REVIEW

ADVANCED FUNCTIONAL MATERIALS
www.afm-journal.de

Tiny Windows in Reticular Nanomaterials for Molecular Sieving Gas Separation Membranes

*Oksana Smirnova, Subham Ojha, Ankita De, Andreas Schneemann, Frederik Haase, and Alexander Knebel**

The current state of reticular chemistry enables the synthesis of a wide range of highly porous nanomaterials for gas separation, including metal-organic frameworks (MOFs), covalent organic frameworks (COFs), porous organic cages (POCs), metal-organic cages (MOCs), and polyhedra (MOPs). This perspective focuses on membrane technology, a key player in energy-efficient gas separations. It explores the world of reticular materials, taking a glance at tiny pore windows with narrow openings, which are ideal for high-resolution molecular sieving, and how to design them. Promising concepts in this field are membranes consisting of neat materials, but also mixed matrix membranes, where polymeric films incorporate reticular fillers, creating cost-efficient membranes. This article sheds light on the potential use of reticular materials as membrane components. The reticular synthesis of MOFs offers the ability to separate gas molecules with minimal size differences effectively. For COFs, the crucial factor lies in reducing their pore size, preferably through functional group modifications. Porous cage compounds can achieve fine distribution from homogeneous dispersions into polymers making them excellent candidates for mixed matrix membranes. This perspective provides strategies and guiding principles for the future of reticular nanomaterials-based membranes, addressing the pressing need for advanced and efficient separation technologies.

1. Introduction

Reticular chemistry, with its diverse facets,[1] significantly impacted materials science and embarked the research community on an unstoppable journey to address crucial molecular separations.[2] Over the past two decades, metal-organic and covalent organic frameworks (MOFs and COFs) have revolutionized adsorptive molecular separation technology multiple times.[3] These advancements have led to the emergence of industrial applications that are poised to effectively tackle modern societal challenges while promoting environmentally sustainable lifestyles combating global warming, and meeting the escalating demand for high-value raw chemicals.[4–6]

The time of making "novel" reticular materials and reporting their adsorption capacity is almost over, which has paved the way toward extremely powerful materials with very high surface areas.[7] Computational guidance will play a pivotal role in driving future research on adsorbent materials, guiding experimental scientists to more specific and specialized reticular materials. What is now at the forefront of materials research with hands-on scientists sets the focus on the variety of younger reticular materials, such as hydrogen-bonded frameworks (HOFs), organic and frustrated frameworks[8,9]; combinations of MOFs with nanotechnology have led to the development of liquids with permanent porosity (PLs),[8,10,11] organic and metal-organic cages and polyhedral (MOCs/MOPs).[12] All these reticular materials possess similar characteristics, such as a high degree of tailorability and chemical tunability, providing ground-breaking inner surface areas and huge pore volumes, which allow for gas and liquid separations, in the future certainly on the industrial scale.

Membranes utilizing reticular materials (MOFs, COFs, HOFs, MOCs, and MOPs) hold great promise for application-based research, particularly in energy-efficient gas separation processes, paving the way for a bright future. **Figure 1** provides an overview of the scope of this perspective illustrating the materials and concepts poised for application in high-potential gas separation membranes.

Many separations need strong improvements to cope with new standards and generate higher revenue on the one hand, while

O. Smirnova, A. Knebel
Friedrich Schiller University Jena
Otto Schott Institute of Materials Research
Fraunhoferstr. 6, 07743 Jena, Germany
E-mail: alexander.knebel@uni-jena.de

S. Ojha, F. Haase
Martin Luther University Halle-Wittenberg
Institute of Chemistry
von-Danckelmann-Platz 4, D-06120 Halle (Saale), Germany

A. De, A. Schneemann
Technical University Dresden
Chair of Inorganic Chemistry I
Bergstraße 66, 01069 Dresden, Germany

A. Knebel
Centre for Energy and Environmental Chemistry Jena (CEEC)
Philosophenweg 7a, 07743 Jena, Germany

The ORCID identification number(s) for the author(s) of this article can be found under https://doi.org/10.1002/adfm.202306202

DOI: 10.1002/adfm.202306202

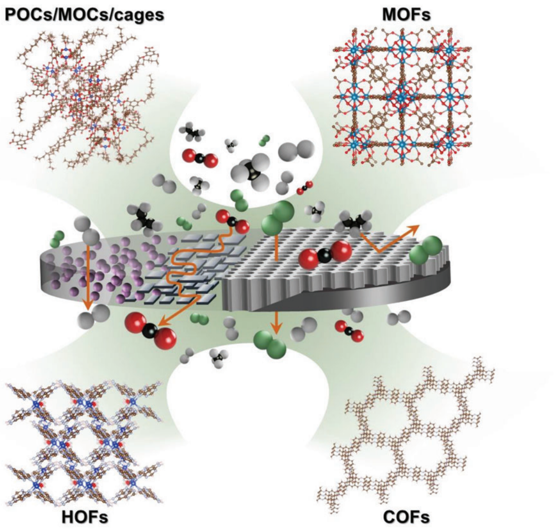

Figure 1. A schematic figure outlining the scope of this perspective: Reticular membrane concepts from mixed matrix membranes on the left, with high potential novel materials classes (POCs/MOCs/cages and HOFs) and the inorganic, supported membranes where MOFs and COFs offer tremendous potential for kinetic sieving.

they need to cut energy and greenhouse gas emissions on the other hand. Reticular materials offer numerous possibilities for integration into existing workflows and have the potential to disruptively replace conventional energy-intensive technologies like (cryogenic) distillation.[13] The utilization of reticular materials in real-world applications has now started to shift the focus away from the fundamental science that laid the base in 1990,[1] with its breakthrough in the late 1990s[14] to more application-based science, as a fundamental understanding developed for the past 25 years.[2] Synthetical chemists start to work together with tech companies and use the tailorability of these materials as an advantageous feature. The data obtained over the years is already strong enough to provide guidance for these designer hybrid materials to specifically lay out their properties.[15] Following their formation[16] and structure–property relationships,[17] scientists found macroscopic properties and transferred this knowledge to any other system. This allowed researchers to build benchmarking frameworks, such as ZIF-8 (Zeolitic Imidazolate Framework 8) for hydrocarbon separation, which has been upscaled into pilot plants **Figure 2**.[18] Further applications arise: NU-1000 (Northwestern University 1000), as one of the most stable MOFs with extremely large pores finds more and more interest in biochemistry,[17] and MOF-303 is well-suited and stable to harvesting water in arid areas[19] or CALF-20 (Calgary Framework 20) for adsorptive CO_2 capture on a larger scale.[3]

Environmental technology focused on carbon capture can significantly cut CO_2 emissions and facilitate the transition from fossil energy to renewable sources.[20] The efficient use of resources[18] and pollutant removal[21] are interlinked, as both contribute to reducing energy consumption and greenhouse gas emissions.

Carbon capture is one of the key technologies to achieve the goal and bridge the gap toward a sustainable world,[5] in which reticular materials play a disruptive and important role. However, reticular materials are equally important for a sustainable chemical production chain[22] and will lead to drastic technological changes. While reticular materials, such as MOFs and COFs, enable energy production by themselves[23] and act as catalysts in chemical production[24] or storage materials,[25] this review will focus only on their use cases for gas-sieving separations. Gas sieving is completely different from gas adsorption, but an equally important technology with strong potential. From this perspective, we want to take a glance through the tiny windows of gas-sieving reticular materials.[18,26,27] A precise tailoring of nanoscopic properties in reticular materials by minimizing the pore windows diameters enables membrane technology.[28]

Designing reticular materials for gas-sieving membrane processes requires reticular chemistry, as it permits the narrowing and tuning of pore windows in the sub-Å range, achieving the exclusion of the tiniest molecules.[29,30] Growing molecular sieving MOF and COF membranes on ceramic substrates initially enabled working membrane technologies,[13] while decreasing costs and improving efficiency led the field toward polymer mixed matrix membranes (MMMs).[31]

While molecular sieving is a well-understood process in zeolites, the molecular gating in MOFs and COFs created an entire own field of reticular design, with the flexibility of these hybrid materials presenting both challenges and opportunities.[27] Technical concepts are essential to produce commercially applicable molecular sieving membranes from MOFs,[30] whether through physical stimuli[32] or specialized synthetic pathways for rigid frameworks.[27,33]

The organic backbones of reticular materials facilitate excellent interaction with polymers and carbons, which have fostered a growing interest in the field. Unifying polymers with reticular materials has demonstrated outstanding results as membrane materials, and an unconventional approach like combining reticular fillers with graphene-derived matrices also shows promise. Mixed matrix membranes offer the advantage of both diffusional and adsorptive separation within the same material.[34,35]

Tackling a few of the many important challenges of the 21st century requires research within the area of highly specialized reticular materials,[36] materials' processability,[10] and disruptive novel separation concepts, mainly involving membranes.[13] While reticular materials enable technology that is required now, such as carbon capture in pre- and post-combustion processes,[37] thinking into the future is equally important. Reticular materials in membranes can be used for direct air capture of CO_2 as a carbon building block to reduce the environmental impact on society.[38] Furthermore, our society runs into many other crises which have not appeared on the map, yet. For instance, the loss of helium-reliant technology—helium is another extremely important, highly valuable element originating from radioactive decay. It cannot be produced otherwise and leaves the atmosphere if not captured.[39] While helium is captured today from natural gas wells, it will deplete at some point, and this is already noticeable today by its constant price increases. Today's helium levels in the atmosphere are as high as they have never been before due to fossil fuel exploitations, and direct air He capture could be another point for small-pore reticular membranes.[40]

Furthermore, tailoring narrow pores even further is of high importance for methane valorization[29,34,41] and for the production of high-value chemicals, such as ethylene and

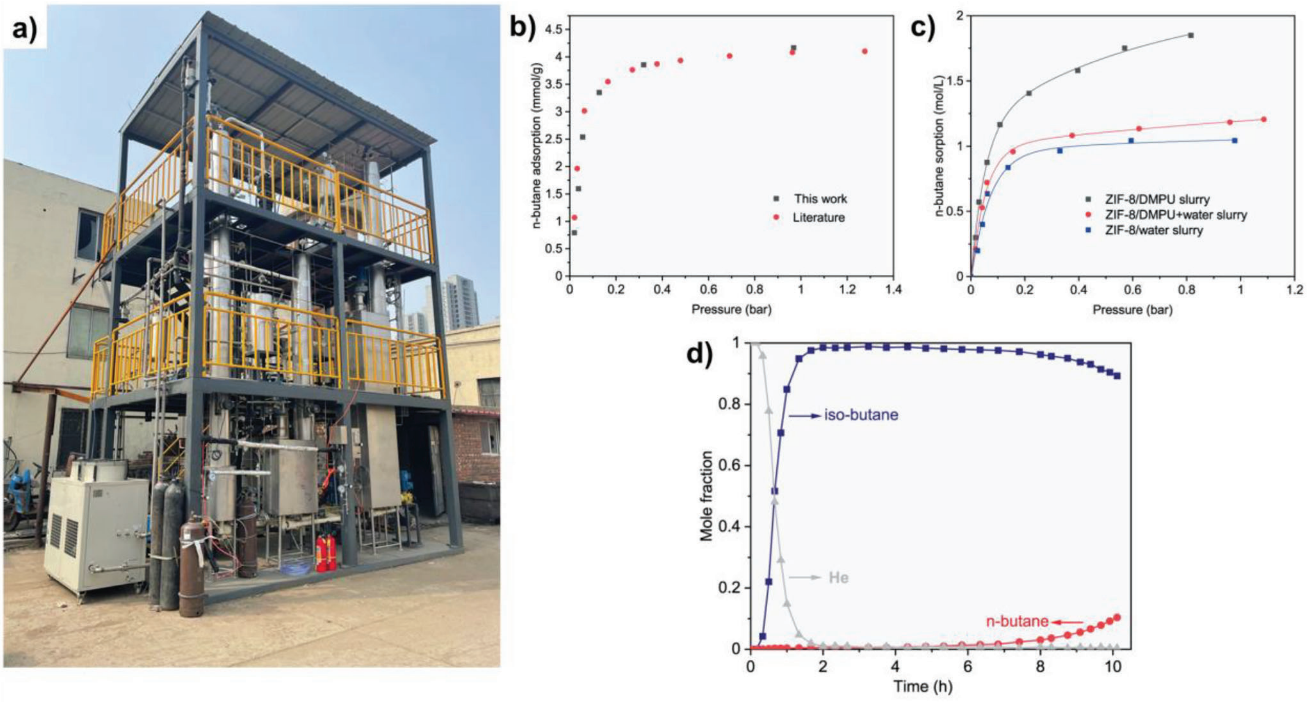

Figure 2. C4 Isomer separation columns using the sorption capacity of ZIF-8 slurries. Breakthrough of curves of b–d) *n*-butane and iso-butane (d) on the columns shown in (a). Adapted with permission.[18] Copyright 2022, Springer Nature.

propylene in the petrochemical sector[27,42] or of propane as a natural refrigerant.[43] The difference in molecular size between ethane/ethylene and propane/propylene lies in the range of 0.2 Å and makes reticular design highly important but also challenging.

The purpose of this perspective is to sharpen the view of the reader and researchers through tiny pore windows. The objective is to demonstrate net-based strategies and synthetic pathways to pore aperture editing with reticular materials. It will become clear that the reticular materials with small window sizes, or strategies to design these, are often forgotten or neglected. For gas separation membranes, these materials become important to sieve the gas molecules with the slightest size difference effectively and enable energy-efficient separation technologies of the future.

2. Excursion: Principles of Membrane Separation

Membranes act as physical barriers placed in a gas stream, separating the upstream (feed gas and retentate (depleted feed gas) side) from the downstream (sweep gas/vacuum and permeate (enriched gas) side). Gas permeation in membranes, whether made of pure reticular materials or polymer-filler composites, follows two physical mass-transport processes:

1) Mass transport in microporous media (<2 nm pore size, IUPAC nomenclature) is primarily governed by the molecular sieving model (kinetic diffusion) determined by pore size and shape.[44]
2) Mass transport in polymer-mixed matrix systems is dominated by the solution-diffusion model. Here, as gas molecules dissolve in dense polymeric matrices, solubility becomes the basis for selectivity.

While a deep understanding of diffusional processes is crucial for membrane permeation, it falls outside the scope of this perspective. To gain practical insights, the Maxwell-Stefan diffusion model, as described by Kapteijn and Krishna, aids in comprehending[45] mass transport through membranes in complex multicomponent gas mixtures.

Gas transport is primarily driven by the chemical potential gradient between the upstream and downstream regions, typically represented by the partial pressures of the gas species. The number of gas molecules (n) of gas species (i,j) that pass through a specific area (A) of a membrane within a specific time (t) is termed flux (f) in formula (1):

$$f = \frac{n_\mathrm{i}}{t \cdot A} \tag{1}$$

A pressure (p) normalization between retentate and permeate pressures (Δp) results in the permeance (Π) as shown in (2), while a further normalization of the permeance with the thickness of the membrane gives the permeability P as shown in (3):

$$\Pi = \frac{n_\mathrm{i}}{t \cdot A} \cdot \frac{1}{\Delta p} \tag{2}$$

$$P = \frac{n_\mathrm{i}}{t \cdot A} \cdot \frac{1}{\Delta p} \cdot d \tag{3}$$

The selectivity (α) of a membrane system is determined by dividing the molar fractions of different gases between the downstream (sweep/permeate side, *d*) and the upstream (feed/retentate side, *u*).

$$\alpha_{\mathrm{i,j}} = \frac{n_{\mathrm{i,d}}/n_{\mathrm{j,d}}}{n_{\mathrm{i,u}}/n_{\mathrm{j,u}}} \tag{4}$$

Usually, the feed gas is overdosed, and the retentate's composition is assumed to remain unchanged from the initial feed composition, simplifying the equation. The selectivity can be determined from single gas measurements and is referred to as "ideal" selectivity, whereas binary mixture selectivity is called "real" selectivity. Generally, in the absence of special competitive effects in gas permeation, the ideal selectivity is always better than the real selectivity of a membrane.

For a more comprehensive understanding, referring to the IUPAC terminology for membranes and membrane processes by Koros, Ma, and Shimizu is highly recommended.[46]

3. Sieving Strategies in Reticular Materials

3.1. Materials Introduction in the Context of Gas Separation

3.1.1. Metal-Organic Frameworks (MOFs)

In this perspective, MOFs constitute the most extensively researched and explored class of materials for gas separation membranes.[13] Therefore, we will focus on highlighting various strategies to enhance the gas separation performance, particularly by reducing the pore window size for precise molecular sieving.

Early works often claimed to achieve "perfect" molecular sieving in their titles.[47] However, current knowledge reveals significant limitations arising from flexibility in these framework materials,[48,49] leading to separation values much lower than expected from theoretical predictions.[15,31] This issue has been especially apparent in ZIF-8 membranes, where applying external stimuli to stiffen the structure resulted in a significantly improved molecular size cut-off.[26,50]

Moreover, surface defects[51] and grain boundaries[52] present significant challenges in the practical applications of MOFs in membranes, especially when used in polymeric mixed matrix membranes, where polymer–filler interactions need thorough investigation.[53] Nevertheless, the versatile nature of reticular chemistry in MOFs holds tremendous potential for highly efficient molecular sieving membranes. We will further discuss MOFs, particularly focusing on pore aperture editing strategies, in the subsequent sections.

3.1.2. Covalent Organic Frameworks (COFs)

Simple organic reactions are essential for the construction of Covalent Organic Frameworks, for instance, the Schiff-Base reaction (imines, COF-LZU-1),[54] trimerization of nitriles (triazines, CTF-1)[55] or boronic acids (boroxine, COF-1).[56] Layered 2D COFs can be easily integrated into separation membranes.[57] Inherently, most of the archetypical crystalline COFs possess large pore windows, since they are often constructed from extended aromatic structures for instance, 1,3,5-triphenylbenzol,[58] triphenylene[59] or pyrene[60] derivatives to name a few common examples, often featuring pore sizes above 2 nm. Even the simplest materials like CTF-1[55] or COF-1[56] constructed from three connecting triazine or boroxine cores and bridged by benzene linkers have pore sizes beyond 1 nm, making the pristine materials unsuitable for many of the key separations introduced by Sholl and Lively.[4] Early on proof-of-concept work on COF membranes focused on the selective sieving of large molecules, i.e., organic dye molecules.[61] The key to maximizing the interaction of industrially relevant molecules for efficient separation technologies using COFs as the active porous material necessitates the drastic downsizing of the pore dimensions as shown in **Figure 3**. With the massive growth of interest in COF materials from different areas of material science, huge progress has been made in developing synthetic concepts for the design of COFs and consequently, a range of methods for systematically downsizing pore openings and diameters has been developed. In the following, we will review the progress made so far in the literature and give an overview of other techniques for decreasing pore diameters that might be applicable to COFs.

The most promising techniques for engineering the pore diameter of COFs, are by a) careful control of the stacking differences of adjacent layers to create hierarchical pore windows, or b) by methodical pore wall engineering for selective interaction with analytes or limiting the apparent pore diameter.[62] Furthermore, the lengths and geometry of the building blocks (Figure 3) play a key role in the design of the pore opening, however, to the best of our knowledge no pristine COFs with inherently small enough pore diameters (<1 Å) for key separations have been prepared. A novel approach is pore-in-pore engineering, where a sugar molecule is inserted within the pore to effectively reduce its pore size.[63] Nevertheless, this approach is still in its infancy, and its applicability to other COFs needs thorough investigation.

3.1.3. Hydrogen-Bonded Organic Frameworks (HOF)

Hydrogen-bonded organic frameworks (HOF) are constructed from multifunctional molecules with their structure is determined by their hydrogen-bonding interactions, with other weak interactions like van der Waals interactions contributing to their crystallization.[64] The directional nature of hydrogen-bonding motifs enables the formation of porous structures accompanied by their structural prediction and design. HOF building blocks are endowed with hydrogen bond donor and acceptor groups leading to hydrogen-bonding motifs such as dimers, trimers, and chains.[64] The hydrogen-bonding motif exhibits polymorphism, resulting in the formation of small pores and heightened structural complexity. This complexity allows for precise structural adjustments based on synthesis conditions, surpassing the level seen in COFs, but not reaching the extensive complexity found in MOFs. Furthermore, HOFs are molecular compounds that readily dissolve and recrystallize, facilitating effortless fabrication and processing. Their solubility also enables the recyclability of HOFs without the need for energy-intensive processes. Despite being molecular materials, HOFs possess permanent porosity, often in the range of microporosity, that enables rapid transport and diffusion.[65] As reticular materials, HOFs offer compelling advantages in the design of porosity and functionality through a rational linker and framework design. This unique characteristic

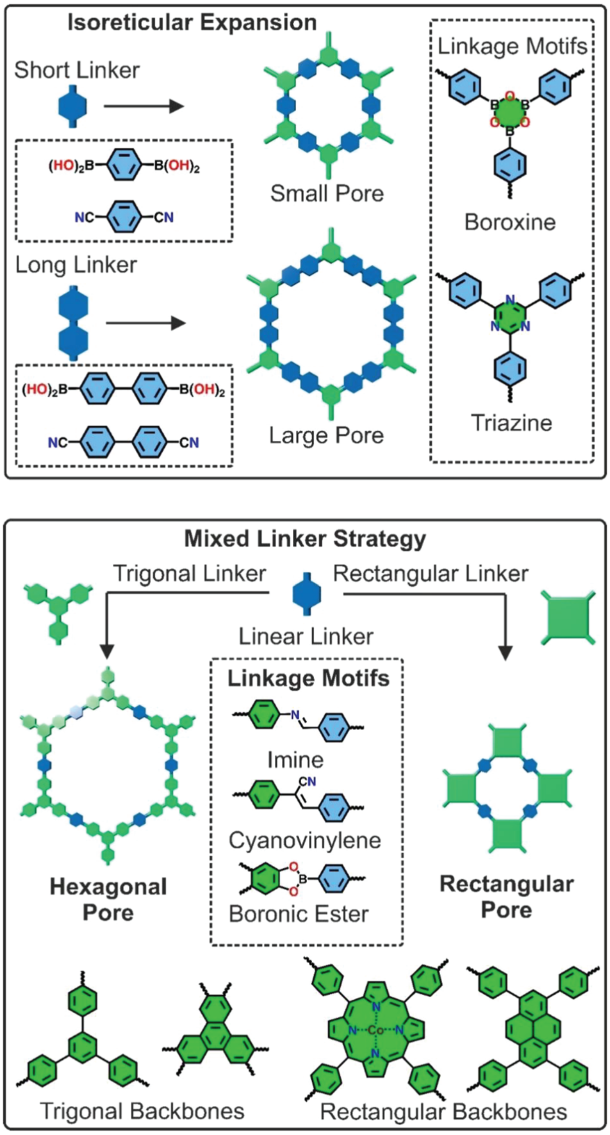

Figure 3. (Top) Schematic depiction of the construction of COFs with different pore sizes via isoreticular expansion by the self-condensation of boronic acids and nitriles. (Bottom) Illustration of the synthesis of COFs with different framework topologies on the example of hexagonal and rectangular pore systems by the combination of two differently functionalized building blocks. At the bottom, some archetypical trigonal and rectangular backbones are shown.

enables precise control over pore sizes, even at the sub-nanoscale, by carefully selecting and arranging the constituent building blocks. One of the key features of reticular design in hydrogen-bonded frameworks is the ability to incorporate functional groups that participate in hydrogen-bonding interactions. These functional groups can be strategically placed within the framework to create specific and tailored interactions with guest molecules enabling selective binding and recognition within the pores. Furthermore, the modular nature of hydrogen-bonded frameworks allows for the assembly of complex architectures using multiple linkers.

Given that all HOFs inherently feature hydrogen-bonding motifs, they selectively interact with guest molecules by acting as hydrogen bond donor, hydrogen bond acceptor, or through other non-covalent interactions. The extent of this interaction heavily depends on the accessibility of the hydrogen-bonding motif itself. Due to the potential complexity and multi-valency of hydrogen-bonding motifs, not all the available hydrogen bond donor or acceptor sites are necessarily involved in hydrogen bonding. In some cases, hydrogen-bonding sites are not involved in structure formation and extend into the pore.[66] These sites can then bind to guests, resulting in stronger and more selective adsorption in the pore.

3.1.4. Metal-Organic Cages/Polyhedra and Covalent Organic Cages

Cavity-containing materials such as cages and macrocyclic compounds can maintain their porosity through their internal cavity even when the assembly of molecules is difficult to predict. Calixarene-based molecules are a prominent example of this,[67] which due to their internal cavity can maintain their porosity in the solid state, although the packing significantly affects the accessible porosity. Cage-based compounds present an advancement on these cavitand molecules, as they are designable and possess multiple pore windows in addition to their internal voids. Cage compounds combine microporosity and solution processability and are therefore extremely desirable for the fabrication of gas separation membranes.

When considering the design of cage compounds for adsorption, they are molecularly defined compounds with an organic or metal-organic backbone that features an internal cavity. These compounds exhibit precise control over their pore size and functions, thanks to their molecular nature. Additionally, their solubility enables their crystallization independently from the synthesis process.[68] To use cage compounds for gas adsorption or separation, they need to be stable toward activation and desolvation. This excludes many types of coordination cages that are only stable in solution.[69] The cages stable toward activation are typically based on chemistries that can be also found for MOF and COF, as these are based on rigid and directional bonds that create stable backbones. Water-stable MOCs with permanent porosity are frequently produced when oxophilic cations like Zr and Cr are used (similar to stable MOF design strategies) or through stable Rh-Paddlewheels. POCs are synthesized by imine condensation of amines and aldehydes with complimentary geometries, boronic acid condensation, and alkene metathesis.[70] The synthesis of these porous cages also uses a reversible assembly of building blocks, which leads to discreet cage molecules in solution instead of extended structures[71] that can then be crystallized in a second step. This innovative approach introduces a novel design methodology for the controlled construction of pre-fabricated molecular pores, ultimately yielding highly porous organic materials.[11,72,73]

3.2. Neat Reticular Membranes with Small Pores

Membranes composed of pure reticular materials, such as MOFs or COFs, fundamentally act as physical barriers that influence the flux of various gas species through their inherent material properties. The driving force behind membrane separation always hinges on chemical potential, with three distinct diffusional effects playing a crucial role in microporous spaces: capillary condensation, surface diffusion, and molecular sieving.[44] In the context of pure reticular materials, the pore window stands as the barrier, exerting the most significant impact on membrane separation and functioning as the rate-limiting step. Earlier reviews by Krishna have delved into diffusion within porous materials.[74] It is imperative to acknowledge that membrane science operates with continuous thin films, ranging in thickness from 1 nm to 100 μm, over areas spanning centimeters to meters. Thus, the diffusion path through a membrane is very short.

Capillary condensation is found in sub-nanometer pore space.[75] In contrast, most MOFs have tiny windows for effective molecular sieving, but also nanometer-sized cages where surface diffusion is a relevant process.[49,74] The film thickness needs to be as low as possible to allow for a fast flux of gases, thereby the influence of sorption selectivity and capillary condensation is lost to a large extent—and what remains is the molecular gate.[76] The neat materials used in membranes are usually supported by porous ceramics such as α-Al_2O_3, or polymeric supports, such as polyamides or polysilanes.[77]

A good example is the MFU (Metal-Organic Framework Ulm University) series, which shows highly confined pores with special features.[78] Especially in the low-temperature regime, the framework MFU-4 shows specific separation features, which can also be enabled in membranes and leads to higher separation factors and higher fluxes.[79] An important property of the MFU-4 series that was discovered recently is the quantum sieving effect, which allows to think about future perspectives of neat-MOF membranes. The separation of H_2 from D_2 is a highly complex problem that needs further evaluation and a technical solution. However, if this could be possible in membranes, continuous separation of isotopes would immensely lower the price for D_2 and deuterated chemical compounds.[80] For MFU-4 it was shown that D_2 gets trapped at very low temperatures in its small cavity (diameter of only 3.88 Å) after passing the narrow and stiff 2.52 Å pore window and could show a sorption selectivity of 7.5.[81] The quantum sieving happens at temperatures of 50 K and could open a whole new world of membranes and open a new field for reticular membrane materials.

Reticular chemistry, however, also enables the exchange of metal-sources to yield isoreticular membrane materials, and on the other hand heteroepitaxial growth. Changing metals, for example, changing the ratio of Zn/Co in ZIF-8 ($Zn(mIm)_2$ with mIm = 2-methylimidazole) and ZIF-67 ($Co(mIm)_2$) based membranes helps to adjust gas-sieving capabilities via synthetic control. Exchanging Zn^{2+} to Co^{2+} influences the grain boundary and intergrowth characteristic of the autoclave-based in situ synthesis of membrane layers, leading to a better molecular sieving membrane due to fewer grain boundary defects.[52] Another approach is the preparation of heterostructures that find use in guest-selective MOF films. The bottom-up layer-by-layer synthesis of heterostructures can yield highly potent, nanoporous designer solids.[82] In membrane science performance increases have been shown by examples, such as hetero-polycrystalline membranes in a combination of the crystal structures of ZIF-7 ($Zn(bIm)_2$ with bIm = benzimidazole) and ZIF-8 in the separation of hydrogen and CO_2.[83] An interfacial binding between two MOF lattices seems to be highly helpful, as it improves the polycrystalline intergrowth and reduces grain boundary defects. The example of ZIF-67 in combination with ZIF-8 allows for better separation performance than the individual MOF membranes.[50] The concepts of "heterobilayer," "MOF-on-MOF," or "epitaxial" MOF membranes, all representing the way of stacking one MOF onto another, are becoming more and more popular, as it is a helpful concept to close defect sites, as found by many groups simultaneously in individual studies. Isostructural MOFs, not only with 3D pore systems but also from 2D Kagome lattices tend to show the same behavior, as shown for Cu^{2+}-based Kagome MOFs constructed from 5-propoxyisophthalate, 5-methoxyisophthalate, and isophthalate.[84]

Additionally, dissolved molecular cages can be used to directly create membranes composed of pure porous molecular materials. This was shown with a pure cage membrane based on five cage compounds such as imine cages constructed from triformylbenzene (TFB) in combination with either (1R,2R)-1,2-cyclohexanediamine (CHDA) (referred to as CC3) or using 2-methyl-1,2-propanediamine (referred to as CC13), but also based on locked reduced amine cages that have improved chemical stability. The membranes were obtained by spin-coating a homogeneous solution onto non-porous or porous substrates such as porous alumina. Here, the cages yielded high H_2 permeance in an MMM, which turned out to be as high as 1.53×10^{-6} mol m^{-2} s^{-1} Pa^{-1} and a CO_2 permeance of 9.2×10^{-7} mol m^{-2} s^{-1} Pa^{-1}. Overall, the measured gas selectivities for the cage thin-film membranes were $CO_2/N_2 = 19$, $CO_2/CH_4 = 10$, $H_2/N_2 = 30$, and H_2/CH_4 close to 20.[65] Freeze drying was used to obtain amorphous materials, which still exhibited interconnected porosity derived from both the internal voids and extrinsic voids. The resulting membranes exhibited molecular sieving performance with high permeance and selectivity, making them suitable for various separation applications.

3.3. Reticular Materials in Composite Membranes

3.3.1. Mixed Matrix Concepts

While various pure reticular materials notably surpass Robeson's upper bound set for polymers in membrane separation[85–87] (**Figure 4**a), the challenge of upscaling remains paramount. While MOF films with polymer mixed matrix membranes may not offer a direct comparison, it does illuminate the advantages of neat materials over mixed matrix systems.

One of the remaining challenges for neat MOF membranes is the large-scale production of membrane areas of several m^2, out of ultra-thin, defect-free polycrystalline films. Moreover, together with challenging productions and prices of the starting materials and building blocks for MOF, COF, or other reticular materials, the highest costs are attributed to the ceramic substrates.[89] The integration of high-performance nano-sized solid materials into relatively inexpensive and easily liquid- or melt-processable polymers to form large and efficient mixed-matrix membranes (MMM) is another strategy that will find its application on the industrial scale more easily. By incorporating reticular materials into the polymer, the flux and selectivity can be increased, which leads to faster and improved processes. The diffusion of gases in

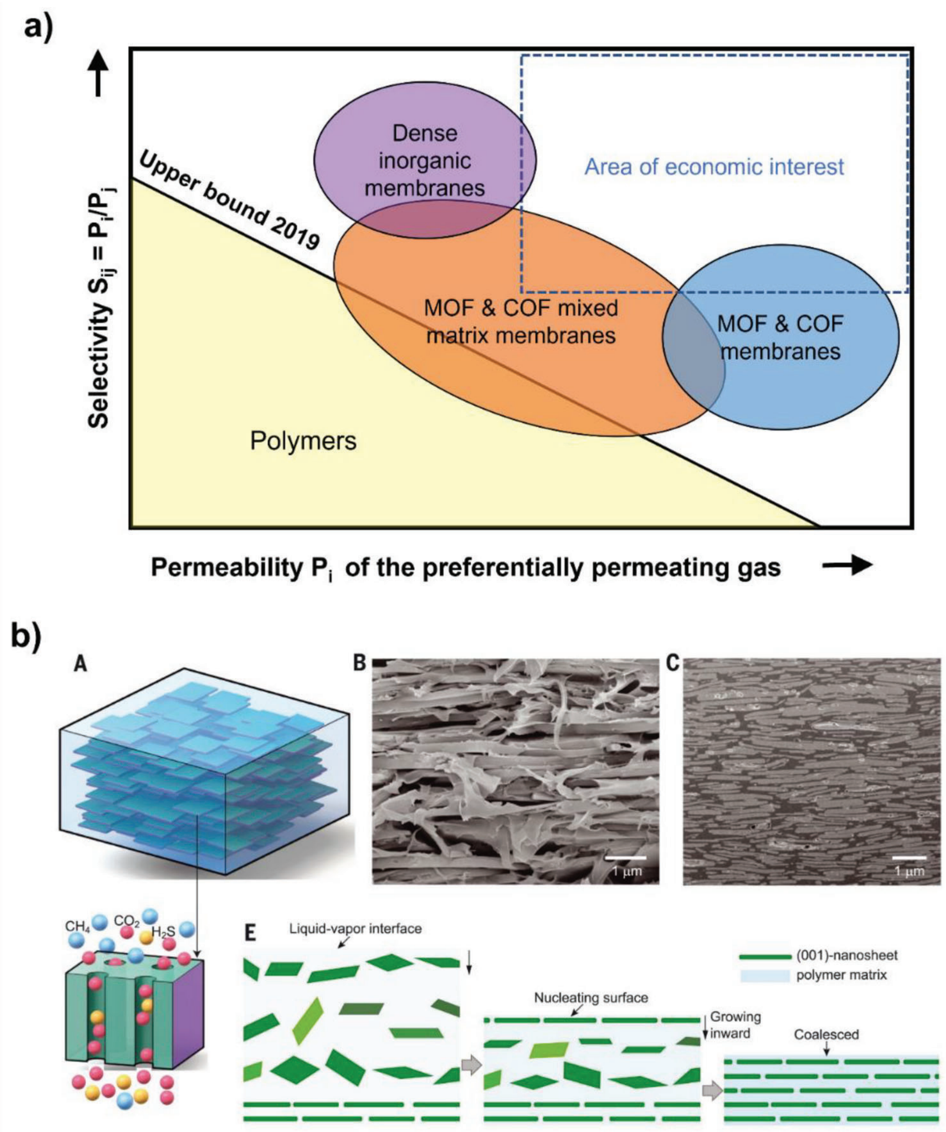

Figure 4. a) The benchmark plot for membrane performances, originally made by Robeson,[85] now since 2019 by McKeown.[88] Even though a comparison to the Robeson upper bound as a benchmark for inorganic, porous membranes is not physically reasonable, as the Robeson upper bound has been developed for solution diffusion in polymer membranes, it gives clear evidence of the benefits of neat MOF, COF, or dense, inorganic membranes over MMMs. Other than it often seems in literature, the neat reticular membranes (MOFs, COFs) are not meant by the term "inorganic membranes." b) High filler loaded MMM made with large sheets of MOFs—the authors call it MMMOF membrane, because it is not clear which part is more influential here. The large MOF sheets offer the dominant gas diffusion pathway through molecular sieving channels, due to their high content in the composite. Adapted with permission.[35] Copyright 2022, AAAS Science.

polymers follows the solution-diffusion model.[90] Using porous materials as fillers leads to gas separation through adsorptive processes and kinetic gas diffusion (molecular sieving) inside the polymer matrix.[91] Tuning the properties of the reticular material and trying different combinations of polymers and fillers, functionalizing them, and changing the physical conditions enable to overcome the benchmark (Figure 4a). The benchmark plot[85,92] from which a selectivity-permeability trade-off is visible, displays (usually on a logarithmic scale) the selectivity of a membrane against the permeability of the preferentially permeating species. In order to bring MMM's performance to the industry-applicable level[86] techno-economic analysis is necessary to define a point at which the developed separation membranes are an economically viable option[10] (Figure 4a).

At first glance, MMM seem to be quite facile since a filler is simply mixed with a polymer and further tested for its properties. However, from a materials perspective, there are many more steps and concepts involved to achieve defect-free MMMs and maximum selectivity and increased permeability. Liu et al.[93] reported outstanding $H_2S/CO_2/CH_4$ and nC_4/iC_4 separation performance for a MMM based on face-centered cubic MOFs, consisting of rare-earth metal clusters (yttrium or europium) and ditopic 1,4-naphthalenedicarboxylate or fumarate as linkers. In this case, the membrane prototypes have been studied under harsh, real feed gas conditions (in particular, with high feed pressure of up to 55 bar and high concentrations of corrosive H_2S) and remained effective, which makes such materials extremely promising for use in natural gas purification. Ghalei et al.[94] managed to achieve a separation factor of 24.1 for CO_2/N_2 for UiO-66-NH_2/PIM-1 MMM. Even though the permeability compared to the neat PIM-1 drops significantly (PIM-1 N_2 = 390 GPU, CO_2 = 3600 GPU, to 5 wt% UiO-66 with N_2 = 72 GPU, CO_2 = 1740 GPU) the increase in selectivity is still worth it and gives a membrane with good performance. Importantly, a part of this study was devoted to the mechanical properties of the membrane, which is crucial when it comes to forming/upscaling/transporting the membranes in industry.[10]

Despite the impressive progress made over the past two decades in MOF and COF membranes,[13] still many challenges persist, and one among them is the complex filler–polymer compatibility. In a seminal study, Moore and Koros[53] described five types of non-ideal effects in MMM leading to a drastic performance decline, often stemming from suboptimal polymer–filler interactions. Among the prevailing issues, a common hurdle is the formation of voids around filler particles, characterized as Case II or "sieve-in-a-cage" morphology.[95] Anticipating this concern can be addressed at the experiment's inception by adhering to the principle of "like interacts with like." Generally, organic polymers tend to exhibit improved compatibility with fillers abundant in organic components, rendering MOFs and particularly COFs prime contenders for MMM fillers due to their predominantly organic composition. This leads us to another guiding principle, as presented by Mahajan and Koros already in the year 2000[96] which gets ignored quite often: there is also a crucial need for a matrix phase selection. This provided concept suggests that the denser or less dense a polymer is, it require fillers with transport properties nearer to the matrix phase.[96] Thus, the conclusion we can draw here is that dense polymers, such as polyimides tend to work better with small window reticular materials, while polymers such as PIM-1 need fillers with faster transport and higher porosity. Nonetheless, the resultant compatibility is contingent upon numerous factors and parameters, necessitating a tailored approach for each system.

Not sufficient filler–polymer interaction can also lead to an undesirable effect of poor filler distribution, mostly due to its agglomeration. This problem becomes especially noticeable when the loading of the filler increases (usually 20% or more),[97–99] although in many cases higher amount of the active component in MMM is required to improve the separation performance.[97,99] Particle size has an impact on agglomeration as well: smaller particles in general are more likely to interact with each other and aggregate.[100] On the other hand, larger particles are frequently reported to demonstrate lower separation selectivity than well-distributed small particles. For instance, Nordin et al. demonstrate higher selectivity in their polysulfone MMMs with smaller particles, while the permeance increases with larger particle size and decreases with smaller particles,[101] bringing up another possible trade-off. Moreover, if the reticular filler materials have a very poor ability to form stable colloidal solutions in the solvent used for casting the membrane, it will most probably cause sedimentation and agglomeration in the membrane itself upon casting.[10,102]

Fortunately, in most cases, filler–polymer (or filler–solvent) compatibility can be improved and defects can be reduced by different treatment approaches, with functionalization being one of them. The ability to attach different functional groups to the components of MMMs, be it the surface of the polymer or MOF, opens new possibilities for tailoring its properties. Thus, adhesion can be significantly increased by introducing various bonding organic nitrogen groups in the structures,[98,99,103] most prominently amines.[94,104] Other groups, such as phenyl acetyl[97] and hydroxyl,[105] were also used to enhance the interaction in suitable systems. Consequently, the filler loading can also be increased by functionalization.[94,99] Sometimes, non-obvious approaches can also improve the polymer–filler interactions: Datta et al.[35] used aligned MOF nanosheets as a filler instead of more common nanoparticles, which not only enhanced the compatibility but also allowed for a higher loading (**Figure 5**b). Important to note that high polymer-filler adhesion might lead to the opposite effect—pore blockage, due to too strong interaction[106] or polymer entering large pores of the MOF.[107]

When it comes to choosing the base polymer for gas separation MMM, the nature of one must be considered first. In general, it is believed that rubbery polymers frequently have higher permeability than glassy polymers.[92] Some examples of high flux rubbery polymers and MOFs combinations studies as MMM are ZIF-8/PDMS (polydimethylsiloxane),[110] ZIF-8/PMPS (polymethylphenylsiloxane)[111] and functionalized UiO-66-NH_2 in PEG/PPG-PDMS copolymer.[112] In contrast, lower flux glassy polymers tend to have higher selectivity,[92] and a significant number of its combinations with MOFs has been reported, such as PEI (polyetherimide) with HKUST-1[113] and ZIF-62,[114] ZIF-20/PSF (polysulfone),[115] Mg-MOF-74/PVAc (polyvinyl acetate),[116] 6FDA-DAM with UiO-66[117] and functionalized ZIF-67,[10] as well as commercial Matrimid with ZIF-8[47] and MOF-5[118] and Ultem with ZIF-8[119] and post-modified MIL-53(Al).[98] Combining polymers of different nature for MMM into copolymers, such as SBS (polystyrene-block-polybutadiene),[120] SEBS (polystyrene-block-poly(ethylene-ran-butylene)-block-polystyrene)[121] and PEBA (polyether-*block*-amide),[122] is another perspective idea. It allows for tuning the properties of the system by tailoring both polymer and filler parts.[123]

It must be pointed out that a critical aspect that can be tackled particularly with reticular materials is polymer–filler compatibility. Therefore, it is necessary to understand the chemistry of both the polymer and the reticular material and combine both aspects positively.

3.3.2. Dissolved Cages

The most used membrane fabrication techniques involve fiber spinning through phase inversion techniques or large-area coatings, which require uniform dispersions of filler particles and polymer solutions. Therefore, it is essential to develop nanoparticle synthesis for MOFs and COFs.[124] Nevertheless, porous molecular materials easily crystallize in small particles and are favorably suited for their incorporation into MMMs. The weak interaction within the molecular crystals is easily broken and reformed without chemical modification and with little energy

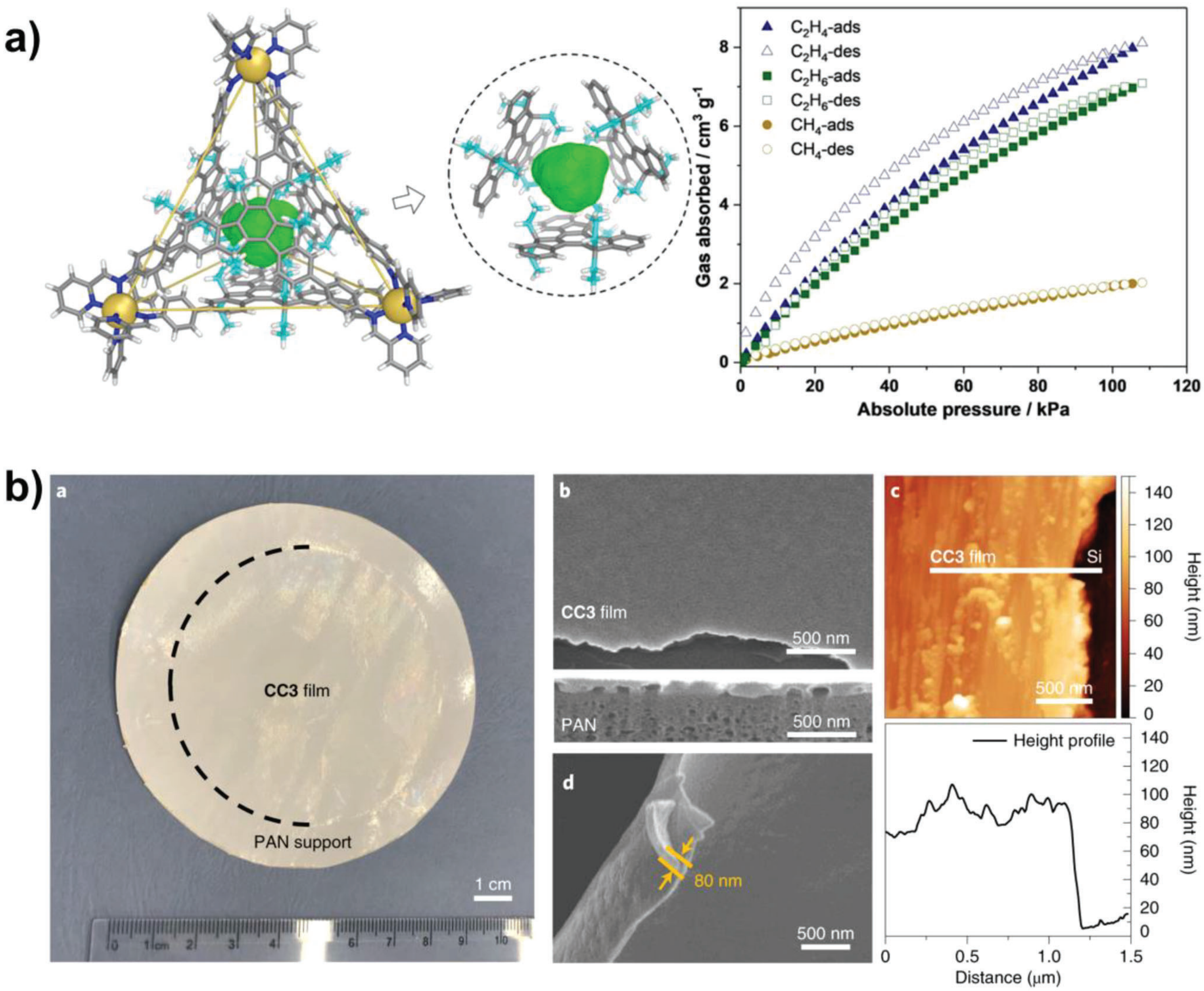

Figure 5. a) An Zn_4L_4 coordination cage with hydrocarbon selective sorption in its cavity. The adsorption is highly favorable for ethane/ethylene and propane/propylene over methane and could be used for methane separation. Adapted with permission.[108] Copyright 2021, Wiley VCH. b) A membrane film made of the organic cage CC3α together with PAN in an interfacial condensation reaction, yielding a defect-free porous organic cage membrane. A photograph, SEM images, and AFM analysis are shown. The film is 80 nm thin and shows responsive behavior. Reproduced with permission.[109] Copyright 2022, Springer Nature.

consumption in the process of dissolution and recrystallization. This enables facile recycling and regeneration of molecular porous materials,[125,126] which gives them a distinct advantage over other materials. The easy crystallization allows the use of wet impregnation of porous substrates or the growth of crystallites in the polymer substrate during or after the evaporation of the solvent via a ship-in-the-bottle approach.[127]

This approach was used for the fabrication of a MMM based on the 6FDA-DAM polymer (6FDA (4,4′-(hexafluoroisopropylidene)diphthalic anhydride), DAM (2,4,6-trimethyl-1,3-diaminobenzene)) with 20% loading of a molecular cage based on triformylebenzene and 1,2-cyclohexanediamine.[128] The preparation involved creating a homogeneous solution of polymer and cage in $CHCl_3$ and simply drop-casting it onto a glass substrate where it slowly evaporates. The cage then forms crystals of the same phase as in bulk in the polymer matrix ranging in size from 0.4 to 1.2 μm for MMM-20 wt% loading. As the cage crystals have an optimal size of pore windows of 4.0–4.4 Å for propane/propene separation, they show good a selectivity factor of >8 at 60 °C, indicating promising potential for feasible applications.

In addition to using cages as dispersed crystallites, they can be dissolved in regular solvents and a co-dissolution with polymers and direct fabrication of membranes with molecularly dispersed cages is possible. This was demonstrated with MOP-18,[129] a metal-organic cuboctahedron based on copper paddle-wheels with an isophthalic acid linker containing a long alkyl chain that imparts good solubility and lessen the driving forces for crystallization. This was used to incorporate molecularly dispersed, or dissolved cages into a Matrimid 5218 polymer-based

MMM. The solubility and good compatibility of the MOP with the polymer due to the long alkyl side chains leads to the ability of the membrane to tolerate up to 80 wt% MOP without separate crystallization of the MOP and with apparently uniform distribution of the MOP within the membrane. In comparison to the pure Matrimid 5218, the Matrimid 5218-MOP MMM exhibits significantly increased gas sorption capacity. This enhancement is attributed to a cooperative effect, where the MMM adsorbs more CO_2 than the pure MOP crystals. These membranes were then used for the separation of certain gases, for instance, the 44 wt% MOP-18/Matrimids MMM has a CO_2/N_2 selectivity of 26.0 at 35 °C ($P(CO_2) = 15.61$ Barrer) and the 33 wt% MOP-18/Matrimids MMM exhibits a CO_2/CH_4 selectivity of 21.9 (with $P(CO_2) = 14$ Barrer), which is better than the pure Matrimid.

3.3.3. Graphene/Graphene Oxide as Matrix Material

While polymer-based mixed matrix membranes are undoubtedly the most extensively studied membrane systems, it's worth considering other combinations involving reticular materials. Graphene and graphene oxide (GO) represent highly ordered ultra-thin carbon layers, offering an excellent epitaxial match with reticular materials. GO, due to its remarkably narrow pore size distribution, presents a high potential for selective gas sieving by itself.[130] In 2010, hybrid MOF/GO nanocomposites were successfully tested for H_2S removal.[131] In 2013, a similar system was reported to demonstrate a significant adsorptive CO_2 separation capability.[23] Further development of these systems yielded a supported 100 nm ZIF-8/GO nanocomposite membrane, serving as a molecular sieve with a CO_2/N_2 selectivity of 7. This marked the pioneering stride toward reticular membrane composites combined with carbon materials.[132] GO notably offers a robust platform for epitaxially grown MOF immobilization. Separation factors of 9.75 and 6.35 for H_2/N_2 and H_2/CO_2, respectively were reported for bulk flexible GO membranes decorated with UiO-66-NH_2 with a H_2 permeance of 3.9×10^{-8} mol m^{-2} s^{-1} Pa^{-1}.[133] Here, truly interesting for gas separation membranes with high performances are the systems where MOFs are intercalated, or intergrown between GO layers. Nano-sized ZIF-8 was grown in between GO layers and yielded membranes with a H_2 permeability of 73 Barrer, thereby reaching a remarkable selectivity of 43 for H_2/CH_4[134] and 26.4 for H_2/CO_2.[135] However, such systems are challenging to fabricate and some interfacial engineering is required.[134,136] The systems are not yet well thought through, but pioneering steps in this direction have been made and carbon-based materials in combination with reticular materials offer promising concepts for membrane technology.

4. Pore Aperture Editing Strategies

4.1. Same Linker Pore Aperture Reduction

Pore space reduction or partitioning by pore surface functionalization—either by pre-synthetic methods or post-synthetic modification—can also be a useful tool for having precise control over the size of the material's pores. Approaches like this are well known for the chemistry of mesoporous silica[137] and metal-organic frameworks.[138] Pre-synthetic methods require the organic synthesis of linker molecules with complex functionality, and the prerequisites are that the attached functional group a) does not interfere with the bond formation, b) does not affect the solubility of the building block in a way that the reaction is inhibited and c) sustains the sometimes harsh conditions of COF synthesis. This approach is in general favorable for robust functionalities that are coupled to the linker backbone using high temperature or strong acid/base conditions and in case weaker covalent bonds are used for the construction of the COF backbone.

The earliest reports of pore space minimization in COFs by pre-synthetic linker design were presented by the research group of Lavigne who tailored the pore surface of an isoreticular series of boroxine-linked COFs with sterically demanding alkyl chains.[139] Controlling the microenvironment of well-designed COF with nanopores (for example, reticular combination of short linker lengths) with functional sites like $-NH_2$, $-OH$, $-SO_3H$, $-COOH$ that can interact with molecules from the fluid phase is also a relatively straightforward and efficient technique toward making COFs amenable for separation techniques.[140,141]

Another useful strategy for regulating the pore diameter was developed by using asymmetric linker molecules as building units to create a hierarchical pore structure.[142] By layering the hierarchical pore systems in an alternating fashion in a membrane, the diffusion pathway remains intact due to the structural isotropy of the COFs while creating minimized pore diameters for effective separations.

The discreet and soluble porous cages can easily be crystallized into microporous solids with high BET surface areas, but due to their internal cavities, they do not require an ordered structure to have well-defined adsorption sites. As the internal cavity is typically larger than the pore windows of the cage, these can be employed to regulate guest diffusion and selectivity. Cages are constructed similarly to MOF and COF from individual linkers that react with each other, the size, shape, and functional groups have a direct influence on the geometry of the formed cage and the geometry and size of the cage windows. For optimal guest selectivity, small pore sizes increase the interaction of the guests with the cage molecule. In cage compounds the design of smaller pores is achieved by small linker molecules, additional functional groups inside the cages, as well as the cage geometry and bulky side groups that block the pore apertures.[73] The internal cavities can be decorated with additional functional groups that introduce stronger and specific interactions with guest molecules through hydrogen-bonding or other non-covalent interactions.[143] This control over pore apertures and internal cavities in POCs and related cage compounds, as opposed to other inherently porous materials, enables significantly better control over guest transit.[73,144] In MOCs/MOPs (used interchangeably) both the organic linker and the metal binding sites play an important role for small pore size. The unsaturated metal sites provide free sites to bind polar molecules which is useful in gas separation. The coordination of Lewis basic molecules on the unsaturated metal presents a straightforward strategy to modulate the pore size and introduce additional functionalities like aliphatic chains that can improve the binding of small hydrocarbon gases (Figure 5).[108] These membranes are highly engineered, and the analysis of MOCs inside these polymer films is challenging, as shown in Figure 5b. Nevertheless, their performance is strong in dye rejection water purification, as shown by He et al.,[109] and also offers promising potential for gas-sieving membranes in the future.

4.2. Mixed Linker Strategies to Reduce Pore Sizes

Keeping all this in mind, pore aperture editing can be performed using reticular chemistry (**Figure 6**). Zhou and co-workers were able to edit the pores in Zr-*fum* (*fum* = fumarate) with a single mesaconic acid (*mes*) linker to remove the ability for methane to diffuse through a membrane.[29] The rigidity of Zr-*fum* and the built-in *mes*-linker lead to a very strong exclusion on the scale of 1.8 cm in diameter and only about 30 nm MOF-film thickness on a ceramic Anodisc support with 20 nm straight pores.[29] This type of framework can be exchanged based on the isoreticular *fcu*-MOF system and synthesized within a few minutes using an electrochemical synthesis route, as described in detail by Zhou et al. in another outstanding work.[145] This enables highly potent molecular sieving membranes using rigid reticular materials with highly defined pore windows.

A unique approach to alter the pore diameter and polarity was conducted by preparation of multivariate β-Ketoenamine linked COFs with varying ratios of non-functionalized and carboxylate-functionalized linker molecules. The frameworks showed adjustable diffusion and adsorption of ammonia in dependence on the abundance of carboxylate groups which can form hydrogen bonds with incoming guest molecules and offer interaction-specific adsorption sites.[146]

4.3. Post-Synthetic Modification to Reduce Pore Size

The post-synthetic pathway requires the presence of receptive sites that can undergo reactions under mild conditions. Generally, this is a favorable method to attach chemically more labile groups to the backbone of COFs and it furthermore allows the attachment of a variety of different groups, making material screenings much easier. A drawback can be that many of the known mild reaction conditions, i.e., click reactions[147] or esterification[148] lead to the inclusion of spacers (i.e., 1,2,3-triazoles or ester bridges) connecting the targeted functionality with the COF backbone, which might be undesired for certain applications. This also allows for size-selective separation and enhances diffusion pathways. Moreover, the pore walls being an interface for controlling the surface interactions during molecular diffusions, the separation can be controlled by specific functionalization to maximize interactions (i.e., increasing retention time of certain analytes on the COFs pore wall) as well as having precise control over the composition.[141,149]

Post-synthetic modification of –OH functionalized COFs by acylation has also been explored to functionalize the COF pores with bulky functional moieties like azobenzene and stilbene to trigger selective adsorption of CO_2 over N_2.[150] Click reactions have been particularly instrumental in pore space reduction by the introduction of responsive groups to the pore walls. Jiang and co-workers explored the well-known CuAAC (Cu(I)-Catalyzed Azide-Alkyne Cycloaddition, also called Husigen reaction) click reactions to functionalize the pore walls. The click reaction of the azide group to ethynyl groups[151] can yield a quantitative functionalization while gradually decreasing the pore windows significantly.[152] Moreover, due to the polar azide groups, an induced layer slipping by 0.8 Å was observed by computational studies. This is thus a hybrid strategy to effectively reduce the pore dimensions.[153] The click reaction between azide and ethynyl has been also used to anchor targeted groups like benzene diimide (BzDI), naphthalenediimide (NDI), and perylenediimide (PDI) potentially opening new avenues for selective separations.[154] Functionalization might not only be a powerful tool to address molecular sieving via molecule-specific interaction sites,[155] functionalization with large side groups can benefit the regulation of diffusion pathways. However, this also poses the limitation that the ordering of the pores can be impeded, and more disorder is induced into the uniform nanochannels. This could in turn also form diffusion barriers for separation techniques, thus reducing the overall efficiency. In this respect, PolyCOFs or PolyMOFs have been an interesting materials concept.[156] Here, the bridging linker molecules are integrated into the backbone of a block-copolymer, and through interfacial polymerization free-standing membranes can be formed. This can yield some interesting features for the design of binder-free separation membranes. Furthermore, the polymer bridges between the linkers of the PolyCOF can regulate the pore diameter. Another technique from the field of metal-organic frameworks that might be applicable to covalent organic frameworks to enhance molecular separations is a technique called pore space partitioning. In this concept, a multitopic co-ligand is coordinatively installed into the pore space, which bridges the pore walls. Unlike the previously mentioned functionalization methods, the pore diameter is changed more drastically, as well as the network topology of the framework. It is well imaginable that post-synthetic cross-linking approaches between the linkages or linkers in COFs can also be exploited for covalent or coordinative pore space partitioning, pushing the COFs pore diameter into the regime suitable for many membrane-based separations.[157]

In hydrogen-bonded organic frameworks (HOFs), post-synthetic modification offers possibilities like other reticular materials based on organic linkers. However, HOFs typically use a single linker with three or more functional groups that participate in hydrogen bonding. Incorporating additional functional groups for post-synthetic modification in such molecules can be challenging compared to materials like MOFs, COFs, and cage compounds that use 2-c linkers. Nevertheless, late-stage functionalization of melamine-based linker molecules with functional groups that can be further modified in the solid state has shown promising results. This approach not only transforms HOFs into chemically robust covalently crosslinked networks, akin to COFs, but also leads to a reduction in pore size. This reduction in pore size could be utilized in the future to tailor the gas adsorption properties rationally.[158]

In organic cages (POCs), similar strategies as those used for COFs can be employed for post-synthetic functionalization of the interior of the pores. Additionally, the reversible linkages in POCs can be modified to improve chemical stability, alter the rigidity of the cages, or decrease the size of internal cavities. This flexibility in chemical modification of covalent bonds in POCs offers

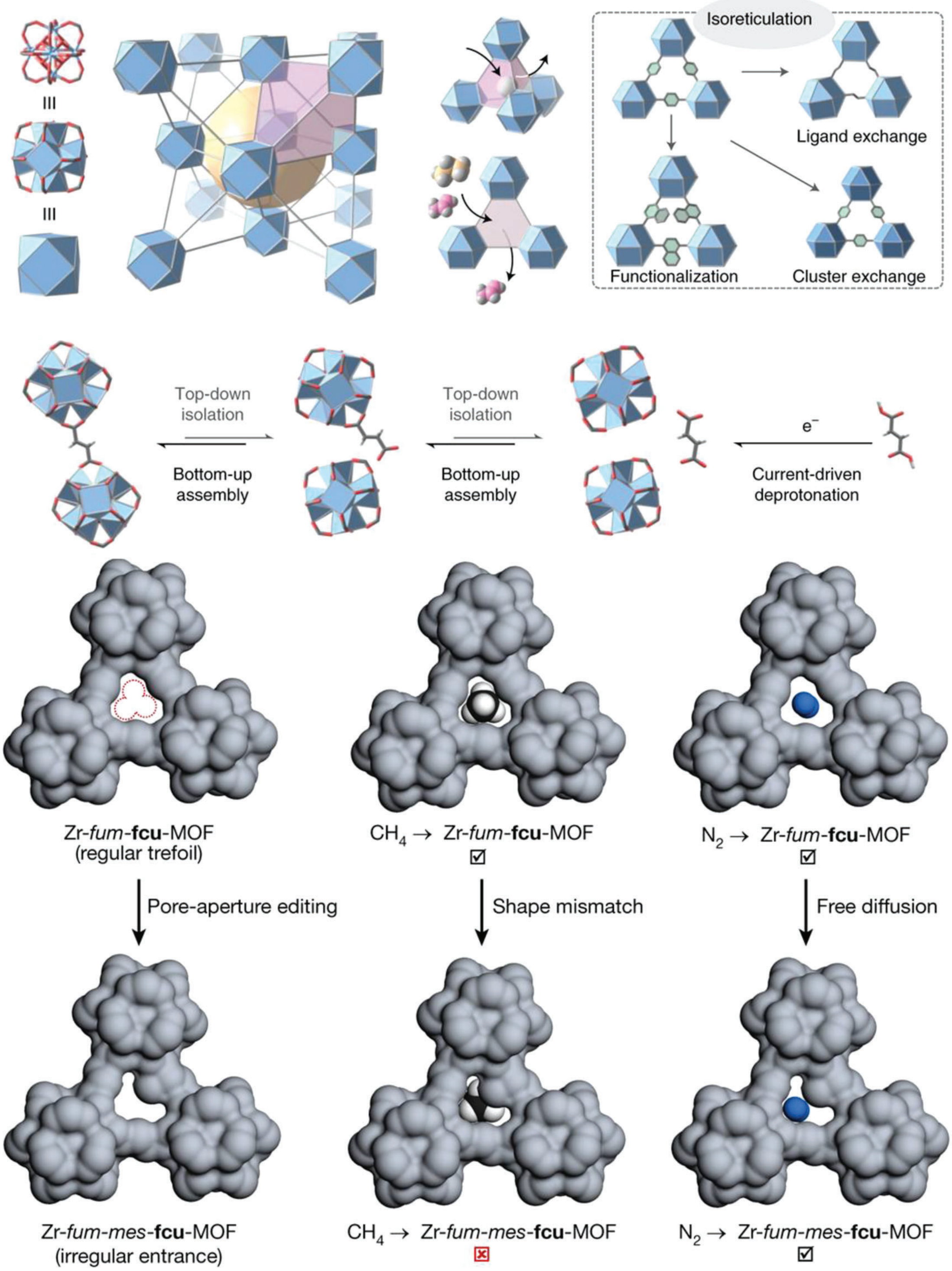

Figure 6. A combination of two images. Reproduced with permission.[29,145] Copyright 2021 and 2022, Springer Nature. The images blend in together to show the concept of reticular chemistry for Zr-based frameworks. On the top part, the electrochemical synthesis allows to define the framework in its functionalities in an isoreticular way, e.g., ligands, clusters, and side-chain functions in membrane films.[145] This concept was further used for the isoreticular synthesis of Zr-fum-fcu with the exact exchange of 1 linker per pore window from fumaric acid to mesaconic acid, which led to excluding methane effectively from penetrating the membrane.[29]

opportunities to fine-tune the pore sizes, thereby enhancing their gas adsorption capabilities.[70,159]

4.4. Pore Aperture Editing Based on Weak Interactions

4.4.1. Layer Stacking in COFs

A key strategy for enhancing the gas separation performance of Covalent Organic Frameworks (COFs) involves precise layer alignment and stacking offset to effectively reduce the pore aperture. The design principles for induced stacking differences in 2D COFs originate from the early theoretical studies, where the main stacking modes adopted by COFs and the slipping nature between the layers induce the synchronous existence of several stacking modes,[160] namely the serrated and inclined modes apart from the AA- and AB-stacking patterns (**Figure 7**). The earliest studies describe changes in the lateral offsets and the developed design principles have been correlated to the dipole density and the length of the linkers.[142,149,161] Experimental studies to complement these theoretical endeavors have found the utility of the induced "self-complimentary π electronic interactions" to tune the interlayer interactions and therefore possibly the stacking differences.[162] Directional slipping to induce offsets requires a close interplay between the geometry, polarity, and conformation of the building units.[163,164] The layer offsets that lead to a lower degree of stacking have been correlated to a loss of planarity of the building units, to linkers with higher dipole moments, or to ionic COFs.[165] In this aspect, it is worth pointing out the utilization of the electrostatic interaction of two counter ionic covalent organic nanosheets (iCONs) in the fabrication of membranes by a layer-by-layer (LbL) approach. The iCONs were deposited on a porous substrate alternately to induce a stacking difference driven by the intralayer repulsions to give segregated (i.e., smaller) pore apertures leading to efficient separation of H_2 and CO_2 (Figure 7c).[166] In this aspect, it is also important to recognize the impact of downsizing the layered 2D CONs to minimize the diffusion barriers and enhance permeation.[167] In addition to the pore space, the interlayer space also plays a key role in this separation technique, whereas an ordered edge on stacking is the preferred form of orientation.

The embedding of pseudorotaxanes into the backbone of COFs has been realized as a technique to control the number of layers in a stack through mechanic bonding, which is also a promising approach to influence the orderliness of the edge on stacks of several layers.[170] Furthermore, the charges in the pseudorotaxanes, also helped to facilitate the precise exfoliation of single stacks held together by mechanical bonds. Stacking offsets can also be mediated by engineering approaches, for instance by a combination of two COFs in a heterostack with different pore apertures in order to tailor the effective pore diameter at the interphase of the two materials.[171] Topological polymerization between the layers can be an interesting way to ensure stacking uniformity after the induced layer offsets to lock the layers into their stacking position by covalent bonding, and this also represents a unique strategy to ensure the increased lifetime of the membranes.[172]

Steric repulsions induced through attached bulky groups on the linker backbones can affect the ordering of the pore system and have been a promising method to tune stacking offsets

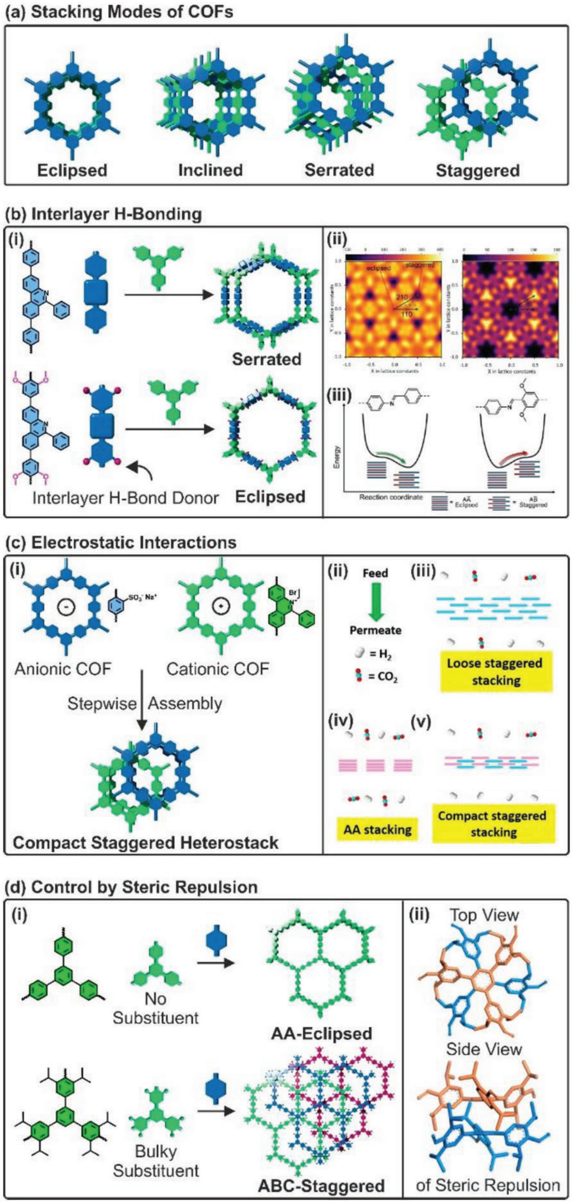

Figure 7. a) Schematic depiction of the most prevalent stacking modes possible in covalent organic frameworks. b-i) Illustration of Interlayer hydrogen bonding as a design principle for tuning the stacking between adjacent COF Layers. ii) Potential energy landscapes of the slipping of two adjacent layers in two isostructural COFs without (left) and with (right) interlayer hydrogen bonds. iii) Depiction of the potential energy changes in dependence on the stacking mode of the COF without hydrogen bond donor (left) and with hydrogen bond donor groups (right). Reproduced with permission.[168] Copyright 2021, American Chemical Society. c-i) Conceptual depiction of designing a COF heterostack with narrow pore size distribution by stepwise assembling cationic and anionic COFs. Schematic depiction of the separation of a feed consisting of ii) H_2 and CO_2 over a iii) loosely staggered COF, a iv) AA stacked (eclipsed) COF, and v) a compact staggered stacking found for the heterostack consisting of anionic and cationic COFs. Adapted with permission.[166] Copyright 2020, American Chemical Society. d-i) Schematic illustration of the use of bulky substituents on the linker to control the stacking by steric repulsion. ii) Top and side view of the arrangement of the substituted linkers in adjacent layers highlighting the steric repulsion. Adapted with permission.[169] Copyright 2018, American Chemical Society.

(Figure 7d).[173,169] This can consequently also provide additional interaction sites for guest molecules by tuning the interlayer interactions. Similarly, studies of the potential energy landscape by computational methods, in combination with experimental work have led to reduced interlayer slipping and eclipsed stacking by the introduction of anchoring groups (i.e., hydrogen bond donors and acceptors) on the backbone (Figure 7b). Further, the hydrogen donor groups (i.e., methoxy groups) also decreased the polarization of the imine-bonds in this specific example and hence reduced the repulsions between adjacent layers.[168] This means that precise control of flexibility of the building units and Van der Waals forces in between the layers have been conducive to effective tuning of the stacking offsets.[174] Rigidity generated by intralayer hydrogen bonding has been an excellent design strategy to control the dipole moments within the COFs plane, further dictating the stacking, and allowing for a rapid, scaled-up synthesis toward a COF material with an established stacking pattern.[175]

Apart from the abovementioned design strategies, solvation effects have also been an interesting pathway to inducing layer offsets,[176] representing a relatively simple method that was generalized for a range of imine-linked COFs by the group of Zhao.[177] An important theoretical study suggesting a mixed linker strategy to reduce the pore width was presented by Wolpert et al.[178] The combination of different advanced characterization methods including diffraction, electron microscopy, total scattering,[179] and solid-state NMR[180] has been employed to detect such stacking changes, which can be advantageously used along with the targeted design principles to successfully reduce the pore aperture for the application of COFs in membrane-based separations.[181] The dominating effect of the apparent pore size by stacking control on gas separation has been theoretically studied to give an important direction to membrane-based applications with the same strategy.[182]

4.4.2. Polymorphism as a Tool to Tune Pore Sizes and Apertures

In contrast to strongly bonded reticular materials such as MOFs and COFs, the class of porous molecular crystals offers a rich polymorphism that can be exploited to tune the properties (i.e., the pore size and metrics, exposed functional groups) from just one common molecular precursor.[183] All these features make molecular porous materials promising candidates for future gas separation applications.

Due to the strong and directional hydrogen bonds in HOFs, the structure, surface areas, and functional groups can be tailored by designing the linker molecules, while the high reversibility leads to highly crystalline structures that allow the easy exploration of the structure-function relationship. The high crystallinity but weaker hydrogen bonds allow the characterization of different polymorphs, which are frequently encountered in HOFs. Functional groups that participate in hydrogen bonding can assemble into different hydrogen-bonding motifs and weak interactions mitigated by crystallization solvents are leading to polymorphism.

Polymorphs generally exhibit comparable thermodynamic stabilities, with distinctions primarily manifesting in the packing, conformation, stacking, interpenetration, and crystal symmetries of molecules, all guided by supramolecular interactions.[183] Nonetheless, these polymorphs can significantly diverge in pore sizes, offering avenues to tailor HOF structures for gas separations.[184,185] On the other hand, polymorphism increases the complexity of the synthesis, particularly since predicting crystal structures in HOFs is notably more difficult than in COFs and MOFs. This unpredictable synthesis somewhat hinders the exploration of structure–function relationships, even though the straightforward crystallization ensures novel structure production.[64,126]

However, this structural flexibility comes with the drawback of potential loss of order or porosity when the strength of hydrogen bonds is inadequate to counteract capillary forces during desolvation.[184] This often necessitates the use of mild or multistep activation procedures in certain HOFs, introducing complexity to their application.[186]

Solubility also conveys significant advantages for purifying them. Rather than relying on synthetic conditions to afford phase pure material, or physically separating impurity phases post-synthetically, solution-based purification techniques can be used. In the realm of POC/MOC chemistry, these include both chromatographic and recrystallization procedures.[187] Due to the intrinsic porosity, cage compounds are incredibly versatile in endowing porosity like functionality. By the choice of a bulky solvent that cannot penetrate the pore apertures, it is even possible to generate porous solutions of cages. Assemblies of cages are used to form porous materials based on direct crystallization, covalent or coordinative crosslinking, and ionic interactions. Direct solvent removal from cage solutions can be used to create ordered crystals or disordered solids. Due to the mostly weak interactions between cages, cage compounds exhibit a rich polymorphism that can be used to control the selectivity for guest molecules by modulating the pore aperture between cage molecules through cage packing. Instead of pure vdW-based assembly, cage compounds can also be externally endowed with functional groups that lead to more directional assembly such as coordinating self-polymerization in MOCs, ionic groups leading to salt-type structures and hydrogen-bonding sites.[127,188] The cages arrangement is extremely important in determining the overall porosity, as the alignment of pore apertures determines in close-packed structures whether a material with accessible pores is formed or in less closely packed arrangements, if additional external porosity can be observed. In extreme cases, cages can be arranged directly or during aging into more closely packed structures, that are completely non-porous solids.[65] The easy structural transformation is related to gating effects during the adsorption of guest molecules.[189] In larger pore cage compounds, there is even polymorphism based on the cage interpenetration where a discrete number of cages are catenated to each other leading to smaller pore apertures.[190]

Methods that lead to disordered solids are also extensively used to create porous materials as the cage provides a well-defined cavity for adsorption, which is complemented by extrinsic porosity in between the cage molecules that depend on the assembly method.[127] Here, crosslinking of MOCs with flexible organic linkers coordinated to metal sites has been used to produce porous gels and solids. Crosslinking can also be achieved by the covalent connection of linker molecules into thermoset polymers.

4.4.3. Interpenetration

Interpenetration within reticular materials refers to the entwining of two or more networks of coordination frameworks within the same space. This characteristic can be strategically harnessed to decrease pore sizes, enhance gas separation performance, and improve selectivity. Despite its unpredictable outcomes, this intriguing strategy remains relatively underutilized. When reticular materials experience interpenetration, the spaces within their frameworks become more constrained due to overlap, leading to a reduction in effective pore size. This size exclusion phenomenon can be exploited to preferentially adsorb or separate gas molecules based on their sizes. Furthermore, interpenetration can facilitate cooperative interactions between the frameworks, resulting in synergistic effects that amplify the gas separation performance beyond what individual reticular materials could achieve on their own.[191]

The degree of interpenetration and the relative orientation of the interpenetrating frameworks can be controlled during synthesis, providing opportunities to finely adjust the pore environment.[184] These tunable pore environments offer possibilities for tailoring the gas separation properties of reticular materials.

In the context of Metal-Organic Frameworks, interpenetration can manifest as either full and static or dynamic, leading to induced fits as observed in "breathing" phenomena.[191] While a comprehensive discussion of interpenetration in MOFs extends beyond the scope of this review, previous literature delves into this topic in detail.[192]

In Covalent Organic Frameworks, interpenetration results in a reduction of pore size, commonly observed in 3D COFs within *dia* and *pts* nets.[193] Additionally, interpenetration can occur in 2D covalently linked nets, subsequently forming 3D catenated networks. An instance of this was observed in a spirofluorene-based *sql* lattice, which interpenetrated in a 3D arrangement.[194] Similarly, 2D structures of an *hcb* net, typically non-interpenetrating, based on a small-pore 3-c triformyl benzene and 2-c phenylene diamine, were shown to interpenetrate into a 3D network by employing tetramethyl phenylene diamine as a 2-c linker.[195] Comparable interpenetration isomerism is evident in HOFs,[185,196] where synthesis conditions can yield either non-interpenetrated 2D *hcb* nets or highly interpenetrated structures with significantly smaller pores compared to non-interpenetrated hexagonal structures. This involves a linker based on the linear hydrogen-bonding motif of a carboxylic acid binding to a pyridine unit.[196] Controlling interpenetration isomerism in HOFs enables pore size reduction. Synthesizing both interpenetrated and non-interpenetrated structures facilitates a direct comparison, revealing enhanced adsorption and selectivity for CO_2 over N_2 and CH_4 in the interpenetrated structures. Even in metal-organic cages and organic cages, instances of interpenetration have been observed, establishing it as a prospective strategy for reducing pore sizes within cage compounds.[197]

4.4.4. Small Pores by Induced Fit and Breathing

Guest-induced fit and breathing effects in reticular materials offer intriguing opportunities to generate small pores and enhance gas separation performance.[198] These dynamic phenomena involve structural changes in the reticular framework in response to the adsorption of guest molecules, resulting in varying pore sizes and selectivity.

Within Metal-Organic Frameworks (MOFs), guest-induced fit and breathing effects have been well-established and extensively studied.[198] A multitude of MOFs showcase "breathing" behavior, where the metal-organic nodes or linkers responsible for the framework's flexibility undergo conformational changes upon gas adsorption or desorption. This dynamic response leads to changes in pore sizes, allowing for selective gas uptake and separation. For a more comprehensive exploration of MOFs and their guest-induced effects, the reader is encouraged to refer to other comprehensive reviews.[48]

In the realm of Covalent Organic Frameworks (COFs), guest-induced fitting and breathing effects are relatively rarer due to the rigid nature of the building block motifs used in their synthesis.[199] Unlike MOFs, where metal-organic nodes often account for breathing behavior, COFs typically employ inflexible linkages that limit such behavior. Nevertheless, there are noteworthy exceptions in COFs, particularly instances where the conformational flexibility of COF linkages, such as imines, permits breathing.[200,201] As an illustration, a 3D *dia* COF constructed from tetrahedral tetraphenylmethane building blocks linked by imine bonds exhibits guest-induced contraction in the presence of THF vapors, resulting in reduced pore size and showcasing an induced fit with the guest molecules.[200]

Additionally, guest-induced breathing has been observed in assemblies of cage compounds, which are also used for gas separation applications. For example, a cage based on a narrow pore imide cage exhibited three distinct phases due to guest molecules being adsorbed into the structure.[202] This guest-induced breathing culminated in the selective adsorption of propyne over propane under ambient conditions. Analogous breathing effects were also observed in metal-organic polyhedra, where substantial structural transformations accompanied gas adsorption.[189]

This characteristic is especially evident in cage assemblies and HOFs, both reliant on weak interactions. This flexibility can lead to extreme structural shifts, yielding forms with large pores, narrow pores, or nonporous structures that can be accessed through recrystallization or direct guest-induced structural changes.[183,203,204] Breathing and gating effects involve changes in pore size in response to external stimuli like pressure, temperature, or guest molecules.[183,205] This phenomenon was observed in a tetraphenylethylene-based HOF containing a nitro groups, where the introduction of various solvents led to the framework's induced fit crystallization around the solvent or its incorporation, as seen with chloroform, tetrahydrofuran (THF), or dimethylformamide (DMF). Notably, this shape persisted after removing THF or chloroform solvent molecules, whereas pores collapsed after DMF removal. In addition to solvent incorporation, multiple co-crystal structures with non-volatile guests were demonstrated.[203]

4.5. Net-Based Strategies for Smaller Pores

4.5.1. Smaller Pores through Highly Connected Linkers and Nodes

Utilizing net-based strategies with highly connected linkers in reticular materials presents a promising approach to creating materials featuring small pores tailored for gas separation applications. This design principle involves utilizing nodes and linkers with high connectivity to reduce pore dimensions.

In the realm of MOFs, the net-based technique is more straightforward due to the prevalence of widely utilized nodes with high connectivity, such as the cuboctahedral zirconium oxo nodes. Coupled with small linear linkers, these nodes can yield exceedingly small pore apertures.[29,145]

However, in the context of COFs, this strategy is much more limited and challenging to implement, primarily due to the scarcity of highly connected organic linkers and their minimum sizes.[199] Despite these constraints, there are notable examples where highly connected linkers have been used to create COFs with reduced pore sizes. For instance, a non-interpenetrated 3D COF was synthesized using tetrahedral adamantane-based amines and triformyl trihydroxy benzene building blocks, yielding pores as small as 7.7 Å—a remarkable feat for COFs.[206] Among the available nets in COFs, the most prevalent are 2D,[199] with hexagonal *hcb* nets resulting in the largest pore sizes. This is even true for small 3-c and 2-c linkers, due to the formation of hexagonal pores requiring 6 sets of 3-c and 2-c linkers to encircle a single pore (1.3 nm for triformyl benzene + hydrazine).[207] However, pore dimensions can be reduced by utilizing 3-c + 3-c linkers instead. The *sql* net yields comparatively smaller pores for similar-sized 4-c and 2-c linkers (ranging from 10 to 18 Å for a porphyrin tetraphenyl amine + terephthalaldehyde).[208] Among the smallest native pores are realized in triangular pores based on linkers presenting a 60° angle between linker arms, as seen in the *hxl* nets, both resulting in comparatively smaller pores based on 6-c + 2-c building blocks (e.g., 1 nm hexa(4-formylphenyl) benzene + hydrazine).[209] Analogously small pores, as in *hxl* net-based COFs can be found in the triangular pores of *kgm*-based COFs, albeit with the addition of a second, larger pore in the structure.[164] Although net-based strategies employing highly connected nodes in COFs are less frequent and more intricate to implement, they offer unique opportunities for creating materials with tailored pore sizes given feasible linker synthesis. Notably, COFs incorporating both highly connected 8-c nodes and interpenetrated structures have been devised[210] as well as those utilizing 6-c 3D nodes based on triptycene cores.[211]

Many HOFs are devised around binding motifs that balance the count of H-bonding donors and acceptors, yielding specific H-bonding units like linear bonds such as the carboxylic acid dimer. These motifs preferentially generate 2D structures reliant on π–π and Van der Waals interactions for stabilization.[184,212] HOFs are an ideal target for synthesizing materials with small pores by combining complex hydrogen-bonding motifs with multifunctional linkers, which serve as highly connected binding motifs, sometimes in a 1D extension.

In these materials, it has been proven that the small pores are essential in creating robust binding sites for targeted guest molecules, essential for efficient gas separation.[213]

This was demonstrated with the facile production of a HOF based on a naphthalene tetracarboxylic acid diimide of aminoterephthalic acid.[214] The para-substituted benzene, alongside the carboxylic acid hydrogen-bonding motif, resulted in the formation of 4 Å small pores, contributing to the membrane's selective separation capabilities. Fabrication of a membrane based on this linker entailed dispersing HOF crystallites in a Matrimid solution in chloroform, loading it at 10 wt%, followed by drop-casting the dispersion. This led to efficient separation performance in terms of hydrogen (H_2) to methane (CH_4) separation, achieving a selectivity of 72.2 of a H_2/CH_4 mixture.

Similarly, small, well-defined pores were generated from a triphenylamine capped with melamines as hydrogen-bonding inducing units, known as UPC-HOF-6—the first reported HOF employed for membrane separation (**Figure 8**a).[215] Melamine units are frequently harnessed in HOF synthesis due to their dual role as hydrogen bond donors and acceptors. These units are renowned for complex binding motifs facilitating the creation of small pores. In the case of UPC-HOF-6, melamine incorporation resulted in W-shaped channels with remarkably small pore windows, measuring only 2.8 × 3.6 Å (Figure 8b). These unique characteristics significantly contribute to the material's exceptional separation performance. The fabrication of a pure HOF membrane using UPC-HOF-6 involved nucleating densely arranged crystallites by leveraging a concentrated material solution on porous Al2O3 substrates. This methodology yielded a membrane with precise structural attributes and enhanced separation properties (Figure 8c).

4.5.2. Small Pores Through Geometrical Frustration

Geometrical frustration in reticular materials represents a design principle capable of substantially decreasing pore sizes by forming sub-stoichiometric compounds with dangling linkages. This phenomenon emerges from the conflicting geometric constraints encountered by the constituent building blocks or linkers within the lattice. The rigidity or steric hindrance of these building blocks, when coupled with incompatible symmetries, induces lattice distortions and introduces periodic topological defects.

Regarding periodic topological defects, certain linkers or linker arms fail to bind with other nodes or linkers, resulting in their protrusion into the pore spaces. As a consequence, the otherwise available pore diameter experiences significant reduction, subsequently influencing the material's gas separation capacities. These topological defects typically align with sub-stoichiometric structures adopting nets, characterized by relatively smaller pore sizes compared to their parent stoichiometric structures.

The impact of geometrical frustration has been found in all reticular materials. For instance, in the realm of COFs, a well-investigated system involves the combination of a flat 4-c linker derived from pyrene or tetraphenyl ethylene with a 3-c linker, yielding sub-stoichiometric small pore 2D structures instead of the expected large pore 3D nets like *tbo*. In a COF combining a pyrene linker with triaryl benzene linkers yields the *bex* net, where pyrene acts as a 2-c linker with two linker arms, diminishing available pore sizes.[216] The analogous combination of a 4-c pyrene linker and a 3-c triphenyl amine linker leads to

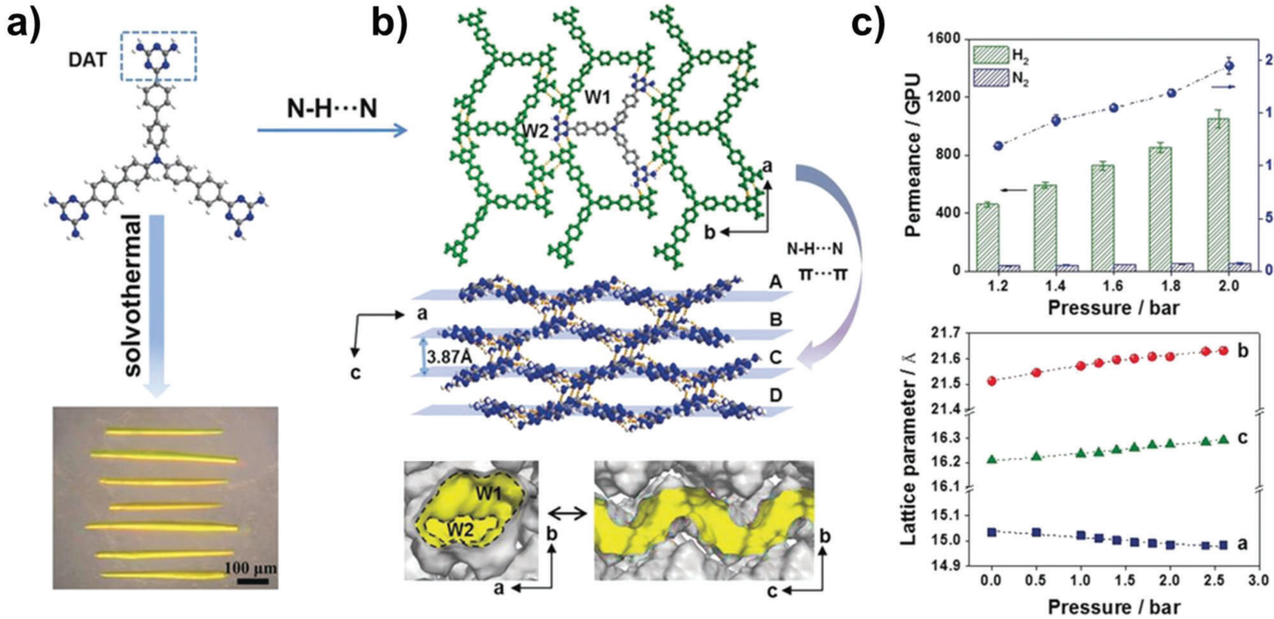

Figure 8. a) The organic building block and photograph of the crystals for UPC-HOF-6. b) 3D structure with a focus on the channel geometry in UPC-HOF-6, a very promising membrane material. c) Separation performance of UPC-HOF-6 membranes in measurements against higher pressure. The structural deformation of the lattice parameter is given, showing the flexibility upon low pressures, which leads to significant performance boosts. Reproduced with permission.[215] Copyright 2020, Wiley VCH.

the creation of 1D ribbons with the triphenyl amine serving as a 2-c linker possessing a dangling linker arm within the pore space.[217] Likewise, coupling a tetraphenyl ethylene-based linker with a triphenyl benzene linker results in a 2D *tth*-defect nets, with the triphenyl benzene linker acting as both a 2-c and a 3-c linker in the structure.[218] An aspect of frustration is polymorphism, explaining the observed different structural outcomes in frustrated systems despite very similar linkers.

A comparable strategy was employed for generating sub-stoichiometric 2D and 3D COFs with dangling functional groups. By utilizing a 6-c flat hexaphenyl benzene-based building block and quasi-tetrahedral 4-c building blocks anchored on methylated biphenyl cores,[219] a sub-stoichiometric *pts* net with dangling functional groups(**Figure 9**b) was achieved. Similarly, combining the 6-c linker with a flat 4-c linker based on tetraphenylethylene led to a sub-stoichiometric sql net (Figure 9a) hosting dangling functionalities. In both structures, the presence of dangling functional groups notably contracted pore sizes (Figure 9c). Both COFs were subsequently evaluated for gas separation using binary mixtures of C_2H_2/CH_4 and C_2H_2/CO_2. These sub-stoichiometric COFs displayed excellent IAST separation for C_2H_2/CH_4 and C_2H_2/CO_2, with values of 306.2 and 4.8 for the 2D *sql* COF, and 8.4 and 3.8 for the 3D pts COF, respectively.

In a similar vein, in the context of MOFs, the manifestation of geometrical frustration has been observed in small pore Truchet tile MOFs, where the angular nature of the linkers contributes to frustration, resulting in the formation of very small, irregularly sized pores.[220] Leveraging frustration as a design tenet, sub-stoichiometric MOFs have been synthesized using pseudo-fivefold symmetrical pentacarboxylic acid derived from a pentaphenyl pyrrole core. This gave rise to MOFs and HOFs with dangling linker arms, displaying exceedingly small pores that significantly influence gas adsorption properties.[221] This approach yielded two copper-based MOFs and a metal-organic HOF, all of which featured dangling linker arms and exhibited very small pores. frustration caused the formation of a metal-containing HOF instead of a fully connected MOF. In this particular system, the largest pores measured 11.3×11.3 Å^2 alongside smaller 4.6×3.8 Å^2 pores. The two MOFs, sharing the same linker and copper ions, were also found to be sub-stoichiometric, with dangling functional groups leading to reduced pore sizes. Despite their disparate structures, both MOFs exhibited very narrow pores, enabling CO_2 adsorption while precluding N_2 uptake. In a different MOF system, the combination of copper paddlewheels and a hexa(carboxy phenyl) benzene linker led to a sub-stoichiometric MOF,[87] which showed very small pores. The presence of dangling functional groups and hydrogen bonding between the linkers effectively sealed the pore space that would otherwise be accessible.

In the realm of HOFs, an instance involving 5-arm melamine-terminated linkers forming a “4-c” network culminated in the contraction of the pore size due to the fifth arm protruding into the pore.[66] Geometrical frustration has also been noted in cage-based compounds, leading to the generation of HOFs through hydrogen bonding, where dangling functional groups reduce pore sizes.[222]

5. Derived Guiding Principles and Conclusion

We want to present materials guiding principles to the reader, which we find promising for the development of reticular materials for membrane-based gas separation. The past two decades of developments in the reticular chemistry of MOFs and COFs, and further the development of MOPs, HOFs, and frustrated frame-

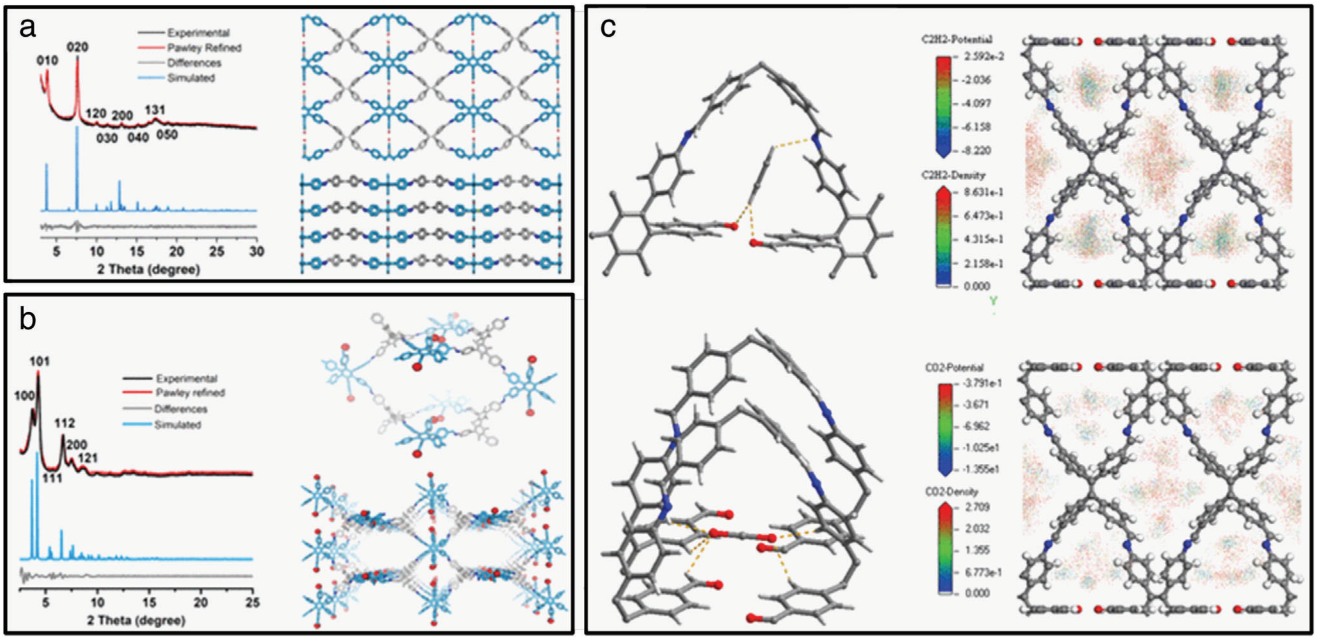

Figure 9. Sub-stoichiometric COFs generated by geometrical frustration as a design principle to improve the gas separation of CO_2 and acetylene through reducing the pore sizes in a pts and sql COF. Reproduced with permission.[219] Copyright 2020, American Chemical Soceity.

work systems have yielded a suite of different methods to control the pore diameters, particle sizes and dispersibility, and polycrystalline films. Although in most cases the goal was not to establish nanochannels for molecular sieving, many of those materials classes can be highly suitable in gas separation membranes. However, a lot of promising resources exist now, which allow to precisely engineer the nanochannels in neat materials, but also in mixed-matrix systems for membrane-based gas separations.

From the current state of literature, we can guide the reader toward interesting and highly promising concepts. The world of reticular materials has shown tremendous variety and possibilities, and we want to encourage researchers to approach materials testing more deliberately and with more sophisticated concepts and ideas.

In exploring the future of structural and property design in reticular materials for gas-sieving applications, two overarching ideas emerge at the forefront of discovery:

i) Pushing the Limits of Control: One avenue of advancement lies in discoveries at the very limits of control. For instance, investigating polymorphism in Metal-Organic Polymer (MOP) and Highly Ordered Framework (HOF) stacking within Covalent Organic Frameworks (COFs) goes beyond the conventional reticular guiding principles. Such novel structural control ventures into uncharted territories that are currently challenging to regulate using reticular chemistry alone. Consequently, further progress in this realm necessitates a return to traditional empirical exploration and optimization methods. By embracing an empirical approach of trial and error, we can unlock the potential of these intricate structures.
ii) The Challenge of Tailoring Properties: On the other front, there exists the ability to achieve full structural control within the unit cell of reticular materials. This enables highly tailored structural designs, offering exciting possibilities. However, an obstacle emerges when attempting to translate this rational design of structures into the rational design of properties. Achieving precise control over the properties of reticular materials remains a complex and relatively unexplored domain. In particular, properties related to gas adsorption require further attention. Many efforts have focused on the application of machine learning techniques to discover novel structures with desired properties, thereby alleviating the need for extensive experimental searches.

We have shown state-of-the-art materials with tremendous potential to be used in gas separation membranes. Throughout the perspective, we provide a look at interesting concepts and try to sharpen the view toward the most promising ones which we assume will end up being the dominating material development scenarios for gas separation membranes. The tiny windows and small pore channels in MOFs, COFs, HOFs, MOCs, and MOPs allow for kinetic separations and membrane technology offers even better energy efficiency for separations, such as carbon capture, methane valorization, and resource-effective/energy-saving raw chemical upgrading, compared to (cryogenic) distillation and half-continuous adsorptive processes (such as pressure-swing). We elucidate the two main areas for the application of reticular materials in gas separation membranes in their advantages and disadvantages: pure or neat thin film membranes and polymer mixed matrix membranes. We demonstrate that MOFs, COFs (and probably HOFs) are highly suitable for supported, pure reticular membranes and offer tremendous potential, while MOCs and MOPs will be rather seen in polymer-filler MMM systems. While MOFs and COFs also offer good compatibility, filler distribution, and the homogeneity of MOCs and MOPs to be the superior materials for MMMs.

As the last point we provided guiding principles for everyone researching the topic of reticular membrane materials and hope to offer interesting starting points for more ideas and better gas separation membranes toward an industrial disruption and finally a broad utilization of reticular materials in membranes.

Acknowledgements

O.S. and A.K. thank the Carl Zeiss Foundation for their support through the "Breakthroughs" program. A.K. is grateful for support by the Free State of Thuringia and the European Social Fund Plus. A.D. and A.S. gratefully acknowledge the support from the Collaborative Research Center "Chemistry of Synthetic 2D Materials" funded by the Deutsche Forschungsgemeinschaft (DFG, German Research Foundation) SFB-1415-651 417590517. A.S. and F.H. gratefully acknowledges the Fonds der Chemischen Industrie (FCI) for their support through the Liebig Fellowship.

Open access funding enabled and organized by Projekt DEAL.

Conflict of Interest

The authors declare no conflict of interest.

Keywords

covalent organic frameworks, gas separation membranes, metal-organic cages, metal-organic frameworks, mixed matrix membranes

Received: June 2, 2023
Revised: September 29, 2023
Published online: October 20, 2023

---

[1] B. F. Hoskins, R. Robson, *J. Am. Chem. Soc.* **1990**, *112*, 1546.

[2] R. Freund, S. Canossa, S. M. Cohen, W. Yan, H. Deng, V. Guillerm, M. Eddaoudi, D. G. Madden, D. Fairen-Jimenez, H. Lyu, L. K. Macreadie, Z. Ji, Y. Zhang, B. Wang, F. Haase, C. Wöll, O. Zaremba, J. Andreo, S. Wuttke, C. S. Diercks, *Angew. Chem., Int. Ed.* **2021**, *60*, 23946.

[3] J.-B. Lin, T. T. T. Nguyen, R. Vaidhyanathan, J. Burner, J. M. Taylor, H. Durekova, F. Akhtar, R. K. Mah, O. Ghaffari-Nik, S. Marx, N. Fylstra, S. S. Iremonger, K. W. Dawson, P. Sarkar, P. Hovington, A. Rajendran, T. K. Woo, G. K. H. Shimizu, *Science* **2021**, *374*, 1464.

[4] D. S. Sholl, R. P. Lively, *Nature* **2016**, *532*, 435.

[5] M. L. Szulczewski, C. W. Macminn, H. J. Herzog, R. Juanes, *Proc. Natl. Acad. Sci. U. S. A.* **2012**, *109*, 5185.

[6] R. Mansoor, M. Tahir, *Energy Fuels* **2021**, *35*, 3675.

[7] Z. Chen, K. O. Kirlikovali, P. Li, O. K. Farha, *Acc. Chem. Res.* **2022**, *55*, 579.

[8] W.-K. Qin, D.-H. Si, Q. Yin, X.-Y. Gao, Q.-Q. Huang, Y.-N. Feng, L. Xie, S. Zhang, X.-S. Huang, T.-F. Liu, R. Cao, *Angew. Chem., Int. Ed.* **2022**, *61*, e202202089.

[9] R. Pallach, J. Keupp, K. Terlinden, L. Frentzel-Beyme, M. Kloß, A. Machalica, J. Kotschy, S. K. Vasa, P. A. Chater, C. Sternemann, M. T. Wharmby, R. Linser, R. Schmid, S. Henke, *Nat. Commun.* **2021**, *12*, 4097.

[10] A. Knebel, A. Bavykina, S. J. Datta, L. Sundermann, L. Garzon-Tovar, Y. Lebedev, S. Durini, R. Ahmad, S. M. Kozlov, G. Shterk, M. Karunakaran, I. D. Carja, D. Simic, I. Weilert, M. Klüppel, U. Giese, L. Cavallo, M. Rueping, M. Eddaoudi, J. Caro, J. Gascon, *Nat. Mater.* **2020**, *19*, 1346.

[11] N. Giri, M. G. Del Pópolo, G. Melaugh, R. L. Greenaway, K. Rätzke, T. Koschine, L. Pison, M. F. C. Gomes, A. I. Cooper, S. L. James, *Nature* **2015**, *527*, 216.

[12] B. S. Pilgrim, N. R. Champness, *ChemPlusChem* **2020**, *85*, 1842.

[13] A. Knebel, J. Caro, *Nat. Nanotechnol.* **2022**, *17*, 911.

[14] a) H. Li, M. Eddaoudi, M. O'keeffe, O. M. Yaghi, *Nature* **1999**, *402*, 276; b) M. Kondo, T. Yoshitomi, H. Matsuzaka, S. Kitagawa, K. Seki, *Angew. Chem., Int. Ed.* **1997**, *36*, 1725.

[15] H. Demir, S. Keskin, *Comput. Chem. Eng.* **2022**, *160*, 107705.

[16] M. G. Goesten, M. F. De Lange, A. I. Olivos-Suarez, A. V. Bavykina, P. Serra-Crespo, C. Krywka, F. M. Bickelhaupt, F. Kapteijn, J. Gascon, *Nat. Commun.* **2016**, *7*, 11832.

[17] T. C. Wang, N. A. Vermeulen, I. S. Kim, A. B. F. Martinson, J. F. Stoddart, J. T. Hupp, O. K. Farha, *Nat. Protoc.* **2016**, *11*, 149.

[18] M. Yang, H. Wang, J. Y. Zuo, C. Deng, B. Liu, L. Chai, K. Li, H. Xiao, P. Xiao, X. Wang, W. Chen, X. Peng, Y. Han, Z. Huang, B. Dong, C. Sun, G. Chen, *Nat. Commun.* **2022**, *13*, 4792.

[19] W. Xu, O. M. Yaghi, *ACS Cent. Sci.* **2020**, *6*, 1348.

[20] C. Hepburn, E. Adlen, J. Beddington, E. A. Carter, S. Fuss, N. Mac Dowell, J. C. Minx, P. Smith, C. K. Williams, *Nature* **2019**, *575*, 87.

[21] G. O. Aksu, H. Daglar, C. Altintas, S. Keskin, *J. Phys. Chem.* **2020**, *124*, 22577.

[22] T. N. Do, C. You, J. Kim, *Energy Environ. Sci.* **2022**, *15*, 169.

[23] R. Kumar, S. Naz Ansari, R. Deka, P. Kumar, M. Saraf, S. M. Mobin, *Chem. - Eur. J.* **2021**, *27*, 13669.

[24] A. Bavykina, N. Kolobov, I. S. Khan, J. A. Bau, A. Ramirez, J. Gascon, *Chem. Rev.* **2020**, *120*, 8468.

[25] K. Suresh, D. Aulakh, J. Purewal, D. J. Siegel, M. Veenstra, A. J. Matzger, *J. Am. Chem. Soc.* **2021**, *143*, 10727.

[26] Z. Lai, *Curr. Opin. Chem. Eng.* **2018**, *20*, 78.

[27] A. Knebel, B. Geppert, K. Volgmann, D. I. Kolokolov, A. G. Stepanov, J. Twiefel, P. Heitjans, D. Volkmer, J. Caro, *Science* **2017**, *358*, 347.

[28] G. Avci, S. Velioglu, S. Keskin, *Appl. Mater. Interfaces* **2018**, *10*, 33693.

[29] S. Zhou, O. Shekhah, A. Ramírez, P. Lyu, E. Abou-Hamad, J. Jia, J. Li, P. M. Bhatt, Z. Huang, H. Jiang, T. Jin, G. Maurin, J. Gascon, M. Eddaoudi, *Nature* **2022**, *606*, 706.

[30] O. Smirnova, S. Hwang, R. Sajzew, A. Reupert, V. Nozari, S. Savani, C. Chmelik, L. Wondraczek, J. Kärger, A. Knebel, *ChemRxiv* **2023**, https://doi.org/10.26434/chemrxiv-2023-b8nnx.

[31] C. Altintas, S. Keskin, A. C. S. Sustain, *Chem. Eng.* **2019**, *7*, 2739.

[32] a) V. Nozari, O. Smirnova, J. M. Tuffnell, A. Knebel, T. D. Bennett, L. Wondraczek, *Adv. Mater. Technol.* **2022**, *7*, 2200343; b) S. Zhou, Y. Wei, L. Li, Y. Duan, Q. Hou, L. Zhang, L.-X. Ding, J. Xue, H. Wang, J. Caro, *Sci. Adv.* **2018**, *4*, 1393.

[33] P. Iacomi, G. Maurin, *Appl. Mater. Interfaces* **2021**, *13*, 50602.

[34] A. Guo, Y. Ban, K. Yang, W. Yang, *J. Membr. Sci.* **2018**, *562*, 76.

[35] S. J. Datta, A. Mayoral, N. Murthy Srivatsa Bettahalli, P. M. Bhatt, M. Karunakaran, I. D. Carja, D. Fan, P. Graziane, M. Mileo, R. Semino, G. Maurin, O. Terasaki, M. Eddaoudi, *Science* **2022**, *376*, 1080.

[36] G. C. Shearer, S. Chavan, S. Bordiga, S. Svelle, U. Olsbye, K. P. Lillerud, *Chem. Mater.* **2016**, *28*, 3749.

[37] L. Meng, T. Kai, S.-I. Nakao, K. Yogo, *Int. J. Greenhouse Gas Control* **2023**, *123*, 103830.

[38] S. Fujikawa, R. Selyanchyn, T. Kunitake, *Polym. J.* **2021**, *53*, 111.

[39] A. Siddhantakar, J. Santillán-Saldivar, T. Kippes, G. Sonnemann, A. Reller, S. B. Young, *Resour., Conserv. Recycl.* **2023**, *193*, 106935.

[40] B. Birner, J. Severinghaus, B. Paplawsky, R. F. Keeling, *Nat. Geosci.* **2022**, *15*, 346.

[41] B. Chen, H. Xie, L. Shen, Y. Xu, M. Zhang, M. Zhou, B. Li, R. Li, H. Lin, *Small* **2023**, e2207313.

[42] P. Bernardo, E. Drioli, *Fuel Process. Technol.* **2021**, *212*, 106624.

[43] A. A. Lysova, K. A. Kovalenko, A. S. Nizovtsev, D. N. Dybtsev, V. P. Fedin, *Chem. Eng. J.* **2023**, *453*, 139642.

[44] A. Ten Bosch, *J. Chem. Phys.* **2005**, *122*, 84711.

[45] F. Kapteijn, J. A. Moulijn, R. Krishna, *Chem. Eng. Sci.* **2000**, *55*, 2923.
[46] W. J. Koros, Y. H. Ma, T. Shimidzu, *Pure Appl. Chem.* **1996**, *68*, 1479.
[47] M. J. C. Ordoñez, K. J. Balkus, J. P. Ferraris, I. H. Musselman, *J. Membr. Sci.* **2010**, *361*, 28.
[48] A. Schneemann, V. Bon, I. Schwedler, I. Senkovska, S. Kaskel, R. A. Fischer, *Chem. Soc. Rev.* **2014**, *43*, 6062.
[49] F. Walenszus, V. Bon, J. D. Evans, S. Kaskel, M. Dvoyashkin, *J. Phys. Chem. Lett.* **2020**, *11*, 9696.
[50] A. Knebel, P. Wulfert-Holzmann, S. Friebe, J. Pavel, I. Strauß, A. Mundstock, F. Steinbach, J. Caro, *Chem. - Eur. J.* **2018**, *24*, 5728.
[51] D. Fan, A. Ozcan, O. Shekhah, R. Semino, M. Eddaoudi, G. Maurin, *J. Membr. Sci. Lett.* **2022**, *2*, 100029.
[52] Q. Hou, S. Zhou, Y. Wei, J. Caro, H. Wang, *J. Am. Chem. Soc.* **2020**, *142*, 9582.
[53] T. T. Moore, W. J. Koros, *J. Mol. Struct.* **2005**, *739*, 87.
[54] S.-Y. Ding, J. Gao, Q. Wang, Y. Zhang, W.-G. Song, C.-Y. Su, W. Wang, *J. Am. Chem. Soc.* **2011**, *133*, 19816.
[55] P. Kuhn, M. Antonietti, A. Thomas, *Angew. Chem., Int. Ed.* **2008**, *47*, 3450.
[56] A. P. Côté, A. I. Benin, N. W. Ockwig, M. O'keeffe, A. J. Matzger, O. M. Yaghi, *Science* **2005**, *310*, 1166.
[57] A. Schneemann, R. Dong, F. Schwotzer, H. Zhong, I. Senkovska, X. Feng, S. Kaskel, *Chem. Sci.* **2020**, *12*, 1600.
[58] B. J. Smith, A. C. Overholts, N. Hwang, W. R. Dichtel, *Chem. Commun.* **2016**, *52*, 3690.
[59] S. Wan, J. Guo, J. Kim, H. Ihee, D. Jiang, *Angew. Chem., Int. Ed.* **2008**, *47*, 8826.
[60] X. Chen, N. Huang, J. Gao, H. Xu, F. Xu, D. Jiang, *Chem. Commun.* **2014**, *50*, 6161.
[61] H. Fan, J. Gu, H. Meng, A. Knebel, J. Caro, *Angew. Chem., Int. Ed.* **2018**, *57*, 4083.
[62] S. Yuan, X. Li, J. Zhu, G. Zhang, P. Van Puyvelde, B. Van Der Bruggen, *Chem. Soc. Rev.* **2019**, *48*, 2665.
[63] H. Fan, H. Wang, M. Peng, H. Meng, A. Mundstock, A. Knebel, J. Caro, *ACS Nano* **2023**, *17*, 7584.
[64] R.-B. Lin, Y. He, P. Li, H. Wang, W. Zhou, B. Chen, *Chem. Soc. Rev.* **2019**, *48*, 1362.
[65] Q. Song, S. Jiang, T. Hasell, M. Liu, S. Sun, A. K. Cheetham, E. Sivaniah, A. I. Cooper, *Adv. Mater.* **2016**, *28*, 2629.
[66] K. E. Maly, E. Gagnon, T. Maris, J. D. Wuest, *J. Am. Chem. Soc.* **2007**, *129*, 4306.
[67] P. K. Thallapally, B. P. Mcgrail, J. L. Atwood, C. Gaeta, C. Tedesco, P. Neri, *Chem. Mater.* **2007**, *19*, 3355.
[68] M. A. Little, A. I. Cooper, *Adv. Funct. Mater.* **2020**, *30*, 1909842.
[69] T. Hasell, A. I. Cooper, *Nat. Rev. Mater.* **2016**, *1*, 16053.
[70] M. Hähsler, M. Mastalerz, *Chem. - Eur. J.* **2021**, *27*, 233.
[71] S. Lee, H. Jeong, D. Nam, M. S. Lah, W. Choe, *Chem. Soc. Rev.* **2021**, *50*, 528.
[72] a) A. A. Festa, L. G. Voskressensky, E. V. Van Der Eycken, *Chem. Soc. Rev.* **2019**, *48*, 4401; b) T. Hasell, J. L. Culshaw, S. Y. Chong, M. Schmidtmann, M. A. Little, K. E. Jelfs, E. O. Pyzer-Knapp, H. Shepherd, D. J. Adams, G. M. Day, A. I. Cooper, *J. Am. Chem. Soc.* **2014**, *136*, 1438.
[73] T. Tozawa, J. T. A. Jones, S. I. Swamy, S. Jiang, D. J. Adams, S. Shakespeare, R. Clowes, D. Bradshaw, T. Hasell, S. Y. Chong, C. Tang, S. Thompson, J. Parker, A. Trewin, J. Bacsa, A. M. Z. Slawin, A. Steiner, A. I. Cooper, *Nat. Mater.* **2009**, *8*, 973.
[74] R. Krishna, *Chem. Soc. Rev.* **2012**, *41*, 3099.
[75] I. Deroche, T. J. Daou, C. Picard, B. Coasne, *Nat. Commun.* **2019**, *10*, 4642.
[76] G. Sastre, J. Van Den Bergh, F. Kapteijn, D. Denysenko, D. Volkmer, *Dalton Trans.* **2014**, *43*, 9612.
[77] X. Ma, P. Kumar, N. Mittal, A. Khlyustova, P. Daoutidis, K. A. Mkhoyan, M. Tsapatsis, *Science* **2018**, *361*, 1008.
[78] S. Biswas, M. Grzywa, H. P. Nayek, S. Dehnen, I. Senkovska, S. Kaskel, D. Volkmer, *Dalton Trans.* **2009**, *33*, 6487.
[79] Q. Qian, A. M. Wright, H. Lee, M. Dinca, Z. P. Smith, *Chem. Mater.* **2021**, *33*, 6825.
[80] S. A. Fitzgerald, C. J. Pierce, J. L. C. Rowsell, E. D. Bloch, J. A. Mason, *J. Am. Chem. Soc.* **2013**, *135*, 9458.
[81] J. Teufel, H. Oh, M. Hirscher, M. Wahiduzzaman, L. Zhechkov, A. Kuc, T. Heine, D. Denysenko, D. Volkmer, *Adv. Mater.* **2013**, *25*, 635.
[82] Z. Wang, J. Liu, B. Lukose, Z. Gu, P. G. Weidler, H. Gliemann, T. Heine, C. Wöll, *Nano Lett.* **2014**, *14*, 1526.
[83] W. Li, P. Su, H. Tang, Y. Lin, Y. Yu, *Small* **2023**, *19*, e2205542.
[84] X. Wang, S. Kusaka, A. Hori, S. Sen, R. Matsuda, *Microporous Mesoporous Mater.* **2022**, *338*, 111950.
[85] L. M. Robeson, *J. Membr. Sci.* **2008**, *320*, 390.
[86] J. Dechnik, C. J. Sumby, C. Janiak, *Cryst. Growth Des.* **2017**, *17*, 4467.
[87] F. M. Amombo Noa, E. Svensson Grape, S. M. Brülls, O. Cheung, P. Malmberg, A. K. Inge, C. J. Mckenzie, J. Mårtensson, L. Öhrström, *J. Am. Chem. Soc.* **2020**, *142*, 9471.
[88] B. Comesaña-Gándara, J. Chen, C. G. Bezzu, M. Carta, I. Rose, M.-C. Ferrari, E. Esposito, A. Fuoco, J. C. Jansen, N. B. Mckeown, *Energy Environ. Sci.* **2019**, *12*, 2733.
[89] J. Caro, M. Noack, in Advances in Nanoporous Materials, (Ed.: S. Ernst), Elsevier, **2010**, pp. 1–96.
[90] B. Seoane, J. Coronas, I. Gascon, M. E. Benavides, O. Karvan, J. Caro, F. Kapteijn, J. Gascon, *Chem. Soc. Rev.* **2015**, *44*, 2421.
[91] D. Schneider, F. Kapteijn, R. Valiullin, *Phys. Rev. Appl.* **2019**, *12*, 044034.
[92] L. M. Robeson, Q. Liu, B. D. Freeman, D. R. Paul, *J. Membr. Sci.* **2015**, *476*, 421.
[93] G. Liu, V. Chernikova, Y. Liu, K. Zhang, Y. Belmabkhout, O. Shekhah, C. Zhang, S. Yi, M. Eddaoudi, W. J. Koros, *Nat. Mater.* **2018**, *17*, 283.
[94] B. Ghalei, K. Sakurai, Y. Kinoshita, K. Wakimoto, A. P. Isfahani, Q. Song, K. Doitomi, S. Furukawa, H. Hirao, H. Kusuda, S. Kitagawa, E. Sivaniah, *Nat. Energy* **2017**, *2*, 1.
[95] a) S. Husain, W. J. Koros, *J. Membr. Sci.* **2007**, *288*, 195; b) A. Knebel, S. Friebe, N. C. Bigall, M. Benzaqui, C. Serre, J. Caro, *Appl. Mater. Interfaces* **2016**, *8*, 7536.
[96] R. Mahajan, W. J. Koros, *Ind. Eng. Chem. Res.* **2000**, *39*, 2692.
[97] S. R. Venna, M. Lartey, T. Li, A. Spore, S. Kumar, H. B. Nulwala, D. R. Luebke, N. L. Rosi, E. Albenze, *J. Mater. Chem. A* **2015**, *3*, 5014.
[98] H. Zhu, L. Wang, X. Jie, D. Liu, Y. Cao, *Appl. Mater. Interfaces* **2016**, *8*, 22696.
[99] A. Kertik, L. H. Wee, K. Sentosun, J. A. R. Navarro, S. Bals, J. A. Martens, I. F. J. Vankelecom, *Appl. Mater. Interfaces* **2020**, *12*, 2952.
[100] J. Sánchez-Laínez, B. Zornoza, S. Friebe, J. Caro, S. Cao, A. Sabetghadam, B. Seoane, J. Gascon, F. Kapteijn, C. Le Guillouzer, G. Clet, M. Daturi, C. Téllez, J. Coronas, *J. Membr. Sci.* **2016**, *515*, 45.
[101] a) N. A. H. M. Nordin, A. F. Ismail, A. Mustafa, R. S. Murali, T. Matsuura, *RSC Adv.* **2014**, *4*, 52530; b) S. Japip, Y. Xiao, T.-S. Chung, *Ind. Eng. Chem. Res.* **2016**, *55*, 9507.
[102] Y. Shi, S. Wu, Z. Wang, X. Bi, M. Huang, Y. Zhang, J. Jin, *Sep. Purific. Technol.* **2021**, *277*, 119449.
[103] a) Q. Xin, J. Ouyang, T. Liu, Z. Li, Z. Li, Y. Liu, S. Wang, H. Wu, Z. Jiang, X. Cao, Z. Jiang, X. Cao, *Appl. Mater. Interfaces* **2015**, *7*, 1065; b) H. R. Amedi, M. Aghajani, *Microporous Mesoporous Mater.* **2017**, *247*, 124.
[104] a) R. Ding, W. Zheng, K. Yang, Y. Dai, X. Ruan, X. Yan, G. He, *Sep. Purific. Technol.* **2020**, *236*, 116209; b) S. Couck, J. F. M. Denayer, G. V. Baron, T. Rémy, J. Gascon, F. Kapteijn, *J. Am. Chem. Soc.* **2009**, *131*, 6326; c) L. Xiang, L. Sheng, C. Wang, L. Zhang, Y. Pan, Y. Li, *Adv. Mater.* **2017**, *29*, 1606999.
[105] N. Tien-Binh, H. Vinh-Thang, X. Y. Chen, D. Rodrigue, S. Kaliaguine, *J. Mater. Chem. A* **2015**, *3*, 15202.

[106] R. Semino, J. C. Moreton, N. A. Ramsahye, S. M. Cohen, G. Maurin, *Chem. Sci.* **2018**, *9*, 315.

[107] M. Fang, C. Wu, Z. Yang, T. Wang, Y. Xia, J. Li, *J. Membr. Sci.* **2015**, *474*, 103.

[108] J.-L. Zhu, D. Zhang, T. K. Ronson, W. Wang, L. Xu, H.-B. Yang, J. R. Nitschke, *Angew. Chem., Int. Ed.* **2021**, *60*, 11789.

[109] A. He, Z. Jiang, Y. Wu, H. Hussain, J. Rawle, M. E. Briggs, M. A. Little, A. G. Livingston, A. I. Cooper, *Nat. Mater.* **2022**, *21*, 463.

[110] M. Zhou, D. Guo, Z. Tang, U. Shafqat, *J. Environ. Chem. Eng.* **2022**, *10*, 106893.

[111] X.-L. Liu, Y.-S. Li, G.-Q. Zhu, Y.-J. Ban, L.-Y. Xu, W.-S. Yang, *Angew. Chem., Int. Ed.* **2011**, *50*, 10636.

[112] I. Hossain, A. Husna, S. Chaemchuen, F. Verpoort, T.-H. Kim, *Appl. Mater. Interfaces* **2020**, *12*, 57916.

[113] Y. Wang, G. Yang, H. Guo, X. Meng, G. Kong, Z. Kang, R. Guillet-Nicolas, S. Mintova, *J. Membr. Sci.* **2022**, *643*, 120070.

[114] C. Ma, Z. Yang, X. Guo, Z. Qiao, C. Zhong, *J. Membr. Sci.* **2022**, *663*, 121069.

[115] B. Seoane, J. M. Zamaro, C. Téllez, J. Coronas, *RSC Adv.* **2011**, *1*, 917.

[116] S. Majumdar, B. Tokay, V. Martin-Gil, J. Campbell, R. Castro-Muñoz, M. Z. Ahmad, V. Fila, *Sep. Purific. Technol.* **2020**, *238*, 116411.

[117] M. Z. Ahmad, M. Navarro, M. Lhotka, B. Zornoza, C. Téllez, W. M. De Vos, N. E. Benes, N. M. Konnertz, T. Visser, R. Semino, G. Maurin, V. Fila, J. Coronas, *J. Membr. Sci.* **2018**, *558*, 64.

[118] E. V. Perez, K. J. Balkus, J. P. Ferraris, I. H. Musselman, *J. Membr. Sci.* **2009**, *328*, 165.

[119] Y. Dai, J. R. Johnson, O. Karvan, D. S. Sholl, W. J. Koros, *J. Membr. Sci.* **2012**, *401–402*, 76.

[120] J. C. Moreton, M. S. Denny, S. M. Cohen, *Chem. Commun.* **2016**, *52*, 14376.

[121] W. S. Chi, S. Hwang, S.-J. Lee, S. Park, Y.-S. Bae, D. Y. Ryu, J. H. Kim, J. Kim, *J. Membr. Sci.* **2015**, *495*, 479.

[122] a) J. Sun, Q. Li, G. Chen, J. Duan, G. Liu, W. Jin, *Sep. Purific. Technol.* **2019**, *217*, 229; b) J. Shen, G. Liu, K. Huang, Q. Li, K. Guan, Y. Li, W. Jin, *J. Membr. Sci.* **2016**, *513*, 155.

[123] R. Nasir, H. Mukhtar, Z. Man, D. F. Mohshim, *Chem. Eng. Technol.* **2013**, *36*, 717.

[124] a) E. Ploetz, H. Engelke, U. Lächelt, S. Wuttke, *Adv. Funct. Mater.* **2020**, *30*, 1909062; b) J. Troyano, A. Carné-Sánchez, C. Avci, I. Imaz, D. Maspoch, *Chem. Soc. Rev.* **2019**, *48*, 5534.

[125] K. Vikrant, V. Kumar, K.-H. Kim, D. Kukkar, *J. Mater. Chem. A* **2017**, *5*, 22877.

[126] I. Hisaki, C. Xin, K. Takahashi, T. Nakamura, *Angew. Chem., Int. Ed.* **2019**, *58*, 11160.

[127] E. Sánchez-González, M. Y. Tsang, J. Troyano, G. A. Craig, S. Furukawa, *Chem. Soc. Rev.* **2022**, *51*, 4876.

[128] Q. Zhang, H. Li, S. Chen, J. Duan, W. Jin, *J. Membr. Sci.* **2020**, *611*, 118288.

[129] E. V. Perez, K. J. Balkus, J. P. Ferraris, I. H. Musselman, *J. Membr. Sci.* **2014**, *463*, 82.

[130] S. K. Alen, S. Nam, S. A. Dastgheib, *Int. J. Mol. Sci.* **2019**, *20*, 5609.

[131] C. Petit, B. Mendoza, T. J. Bandosz, *ChemPhysChem* **2010**, *11*, 3678.

[132] Y. Hu, J. Wei, Y. Liang, H. Zhang, X. Zhang, W. Shen, H. Wang, *Angew. Chem., Int. Ed.* **2016**, *55*, 2048.

[133] M. Jia, Y. Feng, S. Liu, J. Qiu, J. Yao, *J. Membr. Sci.* **2017**, *539*, 172.

[134] D. Liu, G. Pang, Z. Tang, S. Feng, *Inorg. Chem. Front.* **2019**, *6*, 2043.

[135] W. Li, Y. Zhang, P. Su, Z. Xu, G. Zhang, C. Shen, Q. Meng, *J. Mater. Chem. A* **2016**, *4*, 18747.

[136] A. Lalitha, J. E. Shin, S. Bonakala, J. Y. Oh, H. B. Park, G. Maurin, *J. Phys. Chem.* **2019**, *123*, 4984.

[137] a) B. G. Trewyn, I. I. Slowing, S. Giri, H.-T. Chen, V. S.-Y. Lin, *Acc. Chem. Res.* **2007**, *40*, 846; b) F. De Juan, E. Ruiz-Hitzky, *Adv. Mater.* **2000**, *12*, 430; c) D. Brühwiler, *Nanoscale* **2010**, *2*, 887.

[138] M. Kalaj, S. M. Cohen, *ACS Cent. Sci.* **2020**, *6*, 1046.

[139] R. W. Tilford, S. J. Mugavero, P. J. Pellechia, J. J. Lavigne, *Adv. Mater.* **2008**, *20*, 2741.

[140] a) A. Nagai, Z. Guo, X. Feng, S. Jin, X. Chen, X. Ding, D. Jiang, *Nat. Commun.* **2011**, *2*, 536; b) C. Liu, Y. Jiang, A. Nalaparaju, J. Jiang, A. Huang, *J. Mater. Chem. A* **2019**, *7*, 24205; c) N. Huang, X. Chen, R. Krishna, D. Jiang, *Angew. Chem., Int. Ed.* **2015**, *54*, 2986; d) S. Chandra, T. Kundu, K. Dey, M. Addicoat, T. Heine, R. Banerjee, *Chem. Mater.* **2016**, *28*, 1489; e) X. He, Y. Yang, H. Wu, G. He, Z. Xu, Y. Kong, L. Cao, B. Shi, Z. Zhang, C. Tongsh, K. Jiao, K. Zhu, Z. Jiang, *Adv. Mater.* **2020**, *32*, 2001284; f) Y. Zhao, Y. Zhao, J. Qiu, Z. Li, H. Wang, J. Wang, *ACS Sustainable Chem. Eng.* **2020**, *8*, 18413.

[141] J. L. Segura, S. Royuela, M. Mar Ramos, *Chem. Soc. Rev.* **2019**, *48*, 3903.

[142] Y. Zhu, S. Wan, Y. Jin, W. Zhang, *J. Am. Chem. Soc.* **2015**, *137*, 13772.

[143] a) B. Htan, D. Luo, C. Ma, J. Zhang, Q. Gan, *Cryst. Growth Des.* **2019**, *19*, 2862; b) N. Schäfer, M. Bühler, L. Heyer, M. I. S. Röhr, F. Beuerle, *Chem. - Eur. J.* **2021**, *27*, 6077.

[144] M. W. Schneider, H.-J. Siegfried Hauswald, R. Stoll, M. Mastalerz, *Chem. Commun.* **2012**, *48*, 9861.

[145] S. Zhou, O. Shekhah, J. Jia, J. Czaban-Jóźwiak, P. M. Bhatt, A. Ramírez, J. Gascon, M. Eddaoudi, *Nat. Energy* **2021**, *6*, 882.

[146] Y. Yang, M. Faheem, L. Wang, Q. Meng, H. Sha, N. Yang, Y. Yuan, G. Zhu, *ACS Cent. Sci.* **2018**, *4*, 748.

[147] B. Gui, X. Liu, Y. Cheng, Y. Zhang, P. Chen, M. He, J. Sun, C. Wang, *Angew. Chem.* **2022**, *134*, e202113852.

[148] L. Guo, S. Jia, C. S. Diercks, X. Yang, S. A. Alshmimri, O. M. Yaghi, *Angew. Chem., Int. Ed.* **2020**, *59*, 2023.

[149] J. Li, Z. Cheng, Z. Wang, J. Dong, H. Jiang, W. Wang, X. Zou, G. Zhu, *Angew. Chem., Int. Ed.* **2023**, *62*, e202216675.

[150] S. Zhao, B. Dong, R. Ge, C. Wang, X. Song, W. Ma, Y. Wang, C. Hao, X. Guo, Y. Gao, *RSC Adv.* **2016**, *6*, 38774.

[151] N. Huang, R. Krishna, D. Jiang, *J. Am. Chem. Soc.* **2015**, *137*, 7079.

[152] Z. Li, T. He, Y. Gong, D. Jiang, *Acc. Chem. Res.* **2020**, *53*, 1672.

[153] H. Xu, X. Chen, J. Gao, J. Lin, M. Addicoat, S. Irle, D. Jiang, *Chem. Commun.* **2014**, *50*, 1292.

[154] M. Martínez-Fernández, E. Martínez-Periñán, J. I. Martínez, M. Gordo-Lozano, F. Zamora, J. L. Segura, E. Lorenzo, *ACS Sustainable Chem. Eng.* **2023**, *11*, 1763.

[155] A. M. Fracaroli, P. Siman, D. A. Nagib, M. Suzuki, H. Furukawa, F. D. Toste, O. M. Yaghi, *J. Am. Chem. Soc.* **2016**, *138*, 8352.

[156] a) Z. Zhang, H. T. H. Nguyen, S. A. Miller, S. M. Cohen, *Angew. Chem., Int. Ed.* **2015**, *54*, 6152; b) Z. Wang, Q. Yu, Y. Huang, H. An, Y. Zhao, Y. Feng, X. Li, X. Shi, J. Liang, F. Pan, P. Cheng, Y. Chen, S. Ma, Z. Zhang, *ACS Cent. Sci.* **2019**, *5*, 1352; c) M. A. Pearson, S. Bhagchandani, M. Dincă, J. A. Johnson, *Mol. Syst. Des. Eng.* **2023**, *8*, 591.

[157] a) Q.-G. Zhai, X. Bu, X. Zhao, D.-S. Li, P. Feng, *Acc. Chem. Res.* **2017**, *50*, 407; b) G. He, R. Zhang, Z. Jiang, Z. Jiang, *Acc. Mater. Res.* **2021**, *2*, 630.

[158] J. Samanta, Y. Zhang, M. Zhang, A. D. Chen, C. Ke, *Acc. Mater. Res.* **2022**, *3*, 1186.

[159] a) X.-Y. Hu, W.-S. Zhang, F. Rominger, I. Wacker, R. R. Schröder, M. Mastalerz, *Chem. Commun.* **2017**, *53*, 8616; b) T. H. G. Schick, J. C. Lauer, F. Rominger, M. Mastalerz, *Angew. Chem., Int. Ed.* **2019**, *58*, 1768.

[160] a) B. Lukose, A. Kuc, J. Frenzel, T. Heine, *Beilstein J. Nanotechnol.* **2010**, *1*, 60; b) B. Lukose, A. Kuc, T. Heine, *Chem. - Eur. J.* **2011**, *17*, 2388.

[161] a) K. Dey, S. H. Kunjattu, A. M. Chahande, R. Banerjee, *Angew. Chem.* **2020**, *132*, 1177; b) B. T. Koo, W. R. Dichtel, P. Clancy, *J. Mater. Chem.* **2012**, *22*, 17460; c) E. L. Spitler, B. T. Koo, J. L. Novotney, J. W. Colson, F. J. Uribe-Romo, G. D. Gutierrez, P. Clancy, W. R. Dichtel, *J. Am. Chem. Soc.* **2011**, *133*, 19416.

[162] X. Chen, M. Addicoat, S. Irle, A. Nagai, D. Jiang, *J. Am. Chem. Soc.* **2013**, *135*, 546.
[163] a) H.-J. Da, C.-X. Yang, H.-L. Qian, X.-P. Yan, *J. Mater. Chem. A* **2020**, *8*, 12657; b) F. Haase, K. Gottschling, L. Stegbauer, L. S. Germann, R. Gutzler, V. Duppel, V. S. Vyas, K. Kern, R. E. Dinnebier, B. V. Lotsch, *Mater. Chem. Front.* **2017**, *1*, 1354.
[164] L. Ascherl, T. Sick, J. T. Margraf, S. H. Lapidus, M. Calik, C. Hettstedt, K. Karaghiosoff, M. Döblinger, T. Clark, K. W. Chapman, F. Auras, T. Bein, *Nat. Chem.* **2016**, *8*, 310.
[165] G. Das, T. Skorjanc, S. K. Sharma, F. Gándara, M. Lusi, D. S. Shankar Rao, S. Vimala, S. Krishna Prasad, J. Raya, D. S. Han, R. Jagannathan, J.-C. Olsen, A. Trabolsi, *J. Am. Chem. Soc.* **2017**, *139*, 9558.
[166] Y. Ying, M. Tong, S. Ning, S. K. Ravi, S. B. Peh, S. C. Tan, S. J. Pennycook, D. Zhao, *J. Am. Chem. Soc.* **2020**, *142*, 4472.
[167] C. Zhang, B.-H. Wu, M.-Q. Ma, Z. Wang, Z.-K. Xu, *Chem. Soc. Rev.* **2019**, *48*, 3811.
[168] S. T. Emmerling, R. Schuldt, S. Bette, L. Yao, R. E. Dinnebier, J. Kästner, B. V. Lotsch, *J. Am. Chem. Soc.* **2021**, *143*, 15711.
[169] X. Wu, X. Han, Y. Liu, Y. Liu, Y. Cui, *J. Am. Chem. Soc.* **2018**, *140*, 16124.
[170] X. Li, H.-S. Xu, K. Leng, S. W. Chee, X. Zhao, N. Jain, H. Xu, J. Qiao, Q. Gao, I.-H. Park, S. Y. Quek, U. Mirsaidov, K. P. Loh, *Nat. Chem.* **2020**, *12*, 1115.
[171] H. Fan, A. Mundstock, A. Feldhoff, A. Knebel, J. Gu, H. Meng, J. Caro, *J. Am. Chem. Soc.* **2018**, *140*, 10094.
[172] Y. Zhu, P. Shao, L. Hu, C. Sun, J. Li, X. Feng, B. Wang, *J. Am. Chem. Soc.* **2021**, *143*, 7897.
[173] F. Auras, L. Ascherl, A. H. Hakimioun, J. T. Margraf, F. C. Hanusch, S. Reuter, D. Bessinger, M. Döblinger, C. Hettstedt, K. Karaghiosoff, S. Herbert, P. Knochel, T. Clark, T. Bein, *J. Am. Chem. Soc.* **2016**, *138*, 16703.
[174] a) A. Kuc, M. A. Springer, K. Batra, R. Juarez-Mosqueda, C. Wöll, T. Heine, *Adv. Funct. Mater.* **2020**, *30*, 1908004; b) A. Mähringer, D. D. Medina, *Nat. Chem.* **2020**, *12*, 985.
[175] X. Li, J. Qiao, S. W. Chee, H.-S. Xu, X. Zhao, H. S. Choi, W. Yu, S. Y. Quek, U. Mirsaidov, K. P. Loh, *J. Am. Chem. Soc.* **2020**, *142*, 4932.
[176] S. Yang, X. Li, Y. Qin, Y. Cheng, W. Fan, X. Lang, L. Zheng, Q. Cao, *ACS Appl. Mater. Interfaces* **2021**, *13*, 29471.
[177] C. Kang, Z. Zhang, V. Wee, A. K. Usadi, D. C. Calabro, L. S. Baugh, S. Wang, Y. Wang, D. Zhao, *J. Am. Chem. Soc.* **2020**, *142*, 12995.
[178] E. Wolpert, A. Tarzia, K. Jelfs, *Chem. Commun. (Cambridge, U. K.)* **2023**, *59*, 6909.
[179] A. M. Pütz, M. W. Terban, S. Bette, F. Haase, R. E. Dinnebier, B. V. Lotsch, *Chem. Sci.* **2020**, *11*, 12647.
[180] C. Kang, Z. Zhang, A. K. Usadi, D. C. Calabro, L. S. Baugh, K. Yu, Y. Wang, D. Zhao, *J. Am. Chem. Soc.* **2022**, *144*, 3192.
[181] M. Fang, C. Montoro, M. Semsarilar, *Membranes* **2020**, *10*, 107.
[182] Y. Wang, W. Wang, Z. Zhang, P. Li, *Appl. Surf. Sci.* **2022**, *571*, 151355.
[183] D. V. Horváth, T. Holczbauer, L. Bereczki, R. Palkó, N. V. May, T. Soós, P. Bombicz, *CrystEngComm* **2018**, *20*, 1779.
[184] P. Li, P. Li, M. R. Ryder, Z. Liu, C. L. Stern, O. K. Farha, J. F. Stoddart, *Angew. Chem., Int. Ed.* **2019**, *58*, 1664.
[185] C. A. Zentner, H. W. H. Lai, J. T. Greenfield, R. A. Wiscons, M. Zeller, C. F. Campana, O. Talu, S. A. Fitzgerald, J. L. C. Rowsell, *Chem. Commun.* **2015**, *51*, 11642.
[186] L. Chen, B. Zhang, L. Chen, H. Liu, Y. Hu, S. Qiao, *Mater. Adv.* **2022**, *3*, 3680.
[187] a) N. Hosono, M. Gochomori, R. Matsuda, H. Sato, S. Kitagawa, *J. Am. Chem. Soc.* **2016**, *138*, 6525; b) G. Zhang, O. Presly, F. White, I. M. Oppel, M. Mastalerz, *Angew. Chem., Int. Ed.* **2014**, *53*, 1516.
[188] J. Troyano, S. Horike, S. Furukawa, *J. Am. Chem. Soc.* **2022**, *144*, 19475.
[189] G. A. Craig, P. Larpent, H. Urabe, A. Legrand, M. Bonneau, S. Kusaka, S. Furukawa, *Chem. Commun.* **2020**, *56*, 3689.
[190] P. Wagner, F. Rominger, J. H. Gross, M. Mastalerz, *Angew. Chem., Int. Ed.* **2023**, *62*, e202217251.
[191] M. Shivanna, Q.-Y. Yang, A. Bajpai, S. Sen, N. Hosono, S. Kusaka, T. Pham, K. A. Forrest, B. Space, S. Kitagawa, M. J. Zaworotko, *Sci. Adv.* **2018**, *4*, 1636.
[192] H.-L. Jiang, T. A. Makal, H.-C. Zhou, *Coord. Chem. Rev.* **2013**, *257*, 2232.
[193] a) Q. Fang, J. Wang, S. Gu, R. B. Kaspar, Z. Zhuang, J. Zheng, H. Guo, S. Qiu, Y. Yan, *J. Am. Chem. Soc.* **2015**, *137*, 8352; b) G. Lin, H. Ding, D. Yuan, B. Wang, C. Wang, *J. Am. Chem. Soc.* **2016**, *138*, 3302.
[194] F. Jin, H. L. Nguyen, Z. Zhong, X. Han, C. Zhu, X. Pei, Y. Ma, O. M. Yaghi, *J. Am. Chem. Soc.* **2022**, *144*, 1539.
[195] Y. Xiao, Y. Ling, K. Wang, S. Ren, Y. Ma, L. Li, *J. Am. Chem. Soc.* **2023**, *145*, 13537.
[196] J. Lü, C. Perez-Krap, F. Trousselet, Y. Yan, N. H. Alsmail, B. Karadeniz, N. M. Jacques, W. Lewis, A. J. Blake, F.-X. Coudert, R. Cao, M. Schröder, *Cryst. Growth Des.* **2018**, *18*, 2555.
[197] M. Frank, M. D. Johnstone, G. H. Clever, *Chem. - Eur. J.* **2016**, *22*, 14104.
[198] R. Kitaura, K. Seki, G. Akiyama, S. Kitagawa, *Angew. Chem., Int. Ed.* **2003**, *42*, 428.
[199] F. Haase, B. V. Lotsch, *Chem. Soc. Rev.* **2020**, *49*, 8469.
[200] Y.-X. Ma, Z.-J. Li, L. Wei, S.-Y. Ding, Y.-B. Zhang, W. Wang, *J. Am. Chem. Soc.* **2017**, *139*, 4995.
[201] a) T. Ma, E. A. Kapustin, S. X. Yin, L. Liang, Z. Zhou, J. Niu, L.-H. Li, Y. Wang, J. Su, J. Li, X. Wang, W. D. Wang, W. Wang, J. Sun, O. M. Yaghi, *Science* **2018**, *361*, 48; b) F. J. Uribe-Romo, J. R. Hunt, H. Furukawa, C. Klöck, M. O'keeffe, O. M. Yaghi, *J. Am. Chem. Soc.* **2009**, *131*, 4570.
[202] Z. Wang, N. Sikdar, S.-Q. Wang, X. Li, M. Yu, X.-H. Bu, Z. Chang, X. Zou, Y. Chen, P. Cheng, K. Yu, M. J. Zaworotko, Z. Zhang, *J. Am. Chem. Soc.* **2019**, *141*, 9408.
[203] Q. Huang, W. Li, Z. Mao, L. Qu, Y. Li, H. Zhang, T. Yu, Z. Yang, J. Zhao, Y. Zhang, M. P. Aldred, Z. Chi, *Nat. Commun.* **2019**, *10*, 3074.
[204] D. Aulakh, J. R. Varghese, M. Wriedt, *Inorg. Chem.* **2015**, *54*, 8679.
[205] Y. Yang, L. Li, R.-B. Lin, Y. Ye, Z. Yao, L. Yang, F. Xiang, S. Chen, Z. Zhang, S. Xiang, B. Chen, *Nat. Chem.* **2021**, *13*, 933.
[206] Q. Fang, S. Gu, J. Zheng, Z. Zhuang, S. Qiu, Y. Yan, *Angew. Chem., Int. Ed.* **2014**, *53*, 2878.
[207] L. Stegbauer, M. W. Hahn, A. Jentys, G. Savasci, C. Ochsenfeld, J. A. Lercher, B. V. Lotsch, *Chem. Mater.* **2015**, *27*, 7874.
[208] S. Lin, C. S. Diercks, Y.-B. Zhang, N. Kornienko, E. M. Nichols, Y. Zhao, A. R. Paris, D. Kim, P. Yang, O. M. Yaghi, C. J. Chang, *Science* **2015**, *349*, 1208.
[209] S. B. Alahakoon, C. M. Thompson, A. X. Nguyen, G. Occhialini, G. T. Mccandless, R. A. Smaldone, *Chem. Commun.* **2016**, *52*, 2843.
[210] Z. Shan, M. Wu, D. Zhu, X. Wu, K. Zhang, R. Verduzco, G. Zhang, *J. Am. Chem. Soc.* **2022**, *144*, 5728.
[211] H. Li, J. Ding, X. Guan, F. Chen, C. Li, L. Zhu, M. Xue, D. Yuan, V. Valtchev, Y. Yan, S. Qiu, Q. Fang, *J. Am. Chem. Soc.* **2020**, *142*, 13334.
[212] B. Wang, X.-L. Lv, J. Lv, L. Ma, R.-B. Lin, H. Cui, J. Zhang, Z. Zhang, S. Xiang, B. Chen, *Chem. Commun.* **2019**, *56*, 66.
[213] a) C. Y. Chuah, H. Lee, T.-H. Bae, *Chem. Eng. J.* **2022**, *430*, 132654; b) Y. Liu, G. Chang, F. Zheng, L. Chen, Q. Yang, Q. Ren, Z. Bao, *Chem. - Eur. J.* **2022**, *29*, e202202655.
[214] W. Li, Y. Li, J. Caro, A. Huang, *J. Membr. Sci.* **2022**, *643*, 120021.
[215] S. Feng, Y. Shang, Z. Wang, Z. Kang, R. Wang, J. Jiang, L. Fan, W. Fan, Z. Liu, G. Kong, Y. Feng, S. Hu, H. Guo, D. Sun, *Angew. Chem., Int. Ed.* **2020**, *59*, 3840.
[216] T. Banerjee, F. Haase, S. Trenker, B. P. Biswal, G. Savasci, V. Duppel, I. Moudrakovski, C. Ochsenfeld, B. V. Lotsch, *Nat. Commun.* **2019**, *10*, 2689.

[217] H. L. Nguyen, C. Gropp, O. M. Yaghi, *J. Am. Chem. Soc.* **2020**, *142*, 2771.
[218] B. Zhang, H. Mao, R. Matheu, J. A. Reimer, S. A. Alshmimri, S. Alshihri, O. M. Yaghi, *J. Am. Chem. Soc.* **2019**, *141*, 11420.
[219] L. Chen, C. Gong, X. Wang, F. Dai, M. Huang, X. Wu, C.-Z. Lu, Y. Peng, *J. Am. Chem. Soc.* **2021**, *143*, 10243.
[220] E. G. Meekel, E. M. Schmidt, L. J. Cameron, A. D. Dharma, H. J. Windsor, S. G. Duyker, A. Minelli, T. Pope, G. O. Lepore, B. Slater, C. J. Kepert, A. L. Goodwin, *Science* **2023**, *379*, 357.
[221] F. Haase, G. A. Craig, M. Bonneau, K. Sugimoto, S. Furukawa, *J. Am. Chem. Soc.* **2020**, *142*, 13839.
[222] W. Gong, D. Chu, H. Jiang, X. Chen, Y. Cui, Y. Liu, *Nat. Commun.* **2019**, *10*, 600.

Oksana Smirnova is currently pursuing her PhD under the supervision of Alexander Knebel within the Carl Zeiss "Breakthroughs" initiative at the Otto Schott Institute of Materials Research, Friedrich Schiller University Jena, Germany. She received her MSc in Nanosystems and Nanomaterials from Saint Petersburg State University, Russia. In Knebels' group, she is currently working on synthesis, gas transport, and optical properties of disordered, stimuli-responsive metal-organic frameworks, with particular interest in metal-organic framework glasses.

Subham Ojha is currently a PhD candidate at Martin Luther Halle-Wittenberg University, Germany. His research focuses on frustrated assembly in reticular materials and to study of highly complex porous materials. He completed his bachelor's in chemistry from Vikram Deb Autonomous College, India in 2018 and master's in chemistry from the Indian Institute of Technology Hyderabad (IITH), India in 2020.

Ankita De was born in 1997 in Kolkata, India. She obtained her master's degree in Chemical Nanoengineering in 2020, from Aix Marseille University in an Erasmus Mundus Joint Master program, where she did her thesis work under the guidance of Prof. Stefan Kaskel at Technische Universität Dresden. Thereafter she started working on her PhD at Technische Universität Dresden under the supervision of Dr. Andreas Schneemann. Her current research focuses on 2D Covalent Organic Frameworks (COFs) and their exfoliation by combining the tools of chemical functionalization and physical interactions and understanding the structure-based functionality of the prepared nanosheets.

Andreas Schneemann grew up in Sprockhövel, Germany. In 2016, he obtained his PhD in inorganic chemistry from Ruhr-University Bochum under the guidance of Roland A. Fischer working on flexible metal-organic frameworks. Afterward, he became a staff scientist at Technische Universität München. In 2017, he joined Mark D. Allendorf and Vitalie Stavila at Sandia National Laboratories in Livermore, California to investigate magnesium borohydrides for hydrogen storage. In 2019, he returned to Germany on a Liebig Fellowship to become an independent young investigator at Technische Universität Dresden, where his primary research focuses on the development of low-dimensional covalent organic frameworks.

Frederik Haase is currently a Junior Professor (W1) exploring frustrated assembly, topochemical reactions, and novel synthetic routes in reticular materials. In 2018, Frederik Haase received his Doctorate in Chemistry from the LMU University of Munich, Germany, which was supervised by Prof. Dr. Bettina at the Max-Planck Institute for Solid State Research in Stuttgart, Germany. Afterward, he joined the group of Prof. Shuhei Furukawa at Kyoto University, Japan as a JSPS-funded postdoc. After a postdoc and group leader stay at Karlsruhe Institute of Technology (KIT), Germany, he started his lab at Martin Luther University Halle-Wittenberg, Germany in 2022.

Alexander Knebel is an independent Carl Zeiss Foundation Research Group Leader within the "Breakthroughs" initiative at the Otto Schott Institute of Materials Science, Friedrich Schiller University of Jena since 2021. He received his PhD in Chemistry of Materials from the Leibniz University Hanover (Germany) in 2018, was a visiting researcher at the KAUST Catalysis Center (Saudi Arabia), and from 2019–2021 postdoc and group leader at the Karlsruhe Institute of Technology (Germany). His research combines reticular materials chemistry, complex physical characterization, and chemical engineering to do cutting-edge membrane science with ordered and disordered metal-organic and covalent organic framework materials.