ACS APPLIED NANO MATERIALS

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Efficient CO_2/CO Separation by Pressure Swing Adsorption Using an Intrinsically Nanoporous Molecular Crystal

Yao-Ting Wang, Said Jalife, Alexandra Robles, Miloš Đerić, Judy I. Wu, Watchareeya Kaveevivitchai, Ognjen S. Miljanić,* and Teng-Hao Chen*

Cite This: https://doi.org/10.1021/acsanm.2c01535 Read Online

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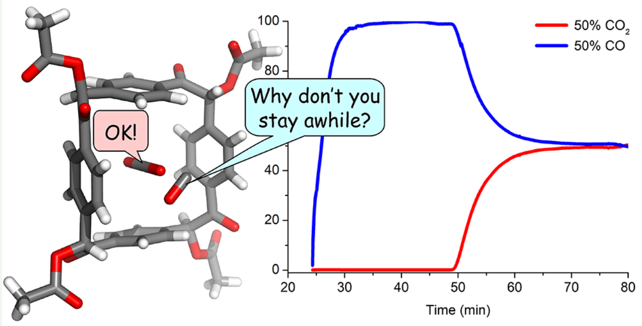
ABSTRACT: The physisorption-based separation of CO_2 from CO is an energy-efficient yet challenging approach to obtain pure CO. We have applied an intrinsically porous molecular crystal (PMC), assembled from the readily synthesized macrocyclic cyclotetrabenzoin acetate to the problem of CO_2/CO separation. This nanoporous material possesses both kinetic (micropore) and thermodynamic (CO_2−π and CO_2−carbonyl interactions) factors needed for selective CO_2 capture. The moderate CO_2−adsorbent interaction allows easy regeneration needed for pressure swing adsorption (PSA). Both trace (1%) and bulk (50%) amounts of CO_2 can be removed from CO_2/CO gas mixtures in PSA processes.



KEYWORDS: *carbon monoxide, CO_2/CO separation, porous molecular crystal, nanoporous materials, pressure swing adsorption*

Carbon monoxide (CO) is an important reagent for the synthesis of industrially valuable chemicals such as oxo-alcohols, acetic acid, phosgene (precursors of polyurethanes and polycarbonate plastics), and various liquid hydrocarbon fuels via the Fischer−Tropsch process.[1] In industry, CO is produced at large scale by steam reforming or water−gas shifting of coal, natural gas, or biomass. These processes generate CO mixed with carbon dioxide (CO_2), whose concentrations can vary from less than 1 vol % to more than 50 vol %. CO_2/CO separation is therefore essential yet challenging since the properties of these two gases are rather similar. Energy-intensive separation processes are behind 40−70% of operating and capital costs in industry and account for about 10−15% of global energy consumption.[2] Thus, the development of economic and energy-efficient separation techniques has become an urgent topic.

The common techniques for CO_2/CO separation include cryogenic distillation, solvent absorption, adsorption, and membrane separation.[2] Most of these processes are associated with significant energy penalties. In contrast, separation processes based on physisorption could have significantly lower cost and energy footprint.[3] Pressure swing adsorption (PSA) is rapidly becoming one of the most promising adsorption-based separation technologies,[4] and the choice of adsorbent is particularly critical for the separation of CO_2 and CO by PSA. Common low-cost adsorbents such as activated carbons and zeolites suffer from low CO_2/CO adsorption selectivity.[5] Cu(I)-modified porous materials[6] and metal−organic frameworks (MOFs) with open-metal sites[7] exhibit high affinity to CO but suffer from competitive CO_2 adsorption.[8] In addition, in these crystalline framework materials, water vapor competes with CO for the unsaturated metal sites and causes structural deformations. Therefore, intensive pretreatment or energy-consuming regeneration is required for the reuse of adsorbents, making them unsuitable for practical applications.[9] So far, CO_2 removal is a preferred strategy for CO_2/CO separation by PSA in contrast to CO adsorption.[10] An ideal CO_2 adsorbent for PSA should be a nanoporous material with uniform and tailored pore sizes for size-exclusive adsorption, moderately strong interactions with CO_2 that would allow both facile CO_2 binding and regeneration, and long-term thermal and hydrolytic stability.

In contrast to the well-established zeolites and MOFs, porous molecular crystals (PMCs) are solution- and vapor-processable, which is desirable for material engineering into devices and industrial production.[11] These crystalline materials are self-assembled from discrete molecules via supramolecular interactions including $\pi\cdots\pi$ stacking, hydrogen bonding, or C−H$\cdots\pi$ interactions. Depending on their structures and crystal packing, they can be divided into intrinsically porous (constructed from molecules with their own cavity, such as

Special Issue: Professor Sir Fraser Stoddart's 80th Birthday Forum

Received: April 8, 2022
Accepted: May 24, 2022

organic cages[12] and macrocycles)[13] and extrinsically porous molecular crystals (formed by the inefficient packing of otherwise nonporous molecules).[14,15] Very recently, Wang and co-workers reported the first use of a microporous hydrogen-bonded organic framework for CO_2/CO separation by breakthrough experiments.[16] To date, the ability of intrinsic PMCs to separate CO_2 and CO has not been studied. While many PMC materials have been proposed and tested as adsorbents in gas separations,[17] their use in PSA separation is rare[18] on account of their moisture sensitivity and inability to sustain repeated adsorption/desorption cycles.

We previously demonstrated that an intrinsic PMC material based on cyclotetrabenzoin acetate (**1** in Figure 1) is an efficient PSA adsorbent for the separation of CO_2 from nitrogen (N_2) and methane (CH_4) gases.[18] In the crystal structure, the linearly aligned 7.1 × 7.1 Å^2 square channels of **1** are lined with the polar carbonyl groups (from adjacent macrocycles) pointing inward in the square pores and creating 5.0 × 5.0 Å square apertures, which endow these materials with kinetic selectivity for CO_2 adsorption. These pores additionally appear quite rigid,[19] as evidenced by minimal (<0.4%) changes in the unit cell parameters upon CO_2 inclusion.[18] This environment results in a high affinity of **1** to the quadrupoles of CO_2 molecules, while the benzene walls of **1** can interact with CO_2 molecules via $\pi\cdots\pi$ stacking. As this PMC material possesses well-tailored kinetic (micropore) and thermodynamic ($CO_2-\pi$ and CO_2−carbonyl interactions) factors for efficient CO_2 capture, we speculated that it would be able to separate CO_2 even from the closely related CO molecule.

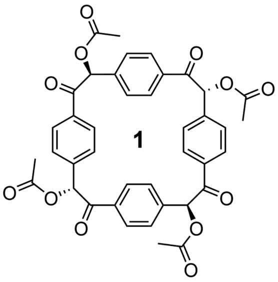


Figure 1. Structure of cyclotetrabenzoin acetate (**1**).

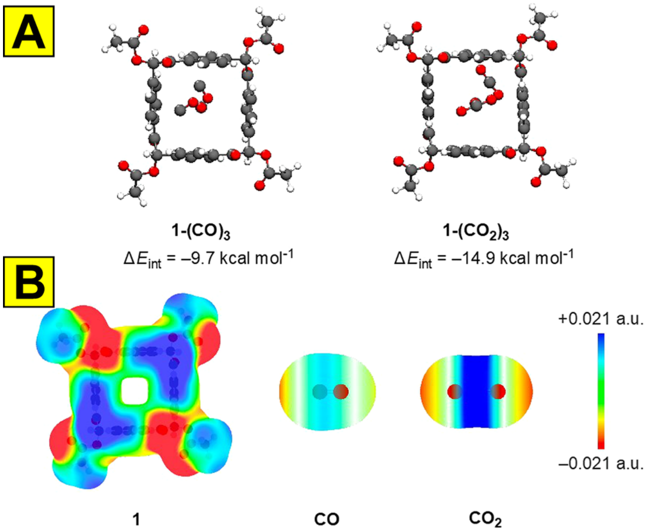


Figure 2. (A) Optimized geometries for **1(CO)$_3$** and **1(CO$_2$)$_3$**. (B) Molecular electrostatic potential (MEP) maps for CO, CO_2, and **1** mapped on the surface of the electron density with an isosurface value of 0.0004 au.

Computed interaction energies (ΔE_{int}) show that macrocycle **1** interacts comparably with one molecule of CO_2 (ΔE_{int} = −7.2 kcal mol^{-1}) and one molecule of CO (ΔE_{int} = −5.5 kcal mol^{-1}), showing only a slight preference for CO_2 encapsulation. Yet, the crystallographic data suggest that up to three guest molecules can be associated with a single molecule of **1**. When three guest molecules are considered, CO_2 capture is notably more favorable (ΔE_{int} = −14.9 kcal mol^{-1}) than that of CO (ΔE_{int} = −9.7 kcal mol^{-1}). Optimized structures of **1(CO)$_3$** and **1(CO$_2$)$_3$** complexes are shown in Figure 2A. All interaction energies (ΔE_{int}) were calculated at the ωB97XD/def2-TZVP//ωB97XD/def2-SVP level of theory using Gaussian16.[20] Interaction energy (ΔE_{int}) values were computed based on the energy of the host−guest complexes from which the energy of an appropriate number of molecules of CO_2 or CO was subtracted. As shown in Figure 2A, in the **1(CO)$_3$** and **1(CO$_2$)$_3$** complexes, one CO_2 or CO molecule is trapped inside the cavity and aligned parallel to the arene rings, and two others are oriented perpendicular to the inner CO_2 or CO molecule. Enhanced association of three CO_2 molecules to **1** can be explained by attractive electrostatic interactions between the oxygen atoms of the outer CO_2 molecules (see Figure 2B, red molecular electrostatic potential (MEP) surface at the O atoms of CO_2) with the arene H atoms of **1** (blue MEP surface), and the C atom of the outer CO_2 molecules (blue MEP surface) with the C═O groups of **1** (red MEP surface). Computed noncovalent interaction (NCI) analyses are supportive of this conclusion (see the Supporting Information).

Encouraged by the computational guidance, we experimentally probed the ability of crystals of **1** to separate CO_2 from CO. The Brunauer−Emmett−Teller (BET) surface area of the microporous crystals of **1** is ∼570 m^2 g^{-1},[21] and the single-component gas adsorption isotherms at 298 K display a preferential uptake of CO_2 over CO (Figure 3A). At 1 bar, the CO_2 uptake of **1** reaches 69 cm^3 g^{-1}, which is much higher than that of CO (5.7 cm^3 g^{-1}). The zero-coverage isosteric heat (Q_{st}) of the CO_2 and CO adsorption was estimated from their adsorption isotherms measured at 273 and 298 K under 1 bar (Figures S12 and S13). The nonlinear CO_2 adsorption isotherm (Figure 3A) and the higher Q_{st} observed for CO_2 (33.7 kJ mol^{-1}) vs CO (12.9 kJ mol^{-1}, Figure 3B) indicate interactions between CO_2 and **1**. Although the CO_2/CO uptake ratio of **1** is not as high as that of ultra-microporous materials, activated carbon, or zeolite 13X (Figure S15),[16] the value of Q_{st} within 30−50 kJ mol^{-1} is indicative of moderate interactions between CO_2 and adsorbent, which allow facile regeneration critical for PSA processes.[22] As shown in Figure 3C, the highly chemically and hydrolytically robust[18] PMC **1** stands among the rare CO_2 adsorbent materials that match the criteria for practical PSA-based CO_2/CO separation, such as MOFs with open-metal sites (Mg-MOF-74[8] and MIL-101).[23]

Ideal adsorbed solution theory (IAST) was used to evaluate the CO_2/CO selectivity of **1** for 50/50 and 1/99 mixtures of these two gases at 298 K.[24] As illustrated in Figure 3D, this PMC displays a high IAST selectivity of 10.1 and 102 for 50/50 and 1/99 mixtures at 1.0 bar, respectively. At lower temperature of 273 K, these selectivities increase to 16.8 and 166, respectively (Figure S16). These values are comparable to those of porous materials with strong CO_2-binding sites,[10]

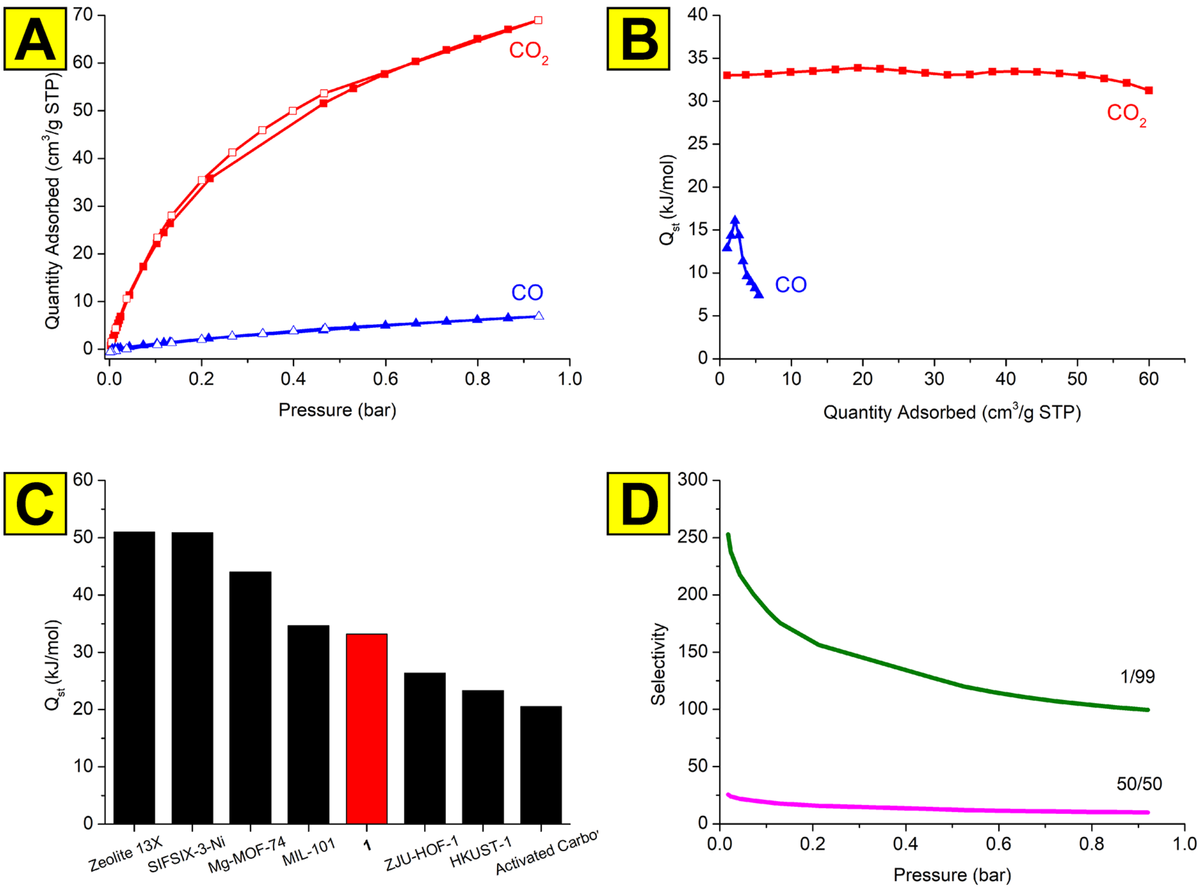


Figure 3. (A) CO_2 and CO sorption isotherms of **1** at 298 K (filled symbols, adsorption; empty symbols, desorption). (B) Isosteric heats of adsorption (Q_{st}) of CO_2 and CO within the pores of **1**. (C) Zero coverage Q_{st} of CO_2 for **1** in comparison with other CO_2 adsorbents studied for CO_2/CO separation. (D) Calculated IAST selectivity of **1** for 50/50 and 1/99 CO_2/CO gas mixtures at 298 K.

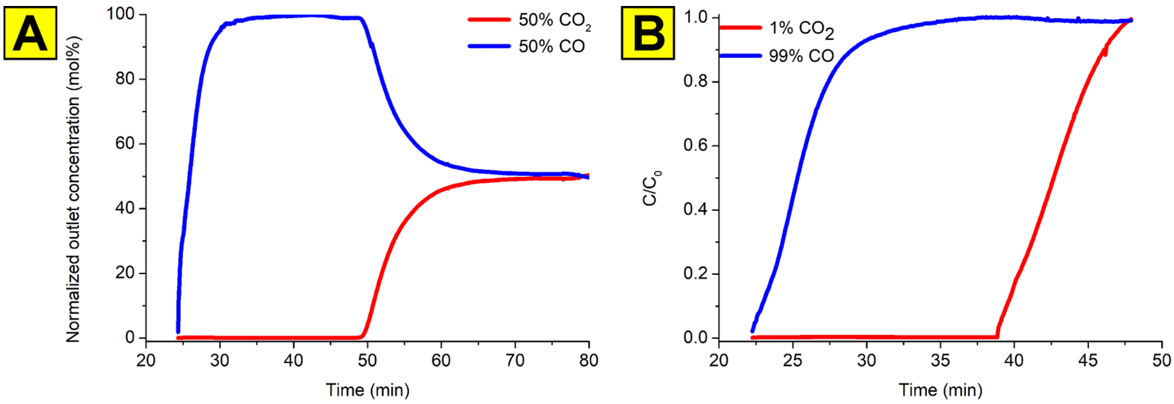


Figure 4. Experimental breakthrough curves for the elution of (A) (50/50, v/v) and (B) (1/99, v/v) CO_2/CO mixtures through a column packed with **1**. Separation conditions: 298 K, 1 bar, flow rates of (A) 3/3 and (B) 0.5/49.5 mL min^{-1}.

making it promising as an efficient adsorbent for CO_2/CO separation.

The separation performance of **1** was further studied in breakthrough experiments of actual 50/50 and 1/99 CO_2/CO mixtures. A column packed with powdered **1** was activated by heating at 303 K for 4 h in vacuo before commencing the breakthrough studies. Eluted gas components were continuously monitored by mass spectrometry. As shown in Figure 4A, this PMC separated CO_2 and CO effectively from a 50/50 mixture at 1 bar and flow rates of 3/3 mL min^{-1}. CO emerged from the adsorbent bed after 24 min, and the highest purity of CO was reached at 35 min. Until 49 min, the outlet concentration of CO_2 remained negligible. After CO_2 started eluting, it reached saturation at 78 min. The breakthrough capacity of **1** is about 57 cm^3 g^{-1}, consistent with the CO_2 uptake of **1** at a partial pressure of 0.5 bar in a single-component isotherm (Figure 3A). This phenomenon can be attributed to the strong CO_2−framework interaction at low pressure. Accordingly, before CO_2 eluted out, about 57 L of CO with >99.99% purity can be produced for 1 kg of **1**, comparable to the performance of ultra-microporous materials.[10] In the case of a 1/99 CO_2/CO mixture, the breakthrough

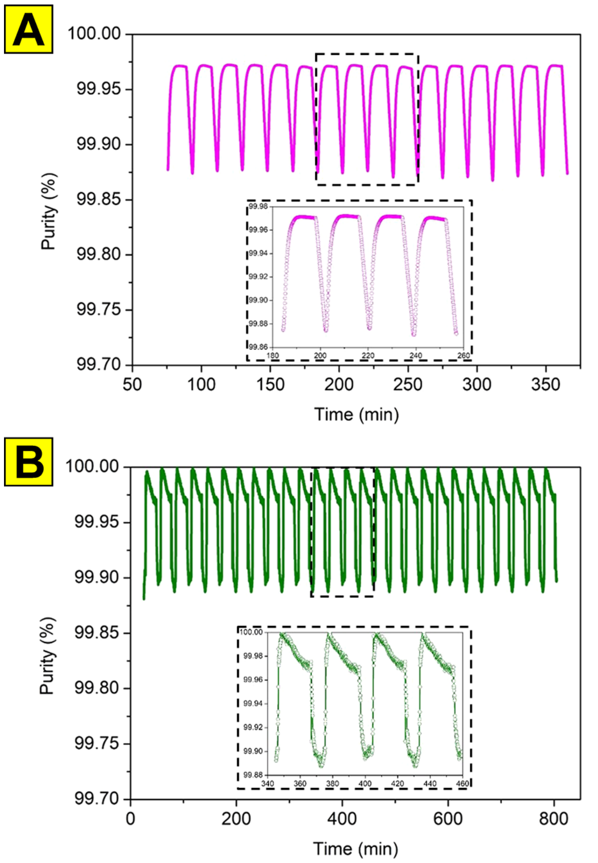


Figure 5. Purity of CO from the cyclic separations of (A) 50/50 (v/v) and (B) 1/99 (v/v) CO_2/CO mixtures with PMC **1** in a PSA apparatus. Separation conditions: 298 K, 1 bar, flow rates of (A) 3/3 and (B) 0.5/49.5 mL min^{-1}.

experiment was carried out at 1 bar and flow rates of 0.5/49.5 mL min^{-1} (Figure 4B). CO eluted out at 22 min, followed by CO_2 at 38.5 min, showing the ability of **1** to efficiently remove a trace amount (1%) of CO_2 impurity from CO. The productivity of pure CO calculated from the breakthrough experiment is about 572 L kg^{-1}, suggesting that PMC **1** could be used in practical CO_2/CO separations. It is noteworthy that after breakthrough experiments, the samples can be readily regenerated at 298 K under a He flow (10 mL min^{-1}) for 7 min, followed by vacuum for 7 min (Supporting Information). The mild and facile desorption conditions are owing to the moderate Q_{st} of CO_2 adsorption, which presumably lowers the energy penalty compared to that of other adsorbents for CO purification under cycling separation processes.

The kinetic cycling CO_2/CO separation of **1** by PSA was performed in a laboratory-scale two-bed system, in which two columns were filled with powdered **1**. Before the cycling processes, the samples were activated by heating at 303 K for 4 h in vacuo, to remove atmospheric impurities. The adsorption step and purging or regeneration step were run alternately and parallelly in the two columns. One complete cycle consisted of two adsorption−desorption processes from two columns, and the operation period was optimized according to breakthrough experiments. The easy regeneration of **1** allowed the desorption of one column before the other one reached its capacity limit. The continuous separation of a 50/50 CO_2/CO mixture at 1 bar, 298 K, and flow rates of 3/3 mL min^{-1} is shown in Figure 5A. Based on Figure 4A, the adsorption step was set to be 18 min long. The downstream eluted gas mixture was continuously analyzed by mass spectrometry. Figure 5A shows that the purity of CO oscillated between 99.87% and 99.97% over eight cycles and 350 min, indicating the stable CO_2/CO separation performance of **1**. The insets in Figure 5 display the data points of the highlighted sections for clarity. For the separation of the 1/99 CO_2/CO mixture at 1 bar and flow rates of 0.5/49.5 mL min^{-1}, the adsorption step was 29 min, and one complete cycle lasted 58 min (Figure 5B). The separation performance was stable over 13 cycles over 800 min, with high purity of eluted CO ranging from 99.88 to 99.99%.

In conclusion, we have shown that a nanoporous crystal assembled by the efficient packing of discrete macrocycle **1** can serve as a selective adsorbent for CO_2, which allows its use in CO_2/CO separation. Computations reveal that **1** more effectively binds to timers of CO_2 than to trimers of CO. As this separation system can be operated and regenerated at ambient conditions and slightly reduced pressure, without the need for temperature swings, it offers the promise of low running costs suitable for PSA technologies. Both trace (1%) and bulk (50%) levels of the CO_2 impurity can be efficiently removed from the CO gas mixtures by PMC **1** in continuous separation cycles. These results demonstrate that an intrinsic PMC can serve as an efficient platform for the continuous separation of CO_2 from CO, paving the way for applications of PMCs in this and other physisorption-based separations of linear gas molecules.[25]

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsanm.2c01535.

Experimental details on breakthrough experiments and gas sorption and computational details (PDF)

■ AUTHOR INFORMATION

Corresponding Authors

Ognjen Š. Miljanić − *Department of Chemistry, University of Houston, Houston, Texas 77204-5003, United States;* orcid.org/0000-0002-7876-9034; Email: miljanic@uh.edu

Teng-Hao Chen − *School of Pharmacy, National Cheng Kung University, Tainan City 70101, Taiwan;* orcid.org/0000-0001-9879-2162; Email: thchen@gs.ncku.edu.tw

Authors

Yao-Ting Wang − *Department of Chemical Engineering, Hierarchical Green-Energy Materials (Hi-GEM) Research Center, National Cheng Kung University, Tainan City 70101, Taiwan*

Said Jalife − *Department of Chemistry, University of Houston, Houston, Texas 77204-5003, United States*

Alexandra Robles − *Department of Chemistry, University of Houston, Houston, Texas 77204-5003, United States*

Miloš Đerić − *Department of Chemistry, University of Houston, Houston, Texas 77204-5003, United States*

Judy I. Wu − *Department of Chemistry, University of Houston, Houston, Texas 77204-5003, United States;* orcid.org/0000-0003-0590-5290

Watchareeya Kaveevivitchai − *Department of Chemical Engineering, Hierarchical Green-Energy Materials (Hi-GEM)*

Research Center, National Cheng Kung University, Tainan City 70101, Taiwan; orcid.org/0000-0001-9775-5909

Complete contact information is available at:
https://pubs.acs.org/10.1021/acsanm.2c01535

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This work was supported by the Ministry of Science and Technology (MOST) of Taiwan under Grant MOST110-2113-M-006-011 (to T.-H.C.) and the Young Scholar Fellowship Program MOST110-2636-E-006-019 (to W.K.). This work was also financially supported by the Hierarchical Green-Energy Materials (Hi-GEM) Research Center from the Featured Areas Research Center Program within the framework of the Higher Education Sprout Project by the Ministry of Education (MOE) and MOST (MOST 109-2634-F-006-020) in Taiwan (to W.K.). This research was supported in part by High Education Sprout Project, Ministry of Education of the Headquarters of University Advancement at National Cheng Kung University (NCKU) (to T.-H.C. and W.K.). We also acknowledge the support from the US National Science Foundation (awards DMR-1904998 to O.Š.M. and CHE-1751370 to J.I.W.) and the National Institute of General Medical Sciences of the National Institute of Health (Grant R35GM133548 to J.I.W.). J.I.W. thanks the Alfred P. Sloan Research Foundation (FG-2020-12811) for support. We acknowledge the use of the Sabine cluster and support from the Research Computing Data Core at the University of Houston.

DEDICATION

This article is dedicated to Prof. Fraser Stoddart on the occasion of his 80th birthday.

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