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A Metal–Organic Framework-Based Material for Electrochemical Sensing of Carbon Dioxide

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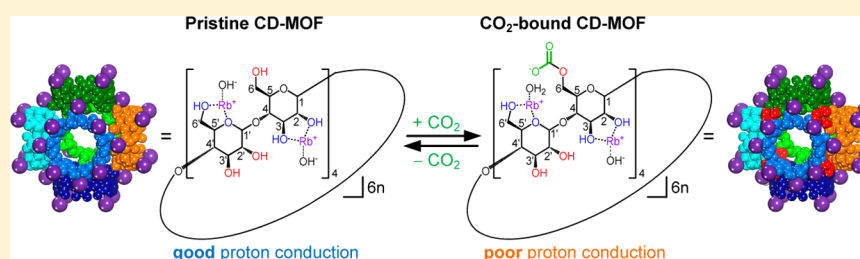
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S Supporting Information



ABSTRACT: The free primary hydroxyl groups in the metal–organic framework of CDMOF-2, an extended cubic structure containing units of six γ -cyclodextrin tori linked together in cube-like fashion by rubidium ions, has been shown to react with gaseous CO₂ to form alkyl carbonate functions. The dynamic covalent carbon–oxygen bond, associated with this chemisorption process, releases CO₂ at low activation energies. As a result of this dynamic covalent chemistry going on inside a metal–organic framework, CO₂ can be detected selectively in the atmosphere by electrochemical impedance spectroscopy. The “as-synthesized” CDMOF-2 which exhibits high proton conductivity in pore-filling methanolic media, displays a ~ 550 -fold decrease in its ionic conductivity on binding CO₂. This fundamental property has been exploited to create a sensor capable of measuring CO₂ concentrations quantitatively even in the presence of ambient oxygen.

INTRODUCTION

The detection of carbon dioxide, a highly oxidized and largely inert gas, has proven difficult within mixtures of multiple gases owing to the presence of competing gas such as oxygen, carbon monoxide and water vapor, all of which are far more chemically active.¹ It stands to reason, therefore, that the clear benefits of having robust and inexpensive devices to provide a quantitative analysis of CO₂ concentrations in admixture with other gases provides more than enough impetus for the continued development of such devices. Much of the present sensing technology depends largely upon spectroscopic methods² which become unreliable when the mixture^{2a,3} of gases contain spectroscopically similar resonances. Alternative methods, such as semiconducting field effect transistors^{2a,b} (FETs), and semiconductive oxide sensors operate⁴ constantly at temperatures in excess of 200 °C (upward of 800 °C) making them both power-hungry and potential ignition sources in areas with flammable or explosive gases.¹ As an alternative, we have investigated the possibility for metal–organic frameworks (MOFs) to act as platforms for sensing analytes at relatively low temperatures.

Not so long ago, we communicated the discovery⁵ of a new γ -cyclodextrin-derived material called CDMOF-2 which exhibits strong but reversible binding of carbon dioxide. Although we were able to demonstrate^{5b} rather crudely a colorimetric response of CDMOF-2 in the presence of CO₂ by taking advantage of the unique chemistry which occurs within this highly porous material, this response is by no means sufficient for practical quantitative analysis. This highly porous material belongs to a rapidly growing family of MOFs, crystalline materials⁶ structured chemically with building blocks—typically clusters of metal ions (components of the nodes) and rigid organics ligands (components of the extendable structural frameworks). MOFs are well regarded for their highly ordered nanoporosity, large internal surface area and postsynthetic modifiability. Accordingly, MOFs have been evaluated as potential nanoporous materials for applications in chemical separations,⁷ gas adsorption,⁸ heterogeneous catalysis,⁹ ion exchange,¹⁰ drug delivery,¹¹ and sensing.^{4c,12} While these

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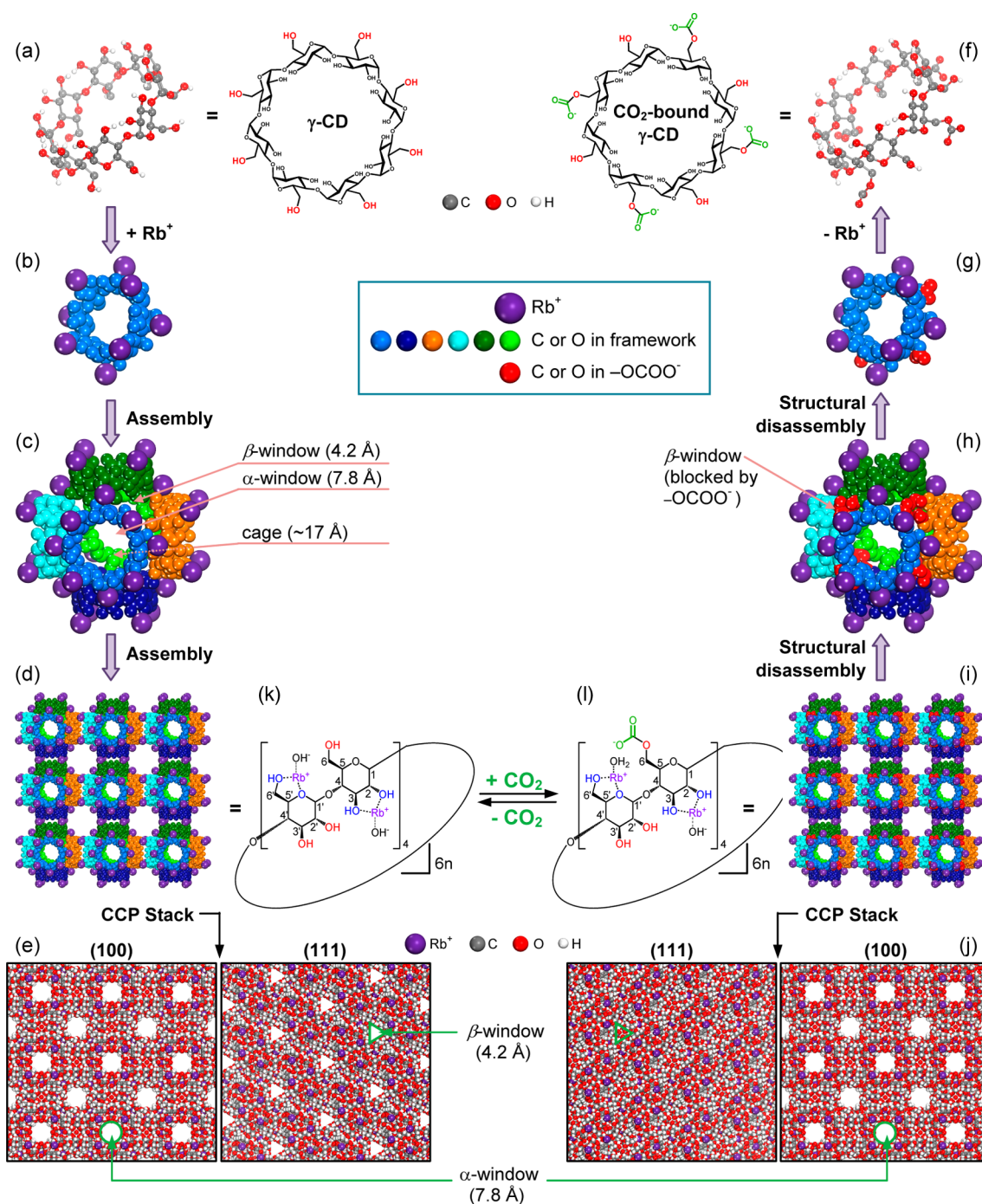


Figure 1. (a) Structural formula of γ -cyclodextrin (γ -CD). (b) Rb^+ -coordinated γ -CD $[(\text{Rb}^+)_4(\gamma\text{-CD})]$. (c) $[(\text{Rb}^+)_4(\gamma\text{-CD})]_6$ unit in which the six γ -CD rings forming the sides of the cube are portrayed in different colors. (d) $[(\text{Rb}^+)_4(\gamma\text{-CD})]_{6n}$ assembled in a planar fashion. (e) Space-filling representation of the CDMOF-2 crystal structure viewed down the 100 and 111 axes, and (f–j) In silico simulated schematic representations of CO_2 -bound CDMOF-2 structures as counterparts of (a–e). Hydrogen atoms only bound to carbon atoms in (a) and (f) and all of hydrogen atoms in (b–e and g–j) are omitted for the sake of clarity. (k and l) Schematic diagram illustrating the equilibrium proposed to exist during the chemisorption of CO_2 by CDMOF-2, expressed in the context of the structural formula of one of the four repeating maltosyl units present in a single γ -CD torus.

materials have proven to be suitable for a host of applications, there are few examples of MOFs utilizing ionic conduction¹³ as a means of chemical detection. For instance, it is surprising that, while MOFs are receiving a lot of attention as a method for CO_2 sequestration,^{5b,7a,14} to the best of our knowledge, there has been only one report of colorimetric sensing^{5b} and no reports of electrochemical sensing of CO_2 by MOFs. Indeed, only one has been reported for ion-conduction-based

sensing,^{12g} but it is just for detection of H_2O rather than CO_2 . Ionic conductivity, as its name implies, depends upon the response of free ions within a bulk material. While this methodology would typically have no applicability in sensing chemical species that are not easily ionized, we have found that a pair of unique attributions of CDMOF-2, namely a very high concentration of free hydroxyl groups and the rapid reactivity of CO_2 to form alkyl carbonic acids within the framework,

produces a viable candidate to detect CO₂ within mixtures of other, typically more reactive gases. Here, we present a method to detect carbon dioxide within CO₂/N₂ and CO₂/Air mixtures utilizing these attributes.

To this end, we have employed electrochemical impedance spectroscopy to measure the changes in proton conductivity as CO₂ levels are altered incrementally around a sample of CDMOF-2. The data show the “as-synthesized” CDMOF-2 displays an approximately 550-fold change downward in its ionic conductivity upon binding to CO₂, more than sufficient to produce a quantitative analysis of the atmospheric content of CO₂.

RESULTS AND DISCUSSION

The majority of MOFs that have been designed for the selective uptake of CO₂ have not exhibited reversible chemisorption–desorption of carbon dioxide. Recently, however, we have elucidated^{5b,d} a mechanism by which a particular metal–organic framework, CDMOF-2, can store CO₂ reversibly by forming labile covalent bonds on the framework. CDMOF-2 can be prepared by reaction of γ -cyclodextrin [γ -CD, see Figure 1a and Section S1 in the Supporting Information] and rubidium hydroxide (RbOH) at room temperature in aqueous methanol (or ethanol). γ -CD is a cyclic oligosaccharide composed of eight α -D-glucopyranosyl residues linked 1,4 to each other. Rb⁺ cations bind with γ -CD tori by coordinating (Figure 1b) to some of the ring oxygen atoms together with some of the secondary and primary hydroxyl groups at C-2, C-3, and C-6 on the glucopyranosyl rings. The coordination sphere round a particular Rb⁺ cation is satisfied by eight oxygen atoms from four different γ -CD tori. See Section S2 in the Supporting Information. This coordination geometry gives rise to a unit cell for CDMOF-2 (Figure 1c), composed of six γ -CD tori and 24 Rb⁺ cations forming a cubic cage inside of which there exists a \sim 17 Å diameter void with two kinds of windows: a large circular one (α -windows) of diameter 7.8 Å and a smaller triangular-shaped one (β -windows) that is 4.2 Å from the apex to the opposite side of the triangle. Body-centered-cubic (bcc) close packing of the unit cells produces a framework with the larger circular α -windows and the smaller triangular-shaped β -windows aligned, respectively, along the 100 and 111 axes in the crystal. ¹³C NMR Spectroscopic investigations revealed that infusion of CO₂ into the extended framework of CDMOF-2 results in covalent bonding of the CO₂ to the noncoordinated free primary hydroxyl groups, forming alkyl carbonic acid (CA) functions on the γ -CD tori to yield CA-CDMOF-2 (Figure 1). On the basis of these observations, we have simulated¹⁵ the crystal structure of CA-CDMOF-2 to reveal the consequences of CO₂ chemisorption along both the 100 and 111 axes (Figure 1e,j).

Generally, MOFs containing hydroxyl functional groups in their frameworks have been found to release protons into their nanopores or nanochannels with relatively low activation energies and thereby exhibit proton conduction.^{13e–g} In a systematic investigation of the ionic conductivity of CDMOF-2, we examined the “as-synthesized” version of CDMOF-2 and a CO₂ gas-infused (Figures 1 and 2) species, CA-CDMOF-2, with methanol or *n*-hexane as a pore-filling solvent. See Supporting Information Section S8. Key to the study is the role of the alkyl CA formed by CO₂-binding. On the basis of the greater acidity of the carbonic acids relative to that of the primary alcohols, we expected that the CO₂-infused CA-CDMOF-2 would show higher conductivity than pristine

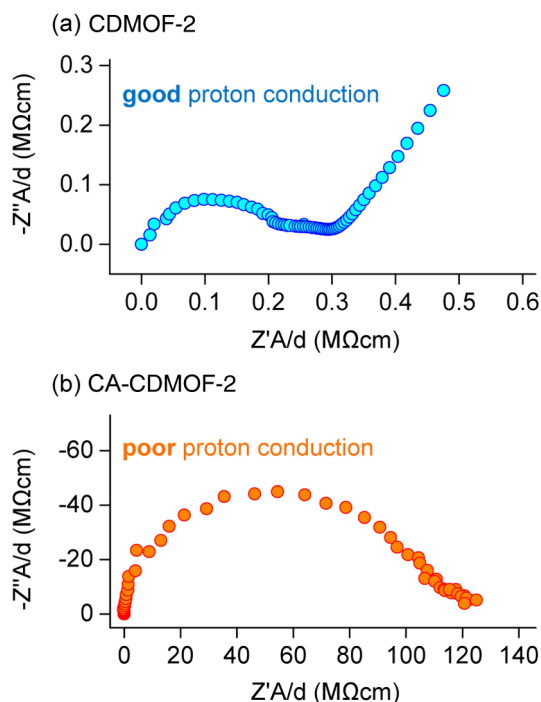


Figure 2. Impedance spectra of (a) a pristine CDMOF-2 and (b) CO₂-infused CDMOF-2 samples following exposure to methanol vapor at room temperature.

CDMOF-2. Contrary to our expectations, we found that CDMOF-2 exhibits a \sim 550-fold higher conductivity compared to that exhibited by CA-CDMOF-2 (see Figure 2 and Table 1). The conductivity of pristine CDMOF-2 was measured to be \sim 4.8 μ S cm^{−1}, while CA-CDMOF-2 is only 9 nS cm^{−1}. We attribute this observation tentatively to the blockage of the hydrophilic, triangular-shaped β -windows with carbonates as the reaction proceeds (Figure 1j). These β -windows are the sole location of all uncomplexed, primary alcohol functions and, consequently, the place where carboxylation occurs primarily.

The tests were conducted under ambient air (ca. 35% humidity). Dry conditions, however, increase the sensitivity: for instance, we have observed that high humidity decreases the sensitivity by a factor of ca. 5. See Section S9 in Supporting Information.

An attractive property of CDMOF-2 is the high degree of reversibility found in the chemisorption of CO₂. This

Table 1. Conductivities of CDMOF-2 Samples Before and After Exposure to Gas-Phase CO₂ for 5 min in Various CO₂ Concentrations

CO ₂ concd (%) ^a	σ (nS cm ^{−1})				
	sample 1	sample 2	sample 3	avg.	ratio
0	4740	4569	5095	4801	550
10	1069	1129	1248	1149	130
20	228	198	223	216	24
30	115	99	110	108	12
40	63	49	57	57	6.5
60	21	24	20	22	2.5
90	11	12	10	11	1.2
100	9	9	8	9	1.0

^aThe concentration of CO₂ gas was controlled by a mass flow controller, diluting with nitrogen gas.

reversibility, which occurs rapidly under very mild conditions, liberating the sequestered CO_2 , is important in the continuous reusability of CDMOF-2. To this end, the cyclic changes in conductivity by a pellet of CDMOF-2 as a result of undergoing multiple chemisorption–desorption experiments of CO_2 were conducted. A pellet sample was prepared and the sample was exposed to CO_2 gas (99.8%, bone dry) for chemisorption, tested, and then heated at $\sim 80^\circ\text{C}$ for desorption and tested again.

The conductivity of pristine CDMOF-2, which initially showed a high value, was decreased by a factor of ~ 550 -fold after CO_2 sorption, but was once again reinstated after CO_2 desorption. This process is completely reversible (Figure 3) over many iterations with no degradation in performance.

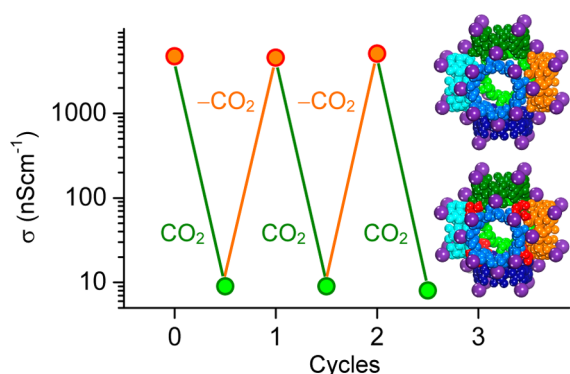


Figure 3. Cyclic change of conductivity of a CDMOF-2 sample following sequential CO_2 -sorption and desorption.

These promising initial experiments suggested to us that this MOF acts as a sensor for CO_2 in the presence of air, from which no effort was made to exclude extraneous nitrogen or oxygen. With these results in hand, we wanted to examine whether the device displays gradual responses to the amount of CO_2 present in a mixture with nitrogen. Thus, we tested the MOF and noted the conduction responses at various CO_2 gas concentrations. The conductivity dropped down sharply (Figure 4) as the CO_2 concentration was increased. Note the exponential scale of the y -axis. The slope shows an approximately exponential decay as the concentration is

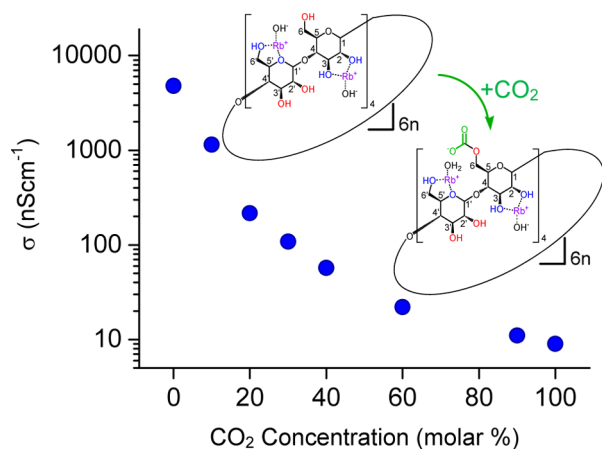


Figure 4. Exponential scale plot of average conductivity values in CDMOF-2 samples after their exposure for 5 min to CO_2 gas, which was diluted with N_2 in various concentrations.

decreased with better sensitivity in the low CO_2 concentration regime, compared with that at high concentrations (lower than 20%, see Section S5 in the Supporting Information). On the basis of this observation, we speculate that the sensitivity will be affected by several factors including: (i) the rate of reaction associated with carboxylation, (ii) the diffusion rate of CO_2 gas into pellets, (iii) the pellet thicknesses, and (iv) the exposure time of the sample to CO_2 gas. On the basis of the assumption that the reaction rate associated with carboxylation is much faster than the CO_2 diffusion rate, we used the slope as a criterion of sensitivity in the low CO_2 concentration region, which is expected to be steep when the pellet thickness is thinner and/or the CO_2 exposure time is longer. While a detailed investigation into pellet geometry is beyond the scope of this communication, we suspect from these observations that thin pellets or films will be more sensitive as a real time detector.

CONCLUSIONS

In summary, we have observed large ionic conductivity from the samples of “as-synthesized” CDMOF-2. The large drop (~ 550 -fold) in the conductivity after CO_2 infusion into these samples is attributed to an encumbrance in the motility of free protons. Additionally, we were able to show a sequential attenuation of the conductivity, together with incremental additions of CO_2 in a mixture of other gases, providing a selective analysis of CO_2 concentrations. The reduced conductivity of CA-CDMOF-2 can be ascribed to the loss of base (coordinated hydroxide) that can catalyze the deprotonation of the methanolic medium and blocking of the secondary β -windows that can significantly reduce mass transfer of the intermedium molecules. The sensitivity of the conductivity change is relatively high at low CO_2 concentration, while the sensor, if fully reversible, follows the desorption of CO_2 . This research seeks to lay the foundation to address the need for an electrochemical means of sensing CO_2 which comes, in part, from an emerging environmental requirement to monitor concentrations at and near high volume, emission point-sources, and from the limitations associated with present state-of-the-art technologies. The value added by using low cost and highly selective materials makes this device an attractive alternative for sensing carbon dioxide. This research has demonstrated that MOFs have a promising future in the field of quantitative sensing applications and that they are capable of showing much higher sensitivities than current methods.^{4a,b}

ASSOCIATED CONTENT

Supporting Information

Experimental details, electrochemical impedance spectra, powder X-ray diffraction patterns, thermal gravimetric analysis, and elemental analysis. 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.

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(15) The crystal structure of CA-CDMOF-2 could not be determined from single crystal X-ray diffraction studies as a consequence of high positional disorder of the bound CO₂. Instead, we simulated the structure based on CP-MAS ¹³C NMR (400 MHz) spectroscopic studies.