

UvA-DARE (Digital Academic Repository)

A Chemically Robust Microporous Zn-MOF for C₂H₂ Separation from CO₂ and Industrially Relevant Four Component Gas Mixtures

Pramanik, B.; Sahoo, R.; Krishna, R.; Das, M.C.

DOI

[10.1002/sml.202411456](https://doi.org/10.1002/sml.202411456)

Publication date

2025

Document Version

Final published version

Published in

Small

License

CC BY-NC-ND

[Link to publication](#)

Citation for published version (APA):

Pramanik, B., Sahoo, R., Krishna, R., & Das, M. C. (2025). A Chemically Robust Microporous Zn-MOF for C₂H₂ Separation from CO₂ and Industrially Relevant Four Component Gas Mixtures. *Small*, 21(8), Article 2411456. <https://doi.org/10.1002/sml.202411456>

General rights

It is not permitted to download or to forward/distribute the text or part of it without the consent of the author(s) and/or copyright holder(s), other than for strictly personal, individual use, unless the work is under an open content license (like Creative Commons).

Disclaimer/Complaints regulations

If you believe that digital publication of certain material infringes any of your rights or (privacy) interests, please let the Library know, stating your reasons. In case of a legitimate complaint, the Library will make the material inaccessible and/or remove it from the website. Please Ask the Library: <https://uba.uva.nl/en/contact>, or a letter to: Library of the University of Amsterdam, Secretariat, Singel 425, 1012 WP Amsterdam, The Netherlands. You will be contacted as soon as possible.

UvA-DARE is a service provided by the library of the University of Amsterdam (<https://dare.uva.nl>)

A Chemically Robust Microporous Zn-MOF for C₂H₂ Separation from CO₂ and Industrially Relevant Four Component Gas Mixtures

Bikram Pramanik, Rupam Sahoo, Rajamani Krishna, and Madhab C. Das*

The separation and purification of acetylene from the light hydrocarbon gas mixtures is considered as one of the most industrially challenging task for the production of fine chemicals. Though metal–organic frameworks (MOFs) are promising candidates for such separation and offer a cost and energy-efficient pathway, achieving the *trade-off* between sorption capacity and separation selectivity along with framework robustness is a daunting task and demands effective design. Herein, a new 3D chemically stable MOF, IITKGP-24 (stable over a wide range of aqueous pH solution, pH = 2–12) is developed, displaying excellent separation selectivity of 13.9 for C₂H₂/CO₂ (50:50) even at ambient conditions and maintained a *trade-off* between sorption capacity and separation selectivity. Most importantly, the breakthrough performance analysis under the industrially relevant gas mixture composition revealed that the developed framework possesses excellent separation of acetylene from not only C₂H₂/CO₂ (50:50) gas mixtures but also from the quaternary C₂H₂/C₂H₄/C₂H₆/CO₂ (25:25:25:25) feed gas streams. Separation of C₂H₂ from such a four component gas mixture by MOFs is unexplored. The exceptional framework robustness, high C₂H₂/CO₂ uptake ratio, low heat of adsorption, and excellent recyclability with easy regenerability made the developed framework promising candidate toward this challenging separation.

of high-purity fine chemicals. However, the traditional industrial separation process is not only energy-intensive but also demands huge capitalization.^[1] Among the light hydrocarbons, acetylene (C₂H₂) is an important chemical feedstock and core raw material in the petrochemical industry, widely used for the production of various essential organic compounds such as vinyl chloride, polyester plastics, α -ethynyl alcohols, acrylic acid, vinyl compounds, etc.^[2] Acetylene is generally produced in the industry via partial combustion of natural gas or steam cracking of naphtha while several impurities (such as ethylene (C₂H₄), ethane (C₂H₆), carbon dioxide (CO₂), etc.) are coexistence as the by-product, which needs to be separated efficiently to obtain high-purity C₂H₂ gas.^[3] However, comparable physicochemical properties of these impurities such as kinetic diameter, polarizability, melting and boiling points make the purification and separation process challenging.^[3,4] Consequently, efficient separation of high-purity C₂H₂ from the

binary C₂H₂/CO₂ gas mixture and quaternary C₂H₂/C₂H₆/C₂H₄/CO₂ gas mixture represents a challenging yet critical task.^[3–5] As employed traditional cryogenic distillation or solvent extraction processes demand intensive cost with high energy consumption, researchers have focused their attention on adsorptive separation technology using solid porous materials to make the separation process *energetically favorable, inexpensive, and environmentally friendly*.^[6–9]

In this regard, metal–organic frameworks (MOFs) have attracted substantial attention for efficient gas separations over traditional porous materials such as activated carbons, porous alumina, zeolites, silica, etc., having their superior structural designability and predictability,^[10–20] highly customizable functionality^[21–31] and many other advantageous features.^[32–46] Most importantly, the well-resolved crystalline structure of MOFs is beneficial for the visualization of host-guest interactions at the molecular level.^[47–57] Although a handful of MOFs have been developed for this targeted separation considering various synthesis strategies including pore confinements, open-metal sites (OMSs), surface functionalization, etc. to avail the high C₂H₂/CO₂ selectivity, most of them suffer from achieving the *trade-off* between sorption capacity and separation

1. Introduction

The separation and purification of light hydrocarbons from their various impurities are of significant interest for the production

B. Pramanik, R. Sahoo, M. C. Das
Department of Chemistry
Indian Institute of Technology Kharagpur
Kharagpur, West Bengal 721302, India
E-mail: mcdas@chem.iitkgp.ac.in

R. Krishna
Van't Hoff Institute for Molecular Sciences
University of Amsterdam
Science Park 904, Amsterdam 1098 XH, The Netherlands

 The ORCID identification number(s) for the author(s) of this article can be found under <https://doi.org/10.1002/smll.202411456>

© 2024 The Author(s). Small published by Wiley-VCH GmbH. This is an open access article under the terms of the [Creative Commons Attribution-NonCommercial-NoDerivs](#) License, which permits use and distribution in any medium, provided the original work is properly cited, the use is non-commercial and no modifications or adaptations are made.

DOI: 10.1002/smll.202411456

selectivity, which demand further exploration.^[2,3,58] In this context, MOFs having polar pore surfaces (–F, –NH₂, accessible N/O sites) are indeed beneficial choices as they are capable of entrapping targeted C₂H₂ gas molecules *via* hydrogen bonding interactions and lead to the high C₂H₂/CO₂ separation selectivity. The presence of stronger dynamic functional binding sites not only can endow specific and selective recognition but also boosting up the adsorbate-adsorbent interaction potentially depending upon the unlike dipole moments, polarizability, and quadruple moments of the various guest molecules. It should also be noted that although MOFs have been widely used for the effective separation of acetylene from the binary C₂H₂/CO₂ (50:50) gas mixtures, their usage as an adsorbent in the purification of acetylene from the quaternary C₂H₂/C₂H₄/C₂H₆/CO₂ (25:25:25:25) gas mixtures remains unexplored and thus demands extensive efforts in designing MOFs toward this particular separation from quaternary gas mixtures both from *academic and industrial* viewpoints.^[59]

On the other hand, in general MOFs are susceptible to degradation in the presence of water/moisture or acidic/basic mediums, and their performances are compromised significantly. However, moisture/water and several acidic/basic impurities are omnipresent in feed gas mixtures for industrial gas separations. Although open-metal sites (OMSs) are beneficial for the selective capture of C₂H₂ gas molecules by π -complexation, the obtained performance could be compromised due to the competitive adsorption of water and C₂H₂ gas molecules in practical separation conditions where water/moisture is omnipresent. Besides, such OMSs will easily get coordinated with water molecules under a humid environment and thus leading to decomposition *via* hydrolysis of metal-ligand bonds. Therefore, the development of chemically robust frameworks is indeed necessary for practical industrial gas separations and demands effective design.^[60] Though a handful of water-stable frameworks have been developed so far, the number is significantly less when considering pH stability. For the development of pH-stable frameworks, a combination of *thermodynamic* and *kinetic stability factors* need to be considered.^[60] In this regard, *mixed ligand approach* employment is undoubtedly a good choice as the employed spacer could construct ample strong metal-nitrogen coordination through the HSAB (hard and soft (Lewis) acids and bases) principle and could act as a pillar for the connection between 2D layers to construct an overall 3D robust framework. Hence, strategic design and development of a 3D chemically stable framework having a polar pore surface (*without any OMSs to avoid degradation and sorption competition*) are of significant interest to obtain an excellent *trade-off* between high C₂H₂ sorption capacity and efficient separation selectivity in an energy and cost-efficient manner.

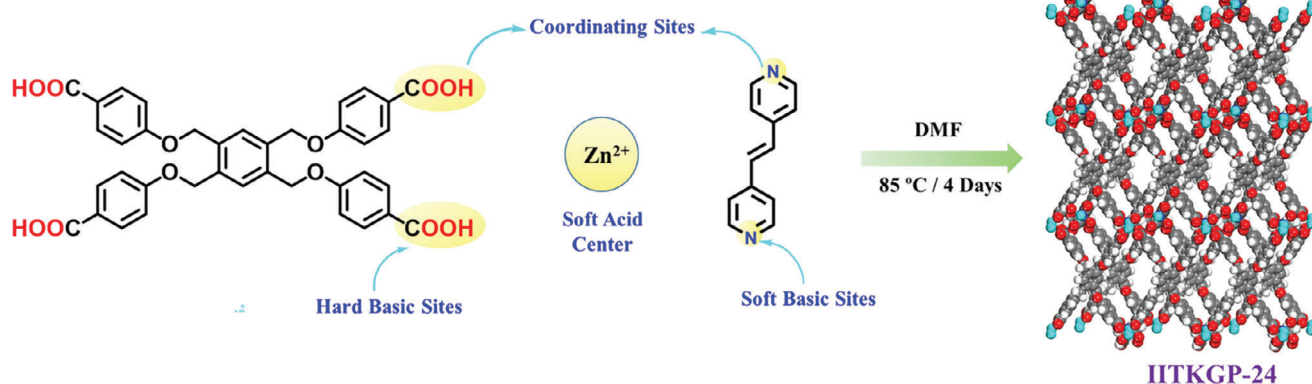
Considering the aforementioned aspects, herein, employing a mixed ligand approach we have strategically developed a 3D chemically robust MOF, **IITKGP-24**, {[Zn₂(H₄L)(bpe)]·3DMF·H₂O}_n, which displayed excellent chemical stability not only in water/moisture but also in presence of wide range acidic/basic solutions (pH = 2–12). The developed activated framework **IITKGP-24a** exhibited a C₂H₂ uptake of (43.6 cc g⁻¹) with a significantly lower uptake of competing CO₂ (15.3 cc g⁻¹) gas under ambient conditions. Notably, **IITKGP-24** showed a higher C₂H₂/CO₂ (50:50) separation selectivity of 13.9 even at ambient conditions, significantly higher than well-known

benchmark MOFs. The in-depth comparison between sorption capacity vs separation selectivity among the previously developed framework projected **IITKGP-24** as one of the best-performing materials toward this direction. Moreover, the high separation selectivity and C₂H₂/CO₂ uptake ratio along with very low heat of adsorption (–29.2 kJ mol⁻¹) made our developed framework as a competing candidate over others. Most importantly, unexplored quaternary C₂H₂/C₂H₄/C₂H₆/CO₂ (25:25:25:25) gas mixtures separation performance analysis demonstrates the outstanding separating ability of **IITKGP-24** and made the developed framework promising toward this challenging separation.

2. Results and Discussion

The solvothermal synthesis of flexible H₄L acid ligand, 1,2-Di(4-pyridyl)ethylene (bpe), and Zn(NO₃)₂·6H₂O in DMF solvent led to high-quality colorless plate-shaped single crystal of **IITKGP-24** (**Scheme 1**). The SC-XRD structural analysis uncovered that the new microporous MOF **IITKGP-24** crystallized in a triclinic crystal system with *P* $\bar{1}$ space group (Table S1, Supporting Information). The asymmetric unit contains two crystallographically different Zn(II) metal centers (Zn1 and Zn2), one full unit of deprotonated flexible carboxylic acid ligand (H₄L), and one full unit of bpe spacer (Figure S1, Supporting Information), leading to the molecular formula of {[Zn₂(H₄L)(bpe)]·3DMF·H₂O}_n. Each of the Zn metal centers is flanked in distorted square pyramidal geometry coordinated with four oxygen atoms (O1, O5, O8, O12 for Zn1, whereas O2, O6, O9, O11 for Zn2) from four different acid units of four H₄L moieties (**Figure 1a**) with Zn–O bond distances of 2.020(4)–2.069(4) Å and one N atom from the employed bpe spacer with Zn–N bond distances of 2.031(5)–2.042(4) Å (Table S2, Supporting Information). Two Zn(II) metal centers are connected *via* acetate (–COO⁻) bridging and forming a paddle-wheel structure of {Zn₂(COO)₄} with the metal–metal (Zn1–Zn2) separation distance of 2.936(1) Å. The acid units are flanked in equatorial directions, whereas bpe spacers occupy axial positions and act as bridging units to connect both the metal centers for the construction of a 3D framework with the SBUs of {Zn₂O₈N₂} (**Figure 1c**). All the bond distances and bond angles around the metal centers in **IITKGP-24** are in the normal range and are listed in Table S2 (Supporting Information). **Figure 1b** displays two different microporous channels (**pore A** and **pore B**) with the dimensions of 4.6 × 5.2 Å² and 2.8 × 3.2 Å² (while considering van der Waals radii) along the crystallographic *b*-axis. Interestingly, the pore channels were decorated with alkoxy oxygen atoms beneficial for favorable H-bonding interaction with the targeted C₂H₂ gas molecules. Furthermore, **IITKGP-24** possesses strong π ⋯ π interactions between two different layers with a separation distance of 3.55 Å (**Figure S2**, Supporting Information). Apart from this, various non-covalent interactions are also present throughout the framework, as tabulated in Table S3 (Supporting Information).

The well-agreement in PXRD patterns of as-synthesized materials with simulated ones confirms the phase purity and high crystallinity of the developed material (**Figure 1d**). As stated earlier, the easy accessibility and the chemical stability of the developed material is an essential concern for any practical application. To verify the easy accessibility of the framework, as-synthesized material was left in a laboratory atmosphere for a



Scheme 1. Schematic representation of developed robust IITKGP-24 framework.

longer time (verified for 3 months for this case), whereas the humid condition stability, hydro-stability, and wide range aqueous pH-stability of the framework were verified to prove the framework robustness of IITKGP-24. The hydro-stability and humid condition stabilities were verified by dipping as-synthesized material in distilled water and placing the framework in a humidity chamber (97% RH) for 3 days, while aqueous pH solutions

stability was verified by dipping the as-synthesized material at different pH solutions (pH = 2–12) for 24 h. Interestingly, the excellent retention of the PXRD patterns of the developed materials was observed in all the cases (Figure 1d), illustrating the admirable robustness of the framework and attributed to the combined effect of the soft-soft interaction between Zn(II)-N coordination (according to the HSAB principle, a *thermodynamic*

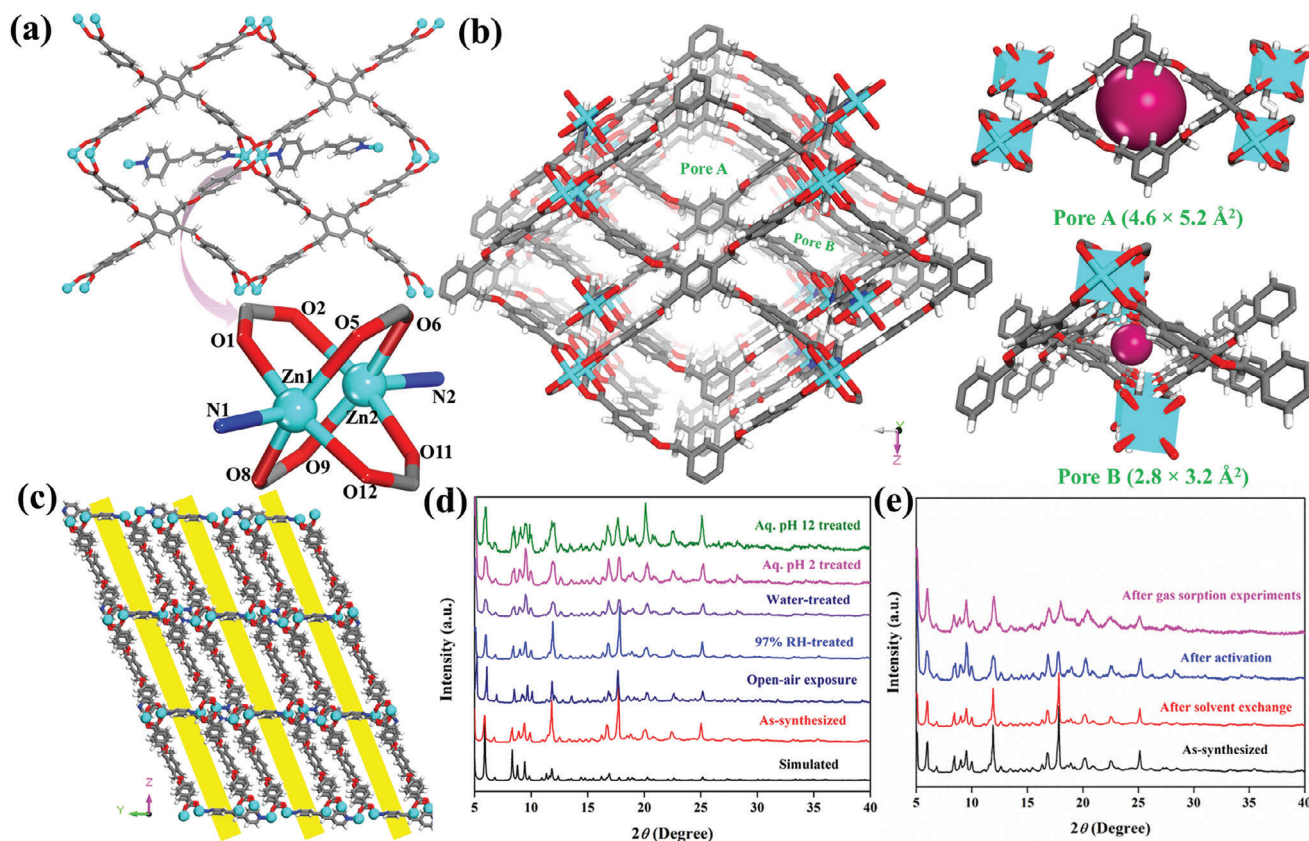


Figure 1. a) Coordination environment of IITKGP-24 and the SBU displaying paddle-wheel structure (Color codes: Zn, Cyan; N, blue; O, red; C, gray; H, white); b) 3D packing diagram of IITKGP-24 displaying two different types of porous channels while viewing along the crystallographic *b*-axis; c) Packing diagram of IITKGP-24 along *a*-axis (yellow color indicates how spacer units connected 2D layers to construct a 3D network); d,e) PXRD comparison plots of IITKGP-24 displaying framework robustness after several treatments (open-air, humidity, water, aqueous pH medium, CHCl_3 exchange, activation and after sorption experiment).

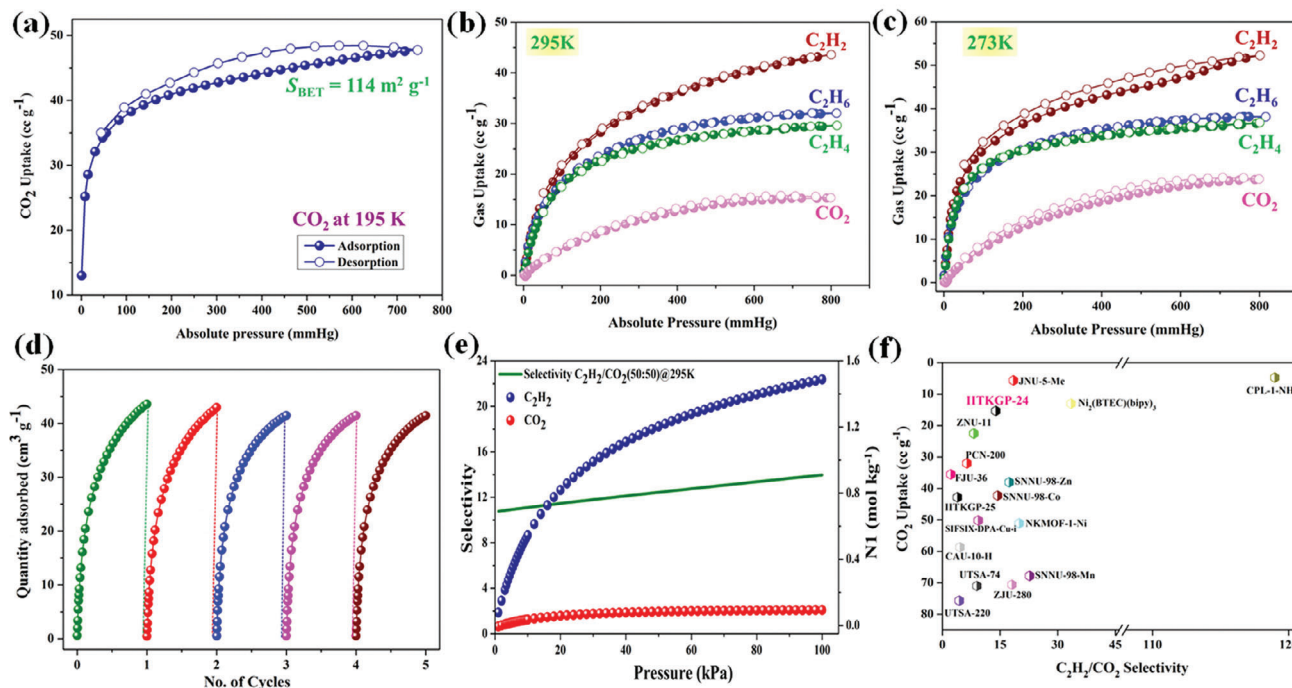


Figure 2. a) 195 K CO₂ sorption isotherm of IITKGP-24a for the BET surface area analysis; b,c) Single component gas sorption isotherms of C₂H₂, C₂H₄, C₂H₆, CO₂ at 295 and 273 K, respectively (closed and open circles represent sorption and desorption, respectively); d) Cyclic adsorption test for C₂H₂ gas at ambient temperature; e) IAST selectivity of IITKGP-24 for C₂H₂/CO₂ (50:50) gas mixtures at 295 K and 1 bar; f) Comparison plot of CO₂ uptake and C₂H₂/CO₂ (50:50) selectivity of IITKGP-24a with well-known reported MOFs at 295 K and 1 bar.

stability aspect) and the presence of ample hydrophobic benzene moieties (a kinetic stability aspect), π – π stacking interactions and several non-covalent interactions throughout the framework.^[60] To obtain the guest-free framework, the as-synthesized material was exchanged with low-boiling dry chloroform (CHCl₃) for three days and activated for 10 h at 80 °C. Excellent framework stability of the IITKGP-24a ('a' indicates activated) was confirmed by an unchanged PXRD pattern with the as-synthesized material following solvent exchange and activation (Figure 1e). Thermogravimetric analysis of as-synthesized material reveals an initial wt loss of 2.1% (calc. 1.5%) below 100 °C attributed to the expel of lattice water molecules followed by the wt loss of 17.8% (calc. 17.9%) at 300 °C corresponding to the removal of lattice DMF molecules, whereas the TGA curve of activated samples (IITKGP-24a) showed successful removal of all guest molecules (Figure S3, Supporting Information). PLATON analysis demonstrates a total of 51% potential solvent accessible volume (1970 Å³) per unit cell volume (3719 Å³), which is fully occupied by DMF and water solvent molecules. To verify the permanent porosity of the framework, 195 K CO₂ sorption study was performed on IITKGP-24a (Figure 2a) and a BET surface area of 114 m² g⁻¹ (Langmuir surface area of 184 m² g⁻¹) was observed with the pore width of 4.8 Å (Figure S4, Supporting Information) having a total pore volume of 0.073 cm³ g⁻¹. The pore width of 4.8 Å is in well accordance with the crystallographic micro-pore dimensions.

The chemically robust nature, microporous channels with specific polar binding sites, and permanent porosity of the developed framework inspired us to analyze the separation performance of the industrially important though challenging C₂ hydrocarbons

over CO₂ gases. At first, single-component gas sorption measurements were performed using the activated sample IITKGP-24a for both temperatures (295 K and 273 K). Interestingly, significant uptake differences were observed between the C₂ hydrocarbons and CO₂ even at room temperature (295 K) with uptakes of 43.6, 29.6, 32.1, and 15.3 cm³ g⁻¹ for C₂H₂, C₂H₄, C₂H₆, and CO₂, respectively, under 1 bar pressure, whereas, the uptake values were 52.3, 36.8, 38.2, and 23.8 cm³ g⁻¹, respectively at 273 K under 1 bar pressure, as displayed in Figure 2b,c. The adsorption and desorption curves are almost coinciding with each other signifying the rigid framework, whereas the steep uptake of C₂H₂ at low pressure demonstrates the favorable host-guest interaction between IITKGP-24a and C₂H₂ gas molecules. The high sorption capacity of C₂H₂ could be attributed to the presence of ample polar alkoxy oxygen atoms and multiple benzene moieties in the framework pore surface, to which C₂H₂ can easily bind through C–H···O and C–H··· π interactions and exhibit selective adsorption of acetylene over others. Furthermore, to verify the recyclability performance of IITKGP-24a, single component gas sorption isotherm study for C₂H₂ has been performed up to five consecutive cycles at 295 K under 1 bar pressure, in which no significant potentiality loss was observed (Figure 2d). Most importantly, the considerably high uptake differences between the C₂H₂ and CO₂ even at ambient conditions (almost three times higher C₂H₂ uptake than CO₂) signifies the potentiality of IITKGP-24a toward challenging C₂H₂/CO₂ gas mixture separation. Besides high sorption capacity and recyclability, the high separation selectivity is also necessary to be maintained. To verify the separation selectivity ideal adsorbed solution theory (IAST) selectivity calculations were performed for both the temperatures with the

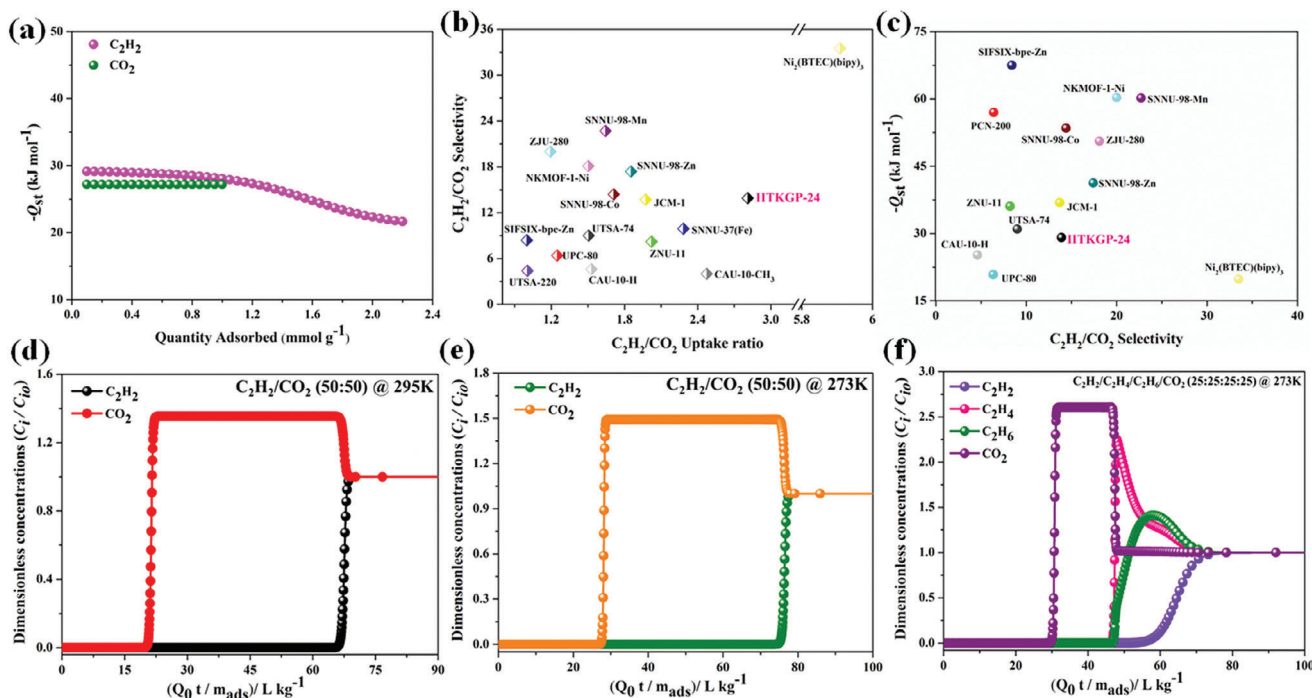


Figure 3. a) Isosteric heat of adsorption (Q_{st}) for C_2H_2 and CO_2 gases. b) Comparison of C_2H_2/CO_2 (50:50) IAST selectivity and C_2H_2/CO_2 uptake ratio at 295 K and 1 bar of **IITKGP-24a**; c) Comparison plot of isosteric heat of adsorption (Q_{st}) of C_2H_2 and C_2H_2/CO_2 (50:50) selectivity of **IITKGP-24a** at 295 K and 1 bar; d) e) C_2H_2/CO_2 (50:50) gas mixtures at 295 K and 273 K temperature, respectively; f) $C_2H_2/C_2H_4/C_2H_6/CO_2$ (25:25:25:25) gas mixtures at 273 K.

dual-site Langmuir model and the corresponding fitting parameters are listed in Table S4 (Supporting Information).

The IAST selectivity for an equimolar mixture of C_2H_2/CO_2 (50:50) was found to be 13.9 and 18.3 at 295 and 273 K, respectively (Figure 2e; Figure S5, Supporting Information). The obtained IAST selectivity of C_2H_2/CO_2 (50:50) for **IITKGP-24a** at 295 K is higher and/or comparable with benchmark MOFs, as tabulated in Table S5 (Supporting Information). The selectivity value is higher than MUF-17 (6.0),^[49] SNNU-37(Fe) (9.9),^[61] ZNU-4 (9.0),^[62] SIFSIX-DPA-Cu-i (9.34),^[63] UTSA-220 (4.4),^[64] FJU-36 (2.2),^[65] sql-SIFSIX-bpe-Zn (8.4),^[66] CAU-10-CH₃ (4.0),^[67] and lower or comparable with SNNU-98-Co (14.4),^[68] SNNU-98-Zn (17.4),^[68] SNNU-98-Mn (22.7),^[68] NKMOF-1-Ni (20.0),^[69] [Ni₂(BTEC)(bipy)₃] (33.5),^[70] ZJU-280 (18.1),^[71] JNU-5-Me (18.5),^[59] and CPL-1-NH₂ (119.0).^[72] The excellent selectivity of **IITKGP-24** toward C_2H_2/CO_2 gas mixtures could be attributed to stronger C–H⋯O and C–H⋯ π interactions between the framework and targeted C_2H_2 gas molecules even under ambient conditions. Although for many frameworks (ZNU-4,^[62] UPC-80,^[73] SIFSIX-DPA-Cu-i,^[63] SNNU-98-Ni,^[68] SNNU-37(Fe),^[61] UTSA-220,^[64] MUF-17,^[49] CAU-10-H,^[67] UTSA-74^[74]) the targeted C_2H_2 uptake was higher than **IITKGP-24a**, at the same time due to the high uptake capacity of competing CO_2 gas molecules they failed to maintain high separation selectivity values and exhibited lower separation selectivity than **IITKGP-24a** (Figure 2f), which makes **IITKGP-24a** as a promising candidate over reported MOFs for this targeted separation.

Besides, high sorption capacity and separation selectivity, lower isosteric heat of adsorption (Q_{st}) is highly desirable to

minimize the regeneration cost and make the process energy-efficient. Interestingly, the lower Q_{st} value of -29.2 kJ mol⁻¹ was obtained for C_2H_2 , whereas the Q_{st} values for other tested gases CO_2 , C_2H_4 , and C_2H_6 were -27.2 , -33.2 , and -30.6 kJ mol⁻¹, respectively, at zero loading pressure under ambient condition (Figure 3a; Figure S6, Supporting Information). The higher Q_{st} value of C_2H_2 than CO_2 for **IITKGP-24a** indicates a stronger binding affinity toward C_2H_2 over CO_2 . The obtained Q_{st} value of C_2H_2 was even lower than the MOFs having high separation selectivity values (such as CPL-1-NH₂ (-50 kJ mol⁻¹),^[72] NKMOF-1-Ni (-60.3 kJ mol⁻¹),^[69] ZJU-280 (-50.6 kJ mol⁻¹),^[71] PCN-200 (-57.0 kJ mol⁻¹),^[75] SNNU-98-Mn (-60.2 kJ mol⁻¹),^[68] SNNU-98-Co (-53.5 kJ mol⁻¹),^[68] ZNU-4 (-50.3 kJ mol⁻¹)^[62]) and keeping the developed framework **IITKGP-24a** one hand upper over other MOFs for this targeted separation. Furthermore, to verify the position of framework **IITKGP-24** among the previously reported benchmark MOFs, we have plotted uptake ratio vs separation selectivity (Figure 3b) and separation selectivity vs Q_{st} values (Figure 3c). As displayed in Figure 3b, **IITKGP-24** maintains a *trade-off* between C_2H_2/CO_2 uptake ratio and selectivity values compared to others. Although [Ni₂(BTEC)(bipy)₃] possesses high C_2H_2/CO_2 uptake ratio and selectivity values among all the developed frameworks so far and appears as the best candidate for this targeted C_2H_2/CO_2 separation, our developed framework **IITKGP-24** could be considering as the second best-performing material in this direction. On the other hand, separation selectivity vs Q_{st} plot indicates [Ni₂(BTEC)(bipy)₃] possesses the high selectivity value despite having a low Q_{st} value, beneficial for practical industrial separation purposes. However, SNNU-98-Zn,

ZJU-280, SNNU-98-Mn possess high separation selectivity and high Q_{st} values as well, thus unable to maintain the *trade-off* between separation selectivity and Q_{st} , whereas **IITKGP-24** maintains a nice *trade-off* between the two (Figure 3c) and likely to employ for C_2H_2/CO_2 practical gas separation purpose. This detailed analysis reveals that our developed framework **IITKGP-24** could be considered as one of the best-performing materials for the targeted C_2H_2/CO_2 separation.

Although single-component isotherms proved the potentiality of our developed framework **IITKGP-24**, it's necessary to validate the superiority under multi-component gas mixtures feed-stock (two and four), as practical industrial C_2H_2/CO_2 gas separation process includes various other C2 impurities and the potentiality of the developed framework is necessary to be retained under that tested condition. Hence, breakthrough performance analysis in the presence of multiple gas mixtures is indeed indispensable though challenging. Considering this, the transient breakthrough analyses were performed to evaluate the actual separation performance for the binary equimolar gas mixtures of C_2H_2/CO_2 (50:50 v/v) and the real mimic of industrial separation composition $C_2H_2/C_2H_4/C_2H_6/CO_2$ (25:25:25:25) at both temperatures 295 K and 273 K (Figure 3d–f; Figure S7, Supporting Information). The methodology used for the transient breakthrough simulations is the same as described in earlier publications^[76–80]; further details are provided in the Supporting Information. As displayed in Figure 3d, CO_2 gas breaks through first from the packed MOF bed with high purity while the pure C_2H_2 gas is retained in the adsorbed bed for a longer time. Purified C_2H_2 may be recovered during the desorption cycle under PSA operations (Figure S8, Supporting Information). The productivity of acetylene gas (of 92% purity) is 1.38 mmol g^{-1} , which is comparable with those obtained from previously developed benchmark MOFs (Table S5, Supporting Information). Similarly, the transient breakthrough separation under 1 bar and 273 K temperature for quaternary $C_2H_2/C_2H_4/C_2H_6/CO_2$ (25:25:25:25) gas mixtures exhibits CO_2 breaks through first with high-purity having the poorest adsorption strength and very less interaction with the employed framework followed by removal of C_2H_4 and C_2H_6 together, while C_2H_2 gas retained in the adsorbed bed for a longest time (Figure 3f).

It should be noted that although quite a few frameworks were employed for two-component C_2H_2/CO_2 gas separation, the potentiality assessment from four-component gas mixtures *via* breakthrough analysis is still unexplored though demandable. Although the difference in breakthrough time parameters of both C_2H_4 and C_2H_6 gas components (eluting same time together) compared to the longest retained C_2H_2 in a column is not too high (45 vs ~58), it could still be considered as a potential candidate for such type of C_2H_2 sieving from four component industrially relevant gas mixture compositions. In general, MOFs show a trend in uptake capacities of these four types of components with the highest and almost equal amount of C_2H_2 and CO_2 uptakes, followed by moderate uptake of C_2H_4 , while C_2H_6 uptake remains the least. As shown before, in single component gas sorption study, **IITKGP-24a** shows the highest uptake for C_2H_2 , the least uptake for CO_2 , and mid to lower uptakes for C_2H_4 and C_2H_6 (with almost equal uptake amounts for C_2H_4 and C_2H_6) and thus enabling for commendable C_2H_2 sieving from four component gas mixtures.

The retention of structural integrity is very important besides obtaining the high potentiality to ensure its practical utility. The PXRD analysis was performed for the post-gas sorption sample to verify the structural integrity of the employed framework, and the unchanged PXRD patterns (Figure 1e) confirm that the developed framework is highly robust in nature and retains its structural integrity during the gas sorption analysis processes.

It should be noted that a perfect sorbent needs to possess a *trade-off* among high sorption capacity, excellent framework robustness and recyclability, high separation selectivity with high purity, and low regeneration cost. Although the developed material **IITKGP-24** didn't possess high C_2H_2 uptake compared to some of the benchmark MOFs under ambient conditions, remarkably low CO_2 uptake capacity, and thus the excellent C_2H_2/CO_2 separation selectivity, framework robustness, easy regenerability, and recyclability of the material made this microporous MOF promising toward challenging C_2H_2/CO_2 and $C_2H_2/C_2H_4/C_2H_6/CO_2$ separations under ambient condition.

3. Conclusion

In summary, a chemically robust 3D microporous MOF **IITKGP-24** has been strategically constructed, which possesses polar pore channels and displays excellent stability not only in water or humid conditions but also in a wide range of pH solutions (2–12). Taking the benefits of high stability and excellent uptake differences the developed framework was employed in C_2H_2 sieving from CO_2 and other C2 hydrocarbons. The material exhibited excellent C_2H_2/CO_2 separation selectivity (13.9 even at room temperature) and capable to maintain excellent *trade-off* between sorption capacity and separation selectivity. Furthermore, breakthrough performances of **IITKGP-24a** under the industrially relevant gas mixture compositions (both binary: C_2H_2/CO_2 as well as quaternary mixtures: $C_2H_2/C_2H_4/C_2H_6/CO_2$) uphold the overall potentiality of the developed framework. The excellent framework robustness with microporosity along with *trade-off* among sorption capacity, separation selectivity, and easy-regenerability made **IITKGP-24** a potential candidate for such industrially important gas mixture separations. A dynamic breakthrough analysis coupled with GCMC simulation could assess a better understanding of this separation phenomenon and the results will be reported in due course. This work will be beneficial for the effective design and development of chemically stable MOFs for various important though challenging gas separations considering the industrial viewpoints.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

Acknowledgements

B.P. thanks the Ministry of Education, Government of India for his PMRF Fellowship (PMRF ID: 2403439). M.C.D. gratefully acknowledges the support received from IIT Kharagpur.

Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available in the supplementary material of this article. **CCDC: 2404969** contains the crystallographic data for **IITKGP-24**. These data are available from the Cambridge Crystallographic Data Center (CCDC) via www.ccdc.cam.ac.uk/data_request/cif.

Keywords

acetylene purification, multi-component separation, pH-stable MOF, physisorbent materials, surface functionalization

Received: November 28, 2024

Revised: December 10, 2024

Published online: December 23, 2024

- [1] D. S. Sholl, R. P. Lively, *Nature* **2016**, 532, 435.
- [2] X. Wang, H. Liu, Y. Li, X. Yang, F. Gao, X. Wang, Z. Kang, W. Fan, D. Sun, *Coord. Chem. Rev.* **2023**, 482, 215093.
- [3] R. Sahoo, M. C. Das, *Coord. Chem. Rev.* **2021**, 442, 213998.
- [4] R. Sahoo, S. Chand, M. Mondal, A. Pal, S. C. Pal, M. K. Rana, M. C. Das, *Chem. - Eur. J.* **2020**, 26, 12624.
- [5] R. Sahoo, S. Mondal, D. Mukherjee, M. C. Das, *Adv. Funct. Mater.* **2022**, 32, 2207197.
- [6] M. C. Das, S. C. Pal, B. Chen, *Joule* **2022**, 6, 22.
- [7] H. Wang, Y. Liu, J. Li, *Adv. Mater.* **2020**, 32, 2002603.
- [8] C. Gu, N. Hosono, J.-J. Zheng, Y. Sato, S. Kusaka, S. Sakaki, S. Kitagawa, *Science* **2019**, 363, 387.
- [9] L. Yang, S. Qian, X. Wang, X. Cui, B. Chen, H. Xing, *Chem. Soc. Rev.* **2020**, 49, 5359.
- [10] R.-B. Lin, S. Xiang, W. Zhou, B. Chen, *Chem* **2020**, 6, 337.
- [11] W. Fan, S. Yuan, W. Wang, L. Feng, X. Liu, X. Zhang, X. Wang, Z. Kang, F. Dai, D. Yuan, D. Sun, H.-C. Zhou, *J. Am. Chem. Soc.* **2020**, 142, 8728.
- [12] S. C. Pal, R. Krishna, M. C. Das, *Chem. Eng. J.* **2023**, 460, 141795.
- [13] A. Pal, S. Chand, M. C. Das, *Inorg. Chem.* **2017**, 56, 13991.
- [14] A. Pal, S. Chand, D. G. Madden, D. Franz, L. Ritter, A. Johnson, B. Space, T. Curtin, M. C. Das, *Inorg. Chem.* **2019**, 58, 11553.
- [15] W. Fan, S. B. Peh, Z. Zhang, H. Yuan, Z. Yang, Y. Wang, K. Chai, D. Sun, D. Zhao, *Angew. Chem., Int. Ed.* **2021**, 60, 17338.
- [16] S. Sharma, S. Mukherjee, A. V. Desai, M. Vandichel, G. K. Dam, A. Jadhav, G. Kociok-Köhn, M. J. Zaworotko, S. K. Ghosh, *Chem. Mater.* **2021**, 33, 5800.
- [17] A. Noonikara-Poyil, H. Cui, B. Wang, Y. Shi, B. Chen, H. V. R. Dias, *Small* **2023**, 19, 2206984.
- [18] M. R. Tchalala, P. M. Bhatt, K. N. Chappanda, S. R. Tavares, K. Adil, Y. Belmabkhout, A. Shkurenko, A. Cadiau, N. Heymans, G. De Weireld, G. Maurin, K. N. Salama, M. Eddaoudi, *Nat. Commun.* **2019**, 10, 1328.
- [19] S. Yang, A. J. Ramirez-Cuesta, R. Newby, V. Garcia-Sakai, P. Manuel, S. K. Callear, S. I. Campbell, C. C. Tang, M. Schröder, *Nat. Chem.* **2015**, 7, 121.
- [20] S. Mondal, R. Sahoo, J. Behera, M. C. Das, *Coord. Chem. Rev.* **2024**, 514, 215924.
- [21] L. Fan, L. Yue, W. Sun, X. Wang, P. Zhou, Y. Zhang, Y. He, *ACS Appl. Mater. Interfaces* **2021**, 13, 40788.
- [22] X.-W. Gu, J.-X. Wang, E. Wu, H. Wu, W. Zhou, G. Qian, B. Chen, B. Li, *J. Am. Chem. Soc.* **2022**, 144, 2614.
- [23] A. Pal, S. Chand, D. G. Madden, D. Franz, L. Ritter, B. Space, T. Curtin, S. C. Pal, M. C. Das, *ACS Appl. Mater. Interfaces* **2020**, 12, 41177.
- [24] L. Zhang, T. Xiao, X. Zeng, J. You, Z. He, C.-X. Chen, Q. Wang, A. Nafady, A. M. Al-Enizi, S. Ma, *J. Am. Chem. Soc.* **2024**, 146, 7341.
- [25] S.-Q. Yang, L. Zhou, Y. He, R. Krishna, Q. Zhang, Y.-F. An, B. Xing, Y.-H. Zhang, T.-L. Hu, *ACS Appl. Mater. Interfaces* **2022**, 14, 33429.
- [26] Y. Wang, S. B. Peh, D. Zhao, *Small* **2019**, 15, 1900058.
- [27] Y. Wei, M. Chang, L.-X. Yun, M. Qiao, R.-K. Liu, D. Liu, J.-X. Wang, J.-F. Chen, *Small* **2023**, 19, 2303848.
- [28] R. Sahoo, S. Mondal, S. Chand, A. K. Manna, M. C. Das, *Small* **2023**, 19, 2304581.
- [29] Y. Ye, Z. Ma, R.-B. Lin, R. Krishna, W. Zhou, Q. Lin, Z. Zhang, S. Xiang, B. Chen, *J. Am. Chem. Soc.* **2019**, 141, 4130.
- [30] Z. Chu, K. Guo, F. Chen, G. Hai, Q. Yang, Z. Zhang, Q. Ren, Z. Bao, *Sep. Purif. Technol.* **2025**, 358, 130467.
- [31] S. Chand, A. Pal, R. Saha, P. Das, R. Sahoo, P. K. Chattaraj, M. C. Das, *Inorg. Chem.* **2020**, 59, 7056.
- [32] S. Laha, N. Dwarkanath, A. Sharma, D. Rambabu, S. Balasubramanian, T. K. Maji, *Chem. Sci.* **2022**, 13, 7172.
- [33] Y. Li, X. Wang, H. Zhang, L. He, J. Huang, W. Wei, Z. Yuan, Z. Xiong, H. Chen, S. Xiang, B. Chen, Z. Zhang, *Angew. Chem., Int. Ed.* **2023**, 62, 202311419.
- [34] S. Chand, A. Pal, M. C. Das, *Chem. - Eur. J.* **2018**, 24, 5982.
- [35] C. H. Hendon, A. J. Rieth, M. D. Korzyński, M. Dincă, *ACS Cent. Sci.* **2017**, 3, 554.
- [36] K. Su, W. Wang, S. Du, C. Ji, D. Yuan, *Nat. Commun.* **2021**, 12, 3703.
- [37] D. Song, F. Jiang, D. Yuan, Q. Chen, M. Hong, *Small* **2023**, 19, 2302677.
- [38] M. Singh, S. Neogi, *Inorg. Chem.* **2022**, 61, 10731.
- [39] R. Das, S. S. Manna, B. Pathak, C. M. Nagaraja, *ACS Appl. Mater. Interfaces* **2022**, 14, 33285.
- [40] H.-Y. Guan, R. J. LeBlanc, S.-Y. Xie, Y. Yue, *Coord. Chem. Rev.* **2018**, 369, 76.
- [41] S. Mondal, R. Sahoo, M. C. Das, *Small*, 2409095, <https://doi.org/10.1002/smll.202409095>.
- [42] S. C. Pal, D. Mukherjee, Y. Oruganti, B. G. Lee, D.-W. Lim, B. Pramanik, A. K. Manna, M. C. Das, *J. Am. Chem. Soc.* **2024**, 146, 14546.
- [43] S. Mondal, B. Pramanik, R. Sahoo, M. C. Das, *ChemSusChem*, 202401248, <https://doi.org/10.1002/cssc.202401248>.
- [44] B. Pramanik, R. Sahoo, Y. Yoshida, A. K. Manna, H. Kitagawa, M. C. Das, *Chem. - Eur. J.*, 202402896, <https://doi.org/10.1002/chem.202402896>.
- [45] R. Sahoo, S. Luo, N. K. Pendyala, S. Chand, Z.-H. Fu, M. C. Das, *Mater. Chem. Front.* **2023**, 7, 3373.
- [46] R. Sahoo, R. Ahmed, A. K. Manna, M. C. Das, *J. Catal.* **2024**, 437, 115641.
- [47] E. D. Bloch, W. L. Queen, R. Krishna, J. M. Zadrozny, C. M. Brown, J. R. Long, *Science* **2012**, 335, 1606.
- [48] B. Li, X. Cui, D. O'Nolan, H.-M. Wen, M. Jiang, R. Krishna, H. Wu, R.-B. Lin, Y.-S. Chen, D. Yuan, H. Xing, W. Zhou, Q. Ren, G. Qian, M. J. Zaworotko, B. Chen, *Adv. Mater.* **2017**, 29, 1704210.
- [49] O. T. Qazvini, R. Babarao, S. G. Telfer, *Chem. Mater.* **2019**, 31, 4919.
- [50] K. Otake, Y. Cui, C. T. Buru, Z. Li, J. T. Hupp, O. K. Farha, *J. Am. Chem. Soc.* **2018**, 140, 8652.
- [51] D. J. O'Hearn, A. Bajpai, M. J. Zaworotko, *Small* **2021**, 17, 2006351.
- [52] J. Xu, Y. Xu, X.-H. Bu, *Small* **2021**, 17, 2102331.
- [53] R. Sahoo, B. Pramanik, S. Mondal, M. C. Das, *Small* **2024**, 20, 2309281.
- [54] S. C. Pal, J.-X. Wang, D. Mukherjee, B. Li, M. C. Das, *Chem. Eng. J.* **2024**, 500, 157054.
- [55] C. Wang, H. Zhang, Y. Wang, J. Wu, K. O. Kirlikovali, P. Li, Y. Zhou, O. K. Farha, *Small* **2023**, 19, 2206116.
- [56] M.-H. Yu, H. Fang, H.-L. Huang, M. Zhao, Z.-Y. Su, H.-X. Nie, Z. Chang, T.-L. Hu, *Small* **2023**, 19, 2300821.
- [57] W. Begum, M. Chauhan, R. Kalita, P. Gupta, N. Akhtar, N. Antil, R. Newar, K. Manna, *ACS Catal.* **2024**, 14, 10427.
- [58] X.-P. Fu, Y.-L. Wang, Q.-Y. Liu, *Dalton Trans.* **2020**, 49, 16598.

- [59] X.-J. Xie, Q.-Y. Cao, Z.-H. Zhang, M.-Y. Zhou, H. Zeng, W. Lu, D. Li, *Chem Bio Eng.* **2024**, *1*, 150.
- [60] B. Pramanik, R. Sahoo, M. C. Das, *Coord. Chem. Rev.* **2023**, *493*, 215301.
- [61] S.-C. Fan, Y.-T. Li, Y. Wang, J.-W. Wang, Y.-Y. Xue, H.-P. Li, S.-N. Li, Q.-G. Zhai, *Inorg. Chem.* **2021**, *60*, 18473.
- [62] N. Xu, J. Hu, L. Wang, D. Luo, W. Sun, Y. Hu, D. Wang, X. Cui, H. Xing, Y. Zhang, *Chem. Eng. J.* **2022**, *450*, 138034.
- [63] J. You, H. Wang, T. Xiao, X. Wu, L. Zhang, C.-Z. Lu, *Chem. Eng. J.* **2023**, *477*, 147001.
- [64] H. Li, L. Li, R.-B. Lin, G. Ramirez, W. Zhou, R. Krishna, Z. Zhang, S. Xiang, B. Chen, *ACS Sustainable Chem. Eng.* **2019**, *7*, 4897.
- [65] L. Liu, Z. Yao, Y. Ye, L. Chen, Q. Lin, Y. Yang, Z. Zhang, S. Xiang, *Inorg. Chem.* **2018**, *57*, 12961.
- [66] M. Shivanna, K.-i. Otake, B.-Q. Song, L. M. van Wyk, Q.-Y. Yang, N. Kumar, W. K. Feldmann, T. Pham, S. Suepaul, B. Space, L. J. Barbour, S. Kitagawa, M. J. Zaworotko, *Angew. Chem., Int. Ed.* **2021**, *60*, 20383.
- [67] S.-Q. Yang, B. Xing, L.-L. Wang, L. Zhou, F.-Y. Zhang, Y.-L. Li, T.-L. Hu, *Chem Bio Eng.* **2024**, *1*, 245.
- [68] J.-W. Wang, S.-C. Fan, H.-P. Li, X. Bu, Y.-Y. Xue, Q.-G. Zhai, *Angew. Chem., Int. Ed.* **2023**, *62*, 202217839.
- [69] Y.-L. Peng, T. Pham, P. Li, T. Wang, Y. Chen, K.-J. Chen, K. A. Forrest, B. Space, P. Cheng, M. J. Zaworotko, Z. Zhang, *Angew. Chem., Int. Ed.* **2018**, *57*, 10971.
- [70] Y. Du, Y. Chen, Y. Wang, C. He, J. Yang, L. Li, J. Li, *Sep. Purif. Technol.* **2021**, *256*, 117749.
- [71] Q.-L. Qian, X.-W. Gu, J. Pei, H.-M. Wen, H. Wu, W. Zhou, B. Li, G. Qian, *J. Mater. Chem. A* **2021**, *9*, 9248.
- [72] L. Yang, L. Yan, Y. Wang, Z. Liu, J. He, Q. Fu, D. Liu, X. Gu, P. Dai, L. Li, X. Zhao, *Angew. Chem., Int. Ed.* **2021**, *60*, 4570.
- [73] C. Jiang, C. Hao, X. Wang, H. Liu, X. Wei, H. Xu, Z. Wang, Y. Ouyang, W. Guo, F. Dai, D. Sun, *Chem. Eng. J.* **2023**, *453*, 139713.
- [74] F. Luo, C. Yan, L. Dang, R. Krishna, W. Zhou, H. Wu, X. Dong, Y. Han, T.-L. Hu, M. O'Keeffe, L. Wang, M. Luo, R.-B. Lin, B. Chen, *J. Am. Chem. Soc.* **2016**, *138*, 5678.
- [75] Q. Li, C. Qiu, F. An, H. Wang, Q. Wang, A. Xiao, L. Wang, L. Zhu, *Sep. Purif. Technol.* **2023**, *324*, 124557.
- [76] R. Krishna, *RSC Adv.* **2015**, *5*, 52269.
- [77] R. Krishna, *RSC Adv.* **2017**, *7*, 35724.
- [78] R. Krishna, *Sep. Purif. Technol.* **2018**, *194*, 281.
- [79] R. Krishna, *ACS Omega* **2020**, *5*, 16987.
- [80] R. Krishna, *Precis. Chem.* **2023**, *1*, 83.