# **Supporting information**

# Post-synthetic metalation in an anionic MOF for efficient catalytic activity and removal of heavy metal ions from aqueous solution

Anindita Chakraborty,<sup>a#</sup> Sohini Bhattacharyya,<sup>a#</sup> Arpan Hazra,<sup>a</sup> Ashta Chandra Ghosh<sup>a</sup> and Tapas Kumar Maji<sup>a</sup>\*

<sup>*a*</sup>*Molecular Materials Laboratory, Chemistry and Physics of Materials Unit, Jawaharlal Nehru Centre for Advanced Scientific Research, Jakkur, Bangalore – 560 064, India.* <sup>#</sup>Both authors contributed equally.

### Materials

All the reagents and solvents employed were commercially available and used as supplied without further purification. Dimethyl-5-hydroxy isophthalate,  $\alpha,\alpha'$ -dibromoparaxylene, dibenzo-18-crown-6, and Zn(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O were obtained from Aldrich Chemical Co.

#### Synthesis of 5,5'-(1,4-phenylenebis(methylene))bis(oxy)diisophthalate:

A mixture of dimethyl-5-hydroxy isophthalate (10.0 mmol),  $\alpha,\alpha'$  dibromo paraxylene (4.96 mmol), dibenzo 18 crown-6 (0.277 mmol) and K<sub>2</sub>CO<sub>3</sub> (2.21g, 16 mmol) were stirred in dry THF (40 ml) at 70°C for 24 hours. After this stirring 20 ml 10 % aquous Na<sub>2</sub>CO<sub>3</sub> solution was added at 0°C under an ice bath. The resulting white solid was filtered and washed with water for several times and finally with diethyl ether and dried under vacuum. Yield: 97% relative to dibromo paraxylene. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 8.29 (s, 2H), 7.83 (s, 4H), 7.48 (s, 4H), 5.16 (s, 4H), 3.93 (s, 12H).

## Synthesis of 5,5'-(1,4-phenylenebis(methylene))bis(oxy)diisophthalic acid (L):

A mixture of 5,5'-(1,4-phenylenebis(methylene))bis(oxy)diisophthalate (2mmol), KOH (20 mmol), 40 ml MeOH and 40 ml distilled water were stirred at 80°C in oil bath for 24 hours. The reaction mixture was filtered to remove any unreacted starting materials and 30 ml 6(M) HCl was added dropwise to filtrate at 0°C under stirring. The white precipitate was filtered and washed with distilled water for several times and dried under vacuum. <sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>):  $\delta$  = 13.29 (br, 4H), 8.05 (s, 2H), 7.69 (s, 4H), 7.47 (s, 4H), 5.21 (s, 4H).



Scheme S1: The reaction pathways of the ligand synthesis.

#### Synthesis of {[(NH<sub>2</sub>Me<sub>2</sub>)<sub>2</sub>][Zn<sub>3</sub>(L)<sub>2</sub>].9H<sub>2</sub>O} (AMOF-1)

Zn(NO<sub>3</sub>)<sub>2</sub>.6H<sub>2</sub>O (0.2 mmol) and L (0.1 mmol) were dissolved in DMF (6 ml), ethanol (3 ml) and distilled water (5 ml) in a 23 mL Teflon-lined stainless steel autoclave and was stirred for 30 minutes. The autoclave was sealed and was kept in an oven at 80 °C for 96 h. After completion of the reaction, the reactor was cooled at RT for 12 h. Colourless crystalline product was collected by filtration. Yield: 60 %, relative to Zn<sup>II</sup>. IR (KBr):  $\tilde{V}$  (cm<sup>-1</sup>) = 3460 (br), 3080 (br), 2782 (w), 1632 (s), 1580 (vs), 1452 (m), 1370 (vs), 1263 (m), 1128 (w), 1036 (m). Elemental analysis shows the following result: C, 45.52; H, 3.89; N, 2.13. Indeed, the observed values are close for {[(NH<sub>2</sub>Me<sub>2</sub>)<sub>2</sub>][Zn<sub>3</sub>(L)<sub>2</sub>].9H<sub>2</sub>O} (cald: C, 45.68; H, 3.98; N, 2.04). This result is in accordance with the thermogravimetric analysis (TGA), which shows a loss corresponding to nine water molecules.

#### **Physical measurements**

<sup>1</sup>H NMR data were measured on a Bruker AV-400 spectrometer with chemical shifts reported as ppm (TMS as internal standard). IR spectra were recorded on a Bruker IFS 66v/S spectrophotometer using KBr pellets in the region 4000-400 cm<sup>-1</sup>. Mass spectra are measured on Bruker Ultraflex II MALDI/TOF spectrometers. The elemental analysis was carried out using a Flash 2000 Organic Elemental Analyzer. Thermogravimetric analysis (TGA) was carried out on METTLER TOLEDO TGA850 instrument in the temperature range of 30- 600 °C under nitrogen atmosphere (flow rate of 50 mL/min) at a heating rate of 5 °C/min. Powder X-ray diffraction (PXRD) patterns were recorded on a Bruker D8 Discover instrument using Cu-Kα radiation. Inductively Coupled Plasma-Optical Emission Spectroscopy (ICP-OES) measurements were recorded on Perkin Elmer Optima 7000dv ICP-OES instrument.

#### **Adsorption measurements**

Adsorption isotherms of CO<sub>2</sub> and N<sub>2</sub> were recorded at 195 K and 77 K respectively with the dehydrated samples using QUANTACHROME QUADRASORB-SI analyser. To prepare the desolvated samples of AMOF-1 (AMOF-1') approximately 70 mg of sample was taken in a sample holder and degassed at 160 °C under  $10^{-1}$  pa vacuum for about 8 hours prior to the measurements. Dead volume of the sample cell was measured with helium gas of 99.999% purity. The H<sub>2</sub>O adsorption isotherms were measured at 298 K in the gaseous state by using BELSORP-aqua-3 analyzer. The different solvent molecules used to generate the vapour were degassed fully by repeated evacuation. All operations were computer controlled and automatic.

#### **Single-crystal X-ray Diffraction:**

A suitable single crystal of compound AMOF-1 was mounted on a thin glass fiber with commercially available super glue. X-ray single crystal structural data were collected on a Bruker Smart-CCD diffractometer equipped with a normal focus, 2.4 kW sealed tube X-ray source with graphite monochromated Mo-K $\alpha$  radiation ( $\lambda = 0.71073$  Å) operating at 50 kV and 30 mA. The program SAINT<sup>1</sup> was used for the integration of diffraction profiles and absorption correction was made with SADABS<sup>2</sup> program. All the structures were solved by SIR 92<sup>3</sup> and refined by full matrix least square method using SHELXL.<sup>4</sup> All the hydrogen atoms were fixed by HFIX and placed in ideal positions. The solvent water molecules were highly disordered and hence could not be located. We have employed PLATON/SQUEEZE<sup>5</sup>

to produce a set of solvent-free diffraction intensities; the structures were then refined again using the data generated. Potential solvent accessible area or void space was calculated using the PLATON<sup>5</sup> multipurpose crystallographic software. All crystallographic and structure refinement data of **1** is summarized in Table S1. All calculations were carried out using SHELXL 97,<sup>4</sup> PLATON,<sup>5</sup> SHELXS 97 <sup>4</sup> and WinGX system, Ver 1.80.05.<sup>6</sup> Selected bond lengths and angles are displayed in Tables S2 and S3.

### **References:**

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Parameter	AMOF-1
Empirical formula	$C_{52}H_{44}Zn_3O_{20}N_2$
Formula weight	1213.06
Crystal system	Triclinic
Space group	P <sup>1</sup> (No.2)
<i>a</i> , Å	9.4533(19)
<i>b</i> , Å	18.614(4)
<i>c</i> , Å	19.976(4)
α, deg	9.4533(19)
$\beta$ , deg	18.614(4)
γ, deg	19.976(4)
<i>V</i> , Å <sup>3</sup>	3223.2(13)
Ζ	2
<i>Т</i> , К	100
$\mu$ ,mm <sup>-1</sup>	1.172
$D_{\text{calcd}}$ ,g/cm <sup>3</sup>	0.147
F (000)	1240
reflections [ $I > 2\sigma(I)$ ]	5987
unique reflections	11141
measured reflections	21940
<i>R</i> <sub>int</sub>	0.090
GOF	1.06
$R_1[I \ge 2\sigma(I)]^{[a]}$	0.1105
$R_{\rm w}[I>2\sigma(I)]^{[b]}$	0.3304

 Table S1. Crystal Data and Structure Refinement for AMOF-1 (CCDC number: 1431244)

 $(R = \sum ||F_{\rm o}| - |F_{\rm c}|| / \sum |F_{\rm o}|, R_{\rm w} = \left[\sum \{w(F_{\rm o}^2 - F_{\rm c}^2)^2\} / \sum \{w(F_{\rm o}^2)^2\}\right]^{1/2})$ 

Zn1-O12	2.563(8)	Zn1-O19	2.332(8)
Zn1-O13	1.983(7)	Zn1-O20_c	2.041(8)
Zn1-O1	1.977(8)	Zn1 -O11	2.004(8)
Zn2-O2	2.149(8)	Zn2-O9	2.254(8)
Zn2-O14	1.986(8)	Zn2-O11	2.151(8)
Zn2-O18	2.083(5)	Zn2-O7	2.000(8)
Zn3-O10	2.559(8)	Zn3-O9	2.051(8)

Table S2. Selected bond distances (Å) for AMOF-1.

 Table S3. Selected bond angles (°) of Compound AMOF-1.

O1 -Zn1-O11	100.6(3)	O11-Zn2-O18	90.9(3)
O1-Zn1-O12	86.6(3)	O9-Zn3-O10	55.6(3)
O11-Zn1-O19	94.9(3)	O11-Zn1-O13	109.1(3)
O7-Zn2-O18	97.8(3)	O11-Zn1-O12	55.8(3)
O7-Zn2-O9	84.5(3)	O1-Zn1-C48	125.0(3)
O7-Zn2-O14	175.1(3)	O9-Zn2-O18	86.2(3)

## Preparation of MII@AMOF-1':

For preparing the different metal ion exchanged compounds, AMOF-1 is activated at 160°C under high vacuum overnight before immersing it in the respective metal ion solutions. 50 mg of activated AMOF-1 (AMOF-1') is immersed in 20 ml 0.01M M<sup>II</sup> (where M is any transition metal/heavy metal cation) solutions in water and the solution is stirred for 24 hours and the solution is changed every 8 hours within these 24 hours. Then it is washed repeatedly with water to remove any unreacted metal solution. The exchanged solids thus obtained were then dried and Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES) analyses were performed with the solids after decomposing them with acid. The % of inclusion of the excgenous metal ions (M<sup>II</sup>) were calculated based on the relative ratio of Zn<sup>II</sup> and M<sup>II</sup>. While performing the exchange experiments with different metal ions, ICP analysis of the exchanging solution were carried for all the metal ions, which showed that any of the

exchanging solution does not show presence of Zn<sup>II</sup> ions. Thus Zn<sup>II</sup> ions do not leach out from the framework and do not exchange with the exogeneous metal cations.

To know the maximum possible uptake capacity of the heavy metal ions by the desolvated AMOF, we have also carried out exchange for prolonged time (7 days). 50 mg of activated AMOF-1 (AMOF-1') is immersed in 20 ml 0.01M M<sup>II</sup> (where M is the heavy metal cations) solutions in water and the solution is stirred for 7 days and the solution is changed daily (to ensure maximum uptake of the heavy metal ions). The exchanged solids thus obtained were then dried and Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES) analyses were performed with the solids after decomposing them with acid (Table S4). For Cu<sup>II</sup> ion also, exchange experiment was carried out for 7 days. However, the extent of exchange (exchange with DMA cation is 49.1%) does not increase compared to 24 hours of exchange, suggesting that one of the two DMA cations is exchangeable.

To quantify the amount of DMA cations in the exchanging solution, we have done ICP analysis of the  $Cu^{II}$  exchanging solution (exchange experiment was carried out for 24 hours). We have immersed 100 mg desolvated AMOF-1' into 10 ml solution of 0.01M  $Cu^{II}$  solution and ICP analysis was carried out with the exchanging solution. We have quantified the amount of N (ammonium chloride solution was used as the standard) from the ICP data and calculated the amount of DMA cations in the exchanging solution (Table S5). The result is in agreement of our previous result that the % exchange of DMA cation is close to 49%.

To understand the kinetics of heavy metal removal efficiency, we have immersed 20 mg AMOF-1' in 20 ml 1 ppm solution of Hg<sup>II</sup>. The solution was not changed and the initial (I ppm) and the residual Hg<sup>II</sup> concentrations in the solution were measured by ICP-OES after certain time interval. ICP-OES data showed that 98.7% removal of Hg<sup>II</sup> occur after 24 hours. Similarly, exchange experiments were carried for Cd<sup>II</sup> and Pb<sup>II</sup> for 24 hours which show 98.2% and 97.6% removal respectively (Table 1 in main manuscript).

**Table S4.** ICP-MS data for heavy metal ion exchange, the % exchange of heavy metal ions

 with DMA cation and uptake capacity of heavy metal ions by AMOF-1'

Heavy metal	Time o	f	No. of M <sup>II</sup> per	Maximum	% exchange of	
(M <sup>II</sup> )	exchange		formula of the	number of	M <sup>II</sup> with DMA	
			exchanged	M <sup>II</sup> possible		
			framework	per formula		
				unit		
Hg <sup>II</sup>	24 hours		0.31	1	31	
	7 days		0.48	1	48	
Pb <sup>II</sup>	24 hours		0.26	1	26	
	7 days		0.42	1	42	
Cd <sup>II</sup>	24 hours		0.29	1	29	
	7 days		0.45	1	45	

The maximum heavy metal ion uptake capacity by AMOF-1' is calculated from the ICP data carried out by with the metal exchanged solids obtained after 7 days of exchange experiments. The uptake capacity for Hg<sup>II</sup>, Pb<sup>II</sup> and Cd<sup>II</sup> are 78 mg, 71 mg and 41 mg per g of the AMOF-1'.

**Table S5.** ICP-MS data for determination of the amount of DMA cations in the exchanging solution of Cu<sup>II</sup> exchange experiment (Done with 100 mg AMOF-1' in 10 mL Cu<sup>II</sup> solution)

Amount of N (ppm)	Amount	of	DMA	cation	Calculated	exchange	%	of
	(ppm)				DMA cation	n		
53.86	354				47			

## Detection of DMA cation in the exchanging solution:

To verify that the metal inclusion in the AMOF occur by cation exchange, we performed cation exchange experiment in DMSO-d6 and immersed AMOF-1' in Cd<sup>II</sup> (diamagnetic and does not interfere in the NMR spectrum) solution. The NMR spectrum of the exchanging solution confirms presence of DMA cation (Fig. S11).

#### **Catalysis study:**

The catalytic activity of the Cu<sup>II</sup>@AMOF-1' catalyst was investigated in one-pot condensation reactions for the synthesis of benzimidazole derivatives by the reaction between *o*-phenylenediamine and different *p*-substituted benzaldehydes. The reaction of *o*-phenylenediamine and benzaldehyde in presence of AMOF-1' shows no conversion of product even after 12 hours and suggest that AMOF-1' could not act as the catalyst and thus PSMet is required to obtain the Lewis acid catalyst Cu<sup>II</sup>@AMOF-1'. We have also carried out reaction with the pristine Cu<sup>II</sup>@AMOF-1' (without any activation) and it does not show any catalytic activity. Thus the Cu<sup>II</sup> UMS are essential for the catalytic reaction and the UMS serve as the active catalytic sites.

The Cu<sup>II</sup>@AMOF-1' sample was activated at 120 °C under 10<sup>-1</sup> pa vacuum for 8 hours to remove any water molecule. A mixture of o-phenylenediamine (1 equivalent) and benzaldehyde (1 equivalent) and activated Cu<sup>II</sup>@1' catalyst (0.05 mol%; the molecular weight of dehydrated Cu<sup>II</sup>(a)AMOF-1' catalyst is calculated based on the ICP data of Cu<sup>II</sup>(a)1' while the activation is carried out at 120 °C under  $10^{-1}$  pa vacuum for 8 hours) were taken in EtOH at RT and stirred for fixed time (monitored by TLC). After the reaction was complete, the solid catalyst was removed by filtration and the quantitative analysis of product conversion is monitored by GC-MS analyser at regular interval of times. The conversion of products with benzaldehyde (X= H) is 62% after 3 h, while after 6 h the product conversion is increased to 97%, suggesting that the conversion takes almost 6 h to complete. Reactions were also carried out for different *p*-substituted benzaldehydes ( $X = NO_2$ , Cl, CH<sub>3</sub> and OCH<sub>3</sub>) using activated Cu<sup>II</sup>@AMOF-1' catalyst for 6 hours. Results suggest that electron withdrawing group at *para* position of aldehyde enhance electrophilic nature of the carbonyl carbon thereby increasing its reactivity and the resulting in high yield of the product (Table 2 in main manuscript). <sup>1</sup>H NMR data were recorded for the first three products ( $X = H, NO_2$ , Cl) after purification and <sup>1</sup>H NMR data analysis confirm the purity of the compounds.

To compare the catalytic activity of  $Cu^{II}@AMOF-1$ ' with homogeneous  $Cu^{II}$  catalyst, we have carried out reaction of *o*-phenylenediamine (1 equivalent) and benzaldehyde (1 equivalent) using dehydrated cupric acetate (0.05 mol%) as a catalyst under the similar reaction condition as employed for the activated  $Cu^{II}@AMOF-1$ ' catalyst. Reaction was carried out in ethanol at room temperature for 6 hours and under this condition we did not find any detectable amount of the desired benzimidazole product through GC-MS analysis.

This reflects the heterogeneous  $Cu^{II}$  (@AMOF-1' is a superior catalyst than the homogeneous  $Cu^{II}$  catalyst.

Catalytic recycling efficiency test of the Cu<sup>II</sup>@AMOF-1' catalyst was carried out using *o*-phenylenediamine and benzaldehyde (X= H). After the 1<sup>st</sup> cycle of reaction, the catalyst was separated by filtration and the recovered catalyst was washed with EtOH thoroughly to remove any unreacted reagent. The recovered catalyst was dried in air and then activated at 120 °C under 10<sup>-1</sup> pa vacuum for 8 hours to perform further reactions under identical conditions. The conversion of the product after 1<sup>st</sup>, 2<sup>nd</sup> and 3<sup>rd</sup> cycles are 97%, 88% and 57% respectively. The PXRD patterns of Cu<sup>II</sup>@AMOF-1' samples after each cycle were recorded (Fig. S10), which suggest that the structural integrity of the framework is maintained after each cycle. The number of Cu<sup>II</sup> ion per formula in Cu<sup>II</sup>@AMOF-1' was determined to be 0.491, before the catalytic reaction (exchange with DMA cation is 49.1%). ICP-OES analyses were also performed after each cycle of the catalytic reaction. The number of Cu<sup>II</sup> ion per formula is 0.487, 0.485 and 0.479 after 1<sup>st</sup>, 2<sup>nd</sup> and 3<sup>rd</sup> cycle respectively, which suggest that no leaching Cu<sup>II</sup> ions occur during the recyclability test and the framework retains its integrity.



Fig. S1. IR Spectra of AMOF-1



Fig. S2. TGA profile for AMOF-1 and Cu<sup>II</sup> @AMOF-1'



**Fig. S3.** The connectivity of the four  $[Zn_3(CO_2)_8]$  SBUs through L ligands. The spatial orientation of the terminal benzene rings of L1 and L2 are highlighted (dihedral angles between the terminal benzene rings of L1 and L2 are 79.8 and 73.5 respectively). Color Code: C: grey; Zn: cyan; O: red



**Fig. S4.** (Left): The 2D network containing the  $[Zn_3(CO_2)_8]$  SBUs connected through L ligands. (Right): Formation of the 3D framework from the 2D nets connected through L ligands along *b* direction.



**Fig. S5.** The view of the crystallographic different DMA cations residing near the junctions of the different channels. After Cu<sup>II</sup> exchange, the Cu<sup>II</sup> ions are anticipated to be present near the carboxylate oxygen atoms (as they could act as possible coordination sites for the Cu<sup>II</sup> ions) shown in the figure.



Fig. S6. Topology of the 2-nodal net of AMOF-1. Color Code: Ligand (L): cyan; trinuclear  $Zn_3$  SBU: blue.



Fig. S7. PXRD patterns of as-synthesized AMOF-1 (black) and the sample immersed in water for 7 days (blue).



Fig. S8. PXRD patterns: black: simulated; blue: as-synthesized AMOF-1, red: AMOF-1', green: Cu<sup>II</sup>@AMOF-1'



**Fig. S9.** PXRD patterns of AMOF-1 (black) and M<sup>II</sup>@AMOF-1' (where M<sup>II</sup> is a heavy metal cation; Pb<sup>II</sup>: red, Cd<sup>II</sup>: pink, Hg<sup>II</sup>: brown).



Scheme S1: The plausible mechanism for synthesis of benzimidazole derivatives using Cu<sup>II</sup>@AMOF-1'. Colour code: Cu: blue; O (from carboxylate of L3 ligand): red.

A plausible reaction mechanism is shown in Scheme S1. Here, the Lewis acidic  $Cu^{II}$  sites immobilized into the pore surface coordinates to the carbonyl oxygen atom of the aldehyde and activates it triggering the attachment of amine group (of *o*-phenylenediamine) to the carbonyl carbon. In the next step, water is removed. In the subsequent step, the second attack of amine followed by oxidation yield final product.



**Fig. S10.** PXRD patterns of Cu<sup>II</sup>@ AMOF-1' (green) and the solid catalyst Cu<sup>II</sup>@ AMOF-1' after 1<sup>st</sup> (blue), 2<sup>nd</sup> (brown) and 3<sup>rd</sup> (pink) cycle of the catalytic reaction.



**Fig. S11.** <sup>1</sup>H-NMR spectra (in DMSO-d6) of the exchanging solution showing DMA cation (see text)



**Fig. S12.** <sup>1</sup>H-NMR spectra (in DMSO-d6) of the benzimidazole derivative formed by the reaction of between *o*-phenylenediamine and benzaldehyde (X=H)



**Fig. S13.** <sup>1</sup>H-NMR spectra (in CDCl<sub>3</sub>) of the benzimidazole derivative formed by the reaction of between *o*-phenylenediamine and *p*-nitrobenzaldehyde ( $X = NO_2$ ).



**Fig. S14.** <sup>1</sup>H-NMR spectra (in DMSO-d6) of the benzimidazole derivative formed by the reaction of between *o*-phenylenediamine and *p*-chlorobenzaldehyde (X = Cl).