Enhanced Thermal Conductivity in a Diamine-Appended Metal–Organic Framework as a Result of Cooperative CO₂ Adsorption

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ABSTRACT: Diamine-appended variants of the metal–organic framework $\text{M}_2(\text{dobpdc})$ ($\text{M} = \text{Mg, Mn, Fe, Co, Zn}$; $\text{dobpdc}^{4-} = 4,4^{'-}\text{dioxidobiphenyl-3,3^{'-}dicarboxylate}$) exhibit exceptional CO₂ capture properties owing to a unique cooperative adsorption mechanism, and thus hold promise for use in the development of energy- and cost-efficient CO₂ separations. Understanding the nature of thermal transport in these materials is essential for such practical applications, however, as temperature rises resulting from exothermic CO₂ uptake could potentially offset the energy savings offered by such cooperative adsorbents. Here, molecular dynamics (MD) simulations are employed in investigating thermal transport in bare and $\text{e-2}$-appended $\text{Zn}_2(\text{dobpdc})$ ($\text{e-2} = \text{N-ethyl ethylene diamine}$), both with and without CO₂ as a guest. In the absence of CO₂, the appended diamines function to enhance thermal conductivity in the $ab$-plane of $\text{e-2}$–$\text{Zn}_2(\text{dobpdc})$ relative to the bare framework, as a result of noncovalent interactions between adjacent diamines that provide additional heat transfer pathways across the pore channel. Upon introduction of CO₂, the thermal conductivity along the pore channel (the $c$-axis) increases due to the cooperative formation of metal-bound ammonium carbamates, which serve to create additional heat transfer pathways. In contrast, the thermal conductivity of the bare framework remains unchanged in the presence of zinc-bound CO₂ but decreases in the presence of additional adsorbed CO₂.

KEYWORDS: metal–organic framework, diamine–$M_2$(dobpdc), heat transfer, CO₂ capture, phonon scattering

INTRODUCTION

Metal–organic frameworks (MOFs) are crystalline, porous solids that exhibit vast chemical and structural tunability, and in tandem with their extremely high internal surface areas, these properties have rendered them promising candidates for a variety of applications, including gas storage, molecular separations, and catalysis.1–3 Recently, diamine-appended frameworks with the formula (diamine)$_2$$M_2$(dobpdc) (also known as diamine–$M_2$(dobpdc); $M = \text{Mg, Mn, Fe, Co, Zn}$; $\text{dobpdc}^{4-} = 4,4^{'-}\text{dioxidobiphenyl-3,3^{'-}dicarboxylate}$) have been shown to capture CO₂ with unprecedented efficiency and selectivity.6–11 In these materials, CO₂ reacts with the metal-bound amine to form a metal-bound ammonium carbamate, which then propagates as ion-paired ammonium carbamate chains that extend along the framework channels.7,9,14 Single-crystal X-ray diffraction structures of $\text{Zn}_2(\text{dobpdc})$, $\text{e-2}$–$\text{Zn}_2(\text{dobpdc})$ ($\text{e-2} = \text{N-ethyl ethylene diamine}$), and $\text{e-2}$–$\text{Zn}_2(\text{dobpdc})$–CO₂ are shown in Figure 1, as determined in ref 9. This unique mechanism gives rise to step-shaped CO₂ uptake, and the material step temperature (isobaric conditions) or step pressure (isothermal conditions) can be tuned based on the choice of appended diamine. As such, these materials are of interest for various challenging separations in industry, including the capture of CO₂ from power plant flue emissions,9,11,15 as they can operate using much smaller pressure or temperature swings and achieve higher working capacities than traditional adsorbents.

One important practical consideration in evaluating the performance of these materials is the rate at which CO₂ can be loaded into the pores without causing a prohibitively sharp temperature increase. Indeed, adsorption of CO₂ is an exothermic process, potentially leading to a considerable increase in the local temperature that is higher than the step temperature in an adsorption isobar curve. To dissipate this heat quickly and maximize the quantity of CO₂ adsorbed, a given framework must have a high thermal conductivity. Additionally, high thermal conductivities can reduce adsorption/desorption cycle times in practical configurations, which can lead to improvements in process efficiency. Previous...
investigations of thermal transport in MOFs have predominantly been limited to materials in the absence of guest molecules,\textsuperscript{16–23} while the few studies that have investigated heat transfer in the presence of an adsorbed gas have considered only physisorbed gases.\textsuperscript{24–27} Our previous studies\textsuperscript{24,26,28,29} have shown that the presence of physisorbed guests introduces new phonon scattering channels resulting from gas-framework collisions, which serve to reduce thermal conductivity. The possible effects of chemisorbed guests on thermal transport in MOFs, however, have remained unstudied.

In this work, we use molecular dynamics (MD) simulations to investigate mechanisms of heat transfer in bare and e-2-appended Zn\textsubscript{2} (dobpdc) (e-2 = N-ethylhexylenediamine), and we apply the Green–Kubo method to predict their thermal conductivities with and without adsorbed CO\textsubscript{2}. Consistent with our previous studies, thermal conductivity in the bare material is diminished in the presence of (noncoordinating) physisorbed CO\textsubscript{2}, whereas it is unchanged in the presence of more strongly adsorbed, zinc-bound CO\textsubscript{2}. Importantly, however, an enhancement in thermal conductivity is observed for e-2–Zn\textsubscript{2} (dobpdc) upon chemisorption of CO\textsubscript{2} resulting from the introduction of new heat transfer pathways along the framework channels. This result is in contrast to the reduction in thermal conductivity that occurs in the presence of physisorbed guests and has important implications for heat management during CO\textsubscript{2} adsorption that is of relevance for practical separation applications.

\section{STRUCTURES AND METHODOLOGY}

In our calculations, we evaluated the thermal conductivity of guest-free Zn\textsubscript{2} (dobpdc) and e-2–Zn\textsubscript{2} (dobpdc), e-2–Zn\textsubscript{2} (dobpdc) with chemisorbed CO\textsubscript{2}, and Zn\textsubscript{2} (dobpdc) in the presence of metal-bound and more weakly physisorbed CO\textsubscript{2}. In the case of Zn\textsubscript{2} (dobpdc), metal-bound CO\textsubscript{2} molecules do not move from their initial density functional theory (DFT)-determined locations in the pores, whereas the other more weakly associated physisorbed CO\textsubscript{2} molecules are those that can diffuse away from their initial random calculated positions. The simulation cell size for each framework was set based on the DFT-relaxed lattice constants. For the interactions between atoms in Zn\textsubscript{2} (dobpdc), e-2–Zn\textsubscript{2} (dobpdc), and e-2–Zn\textsubscript{2} (dobpdc)–CO\textsubscript{2}, we used a modified version of the DREIDING force field,\textsuperscript{30} in which the equilibrium distances between atoms were adjusted to the DFT-relaxed structures. Among other general force fields, we picked DREIDING as it allows for the description of existing hydrogen bonds. The required charges on atoms were obtained using the DDEC algorithm,\textsuperscript{31} wherein partial atomic charges are calculated using the electron densities obtained from van der Waals (vdW)-corrected DFT calculations. The CO\textsubscript{2} molecules loaded within Zn\textsubscript{2} (dobpdc) were modeled using the TraPPE force field.\textsuperscript{32} The initial atomic configurations for the MD simulations involving metal-bound CO\textsubscript{2} adsorbed in Zn\textsubscript{2} (dobpdc) were taken from snapshots of equilibrated DFT calculations.

For the DFT calculations, we used a plane-wave basis and projector augmented-wave (PAW)\textsuperscript{33,34} pseudopotential with the Vienna ab-initio Simulation Package (VASP) code.\textsuperscript{35–38} We performed structural relaxations with a vDW dispersion-corrected functional (vdW-DF2)\textsuperscript{39} as implemented in VASP. For all calculations, a Γ-point sampling of the Brillouin zone and a 600-eV plane-wave cutoff energy were employed. We explicitly treated 12 valence electrons for Zn (3d\textsuperscript{10}4s\textsuperscript{2}), six for O (2s\textsuperscript{2}2p\textsuperscript{4}), five for N (2s\textsuperscript{2}2p\textsuperscript{3}), four for C (2s\textsuperscript{2}2p\textsuperscript{2}), and one for H (1s\textsuperscript{1}). All structural relaxations were performed with a Gaussian smearing of 0.05 eV.\textsuperscript{40} The ions were relaxed until the Hellmann–Feynman forces were less than 0.02 eV Å\textsuperscript{−1}. The Green–Kubo method was applied to predict thermal conductivity.\textsuperscript{41} This method involves calculating the instantaneous heat flux in an equilibrium MD simulation. The partial enthalpy terms required to analyze multicomponent systems were implemented as discussed in refs 24, 26, 42, 43. The MD simulations were performed using a version of the Large-scale Atomic/Molecular Massively Parallel Simulator\textsuperscript{44} software, which can correctly implement heat flux for many-body potentials. To gain further insight into the thermal conductivity predictions, we also calculated the corrected diffusivity (which is associated with molecular mobility) of metal-bound CO\textsubscript{2} in Zn\textsubscript{2} (dobpdc).\textsuperscript{45} The corrected diffusivity is based on a Green–Kubo relation and is defined as the time integral of the center of mass velocity autocorrelation function for the gas component. Details of the Green–Kubo calculations for both thermal conductivity and diffusivity are provided in the Supporting Information. For determining thermal conductivity, a system size of 4 × 4 × 6 (in crystallographic directions a, b, and c) unit cells was used. See Figure 2 for snapshots of the simulation cells for e-2–Zn\textsubscript{2} (dobpdc)–CO\textsubscript{2} and Zn\textsubscript{2} (dobpdc) with metal-bound CO\textsubscript{2}. The systems were initially equilibrated under NPT (constant pressure–constant temperature) conditions at a temperature of 300 K and atmospheric pressure for 500 000 time steps; under NVT (constant volume–constant temperature) conditions at a temperature of 300 K for 300 000 time steps; and for 200 000 time steps under NVE (constant volume–constant energy) conditions. Finally, NVE simulations were run for an additional 300 000 time steps.
and discussed in the text. Zn\(_2\)(dobpdc) with and without CO\(_2\) loading. The parameters respectively.

**RESULTS AND DISCUSSION**

Predicted thermal conductivities in the crystallographic directions \(a\), \(b\), and \(c\) of (a) e-2–Zn\(_2\)(dobpdc)–CO\(_2\) and (b) CO\(_2\) bound at the open Zn\(^{2+}\) sites within Zn\(_2\)(dobpdc). Light blue, red, blue, gray, and light gray spheres represent Zn, O, N, C, and H atoms, respectively.

1 000 000 time steps, where the heat current was calculated every five time steps. For all cases, this procedure was performed for four simulations starting from random velocity distributions.

**Figure 2.** Simulation box with 4 × 4 × 6 unit cells (in crystallographic directions \(a\), \(b\), and \(c\)) of (a) e-2–Zn\(_2\)(dobpdc)–CO\(_2\) and (b) CO\(_2\) bound at the open Zn\(^{2+}\) sites within Zn\(_2\)(dobpdc). Light blue, red, blue, gray, and light gray spheres represent Zn, O, N, C, and H atoms, respectively.

**Figure 3.** Calculated thermal conductivities of Zn\(_2\)(dobpdc) and e-2–Zn\(_2\)(dobpdc) with and without CO\(_2\) loading. The parameters \(k_a\), \(k_b\), and \(k_c\) correspond to the crystallographic \(a\), \(b\), and \(c\) directions as discussed in the text.
that in the presence of CO\textsubscript{2}, the unique chemisorption complex mechanism that also involves the formation of ammonium carbamate chain formation. However, we note that certain frameworks follow a similar mechanism of ammonium thermal transport in diamine-appended materials for practical applications.

### CONCLUSIONS

In summary, we have used MD simulations to investigate thermal transport in the frameworks Zn\textsubscript{2}(dobpdc) and e-2–Zn\textsubscript{2}(dobpdc) both without and with CO\textsubscript{2} as a guest. We find that in the presence of CO\textsubscript{2}, the unique chemisorption mechanism in e-2–Zn\textsubscript{2}(dobpdc) serves to enhance the thermal conductivity in the direction of the framework channels, whereas adsorption of CO\textsubscript{2} in the bare material has no effect on or decreases the thermal conductivity. These results point to enhanced thermal management as an additional advantage of these diamine-appended materials for practical applications. Indeed, upon CO\textsubscript{2} uptake, most diamine–M\textsubscript{2}(dobpdc) frameworks follow a similar mechanism of ammonium carbamate chain formation. However, we note that certain other appended diamines, such as 2,2-dimethyl-1,3-diaminopropane, have been shown to react with CO\textsubscript{2} via a more complex mechanism that also involves the formation of carboxylic acid pairs.\textsuperscript{11} In the future, we plan to investigate the effects of these differing chemisorption mechanisms on thermal transport in diamine–M\textsubscript{2}(dobpdc) frameworks.

### ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsami.0c10233.

Additional information on simulation methodology (PDF)

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