Supporting Information

Amine Functionalized Zirconium Metal-Organic Framework as an Effective Chemiresistive Sensor for Acidic Gases

Marilyn Esclance DMello^[a,b], Nalini G. Sundaram^[a] Akash Singh,^c Abhishek K. Singh,^c and Suresh Babu Kalidindi^{*[a]}

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1. General information

1.1.Reagents

Zirconium tetrachloride anhydrous (ZrCl₄), Hydrochloric acid (HCl, 35 %), Benzoic acid and Methanol (CH₃OH, 99%) was purchased from Merck Life Science Pvt. Ltd. Mumbai, India. Terephthalic acid (C₈H₆O₄) was provided by SDFCL, Mumbai. 2-aminoterephthalic acid (C₈H₇NO₄ 99 %) was purchased from Alfa Aesar. 2-hydroxyterephthalic acid was supplied by TCI chemicals. N, N Dimethylformamide (DMF, HCON(CH₃)₂) was bought from Avra Synthesis Pvt. Ltd, Hyderabad, India.

1.2.Characterization

Powder X-ray diffraction (PXRD) patterns were recorded on Bruker with Cu K α radiation (λ = 1.5418 Å) operating at 20 kV and 10 mA. The specific surface area, pore volume and pore size of the samples were measured using a BELSORP-mini II instrument. FTIR was measured using Bruker Alpha-T.

2. Synthesis methods

2.1. Synthesis of UiO-66 (Zr)

In a typical synthesis, $ZrCl_4$ (0.233 g, 0.99 mmol) was dissolved in 0.16 mL of conc. HCl and 10 mL DMF solvent in a 30 mL screw-cap glass vial. This was followed by the addition of terephthalic acid (0.181 g, 1.08 mmol) and benzoic acid (0.244 g, 1.99 mmol) to the above solution. Once all the precursors were dissolved, the vial was sealed and placed in the oven at 120 °C for 48 hrs. The precipitate was washed with DMF and methanol thrice and dried under vacuum to give a white colour product of UiO-66.

2.2. Synthesis of NH₂-UiO-66 (Zr)

In a typical synthesis, $ZrCl_4$ (0.233 g, 0.99 mmol) was dissolved in 0.16 mL of conc. HCl and 10 mL DMF solvent in a 30 mL screw-cap glass vial. This was followed by the addition of 2-aminoterephthalic acid (0.181 g, 0.99 mmol) and benzoic acid (0.244 g, 1.99 mmol) to the above solution. Once all the precursors were dissolved, the vial was sealed and placed in the oven at 120 °C for 48 hrs. The precipitate was washed with DMF and methanol thrice and dried under vacuum to give a cream colour product of NH₂-UiO-66.

2.3. Synthesis of OH-UiO-66 (Zr)

In a typical synthesis, ZrCl₄ (0.233 g, 0.99 mmol) was dissolved in 0.16 mL of conc. HCl and 10 mL DMF solvent in a 30 mL screw-cap glass vial. This was followed by the addition of 2-hydroxyterephthalic acid (0.181 g, 0.99 mmol) and benzoic acid (0.244 g, 1.99 mmol) to the above solution. Once all the precursors were dissolved, the vial was sealed and placed in the oven at 120 °C for 48 h. The precipitate was washed with DMF and methanol thrice and dried under vacuum to give a white colour product of OH-UiO-66.

2.4. Synthesis of NH₂-OH-UiO-66 (Zr)

In a typical synthesis, ZrCl₄ (0.233 g) was dissolved in 0.16 mL of conc. HCl and 10 mL DMF solvent in a 30 mL screw-cap glass vial. This was followed by the addition of 2-aminoterephthalic acid (0.09 g), 2-hydroxyterephthalic acid (0.09 g) and benzoic acid (0.244 g) to the above solution. Once all the precursors were dissolved, the vial was sealed and placed

in the oven at 120 °C for 48 hrs. The precipitate was washed with DMF and methanol thrice and dried under vacuum to give a pale yellow colour product of NH₂-OH-UiO-66.



3. Characterization

Figure S1: Characterization data of as-synthesized bulk OH- UiO-66 (Zr): (a) PXRD patterns of simulated (black) and as-synthesized OH- UiO-66 (Zr) (violet), (b) Nitrogen adsorption-desorption isotherm, c) MP plot and d) Scanning electron microscope image.

The crystalline structure of bulk OH-UiO-66 was examined by powder X-ray diffraction (PXRD) (figure S1a). The crystallographic phase match very well with the simulated pattern. Figure S1b shows the nitrogen adsorption-desorption curves wherein the OH-UiO-66 showed type I isotherm of microporous nature having BET surface of 1027 m²g⁻¹. This variation in surface area is expected in OH-UiO-66 compared to that of UiO-66 due to functionalized BDC linker that in turn cloak the

small triangular windows to some extent. The calculated mean pore volume of OH-UiO-66 is 0.45 cm³g⁻¹ that is obtained from the micropore plot given in figure S1c. Figure S1d shows the scanning electron microscopy (SEM) images of OH-UiO-66. The morphology of OH-UiO-66 had irregular and octahedral-like crystals sized 400-500 nm similar to UiO-66.



Figure S2: Characterization data of as-synthesized bulk UiO-66 (Zr): (a) PXRD patterns of simulated (black) and as-synthesized UiO-66 (Zr) (pink), (b) Nitrogen adsorption- desorption isotherm, c) MP plot and d) Scanning electron microscope image.

The crystalline structure of bulk UiO-66 was examined by powder X-ray diffraction (PXRD) (figure S2a). The crystallographic phase match very well with the simulated pattern. Figure S2b shows the nitrogen adsorption-desorption curves wherein the UiO-66 showed type I isotherm of microporous nature having BET surface of $1326 \text{ m}^2\text{g}^{-1}$. The calculated mean pore volumes of UiO-66 is 0.59 cm³g⁻¹ that is obtained from the micropore plot given in figure S2c. These values match

very well with the reported literature.¹ Figure S2d shows the scanning electron microscopy (SEM) images of UiO-66.The morphology of UiO-66 had irregular and octahedral-like crystals sized 150-200 nm.



Figure S3: Fourier Transform Infra-Red (FTIR) spectra of UiO-66, NH₂-UiO-66 and OH-UiO-66.

The successful functionalization of amine and hydroxo groups was confirmed by FTIR analysis of UiO-66, NH₂-UiO-66 and OH-UiO-66 and the results are presented in figure S3. Compared with the FTIR spectrum of pristine UiO-66, in the lower frequency range, the peaks centred at 1259 cm⁻¹ and 1244 cm⁻¹ corresponds to the characteristic C-N stretching of aromatic amines and C-O stretching of aromatic alcohols respectively.²



Figure S4: Characterization data of as-synthesized NH₂-OH- UiO-66 (Zr): (a) PXRD patterns of simulated (black) and as-synthesized NH₂-OH- UiO-66 (Zr) (blue), (b) Nitrogen adsorption-desorption isotherm and c) MP plot.

The crystalline structure of bulk NH₂-OH-UiO-66 was examined by powder X-ray diffraction (PXRD) (figure S4a). The crystallographic phases match very well with the simulated pattern.

Figure S4b shows the nitrogen adsorption-desorption curves wherein the NH₂-OH-UiO-66 showed type I isotherm of microporous nature having BET surface of 1007 m^2g^{-1} . This variation in surface area is expected in NH₂-OH-UiO-66 compared to that of UiO-66 due to functionalized BDC linker that in turn cloak the small triangular windows to some extent. The calculated pore volume of NH₂-OH-UiO-66 is 0.25 cm³g⁻¹ that is obtained from the micropore plot given in figure S4c.

Characterization of the Pellets:

The pellets were characterized using powder X-ray diffraction (PXRD), scanning electron microscopy (SEM) and nitrogen sorption isotherms at 77 K to calculate the BET surface area and pore volume (Figures S5- S7). The surface areas were determined by the BET method and total pore volume (Vt) was determined using the adsorption branch of N₂ isotherm curve at the $p/p_0 = 0.99$ single point. Mesopore volume (V_{meso}) of the pellets were obtained from Barrett–Joyner–Halenda (BJH) adsorption and the corresponding micropore volume (V_{micro}) was obtained from the micropore plot (MP Plot). Table 1 summarizes the calculated BET surface area and pore volumes of the three samples in bulk powders and pellets.



Figure S5: Powder X-ray diffraction patterns of NH₂-UiO-66 (Zr) bulk (black) and pellet (green)

Figure 1 and S5 shows the powder X-ray diffraction data collected to ensure that the crystal structure remained intact after pelletization. All 2θ peaks were consistent with the as-synthesized bulk powder of NH₂-UiO-66, indicating that the crystal structures remain intact. However, a significant broadening of the Bragg peak at 2θ lower than 10° was observed. This points towards a partial loss of crystallinity after pelletization. This pressure-induced decrease in crystallinity was also identified in nitrogen sorption studies (figure 1b,c). The N₂ isotherm data indicates that the compression pressure has some effect on the overall surface areas and porosity. N2 adsorptiondesorption isotherms of a mode intermediate between type I, which is related to microporous materials, and type IV, which is related to mesoporous materials were observed. The presence of a pronounced hysteresis loop of intermediate between H2a and H2b type in the N₂ isotherms is indicative of a mesoporosity.³ Furthermore, the calculated BET surface area of NH₂-UiO-66 pellet is 704 m²g⁻¹ and retained 65 % of surface area of bulk powder. The total pore of NH₂-UiO-66 pellet is $0.52 \text{ cm}^3\text{g}^{-1}$ wherein, $0.13 \text{ cm}^3\text{g}^{-1}$ is contributed from microporous volume calculated from MP plot (figure 1c insight) and 0.39 cm³g⁻¹ from mesoporous volume calculated from BJH plot (figure 1c). Figure 1d,e shows the scanning electron microscopy (SEM) images of NH₂-UiO-66 bulk and pellet, respectively. NH₂-UiO-66 bulk and pellet showed irregular and octahedral-like crystals sized 150-200 nm and hence did not show any significant difference in morphology before and after pelletization.



Figure S6: Characterization data of OH-UiO-66 (Zr) (pellet): (a) PXRD patterns of bulk (black) and pellet (purple), (b) Nitrogen adsorption- desorption isotherm, c) MP Plot, d) BJH Plot, e) Scanning Electron Microscopy (SEM) images of cross-section view of the pellet.

Figure S6a shows the powder X-ray diffraction data collected to ensure that the crystal structure remained intact after pelletization. All 2θ peaks were consistent with the as-synthesized bulk powder of OH-UiO-66, indicating that the crystal structures remain intact. However, a significant broadening of the Bragg peak at 2θ lower than 10° was observed (highlighted in yellow box). This points towards a loss of partial loss of crystallinity after pelletization. This pressure-induced decrease in crystallinity was also identified in nitrogen sorption studies (figure S6b-d). The N₂ isotherm data indicates that the compression pressure had little effect on the overall surface areas and porosity. N₂ adsorption- desorption isotherms of a mode intermediate between type I, which is related to microporous materials, and type IV, which is related to mesoporous materials were observed. The presence of a pronounced hysteresis loop intermediate between H2a and H2b type in the N₂ isotherms is indicative of a mesoporosity.³ Furthermore, the calculated BET surface area of OH-UiO-66 pellet is 673 m²g⁻¹ and retained 65 % of surface area of bulk powder. The total pore of OH-UiO-66 pellet is 0.49 cm³g⁻¹ wherein, 0.11 cm³g⁻¹ is contributed from microporous volume calculated from MP plot (figure S6c) and 0.38 cm³g⁻¹ from mesoporous volume calculated from BJH plot (figure S6d).). OH-UiO-66 bulk and pellet showed irregular and octahedral-like crystals sized 400-500 nm and hence did not show any significant difference in morphology before and after pelletization.



Figure S7: Characterization data of UiO-66 (Zr) (pellet): (a) PXRD patterns of bulk (black) and pellet (pink), (b) Nitrogen adsorption- desorption isotherm, c) MP Plot, d) BJH Plot, e) Scanning Electron Microscopy (SEM) images of cross-section view of the pellet.

Figure S7a shows the powder X-ray diffraction data collected to ensure that the crystal structure remained intact after pelletization. All 2θ peaks were consistent with the as-synthesized bulk powder of OH-UiO-66, indicating that the crystal structures remain intact. However, a significant broadening of the Bragg peak at 2θ lower than 10° was observed (highlighted in yellow box). This points towards a loss of partial loss of crystallinity after pelletization. This pressure-induced decrease in crystallinity was also identified in nitrogen sorption studies (figure S7b-d). The N₂ isotherm data indicates that the compression pressure had little effect on the overall surface areas and porosity. Furthermore, the calculated BET surface area of UiO-66 pellet is 716 m²g⁻¹ and retained 54 % of surface area of bulk powder. The total pore of UiO-66 pellet is 0.43 cm³g⁻¹ wherein, 0.29 cm³g⁻¹ is contributed from microporous volume calculated from MP plot (figure S7c) and 0.14 cm³g⁻¹ from mesoporous volume calculated from BJH plot (figure S7d). UiO-66 bulk and pellet showed irregular and octahedral-like crystals sized 150-200 nm and hence did not show any significant difference in morphology before and after pelletization.

MOF	Bulk	Pellet	Bulk Pore	Pellet Pore	Pellet Pore	Pellet Pore
	Sbet	Sbet	Volume	Volume	Volume	Volume
	(m ² /g)	(m²/g)	(Vtotal) (cm ³ /g)	(V _{total})(cm ³ /g)	(Vmicro)(cm ³ /g)	(V _{meso})(cm ³ /g)
			at <i>p/p</i> _=0.9			
UiO-66 (Zr)	1326	716	0.59	0.43	0.29	0.14
NH ₂ -UiO-66	1073	704	0.48	0.52	0.13	0.39
(Zr)						
OH-UiO-66	1027	673	0.45	0.49	0.11	0.38
(Zr)						

Table S1: BET Surface area and pore volumes calculated from N₂ sorption studies of bulk and pellet sensors.

4. Gas sensing measurements

UiO-66, NH₂-UiO-66, and OH-UiO-66 powder materials were tested for chemiresistive sensing of acidic gases including SO₂, NO₂ and CO₂. These powders were weighed and pressed into pellets of uniform thickness. 150 mg of the material was weighed and pressed between two steel rods of 1 cm diameter using a hydraulic pellet press. A pressure of 75 Kg/cm² was applied for about 10 seconds. The thickness of the powder pellets typically was 1 mm. The pellets of all the materials studied in this work were prepared with the same quantity, pressed with same pressure and obtained the same thickness to an extent of uniform thickness. A silver conductive adhesive paste purchased from Alfa Aesar with Sheet resistance: <0.0250hm/square @ 0.001 in thick was used to give the contacts in this study. Small silver dots (diameter of 1 mm) were placed on the upper surface of the pellet using a tooth pick. The gas sensing measurements were recorded by resistance change in the presence and absence of target gas by using a Keithley source meter (Model No. 2450). Alicat Mass Flow Controllers (MFCs) were used to control the gas flow and target gas concentration into the gas reactor chamber and the sensor responses were continuously monitored by a computer-controlled data acquisition system.

Gas sensing measurements were carried out as follows: Nitrogen gas was chosen both as reference and diluting gas to test the desired concentrations of SO₂ and NO₂. For CO₂ gas, argon was chosen as reference and diluting gas. The MOF pellet was placed on the graphite heating block into the gas reaction chamber and the probes were placed unto the silver contacts. The pellets were stabilized under nitrogen (for SO₂ and NO₂)/ argon (for CO₂) atmosphere with slow heating from room temperature to the desired temperature (150 °C) of sensing. A calculated amount of target acidic gas was injected into the chamber through the gas inlet. The mixing chamber was used to mix the target gas with reference gas uniformly and hence vary the desired gas concentrations during measurements.



Figure S8: A scheme of chemiresistive gas sensing device

Calculation of response percentage of all the sensor materials studied in this work.



Figure S9: A scheme of chemiresistive gas sensing device

The response of a chemiresistive sensor is calculated by the change in electrical resistance (R) (output resistance) based on the resistance (R) of chemiresistor before and after analyte exposure

when placed between two electrodes (in this case: probes) and an input potential bias (V) is applied.

The Response of the sensor was defined as

% Response=
$$\frac{[R_a - R_g]}{R_a}$$
 x 100

Where, R_a = Resistance of the sample in the presence of nitrogen or argon R_g = Resistance of the sample in the presence of target gas

The Response Time (Speed of response) is defined as the time required for a sensor to reach 90 % of total response of the signal such as resistance upon exposure to the target gas. $T_R = T_2 - T_1$

The Recovery Time is defined as the time required for a sensor to return to 90 % of original baseline signal upon removal of target gas.

Recovery Time = T_4 - T_3



Figure S10: Gas sensing study of UiO-66(Zr) with 10 ppm SO₂ at an operating temperature of 150° C.



Figure S11: Resistance values of NH₂-UiO-66 (Zr) at various temperatures.



Figure S12: Response- Recovery plots of NH_2 -UiO-66 (Zr) with different concentrations (10 ppm to 1 ppm) of SO₂ at operating temperature of 150 °C and 5 V bias.



Figure S13: Response- Recovery plot of NH₂-UiO-66 (Zr) with 10 ppm SO₂ at operating temperature of 150 $^{\circ}$ C, a) Bias of 1 volt and b) Bias of 3 volts.



Figure S14: Comparison of gas sensing characteristics (Response %, Response time and Recovery time) of NH_2 -UiO-66 (Zr) for 10 ppmSO₂ concentration at different voltage (1 V, 3 V and 5 V.





Figure S15: Response- Recovery plot with 10 ppm SO₂ at operating temperature of 150 °C a) OH- UiO-66 (Zr) and b) NH₂-OH-UiO-66 (Zr).



Figure S16: Comparison of Response % of NH₂-UiO-66 (Zr), OH-UiO-66 (Zr) and NH₂-OH-UiO-66 (Zr) for 10 ppmSO₂ concentration.

Sensing Material	Gas	Average	Average	Average
	Conc.	Response %	Response time	Recovery time
	10	21 4 2 5		
NH ₂ -UiO-66 (Zr)	10 ppm	21.6±2.7	26.8 ± 5.4	46.1±3.9
	SO_2			
NH2-UiO-66 (Zr)	10 ppm	7.6 ± 0.4	35.9 ± 4.8	41.0 ± 3.5
	NO_2			
NH2-UiO-66 (Zr)	5000 ppm	11.48 ± 2.2	30.1 ± 4.2	51.6 ± 4.4
· · ·	CO			
	CO_2			
0H-Ui0-66 (7r)	10 ppm	4.09 ± 0.4	17 5+ 3 5	14.5 ± 10.5
011-010-00 (21)	10 ppm	4.09±0.4	17.5± 5.5	14.5±10.5
	SO_2			
NH ₂ -OH-UiO-66	10 ppm	7.16 ± 1.1	17.0 ± 6.2	15.0 ± 2.3
(Zr)	SO_2			

 Table S2: Error calculations of % response, recovery time and response time



Figure S17: HOCO-LUCO band positions of UiO-66(Zr), NH₂-UiO-66(Zr) and HOMO-LUMO positions of SO₂, NO₂, and CO₂ gases are shown. The band positions are with respect to vacuum level. Basing on the relative band positions stronger interaction is expected between SO₂ and NH₂-UiO-66(Zr).

Table S3: Summary of literature showing chemiresistive sensors studied for SO₂ and NO₂sensing.

Sensor	Conc. of	Operating	Response	R _s Time	R _c Time	References
Materials	Gas	temperature		(sec)	(sec)	
	(ppm)	(°C)				
5 wt% MgO	0.1 ppm SO ₂	400	20 %	250 *	625 (70%	S.C. Lee et al.,
and 2 wt%					recovery)	Sensors and
V ₂ O ₅ SnO ₂						Actuators B, 160,
						2011, <i>1328–1334</i>
LaCaFeO	3 ppm SO ₂	275	50 %	86	110 (90%	Palimar S, et. al.,
					recovery)	Dalton
						Transactions, 45(34),
						2016 , 13547-13555
SnO ₂ -0.15wt	5 ppm SO ₂	350	45 %	Not		S. Das et al., Talanta,
% V2O5				provided		75, 2008 , 385–389
WO 1 (0/	900	400	1.4	200*	200*	
WO3-Iwt%	800 ppm	400	14	300*	300*	Shimizu, Y et. al.,
Ag loading	SO_2					Sensors and
						Actuators B:
						Chemical, 77(1-2),
						2001 , 35-40.
CeO ₂	500 ppm	550	-	600*	300*	E.B. Vrirhegyi et al.,
	SO_2					Sensors and Actiators
						<i>B</i> , 24-25, 1995 , 631-
						635
WO ₃	10 ppm SO ₂	260	9.3 %*	300*	300*	Abdelhamid Boudiba
						et al., Procedia
						Engineering, 47,
						2012 , 1033 – 1036

Edge-	500 ppm	Room	28 %*	7	70	F.Shen. et.al.,
tailored GO	SO_2	temperature				Nanoscale, 2013, 5,
nanosheets						537-540
0.1 wt%	20 ppm NO ₂	250	0.16	Not		R. Vyas, et.al.,
CNT on ZnO				provided		Advanced Materials
						Research, 585, 2012,
						235-239
CNT thin	0.1 ppm	165	4.3 %	Not		Valentini et al., Appl.
films	NO_2			provided		Phys. Lett.,82,6, 2003
Mesoporous	3 ppm NO ₂	35	23 %	>600		L.G. Teoh et al.,
WO3 film						Sensors and
						Actuators B, 96, 2003 ,
						219–225
NiO thin	10 ppm	160		Not		I. Hotovy et al., Thin
films	NO_2			provided		Solid Films, 418,
						2002 , 9–15
Al/CNT	1 ppm NO ₂	-	10 %*	Not		J. Suehiro et
				provided		al.,Sensors and
						Actuators B, 114,
						2006 , 943–949
Cu ₂ O-rGO	2 ppm NO ₂	Room	67.8	500*	600*	S. Deng, et.al., J. Am.
		temperature				Chem. Soc. 2012,
						134, 4905–4917
Porous WO ₃	5 ppm NO ₂	250	111.34	400*	250*	Van Tong, et.al,
nanorod						Sensors and
bundles						Actuators B:
						Chemical, 2013, 183,
						372-380.
ZnO-rGO	5 ppm NO ₂	Room	25.6 %	165	499	S. Liu et al., Sensors
		temperature				and Actuators B 202,
						2014 , 272–278
Co ₃ O ₄ -rGO	60 ppm	Room	80 %/no	400		Chen, N,
	NO_2	temperature	recovery			et.al, Sensors and
						Actuators B:
						Chemical, 2013 , 188,
						902-908.

SnO ₂ -	5 ppm NO ₂	50	3.31	135	200	H. Zhang et al,
nanoparticle						Sensors and
-rGO						Actuators B 190,
						2014 , 472–478
WO ₃ · <i>x</i> H ₂ O	1 ppm NO ₂	300	190.7 %	150*	100*	Z. Liu et al., Sensors
nanorods						and Actuators B 140,
microsphere						2009 , 514–519
S						
Graphene	100 ppm	Room	9 %	250*	500*	G. Ko et al., Current
based SiO ₂	NO_2	temperature				Applied Physics, 10,
						2010 , 1002–1004
In ₂ O ₃	1 ppm NO ₂	250	2.57 %	Not		P. Xu et al., Sensors
nanowire				provided		and Actuators B, 130,
						2008 , 802–808
Ozone	200 ppm	Room	17 %	1800*	1800*	M.G. Chung et al.,
treated	NO_2	temperature				Sensors and
graphene						Actuators B, 166–167
						, 2012 , 172–176
SnO ₂ hollow	2 ppm NO ₂	300	81.4	55		N.G. Cho et al.,
nanofibres						Sensors and
						Actuators B, 160,
						2011 , 1468–1472
ZnO	100 ppm	250	37 %	270	240	E. Oh et al, Sensors
nanorod	NO_2					and Actuators B, 141,
						2009 , 239–243
Flower-like	11.5 ppm	190	350	21	29	M. Chen et al.,
ZnO						Sensors and
						Actuators B, 157,
						2011 , 565– 574
9:1 In ₂ O ₃ –	2 ppm NO ₂	250	-	<5		G. Sberveglieri et.al,
	- FF					•
SnO ₂	- FF 2					Sensors and
SnO ₂	- FF					Sensors and Actuators, 15, 1988 ,

*Calculated from Response-Recovery curves

9. Charge density analysis calculations: formation of charge transfer complex

We performed the Bader charge analysis to explain the charge transfer phenomenon. In this regard, first, we put the SO₂ molecule nearby the -NH₂ functionality of the NH₂-BDCH₂ and performed volume optimization. Monkhorst-Pack k-point has been used with a very dense grid (19×15×11) for the convergence of charge density. The charge density has been shown in Fig S18. We observed that SO₂ is moving closer to the -NH₂ functionality. We found that SO₂ is positively charged (+1.4) whereas NH₂ functionality in linker is negatively charged (-1.4). Therefore this analysis predicts formation of charge transfer complex between SO₂ gas and amine functionality of the linker.



Figure S18. The calculated charge density of the linker. Black dotted lines represent the unit-cell.

We have performed the structural relaxation and electronic structure calculations using density functional theory (DFT) with the Perdew-Burke-Ernzerhof generalized (PBE) using the Vienna ab initio Simulation Package (VASP) ⁴⁻⁵ code with the standard frozen-core projector augmented-wave (PAW) method. The kinetic energy cutoff for the plane wave basis functions has been set to 600 eV. All atoms are fully relaxed until the component of Hellmann Feynman forces on them is below than 0.005 eV/Å. The cell shape and internal positions are also optimized. Monkhorst-Pack k-point has been used with a very dense grid (13×11×7) for structural relaxation and as well as the convergence of charge density. The calculated indirect direct band gap of amine functionalized bezene dicarboxylic acid (NH₂-BDCH₂) is 1.96 eV within the PBE limit. In density functional theory, exchange-correlation functional like the local-density

approximation (LDA) and generalized gradient approximation (GGA) is known to significantly underestimate the band gaps. Therefore, in order to correct the band gap, we performed computationally very expensive hybrid density functional approach (HSE06)⁶⁻⁷, proposed by Heyd, Scuseria, and Ernzerhof, provide an accurate description of the electronic structure and band gaps of semiconductors and show good quantitative agreement with experiment. The calculated HOMO and LUMO band positions are -5.41 eV and -2.6 eV respectively with respect to vacuum level. HSE06 gives an indirect band gap (between Y to F; Fig S19.) of 2.76 eV amine functionalized linker and is obtained with a mixing parameter of 30% and a screening parameter of 0.2 Å⁻¹. These values and band structure of NH₂-BDCH₂ are in very good match with the reported calculated values for NH₂-UiO-66(Zr)⁸ MOFs, this suggest that frontier orbitals of MOF are highly localized on the organic linker.



Figure S19. The electronic band structure and density (left) and density of states (right) of the linker. The Fermi level (horizontal red dotted line) is set to 0 eV. The Vertical dotted lines represent the symmetrical k- points path in the Brillouin zone.

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