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Coordination preferred open metal sites containing porous coordination polymers for selective gas/solvent adsorption

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ABSTRACT

Three isostructural PCPs with molecular formula, $Zn_2M_2(\mu_3-OH)_2(BTMB)_2 \cdot Guest$ ($M = Zn$ (**1**), Co (**2**) and Ni (**3**)) ($BTMB^{3-} = 1,3,5$ -benzenetris(*m*-benzoate)) were synthesized by refluxed conditions at 125 °C. The obtained products were characterized by PXRD, TGA, and FTIR. These PCPs synthesized by this new synthetic method containing unique mono-metallic, $[Zn_4(\mu_3-OH)_2]^{6+}$ and bimetallic cluster cores $[Zn_2M_2(\mu_3-OH)_2]^{6+}$ ($M = Zn, Co$ or Ni) with coordination-free open metal sites (OMSs). They also exhibited specific adsorption isotherms with varying surface areas using CO_2 gas adsorption study. This might be due to the different metal ions present in the framework along with their different number of open metal Lewis acidic sites in the degassed state. The CO_2 gas adsorption BET surface areas found to be 295, 317 and 272 $m^2 g^{-1}$ and their CO_2 gas adsorption Langmuir surface areas found to be 570, 662 and 560 $m^2 g^{-1}$, respectively for **1**, **2** and **3** analogs. By utilizing this coordination preferred OMSs, we carried out various gas and solvent adsorption study for these three PCPs. The gas adsorption profiles of these PCPs indicated that the adsorption profile is type 1 and also the amount of gas adsorbed was different for three different metals ions used in these PCPs. Whereas, the solvents adsorption isotherms showed type-V of isotherm with aromatic solvents exhibited a unique gate-opening profile and aliphatic solvent molecules shown gate closing behavior.

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1. Introduction

Porous coordination polymers (PCPs)/metal-organic frameworks (MOFs) are emerged [1–10] as potential materials of the decade. Last twenty years a revolution in the production of new porous materials has come due to the development of PCPs as a potentially feasible alternative to conventional porous materials. However, the most potential materials are limited because of their instability [11–13] with respect to moisture/chemicals etc. Moreover, they also lack the open metal sites (OMSs) after removal of the guest solvent in the degassed state. To overcome these drawbacks, recently various post-synthetic modification (PSM) approaches [14–18] were reported for stabilizing these PCPs/MOFs. In these PSM functionalized MOFs, the introduction of hydrophobic alkyl chains via PSM enhanced the moisture resistance along with some interesting physical properties [14–18]. However, in most of the PSM methods, the introduction of lengthy

alkyl chains into the framework leads porosity to lose some extent. Alternatively, we developed [19–21] a new methodology and achieved the first superhydrophobic PCPs/MOFs, which exhibit great stability towards the moisture, chemicals and thermal conditions.

MOFs/PCPs with OMS always found to be very precious in the research area of porous materials [22–24], particularly for gas storage, separation, catalysts, and sensors etc. The reduced symmetry linker provided [25] new metal-oxygen-metal (M–O–M) clusters containing MOF/PCPs. The M–O–M bonded inorganic backbone with OMS of the MOFs/PCPs plays an important role in interacting with guest gas/solvent molecules and also provides exceptional thermal and chemical stability to the framework. In many MOFs/PCPs reported in the literature, the inorganic component can be just a single coordinating metal ion. In fact, in such type of MOFs/PCPs, after removal of the guest solvent molecules lead the destruction of the structure or shown with low thermal stability [11–13]. By utilizing this reduced symmetry linkers concept [25] we designed an interesting ligand, Benzene-1, 3, 5-tris

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(*meta*-benzoic acid) (**H₃BTMB**), incorporated the coordinating linker carboxylate group at only at *meta*-position. Later, using this newly synthesized reduced symmetry ligand, **H₃BTMB**, we reported [19–21] few superhydrophobic **PCPs/MOFs** with high thermal stability. Moreover, they also possess unique mono-metallic, $[\text{Zn}_4(\mu_3\text{-OH})_2]^{6+}$ and bimetallic, $[\text{Zn}_2\text{M}_2(\mu_3\text{-OH})_2]^{6+}$ (**M = Co or Ni**) μ_3 -hydroxo-clusters with open metal sites. On other hand, **PCPs** with a similar molecular formula of benzene-1,3,5-tribenzoic acid (**H₃BTB**) has been extensively reported in the literature were found to be instability with respect to moisture and lack **OMSs**.

In this study, we report a simple new refluxed synthetic method for the synthesis of these interesting **PCPs**, $\text{Zn}_2\text{M}_2(\mu_3\text{-OH})_2(\text{BTMB})_2 \supset \text{Guest}$ (**M = Zn (1), Co (2) and Ni (3)**) ($\text{BTMB}^{3-} = 1,3,5$ -benzenetriis(*m*-benzoate)). We also discussed the characterization, thermal and adsorption properties of these **PCPs**. Further, we also report the coordination preference oriented adsorption properties of these **PCPs** with gas molecules and as well as solvent molecules with respect to the temperature.

2. Experimental

2.1. Chemicals used in this work

$\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ were purchased from Finar India LTD. *N,N*-dimethylformamide (DMF) and methanol (MeOH), toluene, cyclohexane and benzene were purchased from Fisher India LTD. All the chemicals used in this study were utilised as received without any further purification.

2.2. Synthesis of $\text{Zn}_4(\mu_3\text{-OH})_2(\text{BTMB})_2 \supset \text{Guest}$ (1)

A solid mixture of $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (120 mg, 0.403 mmol) and **H₃BTMB** (88 mg, 0.2 mmol) was dissolved in a mixture DMF/MeOH/H₂O (2:1:1) of 20 mL solvent in a round bottom flask. To the reaction mixture 160 μL of NaOH (0.01 M) deprotonating agent was added. The initial pH of the reaction mixture was 6.0. The whole reaction mixture was refluxed on an oil bath at 125 °C, over a period of 24 hrs. The product was cooled to room temperature and filtered by washing with methanol. The product was dried in air and isolated as a homogeneous colorless powder. Yield: 113 mg, 69% based on the ligand **H₃BTMB** weight.

2.3. Synthesis of $\text{Co}_2\text{M}_2(\mu_3\text{-OH})_2(\text{BTMB})_2 \supset \text{Guest}$ (2) and $\text{Ni}_2\text{M}_2(\mu_3\text{-OH})_2(\text{BTMB})_2 \supset \text{Guest}$ (3)

Similar reaction conditions employed for the synthesis of $\text{Zn}_4(\mu_3\text{-OH})_2(\text{BTMB})_2 \supset \text{Guest}$ (1) were used to synthesize other two **MOFs/PCPs**, $\text{Co}_2\text{M}_2(\mu_3\text{-OH})_2(\text{BTMB})_2 \supset \text{Guest}$ (2) and $\text{Ni}_2\text{M}_2(\mu_3\text{-OH})_2(\text{BTMB})_2 \supset \text{Guest}$ (3). For, $\text{Co}_2\text{M}_2(\mu_3\text{-OH})_2(\text{BTMB})_2 \supset \text{Guest}$ (2) the product was a homogeneous violet color powder yielded, 123 mg, 76% based on the ligand **H₃BTMB** weight. For, $\text{Ni}_2\text{M}_2(\mu_3\text{-OH})_2(\text{BTMB})_2 \supset \text{Guest}$ (3), the product was a homogeneous green color powder yielded, 117 mg, 72% based on the ligand **H₃BTMB** weight.

2.4. General characterization techniques

The powder X-ray diffraction (PXRD) patterns recorded using a Rigaku RINT powder X-Ray diffractometer with using $\text{Cu K}\alpha$ radiation. Thermo-gravimetric analyses (TGA) carried out using a Hitachi STA 7200 under N_2 flow with 10 K min^{-1} ramp rate. Gas adsorption isotherms carried out using Belsorp Mini volumetric adsorption instrument, BEL JAPAN INC, Japan. FTIR spectra recorded at 298 K temperature by using Cary 639 FTIR with Diamond ATR, Agilent Technologies, USA.

3. Results and discussion

3.1. Synthesis

Synthesis of three **PCPs**, $\text{Zn}_2\text{M}_2(\mu_3\text{-OH})_2(\text{BTMB})_2 \supset \text{Guest}$ (**M = Zn (1), Co (2) and Ni (3)**) were achieved similar to previously reported [19–20] procedure but with different synthetic conditions. Previously these compounds synthesized by the solvo-thermal methods using glass vials and/or Teflon lined auto claves. In this study, we used different method of refluxed synthetic conditions at 125 °C. However, when we employed the same temperature of 100 °C, we got the products slightly lower yields of 55, 63 and 62%, respectively for $\text{Zn}_2\text{M}_2(\mu_3\text{-OH})_2(\text{BTMB})_2 \supset \text{Guest}$ (**M = Zn (1), Co (2) and Ni (3)**). The products synthesized by the refluxed conditions were used for all the gas and solvent adsorption studies.

3.2. Characterization

Powder X-ray diffraction (PXRD) patterns of $\text{Zn}_2\text{M}_2(\mu_3\text{-OH})_2(\text{BTMB})_2 \supset \text{Guest}$ (**M = Zn (1), Co (2) and Ni (3)**) are similar to previously reported [19–20] compounds, indicating that they are iso-structural (Fig. 1) with respective compounds and also confirmed their phase purity. Upon degassing the PXRD patterns of $\text{Zn}_2\text{M}_2(\mu_3\text{-OH})_2(\text{BTMB})_2 \supset \text{Guest}$ (**M = Zn (1), Co (2) and Ni (3)**) at 250 °C, are crystalline in nature confirmed the stability of the frameworks after removal of the coordinating solvent. The PXRD result revealed that these three **PCPs**, 1–3, synthesized by the new refluxed synthetic conditions were isostructural frameworks with phase purity. Thermo-gravimetric analysis (TGA) measured for $\text{Zn}_2\text{M}_2(\mu_3\text{-OH})_2(\text{BTMB})_2 \supset \text{Guest}$ (**M = Zn (1), Co (2) and Ni (3)**) under N_2 gas atmosphere with a heating rate of 10 °C per min (Fig. 2). We were more excited after examined the TGA profiles carefully of all these three interesting **PCPs** synthesized by the refluxed method. In all the three compounds, the solvent of crystallization removed below 134 °C. However, DMF solvent molecules coordinated to the metal ion of the $[\text{Zn}_4(\mu_3\text{-OH})_2]^{6+}$ and $[\text{Zn}_2\text{M}_2(\mu_3\text{-OH})_2]^{6+}$ clusters, evacuated at different temperatures between 134 and 270 °C depending on the nature of the metal ions coordinated with DMF in these **PCPs/MOFs**. The coordinated DMF solvent molecules evacuated at 204 °C, 220 °C

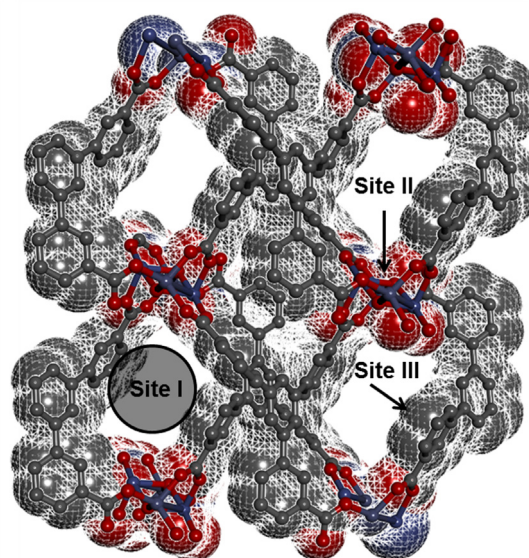


Fig. 1. The possible interactive sites in the degassed phase for three **PCPs**, $\text{Zn}_2\text{M}_2(\mu_3\text{-OH})_2(\text{BTMB})_2$.

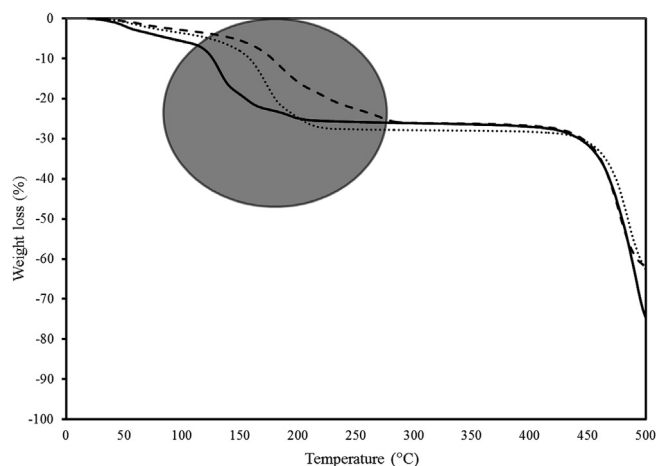


Fig. 2. The TGA plots for three PCPs, $Zn_2M_2(\mu_3-OH)_2(BTMB)_2$ ($M = Zn$ (1) (solid line), Co (2) (dotted line) and Ni (3) (dashed line) measured under N_2 atmosphere and $10^\circ C/min$ (heighted area shows coordinated solvent lost at different temperatures).

and $275^\circ C$, respectively for three PCPs, $Zn_2M_2(\mu_3-OH)_2(BTMB)_2 \supset Guest$ ($M = Zn$ (1), Co (2) and Ni (3)). The interesting point in these three, PCPs analogues is that, they exhibit incongruity in releasing the temperature of their coordinated solvents molecules, indicating that the interactions between the OMSs and the coordinated guest solvent molecules were certainly dissimilar. Based on this interesting observation of having similar structures but exhibits dissimilar interactions with open metal sites and solvents guest molecules, we are interested to study for their gas separation and solvent separation properties.

3.3. Gas adsorption study

The three compounds, $Zn_2M_2(\mu_3-OH)_2(BTMB)_2 \supset Guest$ ($M = Zn$ (1), Co (2) and Ni (3)) shown no adsorb for N_2 gas at 77 K, similar to reported PCPs [19–20]. The porosity of the series of PCPs 1–3, confirmed to a type-I isotherm using CO_2 gas adsorption isotherms carried out at 195 K (Fig. 3). More interestingly, the BET surface areas [19,20] (295 , 317 and $272\text{ m}^2\text{g}^{-1}$) and Langmuir surface areas

(570 , 662 and $560\text{ m}^2\text{g}^{-1}$) also varied with metal ion present in the framework of the PCP, which is in agreement with the TGA results. Among the three PCPs, Co (2), analogue shows the highest surface area, followed by Zn (1) and Ni (3), respectively. But as per TGA results, Ni (3) analogue showed stronger OMSs and better guest interactions. The low surface area of Ni (3) analog could be due to the loss of crystallinity after degassed state. We also carried out CO_2 adsorption isotherms at 273 K and 298 K for all the three PCPs, $Zn_2M_2(\mu_3-OH)_2(BTMB)_2 \supset Guest$ ($M = Zn$ (1), Co (2) and Ni (3)), in order to understanding OMSs interactions with CO_2 gas molecules at different temperature (Fig. 4). The CO_2 adsorption at 195 K, 273 K and 298 K for Zn (1) analogue was 102 , 27 and 15 mLg^{-1} , respectively. The CO_2 adsorption at 195 K, 273 K and 298 K for Co (2) analogue was 114 , 30 and 17 mLg^{-1} , respectively. Similarly, the CO_2 adsorption at 195 K, 273 K and 298 K for Ni (3) analogue was 90 , 29 and 16 mLg^{-1} , respectively. These results are also very good agreement with TGA analysis. Among the three PCPs, Co (2), analogue shows highest adsorption, followed by Zn (1) and Ni (3), respectively at the temperature of 195 K. However, at 273 K and 298 K, Ni (3) analogue also adsorbed as equal Co (2) analogue and better than Zn (1) analogue (Fig. 3 and Fig. 4), which is a clear indication of the strong OMSs and better gas interactions in case of Ni (3) analogue in agreement with TGA analysis. The difference in the coordination behaviour and also unique gas interactions might be due to the difference in their electronegativity of these three metals ($M = Zn$ (1), Co (2) and Ni (3)).

3.4. Solvent adsorption study

We are also interested to study about these three PCPs, $Zn_2M_2(\mu_3-OH)_2(BTMB)_2 \supset Guest$ ($M = Zn$ (1), Co (2) and Ni (3)), coordination preferred interaction with various solvents molecules. For this study we choose three different 6-membered ring containing organic solvents with somewhat comparable molecular size, but differ in their polarity like either aromatic or aliphatic solvents such as benzene, toluene, and cyclohexane. The adsorption profiles of these three PCPs carried out at 298 K on the evacuated samples were shown in Fig. 5. Peculiarly, the solvent adsorption isotherms for the aromatic molecules such as benzene and toluene had shown a gate opening behavior of Type-V adsorption profile [26] with large hysteresis. Whereas, the aliphatic molecules such as

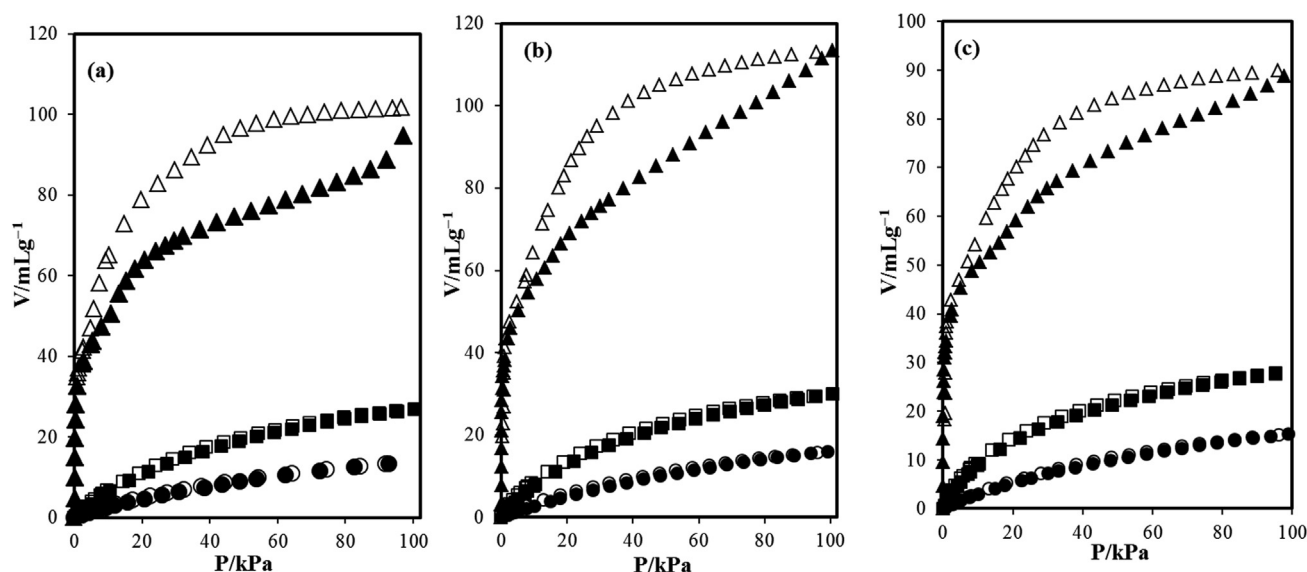


Fig. 3. The CO_2 adsorption isotherms for three PCPs, $Zn_2M_2(\mu_3-OH)_2(BTMB)_2$ at 195 K (triangular), 273 K (square) and 298 K (circular) for (a) Zn (1), (b) Co (2) and (c) Ni (3). Open and filled symbols represent desorption and adsorption profiles, respectively.

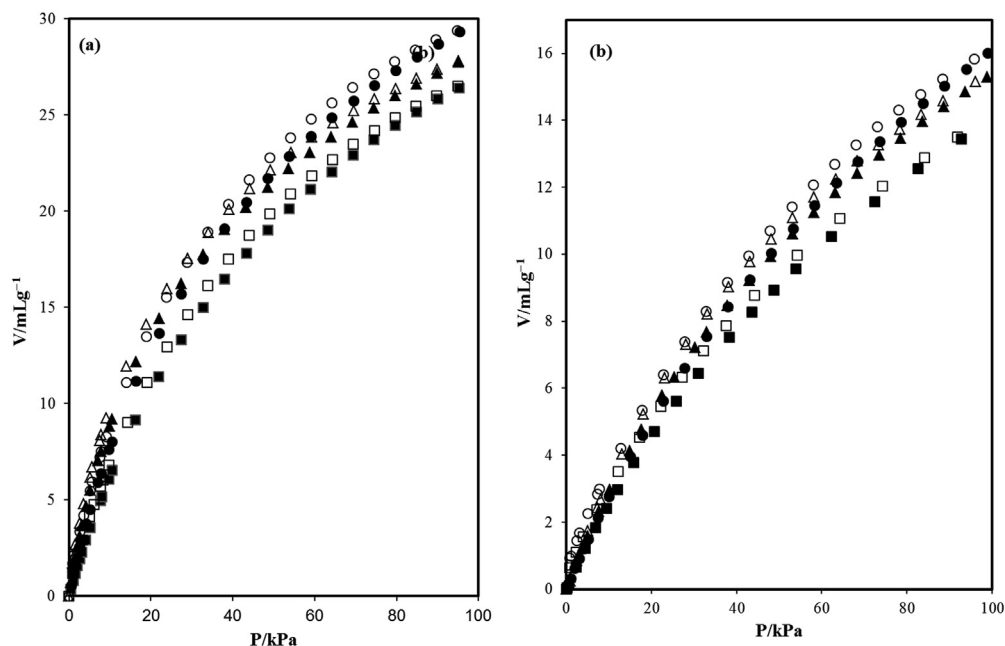


Fig. 4. The CO₂ adsorption isotherms for three PCPs, Zn₂M₂(μ₃-OH)₂(BTMB)₂ (M = Zn (1) (square), Co (2) (circular) and Ni (3) (triangular)) at (a) 273 K and (b) 298 K. Open and filled symbols represent desorption and adsorption profiles, respectively.

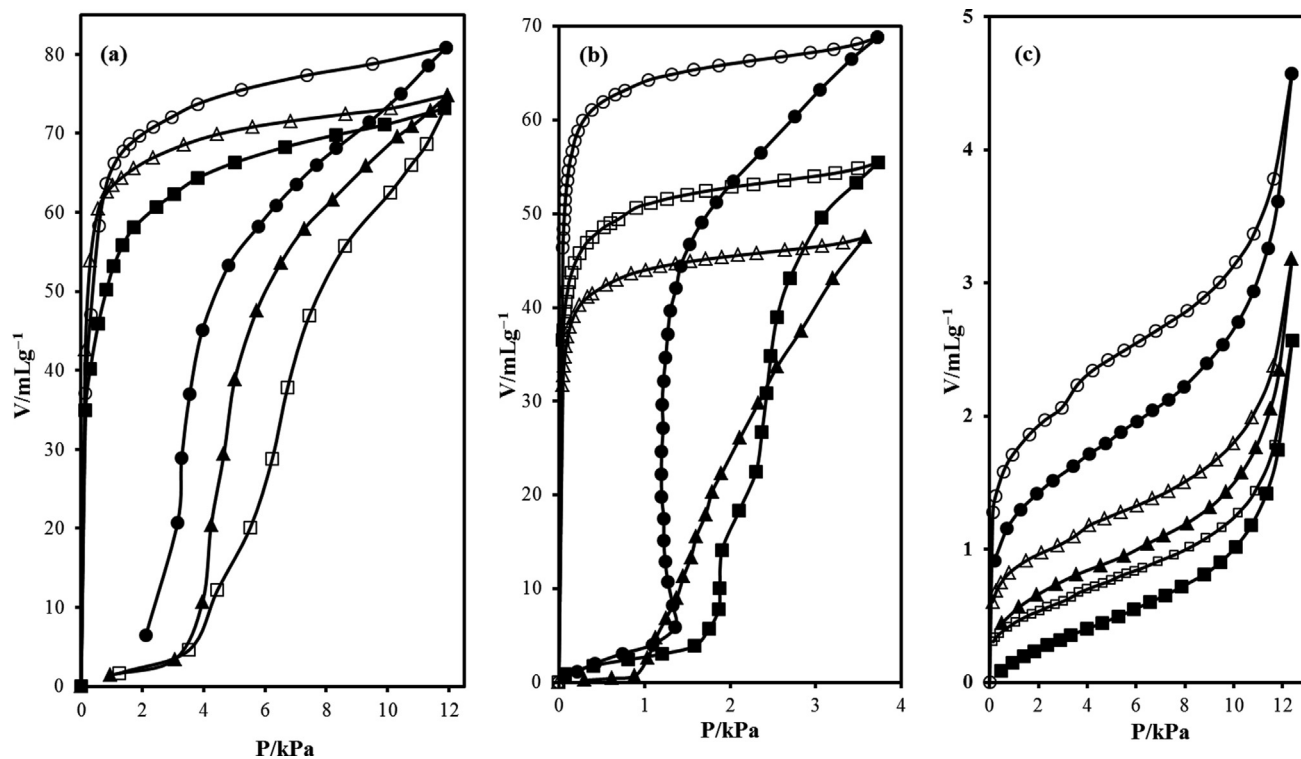


Fig. 5. The solvent adsorption isotherms for three PCPs, Zn₂M₂(μ₃-OH)₂(BTMB)₂ (M = Zn (1) (square), Co (2) (circular) and Ni (3) (triangular)) at 298 K for (a) benzene (b) Toluene and (c) cyclohexane. Open and filled symbols represent desorption and adsorption profiles, respectively.

cyclohexane exhibited gate closing performance and the aliphatic molecules could not able to enter into the pores of the framework. These organic solvent adsorption profiles are unique and entirely different from their gas adsorption profiles. The benzene adsorptions at 298 K for three PCPs, 1–3, were 75, 80 and 75 mLg⁻¹, respectively (Fig. 5a). Similarly, the toluene adsorptions at 298 K for three PCPs, 1–3, were 56, 69 and 48 mLg⁻¹, respectively

(Fig. 5b). Based on these two solvents adsorptions on these PCPs, 1–3, clearly indicated the amount of solvent adsorbed were different for different metal ions, Co (2) analogue adsorbed highest amount solvent. Moreover, all the adsorption profiles shown with large hysteresis indicated the OMSs shown strong affinity towards these solvents. The aliphatic solvents such as cyclohexane adsorptions at 298 K for three PCPs, 1–3, were very low (3, 5 and 2 mLg⁻¹)

(Fig. 5a). The above results revealed that, the aliphatic organic molecules such as cyclohexane excluded from the pores by aromatic hydrocarbon surface of these **PCPs** towards the solvent interactive surface.

The combined solvent adsorption profiles of three solvents (benzene, toluene, and cyclohexane) on the degassed samples performed at room temperature of three individual **PCPs** are shown in Fig. 5. All the three compounds have shown good adsorption towards the aromatic solvent molecules such as benzene, but no adsorption towards the aliphatic solvents such as cyclohexane. Moreover, benzene molecules adsorbed largely than toluene molecules due to high steric hindrance and also the presence of aliphatic methyl group in the toluene molecule. Moreover, the aromatic rich hydrocarbon surface caused by BTMB ligand moiety in these three MOFs/PCPs, reject the aliphatic solvents like cyclohexane. These results clearly indicated that, these **PCPs** can potential separate aromatic solvents from aliphatic solvents.

4. Conclusions

Three **PCPs** with molecular formulas, $\text{Zn}_2\text{M}_2(\mu_3\text{-OH})_2(\text{BTMB})_2 \supset \text{Guest}$ ($\text{M} = \text{Zn}$ (**1**), Co (**2**) and Ni (**3**)) ($\text{BTMB}^{3-} = 1,3,5\text{-benzenetriis}(m\text{-benzoate})$) were synthesized by the refluxed conditions at 125° C. These **PCPs** synthesized by this new refluxed synthetic method containing unique mono-metallic, $[\text{Zn}_4(\mu_3\text{-OH})_2]^{6+}$ and bimetallic cluster cores $[\text{Zn}_2\text{M}_2(\mu_3\text{-OH})_2]^{6+}$ ($\text{M} = \text{Zn}, \text{Co}$ or Ni) with coordination-free open metal sites (OMSs). They also exhibited specific adsorption isotherms with varying surface areas using CO_2 gas adsorption study. This might be due to the different metal ions present in the framework along with their different number of open metal Lewis acidic sites in the degassed state. The CO_2 gas adsorption **BET** surface areas found to be 295, 317 and 272 m^2g^{-1} and their CO_2 gas adsorption Langmuir surface areas found to be 570, 662 and 560 m^2g^{-1} , respectively for 1, 2 and 3 analogs. By utilizing this coordination preferred **OMS**, we studied CO_2 gas and solvent adsorption study for these three **PCPs**. The gas adsorption profiles of these **PCPs** indicated that, the adsorption profile is type-1 and also the amount of gas adsorbed was different for three different metals ions used in these **PCPs**. Similarly, the solvents adsorption isotherms showed type-V, with aromatic solvents exhibited a gate-opening profile and aliphatic solvent molecules displayed gate closing performance. We strongly believe that, the present study furnish a roadmap to design of novel porous materials for various applications especially for the gas/solvent storage, separation and catalysts.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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