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Selective CO_2 Adsorption in a Robust and Water-Stable Porous Coordination Polymer with New Network Topology

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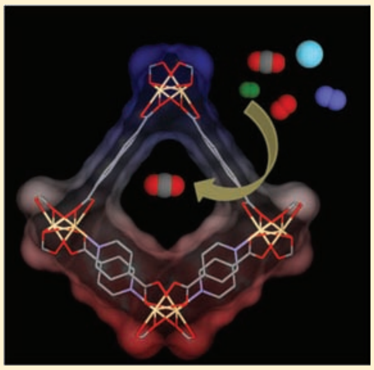
S *Supporting Information*

ABSTRACT: A robust and water-stable porous coordination polymer $[Cd(NDC)_{0.5}(PCA)]\cdot G_x$ (**1**) (H_2NDC = 2,6-napthalenedicarboxylic acid, HPCA = 4-pyridinecarboxylic acid, G = guest molecules) with new network topology has been synthesized solvothermally. The framework is 3D porous material and forms a 1D channel along the *c*-axis, with the channel dimensions ~9.48 × 7.83 Å^2. The compound has high selectivity in uptake of CO_2 over other gases (H_2, O_2, Ar, N_2, and CH_4). The framework is highly stable in presence of water vapor even at 60 °C. The high CO_2 selectivity over other gases and water stability makes the compound promising candidate for industrial postcombustion gas separation application.



INTRODUCTION

Carbon dioxide (CO_2) is a major greenhouse gas that mainly contributes to the global warming causing climate changes, which is one of the greatest environmental challenges facing worldwide.[1] Human activities, mainly burning of fossil fuels are largely increasing the concentration of CO_2 in the atmosphere. Carbon capture and storage (CCS), where carbon dioxide is removed from industrial flue gases. has attracted considerable attention as it is technologically feasible and could play a significant role in reducing greenhouse gas emissions.[2] Separation of CO_2 from power plant flue gas containing water-saturated N_2 with some amount of O_2 and other gases is the key technical challenge. Currently, several methods like adsorption, amine scrubbing, and membrane separation are used in CCS technology to remove CO_2 from industrial flue gases. Amine scrubbing and membrane separation methods are very energy intensive, and capture in these methods alone requires 25−40% energy of a plant and also causes environmental issues due to solvent loss and chemical degradation. Adsorption method is a very promising for CCS technology considering energy required, cost, and properties of adsorbents.[3] Enhancing the separation efficiency has the greatest potential to reduce the overall cost of the CO_2 capture process. To make the process practical, a stable adsorbent with low cost, molecular-level control of CO_2 selectivity to the relevant gas mixtures, especially at low pressure (the partial pressure of CO_2 in the flue gases is 0.1−0.2 atm), is very important.

For the last two decades, porous coordination polymers (PCPs) or metal−organic frameworks (MOFs) emerged as a new type of porous materials and a very promising candidate for CCS technology. These compounds built from metal ions and organic ligands, which are tailorable, low-density solids with extremely high surface area, are potentially useful for gas separation and storage and catalysis.[4−19] A large number of highly porous MOFs have been synthesized, which store a large amount of CO_2, but those materials can simultaneously take up significant amount of other gases also.[20] Separation processes of CO_2 from other gases, viz. CO_2/N_2 (postcombustion), CO_2/H_2 (precombustion), CO_2/O_2 (air separation), and CO_2/CH_4 (natural gas purification), have high technological and industrial importance. Several parameters of gases are important in achieving these separations, like kinetic diameters of gases and their electric properties, i.e., quadrupole moment and polarization.[2b,21] In addition to these, for most of the adsorbent materials, selectivity of a separation process is determined by a combination of adsorption and diffusion selectivity.[2b,c] To design suitable adsorbents for CCS technology, we need to consider all these above criteria. Adsorbents with high CO_2 separation efficiency and stability in presence of water vapor (similar to flue gas mixture temperature ~60 °C) are still rare.[2b,22] Herein we report synthesis, structural characterization, and gas sorption properties of $[Cd(NDC)_{0.5}(PCA)]\cdot G_x$ (compound **1**, Figure 1) having new network topology built with two different ligands that exhibits permanent porosity, water stability, and highly selective CO_2 adsorption properties at low pressure and 273 K.

EXPERIMENTAL SECTION

Materials and Measurements. All the reagents and solvents were commercially available and used without further purification. FT-IR spectra were recorded on NICOLET 6700 FT-IR spectrophotometer using KBr pellets. X-ray powder pattern were measured on Bruker D8 Advanced X-ray diffractometer at room temperature using Cu Kα radiation (λ = 1.5406 Å), Thermogravimetric analyses was

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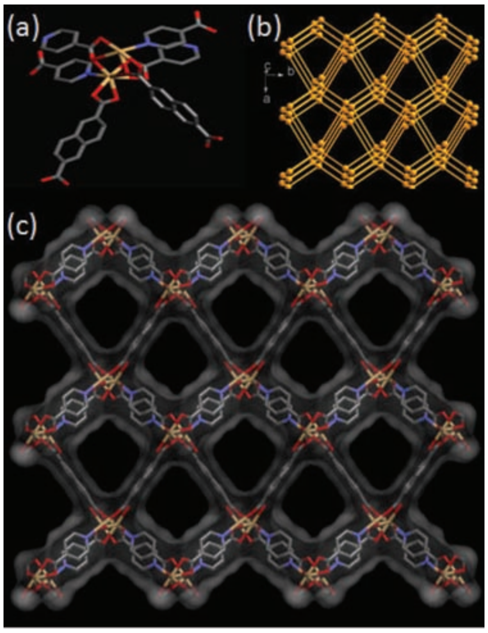

Figure 1. (a) Coordination environment, (b) framework topology, and (c) view of the microporous framework of compound **1**: cadmium, yellow; carbon, gray; nitrogen, blue; oxygen, red. Hydrogen atoms and disorder solvents are omitted for clarity.

recorded on a Perkin-Elmer STA 6000 TGA analyzer under N_2 atmosphere with a heating rate of 10 °C/min.

Synthesis of [Cd(NDC)$_{0.5}$(PCA)]·G$_x$ (1). Single crystal of **1** was prepared by reacting 1 mmol of $Cd(NO_3)_2 \cdot 4H_2O$, 1 mmol of 4-pyridinecarboxylic acid (*pca*), and 0.5 mmol of 2,6-napthalenedicarboxylic acid (*nda*) in 6 mL of DMF–EtOH (1:1) by the solvothermal technique, in a Teflon-lined autoclave . The autoclave was heated under autogenous pressure to 120 °C for 2 days and then cooled to RT by 24 h period. Upon cooling to RT, the desired product appeared in ~20% yield. Compound **1** can be also prepared with better yield (~45%) using DEF as solvent, which was used for further studies.

X-ray Structural Studies. Single-crystal X-ray data of **1** was collected at 150 K on a Bruker KAPPA APEX II CCD Duo diffractometer (operated at 1500 W power: 50 kV, 30 mA) using graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). Crystal was on nylon CryoLoops (Hampton Research) with Paraton-N (Hampton Research). The data integration and reduction were processed with SAINT software.[23] A multi-scan absorption correction was applied to the collected reflections. The structure was solved by the direct method using SHELXTL[24] and was refined on F^2 by full-matrix least-squares technique using the SHELXL-97[25] program package within the WINGX[26] program. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were located in successive difference Fourier maps, and they were treated as riding atoms using SHELXL default parameters. The structures were examined using the *Adsym* subroutine of PLATON[27] to ensure that no additional symmetry could be applied to the models. Identification of the guest entities within the voids of the frameworks was not possible by modeling electron densities due to the disorder contents of the large pores in the frameworks. The routine SQUEEZE was applied to the structures in order to remove diffuse electron density associated with badly disordered solvent molecules. Because of the poor crystal quality, the maximum residual electron density value is remaining high. We tried with several crystals from different batches and every crystal showing the same problem. Supporting Information Table S1 contains crystallographic data for **1**.

Low Pressure Gas Sorption Measurements. Low pressure gas sorption measurements were performed using BelSorpmax (Bel Japan). All of the gases used were of 99.999% purity. To obtain a guest-free sample, **1** was exchanged several times with acetonitrile for two days. The sample was then air-dried and TGA was recorded to confirm the guest exchange. The acetonitrile exchanged sample was then heated at 120 °C under vacuum for 5 h to get guest-free compound **1C**. Prior to adsorption measurement, the guest-free sample **1C** was pretreated at 120 °C under vacuum for 5 h using BelPrepvacII and purged with N_2 on cooling. Between the experiments with various gases, the outgassing procedure was repeated for ca. 5 h. The N_2, H_2, Ar, and O_2 gas sorption isotherms were monitored at 77 K and 273 K. The adsorption isotherms for the CO_2 gases were measured at 195 K, 273 K, and 298 K. CH_4 was measured at 273 K. Surface area and pore size distribution were calculated using BelMaster analysis software. The virial graph analysis was done according previously reported leterature.[28]

Stability in the Presence of Water Vapor. The stability of compound in presence of water vapor was checked at 60 °C. The desolvated sample was taken in glass vial and kept in slightly bigger screw cap bottle containing water. The bottle was heated at 60 °C, and the PXRD was recorded after different time intervals. TGA was recorded after 24 h to confirm the hydrated phase. The sample was then heated in vacuum at 120 °C for 5 h to get dehydrated phase. Removal of guest water was confirmed by TGA, and framework stability was confirmed from PXRD pattern.

■ RESULTS AND DISCUSSION

Compound **1** was synthesized by solvothermal reaction of 2,6-napthalenedicarboxylic acid (H_2NDC), 4-pyridinecarboxylic acid (HPCA), and $Cd(NO_3)_2 \cdot 4H_2O$ in DEF or DMF–EtOH mixture solvent. Colorless crystals were collected and characterized by single crystal X-ray diffraction technique, and phase purity of the bulk material was confirmed by powder X-ray diffraction (PXRD) and thermogravimetric analysis (TGA) (Supporting Information, Figures S8 and S9). Single-crystal X-ray structure analysis revealed that **1** crystallizes in monoclinic crystal system, space group $P2_1/c$, and formulated as [Cd(NDC)$_{0.5}$(PCA)]·G$_x$ (G = disorder guest molecules) The asymmetric unit of **1** consists of one-half NDC, one PCA, and one Cd(II) ion and disorder solvents. Despite its toxicity, Cd(II) was used because of its versatile coordination properties. Each metal ion exhibited seven coordinated distorted pentagonal bipyramidal geometry with NO_6 donor set, bonding from two bidentate carboxylate units from two different ligands, and two bridging carboxylate oxygen from another set of each ligand, and the seventh coordination was occupied by the nitrogen atom of one PCA ligand. These bridging bonds extended the metal centers to make a metal-carboxylate chain along the *c*-axis. Other ends of both the ligands of the metal-carboxylate chain were connected with four different metal-carboxylate chains, and this continuous network formed the assembled three-dimensional (3D) structure (Figure 1).

The resultant 3D framework is porous and forms 1D channels along *c*-axis, with the channel dimensions ~9.48 × 7.83 Å^2 (the channel size is measured by considering the van der Walls radii for constituting atoms). The cavities of the framework are occupied by disordered solvent molecules, and PLATON[29] analysis revealed that the 3D porous structure was composed of large voids of 1505.2 Å^3 that represent 34.9% per unit cell volume.

Topological analysis using TOPOS software identified that the structure has a new topological network with uninodal 9-c net, which can be presented as a Schläfli symbol $3^9\ 4^{17}\ 5^{10}$ (td10 = 3569) (Figure 1b). This network is identified by the code **skg1** in the TOPOS TTD database[30] (see Supporting Information for TOPOS analysis result).

PXRD of the bulk phase of compound **1** and simulated pattern matched indicating the phase purity, which is also supported by SCXRD analysis of randomly selected crystals. The TGA curve indicates that the compound is stable up to 300 °C, which was also confirmed by variable temperature PXRD (Figure 2). The desolvated phase **1A** was generated by heating the compound for 16 h at 180 °C under reduced pressure, and solvent removal was confirmed by TGA data. From PXRD data, it is clear that compound is very stable after removal of guest molecules. Desolvated form of the compound also generated by exchanging DEF with low boiling solvents (MeOH and MeCN), and then solvents were removed at lower temperature under vacuum to avoid any partial damage to the framework. Stability of **1B** and **1C** (**1B** and **1C** are **1** exchanged with MeOH and MeCN, respectively, and then desolvated at 120 °C) were again confirmed by TGA and PXRD data.

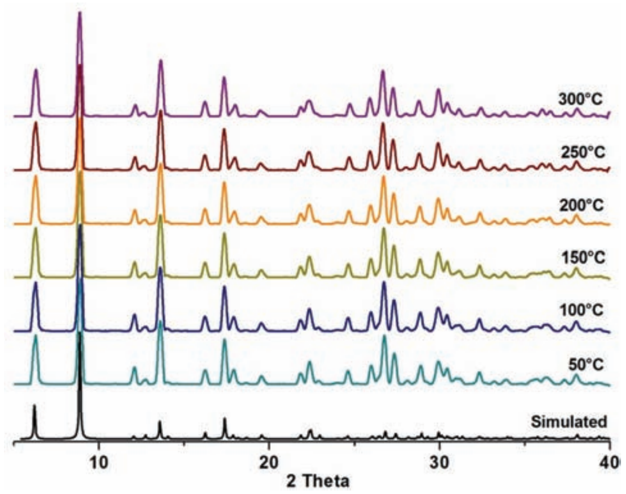

Figure 2. Variable temperature PXRD pattern of **1**.

Desolvated compound is stable in open air even after months. To check the water stability of the framework, we kept compound **1A** in a closed vessel exposed to water vapor for 24 h at 60 °C. TGA data indicates that the water exposed phase takes ~10% H_2O and PXRD pattern remains unchanged, indicating compound maintains the framework. This compound also maintains the framework after dehydrating the exposed phase, which was again confirmed from TGA, PXRD, and CO_2 sorption data (Figure 3, Supporting Information Figures S10 and S18). The water sorption was also measured at 298 K, which shows that the compound takes about 80 mL of H_2O (Supporting Information Figure S17).

The porosity and gas adsorption properties were measured volumetrically at different temperature. To find the best method to activate the sample, we measured CO_2 adsorption isotherm at 195 K for all three evacuated phases (**1A**, **1B**, and **1C**) (Figure 4). All isotherms show type I behavior as expected for material with micropores, but in the case of **1B**, the amount is less. Among **1A** and **1C**, although the adsorption amount is same, for the previous one it is very much dependent on activating time and temperature, so we did all other adsorption measurements using **1C**. Adsorption isotherms of several gases were measured at different temperature. Surprisingly, the adsorption isotherms of Ar (kinetic diameter = 3.5 Å), H_2 (2.8 Å), and N_2 (3.6 Å) at 77 K reveal no inclusion of guest molecules, although this rigid framework has much bigger pore size than the kinetic diameter of above gases. We determined pore size distribution of the compound (Supporting Information Figure S14). Interestingly, a significant amount of CO_2 (80 cm^3/g) and CH_4 (40 cm^3/g) uptake were observed at 195 K.

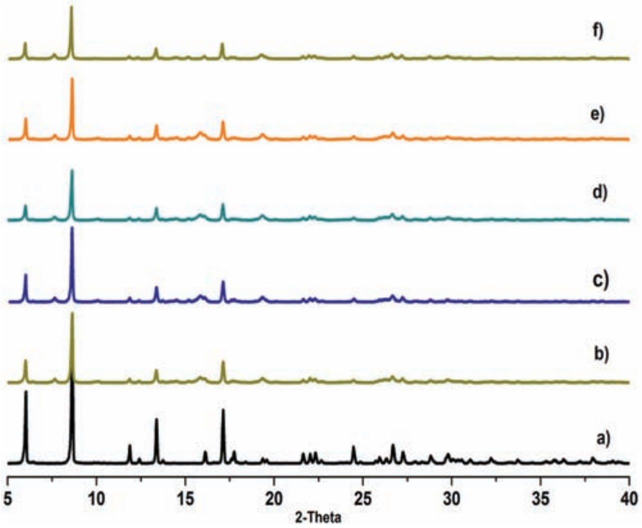

Figure 3. Powder X-ray diffraction (PXRD) patterns of **1**. (a) **1C**: after exposed to H_2O vapor at 60 °C for (b) 1 h, (c) 5 h, (d) 8 h, (e) 24 h, and (f) dehydrated form after heating at 120 °C for 6 h.

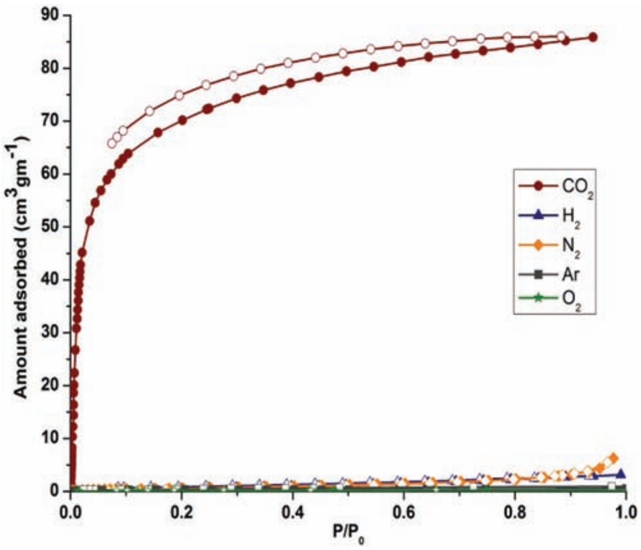

Figure 4. Gas adsorption isotherms of **1C**: CO_2 (195 K), H_2 (77 K), N_2 (77 K), Ar (77 K), and O_2 (77 K) (filled symbols, adsorption; open symbols, desorption).

As reported previously also by Kitagawa group,[31] this unusual adsorption selectivity may be due to the strong interactions of incoming guest molecules (CH_4, H_2, N_2, Ar and O_2) with the pore windows at 77 K, which prevents the next incoming guest molecules to enter into the pore. CO_2 with a large quadrupole moment interact strongly with the host framework and maybe a good polarizability value, also allows CH_4 to interact with the framework, which makes it possible to enter into the pore. The empty pore of the host framework with large π−electron clouds of the naphthalene ring from the NDC ligand, polar functional groups of two ligands, and Cd(II) generates a suitable electronic environment, which favors interaction of CO_2 and CH_4 with the framework.[32,33] CO_2 interacts more strongly than CH_4 with the framework due to the existence of a quadrupole

Table 1. Virial Graph Analysis of Compound 1A

temperature (K)	adsorbate	A_0 ln(mol g^{-1} Pa^{-1})	Henry's const K_H (mol g^{-1} Pa^{-1})	R^2	S_{ij}[a]
273	CO_2	−17.45994	2.6×10^{-8}	0.988	
273	CH_4	−20.79051	9.3497×10^{-10}	0.846	28
273	H_2	−23.04742	9.7866×10^{-11}	0.972	266
273	N_2	−21.43169	4.9242×10^{-10}	0.964	53
273	Ar	−21.47874	4.6979×10^{-10}	0.986	55
273	O_2	−22.57957	1.5622×10^{-10}	0.822	166

[a] The selectivity for CO_2 (i) over different gases (j) calculated as $S_{ij} = K_H\ (CO_2)/K_H(j)$.

moment for the former but not for CH_4, and consequently adsorption amounts are much more in case of CO_2 than CH_4 at different temperatures. The favorable interactions have facilitated this compound to be highly selective for CO_2 over other gases. Adsorption amounts of other gases (H_2, O_2, N_2 and Ar) are negligible, which is desirable for separation of CO_2 from gas mixture. The Henry's law selectivities of CO_2/CH_4, CO_2/H_2, CO_2/N_2, CO_2/Ar, and CO_2/O_2 separation were calculated based on equation $S_{ij} = K_H(CO_2)/K_H(j)$.[28] (Table 1 and Figure 5). The Isosteric heat of adsorption for CO_2 was found to be 20 kJ/mol for low loading (Supporting Information Figure S15).

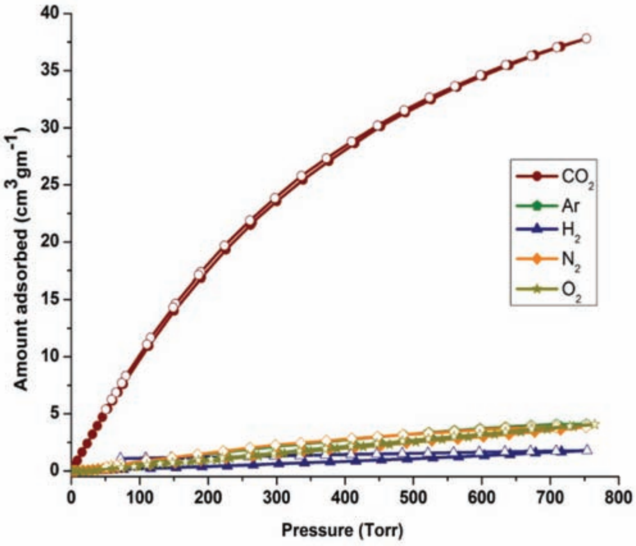

Figure 5. Adsorption isotherms for different adsorbate in **1C** at 273 K (filled symbols, adsorption; open symbols, desorption).

The CO_2/CH_4 separation selectivity of **28** is among the few highest values reported in the literature, which makes the compound a potential candidate for natural gas purification (Supporting Information Figure S12).[2c] The CO_2/H_2 separation selectivity is found to be 266, thus the compound can be used in precombustion CCS technology. The CO_2/N_2 selectivity is 53 times, making it a potential candidate in postcombustion CCS technology. The separation selectivities for CO_2/Ar and CO_2/O_2 are 55 and 166, respectively, which is important in air separation processe. The high selectivity for CO_2 over H_2, N_2, Ar, O_2, and H_2O stability makes the compound a promising candidate for industrial postcombustion CCS technology.

In conclusion, we have successfully synthesized and characterized a novel robust water-stable 3D framework with new network topology. The compound exhibits a very high selectivity for CO_2 over other small gases, including CH_4, H_2, N_2, Ar, and O_2. Selective capture of CO_2 and water stability makes the compound a promising candidate for industrial gas-separation applications.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

X-ray crystallographic data of **1** in CIF format, thermal analysis, X-ray powder diffraction patterns, topology analysis, adsorption isotherms of **1**, and FT-IR of both the ligands and **1** and **1′**. This material is available free of charge via the Internet at http://pubs.acs.org.

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