* also reported a highly porous metal-organic framework  $[\text{Zn}_4(\mu_4\text{-O})(\text{bdc})_3] \cdot (\text{DMF})_8(\text{C}_6\text{H}_5\text{Cl})$  better known as MOF-5 (bdc = benzene-1,4-dicarboxylate; DMF = *N,N*-dimethylformamide).<sup>33</sup> The framework of MOF-5 is so robust that a fully desolvated structure could be characterized by single-crystal X-ray analysis as well.<sup>33</sup>

Permanently porous, solvent-free, robust and crystalline frameworks have become recurring themes in MOF research, but before the turn of the millenium these features still needed to be ascertained in this new family of porous coordination polymers/metal-organic frameworks. The seminal work reported by Kepert and Rosseinsky has influenced many researchers in the field of coordination polymers and MOFs over the years and has led to over 260 citations of their paper by now.<sup>34</sup> Solid-state reactivity and structural transformations involving coordination polymers had a first highlight with the Kepert and Rosseinsky publication and the field continues to flourish. Nowadays structural transformations in coordination polymers induced



**Fig. 3** Space-filling representation with H atoms included in the network of the ethanol-solvated structure of  $[\text{Ni}_2(4,4'\text{-bipy})_3(\text{NO}_3)_4]$  in two viewing directions. Left: corresponding to Fig. 2a, right: corresponding to Fig. 1c, left. For better differentiation the ethanol solvent molecules are depicted in green color.

by the removal or exchange of guest molecules, by the exposure to reactive vapors and by external stimuli such as heat, light or pressure, are exploited for their concomitant changes in physical properties such as color, magnetism, luminescence, chirality, porosity, etc.<sup>35</sup>

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