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## A single-crystal-to-single-crystal transformation affording photochromic 3D MORF crystals

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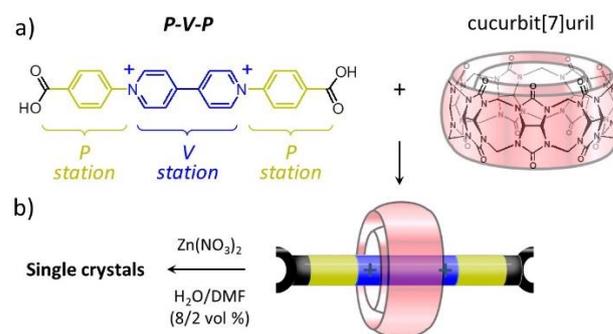
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**Metal-Organic Framework (MOF) type crystals in which rigid, viologen-based pillars are surrounded by cucurbit[7]uril (CB[7]) macrocycles are described. These Metal-Organic Rotaxane Frameworks (MORF) are obtained by desolvation of a crystal precursor featuring a network already near-optimal toward 3D Metal-Ligand reticulation and show reversible photochromism.**

Predicting the arrangement of molecules in the solid state has remained a tremendous challenge<sup>1</sup> until recently when several design principles have arisen toward getting hybrid, metal-ligand coordination polymers.<sup>2</sup> While the crystallization of organic compounds often relies on weak supramolecular interactions,<sup>3</sup> the impact of which remains difficult to establish compared to packing effects, the construction of coordination polymers relies on the formation of, comparatively stronger, metal-ligand bonds. In this context, the family of Metal-Organic Framework (MOF) crystals<sup>4</sup> has largely developed over time to become a mature research field where much of the activity is centred on (i) tuning the void space often available after material activation and (ii) using it for example for gas storage,<sup>5</sup> liquid separation,<sup>6</sup> water capture<sup>7</sup> or controlled drug release.<sup>8</sup> One subfield of MOF research is focused on arranging entangled structures along the pillars of the frameworks. Doing so, the pillars can possess a rotaxane architecture,<sup>9</sup> affording Metal-Organic Rotaxane Frameworks (MORF).<sup>10</sup> Recent advances include the pre-organization of rotaxanes or pseudo-rotaxanes in the form of a thread carrying carboxylic acids and a ring, often a crown-ether, before crystal growth with relevant metal ions.<sup>11</sup> Dynamics studies showed possible ring rotation<sup>12</sup> and translation<sup>13</sup> along the pillars of the crystals with temperature. Another strategy relied on the pre-synthesis of a highly porous MOF crystal carrying functional groups amenable for

subsequent linkage of rotaxanes in the pores of the crystals.<sup>14</sup> Ring movements were shown to operate with the right stimulus. Among the different rings available for MORF construction, the recent family of macrocycles cucurbit[*n*]urils (CB[*n*]) presents several advantages.<sup>15</sup> MORF crystals featuring CB[6] as the ring were introduced in 1997 in the form of 1D-MORF crystals.<sup>16</sup> A little later, 2D-<sup>17</sup> and 3D-versions<sup>18</sup> were reported before a revival of this chemistry in recent years.<sup>19</sup> But these examples relied on the recognition properties of CB[6] toward a di-cationic guest flanked with two chelate ligands. To the best of our knowledge, there are no examples of CB[7] based 3D-MORF. On the other hand, another subfield of the CB[*n*] chemistry has focused on viologens and derivatives<sup>20</sup> due to the good recognition of this motif by CB[7].<sup>21</sup> Owing to the responsiveness of the viologen function to various stimuli (light, chemicals, redox, temperature),<sup>22</sup> we hypothesized that a relevant viologen•CB[7] pseudo-rotaxane (Fig. 1) could be organized with the right metal ion into 3D-MORF crystals, and show stimuli-responsive properties.



**Fig. 1.** Structures of (a) guest compound *P-V-P* and of CB[7], followed by the procedure (b) for single crystals preparation.

Following initial work about silver<sup>23</sup> and pH<sup>24</sup> responsiveness of a CB[7]-viologen pseudo-rotaxane, we describe herein the preparation of Zn-based 3D-MORF crystals featuring CB[7] and rigid pillars derived from a viologen core (Fig. 1).

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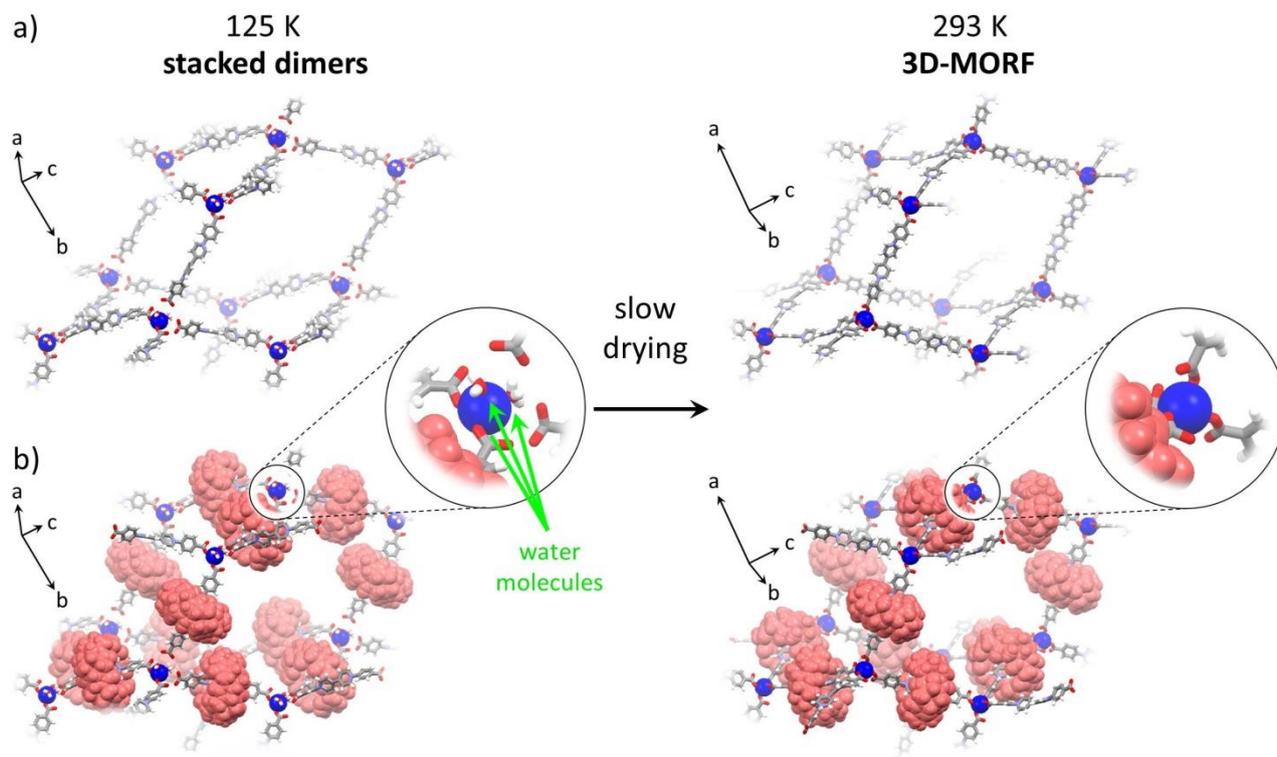
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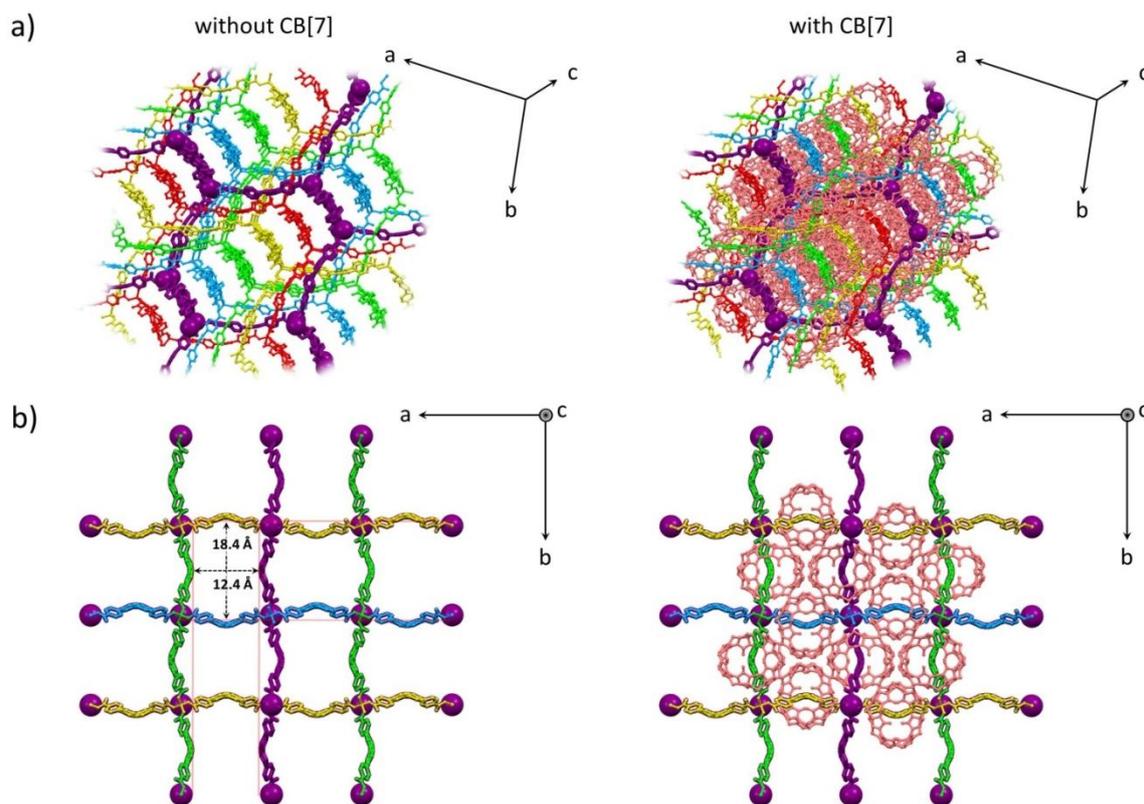
Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/x0xx00000x

The synthesis of the pillar compound **P-V-P** (chlorine salt) is described in supporting information.  $^1\text{H}$  NMR showed about quantitative binding at 1 equiv of CB[7]. With 2 equiv CB[7], stations *P* are occupied and so a 1:1 stoichiometry was selected. As already reported for similar compounds,<sup>23</sup> **P-V-P** binds CB[7] with a relatively good affinity,  $K_a \approx 3.8 \times 10^5 \text{ M}^{-1}$  as checked by  $^1\text{H}$  NMR (competition with 1-butyl-3-methyl-imidazolium chloride, Fig. S1, supporting information). A strong affinity between the host and the guest was an important requisite to warrant homogeneous crystal growth, incorporating the rings in a reliable way all along the procedure. A screening of >40 experimental conditions, varying the nature of the metal ion ( $\text{Cu}^{2+}$ ,  $\text{Fe}^{2+}$  or  $\text{Zn}^{2+}$ ), the concentration of host and guest, the host:guest ratio (between 1.04 and 1.20), and the ratio between water and DMF (Table S2, supporting information), allowed to identify a few cases for which single-crystals could be obtained. A few set of conditions was suitable for crystal growth with zinc, **P-V-P** and CB[7]. At 5 mM **P-V-P**, 1.2 equiv CB[7] and 6.4 equiv  $\text{Zn}(\text{NO}_3)_2 \cdot 6 \text{H}_2\text{O}$  in a water/DMF mixture (8/2 vol%), single crystals were obtained reproducibly (see supporting information) and analysed by X-ray diffraction at low temperature (Fig. 2, left). A network featuring Zinc atoms with **P-V-P** surrounded by CB[7] was obtained, but the Zn nodes are also coordinated by three water molecules (one was disordered), hence preventing total metal-ligand reticulation. The basic unit is composed of a zinc ion connected by two **P-V-P**•CB[7] complexes and three water molecules. However, upon coming back to room temperature overnight in the diffractometer, the structure changed to a 3D-MORF arrangement showing full reticulation of the metal-ligand framework (Fig. 2, right). The crystals now belong to the  $I\bar{4}2d$  tetragonal space group with unit cell parameters  $a =$

$32.6797(2) \text{ \AA}$  and  $c = 13.5625(2) \text{ \AA}$ . The zinc nodes are no longer carrying water molecules which disappeared from the framework suggesting a slow drying under air stream overnight. The other striking feature of this structure is that, as for the structure determined at 125 K, all the **P-V-P** molecules are surrounded by CB[7] according to a rotaxane topology. A careful examination of the former structure (125 K) showed that each component of the future network was already arranged in a relevant fashion so that the energetic cost of reorganization to metal-ligand coordination is presumably limited. The environment around the zinc nodes changed from penta-coordinated (two carboxylic acid oxygen atoms and three water oxygen atoms) to tetracoordinated (four carboxylic acid oxygen atoms). However, interpenetration also occurred, as commonly observed for frameworks with large void spaces. The crystal structure at 293 K shows 5-fold interpenetration (Fig. 3a) but there is still enough space in the form of large corrugated channels (Fig. 3b, left) of approximate dimensions  $\sim 1.2 \times 1.8 \text{ nm}$ . The channels are filled with CB[7] macrocycles that are threaded along the **P-V-P** pillars of the framework (Fig. 3b, right). It seems CB[7] is able to reduce the level of interpenetration, passing from 13-fold (Cd-**PVP** MOF)<sup>25</sup> to 5-fold. Isothermal thermogravimetric analysis (isothermal TGA) was performed to determine on which timescale the crystals corresponding to the low-temperature form are dehydrated. At room temperature, the  $\text{Zn} \cdot \text{P-V-P} \cdot \text{CB}[7]$  crystals are dehydrated and transformed to the 3D-MORF structure after a few hours (Fig. S2, supporting information). Powder X-ray diffraction was measured on a batch of dehydrated (3D-MORF) crystals.

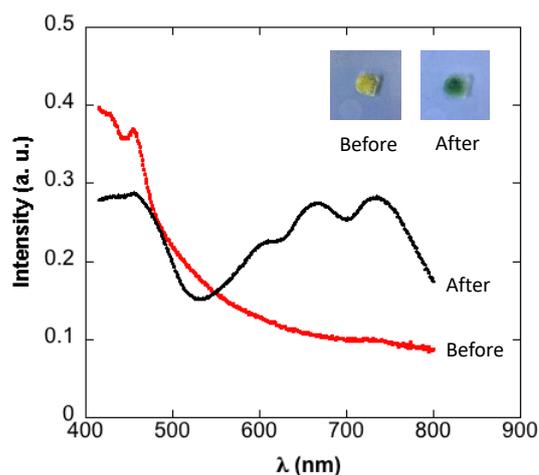


**Fig. 2.** Single-crystal-to-single-crystal transformation of stacked dimetallic-Host-Guest dimers (left) toward the 3D-MORF structure. The pseudo-diamondoid network and reticulated one are shown in a) (CB[7] removed for clarity) and in b) with CB[7] (only one network is shown, for interpenetration, see text).



**Fig. 3.** 5-fold interpenetration of the Zn•P-V-P•CB[7] 3D-MORF (a) without (left) and with (right) CB[7]. Another view (b) of the interpenetrated framework without (left) and with (right) CB[7] along the *c* crystallographic axis.

Reflections from the experimental diffractogram match generally well with those of the theoretical one derived from the single-crystal structure (Fig. S3, supporting information). To our knowledge, we are not aware of previous reports featuring CB[7] 3D-MORF or CB[7]-viologen MORF crystals. The colour of the 3D-MORF crystals changed when exposed to sunlight or UV light. Placed in a Rayonet© photochemical reactor ( $\lambda = 305$  nm), the crystals become green. Actually, MOFs containing viologen ligands present interesting colouration properties induced via light,<sup>26</sup> heat,<sup>27</sup> or pressure.<sup>28</sup> These properties are assigned to short distances between electron donor/acceptor functions, favouring electron transfer to the viologen.<sup>29</sup> The induced cationic radical viologens are stabilized in the MOF structure<sup>30</sup> and colour the crystals from green to blue. In this work, we have observed a similar colour change of the MORF crystals under UV-irradiation, from pale yellow to green, with a sharp absorption band centred at 454 nm for the yellow crystals and two broad bands with maximum at 730 and 668 nm associated with a shoulder at 602 nm for the green crystals (Fig. 4).<sup>25, 28a</sup>



**Fig. 4.** Solid UV-vis spectra before and after photoirradiation with UV source (inset, photos of a 3D-MORF crystal, respectively before and after irradiation)

The colour change is reversible (timescale of minutes after switching the UV light source off), and reversible photoinduced electron transfer is the favoured explanation now. However, oxygen diffusion inside the crystals and viologen oxidation back to the 2+ charge state cannot be ruled out.<sup>31</sup> EPR spectra recorded before and after photoirradiation at 305 nm showed respectively no, and one signal at  $g \approx 2.0032$ , indeed suggesting that reduction of the viologen pillars is involved in the colour change (Fig. S4, supporting information).<sup>25</sup>,<sup>32</sup> Previous reports suggest that the carboxylic acid functions are the electron donors in photoswitchable MOFs,<sup>25-26, 26d, 28c, 33</sup> but more investigations are needed to ascertain the nature of the electron donor in this case.

Here we have shown that 3D-MORF type crystals can be grown using CB[7] as ring molecules and a viologen derivative as the pillars. With a modest screening of experimental conditions, we have found suitable experimental parameters favouring crystal growth of a precursor of the designed MOF structure. Gentle dehydration enabled zinc nodes to fully connect to the pillars, affording the targeted 3D-MORF crystals featuring CB[7] molecules around the pillars. The presence of viologen fragments endowed the crystals with photochromism, which could open interesting perspectives in inkless printing<sup>34</sup> or transient writing/erasing for data encryption.<sup>35</sup>

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## Conflicts of interest

There are no conflicts of interest to declare.

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