Why Porous Materials Have Selective Adsorptions: A Rational Aspect from Electrodynamics

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Supporting Information

ABSTRACT: Gas storage/separation is a typical application of porous materials such as metal organic frameworks (MOFs). The adsorption/separation behavior results from the host—guest and/or guest—guest interaction and equilibration (host, porous material; guest, adsorbates). Although the driving forces for gas adsorption have been investigated, a detailed picture of interactions between gas molecules and MOFs has not clearly emerged. Herein, a new cobalt microporous MOF [Co(tipb)(adc)]·(DMF)·(H2O)1.5, which possesses a rare self-inter-penetrated graft topology, has been prepared with both tipb and H2adc ligands (tipb = 1,3,5-tris(p-imidazolylphenyl)benzene, adc = 9,10-anthracenedicarboxylate). This MOF shows high stability and exceptional selective adsorption of CO2 over N2, O2, and CH4. In particular, a theoretical assumption of a "regional dynamic electric field effect" is proposed to clarify the selective adsorption. Moreover, we suggest that the proposed effect may be one of the most important factors impacting gas separation and storage in porous materials.

INTRODUCTION

In view of energetic, biological, and environmental factors, gas separations and storage play significant roles in industry and daily life.1,2 In particular, as one kind of greenhouse gas and a renewable carbon source, CO2 has attracted much attention. The separation of CO2 over N2/O2 for its enrichment and recovery as well as that over CH4 for biogas upgrade have motivated strong interest in the development of novel porous materials such as metalorganic frameworks (MOFs). Their potential is due not only to their fascinating structural architectures and topologies but also to their tailorability, structures, properties, and associated potential applications.3–6 As good candidates for gas separations and storage, the driving force for gas adsorption in MOFs has been investigated and various strategies have been developed to improve their working capacity and selectivity.12–16 The adsorption/separation behavior results from the host—guest and/or guest—guest interaction and equilibration (host, porous material; guest, adsorbates). However, a clear picture of the interactions between gas molecules and the framework has not emerged, and some explanations of selective gas adsorption in MOFs are somewhat ambiguous, except for the pore size exclusion effect17,18 or quadrupole moment19–22 of gas molecules (see the Supporting Information for more details), particularly in cases where special adsorption behaviors were observed. Herein, a new CoII-based MOF [Co(tipb)(adc)]·(DMF)·(H2O)1.5 (I, tipb = 1,3,5-tris(p-imidazolylphenyl)benzene; adc = 9,10-anthracenedicarboxylate) is presented where a high adsorptive selectivity of CO2 over N2, O2, and CH4 was observed at different temperatures. Most importantly, the selective adsorption could be reasonably well explained by the presence of the "regional dynamic electric field effect" in the framework. Furthermore, as electric fields commonly exist in all porous materials, this effect can be considered as a universal/common influence factor for gas adsorption in porous materials.

RESULTS AND DISCUSSION

Syntheses and Structural Characterization of 1. The solvothermal reaction of Co(NO3)2·6H2O, tipb, and H3adc in N,N′-dimethylformamide (DMF) resulted in the formation of red prismatic crystals of I. X-ray crystallographic analysis revealed that only one crystallographically independent CoII...
center is involved in the fundamental asymmetric unit. CoII locates in the center of a distorted octahedral coordination geometry, defined by three nitrogen atoms from three independent tipb ligands and three oxygen atoms from two different adc− ligands (Figure S1). Each tipb ligand connects three CoII atoms, according a 63 layer parallel to the ab plane (Figure S2). The 63 layers packed in an ABCD fashion were interconnected by adc− ligands to give an overall three-dimensional (3D) framework with one-dimensional (1D) channels (0.96 × 0.73 nm in size) along the c axis (Figure 1). After removing the DMF and H2O molecules from the channels, PLATON calculations show that the porous structure of 1 composes a void of 3706.0 Å3 that represents 35% per unit cell volume [10586.0 Å3]. Taking into account the vdW surface, the free volume is 5352.4 Å3, occupying ∼51% volume of a unit cell. Topology analysis (see the Supporting Information for more details) revealed that the framework of 1 could be simplified into a rare self-interpenetrated gra net (Figure S4). Additionally, a stability test confirmed that 1 has high thermal and chemical stability (see the Supporting Information for more details).

Selective Gas Adsorptions. In order to characterize the nature of the pores and gas adsorption properties of 1, isotherms are measured for N2, H2, O2, CH4, and CO2. The N2 adsorption isotherm of activated 1 is measured at 77 K (Figure S10). It shows a classic type I isotherm with a Brunauer–Emmett–Teller (BET) surface area of 514 m2 g−1 and Langmuir surface area of 680 m2 g−1. The fit of the adsorption data to the Horvath–Kawazoe method demonstrated the pore width distribution from about 0.5 to 0.9 nm (Figure S11). At 195 K, 1 exhibits a type I isotherm toward CO2 gas and gives an uptake of 28.51 wt % (145 cm3 g−1 at STP) at 620 mmHg. Most interestingly, 1 shows high adsorption selectivity for CO2 over N2 and O2 as shown in Figure 2. The adsorption selectivities are calculated via ideal adsorption solution theory (IAST). The CO2/N2 (in a 15:85 molar ratio) selectivity is estimated as 2094 at 195 K (80 KPa) and 27.8 at 273 K (100 KPa). The predicted CO2/CH4 selectivity is 113 at 195 K (80 KPa), 7.4 at 273 K (100 KPa), and 5.4 at 303 K (100 KPa) from equimolar gas-phase mixtures (Figures S14–16). At 303 K, almost no N2 and O2 is adsorbed (Figure S13). It is insignificant to calculate the selectivity.

Assumption of a Regional Dynamic Electric Field Effect. Compound 1 indeed has shown remarkable adsorptive selectivity for CO2, and the selective adsorption orders are CO2 > CH4 > N2/O2 at different temperatures. However, the origin of the selectivity could not be attributed to a size/shape-based effect since the kinetic diameters of CO2, CH4, N2, and O2 are all much smaller than the diameter of the channel of 1.

By checking carefully the structure of 1, the selective adsorption is assumed to originate from the interactions between the gas molecules and the local electric fields of the framework: Commonly, electronegative atoms or groups tend to distribute around electropositive metal centers symmetrically due to the electrostatic repulsion of the homocharges, forming symmetrical structures such as the classical paddlewheel26,27 secondary building unit (SBU). However, in 1 the steric hindrance of coordinated imidazole rings may compel the electronegative carboxyl groups to locate on one side of the CoII atoms (Figure S5). This results in a separation of positive and negative charge centers in this region and accordingly leads to regional electric fields around the CoII atoms (Figure 3a).

This phenomenon can be defined as "unequal coordination." As shown in Figure 3b, the CoII centers are quite close to the wall of the 1D channel, and the distance between the nearest...
CoII is 8.4 Å. Therefore, a cutoff of the regional electric field was set to be ∼8.4 Å (the minimum diameter, Figure 3b). In this region, the electric field should be dominated by the permanent dipole located around the metal center. The strength of the permanent dipole moment is evaluated using a cluster model (see the Supporting Information for more details). The first-principles calculation indicates a large dipole moment (Figure S19) of ∼12.7 D. This large dipole moment suggests a strong electric field around the CoII centers.

To confirm the existence of the electric field, the electrostatic potential of the cluster model was calculated by density functional theory (DFT) (Figure 4a). The distribution of the electrostatic potential is not even. The carboxyl O atoms exhibit strong electronegativity, while the aromatic H atoms are slightly electrically positive. As illustrated in Figure 4b, the contours of electrostatic potential indicate the direction and strength of the electric field, which varies locally according to the position in the plane. These results suggest that that there exists a nonuniform electric field around the CoII center defined as a regional electric field. The term "regional" refers to the local environment of the porous material and to the subsequent effect on the electric field characteristics.

It should be pointed out that the permanent electrical dipole near CoII is the most obvious source of the regional electric field, but it is not the only one. From the calculated results (Figure 4), the imidazole rings and anthracene nucleus are also important for the formation of the regional electric fields in I. This indicates that the electric fields may be originated from a variety of effects. The electric field and the potential gradient play important roles in gas adsorption in I.

For gas molecules diffusing inside the regional electric field, the interaction between a gas molecule and the electric field can be expressed by the multipole expansion of the energy of a charge distribution28 (Figure 5)

\[
W = q\Phi(0) - p \cdot E(0) - \frac{1}{6} \sum_i \sum_j Q_{ij} \frac{\partial E_i}{\partial X_j}(0) + \ldots
\]

In the equation, \(q\) is the total charge while \(p\) and \(Q_{ij}\) are the electric dipole moment and the quadrupole moment tensor components of a gas molecule. In our study, the charge of gas molecules is zero, and the effect of other higher order multipoles can be neglected compared with the dipole/quadrupole moments. Therefore, the major contribution comes from the interaction of the dipole/quadrupole of the gas molecules and the regional electric field. Moreover, for nonpolar gas molecules, their permanent electric dipole moments are equal to zero. However, in an external electric field, nonpolar gas molecules can be polarized to give induced dipole moments, as well as instantaneous dipole moments. These two types of dipoles are related to the polarizability of the gas molecules. They are also of importance in the MOF–gas interactions.

As both the polarizability and the quadrupole moment of CO₂ are larger than those of CH₄, N₂, and O₂ (Table S1), CO₂ should have stronger interaction with the regional electric field in the 1D channels of I. This can explain the order of adsorption selectivity for CO₂ over CH₄/N₂/O₂. On the other hand, although the quadrupole moment of CH₄ is zero, the polarizability of CH₄ is far larger than that of N₂ and O₂. As a
result, the combined interaction of the gas molecules and the framework has an order of CO\textsubscript{2} > CH\textsubscript{4} > N\textsubscript{2}/O\textsubscript{2}.

This is verified by periodic DFT calculations (see the Supporting Information for more details): The calculated interaction energy is \(-4.2\) kcal/mol for N\textsubscript{2}, \(-6.2\) kcal/mol for CH\textsubscript{4}, and \(-7.8\) kcal/mol for CO\textsubscript{2}. The calculated values are in good agreement with the experimental results and can be attributed to the effect of the regional electric field. Notably, the dipole moments play more important roles than the quadrupole moments in this case.

In summary, the presence of a regional electric field can reasonably explain the selective adsorption order of CO\textsubscript{2} > CH\textsubscript{4} > N\textsubscript{2}/O\textsubscript{2} in I. It should be pointed out that the explanation above does not involve specific porous materials. It can be expressed as a universal hypothesis, which may apply to other MOFs and porous materials as discussed next.

As shown in I, the electric fields originated from a variety of effects. It mainly involves two aspects (Figure 5). One aspect is the host framework of porous materials: as we discussed, the regional electric field can be originated from the unequal coordination. Also, it may be generated by unsaturated metal centers\cite{29-31} in some MOFs. Moreover, it can be produced by polar ligands and/or groups\cite{32-35} in porous materials: some investigations have shown that polar groups such as acrylamide and carboxyl groups could enhance the CO\textsubscript{2} uptake and the corresponding heat of adsorption. In addition, there are some other triggers such as ionic frameworks,\cite{36-38} delocalization of \pi electrons, instantaneous dipole moment of the groups in the framework, etc. Another aspect is guest molecules or/and adsorbates. The adsorbed/encapsulated polar molecules or ions in MOFs are important sources of electric fields: for example, recent studies have confirmed that small amounts of water can help to enhance the adsorption of CO\textsubscript{2} in HKUST-1.\cite{39,40} The adsorbed adsorbates will interact with adsorbates which are going to be adsorbed (van der Waals force). Consequently, electric fields may exist extensively in MOFs, and the fields are dynamic. The current research of multipoint interactions also substantiated the origins of electric fields are various.\cite{41,42}

The interactions between the framework and the gas molecules can be described as a regional dynamic electric field effect. The term “dynamic” refers to the electric fields of effective adsorption space that are variable for the polarity of the guests and/or other influencing factors.

The assumption can also be extensively applied to explain the adsorption of other polar/nonpolar molecules. For polar molecules, the permanent dipole will play a leading role in the interaction between electric field and polar molecules. Some reported results of MOFs materials in HKUST-1 and Ni/DODBDC boronate that H\textsubscript{2}O is more easily adsorbed than CO\textsubscript{2}.\footnote{43} This may be attributed to the strong permanent dipole moment of H\textsubscript{2}O (about 1.85 \times 10\textsuperscript{18} esu-cm). While, for gas molecules with a weak permanent dipole such as CO, the effect of instantaneous dipole, induced dipole, and quadrupole moment shall be the crucial factors. For example, though the permanent dipole of CO\textsubscript{2} is zero, both its polarizability and its quadrupole moment are higher than that of CO. Considering all factors, CO\textsubscript{2} shall have a stronger interaction with MOFs than that of CO, which has been proved by previous studies.\cite{44,45} Besides, there are no significant correlations between the selective adsorption order and the ionization energy of the adsorbates (Table S1). Thus, the effect of induced dipole moments is far greater than instantaneous dipole moments in our research system.

Besides MOFs materials, the assumption can be used to explain the adsorption behavior in other porous materials. For instance, partially charged single-walled carbon nanotubes by methylene blue encapsulation can enhance the CO\textsubscript{2} absorbivity.\cite{46} Zhou et al. grafted a porous polymer network with polar sulfonic acid (PPN-6-SO\textsubscript{3}H) and its lithium salt (PPN-6-SO\textsubscript{3}Li), which exhibit a significant increase in isosteric heats of CO\textsubscript{2} adsorption and CO\textsubscript{2}-uptake capacities.\cite{47} Cooper et al. reported a series of conjugated microporous polymers (CMP) networks.\cite{48} The carboxylic acid-functionalized network shows the highest isosteric heat of sorption for CO\textsubscript{2}. All these results could be rationally attributed to the presence of a regional dynamic electric field in these materials and explained with the assumption.

\section*{CONCLUSIONS}

In conclusion, we successfully synthesized a new MOF which presents an interesting self-interpenetrated gra topology and exceptional adsorption selectivity for CO\textsubscript{2}. It is found that the selectivity is closely related to the effect of a regional dynamic electric field present in the framework. The factors that influence physical adsorption were discussed in detail from the point of electrodynamics: The regional dynamic electric fields exist extensively in MOFs and other porous materials, and the intrinsic properties of adsorbates (such as polarizability, quadrupole moment) are the crucial factors that influence gas adsorption. According to the regional dynamic electric field effect, the adsorption capacity and selectivity could be enhanced by brightening the electric field intensity and potential gradient of the effective adsorption space of porous materials through structure modification, which is the central advantage of MOF materials.
**EXPERIMENTAL SECTION**

Synthesis of [Co(tpb)(adc)][DMF]$_3$(H$_2$O)$_{1.5}$ (1). A mixture of Co(NO$_3$)$_2$·6H$_2$O (29.1 mg, 0.1 mmol), tpb (50.4 mg, 0.1 mmol), H$_2$adc (27.0 mg, 0.1 mmol), and 2 drops of pyridine in 5 mL of DMF was sealed in a 16 mL Teflon-lined stainless steel container and heated at 160 °C for 3 days. The container was then cooled to room temperature at a rate of 0.1 °C/min, and the red crystalline product was separated by filtration, washed with DMF, and dried in air. Yield: 62% (based on tpb). Despite extensive efforts, elemental analyses are not well reproduced, presumably because the solvent molecules in the frameworks are variable. IR (KBr pellets, cm$^{-1}$): 3134, 1664, 1598, 1521, 1400, 1309, 1061, 963, 833, 656.

**Calculation of Electric Dipole Moment.** The cluster model of 1 was extracted from the periodic framework for evaluation of the strength of the dipole moment. Taking into account the entire conjugation effect, 1 includes all the nearly coplanar molecular fragments. A single-point DFT calculation was performed using the B3LYP functional (Becke three-parameter exchange hybrid functional combined with the Lee−Yang−Parr correlation functional) with the 6-31G(d) basis set for C, H, O, and N atoms and the Stuttgart RSC 1997 effective core pseudopotential for Co atoms. The result shows that the centers of positive electrical charge and negative charge are near Co$^{II}$. The direction of the dipole moment is from the oxygen atoms to the cobalt atom (Figure S19). Notably, the magnitude of the dipole moment is as large as ~12.7 D, which is rarely reported in other MOF systems.

**Calculation of Binding Energy.** Periodic density functional theory (DFT) calculations were performed using the Vienna *ab initio* Simulation packages, in which the Kohn−Sham equations are solved by self-consistent algorithms. The exchange-correlation functional used in calculations was in the framework of the generalized gradient approximation (GGA) proposed by Perdew and Wang (PW91). Valence electrons were described by a plane wave basis set with a cutoff energy of 400 eV, while inner core electrons were described by using Vanderbilt’s ultrasoft pseudopotentials for computational efficiency. A 2 × 2 × 2 Monkhorst–Pack k-point mesh was used for Brillouin zone sampling in the reciprocal space. A conjugation gradient algorithm was applied to ionic relaxation and until the energy difference was less than 10$^{-4}$ eV. An semiempirical dispersion potential was added to the conventional Kohn−Sham energy for evaluation of van der Waals (vdW) interactions in the DFT calculations. The framework atoms were fixed to their positions in the crystal structure, whereas the gas molecules were relaxed to reach a local minimum energy configuration. The binding energy is calculated by the following equation: $E_{bind} = E_{frwk/gas} - E_{frwk} - E_{gas}$ in which $E_{frwk}$ is the total energy of the framework and the adsorbed gas molecule(s), $E_{frwk}$ is the energy of the framework, and $E_{gas}$ is the energy of the gas molecule(s).

**ASSOCIATED CONTENT**

1. **Supporting Information**

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorg-chem.6b02746.

- Experimental details, crystallographic data, supplementary figures, IR, TGA, PXRD, adsorption data, calculation and modeling (PDF)
- Crystallographic data for 1 (CIF)

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**Notes**

The authors declare no competing financial interest.

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