Cation-Exchange Approach to Tuning the Flexibility of a Metal–Organic Framework for Gated Adsorption

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ABSTRACT: Achieving tailorable gated adsorption by tuning the dynamic behavior of a host porous material is of great interest because of its practical application in gas adsorption and separation. Here we devise a unique cation-exchange approach to tune the dynamic behavior of a flexible anionic framework, [Zn2(bptc)(datrz)]− (denoted as MAC-6, where H2bptc = [1,1′-biphenyl]-3,3′,5,5′-tetracarboxylic acid and Hdatrz = 3,5-diamine-1H-1,2,4-triazole), so as to realize the tailorable gated adsorption. The CO2 adsorption amount at 273 K can be enhanced by exchanging the counterion of protonated dimethylamine (HDMA+) with tetraethylammonium (TEA+), tetrabutylammonium (TBA+), and tetramethylammonium (TMA+), where the adsorption behavior is transferred from nongated to gated adsorption. Interestingly, the $P_{opt}$ for gate-opening adsorption can be further tuned from 442 to 331 mmHg by simply adjusting the ratio of HDMA+ and TMA+. The origin of this unique tunable property, as revealed by X-ray diffraction experiments and structure models, is rooted at the cation-responsive characteristic of this flexible framework.

1. INTRODUCTION

Metal–organic frameworks (MOFs), which consist of metal ions or clusters coordinated to organic ligands, have emerged as an exciting family of crystalline porous materials.1–7 One of their unique properties is the framework flexibility.8–12 They can undergo a reversible structural change accompanied by responsive physical or chemical properties by application of an external stimulus.13–21 Gate-opening adsorption is one such interesting property. Generally, it involves a structural transformation from closed-pore (cp) to open-pore (op) form, giving a huge step-up increase of the uptake amount at a certain pressure ($P_{opt}$).22–25 This special adsorption behavior is highly desired because of their possible practical applications in selective adsorption and molecular sensing.26–29 In this context, synthesizing flexible frameworks and tuning framework dynamics have become an important pursuit. Several approaches have been developed, including the following: (i) the ligand replacement approach, where the ligand containing a branched side-chain group is used to replace the original one, such as [Zn2L2(dabco)]30,31 MIL-53,32–34 etc.,35–38 and then the relationship between the side-chain groups and framework dynamics as well as gas adsorption are investigated; (ii) the solid–solution approach, where the functionalized ligand is mixed with the parent one in a crystalline matrix to allow the framework dynamics as well as the adsorption behaviors to be tailored by changing their ratio.39–43 Although these studies have provided some useful guidelines in tuning the structural dynamics, remodeling of the framework is commonly required, which means a tedious and irreversible pathway with potential undesirable results.

Compared with the chemical functionalization of flexible skeletons, the cation-exchange approach is a method to produce dynamic switchable structures that can be easily and reversibly achieved via a postsynthetic exchange.44–46 Because of the framework flexibility, the changes of the cationic features could affect the hosts, allowing fine control over the framework between the cp and op states. Very uniquely, if the exchanged cation can support the flexible framework in the op state or partition the large pores into small ones, the adsorption capacity would be greatly enhanced.47–49 All of these properties illustrate the advantage of the interdependent coexistence of exchangeable cations and a host flexible framework that could make the structural transformation possible to generate unprecedented properties.

Here, we aim to switch the framework dynamic behavior to realize tailorable-gated adsorption by a cation-exchange approach. {HDMA+}[Zn2(bptc)(datrz)]−·2H2O}n (denoted as

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Figure 1. (a) Crystal structure of HDMA@MAC-6 (from left to right: 1D chain structure built of paddle-wheel and triazolate-dinuclear units and 3D structure showing in a space-filling mode and its 3,6-connected fby net). (b) Crystal structure of HDMA@MAC-6′ (from left to right: 1D chain structure built of deconstructed paddle-wheel and triazolate-dinuclear units and 3D structure in cp form and its topology). Corresponding reduced building blocks for the structure: (c) 6-connected node for the paddle-wheel unit; (d) self-dual 3-connected node for the bptc ligand; (e) 6-connected node for the triazolate-dinuclear unit.

HDMA@MAC-6, where HDMA = protonated dimethylamine, 
H₂bptc = \([1,1\text{-}\text{biphenyl}]\text{-}3,3',5,5'\text{-}4\text{-}tetracarboxylic acid, and Hdatrz = 3,5-diamine-1HH-1,2,4-triazole), an op state framework that can be transformed into a cp form of \(\text{HDMA}^+\text{[Zn}_2\text{(bptc)}\text{-}O_2\text{]}\mathrm{H}_2\text{O}\) \(\text{Hdatz} = 3,5\text{-diamine-1H-1,2,4-triazole},\) an op state framework that can be transformed into a cp form of \(\text{HDMA}^+\text{[Zn}_2\text{(bptc)}\text{-}O_2\text{]}\mathrm{H}_2\text{O}\) (HDMA@MAC-6’), is selected in this study. The cation-dependent framework dynamic behaviors, including cation-exchange-induced and thermo-induced crystal structural transformation, have been extensively studied. It is revealed that the cp form shows a nearly linear relationship with the cations of HDMA+, tetramethylammonium (TMA+), tetraethy lammonium (TEA+), and tetrabutylammonium (TBA+). The CO₂ adsorption behavior on this flexible host framework is fine-tuned from nongated adsorption in the case of HDMA+, TEA+, and TBA+ to gated adsorption in the case of TMA+. Finally, by controlling the exchange extent of TMA+, the gate-opening pressure \(P_0\) for CO₂ adsorption is successfully tailored from 442 to 331 mmHg.

2. EXPERIMENTAL SECTION

Materials and General Methods. All reagents were purchased from commercial sources and used as received. Fourier transform infrared (FT-IR) spectra were measured on a Nicolet 470 FT-IR spectrometer in the range 4000–400 cm⁻¹ with KBr pellets. Thermogravimetric analyses (TGA) were carried out on a Mettler-Toledo TGA/SDTA 851 analyzer under a N₂ atmosphere (50 mL/min) with a heating rate of 10 K min⁻¹. Powder X-ray diffraction (PXRD) patterns were measured on a Bruker D8 powder diffractometer with Cu Kα radiation (\(\lambda = 1.5406 \AA\)). Solid-state \(^{13}\text{C}\) NMR spectra were measured on a JOEL ECA400 spectrometer. For solution-state \(^1\text{H}\) NMR characterization, the mother liquor of the obtained crystals was replaced with fresh acetone (10 mL) three times. Crystals were then collected by filtration and degassed at 140 °C for 2 h to evaporate other guest molecules. The obtained samples were then digested by \(\text{D}_2\text{SO}_4\) and then dissolved in 1 mL of \(\text{CD}_3\text{OD}\). Raman spectra were recorded on Renishaw (785 nm). Gas adsorption of CO₂ was measured on an ASAP 2020 gas adsorption analyzer (Micromeritics). Before adsorption, all samples (about 50 mg) were activated in fresh acetone and then degassed at 413 K for 10 h. Helium gas was used for estimation of the dead volume. High-pressure CO₂ (10 bar) adsorption was measured on an IGA adsorption apparatus. Before each adsorption experiment, all samples were degassed at 413 K for 10 h, and the adsorption was carried out at 298 K.

Synthesis of \((\text{CH}_3)_2\text{NH}_2\text{[Zn}_2\text{(bptc)}\text{(datrz)}\text{]}\cdot2\text{H}_2\text{O} \text{(HDMA@MAC-6)}, \text{Zn}({\text{OAc}})_2\cdot2\text{H}_2\text{O} (0.4 \text{ mmol, 0.089 g}), \text{H}_2\text{bptc (0.2 mmol, 0.067 g), and Hdatrz (0.2 mmol, 0.021 g) were dissolved in N}_2\text{-dimethylformamide (DMF; 4.5 mL), the solution was stirred at room temperature for 10 min, and then 0.5 mL of water (H}_2\text{O) was added. Then 0.3 mL of nitric acid was added, and the mixture was further stirred for another 10 min. Finally, the mixture was sealed in a Teflon-lined stainless steel autoclave (15 mL) and heated at 140 °C for 3 days, followed by cooling to room temperature. Block colorless crystals were collected by filtration and washed with DMF (5 mL × 3) and acetone (5 mL × 3). Yields: 82% based on zinc(II). Elem anal. Calcd for HDMA@MAC-6 \((\text{C}_20\text{H}_{22}\text{N}_6\text{O}_{10}\text{Zn}_2)\): C, 37.70; H, 3.48; N, 13.19. Found: C, 37.45; H, 3.68; N, 13.23."

Postsynthetic Cation Exchange. HDMA+ in HDMA@MAC-6 was replaced by TMA+, TEA+, and TBA+ cations via postsynthetic cation exchange to yield TMA@MAC-6, TEA@MAC-6, TBA@MAC-6, and HDMA@MAC-6, respectively. For example, a solution of TMABr·H₂O (0.3 M) was prepared. Cation exchange was performed as follows: (a) as-synthesized HDMA@MAC-6 (50 mg) was rinsed with DMF (5 mL × 3); (b) the material was soaked in a N₂ atmosphere (50 mL/min) with a heating rate of 10 K min⁻¹. Powder X-ray diffraction (PXRD) patterns were measured on a Bruker D8 powder diffractometer with Cu Kα radiation (\(\lambda = 1.5406 \AA\)). Solid-state \(^{13}\text{C}\) NMR measurement was carried out on a Bruker AVANCE III 400WB apparatus. Solution-state \(^1\text{H}\) NMR spectra were measured on a JOEL ECA400 spectrometer. For solution-state \(^1\text{H}\) NMR characterization, the mother liquor of the obtained crystals was replaced with fresh acetone (10 mL) three times. Crystals were then collected by filtration and degassed at 140 °C for 2 h to evaporate other guest molecules. The obtained samples were then digested by \(\text{D}_2\text{SO}_4\) and then dissolved in 1 mL of \(\text{CD}_3\text{OD}\). Raman spectra were recorded on Renishaw (785 nm). Gas adsorption of CO₂ was measured on an ASAP 2020 gas adsorption analyzer (Micromeritics). Before adsorption, all samples (about 50 mg) were activated in fresh acetone and then degassed at 413 K for 10 h. Helium gas was used for estimation of the dead volume. High-pressure CO₂ (10 bar) adsorption was measured on an IGA adsorption apparatus. Before each adsorption experiment, all samples were degassed at 413 K for 10 h, and the adsorption was carried out at 298 K.

3. RESULTS AND DISCUSSION

Interconvertible op and cp Forms with Integrated Framework Stability and Flexibility. The crystal structure of HDMA@MAC-6, as determined in our previous study,\(^{30}\) ...
exhibits a 3D porous framework containing 1D rhombic channels in an op form where the HDMA$^+$ cations reside. The paddle-wheel dimer and triazolate-dinuclear units are alternatively connected to each other via the connection of the $\mu_{1,2,4}$-triazolate ligand (Figure 1). The bptc ligand bridges two paddle-wheel secondary building units (SBUs) and two triazolate-dinuclear SBUs in a trans model (Figure S1). PXRD patterns confirm completion of the bulk crystal transformation at 90 °C (Figure 2a), which is

\[ \text{[HDMA}^+\text{][Zn}_2\text{(bptc)(datrz)(H}_2\text{O)}_{0.5}\text{]}^{-\text{H}_2\text{O}}]_n \] (HDMA@MAC-6$'$) with the 1D rhombic channels in the cp form. The main peak reflection, which corresponds to the (11−1) plane (the $h$ parameter, distance of the parallel edge of the rhombic channel, is calculated by the Bragg diffraction equation). HDMA molecules are shown in pink; hydrogen atoms and H$_2$O molecules are omitted for clarity.

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Cation-Dependent Framework Dynamics. The integrated stability and flexibility make HDMA@MAC-6 an excellent candidate structure for studying the dynamic responses to different guest cations.

Postsynthetic cation exchange of HDMA@MAC-6 with TMA$, TEA$, and TBA$'$ in a DMF/H$_2$O solution is carried out, leading to the isolation of TMA@MAC-6, TEA@MAC-6, and TBA@MAC-6, respectively. TGA results indicate that all of these compounds are stable up to 300 °C, similar to HDMA@MAC-6 (Figure S5). The characteristic bands assigned to $\nu$$_{(\text{C−H})}$ of the alkyl groups are observed from FT-IR spectra in the range of 2700−3000 cm$^{-1}$ (Figure S6). The gradually enhanced absorption band agrees well with the increased numbers of alkyl groups from HDMA$^+$ to TBA$, indicating the inclusion of corresponding cations. According to the solid-state $^{13}$C NMR spectra (Figure S7), the signal at 33.9 ppm, which is assigned to C(−C$_3$H$_7$)$_2$ of HDMA$^+$, disappears after exchange with TMA$, and a new signal at 53.9 ppm assigned to C(−C$_3$H$_7$)$_2$ of TMA$'$ is observed. Complete cation exchange is further proven by the $^1$H NMR spectra (Figure S8). HDMA$^+$ shows a signal at 2.42 ppm assigned to H(−CH$_3$)$_2$. For cation-exchanged products, this signal disappears, and new hydrogen signals ascribed to the corresponding cations are observed.

Using the number of hydrogen atoms in the bptc ligand as a reference, the ratio of bptc ligands and exchanged cations is determined to be 1:1 for each case, confirming complete exchange.

The structural changes are detected by PXRD analysis. The PXRD pattern of TMA@MAC-6 shows the main diffraction peak at 2$\theta$ = 8.68° (Figure 3a), which has a 0.5° shift to higher angle compared with that of HDMA@MAC-6. In contrast, the main diffraction peak shifts to a smaller value for TEA@MAC-6 (2$\theta$ = 7.85°) and TBA@MAC-6 (2$\theta$ = 7.79°), indicating a pore expansion. These results demonstrate the cation-responsive fitting of this flexible host framework during the inclusion of different cations. Temperature-dependent PXRD patterns of those three cation-exchanged products exhibit a distinct structural transformation as a response to the temperature (Figure 3b,c). The diffraction peaks of TMA@MAC-6 show no

[Figure 2](#) Temperature-dependent PXRD patterns of HDMA@MAC-6. (b and c) Structures of HDMA@MAC-6 and HDMA@MAC-6 after being cleaved through the (11−1) plane (the $h$ parameter, distance of the parallel edge of the rhombic channel, is calculated by the Bragg diffraction equation). HDMA molecules are shown in pink; hydrogen atoms and H$_2$O molecules are omitted for clarity.

[Figure 3](#) PXRD patterns showing the distinct framework dynamics: (a) cation-exchanged samples of TMA@MAC-6, TEA@MAC-6, and TBA@MAC-6 compared with that of HDMA@MAC-6; (b−d) thermo-induced structural transformations of TMA@MAC-6, TEA@MAC-6, and TBA@MAC-6, respectively.
obvious shift when the temperature increases from room temperature to 90 °C. The crystal structure transformation occurs when the temperature increases from 90 to 140 °C, in which the main diffraction peak shifts to 9.82°. However, the structural changes of TEA@MAC-6 and TBA@MAC-6 occur at 90 °C, showing main peak shifts of 1.58° and 0.74°, respectively, to higher angle.

To better illustrate the cation-exchange responses of this host framework, a rhombic channel model is constructed by using HDMA@MAC-6 as the reference, and the calculated structural parameters are deposited in Table 1 and Figure 4. The value of
adsorption. Whether this gate-opening pressure contrast, gate-opening adsorption is not observed for TEA@MAC-6 drastically to 4.69 mmol/g at 2.0 bar for TMA@MAC-6 increases slowly to 1.34 mmol/g at 1.01 bar and then increases a strong cation-to-host exchange with TMA+, while it gives a positive pore expansion with breathing amplitudes of +11.76% and +14.39% after inclusion of TEA+ and TBA+, respectively. Then, compared with the cation-exchange state, the thermo-induced framework breathing amplitude for each sample is calculated, giving the order of HDMA@MAC-6 (−46.81%) > TEA@MAC-6 (−32.72%) > TBA@MAC-6 (−20.88%) > TMA@MAC-6 (−19.16%). Furthermore, a plot of the calculated kinetic diameter of guest cations versus the closed state of the host framework (d′/D′) shows a linear relationship for HDMA@MAC-6, TEA@MAC-6, and TBA@MAC-6 (Figure 4c), indicating that the closed state of the host framework depends on the size of the included cation. However, TMA@MAC-6′ deviates slightly from the fitted line (theoretically calculated d′/D′ = 0.40 for TMA+). We ascribe this deviation to the possible partial overlay of TMA+ in the channel, which supports the flexible framework. All of the above studies have clearly demonstrated the strong interdependent relationship between the dynamic behavior of the host flexible framework and the included guest cations, showing a strong cation-responsive fitting of this flexible framework in the crystal-to-crystal transformation. Tailoring the Gate-Opening Adsorption. CO2 adsorption measurements are then carried out using the cation-exchanged samples in the cp form. At 273 K, HDMA@MAC-6′ shows an uptake of 0.45 mmol/g at 800 mmHg (Figure S9). In contrast, TMA@MAC-6′, TEA@MAC-6′, and TBA@MAC-6′ give uptake amounts of 3.66, 1.34, and 0.85 mmol/g, respectively (Figure S5a), confirming enhancement of the CO2 capacity after cation exchange. Interestingly, gate-opening adsorption is observed for TMA@MAC-6′, which shows a Pgo pressure at 331 mmHg with an uptake amount of 1.22 mmol/g, and then it reaches 3.28 mmol/g at 496 mmHg. However, the adsorption isotherm shows no gated adsorption at 298 K, and the uptake amount is only 1.12 mmol/g at 800 mmHg. The PXRD pattern after adsorption at 273 K shows that the diffraction peak with a 2θ value of 9.83° shifts to a small angle at 8.79°, indicating a transformation from the cp to op form of the host framework induced by CO2 adsorption (Figure S5b), while the structure remains unchanged at 298 K. We speculate that the low uptake at 298 K might not be sufficient enough to induce a framework transformation for gated adsorption. High-pressure adsorption is then carried out at 298 K to validate the speculation (Figure S10). As expected, gate-opening adsorption is observed, where the uptake amount increases slowly to 1.34 mmol/g at 1.01 bar and then increases drastically to 4.69 mmol/g at 2.0 bar for TMA@MAC-6′. In contrast, gate-opening adsorption is not observed for TEA@MAC-6′ and TBA@MAC-6′, whose uptakes are 1.53 and 0.70 mmol/g at 10 bar, respectively. The above studies demonstrate a strong cation-to-host effect for gate-opening adsorption. TMA@MAC-6′ has distinguished itself for gate-opening adsorption. Whether this gate-opening pressure Pgo can be precisely tailored deserves our further exploration. Previously, it was shown that Pgo can be tailored by tuning the affinity of the host pore surface by a solid–solution approach.28,40,41 Here, we show another feasible approach to tailoring Pgo by just tuning the cation-to-host effect, which is achieved by simply controlling the exchange content of TMA+ in the structure. Cation-exchange products of (HDMA)x(TMA)y@MAC-6 (x = 0.37, 0.69, and 0.90) are isolated by controlling the exchange time. The PXRD pattern shows that the main diffraction peak of (HDMA)x(TMA)y@MAC-6 gradually shifts from 8.33 to 8.42° with an increase of the ‘TMA’ amount (Figure S11b), indicating a homogeneous cation-exchange process rather than a mixed phase of HDMA@MAC-6 and TMA@MAC-6. After degassing, it shows that the 2θ value shifts from 10.13 to 9.83° with an increase of the exchanged TMA+. The calculated d′/D′ values for (HDMA)x(TMA)y@MAC-6 are 0.44, 0.45, and 0.46, respectively, which still deviate slightly from the fitted linear line. Given these samples, CO2 adsorption is then carried out at 273 K. When x is changed from 0.37 to 1, the gate-opening pressure (Pgo) for CO2 correspondingly varies from 442 to 331 mmHg (Figure 6). This means that Pgo for CO2 adsorption depends on the exchanged amount of TMA+. With more TMA+ included, it would be easier to produce a host framework dynamic transformation from the cp to op form. In addition, all samples show an uptake amount of ~3.66 mmol/g at 800 mmHg with a similar desorption isotherm. The result indicates that, although the gate-opening adsorption behavior depends on the amount of exchanged TMA+, the uptake capacity and desorption behavior do not. We ascribe this phenomenon to the unique cation-to-host effect in tailoring the adsorption behavior of a flexible host framework. In the cp form, there should be a strong intimate relationship between the host and the included cation; thus, the adsorption behavior is strongly coupled with its cp form, whose state is determined by the included cation, while this cation-dependent effect becomes weak after gate opening and the adsorbed CO2 takes charge to determine the op form of this flexible host framework. As a result, the uptake amount and desorption behavior are less affected by the exchange content of TMA+. The above results suggest that the cation-exchange approach is a feasible way of tailoring Pgo for gate-opening adsorption without affecting the uptake amount and desorption behavior.
4. CONCLUSIONS

Developing novel methods to realize tailorable gated adsorption in a soft crystalline porous material is important for adsorption and separation. In this work, we have demonstrated a cation-exchange approach to tuning the host framework dynamics to realize tailorable gate-opening adsorption properties. In contrast to the conventional approach of chemical modification, this approach highlights the significance of exchangeable guests for tailoring the gate-opening properties. On the basis of the cation-to-host effect, the dynamic behavior of a flexible host framework can be fine-tailored. The appropriate intimate contacts between the flexible framework and the included cations are important to allow the possibility of the cation-to-host effect to be transmitted. In addition, a proper portrayal of the cation-dependent state of the host framework is helpful for a comprehensive understanding of the interdependent relationship as well as the crystal-to-crystal structural transformation. Our results demonstrate that, by taking advantage of the interdependent coexistence of included cations and flexible host framework, the cation-dependent approach is an efficient and feasible way of creating advanced soft crystalline porous materials for tailorable gated adsorption.

ASSOCIATED CONTENT

Supporting Information
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Experimental details as reported in the text as well as additional characterization data (PDF)

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Notes
The authors declare no competing financial interest.

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