

SI Supporting Information

# Nano-Sized Channels Resulting from the Packing of Discrete 3d–4f Metal Complexes in Crystals

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**ABSTRACT:** The crystal packing of the heterobinuclear complexes  $[M^{II}Dy^{III}(valpn)(hfac)_2(pb)] \cdot 0.67H_2O \cdot (solvent)$  generates large and small channels (M = Zn 1a and Cu 2; hfac<sup>-</sup> = hexafluoroacetylacetonate; valpn<sup>2-</sup> is the dianion of the Schiff base that resulted from the condensation reaction between *o*-vanillin and 1,3-diaminopropane; and pb<sup>-</sup> = 1-pyrenebutyrate). The large channels are padded by CF<sub>3</sub> groups arising from the hfac<sup>-</sup> ligands. The diameter of the almost circular cross-section of the large channels is about 1.2 nm, considering the van der Waals surface. The crystals 1b, resulted from removing the solvent molecules from 1a, were found to host iodine molecules into the small channels:  $0.33I_2/[ZnDy]$  1c. In compounds 1a, 1b, 1c, and 2, the 3d metal ions (Zn<sup>II</sup> and Cu<sup>II</sup>) show a square-pyramidal geometry. If the 3d metal ion is nickel(II), with an octahedral geometry, the packing of the molecules,  $[Ni^{III}Tb^{III}(MeOH)(valpn)-(hfac)_2(pb)]\cdot3$ , is different, without formation of channels. In all these compounds, the segregation of the trifluoromethyl groups was observed.

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The search for synthetic approaches leading to (nano)porous molecular crystals is one of the most important problems in crystal engineering. The high interest in such materials arises from their ability to interact selectively with various molecules, leading to applications in separation processes, gas storage, slow release of drugs, and catalysis.<sup>1-4</sup> The desired porosity can be achieved in different ways: (1) construction of neutral and, preferably, non-interpenetrating 3D coordination polymers, with tunable distances between the nodes (metal centers)<sup>5,6</sup> and (2) 2D or 3D covalent organic frameworks.<sup>3,7</sup> Such porous materials are constructed from directional coordinative or covalent bonds. Weak, non-covalent, but directional interactions can also generate solid-state architectures with nano-sized pores. These interactions can be hydrogen bonds (hydrogen-bonded organic frameworks),<sup>8-11</sup> halogen bonds (halogen-bonded organic frameworks),<sup>12,13</sup> or a convolution of them<sup>14</sup> and are established between complementary donor-acceptor groups belonging to the same molecule or two different molecules. In other words, the packing of discrete molecules, driven by specific intermolecular interactions, can generate porous architectures. Channels with various sizes can also result from the stacking of large cyclic molecules on top of each other. Classical examples are pillar[n] arenes, <sup>15</sup> metallo- and metallacalixarenes, <sup>16,17</sup> calixarenes,<sup>18</sup> and cyclodextrines.<sup>19</sup> Another interesting case is provided by rigid, large (24- and 33-membered) rings containing chalcogen heteroatoms (S and Se). The packing

of these molecules, supported by chalcogen-chalcogen directional forces, leads to nanoporous crystals.<sup>20</sup> A comprehensive and interesting review on porous organic materials, with porosity arising in the absence of covalent or coordinative bonds, has been published recently by Little and Coper.<sup>21</sup>

In a recent paper, we reported on two luminescent binuclear  $[Zn^{II}Ln^{III}]$  complexes (Ln = Eu and Tb) with one of the ligands carrying a pyrene group, which enables their attachment on graphene.<sup>22</sup> These compounds are obtained starting from binuclear complexes containing an acetato ligand that acts as an additional bridge between the two metal ions:  $[ZnLn(valpn)(hfac)_2(CH_3COO)]$ , where valpn<sup>2-</sup> is the dianion of the Schiff base that resulted from the condensation reaction between o-vanillin and 1,3-diaminopropane, hfac<sup>-</sup> = hexafluoroacetylacetonate.<sup>23</sup> The family of 3d-4f binuclear complexes designed by Matsumoto and co-workers<sup>23</sup> is actually larger, counting systems with other 3d metal ions (Cu<sup>II</sup>, Co<sup>II</sup>, and Ni<sup>II</sup>). We have shown that the acetato bridge from such [M<sup>II</sup>Ln<sup>III</sup>] binuclear systems (M = Co and Ni) can be easily substituted by other carboxylato ligands.<sup>22,24</sup> In this paper, we describe a new case of porosity generated by the

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#### Scheme 1. Synthetic Route for Complexes



packing of discrete molecules that are obtained by replacing the acetato ligand in  $[M^{II}Dy^{III}(valpn)(hfac)_2(CH_3COO)]$  complexes with the anion of 1-pyrenebutyric acid (Hpb) (M = Cu and Zn). For comparison, a third compound,  $[Ni^{II}Tb^{III}(valpn)(hfac)_2(CH_3COO)]$ , has been synthesized, and we found that its crystal packing is different from the one observed with the two other compounds.

#### EXPERIMENTAL SECTION

**Syntheses.** All reagents and solvents for synthesis were commercially purchased and used without further purification. The precursors,  $[M^{II}Dy^{III}(valpn)(hfac)_2(CH_3COO)]$  (M = Cu and Zn) and  $[Ni^{II}Tb^{III}(valpn)(CH_3OH)(hfac)_2(CH_3COO)]$ , have been synthesized according to the procedure reported by Matsumoto and coworkers.<sup>23</sup>

Synthesis of  $[Zn^{II}Dy^{III}(valpn)(hfac)_2(pb)]\cdot 0.67H_2O\cdot(Solvent)$  1a. A solution containing  $[Zn^{II}Dy^{III}(valpn)(hfac)_2(CH_3COO)]$  (0.0900 g, 0.0867 mmol) dissolved in 10 mL of CH<sub>2</sub>Cl<sub>2</sub> was mixed with a solution containing 1-pyrenebutyric acid (Hpb, 0.0250 g, 0.0867 mmol) dissolved in 10 mL of CH<sub>2</sub>Cl<sub>2</sub>, and then, another 10 mL of MeOH was added. The mixture was stirred for 1 h and then was filtered off. The resulting yellow solution was left to evaporate in the open air. After several days, yellow single crystals of 1a were obtained. These single crystals were heated to 150 °C, for 48 h, in order to remove the solvent from the channels. The resulting crystals of 1b were yellow as 1a but without their shine. Then, one single crystal of 1b was put in a small beaker and then inserted into a larger one containing iodine crystals. In this manner, an iodine atmosphere was obtained. After several days, the crystals 1c were obtained by adsorbing the iodine molecules into the channels of 1b.

Selected IR data for **1a** (KBr, cm<sup>-1</sup>): 3313 (w), 3249(w), 3138(mw), 3039(mw), 2940(m), 2854(mw) 1658(ms), 1628(ms), 1575(m), 1555(m), 1502(m), 1477(ms), 1437(m), 1406(m), 1346(mw), 1306(m), 1253(s), 1202(s), 1143(vs), 1095(ms), 1069(m), 970(m), 950(m), 918(w), 849(m), 794(m), 736(m), 660(m), 630(m), 583(m), 525(mw), 463(mw), 426(w).

Synthesis of  $[Cu^{II}Dy^{III}(valpn)(hfac)_2(pb)] \cdot 0.67H_2O \cdot (Solvent)$  2. A solution containing  $[Cu^{II}Dy^{III}(valpn)(hfac)_2(CH_3COO)]$  (0.0900 g, 0.0867 mmol) dissolved in 10 mL of CH<sub>2</sub>Cl<sub>2</sub> was mixed with a solution containing 1-pyrenebutyric acid (0.0250 g, 0.0867 mmol) dissolved in 10 mL of CH<sub>2</sub>Cl<sub>2</sub>, and then, another 10 mL of MeOH was added. The mixture was stirred for 1 h and then was filtered off.

The resulting green solution was left to evaporate in the open air. After several days, green single crystals were obtained.

Selected IR data (KBr, cm<sup>-1</sup>): 3421(mw, b), 3134(w), 3043(w), 2986(w), 2939(m), 2866(w), 1658(ms), 1628(ms), 1570(ms), 1506(ms), 1479(ms), 1406(m), 1344(mw), 1301(m), 1253(s), 1198(s), 1145(vs), 1095(m), 1072(m), 970(w), 950(m), 851(m), 796(m), 741(m), 659(m), 634(mw), 584(m), 528(w), 464(w).

Synthesis of  $[Ni^{II}Tb^{III}(MeOH)(valpn)(hfac)_2(pb)]$ -3. A solution containing  $[Ni^{II}Tb^{III}(valpn)(CH_3OH)(hfac)_2(CH_3COO)]$  (0.1030 g, 0.0867 mmol) dissolved in 10 mL of  $CH_2Cl_2$  was mixed with a solution containing 1-pyrenebutyric acid (0.0250 g, 0.0867 mmol) dissolved in 10 mL of  $CH_2Cl_2$ , and then, another 10 mL of MeOH was added. The mixture was stirred for 1 h and then was filtered off. The resulting blue solution was left to evaporate in the open air. After several days, blue single crystals were obtained.

Selected IR data (KBr, cm<sup>-1</sup>): 3647(w), 3447(w), 3041(w), 2939(mw), 2852(w), 1656(ms), 1633(m), 1608(mw), 1566(m). 1504(m), 1473(ms), 1438(m), 1406(m), 1346(w), 1303(m), 1255(s), 1207(s), 1145(vs), 1097(m), 1072(m), 1026(w), 952(mw), 846(m), 794(mw), 738(m), 661(m), 636(mw), 582(m), 526(w), 464(w), 430(w).

**Physical Measurements.** IR spectra were recorded on an FTIR Bruker Tensor V-37 spectrophotometer (KBr pellets) in the range of 4000–400 cm<sup>-1</sup>. Diffuse reflectance spectra were recorded on a Jasco V-670 spectrophotometer using MgO as a standard. Powder X-ray diffraction (PXRD) data were recorded on a Proto diffractometer (Cu  $K\alpha$  radiation).

The heating curves [thermogravimetry (TG) and differential thermal analysis (DTA)] were recorded using a Labsys 1200 SETARAM instrument over the temperature range of 30-900 °C using a heating rate of 10 °C min<sup>-1</sup>. The measurements were carried out in a synthetic air atmosphere (flow rate of 16.66 cm<sup>3</sup> min<sup>-1</sup>) by using alumina crucibles.

Small-angle X-ray scattering (SAXS) measurements were performed using a 9 kW Rigaku SmartLab diffractometer in  $\theta/2\theta$  mode from 0 to 3°. The step and speed were fixed at 0.004° and 0.1°/min, respectively, to obtain a high number of points. The scattering vector, q, was calculated as a function of the scattering angle,  $\theta$ :

$$q = \frac{4\pi \sin\theta}{\lambda} \tag{1}$$

where  $\lambda = 0.154$  nm is the wavelength of the monochromatic Cu K $\alpha_1$  radiation.

Gas sorption measurements were performed on Quantachrome Autosorb iQ MP. The samples were activated by heating to 120  $^\circ$ C for 3 h under vacuum.

Vapor sorption measurements were performed on a Quantachrome VSTAR after activation at 120  $^\circ$ C for 3 h.

**Single-Crystal X-ray Crystallography.** X-ray diffraction data were collected at 293 K on a Rigaku XtaLAB Synergy-S diffractometer operating with a Mo K $\alpha$  ( $\lambda = 0.71073$  Å) micro-focus sealed X-ray tube. The structures were solved by direct methods and refined by full-matrix least-squares techniques based on  $F^2$ . The non-H atoms were refined with anisotropic displacement parameters. Calculations were performed using SHELX-2014, SHELX-2018, and Olex2 crystallographic software package.<sup>25–27</sup> Supplementary X-ray crystallographic data in CIF format have been deposited with the CCDC with the following reference numbers: 2237896–2237900. A summary of the crystallographic data and the structure refinement for all crystals is given in Table S1.

# RESULTS AND DISCUSSION

The three new compounds have been obtained by ligand exchange, namely, by reacting the  $[M^{II}Dy^{III}(valpn)-(hfac)_2(CH_3COO)]$  precursors with 1-pyrenebutyric acid (Hpb):  $[ZnDy(valpn)(hfac)_2(pb)]\cdot 0.67H_2O\cdot(solvent)$  1a,  $[CuDy(valpn)(hfac)_2(pb)]\cdot 0.67H_2O\cdot(solvent)$  2,  $[NiTb-(MeOH)(valpn)(hfac)_2(pb)]\cdot 3$  (Scheme 1). The acetato ligand is replaced by 1-pyrenebutyrate. The synthesis is based on our observation concerning the easy substitution of the acetato bridge by other monocarboxylato ligands.<sup>22,24</sup> We did not succeed to obtain single crystals for the [NiDy] derivative.

The solvent molecules from 1a have been removed by gentle heating, giving crystals 1b,  $[ZnDy(valpn)(hfac)_2(pb)]$ . We employed three different 3d metal ions in order to reveal the role, if any, played by their stereochemical preferences on the packing of the molecules in the crystal. Within the [ZnLn] and [CuLn] series, the 3d metal ions show a square-pyramidal coordination geometry. The structure of 1a was measured immediately for crystals removed from the solution. The crystal structures of compounds 1a and 2 are very similar (see Figure 1 for the structure of 1a and Table S1 for crystallographic data and Figure S1 for 2 and 3). The 3d metal ion  $(Zn^{II} \text{ or } Cu^{II})$  is hosted into the N<sub>2</sub>O<sub>2</sub> compartment, forming the basal plane of the pyramid, while the Dy<sup>III</sup> ion occupies the large, open compartment. The two metal ions are



**Figure 1.** Crystal structure of compound **2** along with the atom numbering scheme; the  $CF_3$  groups have been omitted for clarity.

triply bridged by two phenoxido oxygen atoms from the Schiff base ligand and by the carboxylato group (syn-syn bridging mode). The apical position of the 3d metal ions is occupied by one oxygen atom from the bridging carboxylato group [Zn1-O9 = 1.983(2) and Cu1-O10 = 2.174(5) Å]; the metalligand bonds within the basal plane are Zn1-N1 = 2.064(3), Zn1-N2 = 2.069(3), Zn1-O1 = 2.067(2), and Zn1-O3 =2.048(2) and Cu1-N1 = 1.965(5), Cu1-N2 = 1.979(5), Cu1-O1 = 1.958(4), and Cu1-O3 = 1.975(4) Å. Other bond distances and angles are collected in Tables S2 and S3. The Dy<sup>III</sup> ions are coordinated by nine oxygen atoms (two from the phenoxido bridges, four from the chelating hfac- ligands, two from the methoxy groups, and one from the bridging carboxylato), with a coordination geometry intermediate between capped square antiprism and muffin, according to the parameters calculated using the SHAPE program (Table S4).<sup>28-30</sup> The Dy-O distances vary between 2.309 and 2.618 Å for 1 and between 2.310 and 2.627 Å for 2. The intramolecular metal-metal distances are  $Zn \cdots Dy = 3.408$ and Cu…Dy = 3.387 Å. The experimental powder X-ray diffractogram for 1b is similar to those simulated for 1a and 1b (Figure S2), showing that the crystalline architectures of 1a and 1b are the same, and the crystalline phase 1b is pure.

The most interesting structural features of compounds 1a, 1b, and 2 arise from the packing of the molecules in the crystals. A view along the crystallographic c axis (Figure 2)



Figure 2. Packing diagram for 1a, view along the crystallographic *c* axis.

reveals the formation of two types of channels, large (A) and small (B). The large channels are lined by  $CF_3$  groups arising from the hfac<sup>-</sup> ligands (Figure 3a). The diameter of the almost circular cross-section of the channels is about 11.8 Å (1.2 nm) considering the van der Waals surface. The small channels are generated by the superposition of layers formed by three [ZnDy] complexes, which form a triangular cross-section (Figure 3b).

The dimension of the large pores has also been confirmed by the Guinier law, applied on the SAXS data. The Guinier approximation allows one to estimate the radius of gyration,  $R_G$ (i.e., the root-mean-square distance of the object's parts from its center of gravity), as follows:<sup>31</sup>

$$I(q) = I(0)e^{-q^2 R_G^2/3}$$
(2)

Thus,  $R_G^2$  is obtained from the slope of the line plotting  $\ln I(q)$  versus q.<sup>2</sup> In our case, the fit (Figure S3) was performed in the high region (red line), where the observation window is closer to 1 nm and small-scale features become visible. On the other hand, at small q values, the observation window is around 60 nm, and only large-scale features of the scattering



**Figure 3.** (a) Details of the packing diagram showing the  $CF_3$  groups lining the large pores. (b) Cross-section of the small channels (the hosted water molecules are not represented).

object can be detected.<sup>32</sup> It was obtained that  $R_G$  is 5.14 Å for small-scale features, which further implies a pore diameter of 14.5 Å with the assumption of the cylindrical pores.<sup>33</sup> This value is close to the one estimated taking into account the van der Waals radii of the atoms.

The water molecules hosted by the small channels  $(0.67H_2O/[ZnDy])$  have been localized in the crystal structure, while the solvent molecules within the large channels are strongly disordered and cannot be localized. Therefore, the structure was refined following the SQUEEZE routine in the PLATON software.<sup>34</sup> The TG and DTA curves indicate the release of solvent molecules in two endothermic steps (Figure S4). The first step involves the loss of unidentified solvent molecules from the large channels in the 50–100 °C temperature range. The second step (100–170 °C) is assigned to the dehydration process (elimination of the water molecules from the B channels: calcd mass loss 0.96, exp. 1.02%). The anhydrous compound melts at 170 °C.

The presence of the large pores prompted us to determine the surface area. The Brunauer-Emmett-Teller measurements (N<sub>2</sub> and CO<sub>2</sub> sorption) led to low values:  $3 \text{ m}^2/\text{g}$  (N<sub>2</sub>) and 10 m<sup>2</sup>/g (CO<sub>2</sub>), which is essentially the outer surface of a powder (see SI, and Figures S5 and S6). At first glance, this is a surprising result, considering the presence of the two types of pores, especially the large pores. According to the crystallographic data, the total solvent accessible volume/unit cell is 2225 Å<sup>3</sup> (24.5%).<sup>27</sup> There are two points to be considered here: (1) first of all, we notice the so-called segregation of the fluorinated groups,<sup>35</sup> which line the walls of the large channels, and (2) the formation of the walls is supported by intermolecular F…F interactions (Figure 4), with the shortest F…F distances varying between 2.917 and 3.295 Å. Both structural motifs, I and II,36 describing the F…F interactions are observed (bottom of Figure 4). The lack of affinity for adsorbed N2 and CO2 molecules could be related to the wellknown inertness of perfluoro surfaces in adsorption processes.<sup>37</sup> To confirm the stability of the crystals, PXRD measurements were performed before and after activation and measurements. The diffraction patterns (Figure S7) show a good agreement, thus proving the stability of crystallinity. Such surfaces, with densely packed carbon-fluorine bonds, are superhydrophobic.<sup>38</sup> Along this line, recently, it was shown



**Figure 4.** Details of the packing diagram in crystal **1a**, showing the F···· F interactions. Bottom left:  $\theta_1$  and  $\theta_2$  angles vary between 127.2° and 172.6°; bottom right:  $\theta_1$  and  $\theta_2$  vary in the ranges 161.0–165.9° and 93.0–110.9°, respectively.

that permeation of water occurs extremely fast through nanochannels padded with fluorine atoms.<sup>38</sup>

The solid-state architecture of the crystals of 1a is preserved after the elimination of the solvent molecules (a single-crystalto-single-crystal process leads to crystals 1b, Table S1). One single crystal of 1b, obtained by heating several crystals of 1a at 160 °C for 1 h, was measured by single-crystal X-ray diffraction (Table S1). All the channels were found to be empty. A small beaker containing dried crystals (1b) was inserted into a larger beaker containing crystals of iodine, and then, the large beaker was covered with a watch glass. Brown crystals, 1c, were obtained and measured by single-crystal X-ray diffraction (Table S1). The iodine molecules were found to be hosted only in the small channels (0.33I<sub>2</sub>/[ZnDy])-Figure 5, each molecule being disordered: one atom lies on a C3 axis (occupation factor 0.33) and the other one is disordered over two positions, each one with an occupation factor of 0.1667]. The large channels remain empty. Geometrical parameters for all compounds are gathered in Tables S2 and S3.

Other vapor sorption experiments dealt with water and hexafluorobenzene. First, water vapor isotherms were recorded, showing a water sorption of 14 mg g<sup>-1</sup> at a relative pressure  $P/P_0$  of 0.92 (0.0228 bar) at 20 °C (Figure 6a). Afterward, C<sub>6</sub>F<sub>6</sub> was used as an adsorbent to test for potential positive fluorophilic interactions, and an uptake of 201 mg g<sup>-1</sup> was measured at a relative pressure of 0.90 (0.07985 bar) at 20 °C (Figure 6a).

To better compare the affinity of **1** to both adsorbents (H<sub>2</sub>O and C<sub>6</sub>F<sub>6</sub>), the adsorption values have been contrasted at the same absolute pressure of 0.022 bar: 14 mg g<sup>-1</sup> of water and 40 mg g<sup>-1</sup> of C<sub>6</sub>F<sub>6</sub> were found from the adsorption isotherms. Converting these values into molar amounts of the substance shows that despite the lower mass, there are still roughly four water molecules to every molecule of C<sub>6</sub>F<sub>6</sub> at the same absolute pressure of 0.022 bar (0.8 mmol g<sup>-1</sup> of H<sub>2</sub>O to 0.2 mmol g<sup>-1</sup> of C<sub>6</sub>F<sub>6</sub>)—Figure 6b.

Does the coordination geometry of the 3d metal ion play any role in the arrangement of the molecules in the crystal? In order to answer this question, we first replaced  $Zn^{II}$  by  $Cu^{II}$ .  $[CuDy(valpn)(hfac)_2(pb)] \cdot 0.67H_2O \cdot (solvent)$  2 is isostructural with compound 1, and their packing diagrams are identical. The  $Cu^{II}$  and  $Zn^{II}$  ions in 1 and 2 have the same coordination numbers and geometries. Within the third compound,  $[NiTb(MeOH)(valpn)(hfac)_2(pb)] \cdot 3$ , the 3d



**Figure 5.** Details of the packing diagram of 1c showing the disordered  $I_2$  molecules hosted in the small channels.

metal ion, Ni<sup>II</sup>, is hexacoordinated (the additional apical ligand is a methanol molecule). The distances around nickel vary between 2.031(7) and 2.219(6) Å, with the longest one being associated with the nickel-methanol bond. The Tb<sup>III</sup> has a coordination number of 9, the associated geometry being similar to that observed in compounds **1a,b,c**, and **2**. The OH group from the coordinated methanol molecule is involved in a hydrogen bond with an oxygen atom arising from a hfac ligand (O5…O11 = 2.885 Å). The intramolecular Ni…Tb distance is 3.420 Å. The crystal packing of the molecules is different from that observed for crystals **1a** and **2**, that is, without channels (Figure 7), while the segregation of the fluorine atoms is again observed (Figure S8).



**Figure** 7. Packing diagram for crystal 3 (view along the crystallographic a axis).

The diffuse reflectance spectra of three compounds (1b, 2, and 3) reveal the spectral characteristics of the metal ions (Figure 8). In compound 1b, the zinc(II) ion does not exhibit d–d transitions, and only the f–f transitions of Dy<sup>III</sup> are observed at 808, 909, 1097, and 1290 nm, which are ascribed to the transitions from the ground level,  ${}^{6}H_{15/2}$ , to  ${}^{6}F_{5/2}$ ,  ${}^{6}(F_{7/2} + H_{5/2})$ ,  ${}^{6}(F_{9/2} + H_{7/2})$ , and  ${}^{6}(F_{11/2} + H_{9/2})$ , respectively. In the case of compound 2, only the f–f band at 1265 nm is observed [ ${}^{6}H_{15/2} \rightarrow {}^{6}(F_{11/2} + H_{9/2})$ ], the other f–f transitions being masked by the large band due to the {  $Cu^{II}N_2O_3$ } chromophore. For compound 3, the d–d transitions for the (pseudo)octahedral Ni<sup>II</sup> ion are observed.

#### CONCLUSIONS

In this paper, we have illustrated with new examples that large channels can result from the packing of discrete molecules,  $[MDy(valpn)(hfac)_2(pb)]$  (M = Cu and Zn), in the crystal. If, instead of square-pyramidal Cu<sup>II</sup> and Zn<sup>II</sup> ions, the octahedral Ni<sup>II</sup> ion is employed, the crystal packing of the [NiTb-(MeOH)(valpn)(hfac)\_2(pb)]·molecules is different, without formation of channels. Interestingly, no  $\pi$ - $\pi$  stacking interactions are established between the pyrene moieties from the pb<sup>-</sup> ligands for the three compounds. On the other hand, a clear tendency of the CF<sub>3</sub> groups to segregate was



Figure 6. (a) Vapor sorption isotherms of  $C_6F_6$  (red) and water (blue) with uptake in mg/g (logarithmic scale of y axis). (b) Vapor sorption isotherms of  $C_6F_6$  (red) and water (blue) with uptake in mmol/g.





observed with all compounds reported here. By removing the solvent molecules from the  $Cu^{II}$  and  $Zn^{II}$  derivatives, the crystallinity of the samples was preserved. We succeeded to fill only the small channels with iodine molecules, while the ability of the large channels for hosting molecules is very low. This lack of affinity for guest molecules could be related to the so-called Teflon effect.

# ASSOCIATED CONTENT

#### **③** Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.cgd.3c00130.

Experimental details; X-ray data collection and the structure refinement for all crystals; selected bond distances and angles; SHAPE parameters; PXRD diffractograms; thermal analysis data; and sorption isotherms (PDF)

#### **Accession Codes**

CCDC 2237896–2237900 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data\_request/cif, or by emailing data\_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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#### Notes

The authors declare no competing financial interest.

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