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Pillared-bilayer porous coordination polymers of Zn(II): enhanced hydrophobicity of pore surface by changing the pillar functionality

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Abstract

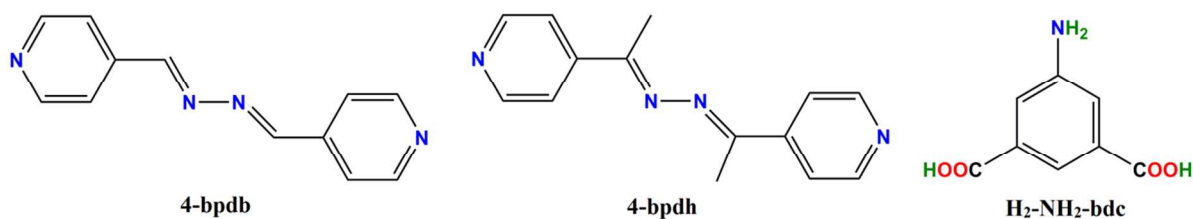
Two new isostructural porous coordination polymers of Zn(II) $\{[\text{Zn}_2(\text{NH}_2\text{-bdc})_2(4\text{-bpdb})]\cdot(\text{H}_2\text{O})_4\}_n$ (**1**) and $\{[\text{Zn}_2(\text{NH}_2\text{-bdc})_2(4\text{-bpdh})]\cdot(\text{H}_2\text{O})_4\}_n$ (**2**) [4-bpdb = 1,4-bis-(4-pyridyl)-2,3-diaza-1,3-butadiene, 4-bpdh = 2,5-bis-(4-pyridyl)-3,4-diaza-2,4-hexadiene and $\text{NH}_2\text{-bdc}$ = 5-amino-1,3-benzenedicarboxylate] have been synthesized using mixed ligand system by solvent diffusion technique and structurally characterized through single crystal X-ray diffraction, variable temperature powder X-ray diffraction and thermogravimetric analysis. Both the coordination polymers are constructed using linear *Schiff* base linkers of similar length having =N–N= base functionalities but only difference is the presence of methyl groups in adjacent carbon atoms of the =N–N= group in 4-bpdh ligand. Single-crystal structure analysis revealed that both the compounds **1** and **2** have two-dimensional (2D) pillared-bilayer framework structure containing 1D channels ($8.3\times 3.8 \text{ \AA}^2$ for **1** and $8.0\times 1.6 \text{ \AA}^2$ for **2**) filled with lattice water molecules. Channel dimension in **2** decreases due the presence of methyl groups. The desolvated frameworks of **1** and **2** are rigid which is evidenced by variable temperature PXRD. Both the compound show type-I CO_2 uptake profile and the difference in CO_2 adsorption uptakes have been corroborated to their void space (27.1% for **1** and 17.1% for **2**). Desolvated forms of compound **1** exhibits remarkably high water adsorption capacity even at low vapor pressure whereas desolvated forms of compound **2** shows very low water vapor uptake, could be ascribed to the hydrophobic nature of the pore surface of **2**.

Introduction

Porous coordination polymers (PCPs) or metal–organic frameworks (MOFs) have become a sizzling topic in the inorganic and materials science due to their versatile structural features, high surface area and predesigned uniform porosities.¹ Such attractive features established these materials as a ‘holy grail’ in context to the searching new porous material which have various meaningful applications like gas storage,² separation,³ electrical conductivity,⁴ sensing,⁵ magnetism,⁶ controlled drug delivery,⁷ heterogeneous catalysis,⁸ proton conductivity,⁹ etc. These functional porous materials are generally constructed by metal ions or their clusters and bridging organic ligands which also known as linkers.¹⁰ The structural features of such porous materials can easily be tuned by changing the organic linkers which are the integral part of their pore walls in such two- or three-dimensional porous frameworks.¹⁰ Unlike other microporous compounds such as zeolites or activated carbons, PCPs or MOFs provide the opportunity for highly tunable architecture as well as the pore surface properties via judicious design of organic linkers by using suitable synthetic methodology. In spite of having several advantages, one striking limitation of the MOFs is that; such porous frameworks are not robust enough and in most of the cases these are prone to collapse in humid environments.¹¹ As a result, several functional MOFs show a sharp decrease in their performance under humid conditions which is frequently observed during the capture of CO₂ from flue gas as it content lot of water vapor (7-9%).¹² Hence, the major challenge lies in MOF chemistry on the rewarding endeavors to synthesize water stable porous MOFs. To achieve this, different strategies are envisaged. Among them two major strategies are; use of high oxidation state metals (e.g. Fe³⁺, Cr³⁺, Al³⁺, Zr⁴⁺, etc.) for carboxylate based MOFs,¹³ and utilization of interpenetration or catenation that narrowing down the pore size.¹⁴ However, there is one other way which took less attention, is the use of hydrophobicity on the linkers *i.e.* the introduction of alkyl, ethyl ester or fluorinated (F, CF₃) groups, to improve the efficacy of MOFs towards water stability.¹⁵

Since last few years, our group shows an immense interest in the design and construction of porous mixed ligand based PCPs of first transition metals using multidentate carboxylate ligands and N,N'-donor linkers with polar functional groups *e.g.* imine, azo, etc.¹⁶ Such pre-designed polar functionalities are found beneficial to improve the gas (especially for CO₂) adsorption and separation properties of such materials. Moreover, it is worth to mention that the mixed-ligand MOFs display some distinctive properties like tunable pore size and chemical

environment and also found to be very flexible, which imparts many interesting properties like gated and stepwise adsorption, selective adsorption so far and so forth.¹⁷ Recently, we have reported a 3D robust porous framework made up with of Cu(II), glutarate dianion and an N,N'-donor ligand which shows a reversible single-crystal-to-single-crystal transformation.^{16a} The pore surface was decorated with '-CH=N-' group and its desolvated form showed selective CO₂ uptake. A slide modification of N,N'- donor ligand using '-CMe=N-' groups instead of '-CH=N-', give same type of 3D porous framework.^{16d} The second compound shows a marked enhancement in CO₂ adsorption and more water repellent character than the first compound which has been achieved by the introduction of hydrophobic methyl groups in the pore wall of the framework.^{16d} To extend our exploration in this area, we have used an amino functionalized trigonal dicarboxylate; 5-amino-1,3-benzenedicarboxylate along with two different above mention N,N'-donor linkers (Scheme 1) with Zn(II). Two isostructural two-dimensional (2D) pillared-bilayer porous frameworks, {[Zn₂(NH₂-bdc)₂(4-bpdb)]·(H₂O)₄}_n (**1**) and {[Zn₂(NH₂-bdc)₂(4-bpdh)]·(H₂O)₄}_n (**2**) are obtained and both of them shows N₂ and CO₂ adsorption appropriate to their pore size. Due to the presence of hydrophobic methyl group in **2** the water adsorption is less with respect to its pore size, which is significant with respect to the design of CO₂ adsorbing materials which can rejects the adsorption of water vapor significantly.



Scheme 1 Ligands used in this work.

Experimental section

Materials and general Method

Zn(NO₃)₂·6H₂O and 5-amino-1,3-benzenedicarboxylic acid (NH₂-H₂-bdc) were obtained from the Sigma-Aldrich Chemical Co. India and used as received. 1,4-bis-(4-pyridyl)-2,3-diaza-1,3-butadiene (4-bpdb) and 2,5-bis-(4-pyridyl)-3,4-diaza-2,4-hexadiene (4-bpdh) were synthesized by reported procedures.¹⁸ Disodium salt of NH₂-bdc was prepared by the addition of NaHCO₃ to NH₂-H₂-bdc ligand in a 2:1 ratio in water and was allowed to evaporate at 100 °C until dryness. All other reagents and solvents were purchased from commercial sources and were used without

further purification. C, H, and N analyses were performed on a Heraeus CHNS analyzer. Infrared spectra were recorded with a Perkin–Elmer Spectrum BX-II IR spectrometer using KBr pellets in the 400–4000 cm^{-1} range. Powder X-ray diffractions were measured at a scanning rate of 5°min^{-1} on a Bruker D8 Discover diffractometer using Cu–K α radiation ($\lambda = 1.5418 \text{ \AA}$). Thermal analyses were carried out with a METTLER TOLEDO TGA 850 thermal analyzer under nitrogen atmosphere with a flow rate of $50 \text{ cm}^3 \text{ min}^{-1}$.

Sorption measurements

The adsorption isotherms of N_2 (77 K) and CO_2 (195 K and 298 K) was measured using the dehydrated sample of **1** and **2** in QUANTACHROME QUADRASORB-SI analyzer. In the sample tube, adsorbent samples **1** and **2** (~100–150 mg) were placed which had been prepared at 403 and 353 K, respectively, under a 1×10^{-1} Pa vacuum for about 6 h prior to measurement of the isotherms. Helium gas (99.999% purity) at a certain pressure was introduced in the gas chamber and allowed to diffuse into the sample chamber by opening the valve. The amount of gas adsorbed was calculated from the pressure difference ($P_{\text{cal}} - P_e$), where P_{cal} is the calculated pressure with no gas adsorption and P_e is the observed pressure at equilibrium. All operations were computer-controlled and automatic.

Water vapor adsorption was also measured at 298 K in the desolvated sample of **1** and **2** by using a BELSORP aqua-3 analyzer. Around 80 mg of samples were activated under similar conditions as mentioned earlier. Water molecules used to generate the vapor were fully degassed by repeated evacuation. The dead volume was measured with helium gas. The adsorbate was placed into the sample tube, then the change of the pressure was monitored and the degree of adsorption was determined by the decrease in pressure at the equilibrium state. All operations were computer controlled and automatic.

Synthesis of $\{[\text{Zn}_2(\text{NH}_2\text{-bdc})_2(4\text{-bpdb})] \cdot (\text{H}_2\text{O})_4\}_n$ (**1**).

An aqueous solution (10 mL) of disodium salt of $\text{NH}_2\text{-bdc}$ (1 mmol, 0.225 g) was mixed with methanolic solution (10 mL) of 4-bpdb (1 mmol, 0.210 g), and the resulting solution was stirred for 20 min to mix well. $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (1 mmol, 0.297 g) was dissolved in 10 mL of water. 6 mL of mixed ligand solution was carefully layered onto a buffer of methanol–water (1:1, v/v, 2 mL), below which an aqueous solution (3 mL) of $\text{Zn}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ in a glass tube, which was sealed and left undisturbed at room temperature. X-ray quality yellow single crystals were obtained from the junction of the layer after 5 days. The crystals were separated and washed with

methanol and dried in air (yield = 82% based on Zn). For the bulk synthesis, aqueous solution of Zn(II) was mixed with above mentioned mixed ligand solution. Then the solution was stirred overnight and the yellow precipitate was filtered and air-dried. Phase purity was confirmed by powder X-ray diffraction and elemental analysis. Anal. Calcd for $C_{28}H_{28}N_6O_{12}Zn_2$ ($M_r = 771.34$): C, 43.60; H, 3.66; N, 10.90%. Found: C, 43.34; H, 3.42; N, 10.93%. IR (KBr pellet, cm^{-1}): 3430(br), 3253-3143(w), 1614(s), 1570(s), 1481(w), 1349(s), 1223(w), 1092(m), 1018(w), 952(w), 783(m), 724(m), 519(m). The IR spectrum of **1** (Fig. S1) shows a broad bands around 3430 cm^{-1} , suggesting the presence of water molecules. Weak two bands around 3253 and 3143 cm^{-1} corroborates the $\nu(NH_2)$ stretching frequency, and a band around 1614 cm^{-1} corresponds to the $\nu(C=N)$ stretching frequency of 3-bpdb ligand.

Synthesis of $\{[Zn_2(NH_2\text{-bdc})_2(4\text{-bpdh})] \cdot (H_2O)_4\}_n$ (**2**).

Compound **2** was synthesized adopting a similar procedure as that of **1**, where we have used 4-bpdh instead of 4-bpdb (1 mmol, 0.238 g). After 7 days, yellow crystals obtained from the middle of the tube and were separated and washed with methanol (yield = 75% based on Zn). The bulk amount of the sample was also prepared by the direct mixing of the Zn(II) salts and corresponding ligand in methanol/water mixed solution with overnight stirring. The phase purity was checked by powder X-ray diffraction and elemental analysis. Anal. Calcd. for $C_{30}H_{32}N_6O_{12}Zn_2$ ($M_r = 799.39$): C, 45.07; H, 4.03; N, 10.51%. Found: C, 44.85; H, 4.18; N, 10.37%. IR (KBr pellet, cm^{-1}): 3408(br), 3262-3142(w), 1618(s), 1564(s), 1482(w), 1366(s), 1228(w), 1109(m), 1030(w), 964(w), 780(m), 730(m), 530(m). The IR spectrum of **2** (Fig. S2) shows broad bands around 3408 cm^{-1} , suggesting the presence of water molecules. Weak two bands around 3262 and 3142 cm^{-1} corroborates the $\nu(NH_2)$ stretching frequency, and a band around 1618 cm^{-1} corresponds to the $\nu(C=N)$ stretching frequency of 3-bpdh ligand.

Crystallographic data collection and refinement

X-ray single-crystal data of **1** and **2** were collected at 298K on a Bruker APEX II diffractometer equipped with a normal focus, sealed tube X-ray source with graphite monochromated Mo-K α radiation ($\lambda = 0.71073\text{ \AA}$) operating at 50 kV and 30 mA. The program SAINT¹⁹ was used for integration of diffraction profiles, and absorption correction was made with the SADABS²⁰ program. Both the structures were solved by SHELXS²¹ using the Patterson method and followed by successive Fourier and difference Fourier synthesis. Full-matrix least-squares refinements were performed on F^2 using SHELXL-97²¹ with anisotropic displacement parameter for all non

hydrogen atoms. During refinement of **1** and **2**, two of the lattice water molecules are found disordered in each structure. In both the cases, their occupancies were fixed at 0.5 before final refinement and were isotropically refined without fixing hydrogen atoms. All the hydrogen atoms except the disordered lattice water hydrogen were fixed geometrically by HFIX command and placed in ideal positions in the case of the four structures. Potential solvent accessible area or void space was calculated using the PLATON multipurpose crystallographic software.²² All the crystallographic and structure refinement data of **1** and **2** are summarized in Table 1. Selected bond lengths and angles for **1** and **2** are given in Tables 2-4. All calculations were carried out using SHELXL 97, PLATON, ORTEP-3v2,²³ WinGX system ver-1.80²⁴ and TOPOS.²⁵

Result and discussion

Structural descriptions of $\{[\text{Zn}_2(\text{NH}_2\text{-bdc})_2(4\text{-bpdb})]\cdot(\text{H}_2\text{O})_4\}_n$ (**1**) and $\{[\text{Zn}_2(\text{NH}_2\text{-bdc})_2(4\text{-bpdh})]\cdot(\text{H}_2\text{O})_4\}_n$ (**2**).

Compounds **1** and **2** are isostructural differing only with respect to the linear linker (4-bpdb and 4-bpdh). Both of them have crystallizes in the monoclinic space group $C2/c$, and the single crystal structure analysis reveals that both the compounds originate a 2D pillared-bilayer coordination frameworks of Zn(II) connected by the 5-aminoisophthalate ($\text{NH}_2\text{-bdc}$) and linear N,N'-linkers, 4-bpdb in the case of **1** and 4-bpdh in the case of **2**. Here, in each case five coordinated Zn(II) center with O_3N_2 binding set is coordinated by three carboxylate O atoms from two $\text{NH}_2\text{-bdc}$, one amine nitrogen from another $\text{NH}_2\text{-bdc}$ ligand and one N atom from N,N'-linker (3-bpdb for **1** and 3-bpdh for **2**) (Fig. 1a for **1** and Fig. 1b for **2**) displaying a highly distorted square pyramidal geometry (Addison parameters²⁶ 0.47 and 0.44 for **1** and **2**, respectively). In **1** and **2**, Zn-O bond length varies from 1.942(3)-2.560(3) Å and 1.931(3)-2.578(3) Å, respectively, and the corresponding Zn-N bond lengths are 2.047(4) and 2.095(4) Å (Table 2); 2.043(3) and 2.128(4) Å (Table 3) for **1** and **2** respectively. The selected bond lengths and bond angles are reported in Table 2 for **1** and Table 3 for **2**. Here each $\text{NH}_2\text{-bdc}$ ligand acts as a bridge between three Zn(II) centers; chelating a Zn(II) center at one end, binding through a single carboxylate oxygen atom at the other end and connecting to another metal center by bridging- NH_2 group. Thus each Zn(II) is linked to three $\text{NH}_2\text{-bdc}$ ligands and each $\text{NH}_2\text{-bdc}$ ligand is bound to three Zn(II) centers forming a 2D $[\text{Zn}(\text{NH}_2\text{-bdc})]_n$ sheet in crystallographic bc plane (Fig. 2 for **1** and Fig. S3 for **2**). The 2D sheets are joined by N,N'-linker (3-bpdb for **1** and 3-bpdh for **2**) to form a 2D pillared-bilayer framework and create 1D channels inside the bilayers

(Fig. 3a for **1** and Fig. 3b for **2**). The thickness of bilayers is ~ 15.23 Å and ~ 15.15 Å for **1** and **2**, respectively. The channels are occupied by guest water molecules in both the cases. In **1**, the dimension of the channel along the *b*-axis is about 8.3×3.8 Å² (Fig. S4) but in **2**, the dimension of the channel reduces to 8.0×1.6 Å² (Fig. S5) as the methyl groups of Meazpy are oriented within the pore. The total solvent accessible void is estimated by PLATON²² to be 926 Å³ which is 27.1% of the total crystal volume of 3415.1 Å³ (for **1**) and 579.1 Å³; 17.1% of the total crystal volume of 3394.0 Å³ (for **2**). Structural analysis with TOPOS²⁵ suggests the 2D metal-carboxylate layer is a 3-c net with Schläfli symbol {6³} (Fig. 4a), where center of gravity of the phenyl ring of the carboxylate and the metal center; both are considered as node. The overall 2D pillared-bilayer framework reveals a 3-nodal 2,3,4-c net with stoichiometry (2-c)(3-c)2(4-c)2 and the corresponding Schläfli symbol for the net is {6³.8².10}2{6³}2{8} (Fig. 4b). The 2D bilayers are further linked together via intermolecular hydrogen bonds between amino group and carboxylate oxygen atoms to generate a 3D supramolecular structure (Table 4). Apart from H-bonding, there are also intramolecular π - π interactions within the 2D bilayers (Fig. S6 for **1** and Fig. S7 for **2**); strengthening the stability of 3D supramolecular construction [cg...cg distance = 3.3307(17)-3.512(3) Å (for **1**) and 3.3456(14)-3.4673(19) Å (for **2**)] (Table 5).

TGA and PXRD Analysis

To examine the thermal stability of the MOFs, thermogravimetric analyses (TGA) were carried out (Fig. 5). TGA of compounds **1** and **2** were performed in the temperature range of 25–600 °C under nitrogen atmosphere. As shown in the crystal structure analysis, both the compounds **1** and **2** comprise four H₂O molecules as guests. In case of **1**, a weight loss of $\sim 9.4\%$ is observed up to 128 °C, which suggests the presence of four guest water molecules (calc. wt% 9.33) and there was no weight loss until 340 °C for the dehydrated sample, showing the successful removal of the solvent molecules during the activation process (Fig. 5). The TGA curve of compound **2** showed a weight loss 9.2% up to 74 °C, corresponds to four lattice water molecules (calc. wt% 9.0). The dehydrated framework of **2** also stable up to 370 °C and then decomposes. The TGA studies clearly indicate the high thermal stability of these pillar-bilayered MOFs (Fig. 5).

We have collected *in situ* variable temperature powder X-ray diffraction (VTPXRD) data of **1** and **2** to study the framework stability at the temperature range of RT-340 °C. The experimental VTPXRD patterns of **1** and **2** are still in good agreement with the simulated PXRD pattern, indicating that the crystal lattice of **1** and **2** remains intact at 340 °C (Fig. 6 for **1** and Fig.

7 for **2**). However, the PXRD patterns of desolvated frameworks of **1** and **2** do not show any change upon exposure to water vapors for seven days (Fig. 6 for **1** and Fig. 7 for **2**).

Adsorption studies

To reveal the porous properties of compounds **1** and **2**, corresponding dehydrated samples were subjected to gas (N₂ and CO₂) and solvent vapor (H₂O), adsorption experiments. N₂ adsorption isotherms at 77 K for **1** and **2** show type-II isotherms indicating only surface adsorption (Fig. 8). Compound **1** do possess sufficient window dimension to allow the diffusion of N₂ but probably the presence of 1D channels imposes enough diffusion barrier to restrict the N₂ adsorption. In case of compound **2** the window dimension is not at all suitable for N₂ (Kinetic diameter~ 3.64 Å) diffusion. But surprisingly, at 195 K both desolvated frameworks of **1** and **2** exhibit a typical type-I profile for CO₂, suggesting a microporous nature of the frameworks (Fig. 9) with respect to CO₂. The CO₂ adsorption capacities of **1** and **2** are about 6.8 wt % (34.5 cm³ g⁻¹) and 3.6 wt % (18.3 cm³ g⁻¹), respectively. The difference between the CO₂ uptakes of **1** and **2** is well anticipated as comparatively larger pores (8.3×3.8 Å²) of **1** with higher solvent accessible void (27.1%) compared to the pore size (8.0×1.6 Å²) and solvent accessible (17.1%) void of compound **2**. The distinct hysteresis in CO₂ adsorption profile for compound **1** can be attributed to the strong interaction between CO₂ quadrupole moment and –C=N–N=C– group. Similar types of interactions and selectivity towards CO₂ have been reported earlier.^{16a,b,d} At room temperature (298 K), CO₂ uptakes are quite low; 1.5 wt% (7.8 cm³ g⁻¹) for **1** and 0.9 wt% (4.8 cm³ g⁻¹) for **2**, respectively with hysteretic isotherms (Fig. S8).

Further to check the nature of the pore surfaces of **1** and **2**, water vapor adsorption experiments have been carried out. Compound **1** was found to show an uptake of ~88 cm³g⁻¹ at very low pressure ($P/P_0 \approx 0.15$), which suggests very high water affinity of the framework. After that, a distinct step was noticed and the final uptake amount reaches 327 cm³g⁻¹ that corresponds to 10.2 molecules of H₂O per formula unit (Fig. 10). The distinct step is probably due to the presence of different adsorption sites in the pore surface. In case of **2** also, the water vapor adsorption profile shows a type I isotherm with a total uptake of 66 cm³g⁻¹ (2.1 H₂O molecules per formula unit; Fig. 10). The water uptake of **2** is very less than that of **1**, and can be well justified not only due to difference in pore size and solvent accessible void as mentioned earlier, but also due to the additional enhanced hydrophobicity in the framework owing to the presence of methyl groups in pores of compound **2**.

Conclusions

In summary, two isostructural 2D pillared-bilayer coordination polymers of Zn(II) have been synthesized from trigonal dicarboxylate 5-amino-1,3-benzenedicarboxylate and two different linear Schiff base linkers. The pore surface of both the MOFs are decorated with =N–N= base functionalities. Here it has been demonstrated that the incorporation of hydrophobic methyl groups on the linker used, have reduced the solvent accessible void in compound **2** as well as reduces its affinity towards water. Desolvated frameworks of both the compounds show different quantities of CO₂ uptake commensurate to their voids. But in case of water adsorption profile the difference is not at par. Compound **1** without the methyl group show extremely high water affinity at low partial pressure at room temperature but the methyl group containing compound **2** adsorbs very low amounts water even in saturated water vapor pressure under the same condition. The high hydrophobicity of pore wall of **2** will reject the inclusion of water vapor as well as inert N₂ but the presence of polar CO₂-philic core (=N–N=) in the pore surface will facilitate the adsorption of CO₂ within the pore. This work provides us an easy but competent method of modifying organic linkers by introducing hydrophobicity to produce highly water-repellent coordination polymers for effective separation of CO₂ from industrial flue gases.

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Electronic supplementary information (ESI) available:

Different figures related to the crystal structure, FT-IR data, and adsorption properties of the compounds reported in this paper are available as ESI. The structure reported in this paper having the CCDC reference numbers 1043965-1043966. For ESI and crystallographic data in CIF or other electronic format see DOI:

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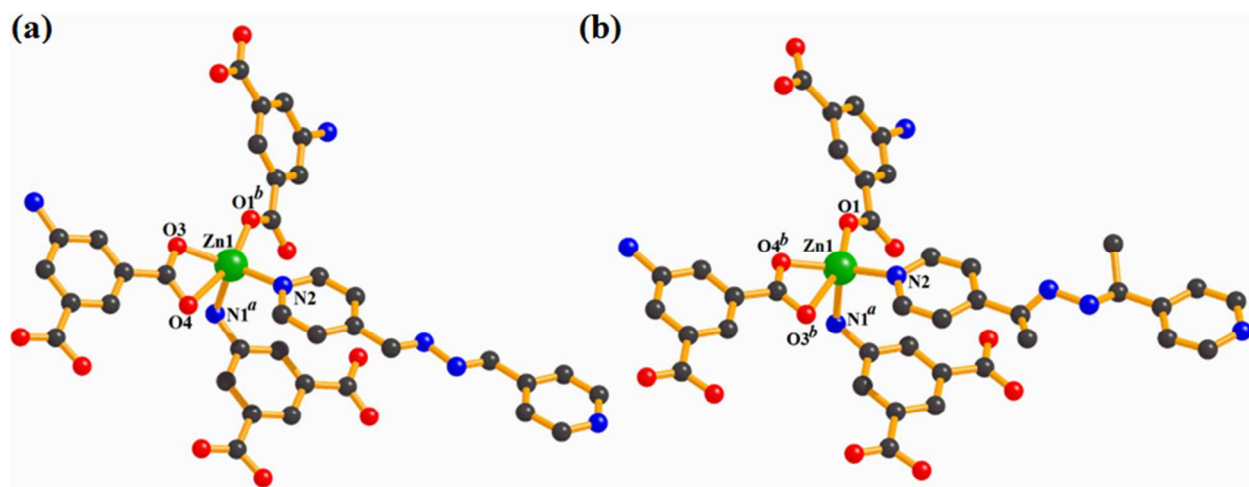
Figures

Fig. 1 View of the coordination environment around Zn(II): (a) for compound **1**, (b) for compound **2**.

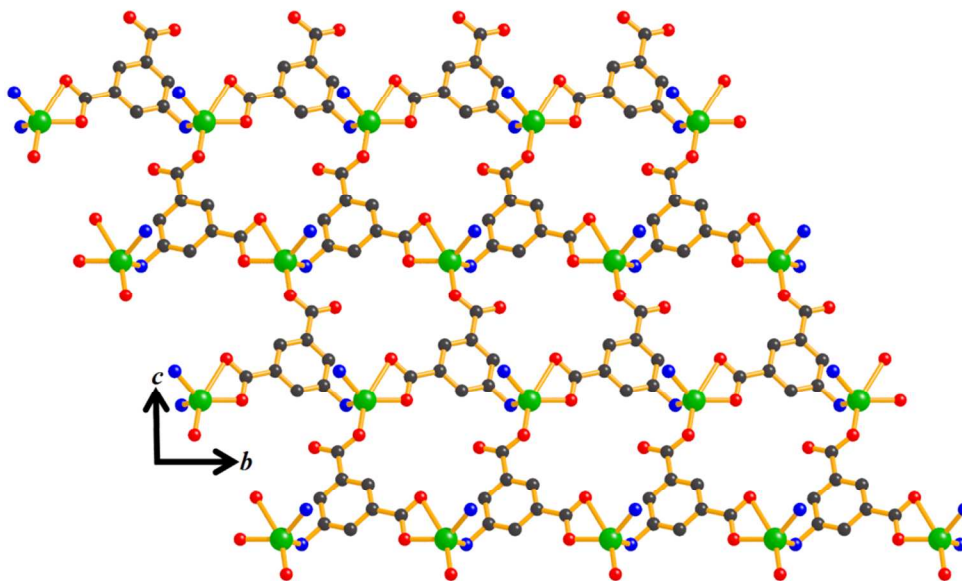


Fig. 2 View of the 2D $[Zn(NH_2\text{-}bdc)]_n$ sheet of **1** in the crystallographic bc plane.

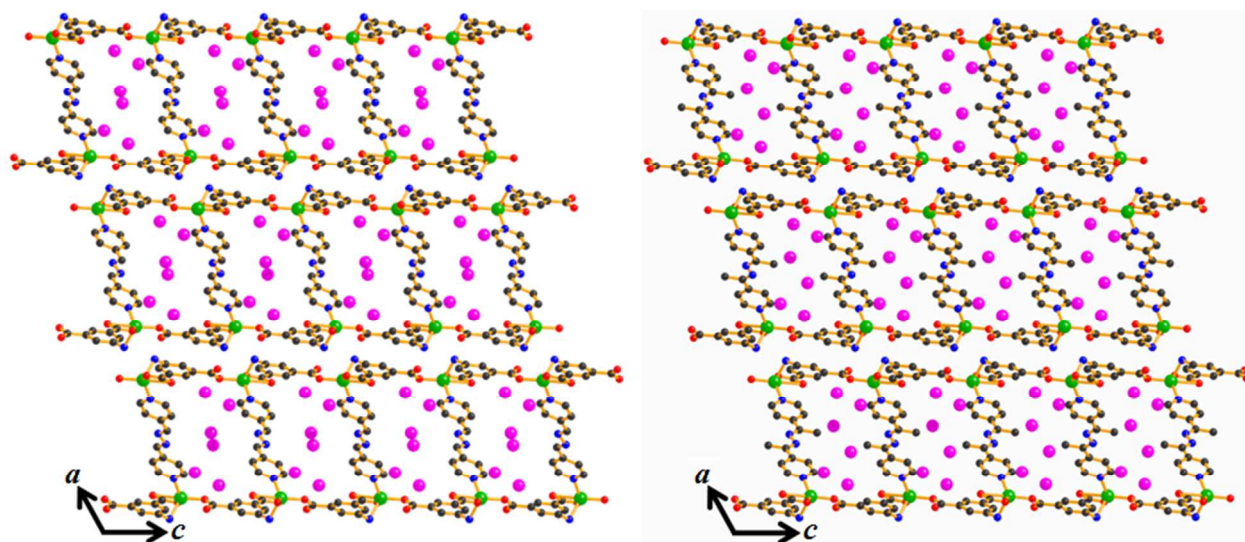


Fig. 3 Stacking of 2D pillared-bilayer framework viewed along b axis: (a) for compound **1**, (b) for compound **2**.

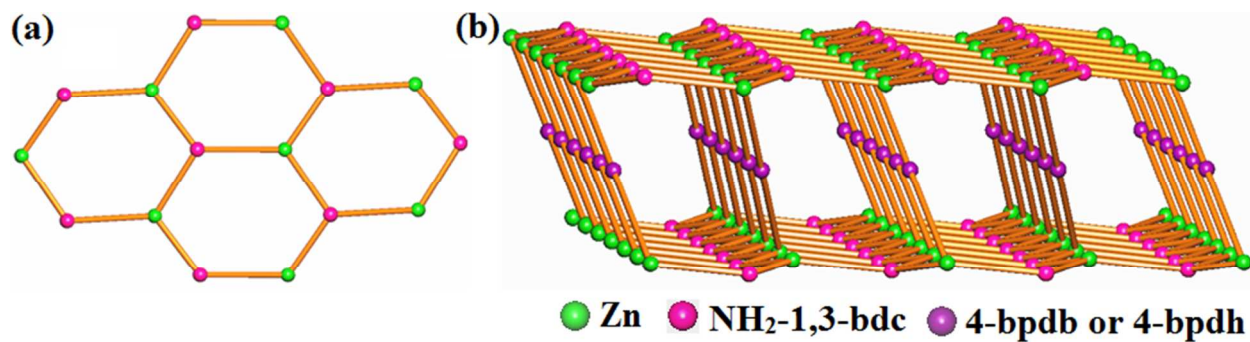


Fig. 4 (a) View of the 3-connected uninodal 2D net of $[\text{Zn}(\text{NH}_2\text{-bdc})]_n$ and (b) 2,3,4-connected 2D net of compound **1** and **2**.

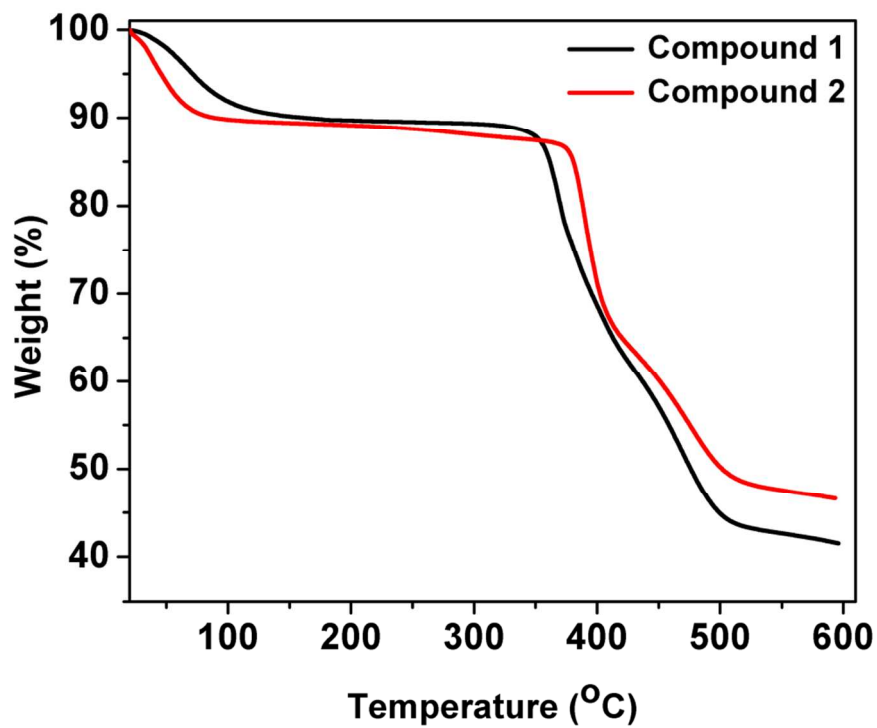


Fig. 5 TGA plots of compounds 1 and 2 measured under nitrogen atmosphere.

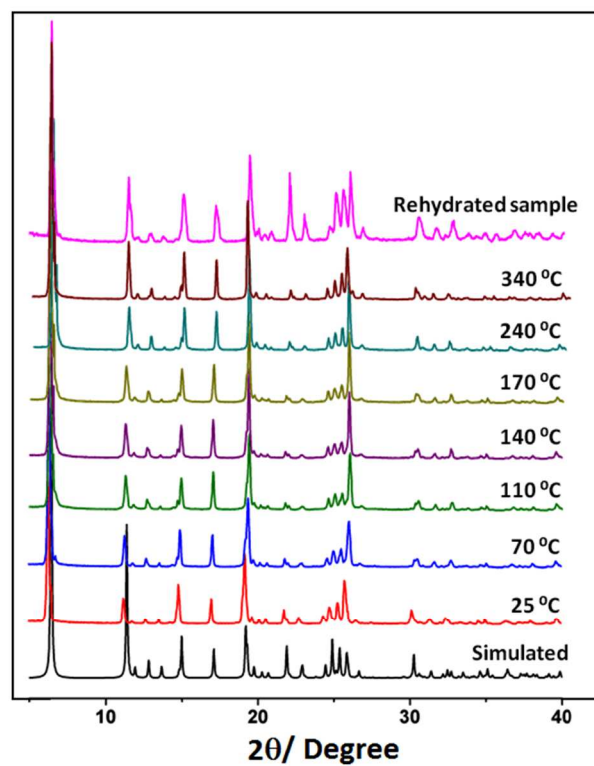


Fig. 6 Variable-temperature PXRD patterns for 1.

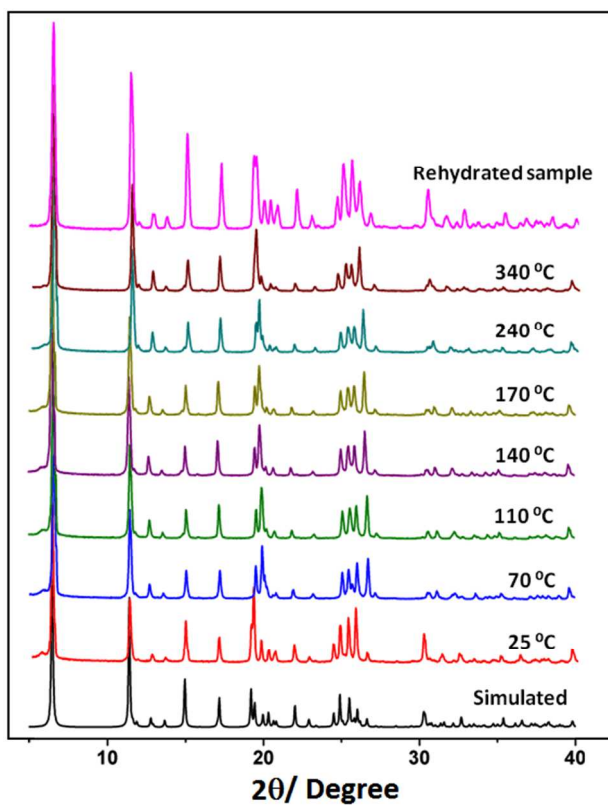


Fig. 7 Variable-temperature PXRD patterns for 2.

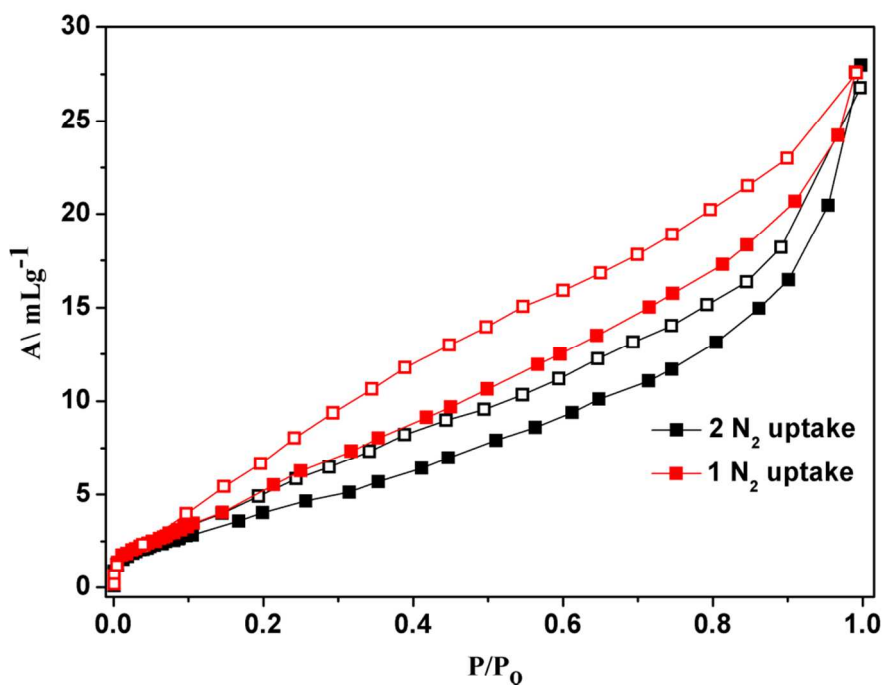


Fig. 8 N_2 adsorption isotherms for 1 and 2 at 77K: adsorption (filled squares), desorption (open squares).

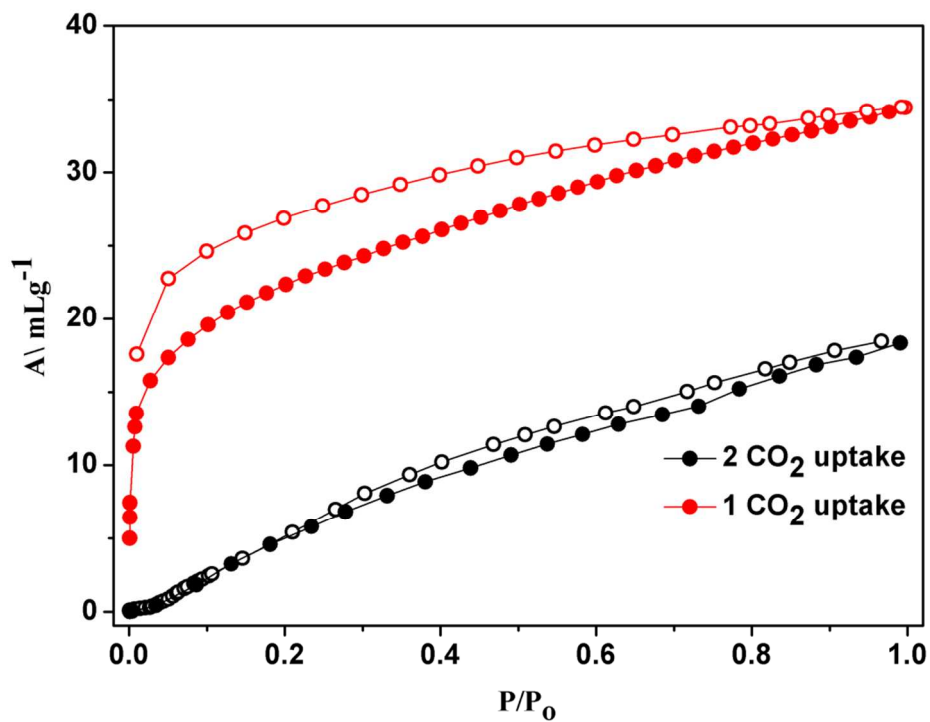


Fig. 9 CO₂ adsorption isotherms for **1** and **2** at 195 K: adsorption (filled circles), desorption (open circles).

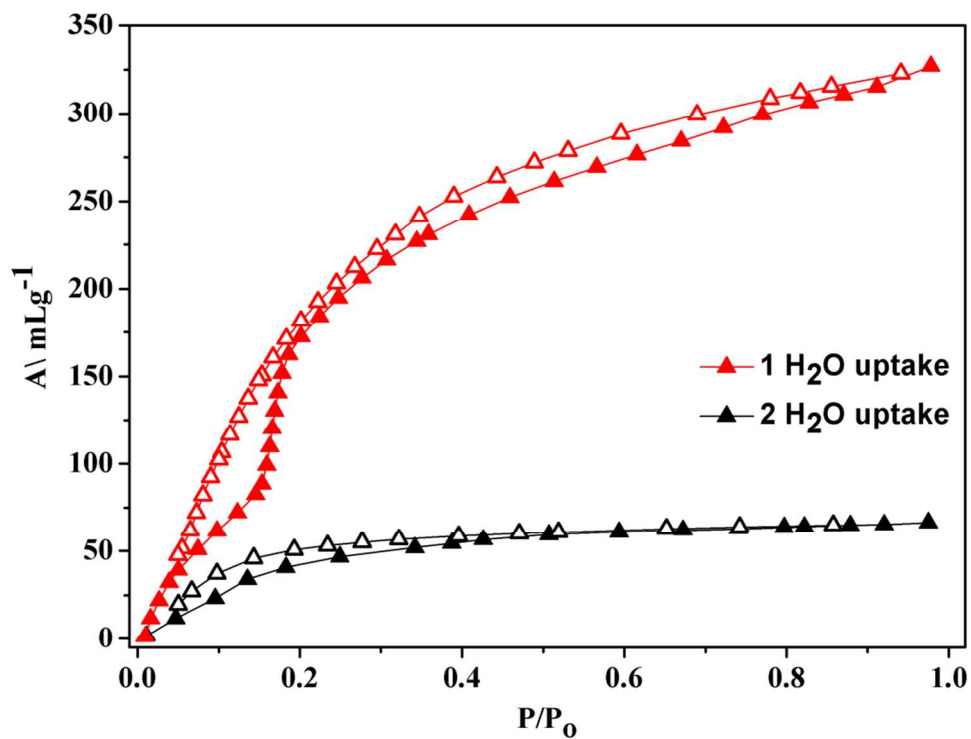


Fig. 10 Water-vapour adsorption isotherms of **1** and **2** at 298 K: adsorption (filled triangles), desorption (open triangles).

Table 1 Crystallographic and Structural Refinement Parameters for Compounds **1** and **2**

	1	2
formula	C ₂₈ H ₂₈ N ₆ O ₁₂ Zn ₂	C ₃₀ H ₃₂ N ₆ O ₁₂ Zn ₂
formula weight	771.34	799.39
crystal system	monoclinic	monoclinic
space group	C2/c	C2/c
<i>a</i> /Å	28.9324(8)	28.825(12)
<i>b</i> /Å	7.7007(2)	7.737(2)
<i>c</i> /Å	16.0837(4)	16.014(6)
α /°	90	90
β /°	107.629(2)	108.23(3)
γ /°	90	90
<i>V</i> /Å ³	3415.16(16)	3392(2)
<i>Z</i>	4	4
<i>D_c</i> /g cm ⁻³	1.485	1.538
μ /mm ⁻¹	1.471	1.484
<i>F</i> (000)	1544	1584
θ range/°	1.5-27.6	1.5-27.6
reflections collected	28097	27675
unique reflections	3941	3923
reflections <i>I</i> > 2 σ (<i>I</i>)	3152	2782
<i>R</i> _{int}	0.033	0.055
goodness-of-fit (<i>F</i> ²)	1.12	1.03
<i>R</i> 1 (<i>I</i> > 2 σ (<i>I</i>)) ^[a]	0.0596	0.0483
<i>wR</i> 2(<i>I</i> > 2 σ (<i>I</i>)) ^[a]	0.2252	0.1544

$${}^aR_1 = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|}, \quad wR_2 = \left[\frac{\sum (w(F_o^2 - F_c^2))^2}{\sum w(F_o^2)^2} \right]^{1/2}.$$

Table 2 Selected Bond Lengths (Å) and Bond Angles (°) for **1**

Zn1-O3	1.983(3)	Zn1-O4	2.560(3)
Zn1-N2	2.047(4)	Zn1-N1 ^a	2.095(4)
Zn1-O1 ^b	1.942(3)		
O3-Zn1-O4	56.20(11)	O3-Zn1-N2	131.33(14)
O3-Zn1-N1 ^a	103.44(14)	O1 ^b -Zn1-O3	103.98(12)
O4-Zn1-N2	87.96(13)	O4-Zn1-N1 ^a	83.65(13)
O1 ^b -Zn1-O4	159.27(12)	N1 ^a -Zn1-N2	103.83(14)
O1 ^b -Zn1-N2	104.05(14)	O1 ^b -Zn1-N1 ^a	109.11(14)

Symmetry code: *a* = *x*, -1+*y*, *z*; *b* = *x*, 1-*y*, 1/2+*z*.

Table 3 Selected Bond Lengths (Å) and Bond Angles (°) for **2**

Zn1-O1	1.931(3)	Zn1-N2	2.043(3)
Zn1-N1 ^a	2.128(4)	Zn1-O3 ^b	2.578(3)
Zn1-O4 ^b	1.983(3)		
O1-Zn1-N2	105.92(12)	O1-Zn1-N1 ^a	105.61(12)
O1-Zn1-O3 ^b	160.55(9)	O1-Zn1-O4 ^b	105.47(10)
N1 ^a -Zn1-N2	102.29(13)	O3 ^b -Zn1-N2	88.14(11)
O4 ^b -Zn1-N2	134.03(12)	O3 ^b -Zn1-N1 ^a	83.80(11)
O4 ^b -Zn1-N1 ^a	100.59(13)	O3 ^b -Zn1-O4 ^b	55.49(9)

Symmetry code: $a = x, -y, -1/2+z$; $b = x, 1-y, -1/2+z$.

Table 4 Hydrogen Bonding Interactions (Å, °) of **1** and **2**

	D-H...A	D-H	H...A	D...A	∠D-H...A
1	N1-H1...O3 ⁱ	0.92(5)	2.17(5)	3.070(5)	166(4)
	N1-H2...O2 ⁱⁱ	0.74(7)	2.32(7)	3.035(5)	163(6)
2	N1-H1...O2 ⁱⁱⁱ	0.89(4)	2.22(4)	3.064(4)	159(3)
	N1-H2...O4 ^{iv}	0.82(5)	2.32(5)	3.073(4)	153(5)

Symmetry code: $i = 3/2-x, 5/2-y, -z$; $ii = 3/2-x, 1/2+y, 1/2-z$; $iii = 3/2-x, -1/2-y, 1-z$; $iv = 3/2-x, -1/2+y, 3/2-z$.

Table 5 π - π Interactions in **1** and **2**

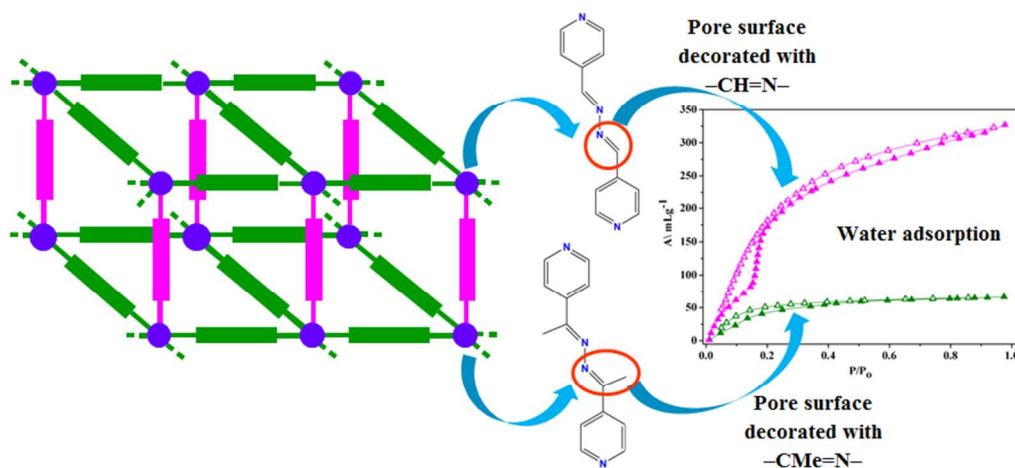
	ring(i) → ring(j)	distance of centroid(i) from ring(j), (Å)	dihedral angle (i,j) (deg)	distance between the (i,j) ring centroids, (Å)
1	R(1) → R(2)i	3.701(3)	18.5(3)	3.512(3)
	R(2) → R(1)ii	3.701(3)	18.5(3)	3.5032(17)
	R(2) → R(2)iii	3.829(2)	0	3.3307(17)
2	R(1) → R(2)iv	3.648(3)	15.9(2)	3.4673(19)
	R(2) → R(1)v	3.648(3)	15.9(2)	3.3501(14)
	R(2) → R(2)vi	3.859(3)	0	3.3456(14)

Symmetry code: $i = x, -1+y, z$; $ii = x, 1+y, z$; $iii = 3/2-x, 3/2-y, -z$; $iv = x, -y, -1/2+z$; $v = x, -y, 1/2+z$; $vi = 3/2-x, 1/2-y, 1-z$.

R(i)/R(j) denotes the ith/jth rings: R(1) = N(2)/C(9)/C(10)/C(11)/C(12)/C(13); R(2) = C(2)/C(3)/C(4)/C(5)/C(6)/C(7).

For Table of Content use**Pillared-Bilayer Porous Coordination Polymers of Zn(II): Enhanced Hydrophobicity of Pore Surface by Changing the Pillar Functionality**

Biswajit Bhattacharya, Ritesh Haldar, Dilip Kumar Maity, Tapas Kumar Maji and Debajyoti Ghoshal*



Two new isostructural porous coordination polymers of Zn(II) have been synthesized using mixed ligand system. Huge difference in water adoption is observed by introducing small hydrophobic group in organic linker.