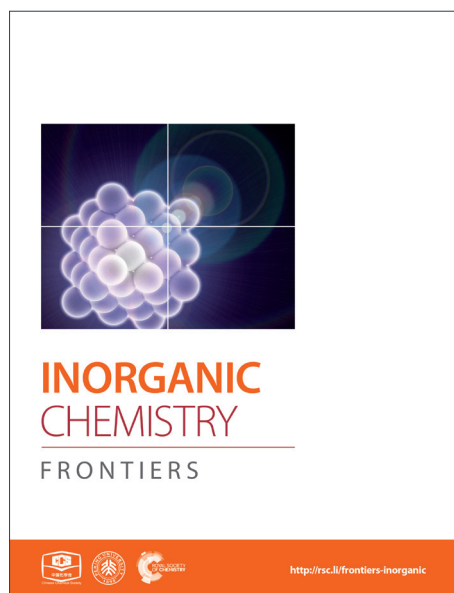
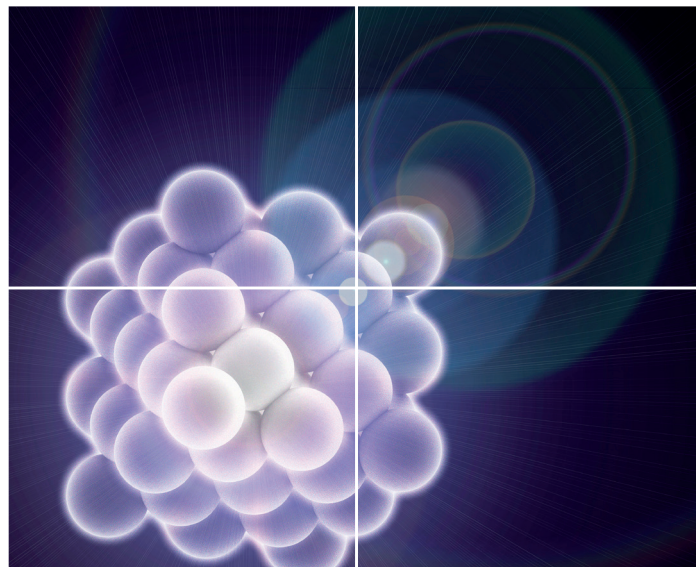


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## Carbon Dioxide Capture in the Presence of Water Vapour in InOF-1

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Kinetic uptake experiments on InOF-1 confirm a maximum of 5.42 wt% CO<sub>2</sub> capture at 30 °C and a significant 2-fold increase (~11 wt %) in CO<sub>2</sub> capture under 20% relative humidity of water vapour. InOF-1 captures CO<sub>2</sub> under humidity conditions (10% and 20% RH) and relatively high temperatures (40 and 50 °C) without any degradation of the crystalline structure which was corroborated by PXRD.

### Introduction

Global warming is one of the biggest threats that our society has to solve since it causes extreme climate change. The cumulative carbon dioxide (CO<sub>2</sub>) emissions in the atmosphere are continuously increasing due to anthropogenic activities and these, unwittingly, generate the undesirable green gas effect.<sup>1</sup> The accelerating global energy demands and consumption of carbon-based fuels are the main trigger to the increasing CO<sub>2</sub> levels,<sup>2</sup> and these energy requirements are expanding promptly due to rapid world population growth, increases in standard of living and the development of technologies, leading to a doubling in the energy demand over the last three decades.<sup>3</sup> Therefore, CO<sub>2</sub> separation and capture have motivated many governments to invest in the development of new methods for efficiently and effectively capturing CO<sub>2</sub>.<sup>4</sup>

Typical absorption in aqueous alkanolamine solutions has been widely used and studied, but it has many major limitations as an adsorbent for industrial CO<sub>2</sub> capture due to its heat instability and corrosion on vessels and pipelines.<sup>5</sup> Thus, the use of porous solids for the adsorption of CO<sub>2</sub> is a timely research area and the search for materials with a high adsorption capacity, structural stability, high tolerance against humidity, fast sorption kinetics and mild regeneration properties, remains a major challenge for practical applications.

Porous coordination polymers (PCPs) or metal-organic frameworks (MOFs) are among the most interesting candidates for gas separation, because their sorption selectivity towards small

molecule adsorbates is directly tunable as a function of the topology and chemical composition of the micropores.<sup>6</sup> Porous metal-organic materials showing high surface area and high pore volume normally show high CO<sub>2</sub> storage capacities at room temperature and relatively high pressures.<sup>7</sup> Although the high CO<sub>2</sub> capacity and selectivity that PCPs show, many gas separation processes in industry involve the exposure to water vapour. However, water molecules can compete with any gas molecules for the active sites (within PCPs) or disrupt the ligand bonding between organic molecules and metal, resulting in the collapse of the structure.<sup>8</sup> Capturing CO<sub>2</sub> from real flue gas (high humidity and high temperature) is indeed a great challenge.

Recently, there is considerable number of PCPs that have shown relatively good stability to water,<sup>9</sup> and some interesting examples are: UiO-66,<sup>10</sup> HKUST-1,<sup>11</sup> MIL-100,<sup>12</sup> MIL-101,<sup>13</sup> and MIL-53.<sup>14</sup> Doonan *et al.*<sup>15</sup> reported a water stable MOF (Cu(bcppm)H<sub>2</sub>O, H<sub>2</sub>bcppm= bis(4-(4-carboxyphenyl)-1H-pyrazolyl)methane) that also showed exceptionally selective separation for CO<sub>2</sub> over N<sub>2</sub>.

However, further than structural stability, direct contact of PCPs to water can seriously reduce their gas storage capacity and water is most often unfavourable to gas separations.<sup>16</sup> The effect of water on the CO<sub>2</sub> capture has only recently been investigated on PCPs.<sup>17</sup> Matzger and co-workers<sup>17b</sup> studied the effect of humidity on the performance of M/DOBDC (M = Zn<sup>II</sup>, Ni<sup>II</sup>, Co<sup>II</sup> or Mg<sup>II</sup>) by collecting N<sub>2</sub>/CO<sub>2</sub>/H<sub>2</sub>O breakthrough curves at different relative humidities. LeVan *et al.*<sup>18</sup> found that a small amount of water did not decrease and may in fact increase the CO<sub>2</sub> capacity of PCPs. Eddaoudi and co-workers<sup>19</sup> demonstrated that a material entitled SIFSIX-3-Cu was a recyclable and moisture stable MOF that showed enhanced CO<sub>2</sub> uptake and selectivity in highly diluted gas streams.

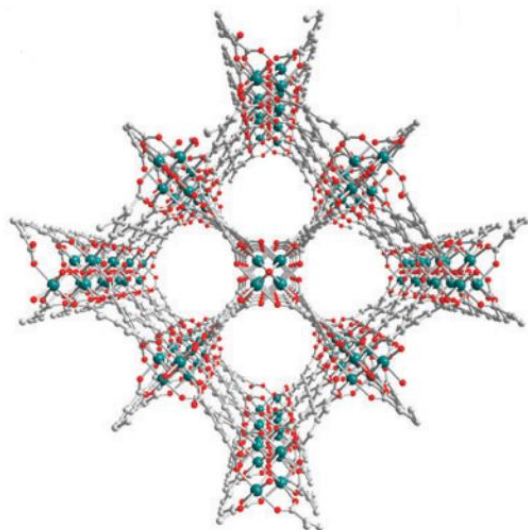
Llewellyn and co-workers<sup>20</sup> investigated the CO<sub>2</sub> adsorption in some PCPs under different relative humidities of water vapour. Certainly, HKUST-1, was shown to degrade in the presence of water vapour, and UiO-66 did not show any enhanced CO<sub>2</sub> uptake.<sup>20</sup> In the case of MIL-100(Fe), a remarkable 5-fold increase in CO<sub>2</sub> uptake was

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observed with increasing relative humidity (RH), 105 mg g<sup>-1</sup> at 40% RH. In addition, Yaghi *et al.*<sup>21</sup> showed that the presence of hydroxyl functional groups increase the affinity of the framework for water. Thus, in the present work we have chosen a material entitled InOF-1,<sup>22</sup> (Fig. 1) a water-stable PCP based on a binuclear [In<sub>2</sub>(μ<sub>2</sub>-OH)] building block (Figure S1, ESI<sup>†</sup>), constructed from a flexible BPTC<sup>4-</sup> ligand (H<sub>4</sub>BPTC= biphenyl-3,3',5,5'-tetracarboxylic acid) and possesses hydroxo functional groups (μ<sub>2</sub>-OH) to study the CO<sub>2</sub> capture in the presence of water vapour.



**Fig. 1** View of the crystal structure of InOF-1 along the *c*-axis (indium: green; oxygen: red; carbon: grey; hydrogen omitted for clarity).<sup>22</sup>

## Experimental

Indium nitrate, In(NO<sub>3</sub>)<sub>3</sub> (156 mg, 0.40 mmol) and biphenyl-3,3',5,5'-tetracarboxylic acid, H<sub>4</sub>BPTC, (33 mg, 0.10 mmol) were dispersed in CH<sub>3</sub>CN (5 ml), DMF (5 ml) and HNO<sub>3</sub> (65 %, 0.2 ml) and sealed in a pressure tube. The clear solution was heated at 85 °C in an oil bath for 72 h. The tube was cooled to room temperature over a period of 12 h and the colourless crystalline product was separated by filtration, washed with DMF (5 ml) and dried in air. Yield: 72 % (based on ligand).

The uncoordinated solvent molecules in the pores of the as-synthesized InOF-1 were exchanged for acetone and this promotes accessibility to the desolvated framework after activation by heating. Thus, thermogravimetric analysis (See Fig. S2, ESI<sup>†</sup>) and bulk powder x-ray diffraction patterns (See Fig. S3, ESI<sup>†</sup>) of as-synthesized and desolvated InOF-1 confirmed that the material consistently retains its structural integrity upon solvent removal. N<sub>2</sub> adsorption isotherms for activated InOF-1 at 77 K were used to calculate the BET surface area (0.01 < *p/p*<sub>0</sub> < 0.04) of 1060 m<sup>2</sup> g<sup>-1</sup>.

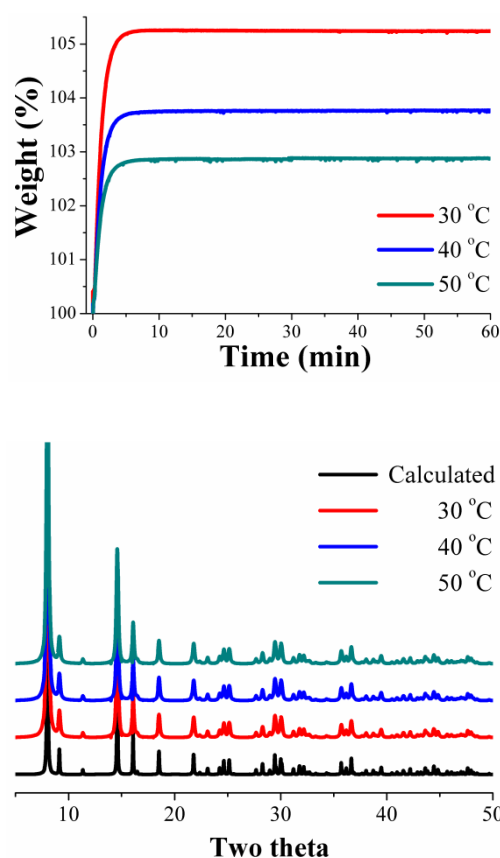
Kinetic uptake experiments were performed by using a thermobalance (Q500 HR, from TA) at different temperatures with a constant CO<sub>2</sub> flow (60 mL min<sup>-1</sup>). Then, acetone-exchanged samples of InOF-1 were placed into the thermobalance and activated by heating from room temperature to 180 °C for 1h and under a flow of N<sub>2</sub> gas. After the activated sample was cooled down, the desired temperature and a constant CO<sub>2</sub> flow (60 mL min<sup>-1</sup>) were set. With a humidity-controlled thermobalance (Q5000

SA, from TA) kinetic uptake experiments at 30, 40 and 50 °C with a constant CO<sub>2</sub> flow (60 mL min<sup>-1</sup>) were carried out on activated samples (180 °C for 1h and under a flow of N<sub>2</sub> gas) of InOF-1.

## Results and discussion

Dynamic and isothermal CO<sub>2</sub> experiments were carried out on InOF-1. Fig. 1, left, shows the kinetic uptake experiments from 30 °C to 50 °C. At 30 °C the material exhibited the maximum weight % gain, which represents the maximum amount of CO<sub>2</sub> captured. This amount corresponds to 5.24 wt%, which was rapidly reached after just 5 min and it was constant until the end of the experiment (60 min). At 40 °C the uptake was estimated to be 3.77 wt%, which was also reached after approximately 5 min (Fig. 2, top). Finally, at 50 °C the maximum uptake was 2.88 wt%.

Clearly, while the temperature is increased (from 30 to 50 °C), the CO<sub>2</sub> weight (%) gradually decreases (Fig. 2, top) from 5.24 to 2.88 wt%. In order to corroborate that this decrease is not due to sample degradation, we have carried out PXRD experiments on each sample after these CO<sub>2</sub> capture experiments. Fig. 2 (bottom) confirms that the crystallinity of the samples after each CO<sub>2</sub> capture experiments was retained.



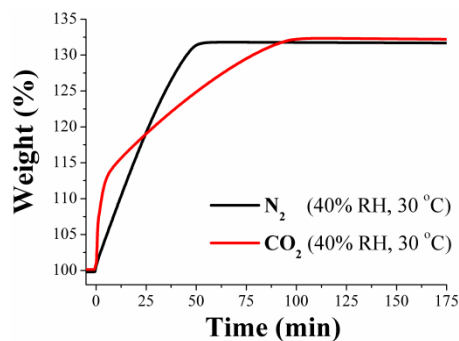
**Fig. 2** (top) Kinetic uptake experiments performed at different temperatures (30, 40 and 50 °C) with a CO<sub>2</sub> flow of 60 mL/min; (bottom) calculated PXRD pattern of InOF-1 and PXRD patterns of each InOF-1 samples after the kinetic CO<sub>2</sub> isotherms were carried out at different temperatures.

Hong *et al.*<sup>22</sup> showed, by PXRD experiments, that InOF-1 is a water stable PCP and this water-stability can be attributed to the presence of the hydroxo functional groups (inside the pores of InOF-1) as previously reported.<sup>17</sup> Thus, kinetic isotherm experiments at 30, 40 and 50 °C, with a constant CO<sub>2</sub> flow, and a relative humidity (RH) of 40% were carried out. It was decided to run these experiments with a 40% RH based on the extraordinary results that Llewellyn *et al.*<sup>20</sup> previously reported (5-fold increase in CO<sub>2</sub> uptake for MIL-100(Fe)).

First, an activated InOF-1 sample (180 °C for 1h and under a flow of N<sub>2</sub> gas) was placed into a humidity-controlled thermobalance. After activation of the material, the equipment was stabilized at 40% RH (30 °C) and a constant CO<sub>2</sub> flow (60 mL min<sup>-1</sup>) was started. Afterwards, we repeated this experimental procedure on a new activated InOF-1 sample and set a constant N<sub>2</sub> flow (60 mL min<sup>-1</sup>). Fig. 3 exhibits the kinetic uptake experiments at 30 °C and 40% RH for CO<sub>2</sub> and N<sub>2</sub>. For both isotherms, it is clear to observe that the material shows a constant increase in weight (while the experiment is continuing in time, see Fig. 3). This increase in weight is due to the contribution of H<sub>2</sub>O and CO<sub>2</sub> or H<sub>2</sub>O and N<sub>2</sub>, respectively.

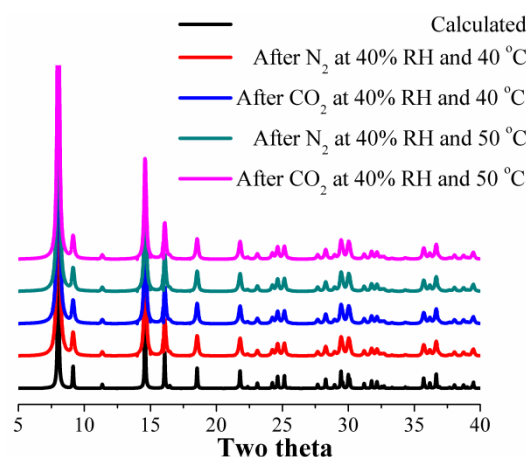
In order to find the maximum CO<sub>2</sub> capture under 40% RH conditions, we need to differentiate the contribution of H<sub>2</sub>O to the weight increase. By taking the difference of the two isotherms (CO<sub>2</sub> and N<sub>2</sub>) we could obtain the CO<sub>2</sub> capture at 40% RH. This is valid if the material does not capture any N<sub>2</sub> at 30 °C. Consequently, by performing a kinetic uptake experiment on a newly activated InOF-1 sample at 30 °C without presence of H<sub>2</sub>O vapor (0% RH) with a constant N<sub>2</sub> flow (60 mL min<sup>-1</sup>) we obtained a N<sub>2</sub> capture of approximately 0.01 wt%. This result is consistent with previous reports where the capture capacity of N<sub>2</sub> capture in PCPs at room temperatures is basically negligible.<sup>23</sup> In Fig. 3, the gradual weight increase for N<sub>2</sub>/H<sub>2</sub>O starts at 0 min and stabilises at ~ 55 min. In the case of CO<sub>2</sub>/H<sub>2</sub>O the weight increase starts at 0 min and stabilises after approximately 110 min.

In contrast, under anhydrous conditions the CO<sub>2</sub> uptake rapidly reached stability (5 min, see Fig. 2, top). This equilibrium discrepancy is due to the nature of the vapour adsorption process that in general takes considerably more time to stabilise than the gas adsorption process in microporous materials.<sup>24</sup> Then, from 110 min until approximately 175 min both isotherms seem to reach a plateau where both uptakes are practically constant (Fig. 3). At 175 min, the maximum amounts of CO<sub>2</sub>/H<sub>2</sub>O and N<sub>2</sub>/H<sub>2</sub>O captured are 132 wt% and 131 wt%, respectively and by taking the difference of these two values (since there is no N<sub>2</sub> uptake at 30 °C) the CO<sub>2</sub> capture in the material is ~ 1 wt%.



**Fig. 3** Kinetic uptake experiments carried out at 30 °C and 40% RH with CO<sub>2</sub> (red line) and N<sub>2</sub> (black line) flows of 60 mL/min, respectively.

Therefore, the CO<sub>2</sub> capture at 40% RH and 30 °C was considerably reduced in comparison to anhydrous conditions (from 5.24 to 1.00 wt%). At 40% RH and 40 °C (See Fig. S4, ESI<sup>†</sup>), as well as 40% RH and 50 °C (See Fig. S5, ESI<sup>†</sup>) the CO<sub>2</sub> capture was approximately the same (~1 wt%). This CO<sub>2</sub> capture reduction is not due to a degradation of the material after each experiment, since PXRD experiments carried out on the samples after the N<sub>2</sub> and CO<sub>2</sub> capture experiments (See Fig.4), showed that the retention of the crystallinity was maintained (See Fig.4).



**Fig. 4** Calculated PXRD pattern of InOF-1 and PXRD patterns of each InOF-1 samples after the kinetic N<sub>2</sub> and CO<sub>2</sub> isotherms at different temperatures.

Then, in closer inspection of the porosity of InOF-1, this corresponds to the microporosity regime with a pore diameter of 7.6 Å.<sup>22</sup> Interestingly, the remarkable result of a 5-fold increase in CO<sub>2</sub> uptake was obtained in a mesoporous material at 40% RH and 30 °C (MIL-100(Fe))<sup>20</sup> which comprises two types of mesoporous cages of free apertures of *ca.* 25 and 29 Å.<sup>20</sup> We then rationalised that at 40% RH the saturation of the micropores in InOF-1, with H<sub>2</sub>O molecules, was completed and therefore, the inclusion of CO<sub>2</sub> molecules, into the micropores, was unfeasible. In order to confirm this hypothesis, we reduced the relative humidity to half (20% RH) and more CO<sub>2</sub> capture experiments were carried out. Then, an activated InOF-1 sample was stabilised, in a humidity-controlled thermobalance, at 20% RH (30 °C) and a constant CO<sub>2</sub> flow (60 mL min<sup>-1</sup>) was started. Later, we replicated this experimental procedure on a new activated InOF-1 sample and set a constant N<sub>2</sub> flow (60 mL min<sup>-1</sup>).

Fig. 5 exhibits the kinetic uptake experiments at 30 °C and 20% RH for CO<sub>2</sub> and N<sub>2</sub>. Again, for both isotherms, the material clearly shows a constant increased in weight. However, this time both isotherms exhibited a much faster weight increase for N<sub>2</sub>/H<sub>2</sub>O and CO<sub>2</sub>/H<sub>2</sub>O than at 40% RH, starting at 0 min and stabilising at ~ 15 min. Thus, from 15 min until approximately 175 min both isotherms reach a plateau where both uptakes are constant (Fig. 5). At 175 min, the maximum amounts of CO<sub>2</sub>/H<sub>2</sub>O and N<sub>2</sub>/H<sub>2</sub>O captured are 112 wt% and 101 wt%, respectively and by taking the difference of these two values (since there is no N<sub>2</sub> uptake at 30 °C) the CO<sub>2</sub> capture in the material is ~ 11 wt%.



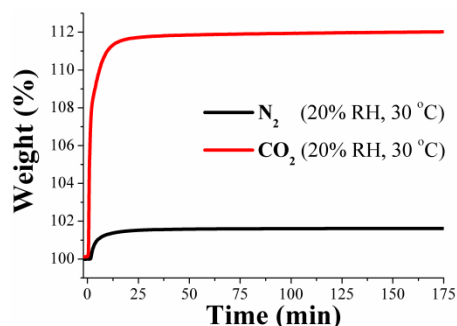


Fig. 5 Kinetic uptake experiments carried out at 30 °C and 20% RH with CO<sub>2</sub> (red line) and N<sub>2</sub> (black line) flows of 60 mL/min, respectively.

Therefore, the CO<sub>2</sub> capture was approximately 2-fold increased with a 20% RH (from 5.24 wt% to 11 wt%) in comparison to anhydrous conditions. Clearly, when the relative humidity was reduced to 20%, the micropores of InOF-1 were partially saturated with H<sub>2</sub>O molecules, allowing CO<sub>2</sub> molecules to enter into the micropores of InOF-1. This enhance in CO<sub>2</sub> uptake in the presence of water can be explained by CO<sub>2</sub> confinement effects induced by bulky molecules (H<sub>2</sub>O).<sup>25</sup> Walton *et al.*<sup>26</sup> proposed that functional groups (*e.g.* hydroxo functional groups inside the pores of InOF-1) act as a directing agent for water in the pores, which allows for more efficient packing. Additionally, we previously observed this enhanced-CO<sub>2</sub> uptake phenomenon in a couple of Sc(III) water stable PCPs.<sup>27</sup>

The cycle stability of the material was investigated by running 11 kinetic uptake experiments on the same sample. Thus, an activated InOF-1 sample (180 °C for 1h and under a flow of N<sub>2</sub> gas) was placed into a humidity-controlled thermobalance and a constant CO<sub>2</sub> flow (60 mL min<sup>-1</sup>) was started at 20% RH. The experiment was stopped after 20 min (only to obtain the maximum CO<sub>2</sub> uptake) and then, this protocol was repeated ten more times (with the same sample) to make a total of 10 cycles. The average CO<sub>2</sub> uptake of the cycles was 11.02 wt% (see Fig. S8 ESI<sup>†</sup>). In addition, PXRD experiments confirmed the retention of the overall framework crystallinity after 10 cycles (see Fig. S9 ESI<sup>†</sup>).

We also performed kinetic uptake experiments at 30 °C and 10% RH finding a maximum CO<sub>2</sub> uptake of approximately 9 wt% (see Fig. S6, ESI<sup>†</sup>). Thus the highest amount of CO<sub>2</sub> capture was obtained under a relative humidity of 20%.

Additionally, we decided to run a CO<sub>2</sub> experiment (60 mL min<sup>-1</sup>) at 20% RH and 30 °C on an activated PCM-14<sup>28</sup> sample (150 °C for 2h, under a flow of N<sub>2</sub> gas). Since PCM-14 is a non-porous coordination polymer, when activated between 25-150 °C, it offered a direct CO<sub>2</sub> capture comparison to InOF-1 (microporous material). Thus, from 0 min to ~180 min the maximum CO<sub>2</sub> uptake (under 20% RH) was 0.8 wt% (see Fig. S7, ESI<sup>†</sup>). This result corroborated that there is no CO<sub>2</sub> sequestration in a non-porous material when the relative humidity is 20% at 30 °C.

Finally, kinetic uptake experiments were performed on InOF-1 at 20% RH and 40 °C (See Fig. 6 top) and 20% RH and 50 °C (See Fig. 6 bottom). The total CO<sub>2</sub> capture values were 8 wt% and 6 wt% (Fig. 6), respectively. Thus, these values represent an approximately 2-fold CO<sub>2</sub> increased (from

anhydrous conditions to 20% RH) from 3.77 wt% to 8 wt% at 40 °C and from 2.88 wt% to 6 wt% at 50 °C. These results are indeed very promising for the application of PCPs in a more realistic CO<sub>2</sub> capture situation like flue gas (high humidity and high temperature).

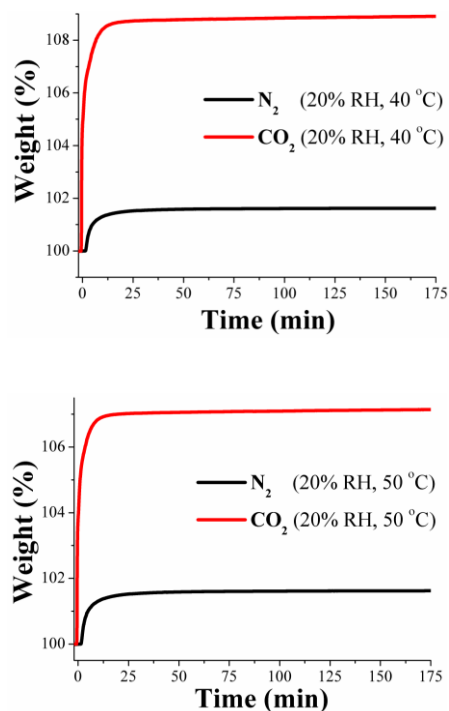


Fig. 6 (top) Kinetic uptake experiments carried out at 40 °C and 20% RH with CO<sub>2</sub> (red line) and N<sub>2</sub> (black line) flows of 60 mL/min, respectively; (bottom) Kinetic experiments carried out at 50 °C and 20% RH with CO<sub>2</sub> (red line) and N<sub>2</sub> (black line) flows of 60 mL/min, respectively.

## Conclusions

In conclusion, InOF-1, a In(III) porous coordination polymer, exhibited a total CO<sub>2</sub> amount of 5.42 wt% at 30 °C shown by kinetic isotherm experiments, which was rapidly reached after approximately 5 min. While increasing the temperature of the kinetic isotherm experiments, the CO<sub>2</sub> capture capacity of InOF-1 decreased to 2.88 wt% at 50 °C. Remarkably, InOF-1 exhibits high stability towards humidity, which was confirmed by PXRD. We attributed this water stability, as previously reported,<sup>21</sup> to the presence of hydroxo functional groups within the pores of InOF-1.

Due to this particularly high water stability, InOF-1 performs CO<sub>2</sub> uptake under relative humidity conditions. Finding the best partial saturation of H<sub>2</sub>O molecules (percentage of relative humidity) into the micropores of InOF-1 is essential to increase the CO<sub>2</sub> uptake. Thus, after testing different relative humidity conditions (40%, 20% and 10% RH) and temperatures (30, 40 and 50 °C), we found that the maximum CO<sub>2</sub> capture was obtained at 20% RH and 30 °C with a total amount of ~11 wt%. Significantly, this CO<sub>2</sub> capture, under humid conditions, represents a 2-fold increase in comparison to anhydrous conditions.

It is also worth to mention that this material captures CO<sub>2</sub> under humidity conditions and relatively high temperatures (40 and 50 °C) which is desirable in a more realistic CO<sub>2</sub> capturing scenario like flue gas. PCM-14 showed non-CO<sub>2</sub> capture under RH conditions,

suggesting that the microporosity provided by InOF-1 is fundamental for this capture process. Since PCM-14 is non-porous coordination polymer, when activated between 25-150 °C, the CO<sub>2</sub> confinement effects induced by H<sub>2</sub>O<sup>25</sup> in porous materials cannot take place unlike in InOF-1, where these effects occur within the micropores as well as the directing effect of the hydroxo functional groups (inside the micropores of InOF-1) which can accommodate CO<sub>2</sub> more efficiently.<sup>26</sup>

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