

Underlying Polar and Nonpolar Modification MOF-Based Factors that Influence Permanent Porosity in Porous Liquids

Hamidreza Mahdavi, Nathan T. Eden, Cara M. Doherty, Durga Acharya, Stefan J. D. Smith,* Xavier Mulet,* and Matthew R. Hill*



Cite This: *ACS Appl. Mater. Interfaces* 2022, 14, 23392–23399



Read Online

ACCESS |

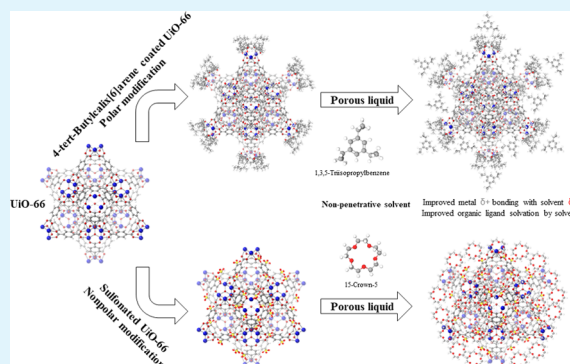
Metrics & More

Article Recommendations

Supporting Information

ABSTRACT: It is increasingly apparent that porous liquids (PLs) have unique use cases due to the combination of ready liquid handling and their inherently high adsorption capacity. Among the PL types, those with permanent porosity are the most promising. Although Type II and III PLs have economic synthetic methods and can be made from a huge variety of metal–organic frameworks (MOFs) and solvents, these nanocomposites still need to be stable to be useful. This work aims to systematically explore the possibilities of creating PLs using different MOF modification methods. This delivered underpinning insights into the molecular-level influence between solvent and MOF on the overall nanocomposite stability. Zirconium-based metal–organic frameworks were combined with two different solvents of varying chemistry to deliver CO₂ sorption capacities as high as 2.9 mmol g⁻¹ at 10 bar. The results of the study could have far-reaching ramifications for future investigations in the PL field.

KEYWORDS: zirconium-based metal–organic frameworks, porous liquids, permanent porosity, MOF modification, gas sorption



INTRODUCTION

Porous liquids (PLs) are a new class of material possessing the fluidity and mass transfer properties of fluids combined with the permanent porosity and molecular sieving properties of the porous solid.¹ PLs attract interest from both academia and industry in various applications such as homogeneous catalysis, novel reaction media, and gas adsorption due to their exceptional physicochemical properties.^{2–4} PLs can be classified into three categories based on the composition and nature of the porous host, namely: Type I PLs, which are neat liquids consisting of a single molecule with permanent pores; Type II PLs, which contain dissolved porous host in excluded solvent from the pores; and the Type III PLs, which are porous host dispersed in a solvent where the solvent is sterically hindered from occupying the pores.^{5–8} The Type II and III PLs hold the most promise among all types of PLs for industrial applications.⁹

Porous hosts such as metal–organic frameworks (MOFs), zeolites, porous carbon, silica nanoparticles, and molecular cages have been studied to form PLs.^{10–13} In each case, the porous hosts are prioritized, where their window size is large enough for guest species penetration but too small for solvent. Since MOF structures possess molecular-sized pores along with a high degree of tunability, they have become the most utilized porous host in PL formation.¹⁴ As a subset of MOFs, zirconium-based metal–organic frameworks (UiOs) are particularly interesting in PL formation as their surface

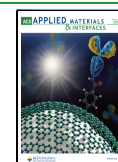
functional groups tunability enables a wider range of solvents to be considered.¹⁵ Besides, solvents with large molecular dimensions such as an ionic liquid, liquid polymer, or deep eutectic solvents often are used to reduce the likelihood of the solvent penetrating the porous host.^{16–19}

Type II and III PLs have facile synthetic methods and can be made from a huge variety of MOFs and solvents, which give rise to nearly infinite variations of MOF-based PLs.⁹ However, solubility and dispersion stability, which are governed by the interaction between the solvent and the porous host, are key parameters for process integration, as settling of the solid porous host would prevent the use of PLs in most existing solvent circulation systems.^{5,6,20} Furthermore, MOF solubility or dispersion in solvents can be limited, leading to fewer stable variations of MOF-based PLs. Thus, it is essential to consider how MOF particle surface chemistry will impact the stability of MOF-based PLs.²¹ Several works have shown that the stability of MOF-based PLs can be improved through postsynthetic modifications.^{22–33} However, these MOF-based PLs suffer from significant viscosity increments and adverse effects on

Received: February 18, 2022

Accepted: April 7, 2022

Published: May 11, 2022



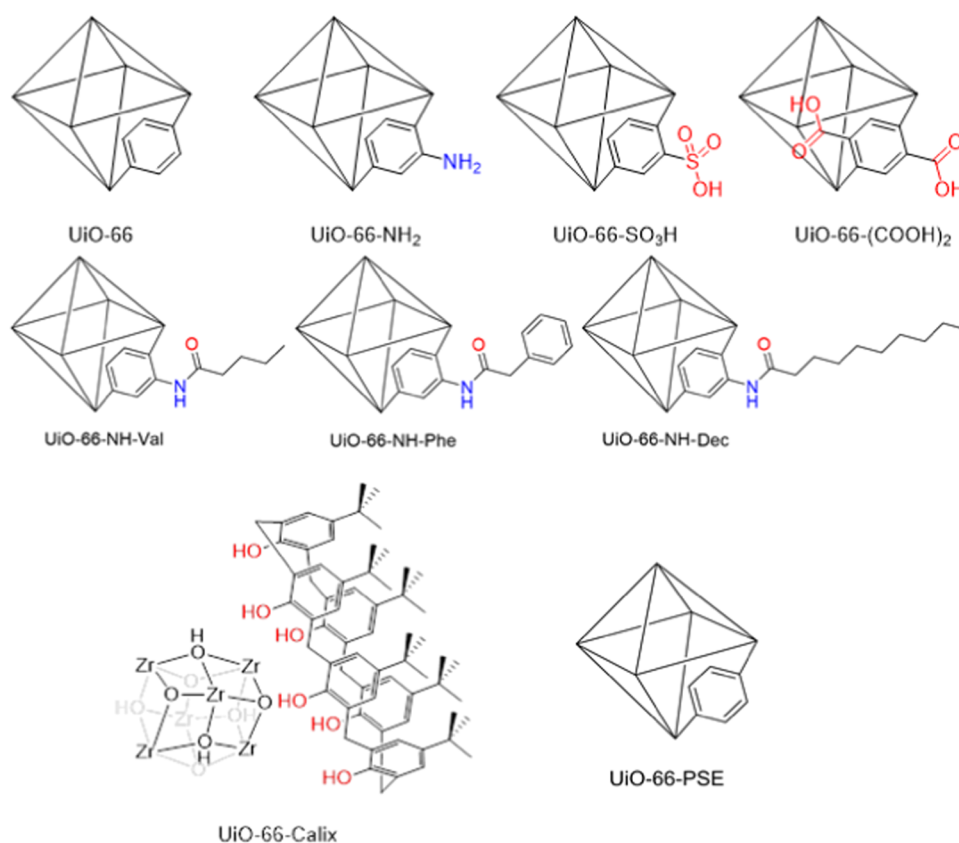


Figure 1. Images of nanosized UiO-66 and its functional derivatives.

pore accessibility.^{34–36} Thus, it is important to systematically explore the possibilities of creating PLs using alternative MOF modification methods.^{21,37–39}

This work focuses on exploring a systematic modification synthetic strategy to make PLs using polar and nonpolar modified MOFs and nonpenetrating solvents. The competitive hydrophilicity/phobicity and van der Waals interactions between the porous host and solvent of the resulting nanocomposites have been investigated using Zr MOFs in two solvents with varying chemistry. All of the 18 candidate porous liquids (Type II/Type III) were prepared at four different porous host concentrations (1–10 wt %) to understand the impact of loading on colloid stability. The studied MOFs were recovered to confirm they were not adversely affected by extended exposure to solvents. High-pressure (10 bar) gas sorption measurements were undertaken for each solvent and compared to the corresponding porous liquid at 10 wt % as an indication of the porosity. We find that UiO-66-Calix_{10%}-TPB and UiO-66-SO₃H_{10%}-CE have an exciting combination of stability and good sorption properties for use in CO₂ gas scrubbing applications.

EXPERIMENTAL SECTION

Nanosized UiO-66 and functional derivatives were synthesized according to literature reports (see Supporting Information S2 for details). In this work, we modified only the linker between different syntheses to reduce variables. Unmodified MOFs, UiO-66, UiO-66-NH₂, UiO-66-SO₃H, and UiO-66-(COOH)₂ were prepared in this way. Then, to investigate additional surface modifications and their effect on being PL candidates, some of these MOFs were modified further. Therefore, the effectiveness of different polar and nonpolar modification methods on stable PL formation was explored. Based on these various methods, amine, sulfonic acid, and dicarboxylic acid

surface functional groups were introduced through presynthetic variation of the organic ligand of UiO-66, while short and long aliphatic, and aromatic surface functional groups through UiO-66-NH₂ underwent three different postsynthetic amidation reactions with acid chlorides to give surface-modified UiO-66-NH-valeryl, UiO-66-NH-phenyl, and UiO-66-NH-decane modification of the external surface of UiO-66-NH₂, and supramolecular amphiphilic macrocyclic surface functional groups through postsynthetic surface grafting using 4-*tert*-butylcalix[6]arene on the external surface of UiO-66, and redistributing the framework's mixture of bound linker/modulator species through postsynthetic annealing of UiO-66 at room temperature in DMF (the synthesis solvent) have been provided (Figure 1). Successful synthesis and modifications were confirmed by Fourier transform infrared (FTIR) spectroscopy, powder X-ray diffraction (PXRD), thermogravimetric analysis (TGA), X-ray photoelectron spectroscopy (XPS), proton nuclear magnetic resonance (¹H NMR), low-pressure gas sorption, and scanning electron microscopy (SEM) images in S5–S11. Besides, 15-crown-5 (CE) (Bp 93–96 °C) and 1,3,5-triisopropylbenzene (TPB) (Bp 232–236 °C) were chosen as solvents due to their differing physicochemical properties (Table S1). A portion of each UiO was added to each solvent at loadings of 1, 2.5, 5, and 10 wt % and sonicated to form an initial dispersion/dissolution. Further details on the solvents used and the preparation of the UiO-based PLs are included in S3 and S4, respectively.

Dispersion/dissolution stability and resistance to particle settling of each of the 18 possible UiO-based PLs were assessed by observing the Tyndall scattering of light and monitoring the natural settling of each UiO-solvent combination left undisturbed overnight. As a result of these screening tests, two PL candidates were evaluated as liquid adsorbents and compared based on the stability and viscosity, avoidance of solvent penetration into MOF pores, sorption capacities, and kinetics for gas sorption. A portion of the MOFs from 10 wt % liquid system of these two candidate PLs was recovered after a solvent exchange with methanol, centrifugation, and washing in triplicate,

followed by overnight vacuum drying under 100 °C. After recovering the MOFs, they were characterized and compared to their synthesized counterparts to check their morphology, surface area, chemical bonding, thermal stability, and pore size by exposure to the solvents. For clarity, this manuscript follows the naming convention of “UiO-66 functionality_{Loading} solvent” (e.g., UiO-66-Calix_{10%}-TPB) for the prepared liquids, while UiOs recovered from combinations are denoted as “UiO-66-functionality_{EX-Solvent}” (e.g., UiO-66-Calix_{EX-TPB}).

RESULTS AND DISCUSSION

Recovered MOF Characterization. The two PL candidates were then recovered and analyzed by the same techniques to investigate the effects of immersion and removal (see Supporting Information S5–S11 for details). FTIR spectra indicate little change to the overall MOF structures, as their characteristic transmittance peaks remain unchanged. Interestingly, PXRD patterns of UiO-66-Calix_{EX-TPB} show higher relative peaks at ~ 12.5 and 14.5° , indicating a change in growth from octahedral crystals to preferential combination along the [220] and [222] axis. The slight broadness of UiO-66-SO₃H_{EX-CE} PXRD pattern peaks is due to a reduction in crystallinity. There are no significant changes in thermal stability, binding energies, and chemical structure of both samples using TGA, XPS, and ¹H NMR, respectively. However, a proportion of 4-*tert*-butylcalix[6]arene and sulfur groups was reduced relative to the terephthalic proton but remained in the same binding energy in XPS and chemical shifts in ¹H NMR. The UiO-66-Calix_{EX-TPB} also showed greatly increased maximum adsorption capacity for N₂ and a slight decrease in surface area. This is confirmed by SEM images that also indicate recovered rod-shaped crystals rather than octahedral as PXRD predicted. The UiO-66-SO₃H_{EX-CE} presented a strong reduction in adsorption capacity for N₂ and surface area as PXRD patterns display crystallinity decrement. The recovery of the UiO-66-SO₃H from CE requires the strong intermolecular bonds between them to be broken, which may result in pores collapsing. In addition, the UiO-66-SO₃H pores are sensitive to the removal of solvents and typically show collapse under mild drying conditions. Therefore, after drying, the pores can collapse to give mostly amorphous material.

Stability. The results of the dispersion/dissolution of each UiO–solvent combination were measured using laser light for the appearance of sediment after sonication and allowing the combinations to stand (Figure 2). Based on the Tyndall effect, laser light was used to determine whether a mixture was colloidal or not. UiO-66-Calix_{10%}-TPB was found to cause minimal scattering of light, whereas the greatest scattering was observed for UiO-66-SO₃H_{10%}-CE. There have been no sedimentations in UiO-66-Calix_{10%}-TPB or UiO-66-SO₃H_{10%}-CE, showing that UiO-66-Calix_{10%}-TPB is a highly stable colloid, while UiO-66-SO₃H_{10%}-CE is a highly stable suspension, and with the presence of empty pores (*vide infra*), a Type II PL and a Type III PL, respectively. According to the findings, 1,3,5-triisopropylbenzene is a particularly compatible media for the hydrophobic UiOs' modification methods. 1,5-Crown-5, on the other hand, is a better compatible media for the hydrophilic UiOs' modification methods. Other UiO–solvent combinations also exhibited varying levels of scattering and sedimentation, indicating the potential to form Type III PLs. The stability of each UiO–solvent combination is presented in Figure 3. As a result of these screening experiments, two UiO–solvent combinations

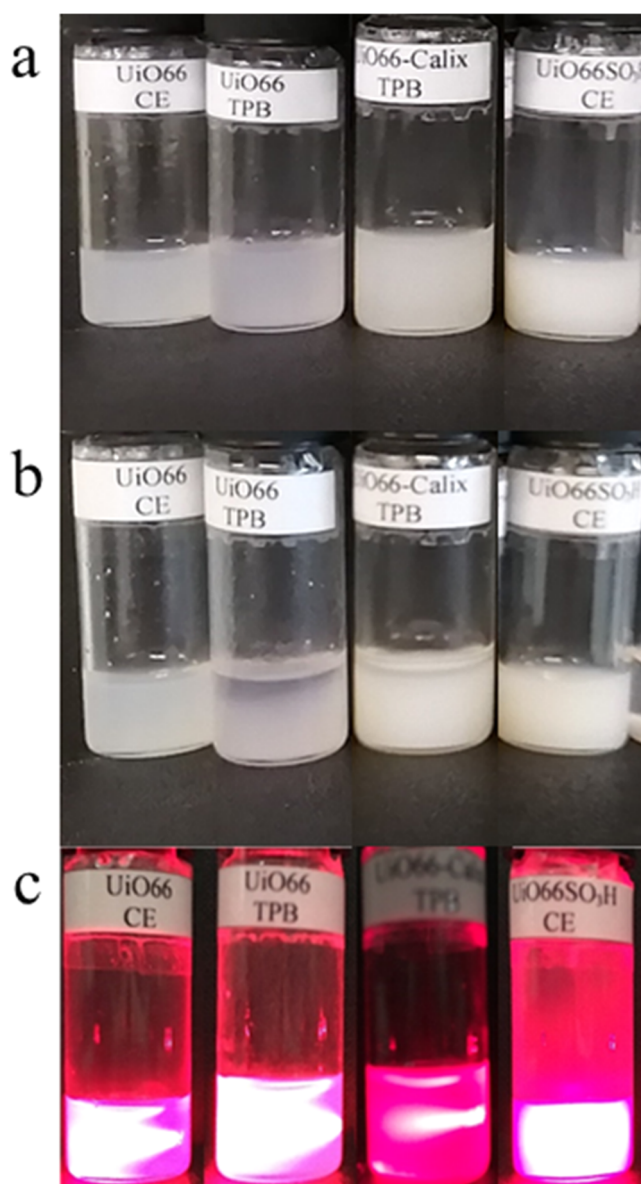


Figure 2. Photographs of select UiO–solvent (1 wt %) combinations (a) immediately following sonication, (b) after allowing to settle, and (c) when exposed to laser light. In addition, we find a gallery of the samples used in the screening process in the Supporting Information (Figure S19).

(UiO-66-Calix_{10%}-TPB and UiO-66-SO₃H_{10%}-CE) were tested further to see what happens when a combination of UiO and solvents does not precipitate.

Mechanistic Insights to Design. Economic synthesis methods and the range of MOFs and solvents allow almost infinite MOF-based PLs formulations to be explored. However, MOFs' solubility or dispersibility in solvents is generally limited. To achieve stable MOF–solvent combinations with acceptable viscosity, open porosity with suitable capacities, and kinetics for guest solubility, these formulations are the key tool to overcome the fundamental challenge of instability. The influence of different MOF modification methods on the competitive hydrophilicity/phobicity and van der Waals interactions between MOF and solvent were systematically investigated to expand the parametric space where functional

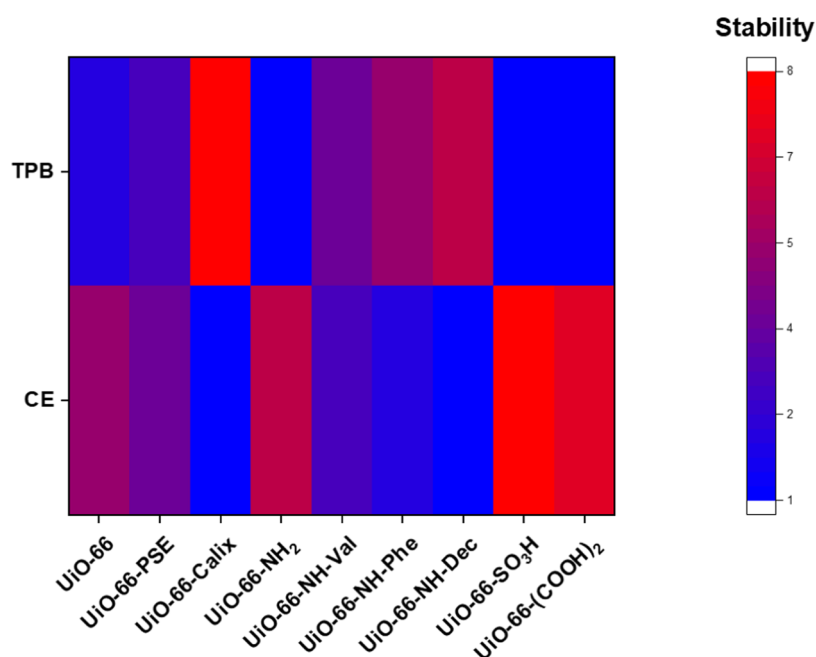


Figure 3. Porous liquid stability index for the prepared UiO–solvent combinations (1 wt % loading), based on Tyndall scattering of light and the natural settling of the UiO overnight.

PLs can be generated. The study's findings might have far-reaching implications for future research into the PL field.

Viscosity. Viscosity is a crucial parameter as it affects the use of PLs in liquid handling settings. The unstable suspended MOFs tend to increase viscosity. The result is that non-modified UiO-66 in both solvents leads to unreliable results due to a large standard deviation, which comes from low dispersion or dissolution and indeed incompatibility between UiO-66 and solvents. In comparison, viscosities of modified UiOs are reliable and consistent and higher than pure solvents as presented in Figure 4 (Figure S20, and Table S6). Although UiO–solvent combinations are increasingly viscous, UiO-66-Calix_{10%}-TPB and UiO-66-SO₃H_{10%}-CE viscosities are still low

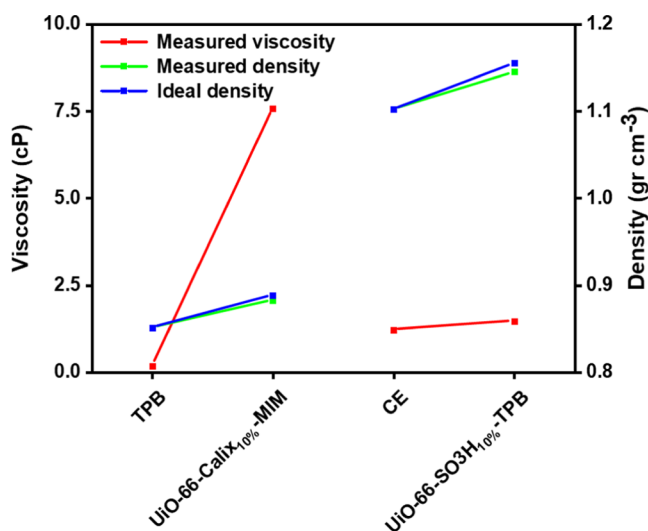


Figure 4. Measured viscosity and ideal and measured densities of UiO porous liquids (10 wt % of UiO to solvent mass; besides, the order of standard deviations values is <5%).

(7.58 and 1.46 mPa s, respectively), owing to their high compatibility with the respective solvents.

Density. The fact that the measured density is lower than the predicted density indicates more porosity in the MOF–solvent combinations compared to the associated solvent.⁴⁰ Figure 4 shows the measured and predicted densities (see Figure S21 and Table S7 for more information). Despite being similar, the measured values are below the confidence interval for the predictions, indicating permanent porosity and avoiding solvent penetration into UiO pores. There were no significant differences observed between the behavior of two samples.

Positron Annihilation Lifetime Spectroscopy (PALS). Positron annihilation lifetime spectroscopy (PALS) gives an accurate and deep intuitive understanding of pore architecture within nanoporous materials. Ortho-positronium (*o*-Ps, bound state between a positron and electron of opposite spin) is established in the empty spaces; the size of the empty spaces can change this species' life span due to annihilation with an electron from the sample of opposite spin. The relative concentrations of the pores are obtainable and given as a percentage (I_3). The PALS results of UiO-66-Calix_{10%}-TPB and UiO-66-SO₃H_{10%}-CE are presented in Figure 5 (Table S8). Based on the PALS results, the suggested structural mechanism is in strong agreement with the density findings. As UiO loading increases, the number of void spaces (intensity) increases in both samples under investigation. In all cases, the lifetimes tended to be shorter than what would be expected for simple additive mixtures. The results demonstrate that the combinations have more, and smaller, void apertures on average than they would have based on the individual components.

High-Pressure Gas Sorption. The permanent porosity in PLs can allow them to possess significant sorption capabilities due to providing extra free volume. Figure 6 shows that these observations are in good agreement with the CO₂ adsorption measurements for PLs. The CO₂ adsorption of TPB and UiO-66-Calix_{10%}-TPB at 10 bar were 1.0 and 1.2 mmol g⁻¹,

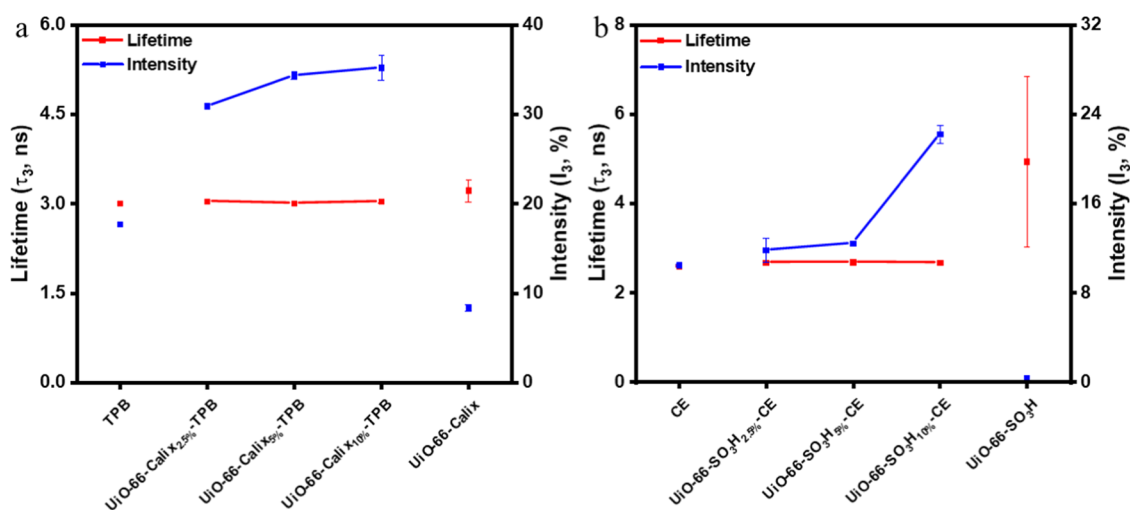


Figure 5. PALS analysis of (a) UiO-66-Calix-TPB and (b) UiO-66-SO₃H-CE PLs (10 wt % of UiO to solvent mass). *UiO-66-SO₃H powders exhibited charging, which affects the measured intensity.

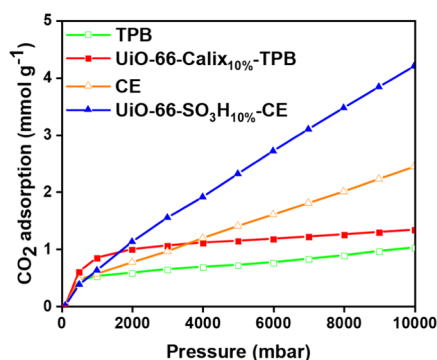


Figure 6. CO₂ sorption capacity of the PLs and solvents at 298 K (10 wt % of UiO to solvent mass).

respectively, 20% higher than the native materials. There is a lower amount of adsorption than the theoretical value due to the partial filling of pores.⁵ The CO₂ adsorption of CE at 10 bar was 2.2 mmol g⁻¹, and UiO-66-SO₃H₁₀%-CE showed a 32% enhancement (2.9 mmol g⁻¹). As a result of extra free volume between UiO-66-SO₃H and CE, the adsorption is higher than expected.²⁴ All of the samples investigated have improved gas adsorption capacity, providing sufficient evidence of solvents with guest accessible porosity.

Comparison of the Current State-of-the-Art Type II and III PLs with This Study. As presented in Table S9, UiO-66-Calix₁₀%-TPB and UiO-66-SO₃H₁₀%-CE provide high adsorption capacities compared to most other Type II and III studies. Furthermore, UiO-66-Calix₁₀%-TPB and UiO-66-SO₃H₁₀%-CE both have low viscosities, high stability, and high solubility and homogeneous dispersity. The combination of all of the aforementioned cases points to the advantages of these PLs over other Type II and III PLs.

Porous Hosts Polar and Nonpolar Modifications Effects on Competitive Hydrophilicity/Phobicity Interactions. The possible interactions of UiO-solvent combinations are strongly dependent on the surrounding solvent and the surface of the MOF.⁴⁰ The exterior surface of UiO-66 contains terephthalate linkers and coordinatively unsaturated Zr centers. It is likely that the imperfect termination of either the metal ion or organic ligands of the alternating framework structure causes the adjacent MOF particles to aggregate under the

influence of electrostatic attraction.⁴¹ Hence, the UiO-66 interaction with adjacent MOFs, as well as their flotation or sedimentation in the solvent, must be overcome through intermolecular interactions. Thus, if there is stronger solvation or chemical binding between UiO and solvent than UiO-UiO, when two UiOs become very close to each other, the van der Waals forces between UiO and UiO emerge as repelling forces that lead to stable dispersions/dissolutions.⁴² Strong intermolecular interactions lead to the dissolution of the porous host in solvent (Type II PL), while weaker interactions cause dispersion of the porous host in solvent (Type III PL).⁵ It is quite interesting that despite the similarity in the base chemical structure of the UiOs, the stabilities of the dispersions/dissolutions prepared in each solvent differ significantly. The hydrophobic TPB and hydrophilic CE solvents can effectively solvate the organic ligands, containing more and stronger hydrophobic and hydrophilic surface functional groups, respectively.⁴³

When polar acidic/basic functional groups are introduced, the side chain becomes more hydrophilic.⁴⁴ As presented in Figure 7a,b, despite the hydrophilic CE solvent's incompatibility with hydrophobic organic linkers, the added sulfonate group enhances the compatibility of the resulting combination. Therefore, CE can solvate the UiO-66-SO₃H weakly. Besides, the CE is sufficiently nucleophilic and possesses good chemical binding affinity for hydrophilic UiO ions and surface functional groups. This implies that the effective van der Waals interactions between Zr⁴⁺ ions of the UiO and sulfur atoms of sulfonate groups with electron-rich oxygen atoms of CE occur at the interface, and consequently, a stable dispersion formation is established (Type III PL).^{21,45,46} On the other hand, the combination of CE and other hydrophilic modified UiOs show weaker behavior in terms of solvation and chemical binding strength.

In contrast, as nonpolar surface functional groups are added, the side chain becomes more hydrophobic.⁴⁴ As presented in Figure 7c,d, the hydrophobic TPB solvent can effectively solvate the UiO-66-Calix due to the high compatibility with the hydrophobic groups including organic ligands' benzene ring and also hydrophobic functional groups. Solvation leads to electron cloud and long-range charge density oscillations around UiO-66, which prevent interpenetration through steric

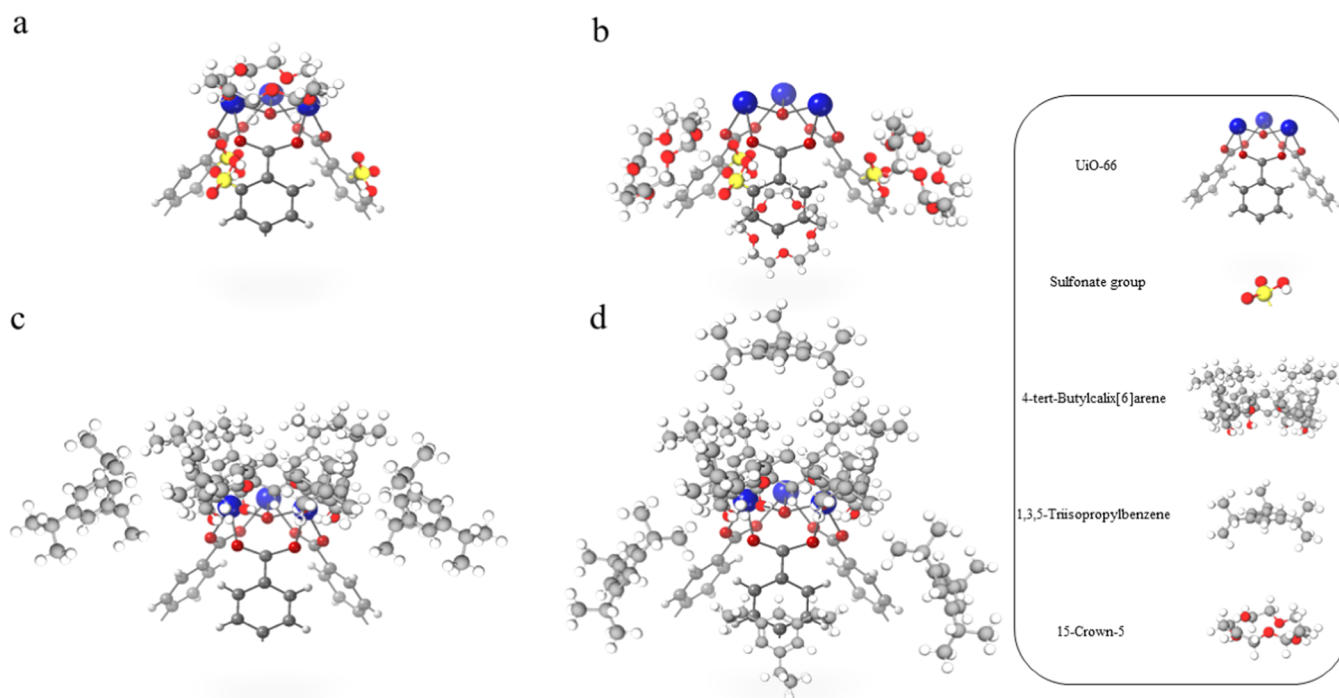


Figure 7. Schematic of the proposed improved mechanisms: (a) chemical binding affinity and (b) solvation of sulfonated UiO-66 (UiO-66-SO₃H) as a polar modification; (c) chemical binding affinity, and (d) solvation of 4-*tert*-butylcalix[6]arene coated UiO-66 (UiO-66-Calix) as a nonpolar modification.

repulsion. Moreover, weak chemical binding between Zr⁴⁺ ions of the UiO-66 and electrons of the benzene causes weak van der Waals interactions, which also contribute to a better dissolution.^{36,41,42,46} As a result, 4-*tert*-butylcalix[6]arene is a macrocyclic supramolecule that renders UiO-66 form a stable Type II PL. However, the solvation and chemical binding strength of other hydrophobic-modified UiO–solvent combinations are weaker.

CONCLUSIONS

While Type II and III PLs attract wide interest due to combining the fluidity and mass transfer properties of fluids with the permanent porosity and molecular sieving properties of the porous host; their stability is generally limited, lessening the possible use cases. Therefore, to expand the parametric space where functional PLs can be generated, a fundamental understanding of how the different MOF modification methods help PL formation is critical. In the foregoing, we reported that the MOF polar and nonpolar modifications influence stable PL formation through hydrophilicity/phobicity and van der Waals interactions between the porous host and solvent.

The hydrophobic TPB solvent can effectively solvate the UiO-66-Calix due to its high compatibility with the hydrophobic groups. Moreover, weak chemical binding causes weak van der Waals interactions, which also contribute to a better dissolution in a stable Type II PL. Although the hydrophilic CE solvent is not compatible with organic ligands, the added sulfonate group of UiO-66-SO₃H enhanced compatibility and therefore solvation. Besides, the high nucleophilicity and chemical binding affinity of CE toward UiO-66-SO₃H lead to van der Waals interactions and consequently a stable dispersion of Type III PL. In contrast, the other UiO–solvent combinations exhibit weaker behavior. Some characteristics of

the modified UiOs were affected by exposure to the solvents due to strong interactions. The measured densities of UiO-based PLs were less than the ideal mixture density. The CO₂ sorption capacities of the UiOs PLs were enhanced than the pure solvents over the entire measured pressure range.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsami.2c03082>.

Further details of the chemicals, UiO synthesis and modifications, solvent, PL preparation conditions, Fourier transform infrared (FTIR) spectroscopy, powder X-ray diffraction (PXRD), thermogravimetric analysis (TGA), X-ray photoelectron spectroscopy (XPS), proton nuclear magnetic resonance (¹H NMR), low-pressure gas sorption, scanning electron microscopy (SEM), PL stability, fluidity properties, density, positron annihilation lifetime spectroscopy (PALS), and high-pressure gas sorption (PDF)

AUTHOR INFORMATION

Corresponding Authors

Stefan J. D. Smith – Department of Chemical and Biological Engineering, Monash University, Clayton, VIC 3800, Australia; CSIRO Manufacturing, Clayton South, VIC 3169, Australia; orcid.org/0000-0001-7465-0565; Email: stefan.smith@monash.edu

Xavier Mulet – CSIRO Manufacturing, Clayton South, VIC 3169, Australia; Email: xavier.mulet2@rmit.edu.au

Matthew R. Hill – Department of Chemical and Biological Engineering, Monash University, Clayton, VIC 3800, Australia; CSIRO Manufacturing, Clayton South, VIC 3169,

Australia; orcid.org/0000-0001-8897-0324;
Email: matthew.hill@monash.edu, matthew.hill@csiro.au

Authors

Hamidreza Mahdavi – Department of Chemical and Biological Engineering, Monash University, Clayton, VIC 3800, Australia; orcid.org/0000-0001-8175-4303

Nathan T. Eden – Department of Chemical and Biological Engineering, Monash University, Clayton, VIC 3800, Australia; orcid.org/0000-0002-1456-1381

Cara M. Doherty – CSIRO Manufacturing, Clayton South, VIC 3169, Australia

Durga Acharya – CSIRO Manufacturing, Clayton South, VIC 3169, Australia; orcid.org/0000-0001-6900-6230

Complete contact information is available at:
<https://pubs.acs.org/10.1021/acsami.2c03082>

Author Contributions

H.M. led the project administration, conceptual and experimental design, analysis, interpretation of results, and writing the draft. N.T.E. participated in UiO synthesis, modifications, and characterization interpretations. C.M.D. and D.A. led the experimental design and data curation of PALS experiments presented. S.J.D.S., X.M., and M.R.H. contributed to the project administration, conceptual and experimental design, analysis, and interpretation of results.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

The authors acknowledge the use of facilities within the Monash X-ray Platform and Monash Centre for Electron Microscopy.

REFERENCES

- (1) Mahdavi, H. R.; Smith, S. J. D.; Mulet, X.; Hill, M. R. Practical Considerations in the Design and Use of Porous Liquids. *Mater. Horiz.* **2022**, DOI: [10.1039/D1MH01616D](https://doi.org/10.1039/D1MH01616D).
- (2) Giri, N.; Del Pópolo, M. G.; Melaugh, G.; Greenaway, R. L.; Rätzke, K.; Koschine, T.; Pison, L.; Gomes, M. F. C.; Cooper, A. I.; James, S. L. Liquids with Permanent Porosity. *Nature* **2015**, *527*, 216.
- (3) James, S. L. The Dam Bursts for Porous Liquids. *Adv. Mater.* **2016**, *28*, 5712–5716.
- (4) Greenaway, R. L.; Holden, D.; Eden, E. G. B.; Stephenson, A.; Yong, C. W.; Bennison, M. J.; Hasell, T.; Briggs, M. E.; James, S. L.; Cooper, A. I. Understanding Gas Capacity, Guest Selectivity, and Diffusion in Porous Liquids. *Chem. Sci.* **2017**, *8*, 2640–2651.
- (5) Shan, W.; Fulvio, P. F.; Kong, L.; Schott, J. A.; Do-Thanh, C.-L.; Tian, T.; Hu, X.; Mahurin, S. M.; Xing, H.; Dai, S. New Class of Type III Porous Liquids: A Promising Platform for Rational Adjustment of Gas Sorption Behavior. *ACS Appl. Mater. Interfaces* **2018**, *10*, 32–36.
- (6) Zhang, J.; Chai, S.-H.; Qiao, Z.-A.; Mahurin, S. M.; Chen, J.; Fang, Y.; Wan, S.; Nelson, K.; Zhang, P.; Dai, S. Porous Liquids: A Promising Class of Media for Gas Separation. *Angew. Chem., Int. Ed.* **2015**, *54*, 932–936.
- (7) O'Reilly, N.; Giri, N.; James, S. L. Porous Liquids. *Chem. - Eur. J.* **2007**, *13*, 3020–3025.
- (8) Smith, S. J. D.; Wood, C. D.; Feron, P. H. M.; Mahdavi, H.; Mulder, R. J.; Doherty, C. M.; Hill, M. R.; Mulet, X. Porous Solid Inspired Hyper-Crosslinked Polymer Liquids with Highly Efficient Regeneration for Gas Purification. *Sci. China Mater.* **2022**, *348*, 1–6.
- (9) Nakanishi, T., *Functional Organic Liquids*; Wiley, 2019.
- (10) Wright, P. A.; Chemistry, R. S. o., *Microporous Framework Solids*; RSC Publishing, 2008.
- (11) Cheetham, A. K.; Férey, G.; Loiseau, T. Open-Framework Inorganic Materials. *Angew. Chem., Int. Ed.* **1999**, *38*, 3268–3292.
- (12) Li, J.-R.; Kuppler, R. J.; Zhou, H. C. Selective Gas Adsorption and Separation in Metal–Organic Frameworks. *Chem. Soc. Rev.* **2009**, *38*, 1477–1504.
- (13) Slater, A. G.; Cooper, A. I. Function-Led Design of New Porous Materials. *Science* **2015**, *348*, No. aaa8075.
- (14) Zhou, H.-C. J.; Kitagawa, S. Metal–Organic Frameworks (MOFs). *Chem. Soc. Rev.* **2014**, *43*, 5415–5418.
- (15) Park, K. S.; Ni, Z.; Côté, A. P.; Choi, J. Y.; Huang, R.; Uribe-Romo, F. J.; Chae, H. K.; O'Keeffe, M.; Yaghi, O. M. Exceptional Chemical and Thermal Stability of Zeolitic Imidazolate Frameworks. *Proc. Natl. Acad. Sci. U.S.A.* **2006**, *103*, 10186.
- (16) Kearsley, R. J.; Alston, B. M.; Briggs, M. E.; Greenaway, R. L.; Cooper, A. I. Accelerated Robotic Discovery of Type II Porous Liquids. *Chem. Sci.* **2019**, *10*, 9454–9465.
- (17) Giri, N.; Davidson, C. E.; Melaugh, G.; Del Pópolo, M. G.; Jones, J. T. A.; Hasell, T.; Cooper, A. I.; Horton, P. N.; Hursthouse, M. B.; James, S. L. Alkylated Organic Cages: from Porous Crystals to Neat Liquids. *Chem. Sci.* **2012**, *3*, 2153–2157.
- (18) Cahir, J.; Tsang, M. Y.; Lai, B.; Hughes, D.; Alam, M. A.; Jacquemin, J.; Rooney, D.; James, S. L. Type 3 Porous Liquids Based on Non-Ionic Liquid Phases - A Broad and Tailorable Platform of Selective, Fluid Gas Sorbents. *Chem. Sci.* **2020**, *11*, 2077–2084.
- (19) James, S.; Tsang, M. Y.; Cahir, J.; Rooney, D. Porous Liquids. U.S. Patent No. US2020/0330919 A12017.
- (20) Kitagawa, S.; Kitaura, R.; Noro, S.-i. Functional Porous Coordination Polymers. *Angew. Chem., Int. Ed.* **2004**, *43*, 2334–2375.
- (21) Liu, S.; Liu, J.; Hou, X.; Xu, T.; Tong, J.; Zhang, J.; Ye, B.; Liu, B. Porous Liquid: A Stable ZIF-8 Colloid in Ionic Liquid with Permanent Porosity. *Langmuir* **2018**, *34*, 3654–3660.
- (22) Li, Y.; Liu, J.; Zhang, K.; Lei, L.; Lei, Z. UiO-66-NH₂@PMAA: A Hybrid Polymer–MOFs Architecture for Pectinase Immobilization. *Ind. Eng. Chem. Res.* **2018**, *57*, 559–567.
- (23) Kalaj, M.; Denny, M.; Bentz, K.; Palomba, J.; Cohen, S. M. Nylon-MOF Composites via Postsynthetic Polymerization. *Angew. Chem., Int. Ed.* **2019**, *131*, 2358–2362.
- (24) Yin, J.; Zhang, J.; Fu, W.; Jiang, D.; Lv, N.; Liu, H.; Li, H.; Zhu, W. Theoretical Prediction of the SO₂ Absorption by Hollow Silica based Porous Ionic Liquids. *J. Mol. Graph. Model.* **2021**, *103*, No. 107788.
- (25) Abánades Lázaro, I.; Haddad, S.; Sacca, S.; Orellana-Tavara, C.; Fairen-Jimenez, D.; Forgan, R. S. Selective Surface PEGylation of UiO-66 Nanoparticles for Enhanced Stability, Cell Uptake, and pH-Responsive Drug Delivery. *Chem* **2017**, *2*, 561–578.
- (26) Venna, S. R.; Lartey, M.; Li, T.; Spore, A.; Kumar, S.; Nulwala, H. B.; Luebke, D. R.; Rosi, N. L.; Albenze, E. Fabrication of MMMs with Improved Gas Separation Properties Using Externally-Functionalized MOF Particles. *J. Mater. Chem. A* **2015**, *3*, 5014–5022.
- (27) Morris, W.; Briley, W. E.; Auyeung, E.; Cabezas, M. D.; Mirkin, C. A. Nucleic Acid–Metal Organic Framework (MOF) Nanoparticle Conjugates. *J. Am. Chem. Soc.* **2014**, *136*, 7261–7264.
- (28) McGuire, C. V.; Forgan, R. S. The Surface Chemistry of Metal–Organic Frameworks. *Chem. Commun.* **2015**, *51*, 5199–5217.
- (29) Wang, S.; Morris, W.; Liu, Y.; McGuirk, C. M.; Zhou, Y.; Hupp, J. T.; Farha, O. K.; Mirkin, C. A. Surface-Specific Functionalization of Nanoscale Metal–Organic Frameworks. *Angew. Chem., Int. Ed.* **2015**, *54*, 14738–14742.
- (30) He, C.; Lu, K.; Lin, W. Nanoscale Metal–Organic Frameworks for Real-Time Intracellular pH Sensing in Live Cells. *J. Am. Chem. Soc.* **2014**, *136*, 12253–12256.
- (31) He, C.; Liu, D.; Lin, W. Nanomedicine Applications of Hybrid Nanomaterials Built from Metal–Ligand Coordination Bonds: Nanoscale Metal–Organic Frameworks and Nanoscale Coordination Polymers. *Chem. Rev.* **2015**, *115*, 11079–11108.
- (32) He, C.; Lu, K.; Liu, D.; Lin, W. Nanoscale Metal–Organic Frameworks for the Co-Delivery of Cisplatin and Pooled siRNAs to Enhance Therapeutic Efficacy in Drug-Resistant Ovarian Cancer Cells. *J. Am. Chem. Soc.* **2014**, *136*, 5181–5184.

(33) Rieter, W. J.; Taylor, K. M. L.; Lin, W. Surface Modification and Functionalization of Nanoscale Metal–Organic Frameworks for Controlled Release and Luminescence Sensing. *J. Am. Chem. Soc.* **2007**, *129*, 9852–9853.

(34) Jeong, U.; Dogan, N. A.; Garai, M.; Nguyen, T. S.; Stoddart, J. F.; Yavuz, C. T. Inversion of Dispersion: Colloidal Stability of Calixarene-Modified Metal–Organic Framework Nanoparticles in Nonpolar Media. *J. Am. Chem. Soc.* **2019**, *141*, 12182–12186.

(35) Morris, W.; Wang, S.; Cho, D.; Auyeung, E.; Li, P.; Farha, O. K.; Mirkin, C. A. Role of Modulators in Controlling the Colloidal Stability and Polydispersity of the UiO-66 Metal–Organic Framework. *ACS Appl. Mater. Interfaces* **2017**, *9*, 33413–33418.

(36) Annapureddy, H. V. R.; Nune, S. K.; Motkuri, R. K.; McGrail, B. P.; Dang, L. X. A Combined Experimental and Computational Study on the Stability of Nanofluids Containing Metal Organic Frameworks. *J. Phys. Chem. B* **2015**, *119*, 8992–8999.

(37) He, S.; Chen, L.; Cui, J.; Yuan, B.; Wang, H.; Wang, F.; Yu, Y.; Lee, Y.; Li, T. General Way To Construct Micro- and Mesoporous Metal–Organic Framework-Based Porous Liquids. *J. Am. Chem. Soc.* **2019**, *141*, 19708–19714.

(38) Zhao, X.; Yuan, Y.; Li, P.; Song, Z.; Ma, C.; Pan, D.; Wu, S.; Ding, T.; Guo, Z.; Wang, N. A Polyether Amine Modified Metal Organic Framework Enhanced the CO₂ Adsorption Capacity of Room Temperature Porous Liquids. *Chem. Commun.* **2019**, *55*, 13179–13182.

(39) Knebel, A.; Bavykina, A.; Datta, S. J.; Sundermann, L.; Garzon-Tovar, L.; Lebedev, Y.; Durini, S.; Ahmad, R.; Kozlov, S. M.; Shterk, G.; Karunakaran, M.; Carja, I. D.; Simic, D.; Weilert, I.; Klüppel, M.; Giese, U.; Cavallo, L.; Rueping, M.; Eddaoudi, M.; Caro, J.; Gascon, J. Solution Processable Metal–Organic Frameworks for Mixed Matrix Membranes Using Porous Liquids. *Nat. Mater.* **2020**, *19*, 1346–1353.

(40) Costa Gomes, M.; Pison, L.; Červinka, C.; Padua, A. Porous Ionic Liquids or Liquid Metal–Organic Frameworks? *Angew. Chem., Int. Ed.* **2018**, *57*, 11909–11912.

(41) Liu, H.; Liu, B.; Lin, L. C.; Chen, G.; Wu, Y.; Wang, J.; Gao, X.; Lv, Y.; Pan, Y.; Zhang, X.; Zhang, X.; Yang, L.; Sun, C.; Smit, B.; Wang, W. A Hybrid Absorption-Adsorption Method to Efficiently Capture Carbon. *Nat. Commun.* **2014**, *5*, No. 5147.

(42) Zhang, H.; Dasbiswas, K.; Ludwig, N. B.; Han, G.; Lee, B.; Vaikuntanathan, S.; Talapin, D. V. Stable Colloids in Molten Inorganic Salts. *Nature* **2017**, *542*, 328–331.

(43) Mahdavi, H.; Zhang, H.; Macreadie, L. K.; Doherty, C. M.; Acharya, D.; Smith, S. J. D.; Mulet, X.; Hill, M. R. Underlying Solvent-Based Factors that Influence Permanent Porosity in Porous Liquids. *Nano Res.* **2021**, 3533–3538.

(44) Chen, W.; Duan, L.; Zhu, D. Adsorption of Polar and Nonpolar Organic Chemicals to Carbon Nanotubes. *Environ. Sci. Technol.* **2007**, *41*, 8295–8300.

(45) Atilhan, M.; Cincotti, A.; Aparicio, S. Nanoscopic Characterization of Type II Porous Liquid and its Use for CO₂ Absorption from Molecular Simulation. *J. Mol. Liq.* **2021**, *330*, No. 115660.

(46) Liu, H.; Pan, Y.; Liu, B.; Sun, C.; Guo, P.; Gao, X.; Yang, L.; Ma, Q.; Chen, G. Tunable Integration of Absorption-Membrane Adsorption for Efficiently Separating Low Boiling Gas Mixtures Near Normal Temperature. *Sci. Rep.* **2016**, *6*, No. 21114.