# Flying MOFs: Polyamine-containing fluidized MOF/SiO<sub>2</sub> hybrid materials for CO<sub>2</sub> capture from post-combustion flue gas

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**Supporting information** 

#### Experimental and general information

#### Chemicals.

All chemicals were used as received from Sigma-Aldrich without further purification. Triethylamine (TEA), N,N-dimethylformamide (DMF), chloroform (CHCl<sub>3</sub>) and methanol (MeOH), branched polyethyleneimine (PEI, M<sub>w</sub> ~ 800), tetraethylenepentamine (TEPA), diethyelenetriamine (DETA), N,N'-dimethylethylenediamine (mmen), trishydroxyphosphine (THP, FeCl<sub>3</sub>·6H<sub>2</sub>O  $AI(NO_3)_3 \cdot 9H_2O_1$ 90%),  $Cr(NO_3)_3 \cdot 9H_2O_1$  $Co(NO_3)_2 \cdot 6H_2O$ ,  $ZrOCl_2 \cdot 8H_2O$ , Zn(NO<sub>3</sub>)<sub>2</sub>·9H<sub>2</sub>O, Fe(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O, Mg(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O, 1,4-benzenedicarboxylic acid (H<sub>2</sub>BDC), 1,3,5benzenetricarboxylic acid (H<sub>3</sub>BTC), 2-aminoterephthalic acid (H<sub>2</sub>BDC(NH<sub>2</sub>)), monosodium 2sulfoterephthalate (H<sub>2</sub>BDC(SO<sub>3</sub>Na)), 2,5-dihydroxyterephthalic acid (H₄DOBDC). 2methylimidazole (HMeIM), benzimidazole (HBnIM) and tetrakis(4-carboxyphenyl)-porphyrin (H<sub>4</sub>TCPP). 1,3,6.8-tetrakis(p-benzoic acid)pyrene (H<sub>4</sub>TBAPy)<sup>1</sup> and 4.4'-dihydroxibiphenyl-3.3'dicarboxylic acid (H<sub>4</sub>DOBPDC)<sup>2</sup> were synthetized according to the published procedure. Mesoporous silica(A) [75-250 µm] was kindly supplied by our commercial partner (physicochemical properties are reported in our previous work<sup>3</sup>). Mesoporous silica was degassed at 120 °C overnight under vacuum to remove the adsorbed water prior to use.

Ligand salt precursors. Na<sub>2</sub>BDC and Na<sub>3</sub>BTC ligand salt precursors were prepared from their acid form in water with the stoichiometric amount of NaOH necessary to deprotonate the carboxylic acid of the organic linker followed by a purification step via precipitation in acetone. Alternatively, ligand salt precursor solutions for H<sub>2</sub>BDC(NH<sub>2</sub>) and H<sub>4</sub>TCPP were directly prepared with the stoichiometric amount of TEA, thereby skipping the step of isolating the ligand salt. H<sub>2</sub>BDC(SO<sub>3</sub>Na) and HMeIM were directly dissolved in water.

#### Characterization techniques.

Scanning electron microscopy (SEM) images were acquired on a FEI Quanta 200 FEG Analytical Scanning Electron Microscope using a beam energy of 15 kV. Transmission electron microscopy (TEM) experiments were performed in a Hitachi 7000 100 kV with AMT digital camera. N<sub>2</sub> sorption isotherms were measured in a Micromeritics ASAP (Accelerated Surface Area and Porosimetry) 2020 System. Samples were weighted into tubes with seal frits and degassed under vacuum (<500  $\mu$ m Hg) with heating. They were initially heated at 150 °C and held for 4 hours, and finally cooled to room temperature and backfilled with N<sub>2</sub>. The samples were re-weighted before analysis. The analysis adsorptive was N<sub>2</sub> at 77K. A multi-point BET surface area was determined from 6 measurements at relative pressures (P/Po) ranging from 0.050 to 0.300 satisfying the four criteria suggested by Rouquerol<sup>4</sup>. Single point adsorption total pore volume was measured near saturation pressure (Po  $\approx$  770 mmHg). Adsorption average pore width was also calculated. Pore size distribution plot was determined by BJH method with Halsey thickness curve equation and Faas BJH correction. **X-ray Fluorescence (XRF)** analysis were performed in a ARL Thermo Scientific (Ecublens, Switzerland) Perform'X Wavelength-Dispersive X-ray Fluorescence (WDXRF) equipped with an X-ray tube 5GN-type Rh target with ultra-thin 30 µm Be window to maximize light element response. 4000 W power supply for 60 kV max or 120 mA max with two detectors (flow proportional and scintillation) and seven analyzer crystals to achieve a broad elemental range. **X-ray diffraction (XRD)** patterns were recorded using a Panalytical Empyrean X-ray diffractometer with Cu K $\alpha$  radiation ( $\lambda$ =1.54778 Å). **Attenuated total reflection (ATR) FTIR** spectroscopy measurements were performed in the range of 4000–400 cm<sup>-1</sup> with a Perkin Elmer Spectrum 100 FTIR spectrometer.

## Solid state synthesis of MOF/SiO<sub>2</sub> hybrid materials

### <u>19 wt.% (Cr)MIL-101(SO<sub>3</sub>H)/SiO<sub>2</sub> (see HyperMOF-A2a in reference<sup>3</sup>)</u>

 $1^{st}$ ) Ligand impregnation: 10 mL of an aqueous solution containing 2 g H<sub>2</sub>BDC(SO<sub>3</sub>Na) was impregnated to 5 grams of evacuated mesoporous silica(A) and was dried at 50 °C under vacuum in a rotavapor for 2 h.

 $2^{nd}$ ) Ligand acidification: the resulting dry material [H<sub>2</sub>BDC(SO<sub>3</sub>Na)/Silica(A)] was placed in a tubular calcination reactor where was first treated with a nitrogen flow saturated with concentrated HCI (37%) for 2 hours at room temperature and after purged with a nitrogen flow for 2 h to remove the excess of HCI.

 $3^{rd}$ ) Metal impregnation: 7.5 mL of an aqueous solution containing 1.5 gr of Cr(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O in 7.5 mL of H<sub>2</sub>O was impregnated to the compound [H<sub>2</sub>BDC(SO<sub>3</sub>H)/Silica(A)]. The resulting solid [Cr(NO<sub>3</sub>)<sub>3</sub>/H<sub>2</sub>BDC(SO<sub>3</sub>H)/Silica(A)] was finally dried at 50 °C under high vacuum in a rotavapor for 2 h. All the impregnation steps were done via incipient wetness impregnation.

 $4^{th}$ ) Synthesis conditions and washing: The solid [Cr(NO<sub>3</sub>)<sub>3</sub>/H<sub>2</sub>BDC(SO<sub>3</sub>H)/Silica(A)] was separated in two 125 mL stainless steel Parr autoclave (> 40 % void space) at 190 °C for 24 h after adjusting the water contain of the solid to 15-20 wt.%. After cooling the autoclave, the resulting products were thoroughly washed with distillated water in a filtration funnel.

5<sup>th</sup>) Washing treatment and activation: the material was washed overnight in a Soxhlet with MeOH. All the materials were activated overnight at 120 °C under vacuum.

A second solid state synthesis was carried out by using 19 wt.% (Cr)MIL-101(SO<sub>3</sub>H)/SiO<sub>2</sub> to obtain 40 wt.% (Cr)MIL-101(SO<sub>3</sub>H)/SiO<sub>2</sub>. To prepare 4.9 wt.%\_(Cr)MIL-101(SO<sub>3</sub>H)/SiO<sub>2</sub>, 0.5 g of H<sub>2</sub>BDC(SO<sub>3</sub>Na) and 0.35 gr of Cr(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O were used instead. Same procedure was followed for preparing 5.6 wt.% (Cr)MIL-100/SiO<sub>2</sub>, 0.2 gr of H<sub>3</sub>BTC and 0.35 gr of CrCl<sub>3</sub>·6H<sub>2</sub>O were used instead.

# 30 wt.% (Zr)UiO-66(NH<sub>2</sub>) (see HyperMOF-E2a in reference<sup>3</sup>)

Solid state synthesis was followed to obtain 37.6 wt.% (Zr)UiO-66(NH<sub>2</sub>) with the following variations: 1<sup>st</sup>) 1.5 gr of H<sub>2</sub>BDC(NH<sub>2</sub>), 2.35 mL of TEA and 10 mL H<sub>2</sub>O; 2<sup>nd)</sup> conventional acidification step; 3<sup>rd</sup>) 2.5 gr of ZrOCl<sub>2</sub>·8H<sub>2</sub>O in 7.5 mL of H<sub>2</sub>O; 4<sup>th</sup>) 15-20 wt.% DMF and 120 °C for 12h; and 5<sup>th</sup>) conventional washing and activation treatment.

Moderate concentrations of  $(Zr)UiO-66(NH_2)$  on SiO<sub>2</sub> were obtained via incipient wetness impregnation in one step of metal and ligand mixture in DMF as following: 20, 40 and 80 mg of H<sub>2</sub>BDC(NH<sub>2</sub>), and 50, 100 and 200 mg of ZrOCl<sub>2</sub>·8H<sub>2</sub>O in 2 mL of DMF per gram of SiO<sub>2</sub> for 1.5, 4.2, and 6.8 wt.% MOF loadings, respectively. The materials also were heated at 120 °C for 12h and conventionally washed/activated. Same procedure was followed for preparing 4.7 wt.% (Zr)UiO-66/SiO<sub>2</sub> (40 mg of H<sub>2</sub>(BDC) and 100 of ZrOCl<sub>2</sub>·8H<sub>2</sub>O in 2 mL of DMF per gram of SiO<sub>2</sub>), 3.5 wt.% (Zr)PCN-222/SiO<sub>2</sub> (50 mg of H<sub>4</sub>TCPP and 100 of ZrOCl<sub>2</sub>·8H<sub>2</sub>O in 2 mL of DMF per gram of SiO<sub>2</sub>), 4.2 wt.% (Zr)NU-1000/SiO<sub>2</sub> (50 mg of H<sub>4</sub>TBAPy and 100 of ZrOCl<sub>2</sub>·8H<sub>2</sub>O in 2 mL of DMF per gram of SiO<sub>2</sub>), 3.9 wt.% (Al)MIL-53(NH<sub>2</sub>)/SiO<sub>2</sub> (40 mg of H<sub>2</sub>BDC(NH<sub>2</sub>) and 100 of Al(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O in 2 mL of DMF per gram of SiO<sub>2</sub>), 5.3 wt.% (Fe)MIL-100/SiO<sub>2</sub> (40 mg of H<sub>3</sub>BTC and 100 of Fe(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O in 2 mL of DMF per gram of SiO<sub>2</sub>),

#### 35.1 wt.% (Zn)ZIF-8 (see HyperMOF-G1a in reference<sup>3</sup>)

Solid state synthesis was followed to obtain 35.1 wt.% (*Zn*)*ZIF-8* with the following variations:  $1^{st}$ ) 2.4 gr of Zn(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O in 10 mL of MeOH;  $2^{nd}$ ) no acidification step;  $3^{rd}$ ) 1.8 gr of HmeIM in 7.5 mL MeOH;  $4^{th}$ ) TEA vapor treatment; and  $5^{th}$ ) conventional washing and activation treatment.

Moderate concentrations of (Zn)ZIF-8 on SiO<sub>2</sub> were obtained via incipient wetness impregnation in one step of metal and ligand mixture in MeOH as following: 60 and 120 mg of HmeIM, and 80 and 160 mg of Zn(NO<sub>3</sub>)<sub>2</sub>·9H<sub>2</sub>O in 2 mL of MeOH per gram of SiO<sub>2</sub> for 4.6 and 7.8 wt.% MOF loadings, respectively. The materials were also treated with TEA vapor and conventionally washed/activated. Same procedure was followed for preparing 4.9 wt.% (Zn)ZIF-7/SiO<sub>2</sub> (80 mg of HmeIM and 80 of Zn(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O in 2 mL of MeOH per gram of SiO<sub>2</sub>) and 5.2 wt.% (Co)ZIF-67/SiO<sub>2</sub> (140 mg of HBnIM and 80 of Zn(NO<sub>3</sub>)<sub>2</sub>·9H<sub>2</sub>O in 2 mL of MeOH per gram of SiO<sub>2</sub>).

#### **Packed-bed reactor**



Scheme S1. Process flow diagram of the RTI's packed bed reactor.

A laboratory-based automated packed-bed reactor (PBR) system (developed by RTI) was used to evaluate the sorbent's  $CO_2$  capture performance by executing multicycle  $CO_2$ absorption/regeneration test conditions with minimal operator interaction. As shown in Scheme 1, the PBR system consists of three main sections: (1) feed gas generation, (2) packed-bed reactor, and (3) gas analysis. The feed gas generation system consists of a bank of electronic gas mass flow controllers and a temperature-controlled water saturator. Water content in the gas stream leaving the saturator is controlled and adjusted by increasing or decreasing the saturator temperature. This arrangement allows for the generation of a wide range of feed gas compositions, including wet and dry gas mixtures. All lines downstream of the saturator are heat traced to avoid H<sub>2</sub>O condensation and to preheat the gas to the reactor conditions. The gas then enters the top of the packed-bed reactor, flows downward through the sorbent bed, and exits the reactor bottom. The packed-bed reactor is a 0.5 in. OD, 8 in. tall stainless-steel tube with temperature control enabled by well-tuned band heaters. A thermocouple is situated in the middle of the sorbent bed to measure the sorbent bed temperature during absorption and regeneration. The reactor effluent is cooled to 10–12°C in a tube-in-tube heat exchanger to remove excess water which is collected in a knock-out pot. Exiting the knock-out pot is a gas stream containing

1–2 vol% H<sub>2</sub>O. The CO<sub>2</sub> and SO<sub>2</sub> concentrations in the reactor effluent were continuously monitored using a Horiba VA-3000 analyzer. Two pairs of solenoid switching valves are used to direct the gas flow through or bypass the reactor and saturator, allowing the PBR to operate highly flexible experimental procedures. Process measurements are taken and control achieved using a RTI-developed data acquisition and process control system.



Figure S1. Image of the PBR.

#### Fluidized-bed reactor



Scheme S2. Process flow diagram of the RTI's visual-fluidized bed reactor system (vFBR).

The system consisted of the gas feed manifold equipped with N<sub>2</sub> and CO<sub>2</sub> mass flow controllers and a water pump. The gas and water feed streams are merged at the heating coil where the water is heated and evaporated, producing a humid gas stream leaving the heater. The humid gas stream is introduced at the bottom of the jacketed 1" ID borosilicate glass (fluidized bed) reactor through a glass frit which serves as a gas distributor and support for sorbent. The reactor jacket is filled with silicone oil and temperature controlled by a circulation bath for both heating and cooling during the test. The reactor effluent leaves the reactor through the top and enters in a cyclone to remove any entrained solids. The gas stream is sent to a condenser to remove water and finally fed to a CO<sub>2</sub> analyzer to monitor the concentration during the experiment. The system is heat-traced to prevent water condensation and equipped with safety limits to mitigate unsafe conditions and equipment damage should an unexpected temperature or pressure excursion occurs. The reactor is loaded with 50 g of sorbent, which fills about 20-30% of the reactor volume in a typical run.



Figure S2. Image of the FBR.

# 2. Characterization

MOF/SiO <sub>2</sub> material	MOF (wt%)	S <sub>BET</sub> (m²/g)
(Cr)MIL-101(SO <sub>3</sub> H)	40.0	865
(Cr)MIL-101(SO <sub>3</sub> H)	19.1	486
(Cr)MIL-101(SO <sub>3</sub> H)	4.9	258
(Zr)UiO-66(NH <sub>2</sub> )	37.6	434
(Zr)UiO-66(NH <sub>2</sub> )	4.2	243
(Zn)ZIF-8	35.1	346
(Zn)ZIF-8	4.6	241
(Cr)MIL-100	4.6	260
(Zr)PCN-222	7.9	297
(Zr)NU-1000	4.2	302

Table S1. MOF loading and surface area for selected MOF/SiO<sub>2</sub>.

 $S_{BET}$  (SiO<sub>2</sub>) = 256 m<sup>2</sup>/g



Figure S3. FTIR spectra for (Cr)MIL-101(SO $_3$ H)/SiO $_2$  at varying loadings compared to pure MOF (100 wt.%)



Figure S4. FTIR spectra for (Zr)UiO-66(NH<sub>2</sub>)/SiO<sub>2</sub> at varying loadings compared to pure MOF (100 wt.%)



Figure S5. FTIR spectra for (Zn)ZIF-8/SiO<sub>2</sub> at varying loadings compared to pure MOF (100 wt.%)

**Table S2**. Resume of the performance and selected characteristics for polyamine coordinated to  $(Cr)MIL-101(SO_3H)/SiO_2$  at varying loadings in a packed bed reactor under simulated flue gas conditions.

MOF	polyamine	Ν	S	N : S	CO <sub>2</sub>	Deactivation	CO <sub>2</sub> :N
(wt.%)	type	(wt.%) <sup>a</sup>	(wt.%) <sup>a</sup>	molar	(wt.%) <sup>b</sup>	(%) <sup>c</sup>	molar <sup>d</sup>
100	TEPA	6.9	6.1	2.6	2.5	28	0.14
40.0	TEPA	5.1	1.2	9.6	3.4	18	0.26
19.1	TEPA	3.1	0.7	10.0	3.4	24	0.43
19.1	DETA	1.7	0.6	6.4	1.1	62	0.31

<sup>a</sup> Calculated by elementary analysis. <sup>b</sup> CO<sub>2</sub> adsorption capacity at the 1<sup>st</sup> cycle measured in a PBR under simulated flue gas conditions. <sup>c</sup> 10 cycles CO<sub>2</sub> adsorption deactivation. <sup>d</sup> Calculated considering one N of the polyamine coordinated to the Cr or sulfonic acid and then non-active for CO<sub>2</sub> capture.

**Table S3.** Resume of the performance and selected characteristics of two PEI/MOF/SiO<sub>2</sub> evaluated for  $CO_2$  capture in a packed bed reactor under simulated flue gas conditions before and after 250-cycle run.

MOF	PEI	MOF	Ν	С	Н	CO <sub>2</sub>	Deactivation
	(wt%)	(wt%)	(wt%)	(wt%)	(wt%)	Capacity	(%) <sup>b</sup>
			[fresh/used]	[fresh/used]	[fresh/used]	(%) <sup>a</sup>	
ZIF-8	-	4.6	1.66	3.79	0.82	-	-
	35	3.0	13.38/12.05	22.36/20.57	4.84/4.35	12.5	8
ZIF-7	-	4.9	1.63	4.46	0.68		
	35	3.2	13.09/11.87	22.24/20.26	4.60/4.38	12.0	12

<sup>a</sup>CO<sub>2</sub> capacity measured at the 50<sup>th</sup> cycle. <sup>d</sup> Deactivation calculated by difference between capacities at the 10<sup>th</sup> cycle and 250<sup>th</sup> cycle.

**Table S4.** Resume of the performance and selected characteristics for PEI/ZIF-8/SiO<sub>2</sub> evaluated for  $CO_2$  capture in a packed bed reactor under simulated flue gas conditions and the presence of contaminants.

	Ν	С	Н	S	CO <sub>2</sub>	Deactivation
	(wt%)	(wt%)	(wt%)	(wt%)	(%) <sup>a</sup>	(%) <sup>b</sup>
fresh	13.38	22.36	4.84	-	-	-
0 ppm	12.05	20.57	4.35	-	12.5	1.7
50 ppm SO <sub>2</sub>	11.74	19.69	4.7	1.8	12.41	31.1
200 ppm SO	9.1	16.0	4.33	6.3	12.86	85.7
200 ppm NO <sub>x</sub>	12.5	20.6	4.5	-	13.29	12.8
1% H₂S <sup>d</sup>	11.3	18.3	5.5	0.4	10.6	1.45

<sup>a</sup> CO<sub>2</sub> adsorption capacity at the 10<sup>th</sup> cycle measured in a PBR under simulated flue gas conditions. <sup>b</sup> 100 cycles CO<sub>2</sub> adsorption deactivation. <sup>c</sup> Dry conditions were used because safety issues because H<sub>2</sub>S cylinder also contains H<sub>2</sub>.



Figure S6. FTIR spectra of TEPA coordinated on bulk (Cr)MIL-101(SO<sub>3</sub>H) before and after 10 cycle run in a packed bed reactor under simulated flue gas conditions.



Figure S7. FTIR spectra for hybrid sorbent  $PEI/(Zn)ZIF-8/SiO_2$  after 100 cycle test under the presence of 0, 50 and 200 ppm of SO<sub>2</sub>.



Figure S8. CO<sub>2</sub> capture for reported bulk MOFs under dry and wet conditions.



Figure S9. CO2 capture under simulated flue gas conditions for 35 wt.% PEI impregnated on Silica(A) (used in this work) compared to Silica(D) and SBA-15.



Figure S10. Scale up from gram to Kg scale of PEI/MOF/SiO<sub>2</sub> fluidized CO<sub>2</sub> sorbent.

	Compound	Commercial- Scale Cost (\$/kg)	Cost per kg sorbent produced (\$/kg)	Cost Ratio to Sorbent Production
Silica	Silicycle 150 Å	15.4	9.24	53.1%
			+9.24	+53.1%
MOF	Zinc Nitrate Hexahydrate	lexahydrate 1.9		0.6%
	2-Methylimidazole	4.9	0.18	1.0%
	Triethylamine	1.5	0.11	0.7%
			+0.35	+2.3%
Solvents	Methanol	0.4	1.02	6.4%
	Chloroform	1.1	1.6	7.9%
			+2.6	+14.3%
Amine	600 MW PEI	22	7.7	30.3%
			+7.7	+30.3%
		Total Cost	19.89	100%



Figure S11. Resume of cost evaluation.

# References

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