Toward MOF@Polymer Core−Shell Particles: Design Principles and Potential Applications

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CONSPECTUS: Compositing MOFs with polymers brings out the best properties of both worlds. The solubility and excellent mechanical properties of polymers endow the brittle, powdery MOFs with enhanced processability, thereby enriching their functions as solid sorbents, filters, membranes, catalysts, drug delivery vehicles, and so forth. While most MOF−polymer composites are random mixtures of two materials with little control over their fine structures, MOF@polymer core−shell particles have recently emerged as a new platform for precise composite design. The well-defined polymer coating can keep the rich pore characteristics of the MOF intact while furnishing the MOF with new properties such as improved dispersibility in various media, tunable surface energy, enhanced chemical stability, and regulated guest diffusion. Nevertheless, the structural and chemical complexity of MOFs poses a grand challenge to the development of a generalizable and feasible strategy for constructing MOF@polymer. Examples in the literature that showcase the presence of a well-defined polymer shell on the MOF with fully reserved porosity are rare. Moreover, methods for coating MOFs with condensation polymers (e.g., polyimide, polysulfone) are severely underexplored, despite their clear potential as membrane materials. In this Account, we present our group's effort over the past 4 years on the synthesis and applications of MOF@polymer composites. We first described a highly generalizable surface polymerization method that utilizes the rapid physisorption of a random copolymer (RCP) to carry initiating groups to the MOF surfaces. Subsequent controlled radical polymerization led to the formation of a uniform methacrylate or styrenic polymer on the MOF with tunable thickness and composition. To utilize the properties of condensation polymers, we pioneered the covalent grafting of polyimide (PI) brushes to UiO-66-NH₂ surfaces. In addition, to circumvent the need for a covalent anchoring group, we further developed an MOF surface grafting method based on mechanical linkage. Instead of connecting to the ligand, polyimide (PI) oligomer was linked to a functionalized linear polymer physically entangled within an MOF, thus realizing surface grafting with PI. Alternatively, PIs, polysulfone (PSF), and polycarbonate (PC) can also be grafted to various MOF surfaces through a metal−organic nanocapsule (MONC)-mediated method using a combination of electrostatic interaction and coordination bonds. To find a rapid and low-cost surface coating method suitable for commercialization, a new approach called non-solvent-induced surface-aimed deposition (NISAP) was developed. The action of the solvent phase separation drives dianhydrides and polyamines to the MOF surface, thus realizing accelerated polymerization and the rapid formation of a polymer coating on the MOF. Finally, we provided an overview of the unique properties and potential applications of MOF@polymer composites, including improved stability, MMMs, porous liquids (PLs), and immobilizing homogeneous catalysts. We hope that this Account can inspire more researchers to further develop and optimize the synthetic strategies for MOF@polymer and uncover its full application potential.
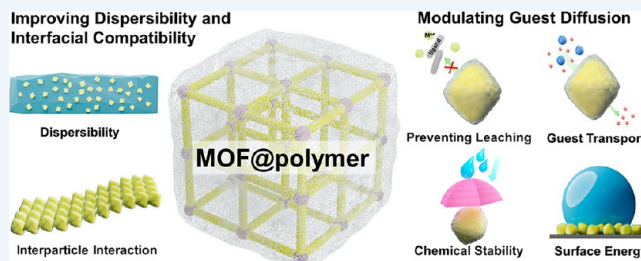
■ KEY REFERENCES

- Wang, H.; He, S.; Qin, X.; Li, C.; Li, T. Interfacial Engineering in Metal-Organic Framework-Based Mixed Matrix Membranes Using Covalently Grafted Polyimide Brushes. *J. Am. Chem. Soc.* **2018**, 140, 17203−17210.[1] *Polyimide brushes were covalently grafted on an MOF surface for the first time to improve the interfacial compatibility, mechanical properties, and gas transport properties of the MMMs.*

- He, S.; Wang, H.; Zhang, C.; Zhang, S.; Yu, Y.; Lee, Y.; Li, T. A Generalizable Method for the Construction of MOF@polymer Functional Composites through Surface-Initiated Atom Transfer Radical Polymerization *Chem. Sci.* **2019**, 10, 1816−1822.[2] *A highly generalizable surface polymerization method was developed to construct MOF@*
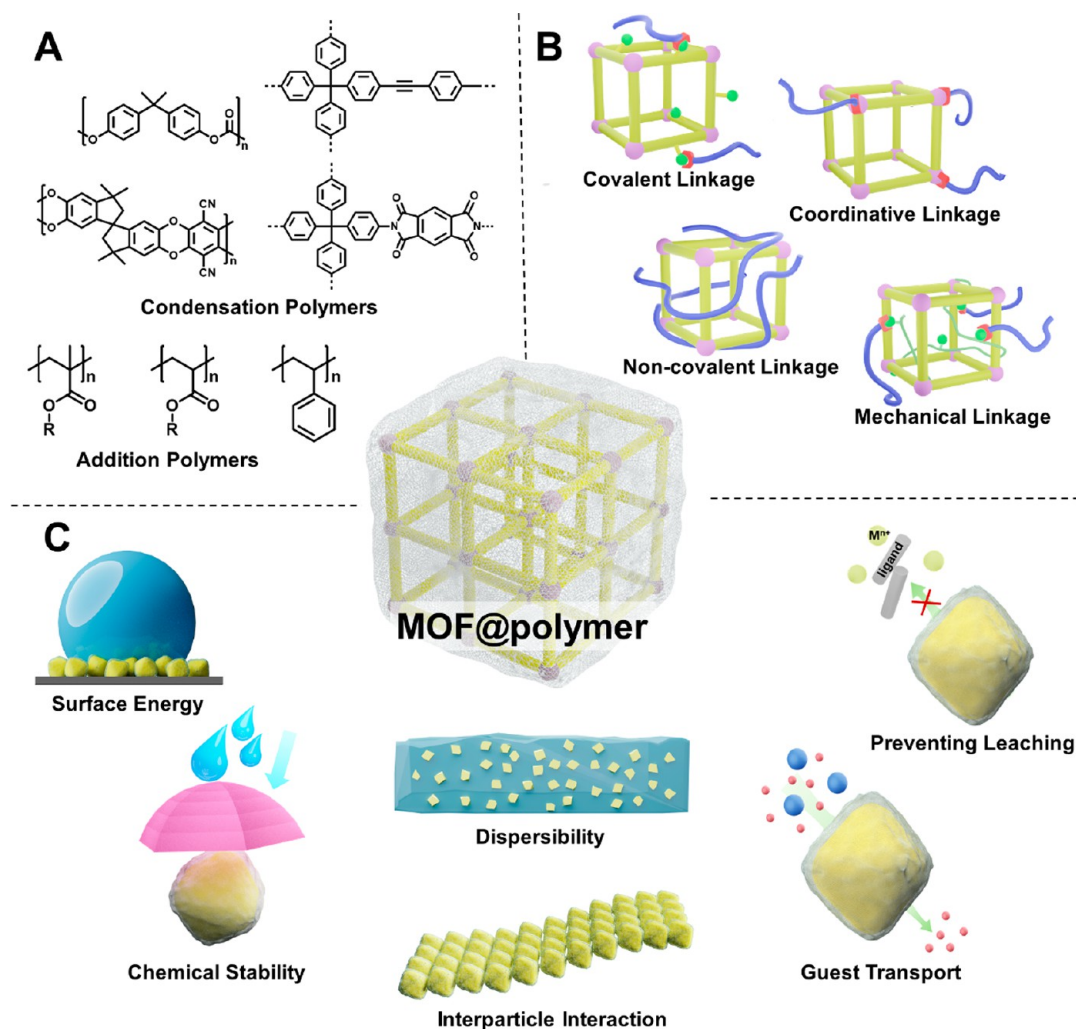
Figure 1. Schematic illustration of (A) various polymer structures, (B) types of linkages at the MOF−polymer interface, and (C) unique functions of the polymer coating.

polymer particles with tunable surface composition and thickness.

- 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.[3] *MOF@polymer particles were dispersed in bulky polydimethylsiloxane liquids to afford type III porous liquids simultaneously possessing fluidity and permanent porosity.*

- Wang, D.; Li, S.; Wu, C.; Li, T. Surface-Seal Encapsulation of a Homogeneous Catalyst in a Mesoporous Metal-Organic Framework. *J. Am. Chem. Soc.* **2022**, *144*, 685−689.[4] *A rapid surface polymerization method was developed to physically seal and immobilize homogeneous catalyst molecules as reusable catalysts.*

1. INTRODUCTION

Metal−organic frameworks (MOFs) are a fascinating class of crystalline porous materials constructed through the molecular assembly of inorganic nodes and multivalent organic ligands.[5−8] The endless combination of molecular building blocks for MOF construction has pushed the limits of MOF materials in terms of surface area,[9] functionality,[10] gas storage capacity,[11] and separation factors[12] beyond what is achievable by traditional porous materials.

Nevertheless, MOFs, like any other crystalline material, exist primarily in a powdery form. This poses a major challenge for subsequent materials' handling and processing.[13,14] To make MOFs suitable for industrial use, MOFs are often dispersed in or mixed with polymers into composites.[15−17] In this context, the dispersibility of MOF particles and their interfacial compatibility with polymers become two determining factors that govern the morphologies of the composites and ultimately their properties and utilities.[1,18−20]

While a majority of the MOF−polymer composites are random mixtures, one special type of composite featuring an MOF core and a thin, yet uniform polymer shell has recently stood out. Due to its unique core−shell architecture, we termed it as MOF@polymer.[2] Apart from a clear core−shell structure, a true MOF@polymer should also feature a clean MOF−polymer phase boundary, meaning that the MOF phase should be free of infiltrated polymer. In this way, the MOF core can fully preserve its pore characteristics. While we are progressing toward that goal, in this Account, we will also include examples that partially retain MOF porosity and emphasize our effort toward a true MOF@polymer composite. In principle, the polymer coating allows MOF@polymer particles to be easily incorporated into
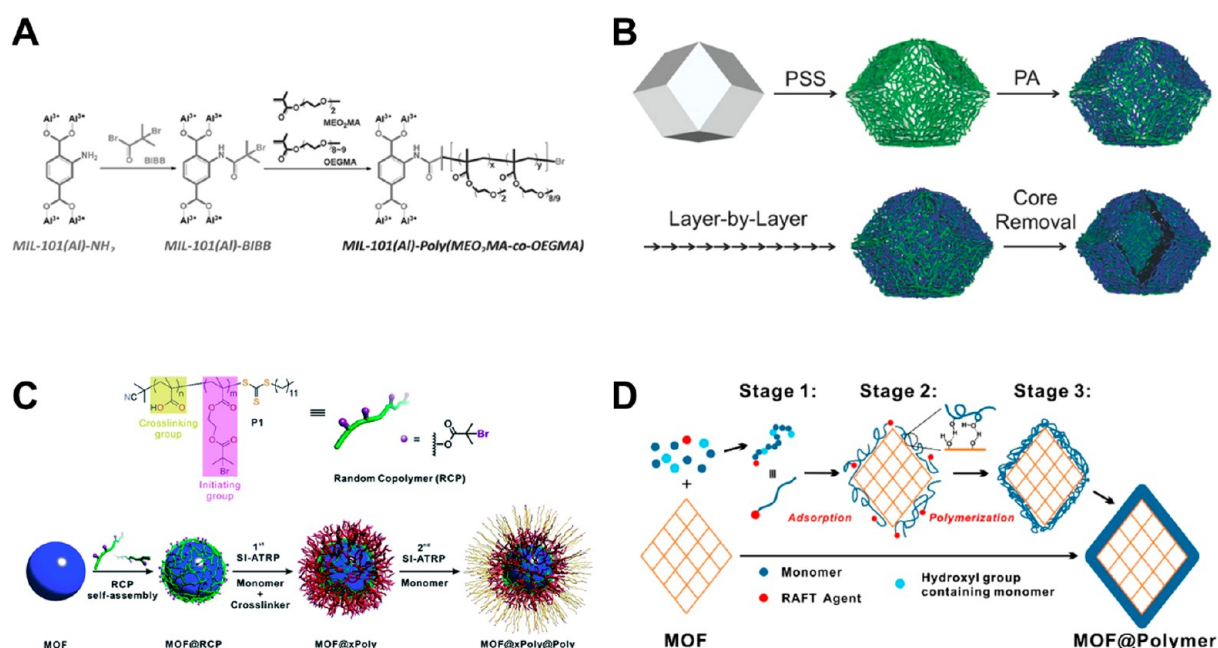
Figure 2. (A) SI-ATRP on MIL-101(Al) based on a covalently anchored initiator. Reproduced with permission from ref 31. Copyright 2015 Wiley-VCH. (B) Schematic illustration of the layer-by-layer assembly of polyelectrolytes on ZIF-8 crystals followed by MOF digestion to form faceted polymer microcapsules. Adapted with permission from ref 37. Copyright 2013 Wiley-VCH. (C) Schematic illustration of noncovalent SI-ATRP. Adapted with permission from ref 2. Copyright 2019 Royal Society of Chemistry. (D) Schematic illustration of MOF surface polymerization through the PISA process. Adapted with permission from ref 28. Copyright 2021 American Chemical Society.

polymer matrixes with improved dispersibility and interfacial adhesion.[3,21,22] Meanwhile, MOF@polymer can also be viewed as a stand-alone composite in which the polymer layer endows the MOF with new functions such as (1) controlling the surface energy,[2,23] (2) regulating guest transport,[24] (3) preventing leaching,[4] (4) improving the chemical stability of the MOF,[2] and (5) modulating interparticle interaction.[25]

Nevertheless, unlike conventional inorganic materials that often exhibit a known surface composition, MOF materials present complex chemistry involving elements all over the periodic table.[26,27] This makes it an arduous task to develop strategies for the construction of MOF@polymer suitable for various polymers and MOFs. That also means that different linkages and interactions need to be taken advantage of for designing an MOF surface coating method. In addition, the open pores of MOFs will allow the infiltration of monomers, thus negatively impacting its porosity. Some of these complications are unique to MOF materials, thereby posing a new set of challenges for polymer chemistry as well as material science.

In this Account, we mainly focus on our recent contributions in the development of innovative strategies to construct MOF@polymer composites and explore their unique functions thereof. First, we presented some of the key strategies to graft addition polymers[2,28] (e.g., methacrylate and styrenic polymers) and condensation polymers[1,4,22,29] (e.g., PI, PSF, and PC) to MOF surfaces using different interfacial interactions (Figure 1A,B). Special emphasis is placed on PI coatings because they are critical to addressing the interfacial compatibility issue in MMMs. Next, the functions of the polymer coatings and the potential applications of MOF@polymer are outlined and discussed (Figure 1C). Finally, the key challenges and potential future directions of these materials are given.

2. STRATEGIES FOR CONSTRUCTING MOF@POLYMER COMPOSITES

Addition and condensation polymers are two main categories of polymers. Incorporating them into MOF@polymer composites requires different synthetic and fabrication methods. In this section, we divide MOF@polymer construction strategies based on these two polymer types.

2.1. Addition Polymers

Methacrylate and acrylate polymers are the most widely studied polymers for MOF surface grafting mainly due to their controllable synthesis, rich selection of monomers, and wide span of physical and chemical properties. The first such example was demonstrated in 2015 by Liu and co-workers in which they functionalized MIL-101(Al)-NH$_2$[30] with a polymerization initiator, α-bromoisobutyryl bromide (BiBB).[31] Copolymers of 2-(2-methoxyethoxy)ethyl methacrylate and oligo(ethylene glycol) methacrylate were then grown off of the BiBB initiating group presented on the MOF through copper-catalyzed atom-transfer radical polymerization (ATRP) (Figure 2A). A similar approach was later adopted by Matzger, Webley, Qiao, and many others.[21,32−34] Alternatively, amine-functionalized MOF can also be prefunctionalized with a methacrylic/acrylic monomer followed by copolymerization with excess monomers to establish a cross-linked and covalently bonded surface polymer coating.[35,36]

The downside of covalent surface modification is the requirement of a prefunctionalized ligand in the MOF, which makes it less generalizable. In comparison, MOF surface modification based on the physisorption of polymers is more universal. This is because the open metal sites (OMSs) presented on the MOF surfaces are often covered by neutral or negatively charged coordinating molecules/ions such as H$_2$O and OH$^-$, which can interact with polymers through hydrogen bonds or electrostatic interaction.[37,38] Due to its simplicity, this
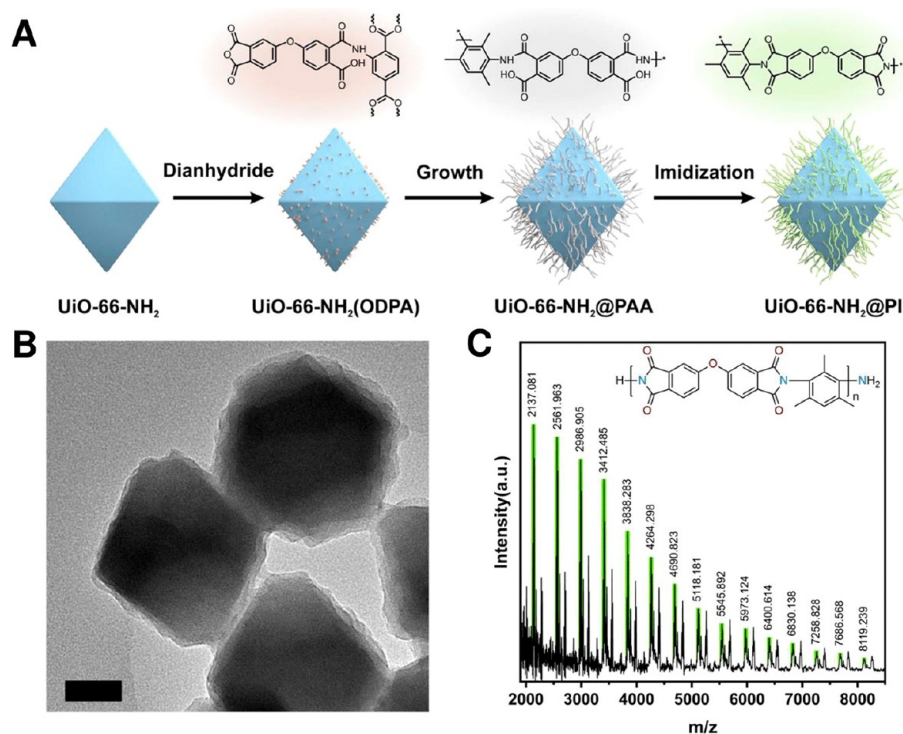
Figure 3. (A) Synthetic procedures of UiO-66-NH$_2$@PI. (B) TEM image of UiO-66-NH$_2$@PI, scale bar 50 nm. (C) MALDI-TOF spectra of the digested UiO-66-NH$_2$@PI. The peaks highlighted in green correspond to the given polymer structure. Adapted with permission from ref 1. Copyright 2018 American Chemical Society.

"noncovalent" approach has been widely adopted to increase the dispersibility of MOF particles in various solvent media. For instance, the physisorption of polyvinylpyrrolidone (PVP) and methacrylate polymers on MOFs can substantially improve the dispersibility of MOF nanoparticles in aqueous media.[38] We also utilized the surface adsorption of methacrylate RCPs containing both carboxylic acid and pyridine pendant groups to facilitate the nucleation and growth of ZIF-8 on Zr, Al, and Cr MOF surfaces into novel core–shell MOFs.[39]

However, apart from the rare example of the layer-by-layer assembly of polyelectrolytes,[37] polymer physisorption often leads to a thin and invisible polymer coating on the MOF (Figure 2B). This aspect greatly limits the in-depth exploration of MOF@polymer materials.

To combine the well-defined characteristics of a covalently grafted polymer coating with the generalizability of a non-covalent modification method, our group developed a non-covalent SI-ATRP method for the fabrication of MOF@polymer.[2] The method first allows an RCP that simultaneously contains a binding moiety (e.g., carboxylic acid) and an ATRP initiator (e.g., BiBB) to predecorate the MOF surface through rapid physisorption. The multipoint hydrogen bond cross-linking between the RCP chains and the MOF–polymer interface warrants the initiating groups firmly staying on the surfaces of the MOF despite the lack of a covalent linkage. Subsequent polymerization from the initiator in the presence of a cross-linking monomer permanently immobilizes the polymer chains on the MOF surface, leading to uniform and well-defined coatings with thickness tunable from a few nanometers to ~100 nm (Figure 2C). We demonstrated the ability to continuously tune the surface wettability of UiO-66 by grafting a hydrophilic polymer such as poly(hydroxyethyl acrylate), a hydrophobic polymer such as poly(1H,1H,2H,2H-perfluorodecyl methacry-

late), or copolymers composed of different monomers. Unlike most other covalent surface polymer grafting approaches that do not have a mechanism to prevent polymer infiltration, our approach limits the macroinitiator on the MOF surface, thus effectively preventing in-pore polymerization. As a result, the porosity of the MOF remains largely unchanged in the form of MOF@polymer.

Despite the success, the above method is a tedious multistep process. For improvement, a facile one-step MOF surface polymerization method was developed.[28] Here, an MOF was mixed with monomers, a reversible addition–fragmentation chain-transfer (RAFT)[40] agent, and a radical initiator in one pot. Note that a small amount of a hydrogen-bond-donating monomer such as 2-hydroxyethyl methacrylate (HEMA) or acrylic acid (AA) must be included in the monomer mixture. In the early stage of polymerization, polymer formed in the solvent. However, the elongation of the RCP chain increases its interaction with the MOF surface through hydrogen bonding, leading to its physisorption on the MOF. Further polymerization occurs on the MOF surface, thereby affording well-defined MOF@polymer particles (Figure 2D). We named this method polymerization-induced surface adsorption (PISA). The porosity of the MOF can also be largely retained during this process.

2.2. Condensation Polymers

While many strategies have been developed for the covalent grafting of chain-growth polymers on MOF surfaces, grafting condensation polymers through step-growth polymerization is still a widely underexplored territory. On the other hand, condensation polymers are fascinating materials often featuring high strength, high heat resistance, high porosity, and high chemical stability.[41] Exploiting condensation polymers as
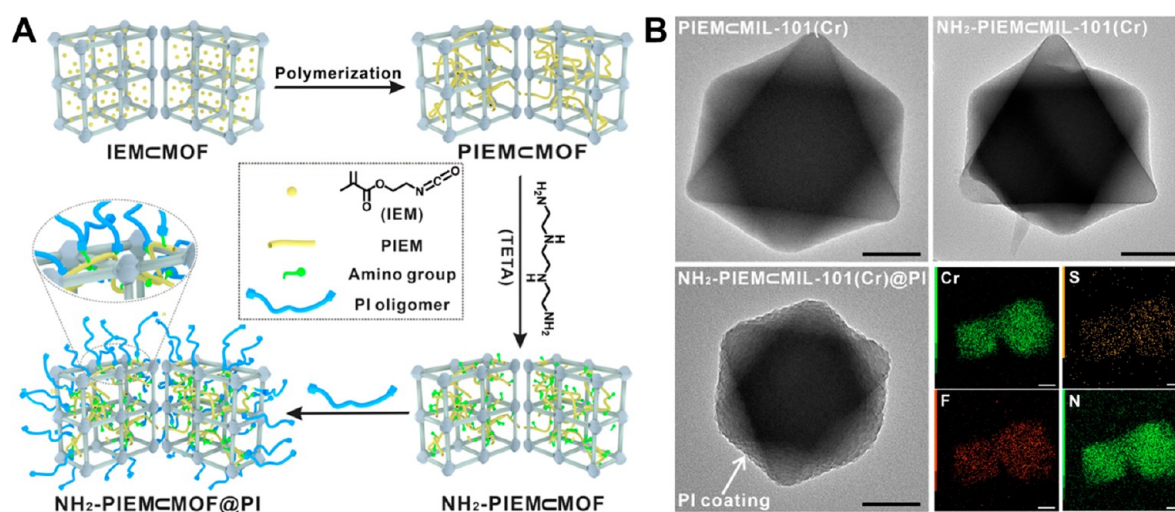
Figure 4. (A) Schematic illustration of MOF surface modification through physical chain entanglement. (B) TEM images of MOF particles in different modification steps and EDS element mapping of NH$_2$-PIEM⊂MOF@PI. Adapted with permission from ref 29. Copyright 2021 Wiley-VCH.
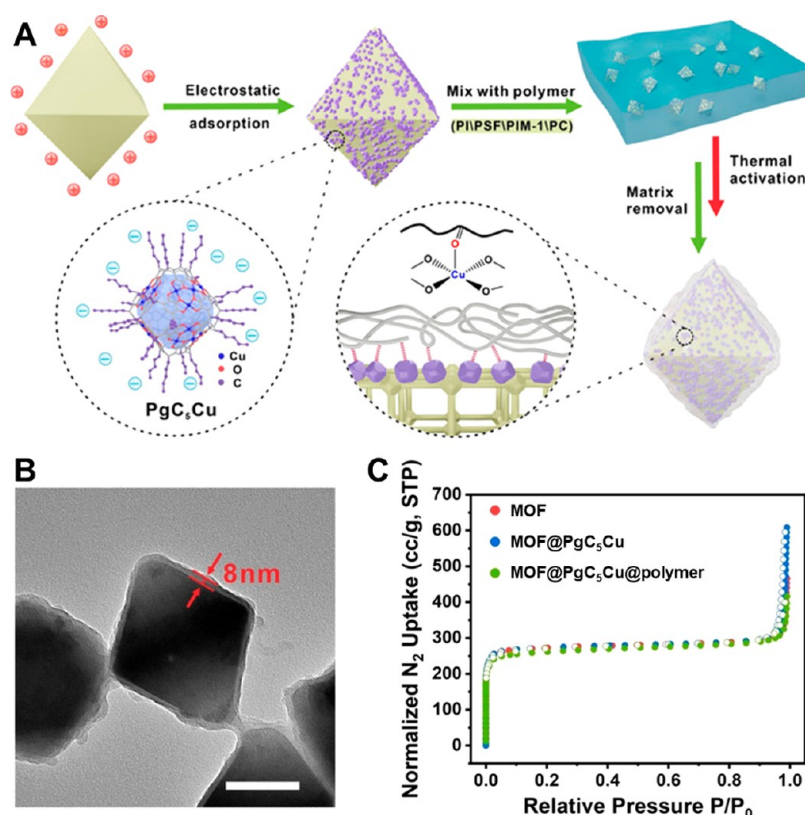

Figure 5. (A) Illustration of the MONC-mediated MOF surface modification with polymer. (B) TEM image of UiO-66-NH$_2$@PgC$_5$Cu@polymer, scale bar 100 nm. (C) N$_2$ adsorption−desorption isotherms of MOF, MOF@PgC$_5$Cu, and MOF@PgC$_5$Cu@polymer normalized to the MOF mass. Reproduced with permission from ref 22. Copyright 2021 Wiley-VCH.

surface coatings may usher in new properties and functions in MOF materials.

In one of the early contributions by Chun et al., a microporous organic network (MON) was coated onto the surface of UiO-66-NH$_2$ through Sonogashira coupling between two monomers, tetra(4-ethynylphenyl)methane and diiodoarene.[23] This is one of the rare early examples of MOF@polymer that unambiguously showed a well-defined core−shell architecture under TEM even after MOF digestion. In addition, crystalline condensation

polymers (e.g., covalent organic frameworks (COFs)) have also been explored as MOF coatings.[42−45]

In 2018, our group presented the first example of covalently grafting PI brushes onto the MOF surface.[1] Establishing a PI coating has special meaning to the field of MMMs as many high-performance polymer matrixes are composed of PIs. Decorating the MOF surface with a PI shell can improve its interaction with the PI matrix, thereby enhancing the gas-separation performance of the MMMs. In the work, an amine-functionalized MOF, UiO-66-NH$_2$, was first reacted with excess dianhydride, 4,4′-
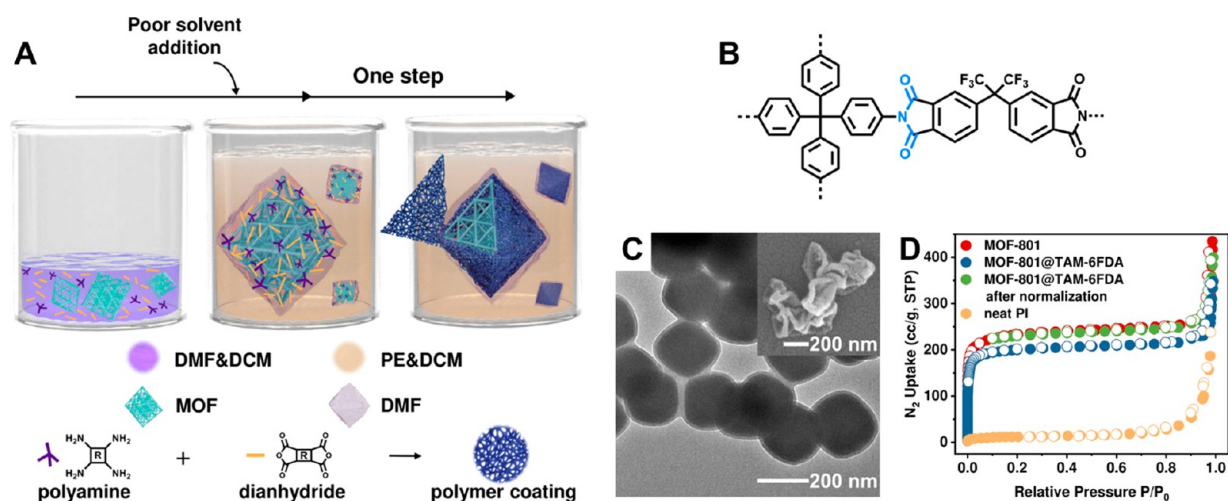
Figure 6. (A) Schematic illustration of the NISAP process. (B) Chemical structure of TAM-6FDA. (C) TEM image of MOF-801@TAM-6FDA. The inset shows the SEM image of the PI capsule after MOF digestion. (D) N_2 isotherms of neat PI and MOF with and without PI coatings. Reproduced with permission from ref 4. Copyright 2022 American Chemical Society.

oxidiphthalicanhydride (ODPA), to present the MOF surface with a more reactive anhydride terminal group. Then, ODPA-functionalized UiO-66-NH$_2$ was copolymerized with ODPA and 2,4,6-trimethyl-m-phenylenediamine (DAM) and later chemically imidized to afford UiO-66-NH$_2$@ODPA-DAM (Figure 3A). The ~5-nm-thick PI coating was clearly visible under TEM with excellent uniformity throughout the sample (Figure 3B). By analyzing the digested sample using matrix-assisted laser desorption/ionization (MALDI) time-of-flight (TOF) spectroscopy, the molecular weight of the PI brushes was found to be in the range of 2−8 kDa and the terminal group was confirmed to be NH$_2$−BDC (Figure 3C). The MOF porosity was nearly unaffected by the surface polymerization process, making it a true MOF@polymer core−shell particle. Co-incidentally, Smith and co-workers reported a similar strategy shortly after.[46] However, unlike our work that used a "grafting from" approach, Smith's work took a "grafting to" approach in which anhydride-terminated telechelic imide oligomers were used for surface grafting.

Despite the success of the covalent grafting of polyimides, the prerequisite for an amino functional group heavily limits the extension of this method to other MOFs. In reality, many MOFs that exhibit promising gas separation potential unfortunately do not contain organic functional groups suitable for covalent grafting. Deliberately introducing a function group into the ligand molecule is either chemically challenging or likely to result in a different MOF phase. Upon examining this challenge, to find a method that is suitable for a wide range of MOFs, a common feature should be relied upon. In this context, we developed a so-called "physical entanglement" strategy to prepare MOF@PI.[29] Instead of relying on a specific functional moiety, this methodology utilizes porosity, a common feature shared by most MOFs, for the surface grafting of polymer. Taking a 3-D mesoporous MOF, MIL-101(Cr), as an example, a reactive monomer, 2-isocyanatoethyl methacrylate (IEM), was first used to impregnate the MOF and was polymerized in situ. The polymer chains formed within the MOF intertwined with the 3-D scaffold of the MOF, preventing them from diffusing out. These polymers were then functionalized with triethylene-tetramine (TETA) to present amine functionality in the pore and on the surface. Anhydride-terminated polyimide oligomers were then covalently grafted to the amines presented on the

MOF surface (Figure 4A). The TEM images showed the formation of a uniform layer of polymer only after the PI grafting step (Figure 4B). Based on this method, a strong connectivity between the MOF and the polymer can be established. This work provided a practical solution for the surface modification on nonfunctionalized MOFs.

As the above method achieves surface grafting at the cost of MOF porosity, a generalizable strategy to construct MOF@PI with fully preserved MOF porosity is highly desired. In addition, strategies for grafting other condensation polymers such as PSF and the polymer of intrinsic microporosity-1 (PIM-1)[47] onto MOF were still not available at the time. In a follow-up work, we designed a surface grafting methodology using a combination of electrostatic interaction and coordinative cross-linking. It was previously found that copper-seamed MONC, PgC$_5$Cu, could coordinatively cross-link the polar functional groups in condensation polymers through its 24 OMSs.[48] We first allow negatively charged PgC$_5$Cu to adsorb to a positively charged MOF surface through electrostatic interaction affording MOF@PgC$_5$Cu.[22] Then MOF@PgC$_5$Cu was mixed with a selected polymer and thermally annealed at 200 °C to initiate coordinative cross-linking (Figure 5A). After a solvent wash, a uniform sub-10-nm polymer coating can be found on each MOF particle (Figure 5B). The success of this strategy was demonstrated on a series of MOFs including MOF-801,[49] UiO-66,[50] MIL-101(Cr), ZIF-67, and UiO-66-NH$_2$ as well as a series of condensation polymers including PIs, PSF, PC, and PIM-1. Since no small molecules were involved in this coating process, the polymer was strictly limited to the MOF outer surface. Therefore, the MOF porosity could be fully retained. This was evidenced by the good agreement between the normalized N_2 adsorption isotherm of UiO-66-NH$_2$@PgC$_5$Cu@polymer and pristine UiO-66-NH$_2$ (Figure 5C). With well-defined core−shell morphology and fully preserved porosity, this represents a definitive example of a true MOF@polymer composite.

While most of the surface polymerization processes take hours to days to complete, developing a method that is fast and efficient with a high monomer utilization rate and minimum steps is highly desirable.[51,52] For that, we developed a one-step rapid surface polymerization method, non-solvent-induced surface-aimed polymerization (NISAP), for the growth of linear

Table 1. Comparison of Various MOF@Polymer Fabrication Methods

fabrication method	MOF	polymer	no. of synthetic steps[a]	reaction time	MOF porosity retention	monomer/polymer utilization rate	ref
noncovalent SI-ATRP	UiO-66-X		2	4−18 h	good	medium	2, 3
	ZIF-8	polymethacrylate					
	ZIF-67	polyacrylate					
	MIL-96	polystyrene					
	MIL-101						
polymerization induced surface adsorption (PISA)	MOF-801		1	24 h	good	medium	28
	MIL-53(Fe)	polymethacrylate					
	MIL-101(Cr)	polyacrylate					
	UiO-66-NH$_2$	polystyrene					
	ZIF-8						
grafting from	UiO-66-NH$_2$	polyimides	3	24 h	excellent	low	1
physical entanglement	MIL-101	polyimides	3	48 h	poor	low	29
MONC-mediated surface cross-linking	UiO-66-NH$_2$	polyimides	3	2 h	excellent	low	22
	ZIF-8	PIM-1					
	ZIF-67	polysulfone					
	MOF-801	polycarbonate					
nonsolvent induced surface polymerization (NISAP)	MOF-801		1	<1 min	excellent	high	4
	UiO-66	polyimides					
	ZIF-8	polyamic acid					
	MIL-101						

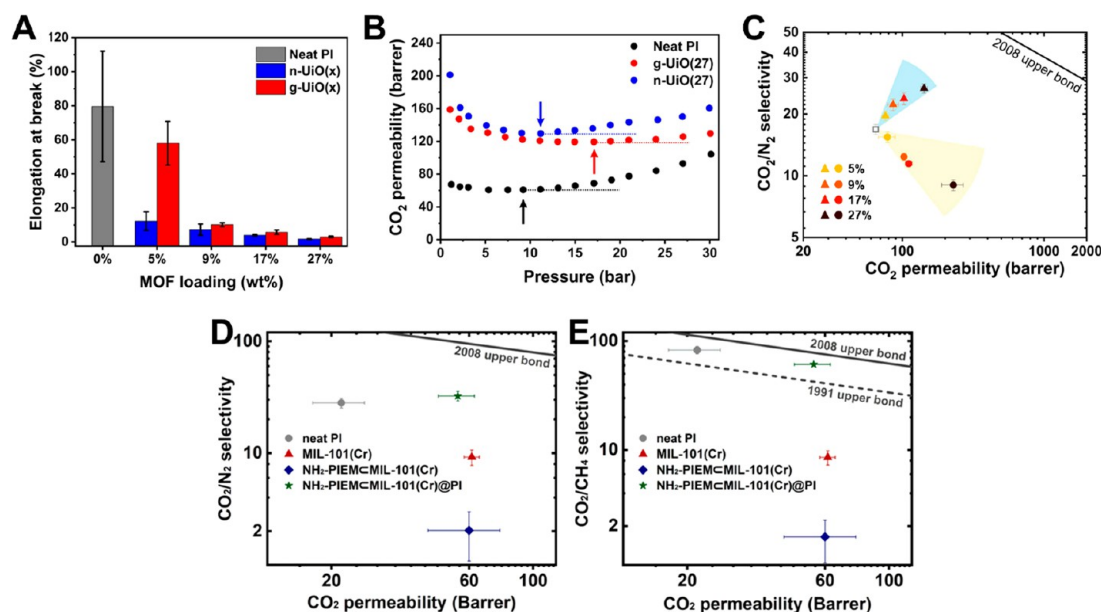[a]Excluding steps for presynthesized polymers and oligomers.

Figure 7. (A) Elongation at break values for the neat ODPA-DAM and MMMs. G-UiO(x) and n-UiO(x) represent PI-grafted and conventional MMM at x wt % MOF loading. (B) Pressure-dependent CO_2 single gas permeation for the neat PI and MMMs. (C) CO_2/N_2 selectivity versus CO_2 permeability of the neat PI (open squares), MMMs with different pure MOF loading (closed triangles), and MMMs with different MOF@polymer loading (closed circles). (A−C) Reproduced with permission from ref 1. Copyright 2018 American Chemical Society. (D) CO_2/N_2 selectivity and (E) CO_2/CH_4 selectivity versus CO_2 permeability of the neat PI membrane and MMMs. (D and E) Adapted with permission from ref 29. Copyright 2021 Wiley-VCH.

or cross-linked PIs on various MOF surfaces.[4] NISAP takes advantage of solvent phase separation to direct and concentrate polyamine and dianhydride monomers on MOF surfaces. Specifically, MOF-801 particles and monomers tetrakis(4-aminophenyl)methane (TAM) and 6FDA were first dispersed/dissolved in the mixture of dimethylformamide (DMF) and dichloromethane (DCM). Upon addition of a poor solvent, petroleum ether (PE), DCM was drawn toward the PE phase whereas DMF would carry all of the monomers and

nucleate on the MOF surfaces as droplets. The sudden increase in monomer concentration accelerated the polymerization reaction leading to the rapid formation of a sub-10-nm polyamic acid coating on MOF-801 (Figure 6A,C). Subsequent chemical imidization then turned polyamic acid into polyimide, thus affording MOF-801@TAM-6FDA (Figure 6B). This method is fast, easily executable, and carried out at room temperature. The synthetic condition involves no protic solvent, making it benign to chemically sensitive MOFs. The utilization rate of the
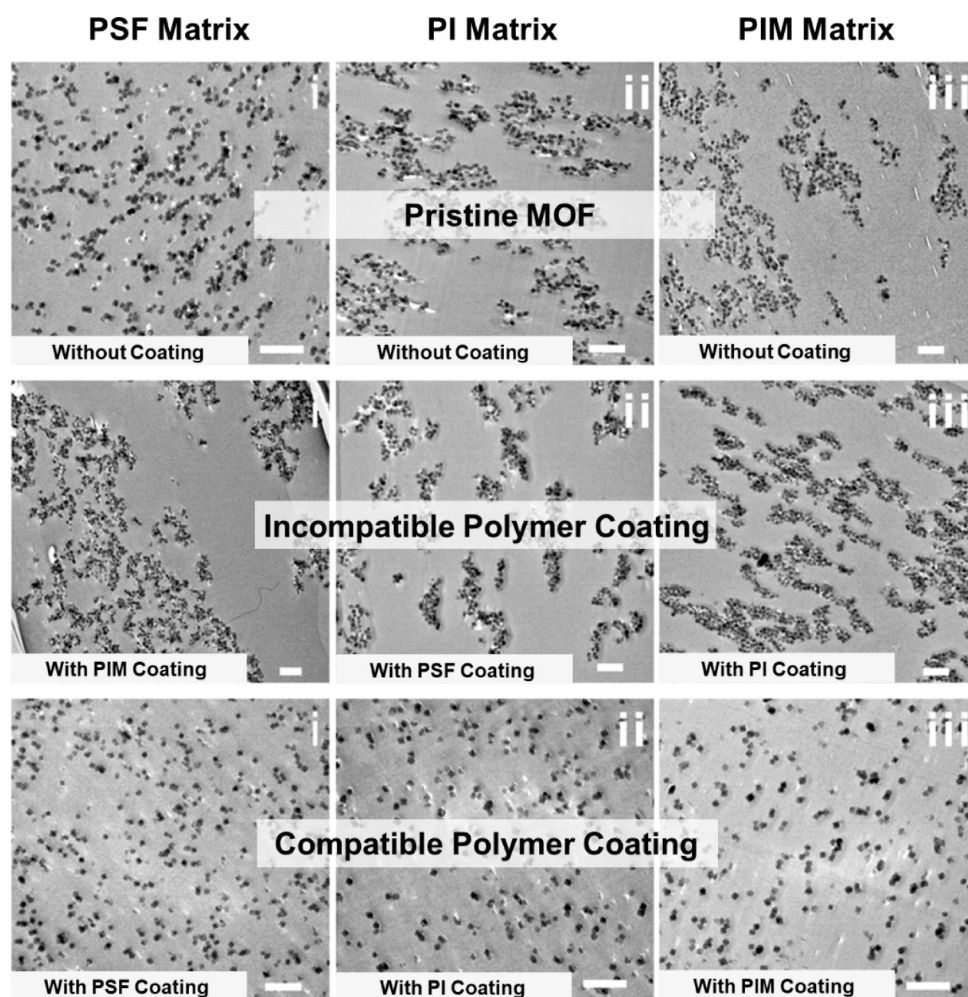
Figure 8. TEM images of ultrathin slices of different UiO-66-NH$_2$ MMMs, scale bar 1 μm. Reproduced with permission from ref 22. Copyright 2021 Wiley-VCH.

monomers can reach above 90%. Again, this surface coating process has no negative impact on the MOF-801 porosity, as revealed by its fully preserved N$_2$ adsorption capacity (Figure 6D).

For better comparison between various MOF@polymer fabrication strategies developed by our group, their main specifications are summarized in Table 1. Certain aspects such as the number of synthetic steps, reaction time, MOF porosity retention, and monomer/polymer utilization rate are essential when considering their applicability under various application scenarios.

3. FUNCTION OF THE POLYMER COATING AND THE POTENTIAL APPLICATIONS OF MOF@POLYMER

3.1. Improving Dispersibility and Interfacial Compatibility

By mimicking the chemical composition of the dispersing media, MOF@polymers can exhibit improved dispersibility and interfacial compatibility compared to their pristine MOF counterpart. This is evident in MOF-based MMMs as poor particle dispersibility and interfacial compatibility are two major obstacles that kept MMMs from performing as expected.[19,53]

There have been many innovative approaches for improving the MMM interfaces. Notable examples include (1) selecting a compatible MOF and polymer pair;[54] (2) small molecular surface modification on MOFs;[55] (3) *in situ* covalent cross-

linking of the MOF surface with the matrix;[56] and (4) using core−shell MOFs.[53] However, optimizing the MMM interface via MOF@polymer is a more generalizable approach.

In 2018, we demonstrated the application of covalently grafted PI brushes to optimize the MMM interface and improve the mechanical and transport properties of the membranes.[1] By incorporating ODPA-DAM brush-grafted UiO-66-NH$_2$ into the ODPA-DAM matrix at 5 wt %, the resultant MMM, g-UiO(5), exhibited 5 times the elongation at break (EAB) value compared to conventional MMM (n-UiO(5)) at the same loading (Figure 7A). Meanwhile, PI-grafted modified MMM was also more resistant to CO$_2$ plasticization at high pressure than conventional MMM (Figure 7B). With the increase in MOF loading, the PI-grafted MMMs exhibited a simultaneous increase in CO$_2$ permeability and CO$_2$/N$_2$ and CO$_2$/CH$_4$ ideal selectivity whereas their pristine MOF counterparts exhibited only increased permeability but decreased selectivity (Figure 7C). This is a strong indication that PI brushes improved the MOF−polymer interface and reduced void defects in the MMM.

In a separate contribution by our group, we demonstrated that PI brushes held by a mechanical linkage can also be used to improve the MOF−polymer interface.[29] By incorporating 6FDA-DDS (DDS represents 4,4′-diaminodiphenylsulfone)-modified MIL-101(Cr) (NH$_2$-PIEM⊂MIL-101(Cr)@PI) into the 6FDA-DDS matrix, substantially enhanced CO$_2$ perme-
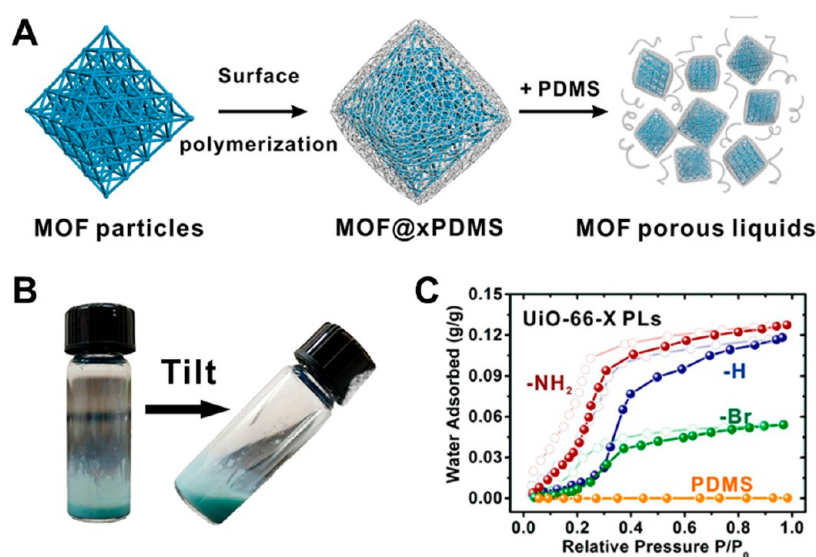
Figure 9. (A) Process of construction of MOF-based type III PLs. (B) Photographs of an upright and tilted vial containing a PL. (C) Water vapor sorption isotherm at 298 K of different MOF porous liquids. Reproduced with permission from ref 3. Copyright 2019 American Chemical Society.

ability was observed while CO_2/N_2 and CO_2/CH_4 selectivities were largely preserved. Comparably, MMM prepared with pristine MIL-101(Cr) witnessed a sharp decline in selectivity with respect to the neat polymer (Figure 7D,E). Apart from PI, Cohen's group demonstrated that UiO-66-allyl grafted with poly(dimethylsiloxane) (PDMS) brushes can also improve its interface with the PDMS matrix, thus leading to enhanced gas transport properties.[57] This method was named corona crosslinking.

Although the MOF dispersibility in MMM was recognized as a critical measure for the quality of the MMM, it was never studied in a quantitative manner. To address this issue, we prepared UiO-66-NH$_2$@polymer samples with PSF, PIM-1, or PI (6FDA-DAM) coatings using a MONC-mediated surface coating and dispersed them in three matrixes.[22] After quantitatively comparing the distribution of free path spacing between MOF particles in the actual MMM samples with the grand canonical Monte Carlo (GCMC) simulated samples, we found that when surface polymer matches with the matrix polymer, ideal MOF particle dispersibility can always be achieved. Otherwise, the aggregation of MOF particles will occur (Figure 8). This work simplifies the MOF–polymer incompatibility issue to the judicious selection of a suitable polymer coating for the MOF, making the interfacial engineering of MMMs a modular process.

Apart from polymer matrixes, the surface polymer coating on an MOF can also improve its dispersibility in liquid media. This is exemplified in one of our recent works that turned MOF@polymer into type III porous liquids (PLs), a colloidal suspension class of porous solids in a bulky solvent that simultaneously exhibit permanent porosity and fluidity (Figure 9A).[58] When we first initiated the type III PL project, we envisioned that liquid PDMS could be an excellent bulky solvent for PLs because (1) it remains fluidic even at high molecular weight; (2) it has relatively low viscosity; and (3) it is nontoxic and chemically and thermally stable. However, the challenge is that most MOFs exhibit a hydrophilic surface while PDMS is hydrophobic. The incompatible interface can cause particle aggregation, thus jeopardizing the colloidal stability and fluidity of the PL. On this basis, we cross-linked a methacrylate polymer

with a PDMS pendant on a series of UiO-66 analogues affording UiO-66-X@xPDMS using a noncovalent-based SI-ATRP approach.[3] Mixing UiO-66-X@xPDMS with liquid PDMS yielded MOF PLs with excellent colloidal stability, thermal stability, and rheological behavior of a liquid (Figure 9B). Most importantly, the characteristic sorption behavior of the MOFs was fully retained in their respective PLs, as exemplified in the water adsorption−desorption isotherms (Figure 9C).

3.2. Modulating Guest Diffusion

MOF@polymer typically shows improved chemical stability over the pristine MOF due to the shielding effect of the polymer shell. For example, by coating UiO-66 with a 7 nm cross-linked polystyrene (PS), the diffusion of H_2SO_4 and NaOH into the MOF can be effectively suppressed.[2] While pristine UiO-66 completely lost its crystallinity after soaking in H_2SO_4 or NaOH for 10 min at room temperature, PS-coated UiO-66 exhibited excellent stability against both the acid and the base at 50 °C for at least 24 h (Figure 10A−C). MOF@polymer has also been shown to improve MOFs' stability toward water.[51,59] Although the polymer barrier may slow down the diffusion of water, it cannot stop water from entering the MOF due to its small kinetic diameter and high polarity. It is likely that the coating prevents the leaching of metal ions and ligands which encourages dynamic repair within the MOF, thereby offsetting the degradation progress. If we could utilize the dynamic repair process to recrystallize the degraded MOF in the gas phase at a high recovery rate, then it is possible to reuse MOF repeatedly, thus extending the lifespan of a MOF.

Based upon this hypothesis, we realized the degradation−reconstruction cycle in MOF@polymer particles for the first time.[60] By encapsulating HKUST-1 particles within a 20 nm cross-linked polystyrene shell (HKUST-1@xPS), the Cu(II) ion and H$_3$BTC could be fully confined within the shell even after the complete degradation of the MOF by acetic acid vapor (Figure 10D). The maintained stoichiometric ratio between the two species allowed HKUST-1 to recrystallize back to its crystalline form within the PS capsule at 73 and 100% recovery rates of its CO_2 and N_2 uptake capacities through an *in situ* methanol vapor-assisted reconstruction step. This degradation−

● **Blocking Aggressive Chemicals**
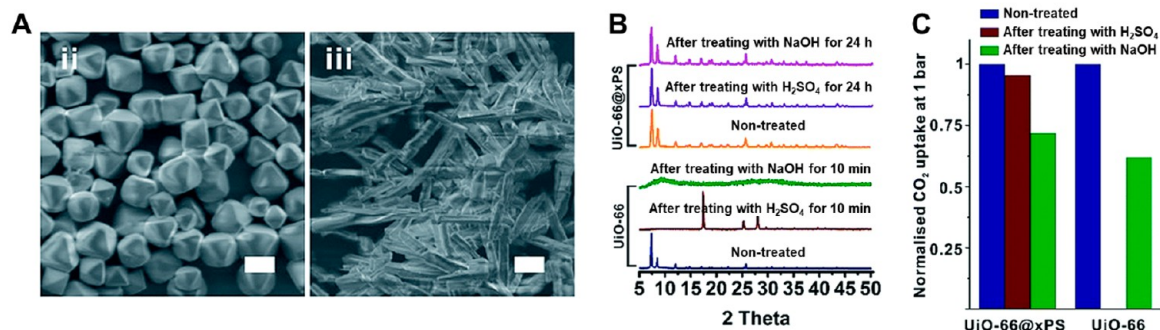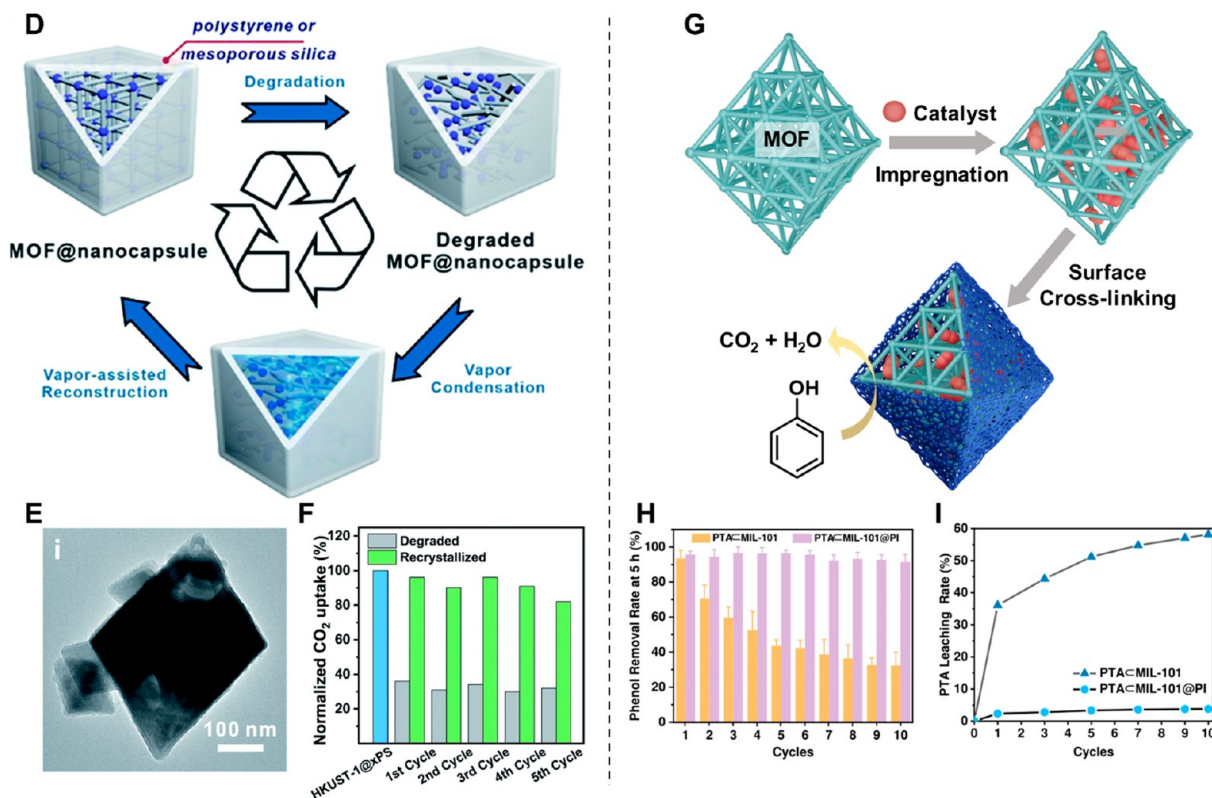

● **Preventing Leaching**

Figure 10. (A) SEM images of (ii) UiO-66@xPS and (iii) UiO-66 after soaking in 1 M H_2SO_4 for 24 h and 10 min, respectively. Scale bars are 1 μm for (ii) and 2 μm for (iii). (B) PXRD patterns and (C) normalized CO_2 uptake at 195 K for UiO-66 and UiO-66@xPS before and after soaking in 1 M H_2SO_4 and 1 M NaOH. (A−C) Reproduced with permission from ref 2. Copyright 2019 Royal Society of Chemistry. (D) Schematic illustration of the *in situ* recycling process. (E) TEM images of HKUST-1@xPS after one degradation−reconstruction cycle. (F) Normalized CO_2 uptake capacity at 0.99 bar and 298 K for HKUST-1@xPS and degraded and reconstructed HKUST-1@xPS over five cycles. (D−F) Adapted with permission from ref 60. Copyright 2022 Royal Society of Chemistry. (G) Homogeneous catalyst immobilization process. (H) Recyclability of PTA⊂MIL-101 and PTA⊂MIL-101@PI for phenol removal. (I) Leaching rate of PTA from PTA⊂MIL-101 and PTA⊂MIL-101@PI. (G−I) Reproduced with permission from ref 4. Copyright 2022 American Chemical Society.

reconstruction cycle could be carried out up to five times with 82% CO_2 uptake capacity retained at the end (Figure 10E,F).

In a recent contribution, we demonstrated that rapid surface polymerization coating can be used to physically confine small molecular species such as dye and homogeneous catalysts in the MOFs that are otherwise prone to leaching. This concept was demonstrated in our recent work in which a homogeneous catalyst, phosphotungstic acid (PTA), was encapsulated and sealed in a mesoporous MOF, MIL-101(Cr), with negligible leaching after applying an ∼8 nm cross-linked PI coating on the MOF surface (Figure 10G).[4] The heterogeneous catalyst not only exhibited catalytic activity similar to that of the

homogeneous PTA but also could be reused at least 10 times without a decrease in its catalytic activity (Figure 10H,I). Unlike other strategies for the immobilization of a homogeneous catalyst in MOFs, this strategy does not require special properties from the MOF, thus making it more generalizable.

4. SUMMARY AND OUTLOOK

While the surface modification of nanomaterials with polymers is not a new concept, constructing MOF@polymer composites with well-defined morphology does put forward new challenges for chemistry as well as materials science due to the complex nature of MOFs. Meanwhile, by combining the rich pore

chemistry of the MOF with the ultrathin functional polymer coating, new properties and applications of MOF materials will emerge. In this Account, we first summarized our recent development of a series of new strategies for the construction of MOF@polymer composites. Then, we rationalized that a well-defined polymer coating can improve many aspects of MOF properties. Despite the significant progress in this research direction over the past several years, challenges remain to be addressed and opportunities are waiting to be discovered. Here we lay out three research directions in MOF@polymer composites that are worth pursuing.

First, research on grafting condensation polymers onto MOFs is still in its infancy. To date, only a handful of papers concern this topic. However, these materials have already showed great promise for gas separation and catalysis. Questions such as how to graft condensation polymers other than polyimides on MOFs and how to control the polymer thickness, grafting density, and uniformity are still waiting to be unveiled. Discoveries in this direction will undoubtedly usher in new opportunities in MOF research, particularly in the direction of membrane science.

Second, MOF@polymer particles can be used to fabricate ultrathin single-component membranes for gas separation. One benefit of these membranes is that their interparticle distance can be precisely regulated by the surface polymer thickness whereas the interparticle interaction can be systematically controlled by the polymer architecture, molecular weight, and grafting density. Since single-component membranes eliminate the use of a matrix, the structural control becomes much easier and more precise. Preliminary results by Cohen's group have already offered a glimpse of single-component membranes fabricated with MOF particles coated with methacrylate polymers.[33] Future efforts should be focused on eliminating membrane defects, testing the gas-transport properties, and using membrane-relevant polymers.

Third, the exploration of MOF@polymer composites for catalysis is also in its nascent period. Apart from the existing example that utilizes the polymer coating to immobilize homogeneous catalysts in the MOF, a well-defined polymer coating can also enrich the function of the composite catalysts at least in the following three aspects: (1) improving the dispersibility of MOF particles for rapid diffusion; (2) enriching substrate molecules through charge or hydrophobic interaction; and (3) serving as a selective layer for selective catalysis. Surface coating with polymers can be a novel strategy for achieving the catalytic properties of MOF-based catalysts.

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Author Contributions

CRediT: **Dongxu Wang** conceptualization (supporting), formal analysis (equal), investigation (equal), validation (supporting), visualization (equal), writing-original draft (equal), writing-review & editing (equal); **Tao Li** conceptualization (lead), formal analysis (equal), funding acquisition (lead), investigation (equal), supervision (lead), validation (lead), visualization (equal), writing-original draft (equal), writing-review & editing (equal).

Notes

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■ REFERENCES

(1) Wang, H.; He, S.; Qin, X.; Li, C.; Li, T. Interfacial Engineering in Metal-Organic Framework-Based Mixed Matrix Membranes Using Covalently Grafted Polyimide Brushes. *J. Am. Chem. Soc.* **2018**, *140*, 17203−17210.

(2) He, S.; Wang, H.; Zhang, C.; Zhang, S.; Yu, Y.; Lee, Y.; Li, T. A Generalizable Method for the Construction of MOF@polymer Functional Composites through Surface-Initiated Atom Transfer Radical Polymerization. *Chem. Sci.* **2019**, *10*, 1816−1822.

(3) 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.

(4) Wang, D.; Li, S.; Wu, C.; Li, T. Surface-Seal Encapsulation of a Homogeneous Catalyst in a Mesoporous Metal-Organic Framework. *J. Am. Chem. Soc.* **2022**, *144*, 685−689.

(5) Hoskins, B. F.; Robson, R. Infinite Polymeric Frameworks Consisting of Three Dimensionally Linked Rod-like Segments. *J. Am. Chem. Soc.* **1989**, *111*, 5962−5964.

(6) Férey, G. Hybrid Porous Solids: Past, Present, Future. *Chem. Soc. Rev.* **2008**, *37*, 191−214.

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

(8) Zhou, H.-C.; Kitagawa, S. Metal-Organic Frameworks (MOFs). *Chem. Soc. Rev.* **2014**, *43*, 5415−5418.

(9) Farha, O. K.; Yazaydın, A. Ö.; Eryazici, I.; Malliakas, C. D.; Hauser, B. G.; Kanatzidis, M. G.; Nguyen, S. T.; Snurr, R. Q.; Hupp, J. T. De Novo Synthesis of a Metal-Organic Framework Material Featuring Ultrahigh Surface Area and Gas Storage Capacities. *Nat. Chem.* **2010**, *2*, 944−948.

(10) Lee, J.; Farha, O. K.; Roberts, J.; Scheidt, K. A.; Nguyen, S. T.; Hupp, J. T. Metal-Organic Framework Materials as Catalysts. *Chem. Soc. Rev.* **2009**, *38*, 1450−1459.

(11) Getman, R. B.; Bae, Y.-S.; Wilmer, C. E.; Snurr, R. Q. Review and Analysis of Molecular Simulations of Methane, Hydrogen, and

Acetylene Storage in Metal-Organic Frameworks. *Chem. Rev.* **2012**, *112*, 703−723.

(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) Ryu, U.; Jee, S.; Rao, P. C.; Shin, J.; Ko, C.; Yoon, M.; Park, K. S.; Choi, K. M. Recent Advances in Process Engineering and Upcoming Applications of Metal-Organic Frameworks. *Coord. Chem. Rev.* **2021**, *426*, 213544.

(14) Ren, J.; Langmi, H. W.; North, B. C.; Mathe, M. Review on Processing of Metal-Organic Framework (MOF) Materials Towards System Integration for Hydrogen Storage. *Int. J. Energy Res.* **2015**, *39*, 607−620.

(15) Kalaj, M.; Bentz, K. C.; Ayala, S., Jr; Palomba, J. M.; Barcus, K. S.; Katayama, Y.; Cohen, S. M. MOF-Polymer Hybrid Materials: from Simple Composites to Tailored Architectures. *Chem. Rev.* **2020**, *120*, 8267−8302.

(16) Yang, S.; Karve, V. V.; Justin, A.; Kochetygov, I.; Espin, J.; Asgari, M.; Trukhina, O.; Sun, D. T.; Peng, L.; Queen, W. L. Enhancing MOF Performance Through the Introduction of Polymer Guests. *Coord. Chem. Rev.* **2021**, *427*, 213525.

(17) Qian, Q.; Asinger, P. A.; Lee, M. J.; Han, G.; Mizrahi Rodriguez, K.; Lin, S.; Benedetti, F. M.; Wu, A. X.; Chi, W. S.; Smith, Z. P. MOF-Based Membranes for Gas Separations. *Chem. Rev.* **2020**, *120*, 8161−8266.

(18) Rezakazemi, M.; Amooghin, A. E.; Montazer-Rahmati, M. M.; Ismail, A. F.; Matsuura, T. State-of-the-Art Membrane Based CO_2 Separation Using Mixed Matrix Membranes (MMMs): An Overview on Current Status and Future Directions. *Prog. Polym. Sci.* **2014**, *39*, 817−861.

(19) Ma, L.; Svec, F.; Lv, Y.; Tan, T. Engineering of the Filler/Polymer Interface in Metal−Organic Framework-Based Mixed-Matrix Membranes to Enhance Gas Separation. *Chem.—Asian J.* **2019**, *14*, 3502−3514.

(20) Wang, Z.; Wang, D.; Zhang, S.; Hu, L.; Jin, J. Interfacial Design of Mixed Matrix Membranes for Improved Gas Separation Performance. *Adv. Mater.* **2016**, *28*, 3399−3405.

(21) Xie, K.; Fu, Q.; He, Y.; Kim, J.; Goh, S. J.; Nam, E.; Qiao, G. G.; Webley, P. A. Synthesis of Well Dispersed Polymer Grafted Metal-Organic Framework Nanoparticles. *Chem. Commun.* **2015**, *51*, 15566−15569.

(22) Li, C.; Liu, J.; Zhang, K.; Zhang, S.; Lee, Y.; Li, T. Coating the Right Polymer: Achieving Ideal Metal−Organic Framework Particle Dispersibility in Polymer Matrixes Using a Coordinative Crosslinking Surface Modification Method. *Angew. Chem., Int. Ed.* **2021**, *60*, 14138−14145.

(23) Chun, J.; Kang, S.; Park, N.; Park, E. J.; Jin, X.; Kim, K. D.; Seo, H. O.; Lee, S. M.; Kim, H. J.; Kwon, W. H.; Park, Y. K.; Kim, J. M.; Kim, Y. D.; Son, S. U. Metal-Organic Framework@Microporous Organic Network: Hydrophobic Adsorbents with a Crystalline Inner Porosity. *J. Am. Chem. Soc.* **2014**, *136*, 6786−6789.

(24) Nagata, S.; Kokado, K.; Sada, K. Metal-Organic Framework Tethering PNIPAM for ON-OFF Controlled Release in Solution. *Chem. Commun.* **2015**, *51*, 8614−8617.

(25) Barcus, K.; Cohen, S. M. Free-Standing Metal-Organic Framework (MOF) Monolayers by Self-Assembly of Polymer-Grafted Nanoparticles. *Chem. Sci.* **2020**, *11*, 8433−8437.

(26) Forgan, R. S. The Surface Chemistry of Metal-Organic Frameworks and their Applications. *Dalton Trans.* **2019**, *48*, 9037−9042.

(27) McGuire, C. V.; Forgan, R. S. The Surface Chemistry of Metal-Organic Frameworks. *Chem. Commun.* **2015**, *51*, 5199−5217.

(28) Li, S.; Zhang, S.; Dai, D.; Li, T. Facile One-Step Metal-Organic Framework Surface Polymerization Method. *Inorg. Chem.* **2021**, *60*, 11750−11755.

(29) Dai, D.; Wang, H.; Li, C.; Qin, X.; Li, T. A Physical Entangling Strategy for Simultaneous Interior and Exterior Modification of Metal-Organic Framework with Polymers. *Angew. Chem., Int. Ed.* **2021**, *60*, 7389−7396.

(30) Férey, G.; Mellot-Draznieks, C.; Serre, C.; Millange, F.; Dutour, J.; Surblé, S.; Margiolaki, I. A Chromium Terephthalate-Based Solid with Unusually Large Pore Volumes and Surface Area. *Science* **2005**, *309*, 2040−2042.

(31) Liu, H.; Zhu, H.; Zhu, S. Reversibly Dispersible/Collectable Metal-Organic Frameworks Prepared by Grafting Thermally Responsive and Switchable Polymers. *Macromol. Mater. Eng.* **2015**, *300*, 191−197.

(32) McDonald, K. A.; Feldblyum, J. I.; Koh, K.; Wong-Foy, A. G.; Matzger, A. J. Polymer@MOF@MOF: "Grafting From" Atom Transfer Radical Polymerization for the Synthesis of Hybrid Porous Solids. *Chem. Commun.* **2015**, *51*, 11994−11996.

(33) Katayama, Y.; Kalaj, M.; Barcus, K. S.; Cohen, S. M. Self-Assembly of Metal-Organic Framework (MOF) Nanoparticle Monolayers and Free-Standing Multilayers. *J. Am. Chem. Soc.* **2019**, *141*, 20000−20003.

(34) Sun, H.; Tang, B.; Wu, P. Development of Hybrid Ultrafiltration Membranes with Improved Water Separation Properties Using Modified Superhydrophilic Metal-Organic Framework Nanoparticles. *ACS Appl. Mater. Interfaces* **2017**, *9*, 21473−21484.

(35) Jiang, W.-L.; Fu, Q.-J.; Yao, B.-J.; Ding, L.-G.; Liu, C.-X.; Dong, Y.-B. Smart pH-Responsive Polymer-Tethered and Pd NP-Loaded NMOF as the Pickering Interfacial Catalyst for One-Pot Cascade Biphasic Reaction. *ACS Appl. Mater. Interfaces* **2017**, *9*, 36438−36446.

(36) Molavi, H.; Shojaei, A.; Mousavi, S. A. Improving Mixed-Matrix Membrane Performance via PMMA Grafting from Functionalized NH_2-UiO-66. *J. Mater. Chem. A* **2018**, *6*, 2775−2791.

(37) Ejima, H.; Yanai, N.; Best, J. P.; Sindoro, M.; Granick, S.; Caruso, F. *Adv. Mater.* **2013**, *25*, 5767−5771.

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

(39) Wang, F.; He, S.; Wang, H.; Zhang, S.; Wu, C.; Huang, H.; Pang, Y.; Tsung, C.-K.; Li, T. Uncovering Two Kinetic Factors in the Controlled Growth of Topologically Distinct Core-Shell Metal-Organic Frameworks. *Chem. Sci.* **2019**, *10*, 7755−7761.

(40) Chiefari, J.; Chong, Y.; Ercole, F.; Krstina, J.; Jeffery, J.; Le, T. P.; Mayadunne, R. T.; Meijs, G. F.; Moad, C. L.; Moad, G. Living Free-radical Polymerization by Reversible Aaddition-Fragmentation Chain Transfer: The RAFT Process. *Macromolecules* **1998**, *31*, 5559−5562.

(41) Hu, Y.; Daoud, W. A.; Cheuk, K. K. L.; Lin, C. S. K. Newly Developed Techniques on Polycondensation, Ring-Opening Polymerization and Polymer Modification: Focus on Poly (lactic acid). *Materials* **2016**, *9*, 133.

(42) Peng, Y. W.; Zhao, M. T.; Chen, B.; Zhang, Z. C.; Huang, Y.; Dai, F. N.; Lai, Z. C.; Cui, X. Y.; Tan, C. L.; Zhang, H. Hybridization of MOFs and COFs: A New Strategy for Construction of MOF@COF Core-Shell Hybrid Materials. *Adv. Mater.* **2018**, *30*, 1705454.

(43) Sun, D.; Jang, S.; Yim, S. J.; Ye, L.; Kim, D. P. Metal Doped Core-Shell Metal-Organic Frameworks@Covalent Organic Frameworks (MOFs@COFs) Hybrids as a Novel Photocatalytic Platform. *Adv. Funct. Mater.* **2018**, *28*, 1707110.

(44) Cai, M. K.; Li, Y. L.; Liu, Q. L.; Xue, Z. Q.; Wang, H. P.; Fan, Y. N.; Zhu, K. L.; Ke, Z. F.; Su, C. Y.; Li, G. Q. One-Step Construction of Hydrophobic MOFs@COFs Core-Shell Composites for Heterogeneous Selective Catalysis. *Adv. Sci.* **2019**, *6*, 1802365.

(45) Zhang, M. Y.; Li, J. K.; Wang, R.; Zhao, S. N.; Zang, S. Q.; Mak, T. C. Construction of Core−Shell MOF@COF Hybrids with Controllable Morphology Adjustment of COF Shell as a Novel Platform for Photocatalytic Cascade Reactions. *Adv. Sci.* **2021**, *8*, 2101884.

(46) Qian, Q. H.; Wu, A. X.; Chi, W. S.; Asinger, P. A.; Lin, S.; Hypsher, A.; Smith, Z. P. Mixed-Matrix Membranes Formed from Imide-Functionalized UiO-66-NH_2 for Improved Interfacial Compatibility. *ACS Appl. Mater. Interfaces* **2019**, *11*, 31257−31269.

(47) McKeown, N. B.; Budd, P. M. Polymers of Intrinsic Microporosity (PIMs): Organic Materials for Membrane Separations, Heterogeneous Catalysis and Hydrogen Storage. *Chem. Soc. Rev.* **2006**, *35*, 675−683.

(48) Wang, H.; Zhang, K.; Li, J. P. H.; Huang, J.; Yuan, B.; Zhang, C.; Yu, Y.; Yang, Y.; Lee, Y.; Li, T. Engineering Plasticization Resistant Gas Separation Membranes Using Metal-Organic Nanocapsules. *Chem. Sci.* **2020**, *11*, 4687−4694.

(49) Furukawa, H.; Gandara, F.; Zhang, Y.-B.; Jiang, J.; Queen, W. L.; Hudson, M. R.; Yaghi, O. M. Water Adsorption in Porous Metal−Organic Frameworks and Related Materials. *J. Am. Chem. Soc.* **2014**, *136*, 4369−4381.

(50) Kandiah, M.; Nilsen, M. H.; Usseglio, S.; Jakobsen, S.; Olsbye, U.; Tilset, M.; Larabi, C.; Quadrelli, E. A.; Bonino, F.; Lillerud, K. P. Synthesis and Stability of Tagged UiO-66 Zr-MOFs. *Chem. Mater.* **2010**, *22*, 6632−6640.

(51) Yang, S.; Peng, L.; Sun, D. T.; Asgari, M.; Oveisi, E.; Trukhina, O.; Bulut, S.; Jamali, A.; Queen, W. L. A New Post-Synthetic Polymerization Strategy Makes Metal-Organic Frameworks More Stable. *Chem. Sci.* **2019**, *10*, 4542−4549.

(52) Wang, W.; Wang, L.; Li, Y.; Liu, S.; Xie, Z.; Jing, X. Nanoscale Polymer Metal-Organic Framework Hybrids for Effective Photo-thermal Therapy of Colon Cancers. *Adv. Mater.* **2016**, *28*, 9320−9325.

(53) Wu, C.; Zhang, K.; Wang, H.; Fan, Y.; Zhang, S.; He, S.; Wang, F.; Tao, Y.; Zhao, X.; Zhang, Y.-B. Enhancing the Gas Separation Selectivity of Mixed-Matrix Membranes Using a Dual-Interfacial Engineering Approach. *J. Am. Chem. Soc.* **2020**, *142*, 18503−18512.

(54) Semino, R.; Moreton, J. C.; Ramsahye, N. A.; Cohen, S. M.; Maurin, G. Understanding the Origins of Metal-Organic Framework/Polymer Compatibility. *Chem. Sci.* **2018**, *9*, 315−324.

(55) 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.

(56) Zhang, Y.; Feng, X.; Li, H.; Chen, Y.; Zhao, J.; Wang, S.; Wang, L.; Wang, B. Photoinduced Postsynthetic Polymerization of a Metal-Organic Framework Toward a Flexible Stand-Alone Membrane. *Angew. Chem., Int. Ed.* **2015**, *54*, 4259−4263.

(57) Katayama, Y.; Bentz, K. C.; Cohen, S. M. Defect-Free MOF-Based Mixed-Matrix Membranes Obtained by Corona Cross-Linking. *ACS Appl. Mater. Interfaces* **2019**, *11*, 13029−13037.

(58) O'Reilly, N.; Giri, N.; James, S. L. Porous Liquids. *Chem.—Eur. J.* **2007**, *13*, 3020−3025.

(59) Castells-Gil, J.; Novio, F.; Padial, N. M.; Tatay, S.; Ruiz-Molina, D.; Marti-Gastaldo, C. Surface Functionalization of Metal-Organic Framework Crystals with Catechol Coatings for Enhanced Moisture Tolerance. *ACS Appl. Mater. Interfaces* **2017**, *9*, 44641−44648.

(60) Song, L.; Chen, L.; He, S.; Zhang, K.; Huang, J.; Chen, Y.; Qin, X.; Zhang, S.; Ma, Y.; Lee, Y. Repetitive in Situ Recycling of Degraded Metal-Organic Frameworks within Nanocapsules. *J. Mater. Chem. A* **2022**, *10*, 6607−6615.

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