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A route to drastic increase of CO<sub>2</sub> uptake in Zr metal organic  
framework UiO-66

Post-synthetic exchange of titanium ions into the zirconium  
MOF UiO-66 has doubled the carbon dioxide capture performance.  
This has been achieved by a strengthening of the interaction, with a  
pore size decrease and the strong attraction of titanium ions being  
chiefly responsible.

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# A route to drastic increase of CO<sub>2</sub> uptake in Zr metal organic framework UiO-66†

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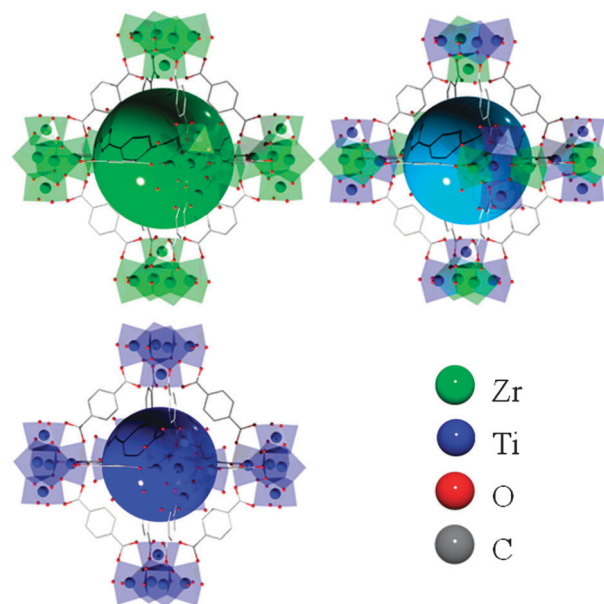
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**CO<sub>2</sub> uptake in zirconium MOF UiO-66 almost doubles with post-synthetic exchange of Zr by Ti. This was due to smaller pore size and higher adsorption enthalpy, with good complementarity between experiment and simulation. Furthermore, the full effect is obtained with ~50% Ti loading, precluding the need to fully substitute frameworks for CO<sub>2</sub> capture.**

Carbon dioxide capture is an important process for mitigating greenhouse gas emissions, and for light gas purifications. Promising capture methods include pressure swing adsorption (PSA),<sup>1</sup> solvent absorption,<sup>2</sup> and gas separation membranes.<sup>3–5</sup> Key to widespread adoption of these technologies is the energy efficiency of the process, particularly for post-combustion CO<sub>2</sub> capture from coal flue gas streams, where the energy costs,<sup>6–8</sup> are well above the thermodynamic minimum.<sup>9,10</sup> Some of the most promising materials being investigated to enhance the efficiency of adsorption-based capture processes include ultra-high surface area materials such as metal organic frameworks (MOFs)<sup>11,39</sup> and porous aromatic frameworks (PAFs).<sup>12,13</sup> They are of particular interest due to the storage capacities attainable being more than three times that of liquid amine absorbents,<sup>14,15</sup> and that for MOFs in particular, their surface chemistry and pore architecture is readily tuneable for optimum CO<sub>2</sub> capture performance.<sup>11</sup>

Many MOFs, which consist of metallic nodes joined in an ordered fashion by organic linker molecules to generate a porous network, are not viable for post-combustion capture applications due to poor hydrothermal stability, which can be ascribed to many systems having comparatively weak metal-linker bonds relative to competitive hydroxylation reactions. However, it has been recently shown that Zr-based MOFs are particularly stable to water vapour, partly due to the reversible arrangement of the Zr<sub>6</sub>O<sub>4</sub>(OH)<sub>4</sub>(CO<sub>2</sub>)<sub>12</sub> cluster upon



**Fig. 1** The Zr-based metal organic framework UiO-66 can undergo post-synthetic exchange with Ti(IV) to deliver heterometallic MOFs, with decreased octahedral cages sizes.

hydroxylation and dehydroxylation, making them attractive candidates for post-combustion capture.<sup>16</sup> Moreover, Zr-based MOFs like UiO-66,<sup>16–18</sup> MIL-140,<sup>19</sup> and PIZOF<sup>20</sup> are air-stable up to 813 K.

Native Zr-MOFs exhibit mid-range CO<sub>2</sub> adsorption capacities of ~1.7 mmol g<sup>-1</sup> at 1 atm and 298 K.<sup>21</sup> These MOFs can be functionalised<sup>21–24</sup> to deliver increased storage capacity, with amine functionalisation for example delivering 3 mmol g<sup>-1</sup> at 1 atm and 298 K.<sup>21</sup> Recently, Cohen *et al.* reported the elegant post-synthetic exchange (PSE) of Zr with Ti ions to deliver a heterometallic MOF with high Ti loading.<sup>22</sup> The smaller Ti ions<sup>25</sup> may decrease the pore sizes within the framework to be closer to the ideal pore sizes for CO<sub>2</sub> adsorption,<sup>26,27</sup> thus enhancing the gravimetric CO<sub>2</sub> uptake of Ti-exchanged UiO-66.

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**Table 1** Surface area and pore volumes of UiO-66(Zr<sub>100</sub>), and Ti-exchanged UiO-66 as a function of Ti(IV) content

Sample name	Ti(IV) content (atomic %)	BET surface area (m <sup>2</sup> g <sup>-1</sup> )	Langmuir surface area (m <sup>2</sup> g <sup>-1</sup> )	Pore volume (cm <sup>3</sup> g <sup>-1</sup> )
UiO-66(Zr <sub>100</sub> ) <sup>a</sup>	0	1390 (1186) <sup>b</sup>	1644	0.70 (0.42) <sup>b</sup>
UiO-66(Ti <sub>32</sub> ) <sup>a</sup>	32	1418	1703	0.78
UiO-66(Ti <sub>44</sub> ) <sup>a</sup>	44	1749	2088	0.94
UiO-66(Ti <sub>56</sub> ) <sup>a</sup>	56	1844	2200	1.18

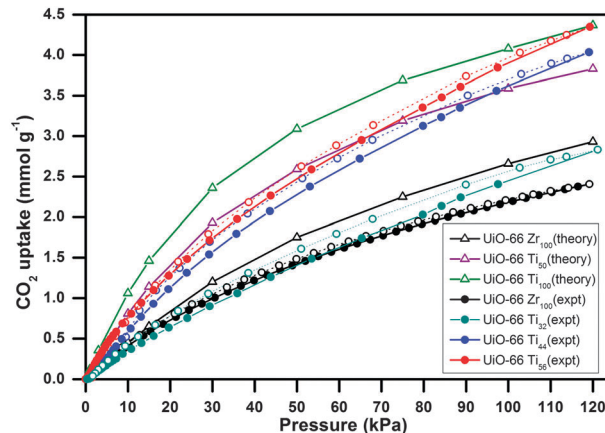
<sup>a</sup> Experimental data. Subscripts refer to atomic % of metal ions in Ti-exchanged UiO-66. <sup>b</sup> Data in parenthesis are obtained from molecular modelling.

Herein we explore this approach as a means to enhance the CO<sub>2</sub> storage capacity of this family of MOFs. Size-modulated UiO-66(Zr<sub>100</sub>) nanoparticles were synthesized according to literature.<sup>28</sup> Thereafter, Zr(IV) ions were post synthetically exchanged with Ti(IV) ions in UiO-66(Zr<sub>100</sub>) at different loading levels by exposing UiO-66(Zr<sub>100</sub>) to a DMF solution of TiCl<sub>4</sub>(THF)<sub>2</sub> for 1, 5, and 15 days at 368 K (Fig. 1). We compared the CO<sub>2</sub> uptake of Ti-exchanged UiO-66 with simulated results obtained from molecular modelling, and also used molecular modelling to predict the changes in pore diameters, CO<sub>2</sub> adsorption enthalpies, and the framework densities of Ti-exchanged UiO-66 and are found to be in qualitative agreement with experiment (see ESI†).

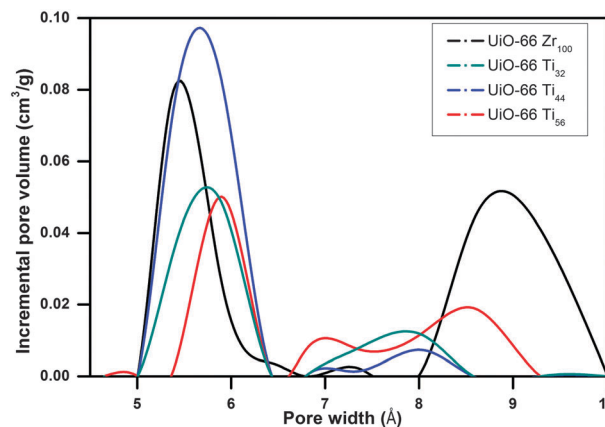
Inductively coupled plasma optical emission spectrometry (ICP-OES) analyses in Table 1 indicate that longer PSE durations increase the Ti(IV) content in Ti-exchanged UiO-66. The trend of increasing Ti content with longer PSE durations was verified with XRF (see ESI†) PXRD data reveals that the crystallinity of Ti-exchanged UiO-66 is comparable to that of UiO-66(Zr<sub>100</sub>) (Fig. S4, ESI†).

The BET surface areas of Ti-exchanged UiO-66 are higher than that of UiO-66(Zr<sub>100</sub>). This is also observed in the work of Cohen and co-workers.<sup>22</sup> The replacement of heavy metals with lighter metals can increase the surface area of MOFs.<sup>29,30</sup> The BET surface areas of UiO-66 and Ti-exchanged UiO-66 studied in this work are significantly larger than those reported in literature.<sup>17,21,22</sup> This can be attributed to the size-modulated UiO-66(Zr<sub>100</sub>) nanoparticles,<sup>28</sup> where the surface areas of size-modulated UiO-66(Zr<sub>100</sub>) nanoparticles are larger than those reported in other literature.<sup>17</sup> Additionally, the interstitial spaces in nano-sized Ti-exchanged UiO-66 and UiO-66(Zr<sub>100</sub>) may contribute to their higher incremental pore volumes observed in Table 1.

The experimental and simulated CO<sub>2</sub> adsorption isotherms at 273 K for UiO-66(Zr<sub>100</sub>), Ti-exchanged UiO-66 and a theoretical UiO-66(Ti<sub>100</sub>) are shown in Fig. 2. The experimental CO<sub>2</sub> uptake of UiO-66(Zr<sub>100</sub>) is measured to be 2.2 mmol g<sup>-1</sup>. With 32 and 56 atomic wt% of Ti(IV) ions in UiO-66(Zr/Ti), CO<sub>2</sub> uptake increases drastically from 2.3 to 4 mmol g<sup>-1</sup>, respectively *i.e.* CO<sub>2</sub> uptake increases by 81%. As the theoretical enhancement in CO<sub>2</sub> gravimetric uptake of UiO-66(Ti<sub>100</sub>) is ~19%, other factors contribute to drastically enhanced CO<sub>2</sub> uptake in Ti-exchanged UiO-66. Meanwhile, the random nature of exchange sites precludes a close match of simulated and experimental results for the heterometallic samples, yet, the trend of enhanced CO<sub>2</sub> uptake with increased Ti loading is clearly observed in both



**Fig. 2** CO<sub>2</sub> uptake can be increased by up to 81% through substitution of Zr atoms with Ti at 273 K. Simulations show that Ti loading increases above that synthetic attainable does not deliver further CO<sub>2</sub> uptake. The empty circles represent desorption data, while the solid circles represent adsorption data.

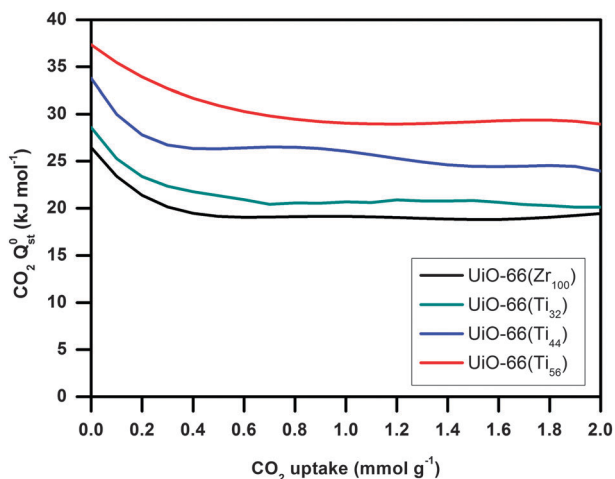


**Fig. 3** Pore size distribution from N<sub>2</sub> gas adsorption, showing that octahedral pores (ca. 9 Å) become significantly smaller following post-synthetic exchange with Ti.

the simulated and experimental data. Notable is that no significant increase for CO<sub>2</sub> uptake is observed in simulations for a theoretical homometallic Ti MOF, a structure not attainable with the present post-synthetic exchange approach.

A decrease in pore size within MOFs can deliver more effective potential energy well-overlap between adsorbent surfaces, and consequently stronger and higher capacity gas adsorption.<sup>31–33</sup> The pore size decrease for the octahedral cages within Ti-exchanged UiO-66 observed in Fig. 3 can be ascribed to the shorter Ti–O<sup>34</sup> compared to Zr–O bonds.<sup>35,36</sup> The pore size distribution, obtained by a DFT fit to N<sub>2</sub> adsorption isotherms, shows two pore sizes at 6 Å and 9 Å, consistent with the tetrahedral and octahedral cages within UiO-66(Zr<sub>100</sub>), respectively.<sup>16</sup> As Ti loading is increased, the tetrahedral cages remain unchanged, whereas the octahedral cages shrink by ~1 Å and become increasingly broader in their distribution. This underlines the randomised nature of the substitution, explaining why significant lattice parameter changes are not observed in XRD (see ESI†).

Fig. 4 shows that the increase in CO<sub>2</sub> adsorption capacity with Ti loading is matched with a similar increase in isosteric



**Fig. 4** Isosteric heat of adsorption as a function of CO<sub>2</sub> uptake increases significantly with Ti loading level.

heat of adsorption across the series, with a  $\sim 10$  kJ mol<sup>-1</sup> enhancement observed. The increases in isosteric heat of adsorptions are also predicted by molecular simulations (Table S4, ESI<sup>†</sup>). Whilst some of this effect can be explained by the inherently stronger adsorption characteristics of Ti(IV) in comparison to Zr(IV),<sup>37</sup> this alone cannot explain the continued increased enthalpy at high CO<sub>2</sub> loadings, where Ti sites will already be saturated. The charge transfer from the metal to the ligand by replacing Zr(IV) with Ti(IV) leads to an increase in CO<sub>2</sub> enthalpy and uptake.<sup>38</sup> (Table S1 and S2 in ESI<sup>†</sup>) This effect correlates well with the diminished pore size, shown in Fig. 3, which will deliver a stronger binding environment for CO<sub>2</sub>.<sup>31,32</sup> This approach may be more promising than typical ligand functionalisation due to these results, as the post-synthetic exchange tailors the entire structure for enhanced CO<sub>2</sub> adsorption regardless of CO<sub>2</sub> partial pressure.

In conclusion, we have shown that the CO<sub>2</sub> uptake of UiO-66(Zr) can be enhanced by 81% *via* post-synthetic exchange with Ti(IV) ions. The trend of enhanced CO<sub>2</sub> uptake in Ti-exchanged UiO-66 is observed in both experimental data and our molecular modelling. The smaller pores in Ti-exchanged UiO-66 enhance the CO<sub>2</sub> isosteric heat  $Q_{st}^0$ , and consequently, increases CO<sub>2</sub> uptake. Additionally, the lower framework density of Ti-exchanged UiO-66 also contributes to higher gravimetric CO<sub>2</sub> uptake. By incorporating Ti(IV) ions into UiO-66, many possibilities are opened up for MOF applications in photocatalytic CO<sub>2</sub> capture and storage, and catalysis.

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## Notes and references

- S. Sircar and T. C. Golden, *Sep. Sci. Technol.*, 2000, **35**, 667–687.
- N. MacDowell, N. Florin, A. Buchard, J. Hallett, A. Galindo, G. Jackson, C. S. Adjiman, C. K. Williams, N. Shah and P. Fennell, *Energy Environ. Sci.*, 2010, **3**, 1645–1669.
- C. H. Lau, P. Li, F. Li, T.-S. Chung and D. R. Paul, *Prog. Polym. Sci.*, <http://dx.doi.org/10.1016/j.progpolymsci.2012.09.006>.

- Y. Xiao, B. T. Low, S. S. Hosseini, T. S. Chung and D. R. Paul, *Prog. Polym. Sci.*, 2009, **34**, 561–580.
- A. W. Thornton, D. Dubbeldam, M. S. Liu, B. P. Ladewig, A. Hill and M. R. Hill, *Energy Environ. Sci.*, 2012, **5**, 7637–7646.
- D. M. D'Alessandro, B. Smit and J. R. Long, *Angew. Chem., Int. Ed.*, 2010, **49**, 6058–6082.
- J. Bao and P. M. Weber, *J. Am. Chem. Soc.*, 2011, **133**, 4164–4167.
- K. Sumida, M. R. Hill, S. Horike, A. Dailly and J. R. Long, *J. Am. Chem. Soc.*, 2009, **131**, 15120–15121.
- P. H. M. Feron, *Int. J. Greenhouse Gas Control*, 2010, **4**, 152–160.
- A. S. Brown and B. C. Freeman, *Environ. Sci. Technol.*, 2011, **45**, 8624–8632.
- K. Sumida, D. L. Rogow, J. A. Mason, T. M. McDonald, E. D. Bloch, Z. R. Herm, T.-H. Bae and J. R. Long, *Chem. Rev.*, 2012, **112**, 724–781.
- T. Ben and S. Qiu, *CrystEngComm*, 2013, **15**, 17–26.
- T. Ben, H. Ren, S. Q. Ma, D. P. Cao, J. H. Lan, X. F. Jing, W. C. Wang, J. Xu, F. Deng, J. M. Simmons, S. L. Qiu and G. S. Zhu, *Angew. Chem., Int. Ed.*, 2009, **48**, 9457–9460.
- K. Konstas, J. W. Taylor, A. W. Thornton, C. M. Doherty, W. X. Lim, T. J. Bastow, D. F. Kennedy, C. D. Wood, B. J. Cox, J. M. Hill, A. J. Hill and M. R. Hill, *Angew. Chem., Int. Ed.*, 2012, **51**, 6639–6642.
- S. R. Caskey, A. G. Wong-Foy and A. J. Matzger, *J. Am. Chem. Soc.*, 2008, **130**, 10870–10871.
- M. Kim and S. M. Cohen, *CrystEngComm*, 2012, **14**, 4096–4104.
- J. H. Cavka, S. Jakobsen, U. Olsbye, N. Guillou, C. Lamberti, S. Bordiga and K. P. Lillerud, *J. Am. Chem. Soc.*, 2008, **130**, 13850–13851.
- H. B. Tanch Jaezet, C. Staudt and C. Janiak, *Dalton Trans.*, 2012, **41**, 14003–14027.
- V. Guillerm, F. Ragon, M. Dan-Hardi, T. Devic, M. Vishnuvarthan, B. Campo, A. Vimont, G. Clet, Q. Yang, G. Maurin, G. Férey, A. Vittadini, S. Gross and C. Serre, *Angew. Chem., Int. Ed.*, 2012, **51**, 9267–9271.
- A. Schaate, P. Roy, T. Preufse, S. J. Lohmeier, A. Godt and P. Behrens, *Chem.-Eur. J.*, 2011, **17**, 9320–9325.
- G. E. Cmarik, M. Kim, S. M. Cohen and K. S. Walton, *Langmuir*, 2012, **28**, 15606–15613.
- M. Kim, J. F. Cahill, H. Fei, K. A. Prather and S. M. Cohen, *J. Am. Chem. Soc.*, 2012, **134**, 18082–18088.
- H. R. Abid, H. M. Ang and S. Wang, *Nanoscale*, 2012, **4**, 3089–3094.
- P. Roy, A. Schaate, P. Behrens and A. Godt, *Chem.-Eur. J.*, 2012, **18**, 6979–6985.
- R. Shannon, *Acta Crystallogr., Sect. A*, 1976, **32**, 751–767.
- Y.-S. Bae, O. K. Farha, J. T. Hupp and R. Q. Snurr, *J. Mater. Chem.*, 2009, **19**, 2131–2134.
- J. R. Li, Y. G. Ma, M. C. McCarthy, J. Sculley, J. M. Yu, H. K. Jeong, P. B. Balbuena and H. C. Zhou, *Coord. Chem. Rev.*, 2011, **255**, 1791–1823.
- A. Schaate, P. Roy, A. Godt, J. Lippke, F. Waltz, M. Wiebcke and P. Behrens, *Chem.-Eur. J.*, 2011, **17**, 6643–6651.
- T. Takei, J. Kawashima, T. Ii, A. Maeda, M. Hasegawa, T. Kitagawa, T. Ohmura, M. Ichikawa, M. Hosoe, I. Kanoya and W. Mori, *Bull. Chem. Soc. Jpn.*, 2008, **81**, 847–856.
- S. S. Kaye and J. R. Long, *J. Am. Chem. Soc.*, 2005, **127**, 6506–6507.
- A. W. Thornton, S. A. Furman, K. M. Nairn, A. J. Hill, J. M. Hill and M. R. Hill, *Microporous Mesoporous Mater.*, 2013, **167**, 188–197.
- A. W. Thornton, K. M. Nairn, J. M. Hill, A. J. Hill and M. R. Hill, *J. Am. Chem. Soc.*, 2009, **131**, 10662–10669.
- Y. Huang, W. Qin, Z. Li and Y. Li, *Dalton Trans.*, 2012, **41**, 9283–9285.
- M. Dan-Hardi, C. Serre, T. O. Frot, L. Rozes, G. Maurin, C. M. Sanchez and G. R. Férey, *J. Am. Chem. Soc.*, 2009, **131**, 10857–10859.
- L. Valenzano, B. Civalieri, S. Chavan, S. Bordiga, M. H. Nilsen, S. Jakobsen, K. P. Lillerud and C. Lamberti, *Chem. Mater.*, 2011, **23**, 1700–1718.
- Y. Gong, L. Andrews, C. W. Bauschlicher, K. S. Thanthirivatte and D. A. Dixon, *Dalton Trans.*, 2012, **41**, 11706–11715.
- R. A. Evarestov, A. V. Bandura and E. N. Blokhin, *J. Phys. Chem. Solids*, 2007, **93**, 012001.
- A. Samanta, T. Furuta and J. Li, *J. Chem. Phys.*, 2006, **125**, 084714–084718.
- R. Lyndon, K. Konstas, B. P. Ladewig, P. D. Southon, P. C. J. Kepernt and M. R. Hill, *Angew. Chem., Int. Ed.*, 2013, DOI: 10.1002/anie.201301126.