LETTER

Adsorption and Release of 1-Methylcyclopropene by Metal−Organic Frameworks for Fruit Preservation

Lue-Lue Huang,[∥] Liang Yu,[∥] Bin Li, Bing-bing Li, Hao Wang,* and Jing Li*

Read Online

ACCESS | Metrics & More | Article Recommendations | Supporting Information

ABSTRACT: Metal−organic frameworks (MOFs) are potentially useful in addressing challenges in food chemistry in light of their tunable pore dimensions and functionalities. Here we demonstrate the adsorption and release of 1-methylcyclopropene (1-MCP) by easily attainable microporous MOFs. The effectiveness of the encapsulation and release system has been validated by a fruit preservation test.
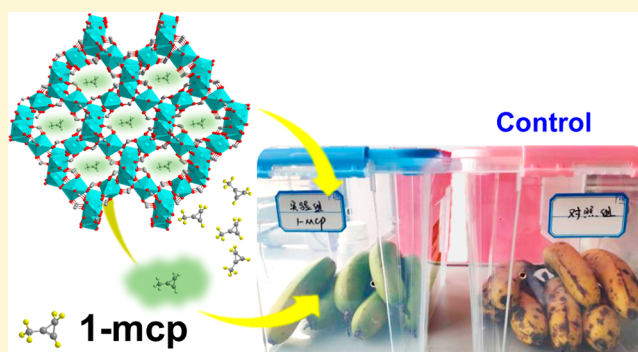
Metal−organic frameworks (MOFs) have attracted tremendous attention over the past two decades in light of their structural diversity, tunable functionality, and potential utility in industrial processes.[1] MOFs have been explored for a variety of possible applications, including gas storage,[2] separation,[3] catalysis,[4,5] and lighting and sensing,[6−8] just to name a few. Besides these applications that have been extensively pursued, MOFs have also been evaluated for uses in areas such as drug delivery,[9,10] health and personal care,[11] food chemistry,[12] and so on. Pan et al. reported a moisture-triggered fragrance release system by encapsulation of the fragrance molecules ethyl butyrate and D-limonene into a microporous, moisture-sensitive MOF.[11] Upon exposure to moisture, the host MOF undergoes structure decomposition and thus slowly releases the fragrance agents. In that study, the authors took advantage of the drawback of a MOF (instability toward moisture) and achieved a proof-of-concept application in personal care. In another study, Li et al. reported the encapsulation and controlled release of a food flavoring agent, allyl isothiocyanate (AITC), by a microporous MOF.[12] The rate of release of AITC from the MOF could be controlled by adjusting the humidity level in the environment.

1-Methylcyclopropene (1-MCP) is a gaseous compound that acts as an ethylene antagonist to inhibit ethylene-triggered events in plants, including fruit degreening and fruit ripening, and has been widely recognized for postharvest application in the fresh-produce industry.[13] Gaseous 1-MCP needs to be encapsulated by a host material and released to the target environment in a controllable manner. Different types of materials have been tested as encapsulation hosts for 1-MCP, with α-cyclodextrin as a representative example. The encapsulation of 1-MCP by α-cyclodextrin, either in the form of a solid encapsulation complex powder for postharvest application or as a liquid formulation for a preharvest process, has been reported. In light of their tunable pore dimensions and surface functionality, MOFs hold particular promise as host materials for the encapsulation and release of 1-MCP in food chemistry.[14] Indeed, MOFs have been explored for the adsorption of ethylene and 1-MCP. Chopra et al. tested the adsorption and release of 1-MCP by two commercially available MOFs, Basolite C300 (Cu-BTC) and Basolite A520 (Al-fum).[15] The authors studied the effect of ethylene desorption from MOFs on ripening of fruits, but the effect of desorbed 1-MCP was not investigated. In this work, we report the adsorption of isobutene (commonly used as a surrogate to quantify 1-MCP) by a group of MOFs with different pore shapes and dimensions. In addition, the effectiveness of 1-MCP encapsulation and release by an easily

attainable MOF was evaluated for postharvest application to bananas.

A series of four three-dimensional (3D) microporous MOFs, including Co-FA, MOF-74-Zn, Ca(SDB), and RPM-3(Zn), were evaluated for their effectiveness in preserving fruits. In general, these four materials feature relatively robust structures with high thermal and moisture stability, facile synthesis, and one-dimensional (1D) channels in the range of 4−10 Å (Figure 1). The MOFs were synthesized according to reported
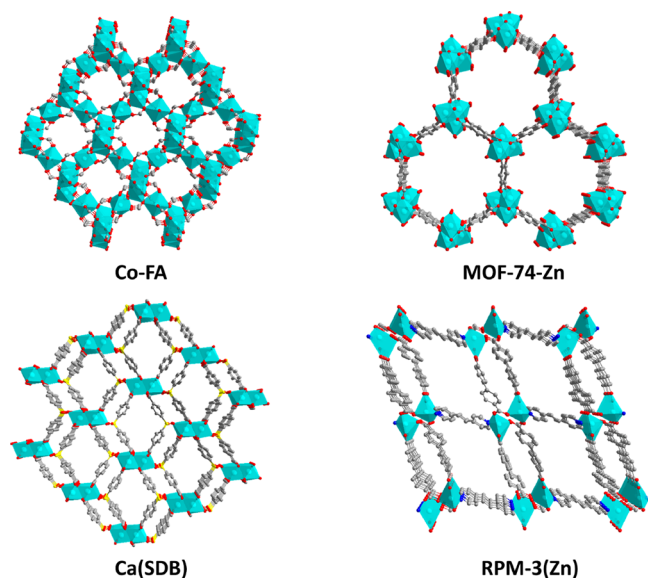

Figure 1. Structures of representative MOFs studied in this work. Color scheme: metal center, cyan; O, red; N, blue; C, gray. Hydrogen atoms have been omitted for clarity.

procedures. Powder X-ray diffraction (Figures S1−S4), thermogravimetric analysis (Figures S5−S8), and porosity measurements (Figures S9−S12) confirmed that the samples were of high quality. Co-FA, built from octahedrally coordinated Co^{2+} ions linked by formate as an organic ligand, is one of the simplest MOFs.[16] The compound features 1D cylindrical channels of ∼5.5 Å, with a Brunauer−Emmett−Teller (BET) surface area of around 300 m^2/g. The synthesis of Co-FA can be easily scaled up with cheap, easily attainable starting materials. MOF-74-Zn is a prototype MOF with open metal sites (OMSs) that is built from Zn^{2+} and 2,5-dihydroxyterephthalate.[17] It possesses 1D hexagonal channels decorated by a high density of Zn^{2+} OMSs with diameter of ∼1 nm. The BET surface area of MOF-74-Zn is around 800 m^2/g. Ca(SDB) (SDB = 4,4′-sulfonyldibenzoate) is composed of corner-sharing calcium polyhedral chains interconnected by SDB^{2-} organic linkers.[18] The overall structure features rhombic channels with a square-shaped cross section having an average size of ∼4.4 Å and a BET surface area of 145 m^2/g. Ca(SDB) possesses exceptional thermal and moisture stability. The flexible MOF RPM-3(Zn) is constructed from Zn^{2+}, 4,4′-biphenyldicarboxylate ($bpdc^{2-}$), and 1,2-bis(4-pyridyl)ethene (bpee).[19] Its structure undergoes reversible gate opening and gate closure upon guest inclusion and removal. In the gate-open state, the rhombic 1D channels have a window size of ∼5 Å × 7 Å, and the structure has a BET surface area of 328 m^2/g.

In our initial screening study to select the best MOF candidate, the adsorption capacity and kinetics of isobutene (as a surrogate for 1-MCP) in the four selected MOF materials

were evaluated because of the commercial availability of isobutene and its similar molecular size and physical properties to 1-MCP. The adsorption measurements were performed on a gravimetric adsorption analyzer with an isobutene partial pressure of 0.5 bar. The MOF samples were first activated at 150 °C under nitrogen to remove residual solvent inside the pores. A gas mixture of nitrogen and isobutene (50:50 v/v, total pressure = 1 bar) was introduced to the activated sample after it was cooled to room temperature. After the adsorption reached saturation, the gas mixture was switched to pure nitrogen so that the adsorbed isobutene could be desorbed. The sample weight was monitored during the process to record the adsorbed amount. The results are shown in Figure 2, where
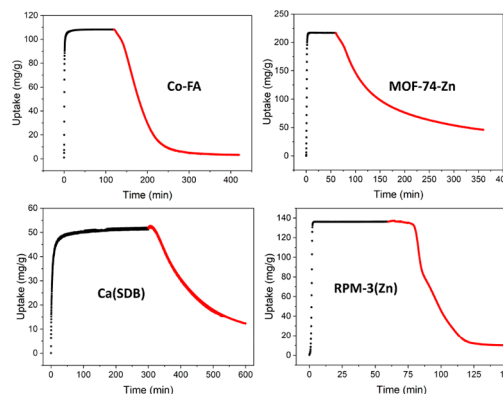

Figure 2. Adsorption−desorption profiles of isobutene on selected MOFs. Black and red curves represent adsorption and desorption, respectively.

the black and red curves represent the adsorption (gas flow with isobutene) and desorption (gas flow with pure nitrogen) branches, respectively. In general, the isobutene adsorption capacities of these MOF materials are notably higher than those observed for host systems using cyclodextrin, which are typically less than 5 wt %. The uptake amounts of isobutene on Co-FA, MOF-74-Zn, Ca(SDB), and RPM-3(Zn) were 109, 217, 52, and 136 mg/g, respectively. It is noted that the adsorption capacities show the same trend as the BET surface areas of the selected MOF adsorbents. The adsorption of isobutene on Co-FA, MOF-74-Zn, and RPM-3(Zn) was very fast and reached equilibrium immediately because of their relatively large pore dimensions, which enable the free passage of adsorbate molecules. In contrast, the adsorption of isobutene on Ca(SDB) displayed notable diffusion restrictions and did not reach equilibrium after 500 min. This is not surprising considering its relatively narrow channels. Similar results were observed for the adsorption of other hydrocarbons.[20] The isobutene uptake capacity on Ca(SDB) is also notably lower than those on the other three MOFs because of its limited porosity.

It can be seen from Figure 2 that the isobutene adsorbed on these MOF adsorbents can be desorbed under a nitrogen flow at room temperature, indicating the physisorptive nature of the adsorption. It is noted that the desorption from Ca(SDB) and MOF-74-Zn is much slower compared with the other two materials, likely because of the slow diffusion in the former and possible strong interactions between carbon−carbon double bonds and OMS in the latter. The high loading amounts of isobutene and subsequently easy desorption make the MOF

Table 1. Effect of the Released 1-MCP on the Quality of Bananas during the 7 day Storage Time

property	0 days	1 days	3 days	5 days	7 days
			Experimental Group		
hardness (kg/cm^2)	1.87 ± 0.02	1.69 ± 0.02	1.55 ± 0.02	1.47 ± 0.01	1.30 ± 0.02
weight loss ratio (%)	0.00	0.23 ± 0.03	0.94 ± 0.04	1.37 ± 0.03	3.10 ± 0.05
TA (%)	0.42 ± 0.01	0.41 ± 0.01	0.37 ± 0.01	0.34 ± 0.01	0.32 ± 0.01
TSS (%)	12.00 ± 0.02	14.00 ± 0.02	14.65 ± 0.01	16.80 ± 0.02	17.50 ± 0.02
vitamin C (mg/100g)	9.40 ± 0.02	9.40 ± 0.02	9.10 ± 0.02	9.00 ± 0.02	8.80 ± 0.01
			Control Group		
hardness (kg/m^2)	1.87 ± 0.02	1.42 ± 0.02	0.86 ± 0.02	0.81 ± 0.03	–[a]
weight loss ratio (%)	0.00	0.38 ± 0.03	1.51 ± 0.05	3.60 ± 0.05	–[a]
TA (%)	0.42 ± 0.01	0.38 ± 0.01	0.28 ± 0.01	0.26 ± 0.01	–[a]
TSS (%)	12.00 ± 0.02	14.90 ± 0.02	17.50 ± 0.02	20.80 ± 0.03	–[a]
vitamin C (mg/100g)	9.40 ± 0.02	8.65 ± 0.01	8.60 ± 0.02	8.40 ± 0.02	–[a]

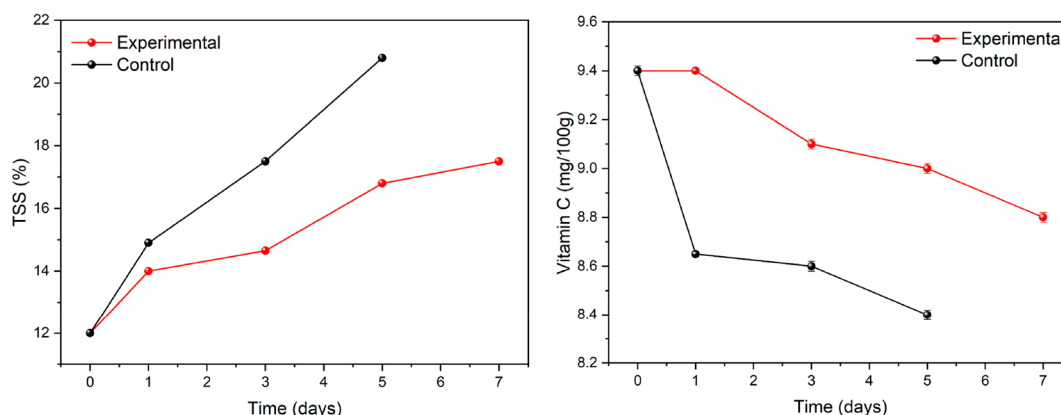[a]"–": the data were not measurable because the banana samples were rotten.
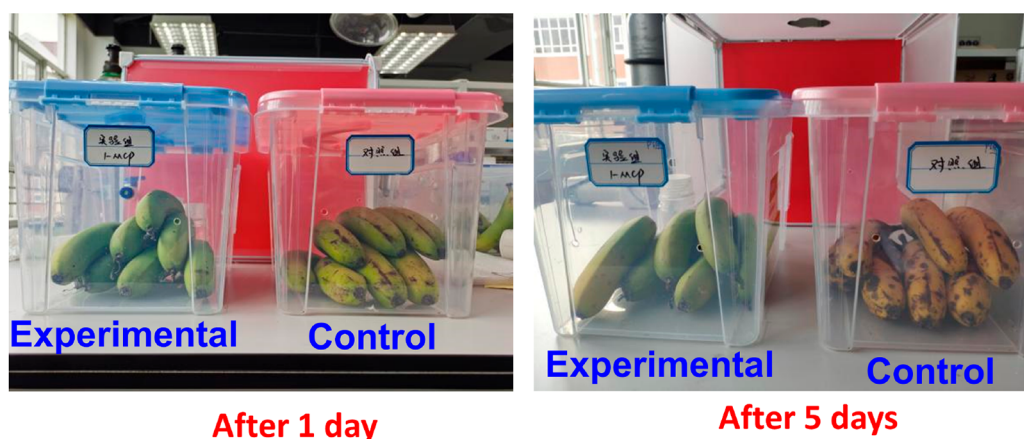
Figure 3. (a) Photograph of bananas in the experimental and control groups after storage for 1 and 7 days. (b) (left) TSS and (right) vitamin C contents of bananas as functions of storage time. The data for day 7 for the control group are not shown because the bananas were rotten.

adsorbents promising for 1-MCP encapsulation and release in food preservation.

On the basis of these results, we then selected Co-FA for further exploration using 1-MCP because of its high adsorption capacity, low cost, and facile scaled-up synthesis. In addition, cycle tests indicated that the material featured good recyclability (Figures S14 and S15). 1-MCP was encapsulated by Co-FA, and its subsequent release for banana preservation was studied. 1-MCP was synthesized from 3-chloro-2-methylpropene and lithium diisopropylamide according to

the reported procedure.[13] The obtained suspension was stored in a refrigerator and could release 1-MCP in situ when dispersed in water. The encapsulation of 1-MCP by Co-FA was performed using a homemade setup (Figure S13). Freshly made Co-FA was dispersed in a glass container and activated at 150 °C under dynamic vacuum. After the MOF was cooled to room temperature, 1-MCP was generated in situ and introduced to the container with activated the Co-FA sample. The system was kept at room temperature for a few minutes to allow the adsorption to reach equilibrium, yielding 1-MCP-

loaded Co-FA (1-MCP@Co-FA). The bananas tested in our study were picked and used directly from banana trees without the application of any preservatives. Two similar bunches of bananas (each bunch contained seven fresh bananas) were placed in two food containers as the experimental and control groups, respectively. Some holes were created in the containers to mimic ventilated food storage rooms. A glass bottle with 1-MCP@Co-FA was placed at the corner of the food container of the experimental group. The glass bottle was sealed using Parafilm with small holes so that the desorbed 1-MCP would slowly diffuse into the food container.

The experimental and control groups were stored at room temperature (~25 °C) for 7 days, during which time certain indicators of the bananas from each group were analyzed every other day. Notable differences were seen by the naked eye. It was noticed that the bananas in the experimental group retained the original greenish color after 7 days. In sharp contrast, the bananas in the control group changed color from green to yellow as time went on and were largely rotten after 7 days. Several indicators of the quality of the bananas, including hardness, weight loss, and contents of titratable acid (TA), total soluble solid (TSS), and vitamin C were monitored. Hardness was tested with a digital fruit hardness tester (GY-4, Hangzhou Zhuoqi Electronic Technology Co., Ltd.). Weight loss was evaluated from the weights of samples with different storage times. The TSS content was evaluated with a hand refractometer (PAL-1, Atago), and the results are presented as % fresh mass. For the determination of TA, 20 g of banana sample paste was diluted with distilled water to a volume of 250 mL, and then 25 mL of filtrate was titrated with 0.1 M NaOH to the pink titration end point. Extraction of ascorbic acid was carried out using 2.5 g/100 g metaphosphoric acid, and 10 g samples were used for the analysis. Ascorbic acid determination was carried out using HPLC. As shown in Table 1 and Figure 3b, in general, the quality of the bananas in the control group decreased rapidly. In contrast, while the quality of the bananas in the experimental group also declined, this occurred much more slowly, and the bananas remained eatable after 7 days. For example, the TSS content of the bananas increased as a function of storage time. However, this process was noticeably slower for the experimental group than for the control group. This indicates that the bananas in the experimental group were also ripening but at a lower rate compared with the control group, which confirms the effectiveness of the 1-MCP released from the MOF material for banana preservation. Other indicators such as the TA and vitamin C contents followed the same trend as the TSS content. It was also noted that the differences of the indicators between bananas in the experimental and control groups show a clear in-trend correlation with the storage time. This suggests the effectiveness of 1-MCP in delaying the ripening of postharvest bananas. PXRD and N_2 adsorption analysis of the postapplication Co-FA revealed that the crystallinity and porosity of the adsorbent were fully preserved during the tests. To further understand the interaction between 1-MCP and the framework, density functional theory calculations were performed. The calculation results indicated that at the most favorable site, 1-MCP interacts with the MOF via hydrogen bonding. The most significant interaction is with the O of the formate groups connected to the metal atoms, as shown in Figure S17. The binding energy was calculated to be 0.49 eV.

In summary, in this work we explored the encapsulation and release of 1-MCP by microporous MOFs for food preservation.

A group of MOFs with various pore shapes and dimensions were tested for the adsorption and desorption of isobutene, a surrogate to quantify 1-MCP. An easily attainable candidate, Co-FA, was selected as a host material for encapsulation and release of 1-MCP. The effectiveness of the released 1-MCP for the preservation of postharvest bananas was investigated. Our study confirmed that 1-MCP released from the MOF host can significantly postpone the ripening of bananas.

■ ASSOCIATED CONTENT

ⓢ Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsmaterialslett.2c00137.

Materials synthesis and characterization and adsorption simulation (PDF)

■ AUTHOR INFORMATION

Corresponding Authors

Hao Wang − *Hoffmann Institute of Advanced Materials, Shenzhen Polytechnic, Shenzhen 518055, China;* ⓞ orcid.org/0000-0001-7732-778X; Email: wanghao@szpt.edu.cn

Jing Li − *Department of Chemistry and Chemical Biology, Rutgers University, Piscataway, New Jersey 08854, United States; Hoffmann Institute of Advanced Materials, Shenzhen Polytechnic, Shenzhen 518055, China;* ⓞ orcid.org/0000-0001-7792-4322; Email: jingli@rutgers.edu

Authors

Lue-Lue Huang − *School of Food and Drug, Shenzhen Polytechnic, Shenzhen 518055, China*

Liang Yu − *Hoffmann Institute of Advanced Materials, Shenzhen Polytechnic, Shenzhen 518055, China*

Bin Li − *School of Food and Drug, Shenzhen Polytechnic, Shenzhen 518055, China*

Bing-bing Li − *School of Food and Drug, Shenzhen Polytechnic, Shenzhen 518055, China*

Complete contact information is available at:
https://pubs.acs.org/10.1021/acsmaterialslett.2c00137

Author Contributions

‖L.-L.H. and L.Y. contributed equally.

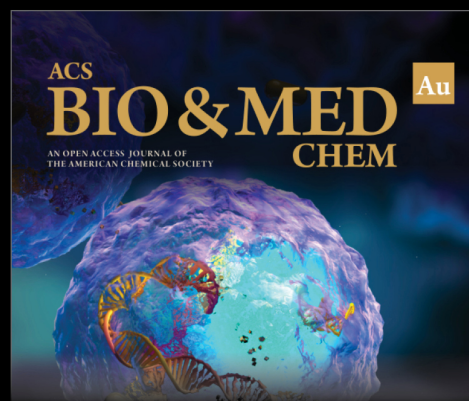### Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

■ REFERENCES

(1) Furukawa, H.; Cordova, K. E.; O'Keeffe, M.; Yaghi, O. M. The Chemistry and Applications of Metal-Organic Frameworks. *Science* **2013**, *341*, 1230444.

(2) He, Y.; Zhou, W.; Qian, G.; Chen, B. Methane storage in metal−organic frameworks. *Chem. Soc. Rev.* **2014**, *43*, 5657−5678.

(3) Adil, K.; Belmabkhout, Y.; Pillai, R. S.; Cadiau, A.; Bhatt, P. M.; Assen, A. H.; Maurin, G.; Eddaoudi, M. Gas/vapour separation using ultra-microporous metal−organic frameworks: insights into the structure/separation relationship. *Chem. Soc. Rev.* **2017**, *46*, 3402−3430.

(4) Yang, D.; Gates, B. C. Catalysis by Metal Organic Frameworks: Perspective and Suggestions for Future Research. *ACS Catal.* **2019**, *9*, 1779−1798.

(5) Li, D.; Xu, H.-Q.; Jiao, L.; Jiang, H.-L. Metal-organic frameworks for catalysis: State of the art, challenges, and opportunities. *EnergyChem* **2019**, *1*, 100005.

(6) Hu, Z.; Deibert, B. J.; Li, J. Luminescent metal−organic frameworks for chemical sensing and explosive detection. *Chem. Soc. Rev.* **2014**, *43*, 5815−5840.

(7) Lustig, W. P.; Li, J. Luminescent metal−organic frameworks and coordination polymers as alternative phosphors for energy efficient lighting devices. *Coord. Chem. Rev.* **2018**, *373*, 116−147.

(8) Lustig, W. P.; Mukherjee, S.; Rudd, N. D.; Desai, A. V.; Li, J.; Ghosh, S. K. Metal−organic frameworks: functional luminescent and photonic materials for sensing applications. *Chem. Soc. Rev.* **2017**, *46*, 3242−3285.

(9) Wang, Y.; Yan, J.; Wen, N.; Xiong, H.; Cai, S.; He, Q.; Hu, Y.; Peng, D.; Liu, Z.; Liu, Y. Metal-organic frameworks for stimuli-responsive drug delivery. *Biomaterials* **2020**, *230*, 119619.

(10) Wang, L.; Zheng, M.; Xie, Z. Nanoscale metal−organic frameworks for drug delivery: a conventional platform with new promise. *J. Mater. Chem. B* **2018**, *6*, 707−717.

(11) Vaughn, J.; Wu, H.; Efremovska, B.; Olson, D. H.; Mattai, J.; Ortiz, C.; Puchalski, A.; Li, J.; Pan, L. Encapsulated recyclable porous materials: an effective moisture-triggered fragrance release system. *Chem. Commun.* **2013**, *49*, 5724−5726.

(12) Wang, H.; Lashkari, E.; Lim, H.; Zheng, C.; Emge, T. J.; Gong, Q.; Yam, K.; Li, J. The moisture-triggered controlled release of a natural food preservative from a microporous metal−organic framework. *Chem. Commun.* **2016**, *52*, 2129−2132.

(13) Neoh, T. L.; Yamauchi, K.; Yoshii, H.; Furuta, T. Kinetics of Molecular Encapsulation of 1-Methylcyclopropene into α-Cyclodextrin. *J. Agric. Food Chem.* **2007**, *55*, 11020−11026.

(14) Sharanyakanth, P. S.; Radhakrishnan, M. Synthesis of metal-organic frameworks (MOFs) and its application in food packaging: A critical review. *Trends Food Sci. Technol.* **2020**, *104*, 102−116.

(15) Chopra, S.; Dhumal, S.; Abeli, P.; Beaudry, R.; Almenar, E. Metal-organic frameworks have utility in adsorption and release of ethylene and 1-methylcyclopropene in fresh produce packaging. *Postharvest Biol. Technol.* **2017**, *130*, 48−55.

(16) Wang, H.; Yao, K.; Zhang, Z.; Jagiello, J.; Gong, Q.; Han, Y.; Li, J. The first example of commensurate adsorption of atomic gas in a MOF and effective separation of xenon from other noble gases. *Chem. Sci.* **2014**, *5*, 620−624.

(17) Rowsell, J. L. C.; Yaghi, O. M. Effects of Functionalization, Catenation, and Variation of the Metal Oxide and Organic Linking Units on the Low-Pressure Hydrogen Adsorption Properties of Metal−Organic Frameworks. *J. Am. Chem. Soc.* **2006**, *128*, 1304−1315.

(18) Banerjee, D.; Zhang, Z.; Plonka, A. M.; Li, J.; Parise, J. B. A Calcium Coordination Framework Having Permanent Porosity and High CO_2/N_2 Selectivity. *Cryst. Growth Des.* **2012**, *12*, 2162−2165.

(19) Lan, A.; Li, K.; Wu, H.; Kong, L.; Nijem, N.; Olson, D. H.; Emge, T. J.; Chabal, Y. J.; Langreth, D. C.; Hong, M.; Li, J. RPM3: A Multifunctional Microporous MOF with Recyclable Framework and High H_2 Binding Energy. *Inorg. Chem.* **2009**, *48*, 7165−7173.

(20) Banerjee, D.; Wang, H.; Gong, Q.; Plonka, A. M.; Jagiello, J.; Wu, H.; Woerner, W. R.; Emge, T. J.; Olson, D. H.; Parise, J. B.; Li, J. Direct structural evidence of commensurate-to-incommensurate transition of hydrocarbon adsorption in a microporous metal organic framework. *Chem. Sci.* **2016**, *7*, 759−765.