

A three-dimensional pillared-layer metal-organic framework: Synthesis, structure and gas adsorption studies



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ABSTRACT

A stable 3D MOF, $\{[\text{Zn}_3(\text{L})_3(\text{DPB})_{1.5}] \cdot 6\text{DMF} \cdot \text{H}_2\text{O}\}_n$ was synthesized using a partially methylated linear rigid linker (**LH₂**) in the presence of the co-linker **DPB** (1,4-dipyridylbenzene) under solvothermal condition. The complex was found to have channels along the crystallographic *a*-axis with the pore surfaces aligned with $-\text{CH}_3$ groups that resulted in a hydrophobic environment inside the cavity. Thermogravimetric analysis and variable temperature powder X-ray diffraction show high thermal stability of the framework. The solvent molecules in the cavity can be evacuated maintaining the structural integrity of the framework to afford a porous structure. Gas (N_2 , CH_4 , CO_2 and H_2) adsorptions were carried out for this MOF. The desolvated framework shows significant CO_2 adsorption over N_2 and CH_4 at 273 K with an isosteric heat of adsorption of ~ 21 kJ/mol, suggesting a strong interaction of the CO_2 molecules with the framework walls.

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1. Introduction

The study of MOFs [1–5] has increased exponentially over the past couple of decades due to their potential practical applications in gas storage [6–11], sensing [12–16], magnetism [17–19], separation [20,21] and even biological studies [22]. These materials often exhibit large internal surface areas. Recently, supramolecular storage of gases such as carbon dioxide, methane or hydrogen has drawn considerable attention and assumed great importance due to concerns over the green house emission, increasing energy demands as well as depletion of the exhaustible reserves of fossil fuels [23–25]. Though zeolites and activated carbon have served this purpose to some extent, yet they have some drawbacks. Zeolites contain hydrophilic pores and lack designable channel surface, whereas activated carbon shows no surface functionalization, wide pore size distribution in an uncontrolled manner in addition to limited accessible surface area and pore volume. In contrast to these conventional materials, metal organic frameworks can be considered as better alternatives since they are completely regular, highly porous and designable in nature [26]. Extensive research has been also been done on coordination polymers to enhance their gas storage capacity in various ways such as incorporation of open metal sites [27,28], increasing the surface area and void

volume [29], utilizing interpenetration as well as functionalizing the organic struts [30,31]. As far as the modification of the organic strut is concerned, it has been observed that replacement of hydrogen atom with functional groups like $-\text{OH}$, $-\text{NH}_2$, $-\text{CF}_3$, etc. lead to an enhancement of molecular interactions with the guest molecules within the framework [32,33]. In this context, frameworks containing partially methylated linkers are not only expected to possess enhanced thermal, light, air, and chemical stability, but also exhibit high gas uptake capabilities [34]. Among the various MOFs, pillar-layer MOFs are one of the best choices in which the pore size and its chemical functionality like hydrophilic/hydrophobic environment of the resultant frameworks can be tuned rationally via thoughtful modification of the pillars [35–40]. In these coordination polymers, the secondary building units (SBUs) are the well-known paddle-wheels $\{\text{Zn}_2(\text{COO})_4\}$, which not only enhance the stability, but also give a well-defined three-dimensional orientation to the framework [41]. Another important factor which contributes to the stability is the interpenetration of frameworks [42,43]. In addition to enhanced stability, interpenetration leads to the formation of new adsorption sites that may exhibit greater gas adsorption properties [44–46]. However, extensive interpenetration is not a desired property as it results in a drastic reduction of the pore size and leading to less gas adsorption.

With these ideas in mind, a linear rigid pre-designed ligand 2',5'-dimethyl-*p*-terphenyl-4,4''-dicarboxylate (**LH₂**) was chosen, that has carboxylate groups at each terminal while the middle aromatic

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ring contains methyl groups (Scheme 1). The terminal carboxylate groups are involved in the coordination to the metal centers whereas the presence of methyl groups discourages extensive interpenetration. As a pillar, the **DPB** (1,4-dipyridylbenzene) co-linker having comparable length to **LH₂** has been used to further strengthen the structure. As Zn(II) ion has a strong tendency to form paddle-wheel structure with carboxylate ligands that provides strength to the overall structure besides larger pore size, it has been chosen in the present study. Herein, we report the synthesis and structural characterization of a triply interpenetrated three dimensional coordination polymer $\{[\text{Zn}_3(\text{L})_3(\text{DPB})_{1.5}] \cdot 6\text{DMF} \cdot \text{H}_2\text{O}\}_n$. There are a number of solvent molecules present in the voids that can be removed through activation to afford a porous structure without destroying the overall framework. It shows high thermal stability, has a highly hydrophobic surface and exhibits permanent porosity with moderate surface area. Nitrogen, carbon dioxide, methane and hydrogen sorption properties were carried out for this porous coordination polymer.

2. Experimental section

2.1. General methods and materials

Reagent grade 1,4-dibromo-2,5-dimethyl benzene, 4-methoxy-carbonylphenylboronic acid, tetrakis(triphenylphosphine)palladium, benzene-1,4-diboronic acid, 4-bromopyridine hydrochloride, $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ were acquired from Aldrich and used as received. All other chemicals and solvents were obtained from S. D. Fine Chemicals, India. Solvents were purified following standard procedures prior to use.

Infrared spectra were obtained (KBr disk, 400–4000 cm^{-1}) on a Perkin-Elmer Model 1320 spectrometer. Thermogravimetric analysis (TGA) was obtained on a Mettler Toledo Star System (heating rate of 5 $^\circ\text{C}/\text{min}$). Microanalyses for the compounds were performed using a CE-440 elemental analyzer (Exeter Analytical Inc.). Variable temperature powder X-ray diffraction patterns for the compound (Cu $\text{K}\alpha$ radiation, scan rate 3 $^\circ/\text{min}$, 293 K) were collected on a Bruker D8 Advance Series 2 powder X-ray diffractometer.

2.1.1. Physisorption measurements

Gas adsorption measurements were performed using automatic volumetric BELSORP-MINI-II adsorption equipment. High purity

gases were used for the adsorption measurements (nitrogen, 99.999%; hydrogen, 99.999%; methane, 99.995%; carbon dioxide, 99.95). Prior to all physisorption measurements the crystals of the sample were immersed in acetone for 96 h at room temperature and additionally activated by heating up to 120 $^\circ\text{C}$ under a high vacuum to remove the solvent molecules.

2.2. Synthesis

The ligand **LH₂** and ancillary ligand **DPB** were synthesized following earlier reported procedures [47,11].

2.2.1. Synthesis of $\{[\text{Zn}_3(\text{L})_3(\text{DPB})_{1.5}] \cdot 6\text{DMF} \cdot \text{H}_2\text{O}\}_n$ (**1**)

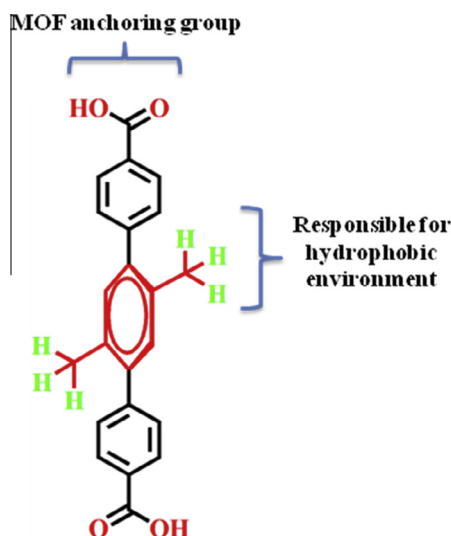
A mixture containing $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (40 mg, 0.13 mmol), **LH₂** (20 mg, 0.06 mmol), 1,4-di(pyridin-4-yl)benzene (**DPB**) (15 mg, 0.06 mmol) in 3 mL of *N,N*-dimethylformamide (DMF) were sealed in a Teflon-lined stainless steel autoclave and heated under autogenous pressure to 85 $^\circ\text{C}$ for 72 h. Then it was allowed to cool to room temperature at the rate of 1 $^\circ\text{C}$ per minute that afforded block-shaped colorless crystals of complex in ~59% yield. The crystals were washed with DMF followed by acetone and air-dried. *Anal.* Calc. for $\text{C}_{108}\text{H}_{110}\text{N}_9\text{O}_{19}\text{Zn}_3$: C, 63.77; H, 5.45. Found: C, 63.69; H, 5.39%. IR (KBr, cm^{-1}): 3611(w), 3420(m), 3074(w), 2912(w), 1706(m), 1638(s), 1610(s), 1553(m), 1488(m), 1407(s), 1223(w), 1175(m), 1099(m), 1016(m), 980(w), 845(w), 715(m).

2.3. X-ray structural studies

Single crystal X-ray data of the complex **1** were collected at 100 K on a Bruker SMART APEX CCD diffractometer using graphite monochromated $\text{MoK}\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$). The linear absorption coefficients, scattering factors for the atoms and the anomalous dispersion corrections were referred from the International Tables for X-ray Crystallography [48]. The data integration and reduction were worked out with SAINT software [49]. Empirical absorption correction was applied to the collected reflections with SADABS [50], and the space group was determined using XPREF [51]. The structure was solved by the direct methods using SHELXTL-97 [52] and refined on F^2 by full-matrix least-squares using the SHELXTL-97 programme [53]. All non-H atoms were refined anisotropically except C90 atom of the complex. The H-atoms connected to carbon atoms were positioned geometrically and treated as riding atoms using SHELXL default parameters. The middle ring of **DPB** molecule and the methyl groups were found to have disorders, hence several DFIX commands were used to fix these distances. To give an account of disordered electron densities associated with solvent molecules in the complex, the “squeeze” protocol in the PLATON [54] package was applied. The contribution of all the solvent atoms has been incorporated in both the empirical formula and formula weight of the complex. The crystal and refinement data are collected in Table 1. Selective bond distances and angles are given in Table S1, (Supporting Information).

3. Results and discussion

The complex was easily synthesized by solvothermal technique in moderate yields. Once isolated, it was found to be stable in air and insoluble in water and common organic solvents. In the IR spectra the complex show strong absorbance between 1706 cm^{-1} and 1408 cm^{-1} attributable to coordinated carboxylate groups as well as carbonyl groups of *N,N*-dimethylformamide molecules present in the channels [55,56]. Broad band near 3620–3390 region suggests the presence of hydroxyl groups of lattice water molecules (Fig. S1) [57].



Scheme 1. Chemical structure of the **LH₂** and **DPB** ligands used to construct the complex **1**.

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