A Family of Rare Earth Porous Coordination Polymers with Different Flexibility for CO_2/C_2H_4 and CO_2/C_2H_6 Separation

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S *Supporting Information*

ABSTRACT: A family of new porous coordination polymers (PCPs) were prepared by the reaction of an acylamide modified ligand (H_3L) and $RE(NO)_3 \cdot xH_2O$ (RE = Y, La, Ce, Nd, Eu, Tb, Dy, Ho, and Tm). PXRD and single-crystal X-ray analyses of them revealed that, besides the La PCP, all other rare earth members gave isomorphous structures. The two types of structural toplogies obtained, although similar, differ in their alignment of acylamide functional groups and structural flexibility. Adsorption experiments and in situ DRIFT spectra showed that rigid frameworks have the typical microporous behavior and poor selective capture of CO_2 over C_2H_4 and C_2H_6; however, the unique La-PCP with structural flexibility and close-packed acylamide groups has a high selective capture of CO_2 with respect to C_2H_6 or C_2H_4 at 273 K, especially at the ambient pressure area (0.1−1 bar).
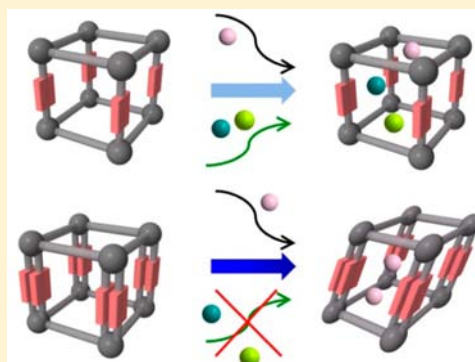
INTRODUCTION

C_2H_4 and C_2H_6 are the important chemical raw materials for the commodity production in the petroleum chemical industry.[1] CO_2, as the main impurity in such hydrocarbon gas (C_2H_4 and C_2H_6) streams, is considered as a barrier of the heat release from gas combustion, and corrosive to gas pipelines.[2] Furthermore, sometimes it further influences the conversion of the products. However, the conventional technologies for the CO_2 capture involving the chemisorption by amine-solution systems incur high cost and pollution in the regeneration process.[3] Moreover, ethane and ethylene can form a maximum pressure azeotrope with carbon dioxide, which hinders carbon dioxide removal by distillation.[4]

Recent progress has shown that porous coordination polymers (PCPs) or metal−organic frameworks (MOFs)[5] are very promising materials for gas storage and separation. This is because their high surface area, periodic, but tunable, pore sizes/type, and functionalizable pore walls. Moreover, their pore surface can be postmodified for the expected applications, such as immobilizing strong recognition sites for higher CO_2 selective capture. Usually, the strategies of tuning the pore surface charge through variation of the metal cations,[6] introducing alkylamine functionality or water molecules onto the coordinatively unsaturated metal center,[7] and employing the amine-based organic building blocks[8] have been frequently used. However, almost all of these strategies have been involved in rigid frameworks, and the separation behavior only located in

the low-pressure areas renders industrial usage difficult. In contrast, some flexible frameworks possess exceptional capability for gas separation.[9] This is because almost no adsorption occurs below the "gate-opening" pressure for the closed structural phase, followed by an abrupt increase in adsorption beyond the gate-opening pressure. The gate-opening pressure is sensitive to different adsorbates. Therefore, the challenge we now face is how to introduce strong recognition sites in the soft porous materials for better CO_2 separation at the ambient pressure region (0.1−1.5 bar).

We have succeeded in controlling structurally and electronically the dynamics of porous coordination polymers for the effective selective sorption of dioxygen and nitric oxide[10] and fine-tuning the gate-opening pressure for CO_2 separation by the solid solution method.[11] Here, a family of new lanthanide frameworks, bearing the functional acylamide group from a tritopic ligand, 4,4′,4″-(benzenetricarbonyltris-(azanediyl)) tribenzoic acid (H_3L), were prepared with the following considerations: First, lanthanides were chosen because of their propensity for forming well-defined 1-D channels with tritopic caboxylate ligands. Second, the introduction of the acylamide groups can increase the flexibility of the structure.[12] Third, the acylamide groups can enhance the CO_2 binding affinity.[8] Structural analyses, gas-sorption measurements, and in

situ DRIFT spectroscopy studies show that the unique and flexible framework (La-PCP) with close-packed acylamide groups represents higher separation ability in comparison with other rigid RE-PCPs possessing a single acylamide site. Thus, the flexible framework with a functional acylamide group will provide a way for constructing PCP materials with the potential separation of CO_2 in the future.

■ EXPERIMENTAL SECTION

General Information. All the reagents and solvents were commercially available and used as received. The IR spectra and in situ DRIFT absorption spectroscopy measurements of CO_2 adsorption were recorded in the range of 4000−400 cm^{-1} on a Nicolet ID5 ATR spectrometer. Thermal analyses were performed on a Rigaku TG8120 instrument from room temperature to 600 °C at a heating rate of 5 °C/min under flowing nitrogen. Powder X-ray diffraction was obtained using a Rigaku RINT powder diffractometer with a Cu Kα anode.

Synthesis of a Series of Rare Earth PCPs. The same process was employed to prepare these nine complexes, except for replacing the metal salt (M(NO$_3$)$_3$·xH$_2$O: M = Y, La, Ce, Nd, Eu, Tb, Dy, Ho, and Tm). Thus, only the synthesis of the lanthanum complex is described in detail here. La(NO$_3$)$_3$·6H$_2$O (17.6 mg, 0.040 mmol), H$_3$L (6 mg, 0.0136 mmol), and several drops of nitric acid were mixed with 2 mL of DMF in a glass container and tightly capped with a Teflon cap and heated at 125 °C for 2 days. After cooling to room temperature, colorless block crystals were obtained and washed with fresh DMF. The phase purity of these series of crystal materials were confirmed by the powder X-ray diffraction pattern (PXRD). Thermogravimetric analysis (TGA) shows that all of them are thermally stable up to 450 °C under a N$_2$ atmosphere (Supporting Information).

Single-Crystal X-ray Study. The single-crystal X-ray diffraction measurement was performed at 223 K with a Rigaku AFC10 diffractometer with a Rigaku Saturn Kappa CCD system equipped with a MicroMax-007 HF/VariMax rotating-anode X-ray generator with confocal monochromated Mo Kα radiation. Data were processed using Crystal Clear TM-SM (Version 1.4.0). The structure was solved by direct methods and refined using the full-matrix least-squares technique using the SHELXTL package.[13] Non-hydrogen atoms were refined with anisotropic displacement parameters during the final cycles. Organic hydrogen atoms were placed in calculated positions with isotropic displacement parameters set to 1.2U_{eq} of the attached atom. The unit cell includes a large region of disordered solvent molecules, which could not be modeled as discrete atomic sites. We employed PLATON/SQUEEZE[14] to calculate the diffraction contribution of the solvent molecules and, thereby, to produce a set of solvent-free diffraction intensities; the structure was then refined again using the data generated. Crystal data as well as the details of data collection and refinements for the complexes are summarized in Table 1 (CCDC numbers for them: 936435−936436.)

Adsorption Experiments. Before the measurement, the sample (about 100−150 mg) was prepared by immersing the as-synthesized samples in fresh DMF for 3 days to remove the uncoordinated ligand and metal ions. The activated sample was obtained by heating the washed sample at 140 °C under a dynamic high vacuum for 30 h. In the low-pressure gas sorption measurement, ultra-high-purity grade were used throughout the adsorption experiments. Gas adsorption isotherms were obtained using a Belsorp-mini volumetric adsorption instrument from BEL Japan Inc. using the volumetric technique. High-pressure adsorption of CO_2, C_2H_4, and C_2H_6 were measured using a BEL Japan adsorption instrument over a pressure range of 0−10 bar at 273 K. Before measurements, about 200 mg samples were loaded into the sample basket within the adsorption instrument and then degassed under high vacuum at 140 °C for 30 h to obtain the desolvated samples.

Table 1. Crystallographic Parameters of Y-PCP and La-PCP

	La-PCP	Y-PCP
space group	$P2_1/c$	$P2/c$
a (Å)	18.582(4)	20.418(4)
b (Å)	34.589(7)	7.9129(16)
c (Å)	16.268(3)	39.212(11)
β (deg)	103.81(3)	121.27(2)
V (Å^3)	10154(4)	5415(2)
Z	4	4
ρ_{calc} (g cm^{-3})	1.016	0.891
$F(000)$	3104	1480
$R_1{}^a$ ($I > 2\sigma$)	0.0647	0.1358
$wR_2{}^b$(all data)	0.2148	0.3821
S	1.132	1.280

$^aR_1 = \sum||F_o| - |F_c||/\sum|F_o|.$ $^bwR_2 = [\sum w(F_o{}^2 - F_c{}^2)^2/\sum w(F_o{}^2)^2]^{1/2}.$

■ RESULTS AND DISCUSSION

Synthesis and Structure. Solvothermal reaction of nine nitric salts with H$_3$L in DMF containing HNO$_3$ afforded block crystals, respectively. PXRD partterns of them show two types of structural topologies among them (Figure 1). Therefore, in this paper, three representative PCPs (Y-PCP and Ho-PCP vs La-PCP) with two different structures were selected for additional measurements.

Single-crystal X-ray diffraction analysis reveals that Y-PCP, formulated as [YLDMF·guest], crystallizes in space group $P2/c$ with a = 20.418(4) Å, b = 7.9129(16) Å, c = 39.212(11) Å, and β = 121.27(2)°. Each Y^{3+} is eight-coordinated by seven oxygen atoms from six carboxyl groups and one DMF molecule. The Y−O bond lengths range from 2.246 to 2.499 Å. The ligand acts as a μ_6-bridge linking six Y^{3+} ions, in which two carboxylate groups adopt μ_2-η_1:η_1-bridging, and one μ_2-η_2:η_1-bridging mode, respectively. Connection behaviors of the ligand then lead to an inorganic chain with edge-shared polyhedra. The adjacent two Y^{3+} ions are bridged by eight ligands, each ligand is connected to three chains, and each chain is linked to the other adjacent six inorganic chains via ligands to form the 3-D framework (Figure 2).

La-PCP crystallizes in the $P2_1/c$ space group, and the coordination geometry of La^{3+} is completed by two chelate carboxylate groups, four bridging oxygen, and one DMF molecules. The ligand also acts as a μ_6-bridge, but all of the carboxylate groups here adopt a μ_2-η_2:η_1-bridging mode, which leads to a slightly helical metal-oxygen chain with edge-shared polyhedra. Because the adjacent two La^{3+} ions are bridged by nine ligands, and each ligand links to three helical chains, another 3-D structure was formed (Figure 2).

Those two structures have almost the same channel size/type along the b axis in Y-PCP and the c axis in La-PCP; more importantly, both of them have rich acylamide moieties outside and inside the crystals (Figure 2). However, the striking difference of them also can be found. In Y-PCP, a rectangular channel with a single wall is present; however, a double-walled channel is present in La-PCP, indicating a side-by-side alignment of acylamide groups. Although other rare earth series, such as Ln(BTB)[15] (H$_3$BTB = 1,3,5-tris(4-carboxyphenyl)benzene) and Ln(BTC)[16] (H$_3$BTC = 1,3,5-benzenetricarboxylic acid), have been reported, all members gave isomorphic crystal structures. Thus, on the basis of the lanthanide contraction effect, we have successfully, for the first time, adjusted the acylamide alignments in similar structures. In addition, the total accessible volumes, calculated
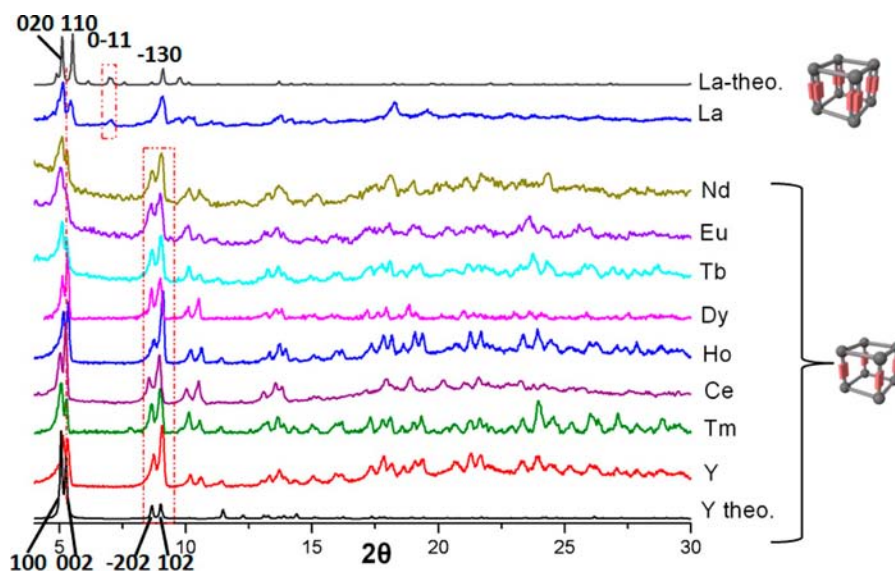
Figure 1. PXRD for a series of Re-L structures: only La-PCP has the close-packed acylamide alignment; all of the other structures have a separated acylamide moiety.
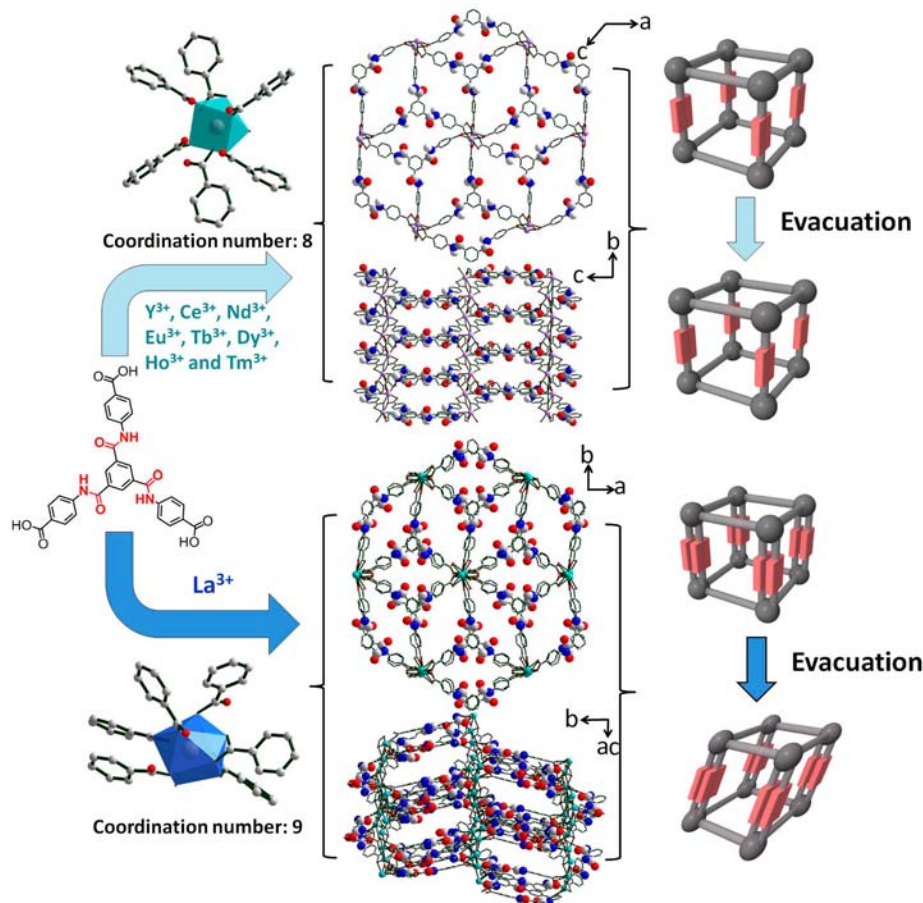
Figure 2. Scheme of the M^{3+}L structures with different acylamide alignments: the coordination number of Y^{3+} in Y-PCP is 8, and the coordination number of La^{3+} in La-PCP is 9. Y-PCP and La-PCP have very similar channel types/sizes, but different acylamide alignments in the structures were observed. The right line shows the expected structural character of the samples before and after evacuation. Red spheres represent oxygen, blue spheres represent nitrogen, and gray spheres represent carbon.

using the PLATON program,[14b] of the Y-PCP and La-PCP are ca. 51.8% and 47.1%, respectively.

Gas Adsorptions and Selectivity Studies. The permanent porosity of Y-PCP and Ho-PCP are revealed by CO$_2$ adsorption at 195 K (Figure 3). Fully reversible type-I isotherms are obtained for them, which indicate their microporous structure with apparent Brunauer−Emmett−Teller (BET: 273 and 243 m^2/g) and Langmuir surface areas
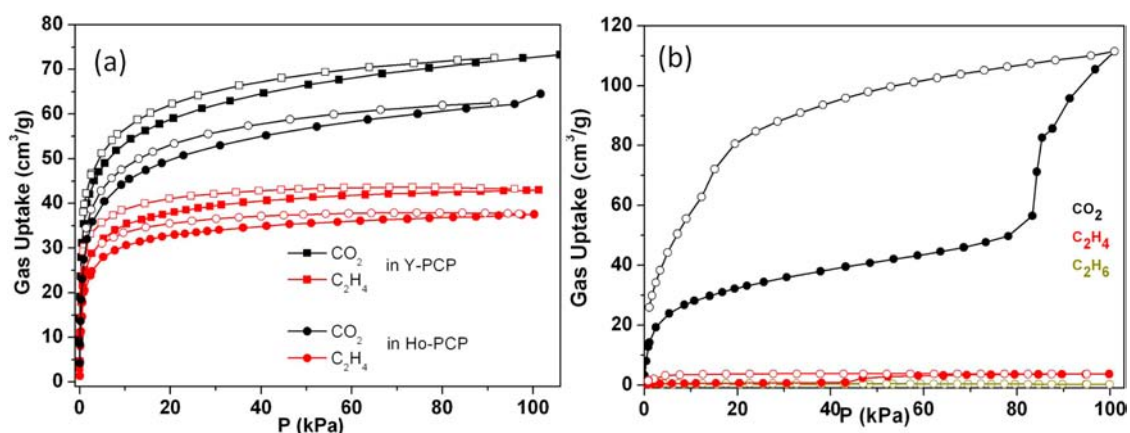
Figure 3. Adsorption isotherms of CO_2, C_2H_4, and C_2H_6 in Y-PCP and Ho-PCP (a) and La-PCP (b) at 195 K.

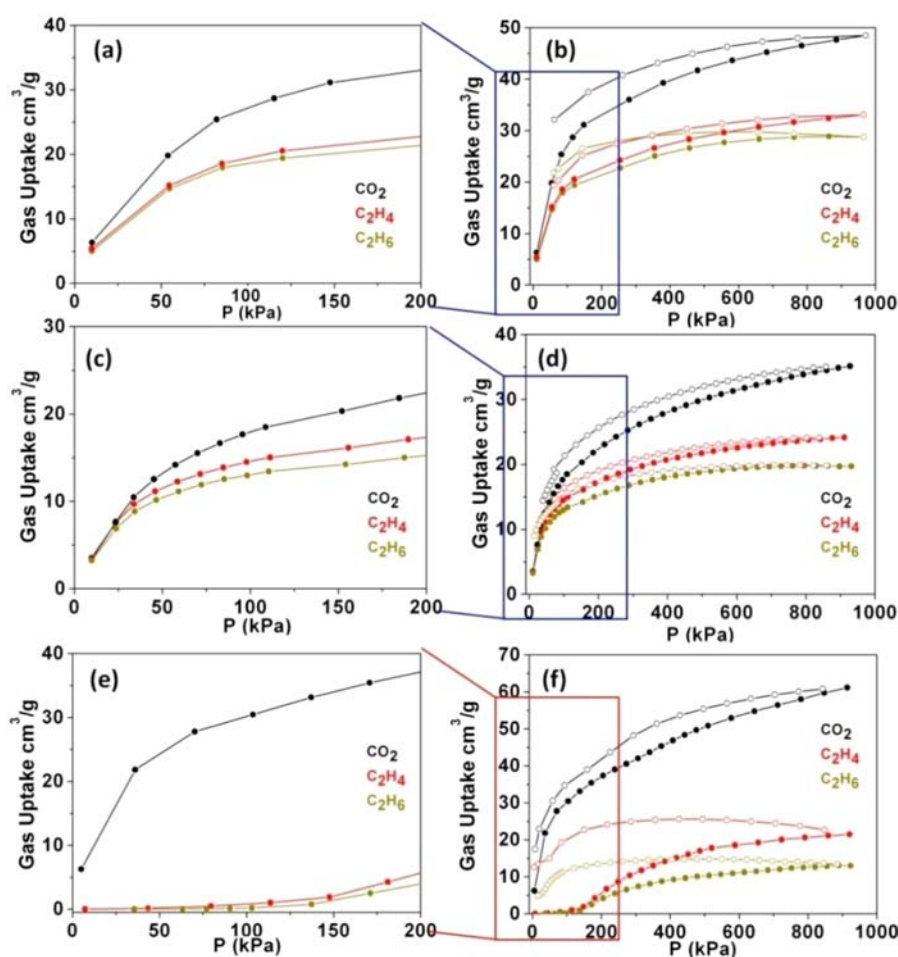**Figure 4.** Adsorption isotherms of CO_2, C_2H_4, and C_2H_6 in Y-PCP (a, b), Ho-PCP (c, d), and La-PCP (e, f) at 273 K.

(423 and 367 m^2/g). However, in La-PCP, the CO_2 adsorption isotherm shows a two-step curve, and the second uptake occurs around 80 kPa. The BET and Langmuir surface areas are 156 and 534 m^2/g (Figure 3). Thus, such a kind of adsorption behavior is regarded as a "gate-opening" phenomenon that is associated with the flexibility of the frameworks.[5d,9d] The S-type methanol adsorption isotherm also indicates the gate-opening behavior.[17] Interestingly, because of the different boiling points of CO_2 and methanol gas, the pressures of the gate-opening are different (Figure S14, Supporting Information). Therefore, the

activated material of La-PCP appears to be the "semiclosed" form, and then undergoes structural transformation to the "open" or as-synthesized form once the crystal obtains sufficient energy from gas adsorbate molecules to overcome the energy barrier.[5d,18] Single-component adsorption isotherms for C_2H_4 and C_2H_6 were also measured at 195 K. As shown in Figure 3, C_2H_4 adsorption isotherms in Ho-PCP and Y-PCP display quick saturation around 10 kPa (Figure 3a); however, there is almost no uptake of C_2H_4 and C_2H_6 in La-PCP even though the pressure reaches to 100 kPa (Figure 3b). More

importantly, in contrast with the gas uptake in each sample, the highly selective discrimination of C_2H_4 and C_2H_6 in La-PCP indicates that La-PCP is a potential candidate for removal of CO_2 in natural gas mixtures. In addition, it is necessary to point out that the main peaks of the PXRD around 6° and 10° (2θ) in the degassed form of Ho-PCP and Y-PCP become slightly broad, indicating the disorder of the framework. However, the current status of them still can trace back to their original crystal structures.

The significant challenge regarding gas separation under ambient temperature and pressure and the excellent distinguishing adsorption behaviors of these three materials encouraged us to examine their selective capture ability of CO_2 in CO_2/C_2H_4 and CO_2/C_2H_6 systems at 273 K. High-pressure adsorption isotherms show that Y-PCP and Ho-PCP are classical rigid microporous materials, and the uptakes of these three gases are almost the same. However, as expected, the adsorption isotherms of La-PCP show an attractive character (Figure 4). For CO_2, a type-I isotherm and the total uptake around 34 mL/g at ~150 kPa were observed. Interestingly, there is almost no adsorption of the C_2H_4 and C_2H_6 before150 kPa, indicating an excellent performance of CO_2 removal from natural gas at amient temperature (273 K) and pressure (0.1−1 bar). In contrast, so many famous frameworks, such as MOF-74,[19] $Zn_2(bmebdc)_2(bipy)$,[20] and Cu-BTTri-en,[7] have been reported for the CO_2 separation or high binding energy; however, the best separation regions are only located at the very low pressure area. This is one of the important barriers for further industrial application. In addition, conventional rigid porous materials[21] exhibit type-I adsorption isotherms for gases, such as CO_2, C_2H_4, and C_2H_6, and the separation behaviors derived from the preferable adsorption sites for C_2H_6, C_2H_4 over CO_2; however, the preferential CO_2 adsorption of La-PCP over C_2H_6 and C_2H_4 is a rare character.[9a]

In Situ Diffuse Reflectance IR Fourier Transform (DRIFT) Spectra Studies. To characterize and understand the different interactions of CO_2 within the pores of Ho-PCP and La-PCP, we performed in situ diffuse reflectance IR Fourier transform (DRIFT) spectroscopy measurements. The spectra were obtained after the introduction of 20 kPa of CO_2 in the cell at 273 K (Figure S15, Supporting Information). Around 2300−2380 cm^{-1}, two strong bands were detected in these two PCPs, which can be assigned as the asymmetric stretching modes of CO_2 ($\nu 3$). This phenomenon is similar to the previous observations in HKUST-1 (2331 and 2342 cm^{-1})[22] and La-BTB.[23] Compared with the spectrum of pure CO_2, some new peaks can be found in M-PCP···CO_2 (M: Ho and La) and La-BTB···CO_2 systems (Figure 5). More interestingly, the number of the new peaks in the M-PCP···CO_2 system is more than that of La-BTB···CO_2 (no functional group in H_3BTB ligand), evidencing the stronger interactions of the acylamide modified framework with CO_2. Furthermore, the number of the new peaks (around 2331.2, 2334.7, and 2344.5 cm^{-1}) in the La-PCP···CO_2 system is more than that of the Ho-PCP···CO_2 system, which revealed the strongest interaction in the La-PCP···CO_2 system among these three structures. These observations may arise from the donation of the close-packed acylamide groups in the flexible host framework, as suggested by the higher CO_2 uptake of La-PCP at the low-pressure area[24] (Figure S15, Supporting Information).

In summary, we have designed and synthesized a family of porous coordination polymers with an acylamide functional group. Structural analyses, gas-sorption measurements, and in
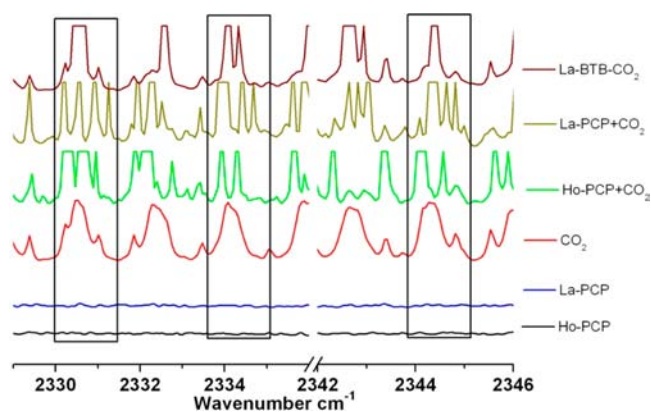
Figure 5. In situ DRIFT spectra of the degassed samples with or without CO_2 (20 kPa) measured at 273 K.

situ IR spectroscopy studies demonstrated that only La-PCP, with a unique side-by-side acylamide alignment and structral flexibility, facilitates the high selective capture of CO_2 with respect to C_2H_4 and C_2H_6 at high pressure and ambient temperature. Thus, based on the inherent designability and diversity of porous coordination polymers, this new strategy, grafting of functional groups into flexible frameworks, will allow for the extension of more sophisticated soft materials for important gas separation.

■ ASSOCIATED CONTENT

ⓢ Supporting Information

X-ray crystallographic file (CIF), experimental details, IR, TGA, PXRD, and gas adsorption isotherms of them. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes
The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

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