Inorganic Chemistry

Article

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A Zn Metal−Organic Framework with High Stability and Sorption Selectivity for CO_2

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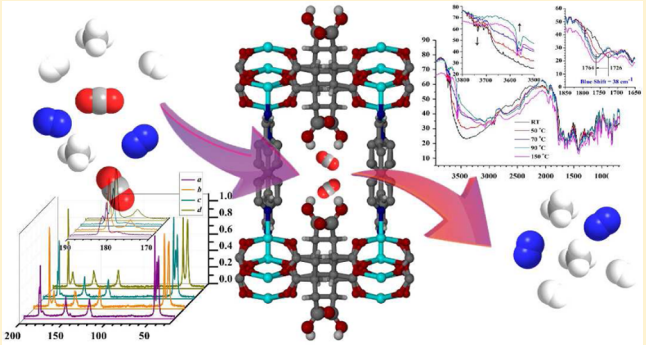
Supporting Information

ABSTRACT: A three-dimensional porous Zn metal−organic framework (**UPC-12**) with high thermal and chemical stability was isolated in high yield and purity from a hydrothermal reaction. **UPC-12** exhibits high selectivity for CO_2 due to the formation of hydrogen bonds between CO_2 molecules and the −COOH groups exposed inside the channels and the effective $\pi-\pi$ interactions between CO_2 molecules and the pillared bipyridine moieties of the MOF. The adsorption−desorption process was studied, for the first time, by both ^{13}C CP-TOSS NMR spectroscopy and in situ DRIFTS.



INTRODUCTION

Capturing CO_2 to prevent global warming due to the greenhouse effect has been one of the most important issues in recent years.[1] Depending on the formation of C−N covalent bonds, alkanol amines have been employed to develop a quite common "amine-scrubbing" strategy/method for selective capture of CO_2 nowadays.[2] However, despite the effective fixation of CO_2 molecules, breaking the C−N bonds to regenerate the adsorbents unambiguously consumes quite a large amount of energy, resulting in significantly increased cost.[2,3] On the other hand, selective separation/removal of CO_2 is also very important and indispensable for the purification of natural gas in industry since the coexisting acidic CO_2 not only significantly lowers the calorific value but also causes serious corrosion of pipelines and equipment.[4] As a consequence, new materials possessing both high selectivity for and facile release of CO_2 are highly desired.

Because of the easy synthesis and low regeneration cost related to the usual physisorption mechanism, porous metal−organic frameworks (MOFs) that selectively adsorb CO_2 have received increasing attention in recent years in gas capture and separation.[5,6] The utilization of open metal sites, flexible frameworks, interpenetrated frameworks, and surface-functionalized frameworks has been found to increase the selectivity and improve the separation of CO_2 from other gases.[7] Among these, the surface functionalization method using different functional groups like −OH, $-NH_2$, and $-SO_2$ to modify the MOF pore surface seems to be the most promising one because of the effective optimization of the CO_2 selectivity and separation ability.[8−12] Unfortunately, most of these porous MOFs are sensitive to moisture and in particular to acidic or basic conditions. Furthermore, it is especially critical to understand the CO_2−host interactions in MOFs for the design and synthesis of porous materials with high selectivity for CO_2. As a choice, solid-state NMR spectroscopy is a powerful technique for detecting adsorbed CO_2 molecules in porous materials, as has been reported in the literature.[13] However, detailed studies of the CO_2 adsorption−desorption process through ^{13}C cross-polarization total suppression of spinning sidebands (CP-TOSS) NMR spectroscopy remain unexplored to date. Moreover, no studies of the CO_2 desorption process through in situ diffuse-reflectance infrared Fourier transform spectroscopy (DRIFTS) have been reported to date. Herein we describe the preparation, structure, and gas adsorption properties, in particular the highly selective CO_2 adsorption, of a porous −COOH surface-decorated MOF, $Zn_2(H_2chhca)(bipy)\cdot 4H_2O$ (**UPC-12**) (UPC = China University of Petroleum, H_6chhca = cyclohexane-1,2,3,4,5,6-hexacarboxylic acid, bipy = 4,4′-bipyridine), with high thermal and chemical stability. ^{13}C CP-TOSS NMR and in situ DRIFTS technologies were employed to study the interactions between the adsorbed CO_2 molecules and the framework at room temperature, which are further rationalized on the basis of theoretical calculations.

Received: June 4, 2015
Published: October 27, 2015

DOI: 10.1021/acs.inorgchem.5b01232
Inorg. Chem. 2015, 54, 10587−10592

EXPERIMENTAL SECTION

Materials and Methods. Commercially available reagents were used as received without further purification. Elemental analyses (C, H, N) were performed with a PerkinElmer 240 elemental analyzer. Thermogravimetric analysis (TGA) was performed under N_2 on a PerkinElmer TGA 7 instrument. ^{13}C CP-TOSS NMR spectra were recorded on a 400 MHz Bruker Avance III spectrometer. In situ DRIFTS spectra were measured on a Nicolet Nexus infrared spectrometer.

Synthesis of UPC-12. $Zn(NO_3)_2{\cdot}6H_2O$ (223 mg), cyclohexane-1,2,3,4,5,6-hexacarboxylic acid (87 mg), and 4,4′-bipyridine (78 mg) in a molar ratio of 2:1:1 and distilled water (8 mL) were mixed in a 25 mL Teflon cup, and the mixture was shaken in an ultrasonic bath for 30 min. The vessel was then sealed and heated at 120 °C for 48 h. The autoclave was subsequently allowed to cool to room temperature. After washing with distilled water and ethanol, plate-shaped transparent colorless crystals were obtained in 90% yield. Elemental analysis of **UPC-12**: calcd C 37.58%, H 3.44%, N 3.98%; found C 37.20%, H 3.36%, N 3.87%.

Single-Crystal Structure Analysis. The crystallographic data and structure refinement parameters of **UPC-12** are summarized in Table 1. Single-crystal X-ray diffraction of **UPC-12** was performed using an Aglient Technologies SuperNova Atlas dual system with a Mo Kα radiation (λ = 0.71073 Å) microfocus source and focusing multilayer mirror optics. The structure was solved by direct methods using SHELXTL and refined by full-matrix least-squares on F^2 using SHELX-97. Non-hydrogen atoms were refined with anisotropic displacement parameters during the final cycles. Hydrogen atoms were placed in calculated positions with isotropic displacement parameters set to 1.2 × U_{eq} of the attached atom. Crystallographic data for the structures reported in this paper (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre (CCDC 1055675).

Table 1. Crystal Data Collection and Structure Refinement for UPC-12

formula	$C_{11}H_{12}NO_8Zn$
M_r	351.58
size [mm^3]	0.17 × 0.14 × 0.11
crystal system	monoclinic
space group	$P2/n$
a [Å]	8.6256(6)
b [Å]	14.0418(7)
c [Å]	10.9059(6)
α [deg]	90.00
β [deg]	105.697(7)
γ [deg]	90.00
V [Å^3]	1271.65(13)
Z	4
$F(000)$	672
ρ_{calcd} [g cm^{-3}]	1.473
[mm^{-1}]	7.45
range [deg]	3.49 to 25.00
reflections collected	2231
independent reflections	1722 (R_{int} = 0.0435)
parameters	203
R_1 [$I > 2\sigma(I)$]	0.0604
wR_2 [$I > 2\sigma(I)$]	0.1729
goodness of fit	1.085

Gas Adsorption Measurements. A freshly prepared sample (~120 mg) was soaked in CH_2Cl_2 for 24 h, and the extract was discarded. Fresh CH_2Cl_2 was subsequently added, and the sample was allowed to soak for another 24 h. This process was repeated three times to remove water solvates. Then the sample was dried under vacuum at 150 °C for 10 h to generate a solvent-free sample. A sample of 100 mg was used for gas adsorption measurements.

Theoretical Calculations. Density functional theory (DFT) calculations were carried out at the PBE-D(Grimme)/DND(3.5) level.[14] The input MOF skeleton without CO_2 molecules was obtained from the single-crystal structure. The CO_2 molecules were added into the input MOF skeleton according to the possible directions of O···H hydrogen bonds in the CIF file of the single-crystal structure. Optimization of the CO_2@MOF supramolecular system was carried out at the PBE-D(Grimme)/DND(3.5) level[14] in DMol^3 Software[15] with the global cutoff radii set to 3.0 Å.

Preparation of the CO_2-Loaded MOF for NMR Measurements. The as-synthesized sample of **UPC-12** was put into zirconia rotor with a diameter of 4 mm. Subsequently, the rotor was placed in the sample tube of the micropore analyzer (ASAP 2020HD88), degassed for 10 h at 150 °C, and backfilled with CO_2. Then the rotor was taken out and capped with the lid quickly for the ^{13}C CP-TOSS NMR investigation.

In Situ DRIFTS Investigation. The as-synthesized sample of **UPC-12** was degassed for 5 h at 150 °C and backfilled with CO_2, and the in situ DRIFTS investigation was performed under an atmosphere of N_2 from room temperature to 150 °C and then back to room temperature. The spectra were recorded at intervals of 20 °C during heating, 40 °C during cooling from 150 to 70 °C, and 20 °C during cooling from 70 °C to room temperature. At every temperature point, two figures were scanned with a resolution of 4 cm^{-1} and a scan time of 128 s.

RESULTS AND DISCUSSION

Description of the Crystal Structure. The hydrothermal reaction of cyclohexane-1,2,3,4,5,6-hexacarboxylic acid (H_6chhca), $Zn(NO_3)_2$, and 4,4′-bipyridine (bipy) led to the isolation of large crystals of **UPC-12** in yields as high as 90%. The powder X-ray diffraction (PXRD) pattern recorded for the single-crystal sample closely matched the simulated one generated according to corresponding single-crystal diffraction results as detailed below, indicating the high purity of this target compound. Single-crystal X-ray diffraction analysis revealed that the three-dimensional (3D) porous framework of **UPC-12** bears a $Zn_2(COO)_4$ paddlewheel secondary building unit (SBU) and that only four of the six carboxylate groups in H_6chhca (with a chair conformation) get deprotonated, resulting in the H_2chhca ligand with two protonated carboxylate groups left (Figures 1 and S1). Each of the four deprotonated carboxylate groups in H_2chhca then bridges two zinc ions, leading to the generation of a two-dimensional (2D) planar supramolecular structure along the *ac* plane with a $Zn_2(COO)_4$ paddlewheel SBU. This layerlike 2D planar structure, as a building block, further packs into a 3D framework with bipy ligands as pillars along the *b* axis, dependent on the coordination bonding interactions between Zn ions of the 2D supramolecular structure and nitrogen atoms of the bipy ligands, with one-dimensional (1D) channels with the dimensions of 4.15 Å × 7.23 Å (from atom to atom). In the case that H_2chhca is simplified as a 4-connected planar linker, the $Zn_2(COO)_4$ paddlewheel SBU as a six-connected node, and bipy as a linear linker, obviously an ***fsc*** topology is employed by the 3D framework of **UPC-12**. At the end of this paragraph, it is worth noting that all of the remaining protonated carboxylate groups for all of the H_2chhca ligands in the 3D framework of **UPC-12** are located inside the 1D channels (Figure 1e), rendering the channels a typical hydrophilic nature. This in turn is responsible for the selective adsorption of CO_2 by **UPC-12** as detailed below.

DOI: 10.1021/acs.inorgchem.5b01232
Inorg. Chem. 2015, 54, 10587−10592

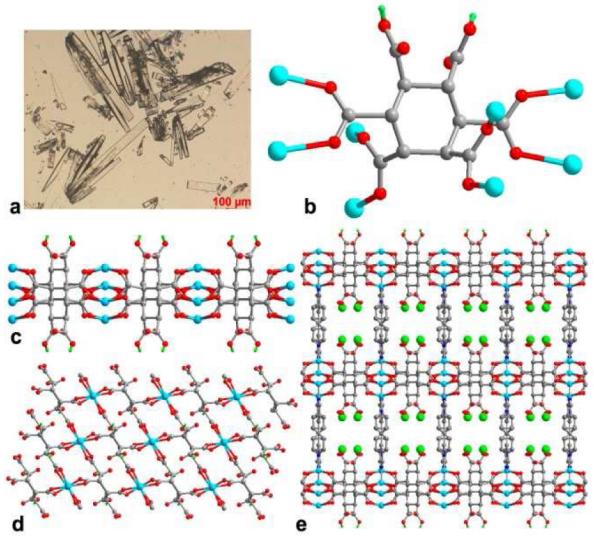


Figure 1. (a) Photograph of the **UPC-12** single crystals. (b) Coordination mode of the H_2chhca ligand. (c, d) 2D layer viewed along the *c* and *b* axes, respectively. (e) 3D porous framework of **UPC-12**, showing the protonated carboxylate groups located inside the channels.

Thermal and Chemical Stability. TGA technology was first used to measure the stability of **UPC-12** in the present case. As shown in Figure S3, the sample remains stable up to 360 °C without decomposing, indicating the high thermal stability of **UPC-12**. This was further confirmed by the temperature-dependent PXRD results. As clearly exhibited in Figure 2, as the temperature increases from 25 to 350 °C, the PXRD pattern remains almost unchanged in terms of both the number and positions of the peaks, indicating the unchanged framework of **UPC-12** over this temperature range. This is also true for crystals of **UPC-12** upon treatment in boiling water or soaking in acidic or basic aqueous solutions over the pH range of 3−12 for 24 h, revealing the high chemical stability of **UPC-12**. This high chemical stability may derive from the tight structure with small channels as well as the existence of protonated carboxylate groups in the framework. Despite the claimed high stabilities of several MOFs, including NO_2-tagged UiO-66, PCN-225, and pyrazole-based Ni-MOF,[16] seldom have porous MOFs been reported to be stable in both acidic and basic aqueous solutions.

Gas Sorption Properties. Because of the 1D channels with exposed −COOH groups involved in the framework together with its high thermal and chemical stabilities, gas uptake measurements on desolvated **UPC-12** for a series of gases including N_2, CH_4, H_2, and CO_2 were carried out to study its gas adsorption properties. According to the adsorption isotherms shown in Figure 3, amounts of 6, 4.6, and 10.5 $cm^3\ g^{-1}$ were deduced for adsorption of N_2 at 77 K, CH_4 at 273 K, and H_2 at 77 K, respectively, indicating the very much restricted adsorption behavior of **UPC-12** for these gases. The restricted sorption behaviors for N_2, CH_4, and H_2 should result from the hydrophilic nature of the channels with a large amount of exposed protons. It should be pointed out that the anomalous behavior of the H_2 desorption isotherm is due to kinetic reasons. However, **UPC-12** can selectively adsorb CO_2 molecules at 196 K with reversible type-I behavior with a Brunauer−Emmett−Teller (BET) surface area of 271.8 $m^2\ g^{-1}$ and a pore volume of 0.126 $cm^3\ g^{-1}$, indicating the high affinity

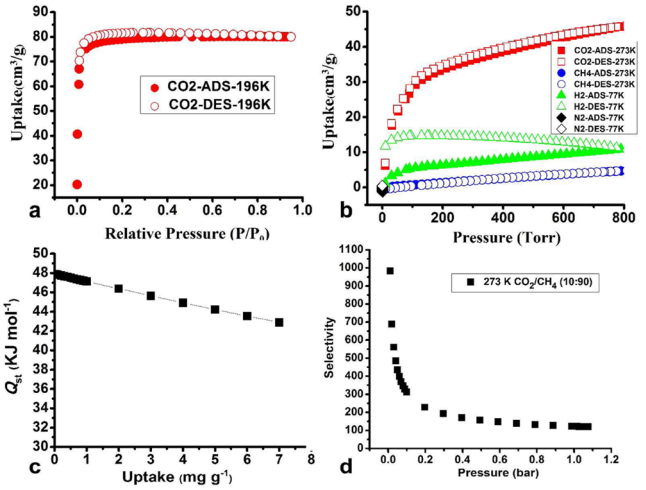


Figure 3. (a) CO_2 adsorption and desorption isotherms at 196 K. (b) Gas adsorption and desorption isotherms for CO_2 at 273 K, CH_4 at 273 K, H_2 at 77 K, and N_2 at 77 K. (c) Isosteric heat of adsorption for CO_2. (d) IAST CO_2/CH_4 selectivities for a 10:90 CO_2/CH_4 gas mixture at 273 K.

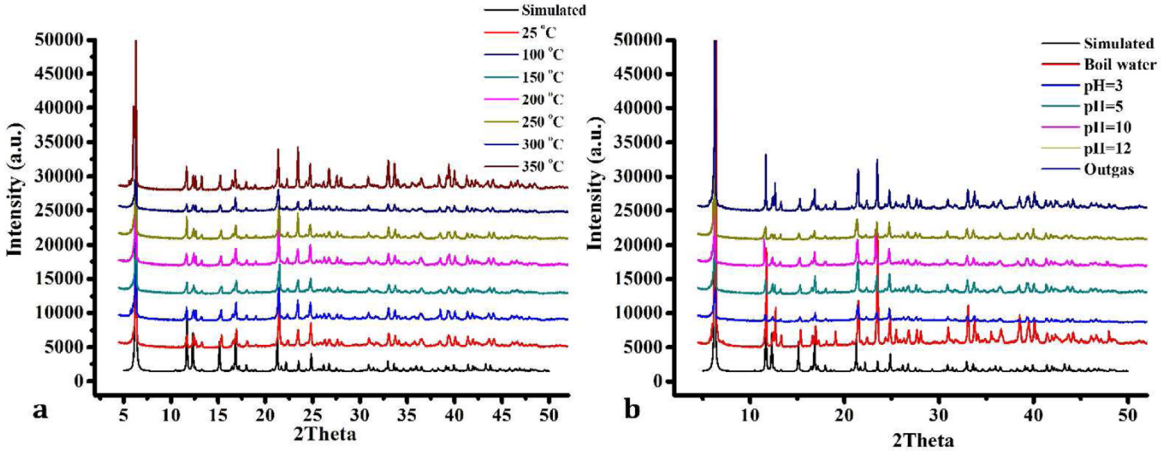


Figure 2. PXRD patterns of **UPC-12**: (a) patterns from room temperature to 350 °C; (b) patterns of samples with distinct chemical treatments.

DOI: 10.1021/acs.inorgchem.5b01232
Inorg. Chem. 2015, 54, 10587−10592

of the **UPC-12** framework for CO_2 molecules. This was further confirmed by CO_2 adsorption measurements at different temperatures. As can be seen in Figure S4, **UPC-12** exhibits typical type-I adsorption behavior for CO_2 at 273, 283, and 295 K with the adsorption abilities of 46, 38.1, and 34 $cm^3\ g^{-1}$. Furthermore, from fits of the CO_2 adsorption isotherms at 273, 283, and 295 K to a virial-type expression, a value of ~48 kJ mol^{-1} for the isosteric heat of adsorption (Q_{st}) of **UPC-12** for CO_2 at zero coverage was derived, suggesting the high selectivity of this single-crystal framework for CO_2.[17] In addition, on the basis of the experimentally recorded adsorption isotherms of **UPC-12** for both CO_2 and CH_4 at 273 K, ideal adsorbed solution theory (IAST) was used to further evaluate the adsorption behavior of **UPC-12** for mixed gas. According to the calculation results for the 10:90 CO_2/CH_4 gas mixture (Figure 3d), in the low pressure range **UPC-12** exhibits excellent selectivities for CO_2 over CH_4 ranging from 689 to 190, revealing the potential application of **UPC-12** in separation of CH_4 from CO_2. Furthermore, **UPC-12** also exhibits excellent selectivity for CO_2 over CH_4 at 295 K (Figure S5), which indicates that the framework of **UPC-12** possesses a high affinity for CO_2 molecules.

Theoretical Investigations. DFT calculations were then performed to rationalize the high Q_{st} and selectivity of **UPC-12** for CO_2 gas. The results showed that the carboxylate groups of the H_2chhca ligand located inside the channels of the framework play a very important role in the high affinity of **UPC-12** for CO_2, as they form hydrogen bonds with the CO_2 molecules adsorbed at positions I, II, III, and IV with OH···O═C═O bond length of 2.48, 2.51, 2.30, and 2.48 Å, respectively (Figure 4). In combination with the $\pi\cdots\pi$ interactions between the π electronic structure of CO_2 (O═C═O) and the π moieties of the pillared bipy ligands in the **UPC-12** framework ($-C_6H_4N-$) with distances in the range of 3.35−3.80 Å, this becomes responsible for the high isosteric heat of adsorption of **UPC-12** for CO_2, with an average binding energy of −54.19 kJ mol^{-1} according to the calculation results. This is in good accordance with the experimental findings as detailed above.

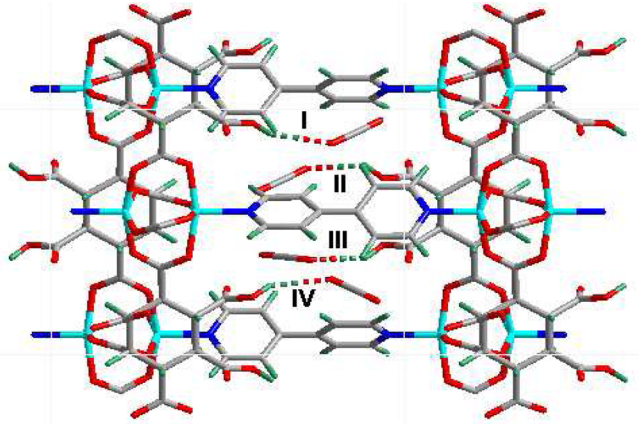


Figure 4. DFT-calculated model of the CO_2 binding sites inside the channels of **UPC-12**.

^{13}C NMR Investigation. The high binding energy revealed for **UPC-12** and CO_2 in the present case seems to suggest a quite strong combination between **UPC-12** and CO_2 (actually, the stable adsorption of CO_2 gas by the MOF framework). As a consequence, solid-state ^{13}C CP-TOSS NMR spectroscopy was employed to probe the CO_2 molecules adsorbed on the **UPC-12** framework at room temperature. As shown in Figure 5, four sets of signals at around 43−48, 123, 151, and 177−182 ppm due to the cyclohexane, bipy (123 and 151 ppm), and H_2chhca carboxylic carbons, respectively, were observed in the ^{13}C NMR spectrum of the empty **UPC-12** single-crystal sample (Figure 5b), which is similar to the spectrum of the as-synthesized sample (Figure 5a). Among the latter set of signals, the peak at 180.9 is attributed to the uncoordinated carboxyl carbons of H_2chhca in the framework, while the peaks at 177.2 and 181.8 ppm are due to the carbons of the Zn-coordinated carboxyl groups. After CO_2 was backfilled into the crystalline sample (which was first activated at 150 °C for 10 h) and kept for half an hour, significant changes in the ^{13}C NMR spectrum occur (Figure 5c) as a result of the formation of hydrogen bonds between the uncoordinated carboxyl groups of H_2chhca and the CO_2 molecules adsorbed inside the channels. The peak at 180.9 ppm disappears, while along with a slight low-field shift the peak at 181.8 ppm becomes sharpened. Also, as a result of the hydrogen-bond formation by the two uncoordinated carboxyl groups left for H_2chhca, the triplet signal at 43−48 ppm due to the cyclohexane carbons becomes a doublet as a result of the concomitant environmental change. In addition, the peak at 123 ppm with almost the same intensity as the one at 151 ppm for the empty **UPC-12** single-crystal sample becomes obviously stronger than that at 151 ppm after treatment of empty **UPC-12** with CO_2. This result appears to suggest that the CO_2 molecules adsorbed resonate at 123 ppm,[18] which overlaps with the peak of the bipy carbons at the same position to intensify the signal. Further support was provided by the following experimental results. The ^{13}C CP-TOSS NMR spectrum after the empty MOF was put in the air at room temperature for 2 h (Figure 5d) is similar to that of the CO_2-loaded MOF, demonstrating that the empty MOF can adsorb CO_2 from the air. In addition, the CO_2-loaded sample was put into a tube and heated to 150 °C under vacuum for 5 h to release the adsorbed

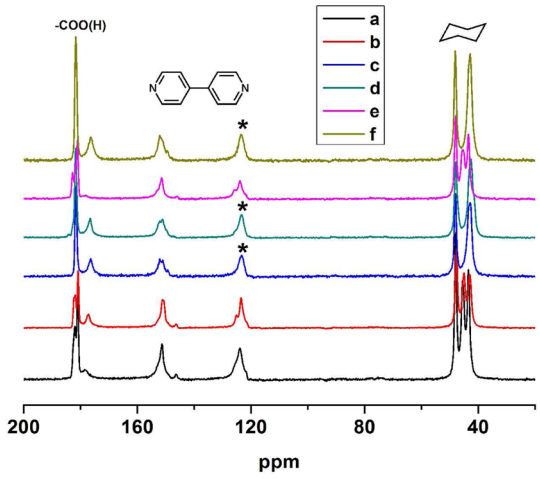


Figure 5. Solid-state ^{13}C NMR spectra of **UPC-12**: (a) spectrum of the as-synthesized sample; (b−d) spectra after the as-synthesized sample was (b) degassed for 10 h at 150 °C, (c) degassed for 10 h at 150 °C and backfilled with CO_2, and (d) degassed for 10 h at 150 °C and allowed to stand for 2 h in air; (e) spectrum after the CO_2-loaded sample was degassed for 5 h at 150 °C and backfilled with H_2O; (f) spectrum after the H_2O-loaded sample was re-degassed for 5 h at 150 °C and re-backfilled with CO_2. Asterisks denote the CO_2 peak combined with one of the bipy peaks.

DOI: 10.1021/acs.inorgchem.5b01232
Inorg. Chem. 2015, 54, 10587−10592

CO_2, and the resulting MOF sample was then directly poured into water to avoid CO_2 contamination. The ^{13}C NMR spectrum of this newly treated sample (Figure 5e) was found to be almost identical with the spectrum of the as-synthesized MOF. Nevertheless, the ^{13}C NMR spectrum of the CO_2-adsorbed sample was completely recovered after this sample was reactivated and re-backfilled with CO_2 (Figure 5f).

In Situ DRIFTS Study. In situ DRIFTS was also utilized to confirm the stable adsorption of CO_2 gas by the **UPC-12** framework. Figure 6 displays the temperature-dependent in situ

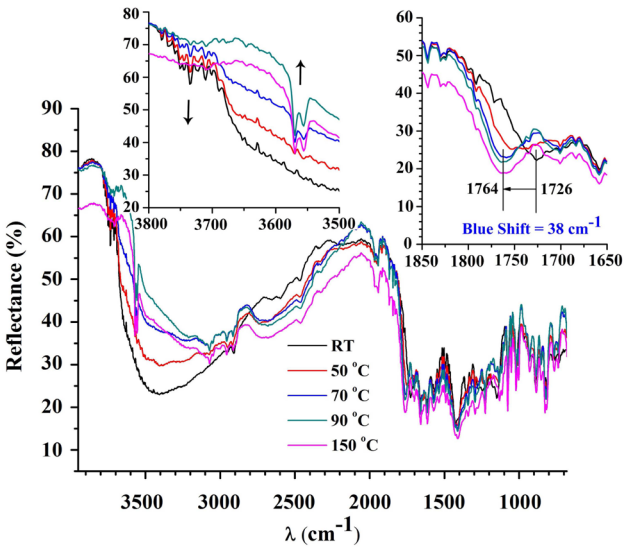


Figure 6. In situ DRIFTS spectra, recorded under a flowing N_2 atmosphere, of a CO_2-loaded sample of **UPC-12** at room temperature and upon heating to 50, 70, 90, and 150 °C.

DRIFTS spectra of the CO_2-loaded sample under a flowing N_2 atmosphere. The observation of the peak at 1792 cm^{-1} due to the asymmetric stretching vibration of CO_2 (ν_1) as well as the absorptions at 3735 and 3750 cm^{-1} due to the combination mode arising from ν_1 and the bending mode of CO_2[19] in the room temperature spectrum clearly demonstrates the existence of the CO_2 molecules adsorbed inside the channels of **UPC-12**. The peak at 1726 cm^{-1} observed in this spectrum is attributed to the carbonyl stretching vibration of the −COOH groups of H_2chhca after hydrogen-bond formation with CO_2 molecules, and it is accompanied by the appearance of a broad O−H stretching vibration peak at 3406 cm^{-1}.[8c] Along with the gradual release of the adsorbed CO_2 by heating of the sample from room temperature to 50, 70, 90, and 150 °C, the absorptions at 3735 and 3750 cm^{-1} gradually lose intensity in the same order and ultimately disappear in the 150 °C in situ DRIFTS spectrum. Meanwhile, the carbonyl stretching vibration peak of the −COOH groups undergoes a gradual blue shift to 1764 cm^{-1}. The blue shift accompanied by the splitting of the one hydroxyl group band into two peaks at 3556 and 3570 cm^{-1} is also well-rationalized by the existence of two types of −COOH groups in **UPC-12** along with loss of the adsorbed CO_2 molecules according to the single-crystal analysis as detailed above. In addition, when the temperature is lowered in a gradual manner from 150 °C to room temperature for the sample also under a flowing N_2 atmosphere, no obvious change is observed in the in situ DRIFTS spectra (Figure S6), confirming again the strong adsorption of CO_2 gas to **UPC-12** due to the intense hydrogen bonding and π−π interactions of the CO_2 molecules with the uncoordinated carboxylate groups and bipy moieties, respectively, of **UPC-12** at room temperature. At the end of this section, it is noteworthy that the present results reveal the great potential of both solid-state ^{13}C CP-TOSS NMR spectroscopy and in situ DRIFTS in monitoring of CO_2 molecules adsorbed in porous MOF structures.

CONCLUSIONS

A porous Zn MOF (**UPC-12**) with exceptionally high thermal and chemical stability was synthesized in high yield and purity via a facile hydrothermal reaction based on low-cost commercially available starting materials. Gas adsorption measurements revealed the high selectivity of **UPC-12** for CO_2 over N_2, CH_4, and H_2 due to hydrogen bonding and effective $\pi\cdots\pi$ interactions of the adsorbed CO_2 molecules with the −COOH groups located inside the channels of the framework and the π moieties ($-C_6H_4N-$) of the pillared bipy ligands of **UPC-12**, respectively, indicating the potential application of this MOF in selective capture/separation of CO_2 over $N_2/CH_4/H_2$. This was further supported by ^{13}C NMR and in situ DRIFTS results and, more importantly, well-rationalized on the basis of DFT calculations. Further studies toward the design and synthesis of functional MOFs with high surface area and large channels decorated with more −COOH groups and therefore further improved selectivity for CO_2 gas are in progress.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorgchem.5b01232.

Details of gas adsorption experiments, calculation of isosteric heat of adsorption and adsorption selectivity, and additional figures (PDF)

Crystal structural data for **UPC-12** (CIF)

The crystal structural data for **UPC-12** have also been deposited with the Cambridge Crystallographic Data Centre (CCDC 1055675).

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Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

Financial support from the National Key Basic Research Program of China (Grants 2013CB933400 and 2012CB224801), the National Natural Science Foundation of China (Grants 21371179, 21271117, and 21290174), the Fundamental Research Funds for the Central Universities (13CX05010A), and NCET-11-0309 is gratefully acknowledged. We are also grateful to the calculating center of the Mining College of Guizhou University for the grant of computer time.

DOI: 10.1021/acs.inorgchem.5b01232
Inorg. Chem. 2015, 54, 10587−10592

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DOI: 10.1021/acs.inorgchem.5b01232
Inorg. Chem. 2015, 54, 10587−10592