Supporting Information –

A Route to Drastic Increase of CO₂ Uptake in Zr Metal Organic Framework UiO-66

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S1. Materials

S1.1. Synthesis of UiO-66

UiO-66 was synthesized according to the work of Behrens and co-workers.¹ 1.00 g (4.48 mmol) of ZrCl₄ and 0.71 g (4.48 mmol) of 1,4-benzenedicarboxylic acid (BDC) were dissolved in 167 mL of dimethylformamide (DMF) and 8.3 mL of deionized water. 8.3 g (68 mmol) of benzoic acid was added. The mixture was heated up at 120 °C for 24 hours. After cooling down to room temperature, a clear phase separation can be observed between the solids and the solvents. The nanoparticles were centrifuged and washed with fresh DMF (at least 8 times). Subsequently, these nanoparticles were dried at 120 °C for 24 hours.

S1.2. Synthesis of TiCl₄(THF)₂

TiCl₄(THF)₂ was synthesized according to the patent of Francesco *et al.*.² 5.0 g (26.4 mol, 2.8968 mL) of TiCl₄ was dissolved in 50 mL of dichloroethane in a 250mL RBF under inert conditions. 7.62 g (105.8 mol, 8.57 mL) of dried tetrahydrofuran (THF) was added at 0 °C to form a yellow solution. 100 mL of sodium dried n-hexane was used to precipitate a yellow powder, which was filtered and washed with n-hexane (2 x 50 mL). It was dried for 2-3 hours over a Schlenk line, and used immediately for post-synthetic exchange.

S1.3. Post-synthetic exchange of UiO-66 with TiCl₄(THF)₂

The post-synthetic exchange of UiO-66 with $TiCl_4(THF)_2$ was carried out according to the work of Cohen and co-workers.³ 0.17gmg (0.3 mmol) of $TiCl_4(THF)_2$ was dissolved in 10 mL of DMF. 0.14 g of UiO-66 was added. The mixture was incubated for 5 and 15 days. The solids were separated from the solvent via centrifugation, and washed with fresh DMF (at least 6 times). The washed solids were immersed in a methanol bath for 3 days. The methanol was replaced every 24 hours. The solids were dried at 40 °C in a vacuum for 24 hours.

S2. Molecular modelling

S2.1 Structural Models

The fully activated structural model of UiO-66 in its hydroxylated form was constructed from the x-ray diffraction data reported by Hafizovic Cavka et al.⁴ Since H atoms cannot be located from x-ray diffraction data, these atoms were added to the organic group and μ_3 -O position to neutralize the overall structure. The constructed periodic model was then optimized by density functional theory (DFT) calculation, in which the both the atomic positions and lattice parameters were fully relaxed. CASTEP⁵ and the GGA-PBE functional⁶ including the dispersion correction were used for the DFT calculations. A kinetic energy plane wave cutoff of 640 eV and 2 x 2 x 2 kpoint sample grid was employed. The convergence criteria for geometry optimization were set as follows; total energy, maximum ionic force, maximum ionic displacement and maximum stress are 1 x 10^{-5} eV per atom, 3 x 10^{-2} eV Å⁻¹, 1 x 10^{-3} Å and 5 x 10^{-2} GPa respectively. The optimized unit cell parameters in UiO-66 matches closely with the experimental and predicted one.⁷⁻⁹ Similarly, the model for the Ti-exchanged UiO-66 is constructed based on the primitive cell of UiO-66. For 50% Ti exchanged UiO-66, half of the Zr atom is replaced with Ti atom and for pure Ti-UiO-66 all the Zr atoms are replaced with Ti atom. Then the structure is fully optimized using DFT calculations. The unit cell parameters for the fully optimized UiO-66, 50% Ti - exchanged and 100% Ti-UiO-66 are 20.885 Å, 20.643 and 20.342 Å. The unit cell parameter of 50 % Tiexchanged UiO-66and 100 % Ti-UiO-66 showed a slight decrease when compared to pure UiO-66. This is due to the shortening of Ti-O bond length when compared to Zr-O.

S2.2 Partial Charge calculations

The partial charges for UiO-66 framework atoms are taken from earlier work.⁸ For 50% Ti-exchanged UiO-66and 100 % Ti-UiO-66, the partial charges are calculated based on fragmental cluster using density functional theory (DFT) as implemented in DMol^{3,10} The DFT calculation was performed on a cluster model cleaved from the unit cell. The PW91 functional along with the Double-ξ numerical polarization (DNP) basis set was used in the DFT calculations, which is comparable to 6-31G(d,p) Gaussian-type basis set. DNP basis set incorporates p-type polarization into hydrogen atoms and d-type polarization into heavier atoms. From the DFT calculations, the atomic charges were evaluated by fitting to the electrostatic potential using the Merz-Kollman (MK) scheme as listed in Table S1 and S2.

S2.3 Methods

The pore volumes of the adsorbents were obtained according to the thermodynamic method proposed by Myers and Monson.¹¹ Universal force field (UFF)¹² was used to describe the Lennard-Jones (LJ) interactions of the framework atoms while the LJ parameters for helium were taken from the work of Talu and Myers.¹³ The accessible surface area is calculated from a simple Monte Carlo integration technique where the center of the mass of the probe molecule with hard sphere is rolled over the framework surface. In this method, a nitrogen probe molecule is used to calculate the accessible surface area. Pore size distribution is calculated using Monte Carlo technique based on the procedure stated elsewhere.¹⁴ The structural properties such as accessible surface

area, free volume, pore limiting diameter, maximum pore diameter and pore size distribution are calculated using the program poreblazer_V3.0.¹⁵

The adsorption of pure CO₂ was simulated by grand canonical Monte Carlo (GCMC) method.¹⁶ Because the chemical potentials of adsorbate in adsorbed and bulk phases are identical at thermodynamic equilibrium, GCMC simulation allows one to relate the chemical potentials of adsorbate in both phases and has been widely used for the simulation of adsorption. The framework atoms are kept frozen during simulation. The LJ interactions were evaluated with a spherical cutoff equal to half of the simulation box with long-range corrections added; the Coulombic interactions were calculated using the Ewald sum method. The number of trial moves in a typical GCMC simulation was 2×10^7 , though additional trial moves were used at high loadings. The first 10^7 moves were used for equilibration and the subsequent 10^7 moves for ensemble averages. Five types of trial moves were attempted in GCMC simulation, namely, displacement, rotation, and partial regrowth at a neighboring position, entire regrowth at a new position, and swap with reservoir. Unless otherwise mentioned, the uncertainties are smaller than the symbol sizes in the figures presented.

Canonical ensemble (NVT) simulation is performed to estimate the isosteric heat of adsorption at infinite dilution. A single adsorbate molecule is subjected to three types of trial moves employed in the NVT simulation, namely, translation, rotation and regrowth. The isosteric heat at infinite dilution is calculated from

$$q_{\rm st}^{\rm o} = RT - \left(U_{\rm total}^{\rm o} - U_{\rm intra}^{\rm o}\right) \tag{1}$$

where U_{total}^{0} is the total adsorption energy of a single molecule with adsorbent and U_{intra}^{0} is the intramolecular interaction of a single gas molecule in bulk phase.

The adsorbate CO₂ was mimicked as three-site model to account for the quadrupole moment. The C–O bond length in CO₂ was 1.18 Å and the bond angle \angle OCO was 180°. The charges on C and O atoms were +0.576e and -0.288e (e = 1.6022×10^{-19} C the elementary charge), resulting in a quadrupole moment of -1.29×10^{-39} C·m². The LJ parameters for CO₂ were $\sigma_{\rm C} = 2.789$ Å, $\varepsilon_{\rm C} = 29.66$ K, $\sigma_{\rm O} = 3.011$ Å, $\varepsilon_{\rm O} = 82.96$ K.¹⁷

The interactions of gas-adsorbent and gas-gas were modeled as a combination of pairwise site-site Lennard-Jones (LJ) and Coulombic potentials. The LJ potential parameters of the framework atoms are adopted from and Dreiding force field.¹⁸ However, the DREIDING force field parameter is not available for Zr and Ti atom, thus the parameter from the Universal force field (UFF)¹⁹ was adopted. To match the experimental CO₂ isotherm the DREIDING force field parameters were rescaled. A reasonably good agreement is obtained between the simulated CO₂ isotherm and experimental data at 298 K in UiO-66(Zr). The same force field parameters were used to predict the CO₂ isotherm in 50% Ti-exchanged UiO-66 and 100% Ti-UiO-66 framework at 273 K and 298 K. This type of adjustment of force field parameters has been widely done in previous works.²⁰⁻²³ Table S3 lists the set of rescaled LJ parameters used in this study. The Lorentz-Berthelot combining rules were used to calculate the cross LJ interaction parameters. Table S4 summarizes the free volume $V_{\rm free}$, accessible surface area, pore limiting and maximum pore diameter and , isosteric heat $q_{\rm st}^0$, calculated in this work

S3. Adsorption isotherms

Gas adsorption isotherms between the range of 0 - 120 kPa were measured by a volumetric approach using a Micrometrics ASAP 2420 instrument. All the samples

were transferred to pre-dried analysis tubes and sealed with Transeal stoppers. UiO- $66(Zr_{100})$ was evacuated and activated at 383 K under a 10^{-6} dynamic vacuum for 24 hours. UiO- $66(Zr_{54}/Ti_{46})$, and UiO- $66(Zr_{51}/Ti_{49})$ were evacuated and activated at 298 K under a 10^{-6} dynamic vacuum for 24 hours. Ultra-high purity N₂ and CO₂ gases were used for these experiments. N₂ adsorption measurements were conducted at 77 K, while CO₂ adsorption measurements were done at 273 and 298 K.

S4. Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES)

The samples were analysed by ICP-OES after ashing at 500 C in a furnace. The ash residue was digesting by a mixture of HNO3, HF, and milli-Q water. Certified multielement solutions were also used to check the accuracy of the calibration and method. As Ti may reach with HF to form TiF_4 ,²⁴ the quantified Ti content obtained from ICP-OES may not be accurate. Hence, we did some back calculations based on Zr content. First, we measured the Zr content in UiO-66(Zr₁₀₀), and determined that there was 30.7 wt. % of Zr. We also measured the Zr content in UiO-66 MOFs that had been exchanged with Ti for 1, 5 and 15 days. The Zr content in these samples is 26.4, 25.1, and 23.9 wt. %, respectively. The differences between Zr content in UiO-66(Zr₁₀₀) and Ti-exchanged UiO-66 were thus assigned to be the quantity of Ti (in wt. %) in the MOFs studied here. To determine the atomic wt. % of Ti in these MOFs, the Ti content in wt. % was multiplied by the Zr/Ti atomic ratio.

For example, Ti content in UiO-66 exchanged with Ti for 15 days is calculated and determined to be:

(30.7 - 23.9)/23.9 *2 = 51 atomic wt.%

S5. X-ray fluorescence (XRF) spectroscopy

XRF analysis was carried out using a Panalytical PW2404 WDXRF. The samples were fused in lithium borate flux and silica was added to increase the sample bulk and make a suitable glass bead. The samples were then analysed with the General Fusion application. The sample weights were between 9 and 28 mg. Hence the weighing errors add an uncertainty between 5 and 10 %. The back calculation approach was also used to determine the Ti content in UiO-66 that has been exchanged with Ti for 1 and 5 days. Due to different sample preparation approaches (ashing in ICP-OES vs. mixing with silica in XRF), the Zr content in the MOFs tested is different. The Zr content in UiO-66 measured by XRF is 25 wt. %, while Zr content in 1 and 5 day samples is 24 and 22 wt.%, respectively. Thus, the atomic wt. % of Ti in these samples is 8 and 24 atomic wt. %, respectively. Taking into consideration the uncertainty (due to weight), the calculated Ti content from XRF results correlate well to those obtained from ICP-OES.

S6. Powder X-ray diffraction (PXRD)

PXRD data were collected using a Philips X'Pert Multipurpose X-Ray Diffractometer ($Cu_{k\alpha}$, $\lambda = 1.54056$ Å) over a 2 θ range of 5 to 40 °. The step time was 69.2 s and the step count was 0.02 °.

Table S1. Atom partial charges in 50 % Ti-exchanged UiO-66 and the atom types arelabelled as shown in Figure S1.

Atom Type	Zr	Ti	01	02	03	O4
Charge	2.509	2.115	-1.509	-0.852	-0.714	-0.589
Atom Type	O5	O6	C1	C2	C3	C4
Charge	-0.698	-0.628	0.812	0.709	0.750	-0.034
Atom type	C5	C6	C7	C8	C9	C10
Charge	-0.083	-0.049	-0.194	-0.145	-0.139	-0.104
Atom type	H1	H2	Н3	H4	Н5	
Charge	0.606	0.168	0.158	0.173	0.169	

Table S2.	Atom	partial	charges	in	100	%	Ti-	UiO	-66	and	the	atom	types	are	labelle	d as
shown in F	igure S	S2.														

Atom Type	Ti	O1	O2	O3	C1	C2
Charge	2.045	-0.580	-1.487	-0.651	-0.164	0.631
Atom Type	C3	H1	H2			
Charge	-0.021	0.179	0.632			

Table S3. Rescaled LJ potential parameter for the framework atoms in UiO-66 and Ti-exchanged UiO-66.

Ti	Zr	С	0	Н
2.69	2.64	3.30	2.88	2.71
7.27	29.52	40.68	40.94	6.50
	Ti 2.69 7.27	Ti Zr 2.69 2.64 7.27 29.52	Ti Zr C 2.69 2.64 3.30 7.27 29.52 40.68	Ti Zr C O 2.69 2.64 3.30 2.88 7.27 29.52 40.68 40.94

Table S4 Framework Density $\rho_{\rm f}$, Free Volume $V_{\rm free}$, Accessible Surface Area, Pore Limiting and Maximum Pore Diameter, and Isosteric heat q_{st}^0 Calculated From This Work.

	V_{free} (cm ³ /g)	Surface Area (m ² /g)	Pore Limiting Diameter (Å)	Maximum Pore Diameter (Å)	CO_2 q_{st}^0 (kJ/mol)
UiO-66(Zr ₁₀₀)	0.42	1180	3.70	7.92	21.34
UiO-66(Ti ₅₀)	0.45	1251	3.66	7.82	23.28
UiO-66(Ti ₁₀₀)	0.46	1260	3.53	7.84	27.56



Figure S1. Cluster used for calculating partial charges on 50 % Ti- exchanged UiO-66 atoms. The terminations of the cluster were saturated with methyl groups to minimize the boundary effects.



Figure S2. Cluster used for calculating partial charges on 100 % Ti-exchanged UiO-66 atoms. The terminations of the cluster were saturated with methyl groups to minimize the boundary effects.



Figure S3 Simulated pore diameters of UiO-66(Zr_{100}) – black, UiO-66(Ti_{50}) – purple, UiO-66(Ti_{100}) – green.



Figure S4 Comparison of experimental CO₂ uptakes of UiO-66(Zr_{100}) (black solid circle), UiO-66(Ti_{32}) (cyan solid circle), UiO-66(Ti_{44}) (blue solid circle), UiO-66(Ti_{56}) (red solid circle) with simulated CO₂ uptake of UiO-66(Zr_{100}) (black empty triangle), UiO-66(Ti_{50}) (purple empty triangle), and UiO-66(Ti_{100}) (green empty triangle) at 298 K.



Figure S5 PXRD data of UiO-66(Zr_{100}) (black), UiO-66(Ti_{44}) (blue), and UiO-66(Ti_{56}) (red).

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