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1 A Palladium-based MOF for the Preferential 2 Sorption of Benzene

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6 KEYWORDS: Metal Organic Framework, Palladium, sorption, benzene, aromatics, volatile organic
7 compounds, Quartz Crystal Microbalance

8 **Abstract**

9 The selective sorption of volatile aromatic compounds is a challenging issue for their total abatement.
10 Despite the well-known affinity of palladium toward rich π systems, the studies dedicated to VOC
11 capture with Pd(II)-based-MOFs are still very scarce. Intending to shed more light on this complex topic,
12 this work compares the adsorption properties of two isostructural MOFs $[\text{Cu}(2\text{-pymo})_2]_n$ and $[\text{Pd}(2\text{-}$
13 $\text{pymo})_2]_n$, and their selectivity for the sorption of linear, cyclic or aromatic VOCs. The combination of
14 both experimental and computational investigations highlights an increasing aromatic affinity over
15 saturated hydrocarbons when palladium is chosen as metal center ($n_{\text{Benzene}}/n_{\text{n-hexane}} = 1.8$ at 0.5 p/p₀) in
16 the MOF framework instead of copper ($n_{\text{Benzene}}/n_{\text{n-hexane}} = 0.7$ at 0.5 p/p₀). Furthermore, $[\text{Pd}(2\text{-pymo})_2]_n$
17 clearly exhibits a preferential adsorption of benzene over toluene ($n_{\text{Benzene}}/n_{\text{Toluene}} = 1.7$ at 0.5 p/p₀), due
18 to the steric hindrance effects of the latter. The present results clearly underline the attractiveness of Pd-
19 based MOFs for the design of selective aromatic adsorbents. Moreover, they also highlight the $[\text{Pd}(2\text{-}$
20 $\text{pymo})_2]_n$ MOF as a relevant candidate for the selective capture of benzene, by a synergistic combination
21 of both charge interactions and steric hindrance effects.

22 **Introduction**

23 Unprecedented environmental threats resulting from human activities are altering the planet with
24 climate change, ozone depletion, deforestation, water scarcity, and increasing pollution of water and air.
25 The growing emission of volatile organic compounds (VOCs) strongly contributes to the deterioration
26 of the environment¹⁻³ and jeopardizes the integrity of living beings⁴⁻⁶. Amongst the organic pollutants
27 classified as VOCs, a particular attention is given to aromatic compounds such as benzene and its
28 derivatives⁷, due to their deleterious effects on human health. These compounds are mainly generated
29 by industrial emissions (e.g. petrochemical processes and derived products such as crude oil, petrol,
30 glues, paints, furniture wax, and detergents) but also by tobacco smoke, gas stations, and motor vehicle
31 exhausts. Benzene is notoriously responsible for a wide range of diseases including leukemia and
32 anemia^{8,9}. It is considered officially as a human carcinogen and the tolerated personal exposure limit is
33 continuously decreasing (100 ppm in 1927, 1 ppm in 2000)¹⁰. Despite a significant effort to reduce their
34 emission, the presence of volatile aromatic compounds is hardly avoidable in urban areas. Moreover, it
35 turns out that indoor exposure to benzene pollution may reach 1.5 times the outdoor street level due to
36 its continuous accumulation in confined spaces¹¹. One of the considered options to preserve individuals
37 from the noxious effects of these pollutants bears on an effective reduction/monitoring of the daily
38 exposure by employing specifically designed materials for their capture and/or detection¹². In this area,
39 the application of activated carbons, zeolites and silica is largely discussed in the literature. However,
40 these materials suffer from either a lack of selectivity (adsorption of a wide range of VOCs) and/or a
41 low adsorption capacity¹³. Despite their low cost, it may be difficult to overcome these aforementioned
42 limitations. Hence, it makes sense to explore the potential of other relevant materials with greater
43 chemical versatility.

44 Metal-Organic Frameworks (MOFs) are hybrid materials which are well known for their rich
45 structural diversity, the versatility of their properties, and their attractive sorption performance. They
46 are composed of inorganic bricks connected through organic ligands to form highly porous structures¹⁴
47 which can be advantageously tuned at the nanoscale to fit properly the requirements of each selected
48 application. For instance, the spacer length adjustment allows to tailor the unit cell dimensions which

49 control both the molecular sieving effect¹⁵ and host-guest interactions by confining guest molecules¹⁶.
50 Furthermore, the affinity to specific adsorbates can be enhanced by a judicious functionalization of
51 ligands¹⁷. It must be underlined that metal centers may also significantly affect host-guest interactions
52 either by the presence of open metal sites or by a specific affinity of the metal for the target adsorbate(s).
53 As an example, the investigation of the CPO-27 series (Ni, Co, Mg, Cu and Zn) for the desulfurization
54 of fuel¹⁸ evidenced that CPO-27(Ni) offers the highest affinity toward thiophene due to strong nickel-
55 sulfur interactions.

56 Amongst different transition metals, palladium holds a special place due to its ability to interact
57 strongly with hydrogen¹⁹ and with conjugated molecules such as alkenes²⁰, alkynes²¹, and aromatics²²
58 *via* π -complexation mechanism. Hence, palladium is a significant asset to boost the sorption selectivity
59 of porous materials for this series of molecules. It has been proven that the incorporation of palladium
60 species (e.g. Pd atoms or nanoparticles, salts, oxides or complexes) within materials is able to catalyze
61 reactions²³, contribute to H₂ sorption, dissociation, and spillover²⁴⁻²⁶, enhance sensor sensitivity²⁷ and
62 promote VOCs capture²⁸.

63 Despite the appealing potentialities of palladium-based materials, only few MOFs with Pd as a metal
64 node were reported in the literature. This is mainly due to their tedious synthesis which often requires
65 post-synthetic modification strategies to circumvent the formation of undesired by-products obtained in
66 one pot synthesis (e.g. isolated PdO or amorphous materials)²⁹⁻³². In order to clearly assess the potential
67 of Pd-MOFs for the abatement of aromatic vapors, especially the benzene removal, the present work
68 reports a comparative study of two isostructural MOFs referred as [Cu(2-pymo)₂]_n³³ and [Pd(2-
69 pymo)₂]_n³² (2-pymo = 2-pyrimidinolate) exposed to four model VOC compounds: n-hexane (linear
70 alkane), cyclohexane (cyclic alkane), benzene and toluene (aromatics). Experimental isotherms obtained
71 by QCM (Quartz Crystal Microbalance) measurements were combined with computational adsorption
72 results in a comprehensive study in order to highlight the role of palladium nodes for the selective
73 sorption/capture of aromatics.

74 **Experimental section**

75 **Materials and methods**

76 All reagents were purchased from commercial suppliers and used without any further purification.
77 The structure and purity of the synthesized materials were verified by Powder X-Ray Diffraction
78 (PXRD), N₂ adsorption-desorption measurements, thermogravimetric analysis (TGA), and Fourier-
79 Transformed infrared (FTIR) spectroscopy. The powder diffraction patterns of crystalline materials
80 were recorded by using PANanalytical X'Pert Pro diffractometer (Ni-filtered Cu-K α radiation, 40 kV,
81 20 mA) from 5 to 50° (2 θ). N₂ adsorption-desorption isotherms were measured at 77 K (liquid nitrogen
82 bath) using Micromeritics ASAP 2020 equipment. Samples were outgassed for 12 h at 130°C under
83 vacuum. Thermogravimetric analyses were carried out with TA instruments SDT 2960 under dry air at
84 a constant heating rate of 5°C/min from 25 to 600°C. FTIR spectra were recorded from 500 to 4000
85 cm⁻¹ (resolution of 4 cm⁻¹) with Nicolet Nexus FT-IR apparatus in reflection mode. Vapor adsorption
86 isotherms were recorded with a Quartz Crystal Microbalance (QCM). The QCM setup is composed of
87 a quartz resonator (AT-cut quartz, 14 mm, 6 MHz) working with a Maxtek TM-400 controller and 0.5
88 L chamber with injected VOC vapors³⁴. The pumping system (Alcatel Drytel 1025), with membrane
89 and turbomolecular pumps, reached pressured below 10⁻¹ Pa for both purge and complete desorption.

90 **Synthesis of [Pd(2-pymo)₂]_n and [Cu(2-pymo)₂]_n**

91 The MOF synthesis protocols reported in literature were followed with only slight modifications and
92 the final materials were analyzed to identify the products and check their purity. [Pd(2-pymo)₂]_n was
93 obtained in two steps: synthesis of [PdCl₂(2-Hpymo)₂] followed by its base-promoted polymerization to
94 [Pd(2-pymo)₂]_n^{30,32}. In more detail, a fresh Na₂PdCl₄ solution was prepared by dissolving PdCl₂ (0.6
95 mmol) in a NaCl solution (1.2 mmol in 10 mL of distilled water) under stirring and left for 12h.
96 [PdCl₂(2-Hpymo)₂] was synthesized by dissolving 2-Hpymo (1.2 mmol) in the freshly prepared
97 Na₂PdCl₄ solution, for 4h at room temperature. The resulting solid was then filtered out and washed
98 with water. The preparation of [Pd(2-pymo)₂]_n was carried out by refluxing a solution containing
99 [PdCl₂(2-Hpymo)₂] (0.4 mmol) and KOH (0.4 mmol) dissolved in 10 mL of distilled water for 20h.
100 The product was filtered out and washed with water, yielding a yellow crystalline powder. [Cu(2-
101 pymo)₂]_n was produced by mixing CuCl₂·2H₂O (1.0 mmol) and 2-Hpymo (2.0 mmol) in 30 mL of

102 NH_4OH solution ($[\text{NH}_3] \approx 25\%$) and stirring at room temperature for 48h³³. The purple solid was then
103 recovered by centrifugation and washed with water.

104 **VOC sorption measurements using QCM**

105 For each MOF material, VOC adsorption isotherms were recorded with QCM set-up equipped with
106 quartz crystals (6MHz, purchased from Neyco) whose surface was covered with the selected MOF
107 powder. Samples were prepared by depositing few drops of a suspension containing 2 mg of the MOF
108 powder in 1 mL of methanol. The coated quartz crystals were then dried at 120°C for 2h. The deposited
109 mass of MOF was estimated by the difference of frequencies measured by QCM before and after
110 deposition, using the Sauerbrey equation³⁵. Before any measurement, the chamber was pumped down
111 to limit vacuum $\sim 10^{-3}$ mbar in order to desorb MOF. Partial pressure was varied from 0 to 0.9 p/p₀ for
112 all four VOCs (n-hexane, cyclohexane, benzene, and toluene). The quartz holder was kept at 25°C
113 during the whole data collection to get the mass uptake isotherm of the sorbed VOC within the MOF.

114 **Computational Methods**

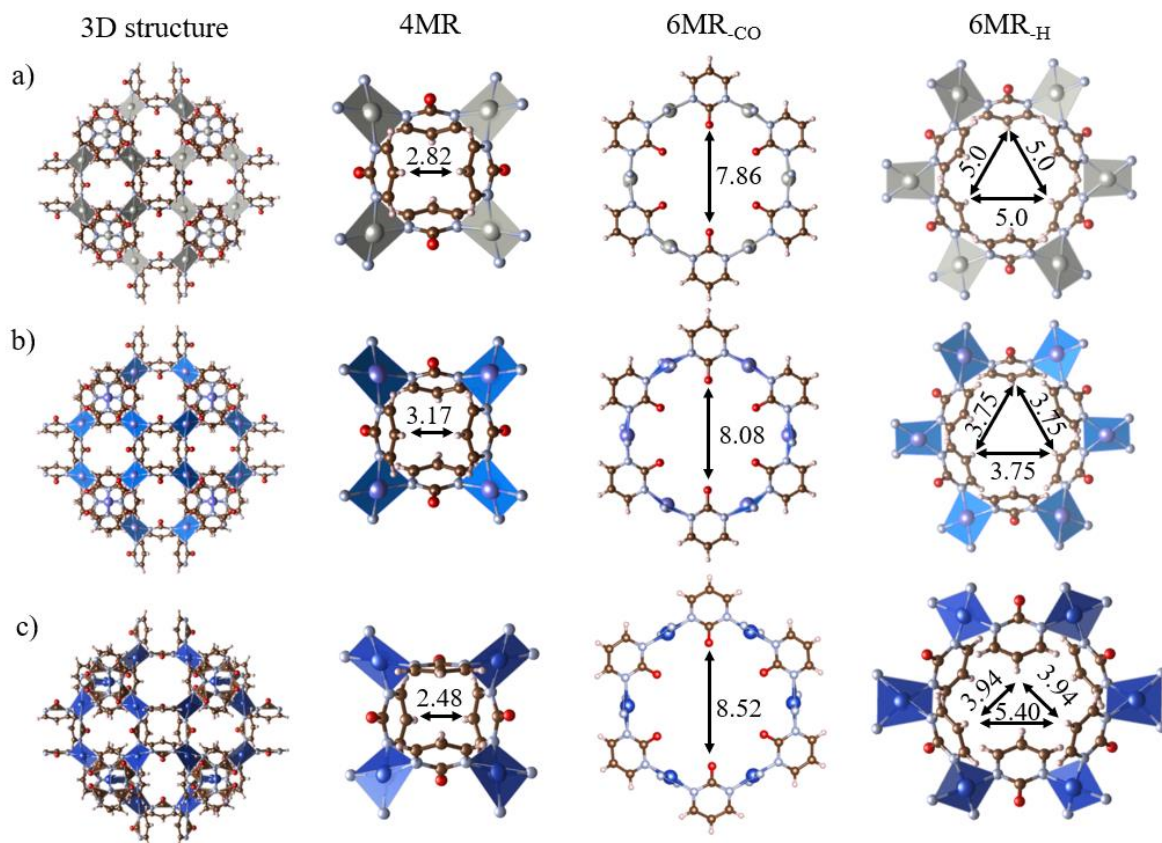
115 Computational methods were used to determine the theoretical microstructural characteristics of
116 solvent-free $[\text{Pd}(2\text{-pymo})_2]_n$, $[\text{Cu}(2\text{-pymo})_2]_n$ (rhombohedral) and $[\text{Cu}(2\text{-pymo})_2]_n$ (cubic) structures.
117 The surface area (SA) and pore volume (V_p) were estimated using RASPA software³⁶. The average
118 occupation profile of all studied adsorbates in the MOF networks (density plot) was depicted through
119 Grand Canonical Monte Carlo (GCMC) simulation. System sizes were selected by considering the Van
120 der Waals cutoff (12Å) and supercells were created with lengths larger than at least twice the cutoff
121 value. More precisely, 2x2x1 and 2x2x2 supercells for $[\text{Cu}(2\text{-pymo})_2]_n$ and $[\text{Pd}(2\text{-pymo})_2]_n$ were
122 considered, respectively. Uncharged United-Atom TraPPE (TraPPE-UA) model^{37,38} was used for n-
123 hexane while benzene was modeled with Explicit-Atom TraPPE (TraPPE-EA) model^{39,40}. Concerning
124 MOF structures, their atoms were taken as single Lennard-Jones sites whose parameters were extracted
125 concomitantly from UFF⁴¹ and Dreiding⁴² force fields. The atomic charge assignment was ensured by
126 the use of the classical “charge equilibration” method. Interactions between MOF structures and
127 hydrocarbon molecules were described by a Lennard-Jones potential using Lorentz-Berthelot mixing
128 rules. The Ewald sum technique was used to compute electrostatic interactions. The simulation was

129 composed of 1,000,000 Monte Carlo steps for equilibration and 1,000 steps for production and the
130 temperature was set at 25°C.

131 **Results and discussion**

132 **Description of the MOF structures**

133 The $[\text{Pd}(2\text{-pymo})_2]_n$ framework results from the polymerization of $[\text{PdCl}_2(2\text{-Hpymo})_2]$ in alkaline
134 medium. The latter is a square-planar complex composed of one Pd(II) atom connected to two chloride
135 atoms and two 2-Hpymo ligands through nitrogen atoms. This Pd-N bond ensuring the connection
136 between the metal and the ligand remains within the resulting MOF structure. The polymerization leads
137 to the formation of a 3D microporous sodalite-type network (**Figure 1**). $[\text{Cu}(2\text{-pymo})_2]_n$ adopts the same
138 topology and thus can be considered as its isoreticular form. Strictly speaking, its structure consists of
139 sodalitic β cages ($\text{O}_{\text{pore}} \approx 9 \text{ \AA}$) connected through four- and six-membered ring windows denoted 4MR
140 and 6MR, respectively (**Table 1**). One may distinguish two types of 6MR windows: *i*) smaller and
141 hydrophilic one decorated by carbonyl groups (6MR_{CO}) and *ii*) larger and hydrophobic one surrounded
142 by C-H groups (6MR_H). Hence, one may consider both MOFs as amphiphilic due to the presence of
143 pores with antagonist water adsorption behaviors. Furthermore, $[\text{Cu}(2\text{-pymo})_2]_n$ exhibits higher
144 flexibility in comparison to its $[\text{Pd}(2\text{-pymo})_2]_n$ analog. Indeed, upon hydration, $[\text{Cu}(2\text{-pymo})_2]_n$
145 undergoes phase transition from cubic to rhombohedral structure³³. In order to complete the comparison
146 between both structures and discuss their accessibility for the transport of the molecular species
147 considered in this work, the size of pore apertures has been estimated from their crystallographic
148 structures (**Table 1**). One may notice that the size of 6MR_{CO} pore aperture is larger for $[\text{Cu}(2\text{-pymo})_2]_n$
149 than for its analog whatever the phase, while only the rhombohedral phase exhibits larger 6MR_H pore
150 apertures.



151
 152 **Figure 1.** Structural description of a) $[\text{Pd}(2\text{-pymo})_2]_n$, b) $[\text{Cu}(2\text{-pymo})_2]_n$ (cubic) and c) $[\text{Cu}(2\text{-pymo})_2]_n$
 153 (rhombohedral). The general 3D structure is given with the three types of windows (4MR: 4 membered-
 154 ring; 6MR: 6 membered-ring). The pore aperture size is noted in Å. Color: grey (palladium), blue
 155 (copper), brown (carbon), white (hydrogen), pale blue (nitrogen), and red (oxygen).

156 **Table 1.** Measured values of pore apertures, theoretical surface area, and pore volume for $[\text{Pd}(2\text{-}$
 157 $\text{pymo})_2]_n$ and $[\text{Cu}(2\text{-pymo})_2]_n$.

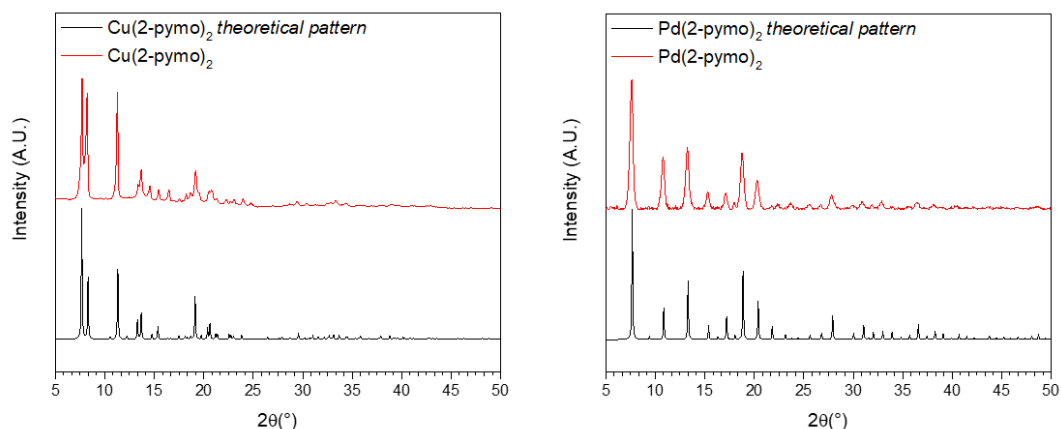
	Phase	4MR (Å)	6MR _{CO} (Å)	6MR _H (Å)	SA (m ² /g)	V _p (cm ³ /g)
$[\text{Pd}(2\text{-pymo})_2]_n$	Cubic	2.82	7.86	5.00/5.00/5.00	694	0.27
$[\text{Cu}(2\text{-pymo})_2]_n$	Cubic	3.17	8.08	3.75/3.75/3.75	571	0.21
$[\text{Cu}(2\text{-pymo})_2]_n$	Rhombohedral	2.48	8.52	5.40/3.94/3.94	406	0.16

158
 159 **Synthesis and characterization of MOFs**

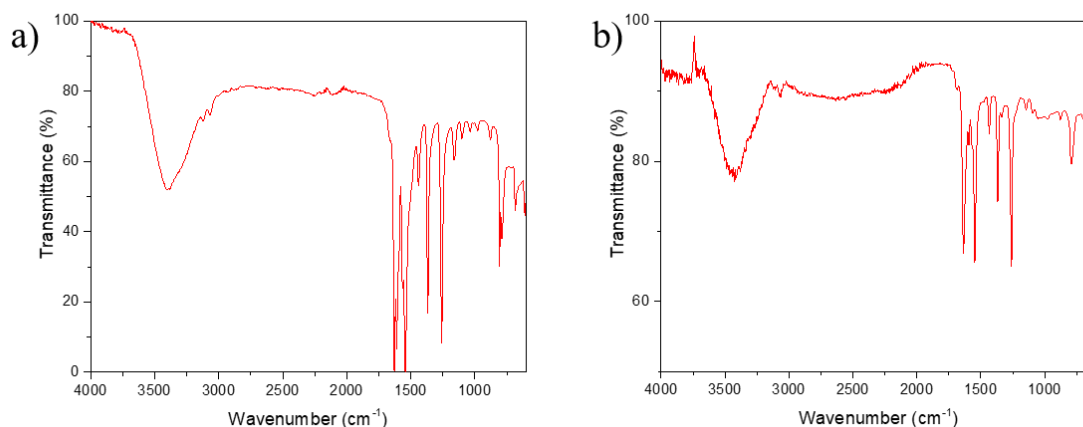
160 XRD patterns of the synthesized materials allowed to identify the crystalline phases and assess their
 161 purity (**Figure 2**). The diffraction pattern of the synthesized $[\text{Cu}(2\text{-pymo})_2]_n$ sample corresponds to the
 162 rhombohedral phase while $[\text{Pd}(2\text{-pymo})_2]_n$ features a cubic phase. Interestingly, both MOFs seem to

163 preserve their structural integrity when stored in air for one month (**Figure S1**), although $[\text{Cu}(2\text{-pymo})_2]_n$
164 shows slight changes in the width and intensity of the diffraction lines. This might be attributed to the
165 higher flexibility of the Cu-based structure in comparison with its Pd-analog. Therefore, adsorbed water
166 (air moisture) within cavities can interact with the structure and induce slight rotation of ligands, thus
167 affecting intereticular distances. FTIR spectra do not exhibit any band corresponding to the free ligand,
168 thus confirming the complete removal of unreacted chemicals (**Figure 3**). Nevertheless, the broad band
169 at 3500 cm^{-1} is attributed to the presence of water molecules remaining within the MOF cavities. Overall,
170 similar absorption spectra were obtained for both materials, essentially caused by their isostructural
171 character. N_2 adsorption-desorption isotherms were measured on outgassed samples (130°C under
172 vacuum) and the BET method was applied to determine the experimental specific surface area (**Figure**
173 **S2**). For both MOFs, the measured surface areas fit values reported in literature (373 vs $350\text{ m}^2/\text{g}^{33}$ and
174 705 vs $600\text{ m}^2/\text{g}^{30,32}$ for $[\text{Cu}(2\text{-pymo})_2]_n$ and $[\text{Pd}(2\text{-pymo})_2]_n$, respectively), although being slightly
175 higher, possibly caused by the reduced amount of defects, PdO and/or better cleaning. Interestingly,
176 these experimental values also fit theoretical ones obtained by simulation (373 vs 406 and 705 vs 694
177 m^2/g for $[\text{Cu}(2\text{-pymo})_2]_n$ and $[\text{Pd}(2\text{-pymo})_2]_n$, respectively). This observation tends to indicate that the
178 MOF activation treatment (outgassing) was efficient as pores are free of any adsorbed species.
179 Thermogravimetric analysis of both MOFs was operated up to 600°C with a gradual temperature
180 increase of $5^\circ\text{C}/\text{min}$ under air flow (**Figure S3**). The TGA profile of $[\text{Cu}(2\text{-pymo})_2]_n$ encompasses three
181 steps. A first dehydration occurs when water vapor is released from the structure between 30 and 110°C .
182 Lately, a second dehydration step takes place up to 250°C after which the structure collapses slowly and
183 decomposes completely above 500°C . Note that a similar TGA profile was reported for HKUST-1
184 (copper based-MOF containing open metal sites), and the second desorption step corresponded to the
185 release of water molecules strongly coordinated to copper sites^{43,44}. However, unlike HKUST-1, both
186 $[\text{Cu}(2\text{-pymo})_2]_n$ and $[\text{Pd}(2\text{-pymo})_2]_n$ do not contain open metal sites. Therefore, in the present case, one
187 may assume that residual water is still present after the first dehydration step due to strong interactions
188 between Cu^{2+} sites and water molecules. Regarding $[\text{Pd}(2\text{-pymo})_2]_n$, the TGA curve exhibits two main
189 steps including desorption of water molecules up to 110°C followed by the structure collapse starting

190 already at 330°C. The absence of the second dehydration step reveals weaker interactions between
191 palladium sites and water, thus resulting in different adsorption behavior compared to its copper based-
192 analog.



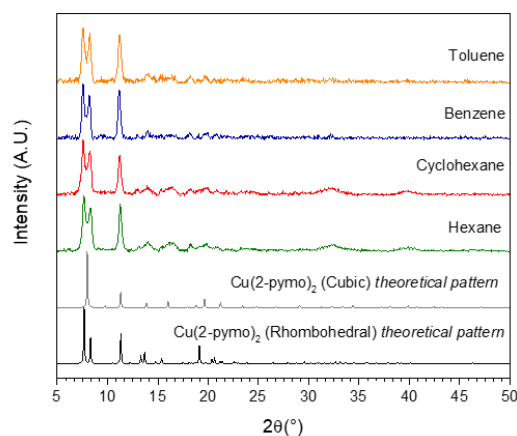
193
194 **Figure 2.** Comparison of experimental XRD patterns of the synthesized MOF powders (red) with the
195 simulated XRD patterns (black).



196
197 **Figure 3.** FTIR spectra of a) $[\text{Cu}(2\text{-pymo})_2]_n$ and b) $[\text{Pd}(2\text{-pymo})_2]_n$.

198 Adsorption of VOCs

199 Both $[\text{Pd}(2\text{-pymo})_2]_n$ and $[\text{Cu}(2\text{-pymo})_2]_n$ were exposed to four VOC vapors cited in **Table 2**. As
200 mentioned before, $[\text{Cu}(2\text{-pymo})_2]_n$ may exhibit cubic or rhombohedral phase depending on the presence
201 of potential guests molecules in its porous structure. Therefore, the PXRD patterns of this material
202 exposed to the selected VOCs (**Figure 4**) were recorded in order to identify the phase to be considered
203 afterward. The presence of rhombohedral phase was confirmed for both compounds.



204

205 **Figure 4.** PXRD patterns of $[\text{Cu}(\text{2-pymo})_2]_n$ exposed to VOCs.

206 Adsorption isotherms derived from QCM show an increase of adsorbed amount at $p/p_0 < 0.2$ followed
 207 by a monotonous slight loading. More specifically for $[\text{Cu}(\text{2-pymo})_2]_n$, the VOC uptake can be ranked
 208 as follows: n-hexane > benzene \gg toluene \approx cyclohexane (**Figure 5.a**). This trend is consistent with
 209 literature findings regarding hydrocarbon selectivity toward apolar type-MOFs. Pirngruber et al.⁴⁵
 210 showed that MOFs exhibiting apolar character such as ZIF-8, tend to adsorb alkanes over alkenes or
 211 aromatics, while ionic MOFs such as CPO-27 (cationic) or RHO-ZMOF (anionic), tend to favor
 212 conjugated molecules over alkanes. Concerning $[\text{Cu}(\text{2-pymo})_2]_n$, different factors can explain its
 213 sorption selectivity ($n_{\text{Benzene}}/n_{\text{n-hexane}} = 0.7$ at 0.5 p/p_0) (**Figure S4**). The high loading of n-hexane is
 214 attributed concomitantly to its smaller kinetic diameter (4.3 Å) and higher flexibility which enhance its
 215 diffusion within the structure and thus allow its accommodation efficiently within pores. In contrast, the
 216 adsorbed amount of toluene is the lowest in the series, in part due to its larger kinetic diameter (5.8 Å)
 217 and its more rigid structure. However, despite their similar kinetic diameters, benzene and toluene
 218 clearly differ in their adsorbed amounts. This phenomenon might be explained by the particularity of
 219 aromatic molecules to organize themselves through π interactions (e.g. π - π stacking)⁴⁶. Indeed, packing
 220 configurations of benzene and toluene strongly differ due to the steric hindrance generated by the $-\text{CH}_3$
 221 group in toluene^{47,48}. The higher content of adsorbed benzene compared to toluene results most likely
 222 from better pore filling caused by higher packing in MOF cages.

223 Some differences are noticed when comparing adsorption isotherms of both isostructural MOFs. The
224 trend observed for $[\text{Pd}(2\text{-pymo})_2]_n$ shows deviations from its Cu-based analog and the VOC adsorption
225 preferences can be ranked as follows: benzene \gg cyclohexane $>$ toluene $>$ n-hexane (**Figure 5.b**). As
226 expected, benzene is clearly the dominant adsorbate within the series. Interestingly, n-hexane and
227 cyclohexane loadings are lower but very similar, indicating a potential weaker affinity of these
228 molecules toward $[\text{Pd}(2\text{-pymo})_2]_n$ ($n_{\text{Benzene}}/n_{\text{n-hexane}} = 1.8$ at 0.5 p/p₀) (**Figure S4**), reaching typically the
229 absorption capacity of benzene $\sim 0.42 \text{ mol}_{\text{Benzene}}/\text{mol}_{[\text{Pd}(2\text{-pymo})_2]_n}$. This hypothesis is reinforced by the
230 differences in adsorption enthalpies for benzene and cyclohexane onto PdCl_2 ($\Delta H_{\text{benzene}}$: 39-46 kJ/mol,
231 $\Delta H_{\text{cyclohexane}}$: 21-29 kJ/mol)²². The lower affinity of cyclohexane can be clearly explained by the lack of
232 π -electrons in the molecule. Similar to $[\text{Cu}(2\text{-pymo})_2]_n$, benzene and toluene do not adsorb in the same
233 manner in $[\text{Pd}(2\text{-pymo})_2]_n$ ($n_{\text{Benzene}}/n_{\text{Toluene}} = 1.7$ at 0.5 p/p₀) (**Figure S4**). Such difference could again
234 result from steric effect, limiting accommodation of toluene molecules in the MOF porous structure and
235 their access to palladium sites. Therefore, one may conclude that the affinity of $[\text{Pd}(2\text{-pymo})_2]_n$ is
236 unambiguously turned to aromatics but more importantly, this particular structure displays significant
237 preference for benzene over toluene. First assumptions might be proposed regarding the benzene
238 sorption mechanisms within $[\text{Pd}(2\text{-pymo})_2]_n$. We may hypothesize that first, benzene chemisorption
239 occurs at low pressures due to the strong interactions with Pd nodes. Then at higher pressure
240 physisorption may be invoked, involving π - π interactions between the “free” and the already
241 chemisorbed benzene molecules. The results indicate that the difference of adsorption uptake is strongly
242 affected by three main characteristics of the VOC molecule: kinetic diameter, flexibility/rigidity and
243 presence/absence of π electrons.

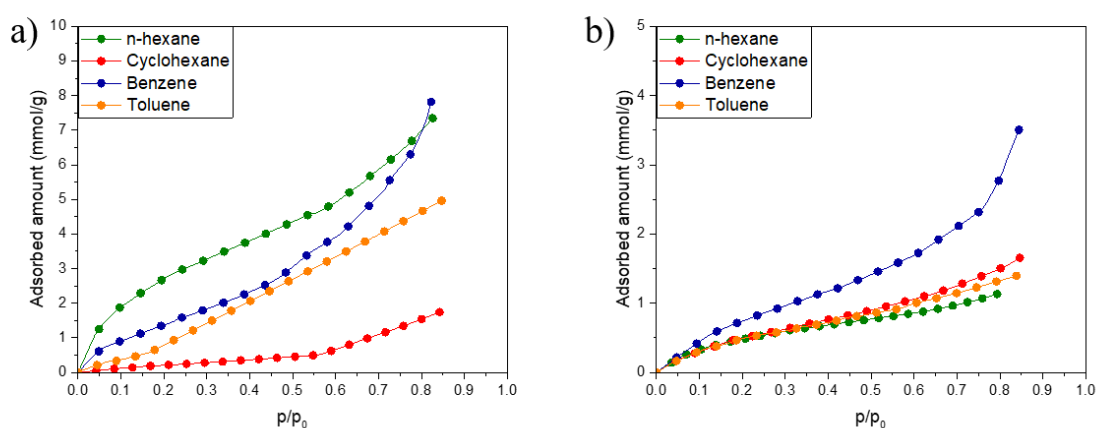
244 It should be highlighted that the overall lower adsorption capacity of $[\text{Pd}(2\text{-pymo})_2]_n$ compared to
245 $[\text{Cu}(2\text{-pymo})_2]_n$ is counterbalanced by its remarkably high selectivity for benzene in the tested VOC
246 series. This is particularly noticeable when comparing the adsorption isotherms per mole of adsorbent
247 (**Figure S4**) but also when VOCs are considered as liquid (in mL) accommodated within the MOF
248 porous structure (**Figure S5**). This finding emphasizes the interest of $[\text{Pd}(2\text{-pymo})_2]_n$ as a preferential
249 benzene sorbent applicable for its favored removal or sensing. In comparison, the Cu-based analog can

250 be used for the simple capture of a broad spectrum of hydrocarbon molecules when no selectivity is
 251 required. It is also noteworthy to realize that the high atomic mass of Pd (106.4 g.mol⁻¹) compared to Cu
 252 (63.5 g.mol⁻¹) contributes to lower the apparent adsorption capacity of [Pd(2-pymo)₂]_n measured in
 253 mmol_{adsorbate}/g_{MOF}. Hence, for a given volume of sorbent, the adsorption capacities of Pd and Cu-based
 254 MOFs are more comparable, and [Pd(2-pymo)₂]_n appears as a competitive material for the design of
 255 devices for the specific capture or detection of benzene.

256 **Table 2.** List of adsorbates, characteristics and kinetic diameters.

Adsorbate	Type	Shape	Flexibility	Kinetic diameter (Å)	Saturation vapor pressure at 25°C (mbar)
n-hexane	Alkane	Linear	Flexible	4.3	199.4
Cyclohexane	Alkane	Cyclic	Flexible	6.0	130.7
Benzene	Aromatics	Cyclic	Rigid	5.8	126.9
Toluene	Aromatics	Cyclic	Rigid	5.8	37.1

257



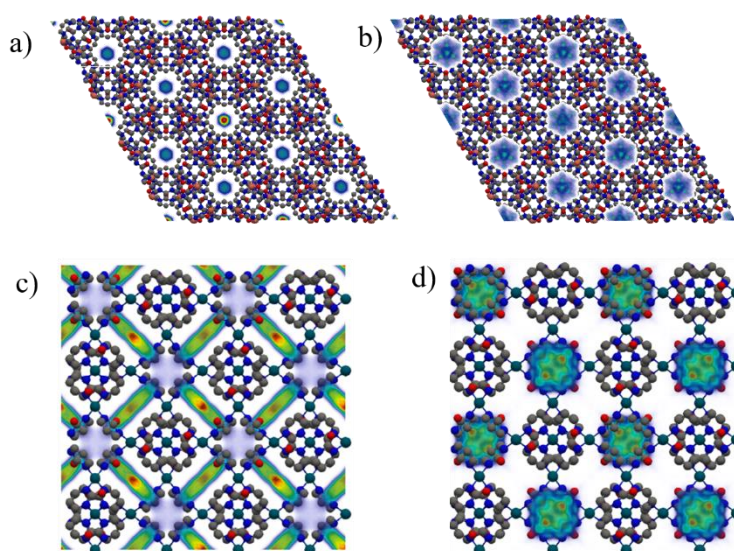
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259 **Figure 5.** Experimental adsorption isotherms of selected VOCs for a) [Cu(2-pymo)₂]_n and b) [Pd(2-
 260 pymo)₂]_n at 25°C.

261 Computational study of the VOC adsorption

262 As described in the experimental part, GCMC simulations were carried out to investigate VOC
 263 adsorption within the MOF structures. Supercells were created from Crystallographic Information File
 264 (CIF) available in the Cambridge Crystallographic Data Center (CCDC) database. As evoked

265 previously, $[\text{Cu}(2\text{-pymo})_2]_n$ can adopt either cubic or rhombohedral structure depending on its exposure
266 to the guest molecule (e.g. water). However, only the rhombohedral topology is observed once in direct
267 contact with the studied series of VOCs. Hence, only this particular structure is exclusively taken into
268 consideration for the simulations. The $[\text{Pd}(2\text{-pymo})_2]_n$ structure keeps the same cubic topology whatever
269 it is solvated or not. As we focused our utmost attention on benzene and n-hexane, the preferential
270 location of these adsorbates was deduced for each MOF by injecting a single molecule into the supercell.
271 GCMC simulations clearly show that benzene and n-hexane are not localized and distributed equally in
272 both structures (**Figure 6**).



273
274 **Figure 6.** Density plots for a) n-hexane and b) benzene in $[\text{Cu}(2\text{-pymo})_2]_n$. Density plots for c) n-hexane
275 and d) benzene in $[\text{Pd}(2\text{-pymo})_2]_n$.

276 The average occupation profiles of n-hexane and benzene reveal a preferential location within the
277 hexagonal channels for $[\text{Cu}(2\text{-pymo})_2]_n$, while the distribution pattern is more diversified in $[\text{Pd}(2\text{-}$
278 $\text{pymo})_2]_n$. Particularly, the benzene molecule seem to be preferentially located at the center of β cages,
279 while the linear n-hexane crosses perpendicularly through the 6MR_H window connecting each cage.
280 It is noteworthy that n-hexane does not pass through the 6MR_CO windows, probably because of their
281 hydrophilicity.

282 Beyond the great value knowledge acquired on adsorption processes, information obtained from
283 GCMC simulations also help to improve these MOFs through rational design for VOC capture purposes.
284 Since steric effect prevents the penetration of toluene in the $[\text{Pd}(2\text{-pymo})_2]_n$ structure, a very precise
285 increase of the ligand length may be a straightforward option if a capture of both benzene and toluene
286 is required. On the other hand, the selectivity toward benzene could also be improved by further repelling
287 other compounds such as n-hexane. As mentioned, n-hexane is only allowed to pass through 6MR_H
288 due to its sufficient hydrophobicity (6MR_CO windows are forbidden). Moreover, replacing the _H
289 group with hydrophilic functions such as carbonyl, hydroxyl or amine, should repel n-hexane and thus
290 allow only benzene accommodation within the pores.

291

292 **Conclusion**

293 This study aims to explore the notorious affinity of aromatics to palladium based-materials and more
294 specifically to MOFs with Pd nodes. In this respect, this work is a valuable contribution to the current
295 state of the art through both experimental and simulation investigations of the aromatic VOCs sorption
296 in a Pd-based MOF. Four VOCs (n-hexane, cyclohexane, benzene and toluene) were examined to assess
297 the sorption properties of two isostructural MOFs: $[\text{Cu}(2\text{-pymo})_2]_n$ and $[\text{Pd}(2\text{-pymo})_2]_n$. QCM
298 measurements showed that benzene exhibits higher affinity to Pd-based MOF while n-hexane has a
299 preference for the Cu-based MOF. Toluene and cyclohexane are adsorbed in lower amounts due to their
300 larger size and/or lower flexibility. GCMC simulations were useful to compare the localization of the
301 adsorbed VOCs in both MOF structures. Benzene and n-hexane occupy hexagonal channels in $[\text{Cu}(2\text{-pymo})_2]_n$,
302 while for $[\text{Pd}(2\text{-pymo})_2]_n$, benzene is localized in the β cages and n-hexane passes through the
303 pore aperture perpendicularly to the 6MR-H. Attractively, the $[\text{Pd}(2\text{-pymo})_2]_n$ MOF clearly exhibits
304 higher selectivity to benzene over other hydrocarbons, with a consistent adsorption capacity in
305 comparison with the same volume of $[\text{Cu}(2\text{-pymo})_2]_n$. Overall, this study validates the highly favorable
306 role of palladium as a metal node in MOF structure for the selective capture of aromatics. In addition, it
307 also demonstrates that the involved charge interactions can be judiciously coupled with steric hindrance
308 effects in the $[\text{Pd}(2\text{-pymo})_2]_n$ MOF network to favor the preferential capture and detection of benzene

309 over toluene. This work paves the way to the design of high-performance materials for applications in
310 specific aromatic adsorbing and/or sensing devices.

311 **Associated Content**

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327 **Author Contributions**

328 The manuscript was written through contributions of all authors. All authors have given approval to the
329 final version of the manuscript.

330 **Notes**

331 The authors declare no competing financial interest. The funders had no role in the design of the study;
332 in the collection, analyses, or interpretation of data; in the writing of the manuscript; or in the decision
333 to publish the results.

334 **Supporting Information**

- 335 • PXRD patterns, IR spectra, TGA, N₂ adsorption-desorption measurements of [Cu(2-pymo)₂]_n and
336 [Pd(2-pymo)₂]_n, PXRD patterns of [Cu(2-pymo)₂]_n exposed to VOCs, computational details for
337 GCMC simulations (PDF).

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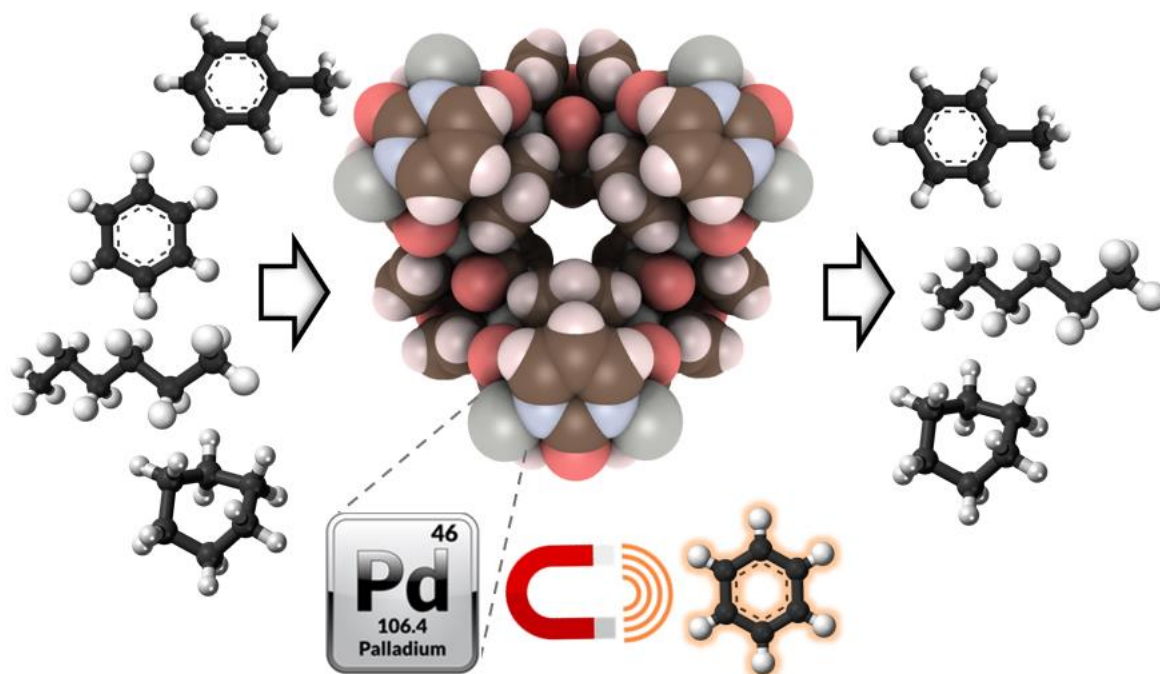
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