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Scaling softness

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Soft porous crystals: flexible MOFs as a new class of adaptive materials

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Soft porous crystals (SPCs), particularly soft metal–organic frameworks (MOFs), represent a promising class of crystalline porous materials distinguished by their structural flexibility, dynamic behavior, and strong responsiveness to external stimuli. These features set them apart from conventional rigid materials and make them highly attractive for advanced technological applications. Despite extensive research on MOFs overall, soft MOFs remain relatively underexplored, and further investigation into their potential is essential for advancing materials science and enabling next-generation technologies. Although both SPCs and their rigid counterparts face common challenges in long-term operational stability (thermodynamic, chemical resistance, and mechanical durability) and large-scale high-quality production, the adaptive properties of SPCs—such as energy efficiency, high selectivity, and high capture efficiency—open up new frontiers for industrial production and real-world applications. In this perspective, to gain a comprehensive understanding of their promising applications, the research landscape is divided based on dosage usage regarding scaling softness, covering both (i) moderate and high-dose applications (storage and separation, catalysis, and energy storage) and (ii) trace or low-dose applications (electronic devices, biomedicine, and nuclear industry), and summarize the key technological fields within each category. It should be noted that high-quality SPCs can typically be obtained at low doses. However, at high doses, the increased presence of defects or disorder may lead to non-uniform structural transformations that propagate through the material. This behavior must be carefully considered in practical applications. Ultimately, an insightful outlook on the promising prospects of SPCs is provided.

Keywords: Soft porous crystals; Metal–organic frameworks; Flexibility; Applications; Industrialization.

1 Introduction

Soft porous crystals (SPCs) are a class of porous materials with ordered periodic structure that exhibit expansion or contraction (global flexibility) or ligand rotation and shuttle (local flexibility) under external stimulation, covering soft porous metal–organic frameworks (MOFs),[1,2] covalent organic frameworks (COFs),[3–6] and/or supramolecular assembly frameworks (SAFs),[7] particularly hydrogen-bonded organic frameworks (HOFs),[8,9] which are constructed from organic linkers and connected by inorganic building units, covalent bonds, or hydrogen bonds. By modifying metal ions (when present), organic ligands, guest molecules, and physical/chemical stimuli, the properties of soft porous motifs—including the flexible structure and function of ligands or frameworks—can be regulated. Such materials are considered ideal for dynamic gas handling operations spanning multiple fields. The inherent flexibility of these frameworks enables adaptive behavior—defined as the ability to undergo reversible structure changes in response to external stimuli such as temperature, pressure, guest molecule presence, or solvent environment, which can lead to conformational adjustments or even reversible structural transformations. One common behavior observed is the dynamic gate effect, where the framework's pore channels act like adjustable "gates": they can reversibly switch between "closed/narrow" and "open/large" states. In this process, the size, shape, or connectivity of the pores dynamically adjusts in response to stimuli (*e.g.*, guest adsorption), thereby overcoming the functional limitations of the rigid counterparts. Generally, in chemical separations, rigid adsorbents rely on size-exclusion or diffusion-limited effects, which can be modulated by adjusting pore size and shape to separate molecules of

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different sizes. By organizing interacting sites in a defined spatial configuration, they can achieve improved recognition properties through enhanced binding affinities for desired guests. Nonetheless, their ability to selectively recognize guest molecules in complex mixtures remains inadequate, especially for species that are smaller than the pore size or display comparable affinities.[10] The structural adaptivity endows SPCs with specific molecular discrimination capability, transforming separation performance from passive sieving to active molecular recognition.[11,12] Soft porous structures with guest-molecule-responsive features display exceptional separation of mixtures with very similar size/physical properties, and obtain ideal selectivity (such as isotope separation of water, CO_2/N_2, C_2H_2/CO_2 and isomers[13–16]). Besides, structural softness endows SPCs with unusual functionalities including negative gas adsorption,[17]
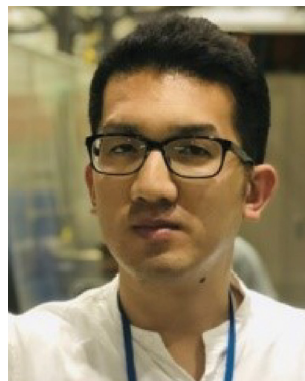
defects and stimuli-responsive behavior.[18] Such features like porosity, structure tunability and flexibility of SPCs enable their promising applications in adsorption, catalysis, separation, sensors, biomedicine, electronics, etc. However, to achieve large-scale industrial application of SPCs, further solutions are required for issues such as cyclic stability, preparation costs, and shaping methods.

Due to their distinct bonding natures, the flexibilities of MOFs, COFs, and HOFs differ from each other in certain aspects. For instance, MOFs are constructed from metal ions/clusters and organic linkers through coordination bonds. The dynamic nature of coordination bonds between metal nodes and organic linkers, the rotation, bending, and/or shuttling of organic linkers, and/or interpenetration effects collectively contribute to the framework flexibility. In contrast, COFs are completely built up from strong covalent

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Ken-ichi Otake earned his Ph.D. in Science from Kyoto University in 2016. After spending two years as a postdoctoral researcher at Northwestern University, he became an Assistant Professor at Kyoto University's Institute of Cell-Material Sciences in 2018. In 2024, he was promoted to Associate Professor within the same institute. He was awarded visiting professorship (assistant professor) from the Chinese Academy of Sciences (CAS) President's International Fellowship Initiative, PIFI, in 2023. His research centers on solid-state chemistry and catalysts, particularly focusing on coordination compounds.

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Ming-Shui Yao currently works at the Institute of Process Engineering (IPE), CAS as a full professor, PI, and serves as the deputy director of State Key Lab of Mesoscience and Engineering. He received his Ph.D. in Materials Science from IPE, CAS. Then he worked at FJIRSM, CAS, Kyoto University as a JSPS fellow (with Prof. Susumu Kitagawa), and University of Birmingham as a Marie Skłodowska-Curie fellow (with Prof. Shangfeng Du, Prof. Robert Steinberger-Wilckens). He does research in the interface chemistry of soft porous crystals and their applications in electrical devices, water treatments and gas-handling operations.

Ming-Shui Yao

Susumu Kitagawa received his Ph.D. at Kyoto University in 1979. He was promoted to Assistant Professor (1979), Lecturer (1983), and Associate Professor (1988) at Kindai University. He became Professor of Inorganic Chemistry at Tokyo Metropolitan University in 1992 and moved to Kyoto University as Professor of Functional Chemistry in 1998. He was a visiting scientist in F. A. Cotton Laboratory, Texas A&M University, from 1986–1987. He is now the vice president for promotion of research of Kyoto University and previously the director of the Institute for Integrated Cell-Material Sciences (WPI-iCeMS) at Kyoto University, launched by the Japanese government.

Susumu Kitagawa

bonds. The softness in COFs typically originates from the varied bond angles of flexible building blocks such as flexible C–O, C–C, or C–N single bonds with degrees of freedom, local dynamic behavior, and/or cooperative rotation and translation of neighbouring building blocks between frameworks within interpenetrated structure.[3–6] Compared with MOFs and COFs, HOFs are self-assembled through weaker hydrogen bonds, making them much more fragile and difficult to stabilize. However, simultaneously, in addition to organic motifs, much of the structural flexibility originates from the weaker H-bonding strength and the wide range of H-bond angles, leading to different flexible behaviors, such as pore size/shape changes, interpenetration/stacking manners, H-bond breaking/reconstruction, and local dynamic behavior.[19]

Among the three categories mentioned above, the research on soft MOFs, also known as flexible MOFs, is the most fascinating part. Soft MOFs are considered the third generation of MOFs. To date, MOF development has advanced to the fourth generation.[2] The in-depth research of MOFs makes people attach great concern over unlocking new features beyond adsorption and separation,[20,21] including structures (hierarchical pore structure, flexibility/softness),[22] functionalities (properties such as sound, light, electricity, magnetism, heat, *etc.*), and other stimuli-responsive properties[23,24] applied in the fields of photocatalysis, memristors, sensors, anti-bacterial, *etc.*[25,26] Besides, MOF derived materials[27] including carbon nanomaterials,[28,29] amorphous and glassy frameworks,[30,31] MOF hybrid materials[32] and metal–organic aerogels[33] have been developed. The history of MOF development can be traced back to the 1990s when the first-generation MOFs emerged; however, these materials are unstable and would collapse upon removing the guest molecules, or the pores are occupied by anions, and the structure is so dense that the guest cannot enter or leave.[34] The second-generation MOFs, termed rigid MOFs, also known as porous coordination polymers (PCPs), will keep the integrity and rigidity of the original structure upon adsorption/extrusion of a guest molecule, usually showing a Langmuir-type isotherm. Interestingly, guest-induced structural transitions are a feature in the third-generation MOFs. Several terms have been proposed to illustrate the adaptive nature of third-generation MOFs, including "soft", "flexible", "dynamic", "stimuli-responsive", and "switchable". These terms are intended to describe solid-state structural changes that are initiated under external stimuli. Such diversity in terminology reflects the ongoing exploration and evolving understanding of these materials within the scientific community. Finally, we use SPC as a general term that encompasses all flexible structures and properties of MOFs, COFs, HOFs, molecular aggregates, and solids. Specifically, the terms "soft MOFs" and "flexible MOFs" refer to the same underlying concept and are therefore used interchangeably throughout this perspective. More generally, softness and/or flexibility can

be defined as the inherent ability of the crystal framework to undergo reversible structural deformations or conformational changes in response to external stimuli (such as temperature, pressure, guest molecules, electric/magnetic fields, or light), while maintaining the integrity of the porous architecture. Regulated organic ligands, along with interdigitation or interpenetration structures, are elaborately designed to achieve softness (global/local dynamics) with unique sorption properties characterized by a hysteretic sigmoidal curve, which can be regarded as a gate-opening phenomenon, accompanied by a phase transformation. Interestingly, the first second-generation MOF to be demonstrated, $[Co_2(4,4'\text{-bpy})_3(NO_3)_4]$,[35] was also the first soft porous crystal with local dynamics.[36] The fourth-generation MOFs are still under study, usually considered the glass MOFs, hybrid MOFs, multiscale MOFs (such as nano-size MOFs), and so on.[1] Thanks to fast-developed characterization techniques, material modelling, and design strategies, it is now possible to rationally construct and tune the flexibility of MOFs, although this remains a challenge. However, it should be noted that, although numerous reports on the application of soft MOFs have been reported, the primary research focus remains on enhancing the performance of traditional separation/storage materials. Additionally, many applications of rigid MOFs have not been fully extended to soft MOFs, primarily due to the lack of conductivity, insufficient research on radiation resistance, the need for improved stability, and high costs in soft MOFs.

The development of SPCs not only represents a technological advancement in the field of porous materials, but also heralds a profound transformation—from traditional "static" functional materials to "dynamic responsive" smart materials. Although the practical applications of SPCs and their rigid counterparts are facing the same challenges of long-term operational stability (thermodynamic, chemical resistance, and mechanical) and the ability to produce high quality in large quantities, their adaptive properties open up new possibilities for industrial production and practical applications because of the advantages of energy efficiency, high selectivity, and high capture efficiency. Deepening application exploration, scaling synthesis, and engineering integration are critical to accelerate industrialization of advanced functional materials and meet high-end manufacturing and sustainability demands. In industrial production, the dosage of materials directly affects their economic viability and practical feasibility, a characteristic known as "dose sensitivity". For SPCs, dose sensitivity varies across different application scenarios. In trace or low-dose, high-value applications (*e.g.* sensing, biomedicine), although the quantity used is small and cost impact is limited, extremely high performance and batch consistency are required. In moderate and high-dose applications (*e.g.* gas separation, waste gas treatment), a balance between performance and cost becomes crucial, with an emphasis on cost-effectiveness. Besides, cost control

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is paramount, and factors such as synthesis cost, recyclability, and scalability determine whether these materials can be practically adopted. Thus, understanding dose sensitivity is key to optimizing SPC applications and enabling their industrial deployment.

In this perspective, we direct our attention to soft MOFs, a highly researched subclass of SPCs. Thanks to soft MOFs' global or local dynamics, these materials exhibit a wide range of unique properties and functionalities that make them highly valuable in various applications. Whether other types of flexibility can be observed to bring about even more applications remains an unknown and eagerly anticipated research direction. To fully appreciate their broad-ranging impact, we categorize their practical applications into two distinct domains: i) moderate and high-dose applications and ii) trace or low-dose applications (Fig. 1). The former category encompasses applications such as storage and separation, environmental pollution control, and catalysis in CO_2 reduction, where properties such as stability, cost-effectiveness, selectivity, green synthesis, and energy efficiency take center stage.[37,38] Meanwhile the latter encompasses research fields including electronic devices and biomedicine, where tailored functionalities should be endowed. It's worth noting that this classification is not absolute and may vary depending on the actual amount used. To expand the applications of SPCs, we have also listed some recently developed areas where rigid MOFs have already found applications. However, the expansion of flexible MOFs remains at an embryonic or nascent stage in these fields—such as memristors, spintronics, energy storage, uranium adsorption and detection—yet they hold significant potential. We believe that this perspective will contribute to advancing the future development of SPCs.
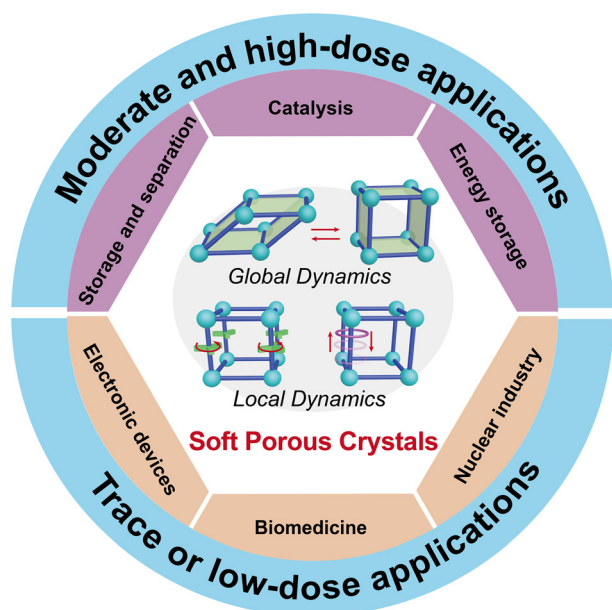

Fig. 1 Overview of topics discussed in this perspective.

2 Moderate and high-dose applications

In these situations, larger quantities (kilograms to tons) of SPCs should usually be synthesized to meet the needs of industrialization. To achieve green and sustainable production of SPCs, various factors should be considered, such as i) selecting cheaper, safer, and/or biologically compatible building blocks; ii) reducing energy consumption; iii) using a non-toxic reaction medium; iv) ensuring easy activation.[39] Here, activation of SPCs refers to the critical process of removing solvent molecules, templates, or other impurities from the pore channels through physical or chemical methods (*e.g.* solvent exchange, drying and thermal treatment). This process aims to preserve the inherent pore structure, keep the pores in an "open" state, and expose more active sites to achieve target functions.

2.1 Storage and separation

Gas storage and separation are the two typical application scenarios of SPCs. Traditional porous materials, such as molecular sieves and activated carbon, are widely used in these two aspects due to the adsorption capability of small molecules. MOFs, as organic–inorganic hybrid materials, feature a large specific surface area, rich chemical functional groups, coordination of unsaturated metal centers, and highly ordered and controllable pore structures, making them more efficient than traditional ones. Unlike most rigid MOFs with fixed pore structures that rely on size-based sieving, soft MOFs can dynamically adjust their pore environments through structural adaptability, enabling more precise molecular recognition. Structural flexibility enables the trigger of structural transformation within soft MOFs under specific stimuli, such as the adsorption of a particular gas molecule.[40] These guest-induced framework deformations (globally or locally) could usually be identified from the S-shape isotherm indirectly: under a specific vapor pressure (threshold pressure), the adsorption capacity of gas increases rapidly, corresponding to the rearrangement of framework structure from a "closed/narrow form" to an "open/large form" at certain temperature. This "gate-opening" phenomenon makes SPCs an ideal candidate in efficient gas storage and separating olefins/alkanes, rare gases, alkane isomers, *etc.* In the following section, some typical examples will be presented to highlight the advantages of soft MOFs in storage and separation applications.

Isotopologues are compounds with identical chemical compositions but only differing in isotopic composition, such as the water isotopologues $D_2O/HDO/H_2O$. Developing effective methods for identifying and separating isotopologues is extremely important in industrial, biomedical, and scientific research. However, it remains a great challenge to separate water isotopologues from each other due to the very similar chemical structure, size, and thermodynamic properties. Soft MOFs featuring reversible
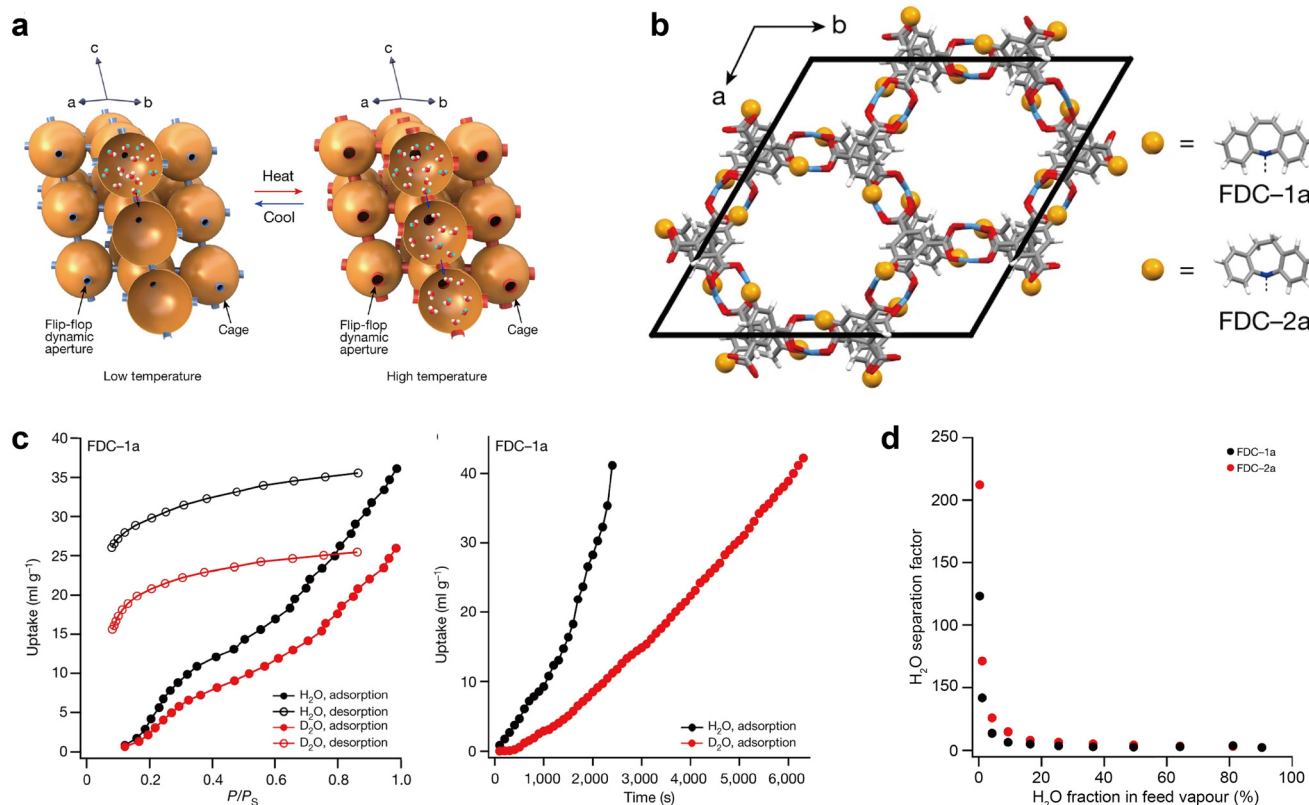
Fig. 2 Soft MOFs for water isotopologue separation. (a) Temperature responsive gate-opening phenomenon with flip-flop dynamic aperture; (b) crystal structures of **FDC-1a** and **FDC-2a** viewed along the c axis; (c) H_2O and D_2O sorption curves (left) and time-dependent H_2O and D_2O adsorption curves (right) at 298 K for **FDC-1a**; (d) H_2O concentration-dependent H_2O separation factor plots for **FDC-1a** and **FDC-2a** in the feed vapor. Reproduced with permission.[41] Copyright 2022, Springer Nature.

structural transformations and dynamic response to specific gas molecules have remarkable potential in isotope separation. In 2022, a "locally flexible" MOFs system (denoted as **FDC-1a** and **FDC-2a**) was constructed to control the diffusion process of water isotopologue molecules through local motion of dynamic gates.[41] By incorporating dynamic "switches" with temperature responsive behavior on the rigid skeleton MOFs (Fig. 2a and b), these materials are endowed with capabilities of highly selective adsorption of H_2O through amplifying their rate differences (Fig. 2c). The dynamic separation coefficient of H_2O from the D_2O/HDO/H_2O ternary mixture system can reach up to 210 at room temperature (Fig. 2d). This design concept is expected to inspire the design of other porous crystal materials and provide inspirations for the adsorption and separation of other isotopologues. In another work, a flexible MOF, DUT-8(Ni), which exhibits isotope-selective gate-opening behavior in response to deuterium (D_2) but not hydrogen (H_2) or hydrogen–deuterium mixtures (HD), was reported.[42] This unique feature, observed through *in situ* neutron diffraction and low-temperature thermal desorption spectroscopy, suggests remarkable potential for D_2-over-H_2 separation with a selectivity of 11.6 at 23.3 K. Theoretical calculations attribute this selective gating mechanism to pronounced nuclear quantum effects. Notably, simulations predict that

the MOF remains closed with HT but opens for DT and T_2, highlighting its efficacy for isotopologue separation. The findings underscore the utility of flexible MOFs in designing energy-efficient and highly selective gas separation processes, particularly for isotopic enrichment applications like those in the nuclear industry and analytical techniques.

Apart from the separation of hydrogen isotopes, H_2 separation from undesired byproducts and H_2 storage also stand as the vital consideration. Hydrogen, with its high energy density, high energy conversion efficiency, zero carbon emissions, and its capability as a high-density energy storage medium, has been regarded as an alternative energy carrier in recent years. However, large-scale H_2 production generates by-products inevitably and the energetic inefficiencies limit H_2 storage, and thus, the efficient storage and separation of H_2 from mixtures are essential.[43,44] Soft MOFs, featuring gate-opening behavior, have been successfully applied on these occasions. In 2023, a multivariate flexible framework designed for efficient hydrogen storage was demonstrated, addressing the challenge of achieving high usable capacity with reduced energy requirements in pressure swing processes.[45] By introducing 2-methyl-5,6-difluorobenzimidazolate linkers into the pre-existing CdIF-13 MOF, the authors created *sod*-Cd(benzimidazolate)$_{1.87}$(2-methyl-5,6-difluorobenzimidazole-late)$_{0.13}$, abbreviated as *sod*-Cd(bim)$_{1.87}$(2M56DFbim)$_{0.13}$ (Fig. 3a).

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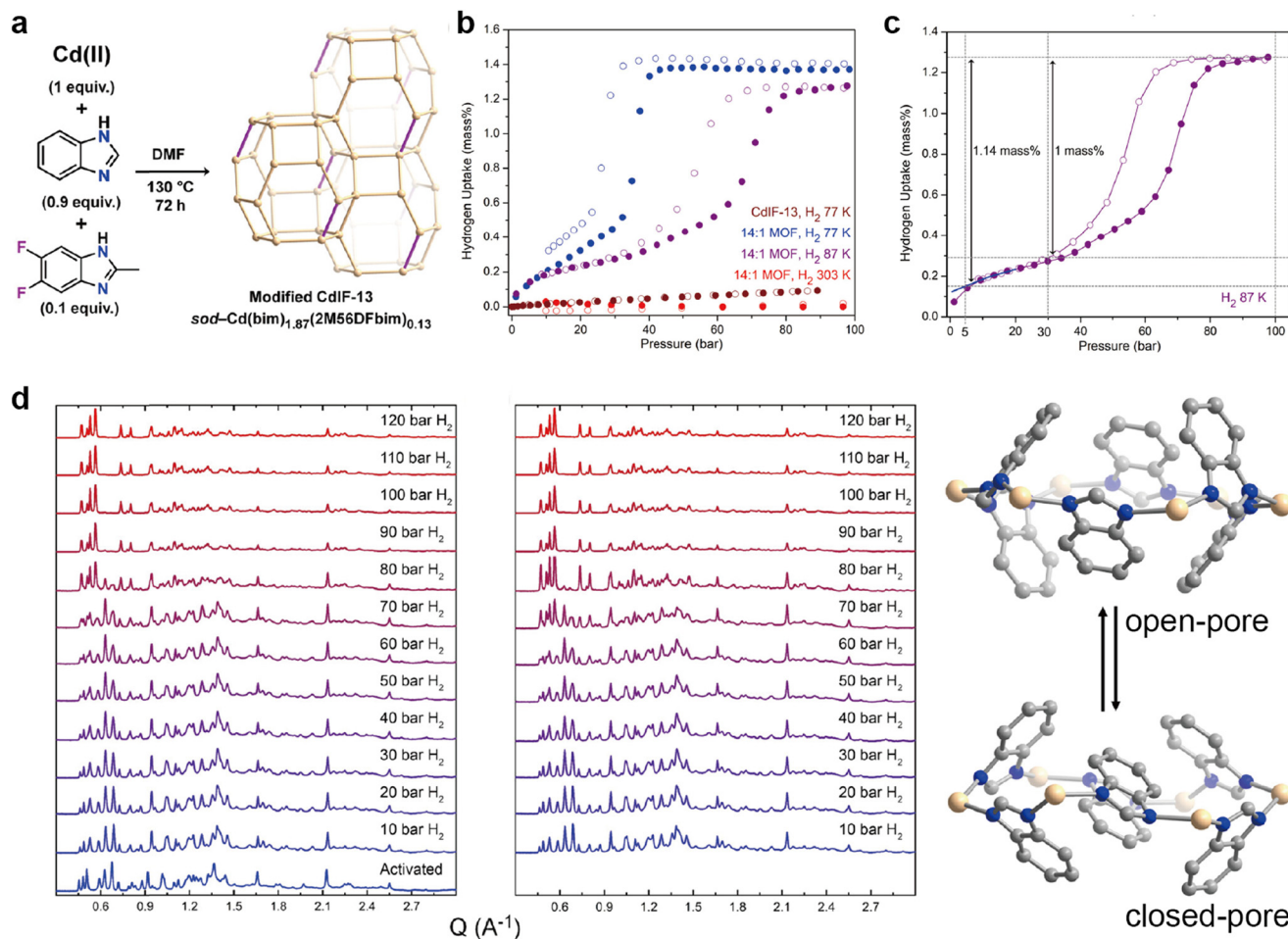**Fig. 3** Soft MOFs for hydrogen storage. (a) General synthetic scheme of modified CdIF-13, sod-Cd(bim)$_{1.87}$(2M56DFbim)$_{0.13}$; (b) and (c) isothermal H$_2$ adsorption–desorption curves for CdIF-13 and sod-Cd(bim)$_{1.87}$(2M56DFbim)$_{0.13}$ at 77 K, 87 K and 303 K, respectively; (d) PSXRD patterns of sod-Cd(bim)$_{1.87}$(2M56DFbim)$_{0.13}$ at various H$_2$ pressures and the corresponding phase dynamic transition. Reproduced with permission.[45] Copyright 2023, American Chemical Society.

This new framework exhibits a significant decrease in the pressure threshold for stepped hydrogen adsorption while preserving a desirable adsorption–desorption profile, with minimal hysteresis. At 77 K, it saturates below 50 bar and shows hysteresis closure at 5 bar, while at 87 K, saturation occurs at 90 bar with hysteresis ending at 30 bar (Fig. 3b and c). These characteristics enable the attainment of usable hydrogen capacities over 1 mass% through a milder pressure swing operation, constituting 85–92% of total capacities. The incorporation of fluorinated linkers lowers the activation energy for the phase change by weakening the interligand C–H⋯π interactions, reducing the adsorption threshold pressure while maintaining structural integrity and favorable adsorption energetics. In contrast, traditional rigid framework HKUST-1 exhibits a usable capacity of only approximately 0.8 mass% under similar pressure swings (77 K, 5–50–5 bar), accounting for about 24% of its total capacity owing to the type-I adsorption–desorption profile. *In situ* variable H$_2$-pressure synchrotron PXRD (PSXRD) measurements were performed to reveal the phase dynamic transition between a closed-pore phase to an open-pore

structure (Fig. 3d). H$_2$ binds *via* sandwich-like interactions between π-rich benzimidazolate rings in six/four-membered pores. This work underscores the potential of the multivariate linker strategy in tuning phase change behaviors of flexible frameworks for enhanced hydrogen storage applications. The design of a MOF nanosheet membrane with regulated structure for precise H$_2$/CO$_2$ separation was reported, achieved by introducing minimal amino groups into Zn$_2$(benzimidazolate)$_4$, optimizing interlayer spacing.[46] Synergistic effects of CO$_2$ adsorption and steric hindrance enhance selectivity while preserving rapid H$_2$ transport paths, setting a new benchmark (separation factor 1158, H$_2$ permeance 1417 GPU) in ultrathin membranes. This method enables customization for desired molecular sieving properties, advancing clean H$_2$ production and climate goals.

CO$_2$ is not only the main greenhouse gas, but also a common industrial gas impurity. The development of technologies for CO$_2$ molecular recognition, separation, capture, and reutilization has significant impacts on sustainable development of human society. By precisely

designing and controlling the flexibility, pore morphology, and interaction sites of MOFs, it is expected to achieve ultra precise molecular recognition and efficient separation of CO_2. For instance, a novel soft MOF, $[Co(3,5-pdc)dpg]_n$ (PCP-3,5-pdc; 3,5-pdc = 3,5-pyridinedicarboxylic acid; dpg = meso-α,β-di(4-pyridyl) glycol), with interdigitated 2-D sheet structure was reported, which can only selectively adsorb CO_2 through gate-opening behaviour over other nine similar molecular probes (N_2, CH_4, CO, O_2, H_2, Ar, C_2H_2, C_2H_4, and C_2H_6).[10] In addition, excellent CO_2 separation and capture performance is also demonstrated when exposed to multiple mixed gases. Based on the characterization and theoretical calculation, the unique affinity towards CO_2 is ascribed to the rational design of narrow-corrugated channels, location of binding sites and suitable structural flexibility. Its narrow-corrugated channels restrict larger molecules but allow favorable electrostatic interactions with CO_2. Specific binding sites (I and II) within these channels stabilize CO_2 through T-shaped configurations. Gate-opening behavior at low temperatures and a Hill coefficient of 4.1 indicate strong cooperative adsorption. DFT calculations confirm more favorable binding energies for CO_2 compared to other gases, enhancing its selectivity in this framework. Calgary Framework 20 (CALF-20) is a highly stable metal–organic framework composed of Zn ions, 1,2,4-triazole, and oxalate ligands, forming a 3D porous structure. It shows high CO_2 adsorption capacity (18% of its weight), excellent selectivity even at 40% humidity, and stability after extensive cycles. Synthesized with low-cost materials, it's the first MOF tested industrially for CO_2 capture, aiding decarbonization in
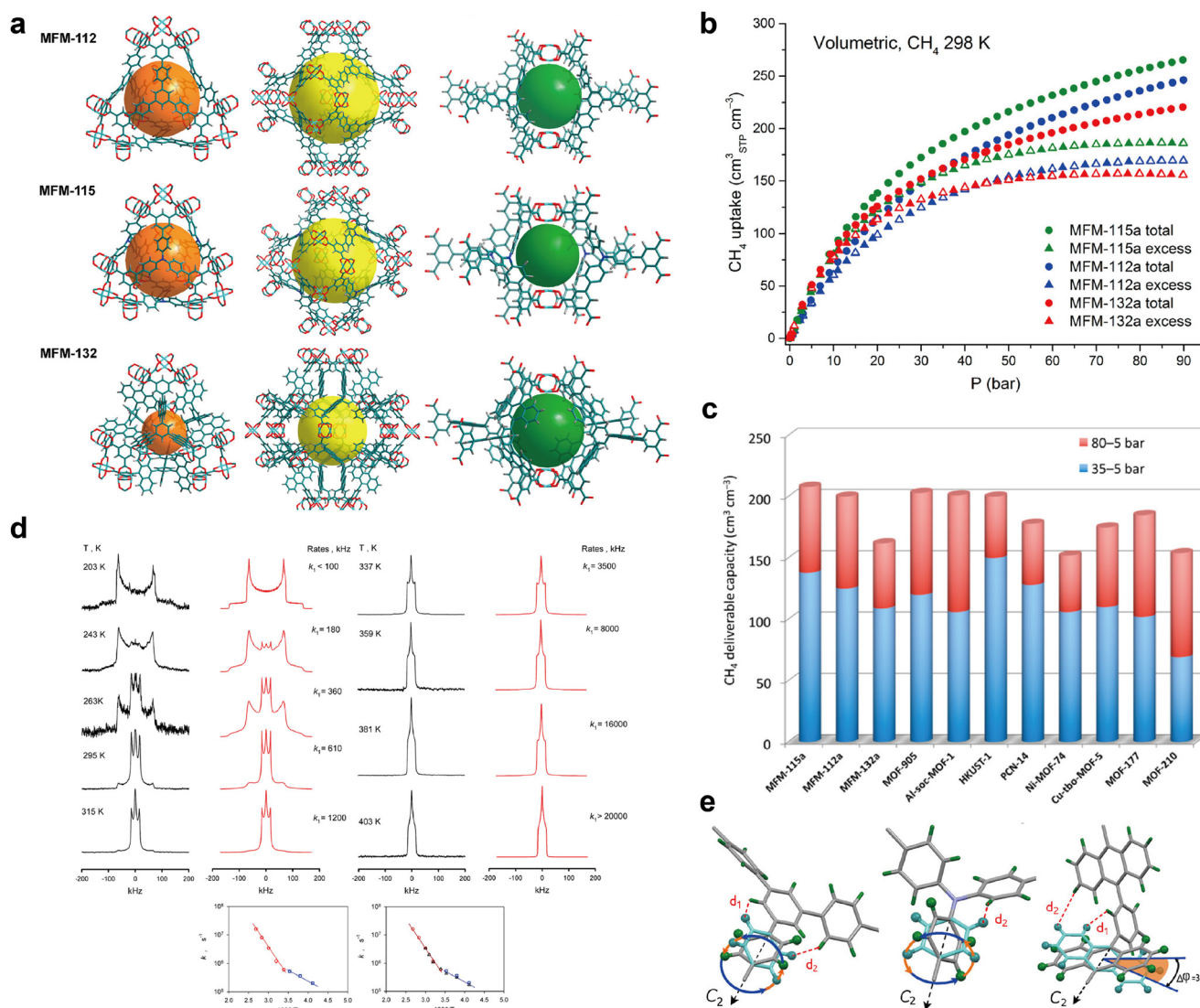

Fig. 4 Soft MOFs for CH_4 storage. (a) Cage structures of the isostructural MFM-112, MFM-115, and MFM-132, respectively; (b) CH_4 adsorption isotherms for MFM series at 298 K; (c) a comparison of the deliverable CH_4 capacity with a variety of reported MOFs at 298 K; (d) temperature-dependent solid state ^2H NMR spectroscopy of deuterated phenylene fragments in guest-free MFM-115a-d_{12} (experimental and simulated) and corresponding Arrhenius curves; (e) rotational models for the partially deuterated MFM series. Reproduced with permission.[49] Copyright 2017, American Chemical Society.

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cement and oil sectors.[47] A recent study has revealed the framework dynamics of CALF-20 through a combination of atomic-scale simulations and experimental investigations. CO_2 is preferentially adsorbed by CALF-20 over water at low RH because its accommodation requires less structural change of the framework than water does, with CO_2 filling the pores before sufficient water induces more structural opening.[48] As simulation methods and characterization techniques continue to advance, the softness of such materials is becoming increasingly understood and well-defined. However, this system does not exhibit efficient adsorption such as an S-shaped adsorption curve. Instead, it is characterized by CO_2 adsorption at low pressure and water adsorption at high pressure, and therefore further development of a softer system is desired.

Natural gas, mostly methane (CH_4), is a vital mobile fuel due to reduced emissions compared with gasoline. Its abundant reserves and established recovery infrastructure augment its attractiveness. However, the broader transport application is hindered by inadequate storage solutions. Soft MOFs hold great potential in enhanced CH_4 storage capacity at low pressure via introducing functional groups/sites, optimizing pore sizes and flexibility, etc. In 2017, a MOF with exceptional methane storage capacity – MFM-115, was demonstrated, featuring $[Cu_2(O_2CR)_4]$ paddlewheels bridged by the isophthalate units from the hexacarboxylate ligands to form cuboctahedra (Fig. 4a).[49] Compared with its analogs with different linker backbone functionalization (MFM-112 and MFM-132), MFM-115 shows an excellent CH_4 uptake of 208 cm^3 (STP) cm^{-3} (v/v) between 5 and 80 bar at room temperature (Fig. 4b), comparable to those reported for most advanced materials (Fig. 4c). Solid state ^2H NMR spectroscopy of partially deuterated isostructural series shows that the rotation rate of the benzene ring in MFM-115 is slower than that in MFM-112 but faster than the nearly static rotation observed in MFM-132 (Fig. 4d and e). This optimized micro-motion state of the structural units is a key reason why MFM-115 exhibits a higher methane adsorption capacity compared to the other two materials. Additionally, in situ neutron powder diffraction experiments were utilized to ascertain the position of methane molecules within MFM-115, confirming that the optimized pore structure enables the dense packing of methane molecules within its voids. In 2019, solvent-induced control of flexible MOF-53 series' breathing was demonstrated, of which the stability perfectly matched with potential industrial applications.[50] By simply increasing the concentration of dimethylformamide (DMF) in water during the synthesis process, the particle size decreases, and stability increases. In the case of MIL-53(Al)-NH_2, the 5.8–65 bar gravimetric CH_4 deliverable capacity increased a remarkable 33% upon introducing 20% DMF, which is promising for natural-gas delivery.

Ammonia (NH_3) is a vital chemical ingredient boasting a myriad of industrial applications, yet it concurrently presents significant environmental risks.[51] The adsorption of NH_3 is not only crucial for environmental protection and production safety, but also constitutes a key technology for achieving efficient and sustainable chemical industrial processes.[52] An environmentally friendly method for synthesizing flexible MOFs, specifically $M(NA)_2$ where M = Zn, Co, Cu, Cd, and NA denotes nicotinate, was presented.[53] Two synthesis techniques – ammonia-assisted synthesis and solvent-evaporated conversion – were employed. These MOFs undergo structural transformations upon dehydration from zero-dimensional supramolecular structures to two-dimensional (Zn, Co) or three-dimensional (Cu, Cd) frameworks. Notably, the transformations of $Zn(NA)_2$, $Co(NA)_2$, and $Cd(NA)_2$ are reversible upon water adsorption. These MOFs exhibit unique NH_3 adsorption characteristics due to their flexibility. $Zn(NA)_2$ demonstrates gate-opening behavior, absorbing NH_3 at 0.22 bar with a two-step uptake reaching 10.2 mmol g^{-1} at 1 bar. $Co(NA)_2$ achieves an exceptional NH_3 uptake capacity of 17.5 mmol g^{-1}, surpassing reported values. $Cu(NA)_2$ and $Cd(NA)_2$ show improved adsorption rates and reach equilibrium faster after multiple cycles, with capacities of 13.4 and 6 mmol g^{-1}, respectively. All MOFs can be regenerated under vacuum at 150 °C for 70 minutes without losing adsorption capacity. Given their green synthesis route, high NH_3 adsorption capacities, and recyclability, $M(NA)_2$ (M = Zn, Co, Cu) are highlighted as promising materials for ammonia capture applications, addressing environmental concerns such as air pollution.

Lithium stands as a strategic metal of paramount importance, particularly in the realm of lithium-ion batteries powering the electric vehicle revolution. With a substantial portion of global lithium resources residing in salt lakes and seawater, the advancement of lithium extraction technologies from these sources is vital to meet the ever-increasing demand for lithium. However, lithium ions coexist with other alkali and alkaline earth metal ions of similar ionic radii, presenting a significant obstacle for traditional separation membranes that typically exhibit a broad range of pore sizes, which poses a challenge to conventional separation techniques. MOF-based membranes with functional design and adjustable pore structures unlock new possibilities in the field of water treatment membrane science.[54] ZIF-8 with easy synthesis has been grown in modified layered double hydroxide (MLDH) defects to form ZIF-8@MLDH composite membranes, achieving high Li^+ permeability (1.73 mol m^{-2} h^{-1}) and Li^+/Mg^{2+} selectivity (31.9), surpassing most 2D membranes for efficient lithium separation.[55] An oriented UiO-67 MOF membrane synthesized with a secondary growth technique on AAO shows rapid Li^+ transport (27.01 mol m^{-2} h^{-1}) and high Li^+/Mg^{2+} selectivity of up to 159.4, enabled by subnanometer pores and distinct ion dehydration mechanisms in the unique channels.[56] A MOF-on-MOF structure strategy has been proposed to create UiO-66-NH_2/ZIF-8 angstrom-scale asymmetric channels for exceptional monovalent ion selectivity, particularly lithium.[57] Nonetheless, these membranes have been tailored for specific separation tasks, and developing MOF-based films with adaptive capability to meet multiple industrial demands is still a challenge. The

integration of soft MOFs, known for their unique flexibility and responsiveness, offers a promising avenue towards membranes that can dynamically adjust their pore structures and functionalities according to changing environmental conditions or diverse feedstocks. Such smart MOF membranes would ideally possess intrinsic mechanisms enabling them to modify their selectivity and permeability in real-time, thereby expanding their applicability across a wide range of separation processes and contributing to more sustainable and efficient industrial practices.

Precise control of the components of soft MOFs is expected to acquire SPCs with suitable flexibility and porosity for targeted utilization, namely crystal engineering, among which linker modification may be the most favorite strategy. For instance, a series of **Zn-CAT** interpenetrated MOFs exhibiting tunable gate-opening and gate-closing pressures (P_{go} and P_{gc}) towards acetylene were reported, achieved by introducing different ratios of functional BDC linkers (functionalized by $-NO_2$ or $-NH_2$) (Fig. 5a).[58] These

modifications enable a facile strategy to tune the filling and release pressures of a gas cylinder in the practical safe range (100–150 kPa at 298 K) (Fig. 5b). In another work, the gate-opening and/or gate-closing pressure could be rationally controlled by substituting the dpe pillar linker of **X-pcu-5-Zn** with other three dipyridyl type ligands.[59]

2.2 Catalysis

In nature, enzyme activity levels can be regulated in response to external stimuli such as temperature, pH, or the presence of specific molecules. This regulatory mechanism allows organisms to effectively respond to environmental changes and optimize the efficiency of biochemical reactions, enabling enzymes to enhance or reduce their catalytic action as needed. Inspired by nature, chemists are searching for smart materials whose catalytic activity could be regulated by external stimuli. In contrast to rigid MOFs with fixed and static active sites, soft MOFs exhibit a unique advantage
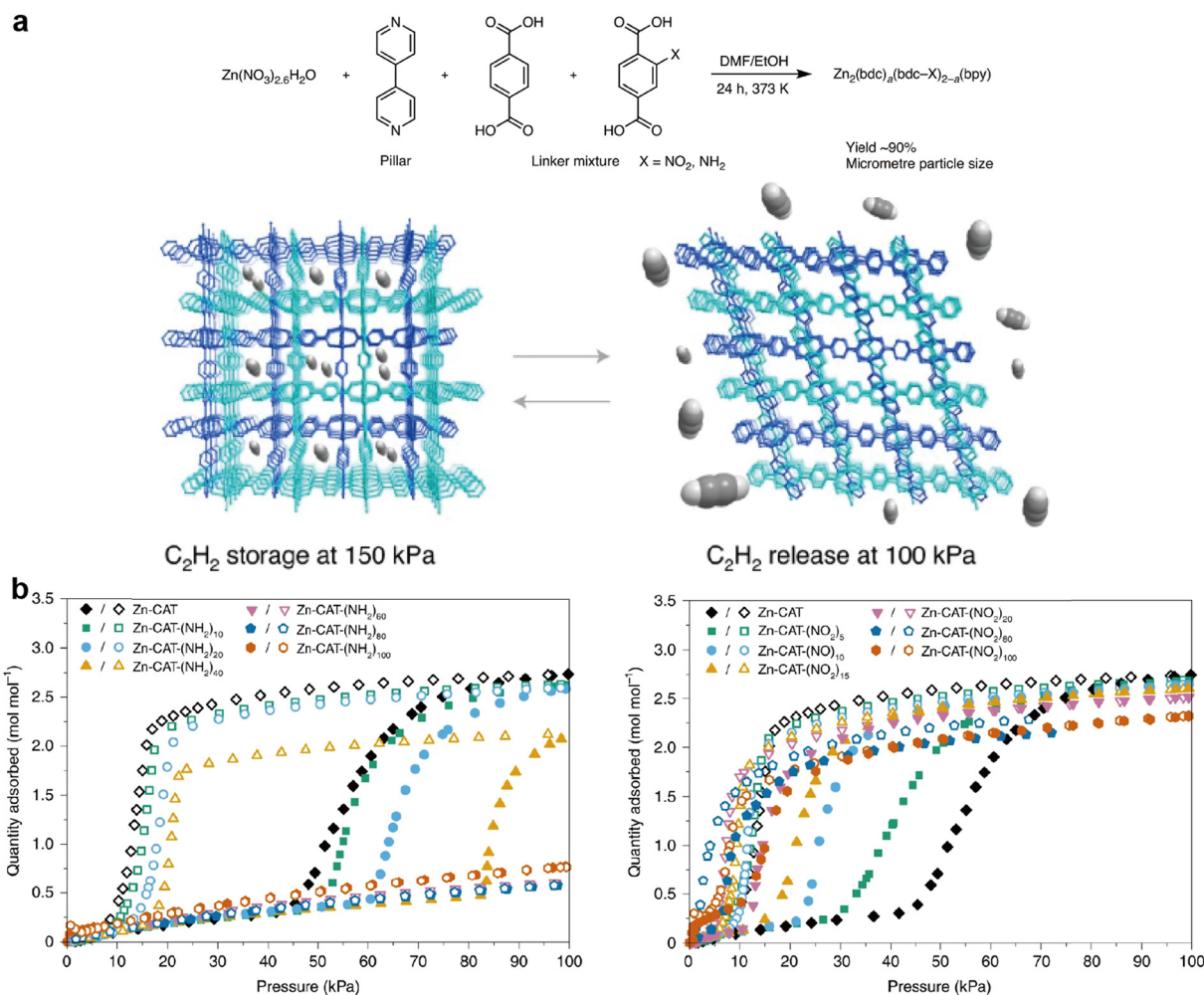

Fig. 5 Linker modification of soft MOFs. (a) Synthetic scheme of Zn-CAT-(X)$_n$ materials with various proportions of functionalized bdc-X linkers (where X is $-NO_2$ or $-NH_2$) and reversible open-pore to closed-pore transition upon acetylene (C$_2$H$_2$) storage and release at varied pressure; (b) C$_2$H$_2$ adsorption isotherms for all Zn-CAT-(NH$_2$)$_n$ and Zn-CAT-(NO$_2$)$_n$ at 273 K, respectively. Reproduced with permission.[58] Copyright 2022, Springer Nature.

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through their ability to undergo structural reorganization in response to external stimuli, thereby dynamically modulating the exposure and alignment of catalytic centers to accommodate substrate interactions. Soft MOFs are a suitable platform because their intrinsic pore environment can be altered through their breathing behavior, which in turn affects their catalytic activity. Thus, the design of soft MOFs with tunable flexibility, high stability, and high efficiency is crucial for the development of biomimetic catalysts. Typically, the modulation of the catalytic performance of soft MOF catalysts can be achieved through several methods.

Post-synthetic modification of MOFs is a commonly used way to introduce new functional groups, chemical moieties, or changes in the pore environment, enhancing the MOF's functionality. This can lead to improvements in catalytic activity, stability, and selectivity, making soft MOFs versatile platforms for applications in catalysis. In 2020, a mesoporous MOF, PCN-808, based on Zr_6 clusters and tetratopic

carboxylate ligands was reported, showcasing accessible coordinatively unsaturated metal sites and intrinsic flexibility, which makes it a prime scaffold for post-synthetic modification via linker installation.[60] Thus, a ruthenium-based metalloligand was installed into the framework's open channels, maintaining mesoporosity (Fig. 6a). The resultant material, PCN-808-BDBR, exhibited high photocatalytic activity in the aza-Henry reaction and efficient conversion of dihydroartemisinic acid to artemisinin across six catalytic cycles (Fig. 6b). Furthermore, the catalytic activity of soft MOF catalysts could also be tuned through the modulation and design of ligand side groups. In 2022, flexible Cu(I) triazolate frameworks as tunable electrocatalysts for CO_2 reduction were constructed (Fig. 6c).[61] By tuning the length of ligand side groups, the C_2H_4/CH_4 selectivity ratio can be tuned from 11.8:1 to 1:2.6, achieving selectivity up to 51%, 56%, and 77%, respectively, without forming Cu-based inorganic species in long-term electrocatalysis tests (Fig. 6d and e). Computational simulations indicate that the
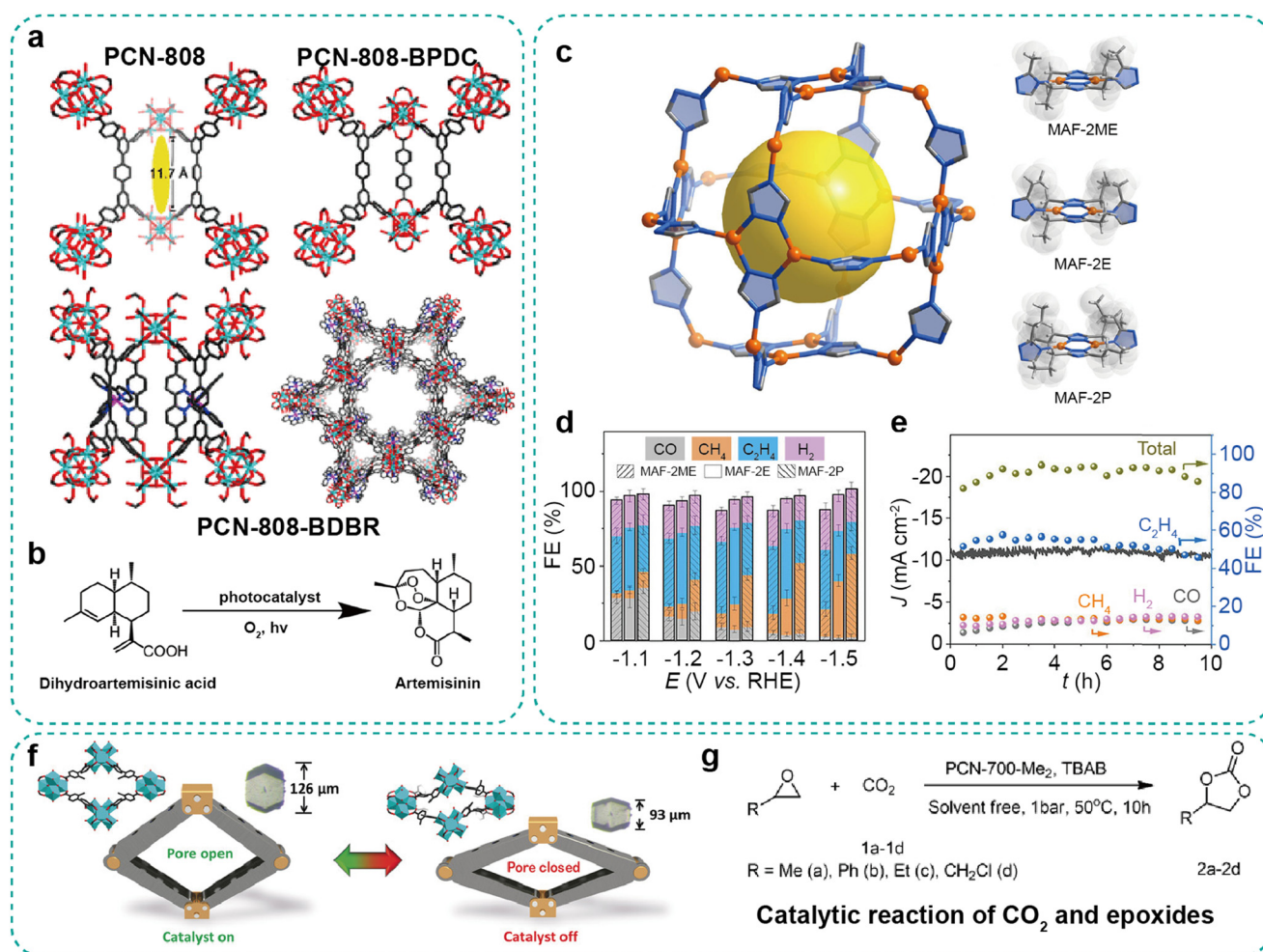

Fig. 6 Soft MOFs for catalysis. (a) Crystal structures of PCN-808 series; (b) photocatalytic oxidation of dihydroartemisinic acid to artemisinin. Reproduced with permission.[60] Copyright 2020, American Chemical Society. (c) Crystal structures of MAF-2 analogs and the corresponding local coordination environments; (d) potential-dependent faradic efficiency of gas products; (e) long term stability of MAF-2 analogs by chronoamperometry. Reproduced with permission.[61] Copyright 2022, Wiley-VCH. (f) Schematic representation of PCN-700-Me$_2$ before and after desolvation; (g) catalytic reaction of CO_2 and epoxides. Reproduced with permission.[62] Copyright 2016, Wiley-VCH.

steric hindrance mechanism, controlled by ligand side groups, impacts the catalyst's flexibility, with the C_2H_4 pathway being more sensitive than the CH_4 one. Apart from the above pore channel modification methods, altering the open and closed pore states within soft MOFs *via* temperature, pressure, or guest molecules is an alternative way to tune the catalytic activity. The flexible zirconium MOFs, the PCN-700 series, were reported to have their catalytic activity turned on and off *via* reversible structural transformations through treatment with trifluoroacetic acid/DMF solution (Fig. 6f). The catalytic performance in cycloaddition reactions of CO_2 with epoxides was studied (Fig. 6g), demonstrating the potential of these materials to function as switchable catalysts inspired by biological systems.[62] The catalytic performance difference between open and closed pore states in soft MOFs, like PCN-700, stems from structural dynamics affecting substrate accessibility to active sites. In the closed pore state, restricted pore size limits substrate diffusion to active sites, reducing catalytic efficiency. In contrast, the open pore state facilitates easier access, enhancing reaction rates. Additionally, the open structure promotes better guest molecule diffusion, preventing product accumulation and inhibition. These structural changes significantly impact the interaction between substrates and active sites, thereby altering catalytic activity. In another work, a series of flexible zirconium-based MOFs was developed, including PCN-605, PCN-606, and PCN-700, serving as bromine nanocontainers.[63] These MOFs demonstrate high bromine adsorption capacities due to the adaptable structure upon bromine uptake. The bromine-pre-adsorbed flexible MOFs extend the storage time of volatile bromine under ambient conditions and can act as a bromine source for bromination reactions, providing improved yields and selectivity compared to liquid bromine.

However, the above progress either demonstrates an "on" and "off" switching effect on catalytic activity or serves as a reservoir for the controlled release of reactants, and the direct utilization of MOF softness and catalysis can fully exploit the adaptive response of the framework structure upon the adsorption of different solvents, substrates, and corresponding product molecules. In a recent study, Zn-DPA, a flexible porous coordination polymer, was shown to efficiently capture and convert CO_2 into cyclic carbonates *via* cycloaddition with epoxides. Its propeller-like ligands rotate to trap CO_2, confirmed by X-ray analysis. It shows high CO_2 affinity, excellent catalytic activity (with a turnover number up to 39 000), rapid dynamics and size selectivity for CO_2 cycloaddition to epoxides, demonstrating efficient CO_2 capture and conversion.[64] As a pioneering work on direct utilization of MOF softness in catalysis, MIL-53(Cr) demonstrates dynamic structural adjustments *via* PXRD and PDF analyses. Solvents with different polarity and size like CH_3CN, DMF, and DMSO alter pore sizes from 7.61 Å to 3.60 Å, affecting catalytic activity. Substrates such as 4-bromoacetophenone and trace water significantly enhance performance, achieving up to 88% yield in CH_3CN and $\geq$99% with water addition. The adaptive

behavior of MIL-53(Cr) reveals its potential for tunable, enzyme-mimicking catalysis.[65]

Although soft MOFs have shown great potential applications in catalysis, there are several areas that require further development and exploration. Firstly, the stability and durability of soft MOFs should be improved over extended periods and under various catalytic conditions, especially in the presence of solvents and at high temperatures. Secondly, the intrinsic catalytic activity of the active sites within MOFs should be enhanced to achieve higher turnover rates and better selectivity through fine-tuning the pore environment. Finally, gaining a deeper understanding of the underlying mechanisms governing the catalytic behavior is crucial for guiding the synthesis and functionalization of these materials.[66]

2.3 Energy storage

In the field of electrochemistry, both batteries and supercapacitors play pivotal roles, serving as two principal energy storage devices that each uniquely contributes to the advancement of modern technology and energy management. To realize highly efficient energy storage and conversion, the pursuit of innovative materials stands as an essential frontier.[67]

In recent years, the exploration and application of MOFs in lithium (Li), sodium (Na), zinc (Zn), and other batteries have witnessed a significant surge, demonstrating their immense potential in next-generation energy storage technologies. The unique structural properties of MOF materials, including high specific surface area, tunable pore sizes, and functionalized surfaces, make them ideal candidates for the development of high-performance battery materials. MOFs and MOF-derived nanomaterials have involved various key components of batteries, including cathodes,[68,69] anodes,[70] electrolytes,[71] separators,[72] *etc.* Soft MOFs exhibit significant advantages over rigid MOFs in battery development and application in the following aspects: i) structural adaptability: soft MOFs possess a dynamic framework that responds to external conditions such as temperature, pressure, and chemical environments. This adaptability allows them to better accommodate volume changes in electrode materials during battery charging and discharging, reducing internal stress and enhancing cycle stability and overall battery life. ii) Pore size tunability: the pore diameter and shape of soft MOFs can be dynamically adjusted through the adsorption or desorption of solvent molecules, optimizing ion transport pathways in batteries, increasing ion diffusion rates, and improving electrochemical reaction efficiency. iii) Enhanced electrochemical performance: due to their structural flexibility, soft MOFs can maintain continuous hydrogen bonding networks, sustaining high proton conductivity even in varying humidity conditions. This is particularly crucial for proton exchange membrane fuel cells, significantly boosting power output and efficiency. For instance, by integrating inherent flexibility and
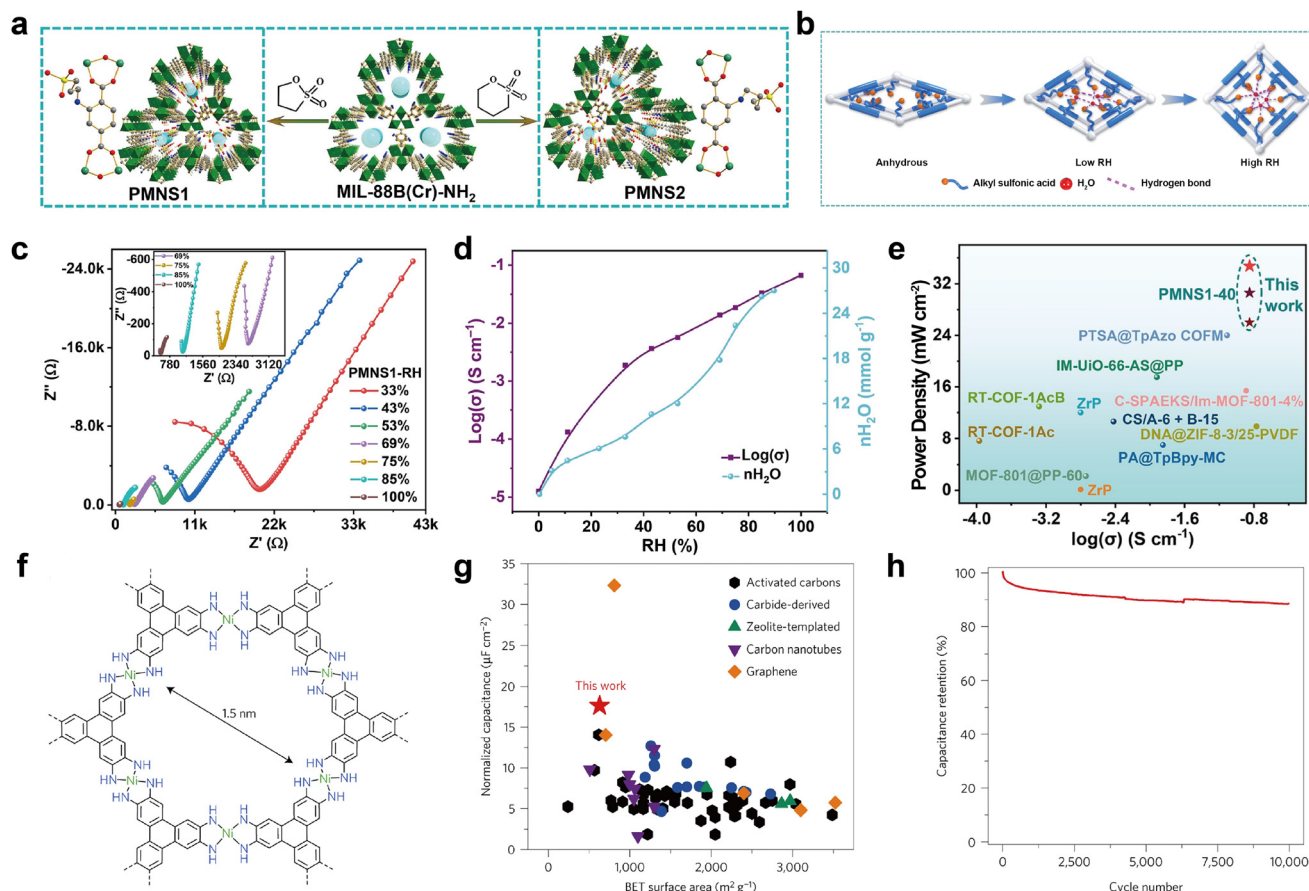
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Fig. 7 Potential application in energy storage of soft MOFs. (a) Synthetic scheme of PMNS1 and PMNS2; (b) dynamic self-adaption of the framework under humidity to form a continuous hydrogen-bonding network; (c) Nyquist plots for PMNS1 in different RH at 25 °C. The inset shows the locally magnified Nyquist plots under high RH; (d) RH-dependent conductivity and water adsorption isotherm for PMNS1 at 25 °C; (e) a comparison of power density and conductivity of the PMNS1-40 membrane with various reported proton-conducting MOFs. Reproduced with permission.[73] Copyright 2021, Wiley-VCH; (f) molecular structure of $Ni_3(HITP)_2$; (g) a comparison of areal capacitance of $Ni_3(HITP)_2$ with various reported electrochemical double layer capacitor materials; (h) capacitance retention for 10 000 cycles at a current density of 2 A g^{-1}. Reproduced with permission.[74] Copyright 2016, Springer Nature.

substructure flexibility through chemical grafting of sultones onto MIL-88B(Cr)-NH_2 nanocrystals (Fig. 7a), PMNS1-40 was constructed, exhibiting a proton conductivity of 1.52×10^{-1} S cm^{-1} at 80 °C under 100% RH. This flexible MOF maintains high conductivity across a wide humidity range due to the dynamic self-adaptation between alkyl sulfonic acid torsion and framework breathing, forming a continuous hydrogen-bonding network (Fig. 7b–d). *In situ* powder X-ray diffraction (PXRD) and temperature-dependent Fourier-transform infrared spectroscopy (FT-IR) reveal that alkyl sulfonic acids dynamically twist, enhancing continuous H-bond networks, crucial for high proton conductivity. Water adsorption induces significant lattice expansion, increasing unit cell volume by up to 69%, facilitating more efficient proton transfer pathways through improved host–guest interactions and structural flexibility. This synergy maintains high conductivity across varying humidity condition. The PMNS1-40 membrane demonstrates long-term durability and achieves a maximum power density of 34.76 mW cm^{-2} as a proton exchange membrane in a direct methanol fuel cell (DMFC) (Fig. 7e).[73]

Despite the promising attributes in the realm of battery technology, soft MOFs encounter certain obstacles in practical battery applications. A primary concern revolves around preserving their structural integrity throughout extended periods of charge and discharge cycles. This requires the soft MOFs to withstand the physical and chemical stresses induced by repeated expansion and contraction without degrading or losing their functional properties. Additionally, the scalability of soft MOF production presents another significant challenge. Achieving economically viable and efficient manufacturing processes capable of producing soft MOFs in large quantities while maintaining quality control is crucial for their widespread adoption in battery technology.

MOFs, distinguished by their porous architecture and high surface area, have emerged as an alternative candidate for crafting electrode materials in supercapacitors. By meticulously engineering the pore size, morphology, and chemical composition of MOFs (including their composites and derived materials), researchers are able to fine-tune the electrochemical properties, significantly elevating the energy

density and power capabilities of supercapacitors. A conductive MOF, Ni$_3$(HITP)$_2$, was highlighted as a promising electrode material for supercapacitors without additional conductive elements or binders (Fig. 7f). This MOF delivers high areal capacitance exceeding most carbon-based materials (Fig. 7g), with over 90% capacity retention after 10 000 cycles (Fig. 7h), which rivals commercial devices.[74] UiO-66-NH$_2$, a type of MOF known for its high stability and large surface area, was successfully integrated with functionalized graphene acid (GA@UiO-66-NH$_2$) *via* amide bonds to create a covalent hybrid material that combines the high conductivity of graphene with the high porosity of MOFs. This combination enhances the specific capacitance and energy density of the supercapacitor while maintaining excellent cycling stability, as demonstrated by tests showing a retention of 88% capacitance after 10 000 cycles.[75] A universal synthesis strategy to transform insulating MOFs into nanostructured conductive MOFs (c-MOFs) was demonstrated. This method allows for the creation of a library of 2D c-MOFs with controlled morphologies and dimensions through a template-directed transformation process. The resultant hierarchically nanostructured Cu-BHT exhibited enhanced performance with improvements of over 225% in specific capacity relative to the bulk c-MOFs.[76] However, the exploration and literature concerning soft MOFs in supercapacitors remain notably sparse mainly due to the following reasons. Firstly, most soft MOFs exhibit lower electrical conductivities compared to their rigid counterparts, which will restrict their efficiency in electrochemical energy storage. Secondly, crafting soft MOFs with precise control over their structures and properties presents a greater challenge than synthesizing rigid MOFs, particularly in maintaining flexibility alongside electrochemical stability. Finally, the dynamic nature of soft MOFs can lead to structural alterations during the charge–discharge cycles, impacting the durability and operational lifespan of supercapacitors probably. Despite these obstacles, soft MOFs possess significant advantages in supercapacitor applications, such as superior adaptability, adjustable porosity during electrolyte ion adsorption–desorption processes, and enhanced ion transport capabilities. Various strategies, including material modification, composite fabrication with conductive polymers, carbon nanotubes, or graphene, and innovative synthesis methods, are expected to enhance the electrical conductivity and mechanical robustness of soft MOFs. It is anticipated that more innovative applications and solutions involving soft MOFs in supercapacitors will emerge, contributing to the development of next-generation tunable energy storage devices.

3 Trace or low-dose applications

Trace or low-dose applications can be categorized into fields such as electronic devices, biomedicine, and the nuclear industry, where samples typically required are in the microgram to milligram range.[77–82] However, there are higher

requirements placed on the preparation and the physical and chemical properties of materials. For electronic devices, soft MOFs typically need to exhibit ionic or electronic conduction and must be available in a high-quality thin film form. In biomedicine, materials are required to maintain extreme stability under challenging conditions, including exposure to water, acidic, and alkaline environments. Additionally, biodegradability and biocompatibility are critical characteristics. For the nuclear industry, radioresistance is the primary and fundamental property, necessitating the use of metals or clusters in high oxidation states to enhance the stability of the framework.

3.1 Electronic devices

Soft MOF films, characterized by their inherent structural flexibility, hold great potential in electronic devices, particularly in advanced switching or sensing applications, where their dynamic responsiveness to external stimuli enables reversible physical and chemical changes—offering distinct advantages over rigid MOF films that lack such adaptability. The successful realization of such devices critically hinges upon the ability to synthesize MOFs onto specific substrates, yielding high-quality thin films that underpin the functionality and performance of the final device. To accomplish this, researchers have dedicated significant efforts to refining and optimizing the methods for fabricating MOF films in electronic devices, with a particular emphasis on enhancing film quality and consistency. In the context of chemiresistive sensors, a common yet somewhat inconsistent approach involves blending MOF powder precursors with suitable solvents, followed by drop-casting the resultant mixture onto substrates pre-patterned with interdigitated electrodes. While this method offers simplicity and accessibility, it often yields devices with a marked degree of variability in performance, undermining the reproducibility and reliability essential for widespread adoption. To date, several bottom-up methods for fabricating nanometer-sized thin film have been well established including interface assistant methods, liquid layer by layer (LBL) growth, modular assembly method, and a combination of the Langmuir–Blodgett (LB) and LBL method, among which LBL is the most popular used approach to fabricate MOF thin films. In this approach, functionalized substrates are alternately immersed in metal node solution and ligand solution for different cycles to acquire MOF films with desired thickness.[83] Interestingly, downsizing MOFs to mesoscale or nanoscale may endow some distinct functionality compared with their bulk counterparts, such as the shape memory effect, structural transformation, magnetic properties and so on.[84] In a typical work, a size-dependent gate-opening phenomenon within a Hofmann-type MOF was discovered.[85] As this material is downsized into a thin film (16 nm) through the liquid-phase layer-by-layer method, a dynamic guest-sorption behavior is observed along the out-of-plane direction to the substrate surface. This gas uptake capability gradually vanishes by increasing the film thickness, which is due to the enlarged surface area and

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decreased diffusion length in the thin film state compared with the bulk state. In another work, $[Cu_2(bdc)_2(bpy)]_n$ bulk crystals exhibit reversible closed pore to open pore transition upon the adsorption and removal of guest molecules.[86] However, when downsizing the crystals to the mesoscale, this MOF loses structural flexibility and keeps an open phase even upon removal of guest molecules, namely the shape-memory effect.

Thus far, MOFs have demonstrated their remarkable versatility and potential in electronic devices, including field-effect transistors, capacitors, memristors, sensors, *etc.* These proof-of-concept implementations underscore the immense scope for exploiting MOFs in advanced electronics. However, previously research efforts have predominantly centered around rigid MOFs, whose inherent rigidity and defined lattice architectures have facilitated their integration into conventional device architectures, while self-adaptive frameworks with unique electrical properties may revolutionize the design and functionality of electronic devices. Nevertheless, the inherent lack of conductivity in soft MOFs constrains their utilization in electronic devices. Strategic material design, hybridization, doping, and functionalization are efficient ways to overcome this

limitation. Control of proton conduction in a soft MOF with a high density of $-SO_3H$ sites, BUT-8(Cr)A, was demonstrated for potential applications in proton exchange membrane fuel cells (PEMFCs).[87] High proton conductivity was achieved both at a much lower relative humidity (RH) of 11% (4.19×10^{-6} cm^{-1}) and elevated temperature (80 °C, 100% RH, 1.27×10^{-1} S cm^{-1}), much higher than that of MIL-101-SO_3H and other rigid MOFs under the same conditions, which was ascribed to the hydrophilic networks and self-adaption behavior of the framework under various levels of humidity. In another work, the preparation and growth mechanisms of substrate-supported conductive Cu-HHTP nanofilms were reported, which exhibit reversal orientations (face-on and edge-on) depending on the ratio of metal ions to organic ligands during the spray assistant LBL preparation process (Fig. 8a and b).[88] More importantly, *operando* grazing incidence wide-angle X-ray scattering (GIWAXS) revealed that the electrical conductivity could be modulated through the guest-induced anisotropic softness along the out-of-plane direction (Fig. 8c–e). In addition, composite methods have also been used to impart conductivity to flexible MOFs. The synthesis of conductive-on-insulating (cMOF-on-iMOF)
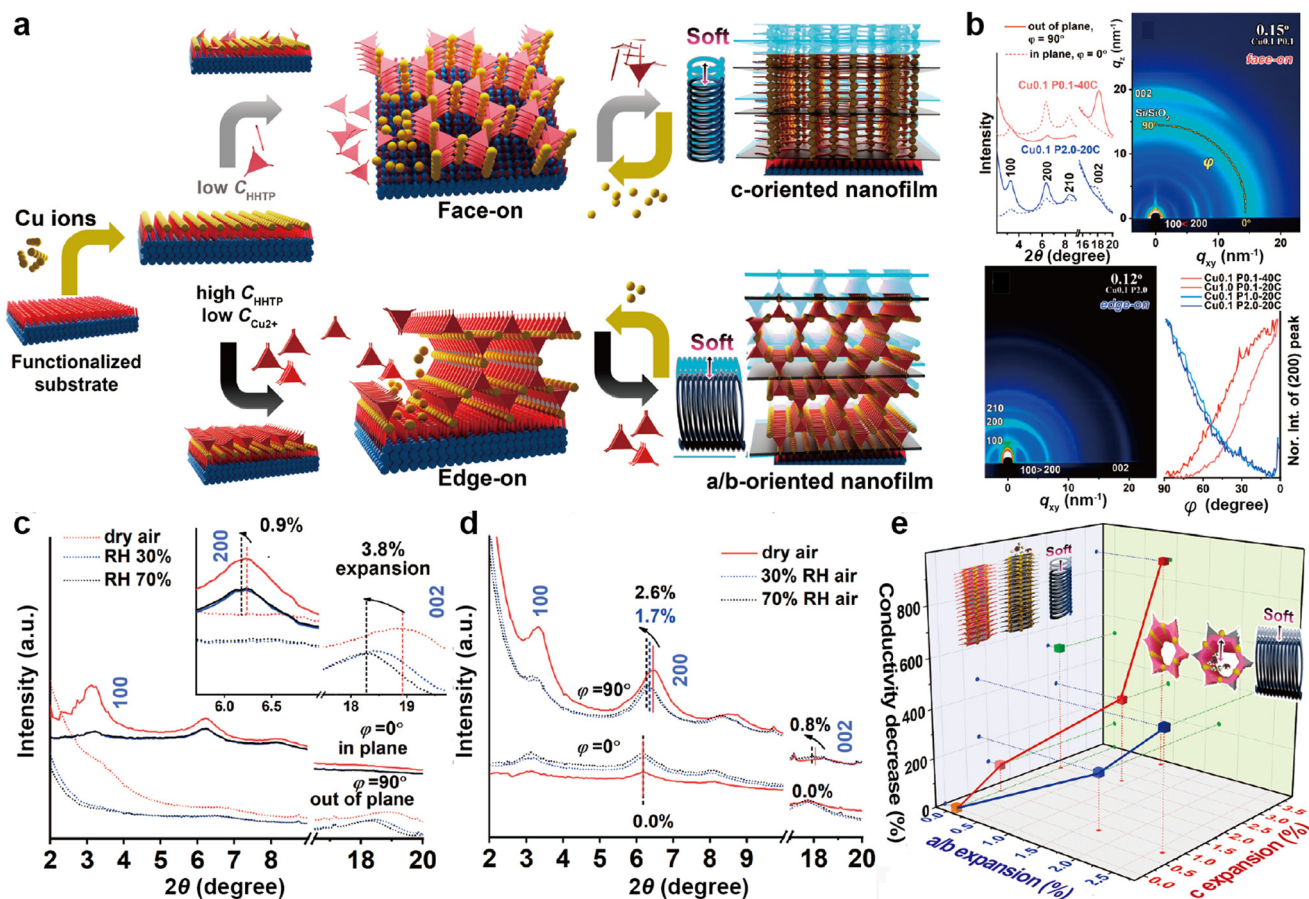

Fig. 8 Softness of conductive MOF nanofilms. (a) Preparation schematic of Cu-HHTP nanofilms with face-on and edge-on orientations; (b) GIWAXS patterns of Cu-HHTP nanofilms with face-on and edge-on orientations, respectively; the in-plane and out-of-plane GIWAXS patterns of face-on (c) and edge-on (d) Cu-HHTP nanofilms upon exposure to different RH. The inset shows the locally magnified GIWAXS patterns of face-on Cu-HHTP nanofilm; (e) the anisotropic lattice expansion-dependent conductivity of face–on and edge-on nanofilms. Reproduced with permission.[88] Copyright 2023, National Academy of Sciences.

heterostructures *via* a seeded layer-by-layer approach was reported, integrating soft porosity and electrical properties within a single material.[89] This integration enhances CO_2 selectivity significantly over pristine iMOF due to a porous interface resulting from molecular hybridization. The flexible iMOF core enables cMOF-on-iMOF heterostructures to exhibit shape memory and sensing flexibility for acetone and CO_2, as evidenced by *operando* GIWAXS analysis of guest-induced iMOF core structural changes. In another study, a H_2S sensing platform fabricated using flexible MIL-88B that is activated by visible light was reported.[90] By varying methanol concentrations during synthesis, the ratio of large pore (lp) to narrow pore (np) phases was adjusted, affecting the material's crystallinity and surface area. The optimized MIL-88B-20% sample demonstrated superior H_2S sensing capabilities compared to other reported MOF-based sensors.

Designing device architectures that exploit the unique properties of soft MOFs without relying on their direct electrical conductivity could be an alternative way to fabricate soft MOF-based devices. For instance, an artificial olfactory sensor utilizing a colorimetric sensor array composed of seven flexible MOFs for highly selective detection of volatile organic compounds (VOCs) was designed (Fig. 9a).[91] This innovative approach capitalizes on the unique colorimetric response of flexible MOFs, enabling the detection of less-reactive VOCs typically undetectable by conventional dye-based sensors (Fig. 9b). The sensor array exhibits excellent reversibility, reusability, and storage stability under varying humidity and time conditions. Moreover, it demonstrates potential for identifying plant diseases, specifically late blight in tomatoes, by differentiating the VOC profiles emitted from infected and healthy leaves. The first example of gas detection by a fluorescence change in organic molecules without any chemical interaction or energy transfer was demonstrated.[92] By introducing a fluorescent reporter molecule, distyrylbenzene (DSB) into the nanochannel of a
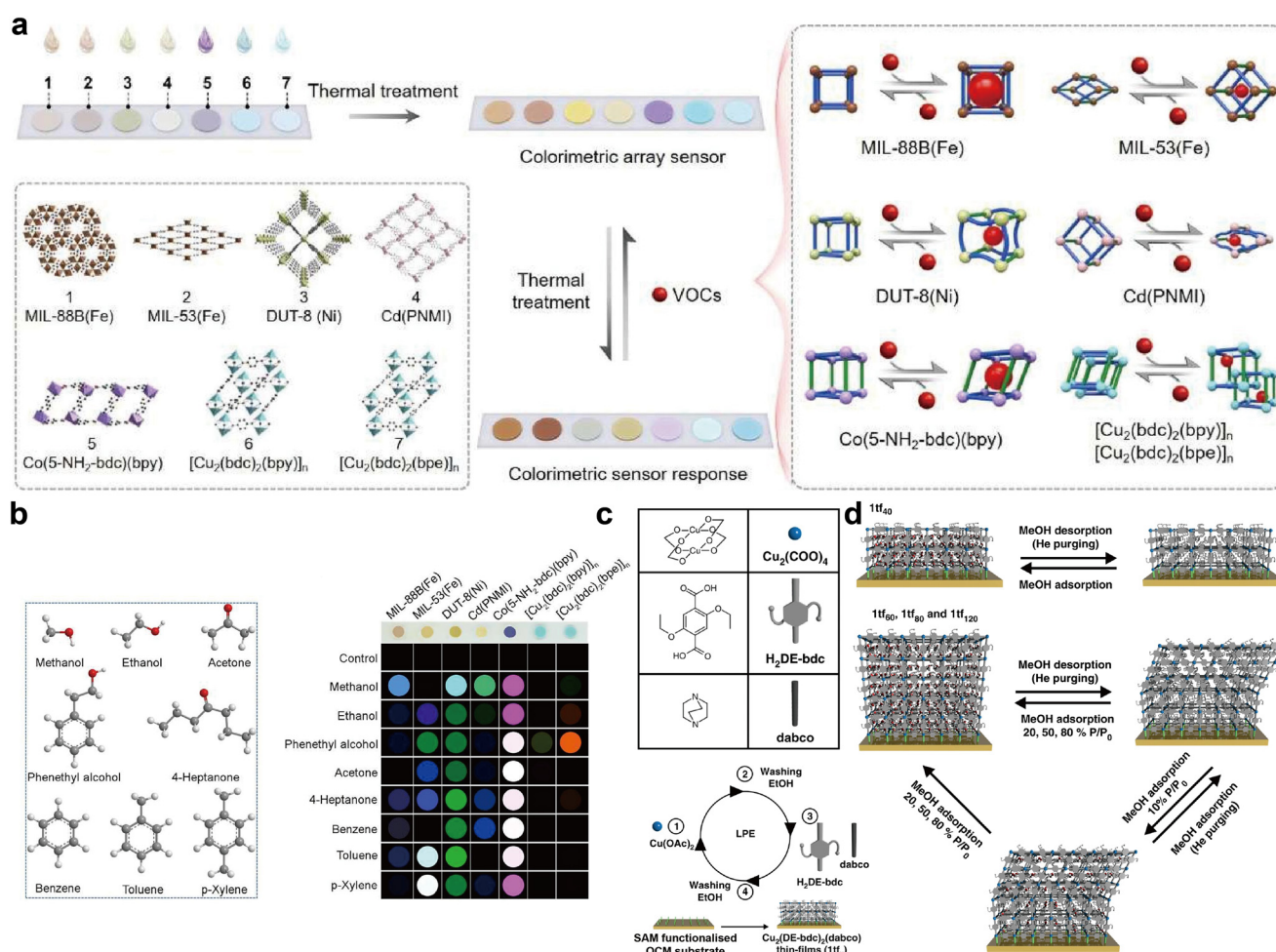

Fig. 9 Soft MOFs for colorimetric sensors and QCM. (a) Illustration of an artificial olfactory sensor utilizing a colorimetric sensor array composed of seven flexible MOFs; (b) molecular structures of target low-reactivity VOCs and differential images of the sensor array upon exposure to different VOCs. Reproduced with permission.[91] Copyright 2022, Elsevier B.V.; (c) schematic representation of the growth of Cu-based alkylether-functionalized MOF crystallites on SAM functionalized QCM substrates through the LPE preparation process; (d) scheme for phase transitions of Cu-based alkylether-functionalized MOF crystallite films with 40 fabrication cycles (up, remains in the open-pore form) and 60 to 120 fabrication cycles (bottom, reversible open-pore to closed pore transition) upon methanol adsorption and desorption cycles. Reproduced with permission.[93] Copyright 2019, Springer Nature.

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soft MOF, this composite selectively adsorbed CO_2 over other atmospheric gases. Upon CO_2 adsorption, a host transformation was triggered, altering the conformation of encapsulated DSB and causing a distinct fluorescence change at a specific pressure threshold. Despite similarities in physicochemical properties, the composite exhibits different fluorescence responses to CO_2 and C_2H_2, enabling their differentiation. This innovative strategy expands the scope of luminescence-based gas sensing and offers a promising platform for versatile, real-time gas detection applications.

Quartz crystal microbalance (QCM) sensors are among the most common mass-sensitive sensors, featuring low cost and favorable sensing performance. The mass of the sensing material coated on the QCM alters upon absorption of target gases. Concurrently, the computer converts this mass change (Δm) into a frequency change (Δf) using the Sauerbrey equation, enabling a clear observation of the sensor's performance.[94] Soft MOFs, with their potential for fine-tuning structural dynamics, enhanced responsiveness, and

orientation-dependent behavior, are considered an attractive alternative compared to their rigid counterparts. In a typical work, the controlled anchoring of flexible, layered-pillared MOFs onto self-assembled monolayer (SAM) functionalized Au-coated QCM substrates was discussed.[93] Through stepwise liquid-phase epitaxy (LPE), Cu-based alkylether-functionalized MOF crystallites were precisely anchored onto these substrates (Fig. 9c). Using in situ grazing incidence X-ray diffraction, the structural transformations during methanol sorption were monitored, revealing a distinct responsiveness different from bulk powders. Thicker films (60–120 deposition cycles) display a reversible phase transition from the large pore (solvent-rich) to the narrow pore (non-solvent rich) state upon polar-guest desorption and re-adsorption, whereas very thin films (40 deposition cycles) inhibit this flexibility (Fig. 9d). Furthermore, the orientation of the film significantly influences the transition. Samples grown along the (110) lattice plane exhibit structural dynamics, while these dynamics are suppressed in MOFs grown along the (001) lattice plane. This work, in
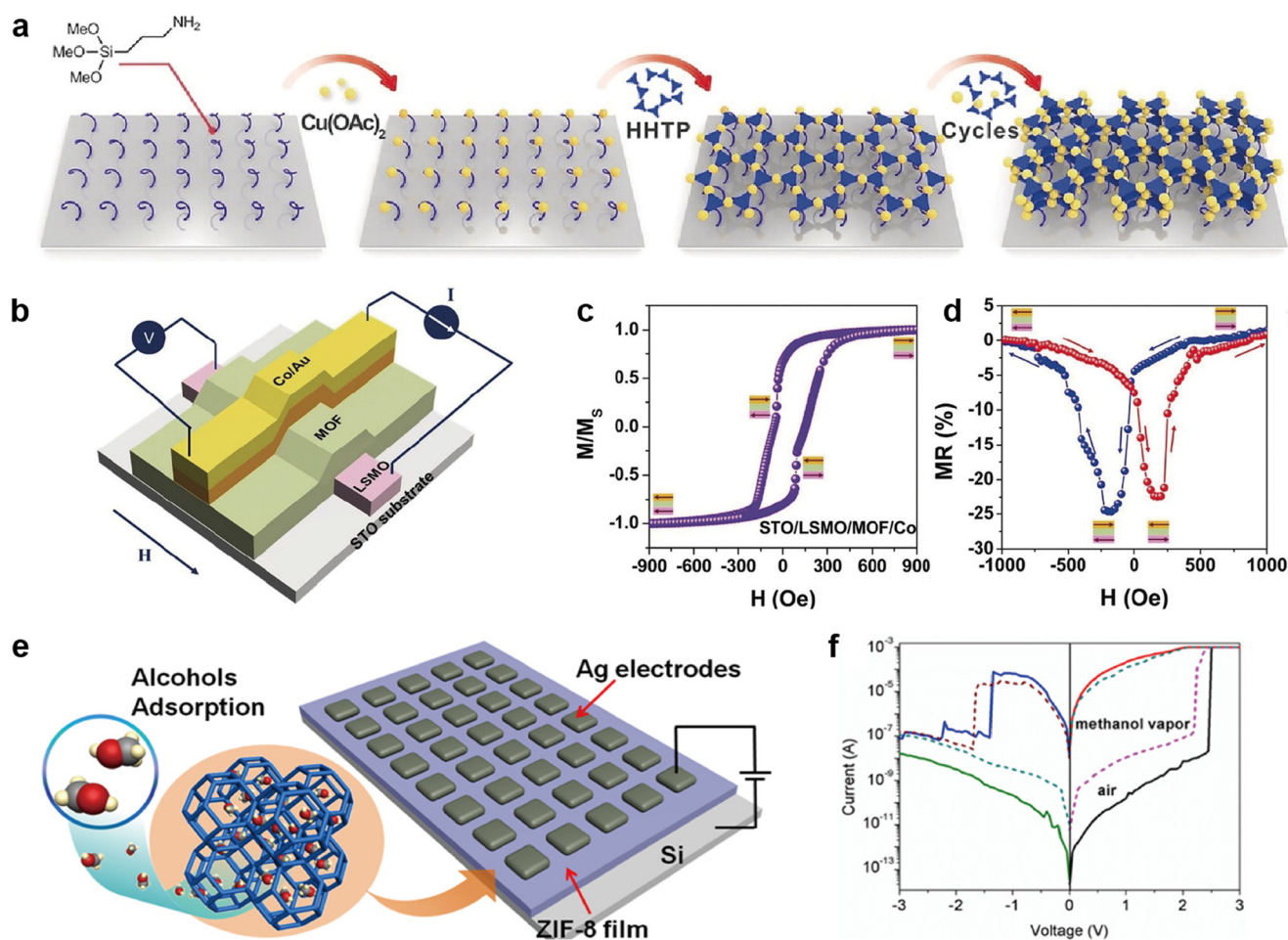

Fig. 10 Potential applications of soft MOFs in spintronics and memristors. (a) Schematic representation of $Cu_3(HHTP)_2$ nonmagnetic spacer layer through layer-by-layer procedure on a functionalized LSMO ferromagnetic electrode; (b) diagram of the 2D c-MOF-based vertical OSVs; magnetic hysteresis loops (c) and the MR loop (d) for the $LSMO/Cu_3(HHTP)_2(100$ nm)/Co OSV at 10 K. Reproduced with permission.[99] Copyright 2021, Wiley-VCH; (e) illustration of ZIF-8 based memory device arrays with alcohol-mediated properties; (f) current–voltage characteristics of the Ag/ZIF-8/Si device in saturated methanol vapor (dashed line) and air (solid line) at room temperature, respectively. Reproduced with permission.[104] Copyright 2016, Wiley-VCH.

understanding thin-film flexibility, is critical for designing tunable MOF-based devices, particularly for applications like selective VOCs sensors.

With the miniaturization of electronic devices nearing their physical limits, the development of new electronic devices in the post-Moore era has become a key area of research focus. Among these, spintronics devices and memristors stand out as prominent examples. Research on MOFs in both spintronics[95] and memristors is still a prospective but an infant field, and investigations into flexible MOFs in these areas are even more nascent. Current research on MOF-based spintronics emphasizes the design of spintronics materials,[96–98] the application of MOFs in spin transport,[99,100] and spin manipulation using MOFs with bipolar magnetic semiconductor (BMS) characteristics.[101] The above research efforts are centered around 2D MOFs due to their high charge mobility through d–π conjunction. In 2020, the use of conductive MOF thin films, $Cu_3(HHTP)_2$, as the nonmagnetic (NM) organic spacer layer to construct organic spin valves (OSVs) with an $La_{0.67}Sr_{0.33}MnO_3$ (LSMO)/$Cu_3(HHTP)_2$/Co structure, was pioneered (Fig. 10b).[99] Employing an *in situ* layer-by-layer assembly technique, they created highly crystalline and oriented thin films with adjustable thicknesses on a 3-aminopropyltrimethoxysilane (3-APTMS) functionalized LSMO ferromagnetic electrode (Fig. 10a). The resulting OSVs exhibited two significant coercivities (H_c) and a negative magnetoresistance (MR) effect of up to 25% at 10 K (Fig. 10c and d), demonstrating adaptability across a range of film thicknesses (from 30 to 100 nm) and higher temperatures (up to 200 K). This work highlights the 2D c-MOFs' potential for further exploration in spin-polarized transport phenomena. For flexible MOFs, most of them are electrical insulators ($\delta < 10^{-10}$ S cm^{-1}), hindering their applications in spintronics. The design of π-conjugated flexible organic linkers is an alternative approach to impart flexibility to conductive MOFs.[102] Additionally, flexible MOFs with magnetic properties need to be urgently explored to progress their applications within the field of spintronics. Recently, a breakthrough in multiferroic materials has been presented by achieving an inverse temperature symmetry-breaking phenomenon in $[FPM][Fe_3(\mu_3\text{-}O)(\mu\text{-}O_2CH)_8]$, where FPM (3-(3-formylamino-propyl)-3,4,5,6-tetrahydropyrimidin-1-ium) acts as a flexible counterion.[103] This material exhibits a ferroelastoelectric phase above its Curie temperature (365 K), demonstrating the coexistence of ferroelasticity and ferroelectricity between 365 K and 426 K. The two-step symmetry breaking, initiated by a conformational flip of FPM cations, enables the material to function at higher temperatures than conventional multiferroics, addressing the limitation of low operating temperatures typically faced by such materials. This development paves the way for the design of novel multiferroic materials suitable for practical applications requiring elevated temperature stability.

To date, memristors based on MOFs can be primarily categorized into three mechanisms: conductive filament switching (*e.g.*, metal and/or carbon filaments),[104,105] charge trapping/de-trapping switching,[106] and light-tunable charge trapping switching,[107] involving several MOFs such as ZIF-8, HKUST-1, Cu-HHTT, Zn-TCPP, *etc.* Given the in-memory computing capabilities of memristor arrays and the substantial advantages of MOFs in sensing applications, developing integrated sensing, storage, and processing (namely in-sensor computing) in a single device within MOFs is promising.[83] By harnessing the host–guest interactions and optoelectronic properties of MOFs, prototype bioinspired olfactory and vision devices have already been realized. In 2016, a resistive switching device with an Ag/ZIF-8/Si structure was reported (Fig. 10e). By leveraging the host–guest interactions between the framework and alcohols, they achieved reversible resistance switching and multilevel information storage (Fig. 10f), which holds promise for application in environmentally responsive smart devices.[104] In 2022, 2D $Zn_2(ZnTCPP)$ MOFs–PMMA composite thin films were utilized as charge-trapping layers to construct a new type of optoelectronic neuromorphic transistor. They were able to simulate human emotional regulation and learning-memory behavior through the modulation of source-drain voltage.[83] Flexible MOFs possess intrinsic advantages in the construction of resistive switching devices and in-sensor computing devices. On the one hand, the reversible dynamic behavior of flexible MOFs in response to external physical or chemical stimuli is expected to result in reversible changes in their charge transport. If these flexible MOFs exhibit different resistances in large-pore and narrow-pore states, they can be utilized to achieve intelligent sensing capabilities in response to external stimuli such as pressure, temperature, odor, and light. On the other hand, downsizing the size of flexible MOF crystallites to the nanoscale can change their adsorption properties and even introduce new intrinsic features that differ from those of bulk MOFs. For example, the shape-memory effect of some flexible MOFs in thin-film states holds promise for applications in write-once-read-many (WORM) memory devices. This science depends on how to functionally control interfaces and how to control the direction and flow of transport of substances, electrons, and ions within other constituent materials. Much progress is expected in this area.[108,109]

3.2 Biomedicine applications

MOFs, with their distinct structural advantages and potential for biofunctionalization, present a broad range of applications in biomedicine, encompassing drug delivery, biomedical imaging, biosensors and diagnostics, bioimaging, and tissue regeneration.[110,111] Soft MOFs have been regarded as a potential platform for drug delivery, largely because their high pore volume and the adaptable pores to accommodate the shape and size of hosted molecules.[112] Furthermore, they can precisely control the rate and location of drug release by responding to external stimuli (such as changes in pH, temperature, light, *etc.*), thereby enhancing treatment efficacy and reducing side effects. For example, the potential drug
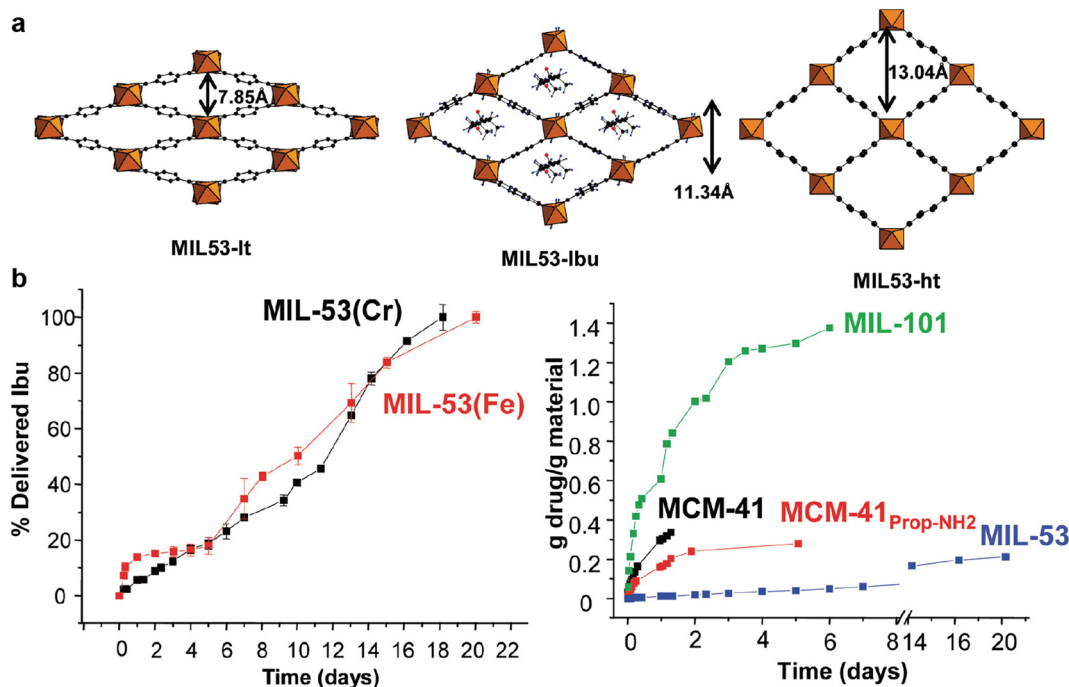
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Fig. 11 Soft MOFs for colorimetric drug delivery. (a) Scheme of the breathing effect of MIL-53(Cr) upon dehydration–hydration; (b) ibuprofen (Ibu) delivery from MIL-53Cr and MIL-53Fe materials (left) compared with other MOFs (right).[113] Copyright 2008, American Chemical Society.

delivery application within soft MOFs was reported for the first time in the year 2008.[113] In this case, the capability in adsorbing (0.21 g ibuprofen per g MOF) and controlled release of ibuprofen (more than three weeks) are both demonstrated in flexible **MIL-53(Cr)** and **MOF-53(Fe)**, which are slower than rigid MOFs MIL-100 and MIL-101 (3 to 6 days), expecting very long therapies (Fig. 11a and b). Both experimental results and DFT calculation revealed that hydrogen bonding between the carboxylic group of ibuprofen and the hydroxyl group of the matrix strongly interact once ibuprofen is inserted. Furthermore, this long-term drug release behavior could be attributed to the adaption of pore size to the guest molecules to enhance the drug–matrix interactions. In another report, a kind of flexible-on-rigid hybrid-phase MOF *via* heteroepitaxial growth was demonstrated, combining distinct MOF phases with partially matched topologies and compensatory structural flexibility.[114] The resulting hybrid-phase MOF was employed to create a dual-drug delivery system with tunable loading ratios and release kinetics. Cell viability assays and combination index analysis in MCF-7 cells demonstrate the system's potential for synergistic, controlled drug delivery.

Despite the significant potential of soft MOFs in drug delivery, several challenges persist. On the one hand, the research into drug loading and release kinetics remains limited, which is crucial for the directed design of these materials. On the other hand, there is a paucity of toxicological studies on soft MOFs in the existing literature, making it difficult to draw definitive conclusions regarding their safety. To progress soft MOFs toward the clinical development stage, it is imperative to conduct systematic *in vivo* studies to evaluate their stability,

degradation mechanisms, and potential side effects on normal organs. With further research and technological advancements, soft MOFs will demonstrate even more possibilities in areas such as real-time monitoring, disease treatment and bioimaging in the future. In addition to the performance of MOF itself, research on hybrid systems, such as creating a biocompatible substance coating to incorporate into biological systems, is also important. This is a typical example of the fourth generation of MOFs.[2,115]

3.3 Nuclear industry

The application of SPCs in the nuclear industry currently appears to be relatively limited, compared to their more established uses in other sectors such as storage, separation, sensing, and catalysis. While SPCs, in general, offer unique properties such as high surface area, tunable porosity, and versatile chemical functionality that could potentially address various challenges faced by the nuclear sector, their deployment in this domain is still in the nascent stages and faces several specific hurdles. Some of the applications could be radiation shielding, radioactive waste management, catalytic decomposition of radioactive substances, radiation detection and sensing, *etc.* Take radiation shielding for example, soft MOFs with high atomic number elements in their metal nodes or organic linkers could potentially be utilized as lightweight, customizable radiation shielding materials. Their tunable porosity and composition allow for the design of materials with optimized attenuation properties for specific types of radiation (*e.g.*, gamma rays, neutrons). The flexibility of

these MOFs may also enable the development of conformal shielding solutions for complex geometries or dynamic environments in nuclear facilities. Next, the applications of traditional rigid MOFs in the nuclear industry will be illustrated, followed by an elaboration on the potential and challenges of soft MOFs in this field. Specifically, the UiO-66 series is widely utilized in the nuclear industry owing to its excellent thermal and chemical stability. The following elaboration on such examples aims to illustrate the current status and demands of MOFs in this field, providing insights for the future design of soft MOFs. For example, modifications and defect engineering strategies enable researchers to introduce local distortions or dynamic

behaviors into the UiO-66-X series through functionality-induced linker rotations.[116]

Facing the energy crisis, nuclear power's high density and low carbon footprint make it a promising alternative. Uranium serves as a critical raw material in the nuclear industry. However, uranium scarcity and safety concerns from radioactivity hinder its sustainable growth.[117] Research on uranium enrichment and removal from seawater and wastewater is vital, but faces challenges from competing metal ions and low concentrations. Enhanced separation techniques are needed to tap these uranium sources effectively.[118] Among plentiful adsorbents, MOFs have attracted tremendous attention in the field of U(VI)
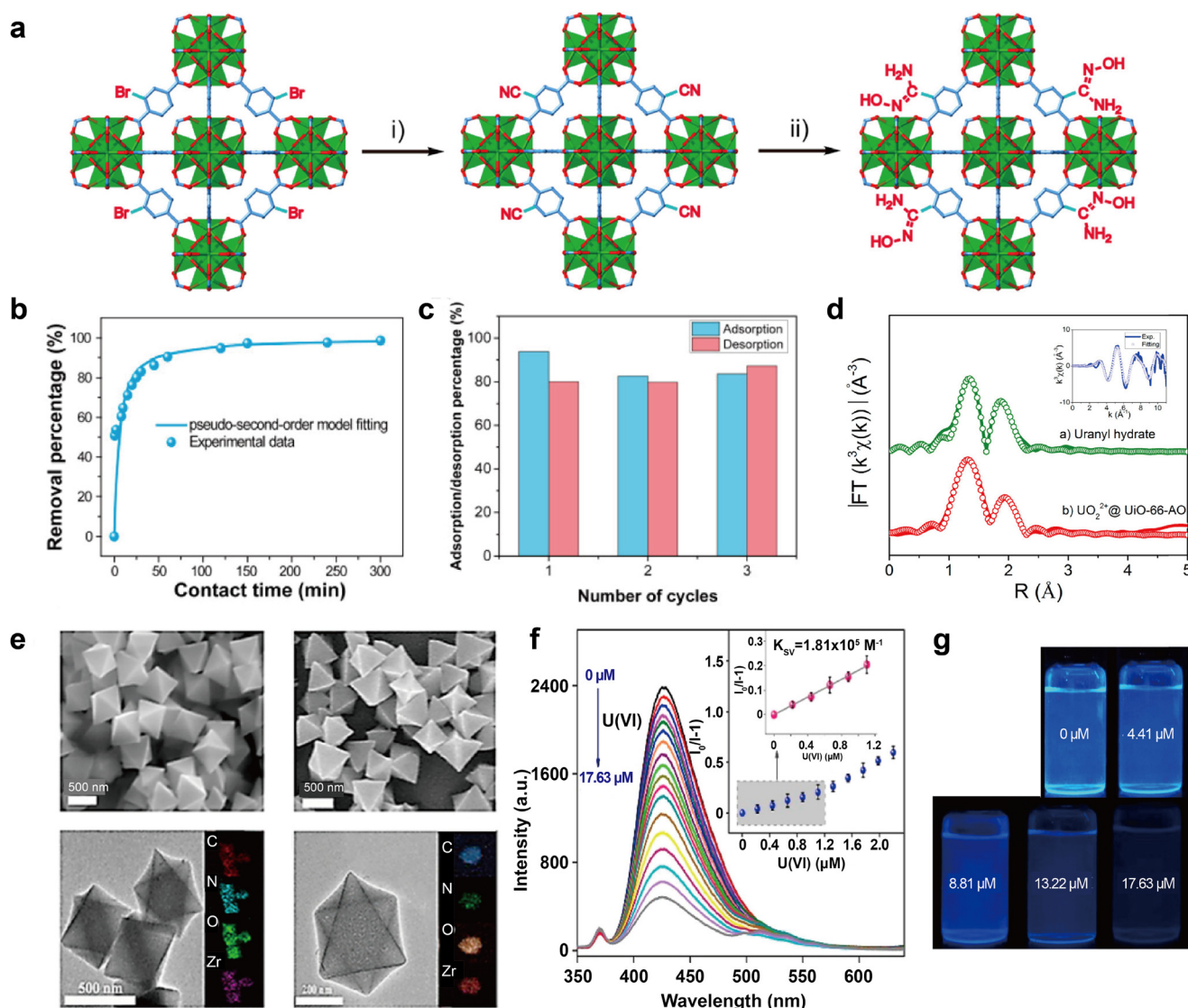

Fig. 12 Potential applications of soft MOFs in the nuclear industry. (a) Synthetic route of UiO-66-AO: i) CuCN, N-methyl pyrrolidone, microwave at 170 °C for 20 min, ii) $NH_2OH \cdot HCl$, CH_3CH_2OH, refluxing for 24 h; (b) time-dependent removal percentage of Bohai seawater by UiO-66-AO; (c) three adsorption/desorption cycles of UiO-66-AO to uranyl for Bohai seawater; (d) comparison of uranium EXAFS spectra for uranyl hydrate and UiO-66-AO adsorbed uranyl. Reproduced with permission.[124] Copyright 2017, American Chemical Society; (e) SEM and TEM images of UiO-66-NH_2 (left) and LTP@UiO-66-NH_2 (right); (f) fluorescence emission spectra of LTP@UiO-66-NH_2 with different concentrations of U(VI). Inset graphs are the corresponding fitting lines at low concentrations (0–1.2 μM); (g) optical photographs of LTP@UiO-66-NH_2 quenched by different concentrations of U(VI) under UV light. Reproduced with permission.[129] Copyright 2022, American Chemical Society.

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adsorption owing to the advantages of controllable pore structure, abundant active adsorption sites and high specific surface areas. To ensure the efficacy and selectivity in uranium enrichment, MOFs should be endowed with the following three features: i) water stability is paramount, as uranium enrichment typically occurs in aqueous environments, demanding that the material withstand hydrolysis to maintain structural integrity and long-term stability; ii) functionalization is essential, requiring the surface or internal pores of the material to contain functional groups that strongly interact with uranium ions, such as carboxylates, phosphonates, and amines, which capture uranium ions efficiently and selectively through coordination, electrostatic attraction, or hydrogen bonding;[119–121] iii) high radioactive stability is vital, which could be tested through structure and crystallinity characterization before and after irradiation exposure.[122,123] Composed of octahedral $[Zr_6\text{-}O_4(OH)_4]$ nodes, UiO-66 stands out as a preeminent example of highly stable MOFs, largely attributable to the high coordination number of its Zr^{4+} centers, which endows the framework with unparalleled robustness and durability. Typically, amidoxime functionalized MOF, UiO-66-AO, was fabricated (Fig. 12a), exhibiting rapid and efficient uranium extraction from seawater.[124] It removes 94.8% uranyl ions in 120 minutes and 99% from seawater with added uranium within 10 minutes (Fig. 12b). Its sorption capacity is 2.68 mg g^{-1} in real seawater samples, showing recyclability over three adsorption/desorption cycles (Fig. 12c). EXAFS analysis reveals that multiple amidoxime ligands chelate uranyl ions, forming hexagonal bipyramid coordination (Fig. 12d). Besides, series such as ZIFs,[125] MILs,[126] and rare earth MOFs[127] have potential in the enrichment of U(VI). Apart from uranium, the nuclear waste contains various other radioactive elements such as plutonium (Pu), strontium-90 (Sr-90), cesium-137 (Cs-137), technetium-99 (Tc-99), and iodine-131 (I-131), and more. These radioactive contaminants can pose serious health risks to humans and cause significant ecological environmental damage if not properly managed. MOFs and their derivatives exhibit a remarkable capacity to selectively trap toxic elements, making them promising candidates for applications in the decontamination of radioactive water.[128]

Soft MOFs, featured in the "breathing effect", are theoretically well-suited for the efficient capture and release of radiative ions. For instance, soft MOFs can dynamically alter their pore dimensions in response to environmental changes, such as humidity levels. This breathing effect enables the material to efficiently capture radiative ions when hydrated, and subsequently release them when the structure dehydrates or dries out, contributing to sustainable nuclear energy development. Nevertheless, the application of soft MOFs in the field of radiative ion enrichment is constrained by several factors. Primarily, the stability of soft MOFs is challenged under extreme conditions, such as in seawater with high salinity or in the presence of strong acids and bases encountered during nuclear waste processing.

Secondly, to achieve efficient radiative ion enrichment, soft MOFs require highly selective functionalization, meaning they must preferentially adsorb specific radiative ions over other coexisting metal ions. This presents a considerable design challenge. Moreover, flexible MOFs must be capable of releasing radiative ions following their adsorption through simple procedures, such as altering temperature or pH, allowing for the collection and further processing of uranium while maintaining the structural integrity for reuse. As research progresses, it's anticipated that more innovative outcomes will emerge focusing on the application of soft MOFs in radiative ion enrichment. These advancements are expected to offer novel solutions for the sustainable development of nuclear energy.

Beyond the extraction of radiotoxic ions, MOFs have also been investigated for their potential in the detection of radioactive ions. The porous nature and tunable functionality of MOFs enable them to serve as sensitive platforms for monitoring radiological contaminants. By engineering specific ligands and metal nodes, MOFs can be customized to respond selectively to targeted radioactive ions such as uranium, plutonium, or other radionuclides. The sensing mechanism covers electrochemical signal and fluorescence quenching or enhancement. For electrochemical sensors, the working principle is fundamentally based on the redox reactions that occur when radioactive ions interact with the electrochemical system.[130] For luminescent sensors, luminescent MOF-based materials are prepared by using lanthanide metal or transition metal as the metal nodes, or combining excellent photoluminescence properties of carbon/metal quantum-dots with MOFs to form nanomaterials/MOF composites.[131,132] In a typical work, an NH$_3$ plasma functionalized UiO-66-NH$_2$ (LTP@UiO-66-NH$_2$) for highly sensitive and selective U(VI) detection in water was developed (Fig. 12e).[129] This technique enhances the material's fluorescence emission and U(VI) binding, demonstrating a remarkable Stern–Volmer constant of 1.81 × 10^5 M^{-1} at 298 K and a detection limit as low as 0.08 μM (19.04 ppb) (Fig. 12f and g). The quenching mechanism behind the heightened sensitivity is attributed to static quenching interactions facilitated by the abundant amine groups on the functionalized framework. Intriguingly, LTP@UiO-66-NH$_2$ exhibits stable and accurate U(VI) detection performance across intraday and interday tests. Its application in real-world scenarios, including tap water and lake water samples, confirms its reliability. Soft MOFs have a great advantage in enhancing the sensitivity of sensors due to their ability to undergo reversible structural changes in response to external stimuli, which can lead to more precise and responsive detection capabilities. Designing functional soft MOFs is crucial for the detection of radioactive ions in water. Even more importantly, the use of higher-valent second building units is essential to enhance their stability in aqueous and radiolytic environments.

Furthermore, monitoring dissolved hydrogen and oxygen of non-radiative water in a nuclear plant's primary loop is

crucial for preventing metal corrosion, monitoring hydrogen buildup to avoid explosion risks, maintaining water quality, and ensuring the integrity of nuclear fuel rods, thus safeguarding operational safety, reliability, and efficiency. Using high-performance hydrogen and oxygen meters for this purpose is essential to safeguard the operational safety, reliability, and efficiency of the nuclear power plant. Selective gas permeation membranes are one of the core materials in these sensors. Through molecular engineering design, incorporating porous materials, such as SPCs, into polymers as fillers instead of traditional organic polymer films enables the construction of mixed-matrix membranes. This method leverages the advantages of both materials, allowing for the customization of the membrane's structure and performance, thereby achieving both high permeability and high selectivity.

4 Perspective

Currently, the research on SPCs is in the hot stage, and various properties are still being unlocked. Through the development history of MOFs, we can see that in recent decades, frameworks with new components and topologies have been designed, synthesized, characterized, and reported one after another, gradually enriching the databases and expanding applications. Compared with traditional porous entities, porous crystals with spatial 3D extension featured designable structure, low density, permanent pores, ultra-high specific surface area, and functionalized pore structure, exhibiting extensive applications in gas storage and separation, catalysis, sensing, drug delivery, *etc.* Promoting new frontiers of application fields and industrialization of MOFs are the two main development trends. Throughout the history of one material, when it transitions from fundamental research to applied research, it is a tricky but common phenomenon that fundamental scientists, or those working at the cutting edge of these fields, will focus more on new frontiers rather than delving deeply into existing applications. There is no doubt that the development of MOFs is following the same path. Although gas storage and separation are the most promising application fields for porous crystals, the major research focus is not on the industrialization of available materials but on transforming to other fundamental aspects, such as electronic devices, spintronics, *etc.* Undoubtedly, while it is urgent to explore new frontiers of MOFs, the importance of industrialization cannot be overlooked. For industrial applications, long-term stability is a critical factor that should be carefully considered. However, many studies focus on single-point analysis, lacking insights into long-term stability. Investigating how structural changes affect framework flexibility offers valuable understanding at the microscopic level and can guide the rational design and synthesis of advanced materials. For example, under repeated adsorption cycles, MIL-53(Al) and ELM-11 exhibited highly stable behavior after 100 cycles, with minimal structural degradation and enhanced catalytic efficiency by trace water.[133] These findings highlight the importance of dynamic structural adaptations in developing robust and sustainable catalysts suitable for industrial applications.

Among porous crystals, MOFs represent the most rapidly advancing and widely studied class, with extensive applications across various fields. Recently, other types of SPCs, such as soft COFs, HOFs, and even zeolites,[134] have also been reported. However, the number of well-documented examples and practical applications for these systems is still limited compared to MOFs. We foresee that, as the field of SPCs continues to evolve, the advancements in soft MOFs will pave the way for major breakthroughs in soft COFs, HOFs, and zeolites in the near future. The following section outlines the future prospects and potential directions for SPCs, focusing on three key aspects: industrialization and material shaping, conductivity and devices, and characterizations and simulations (Fig. 13).
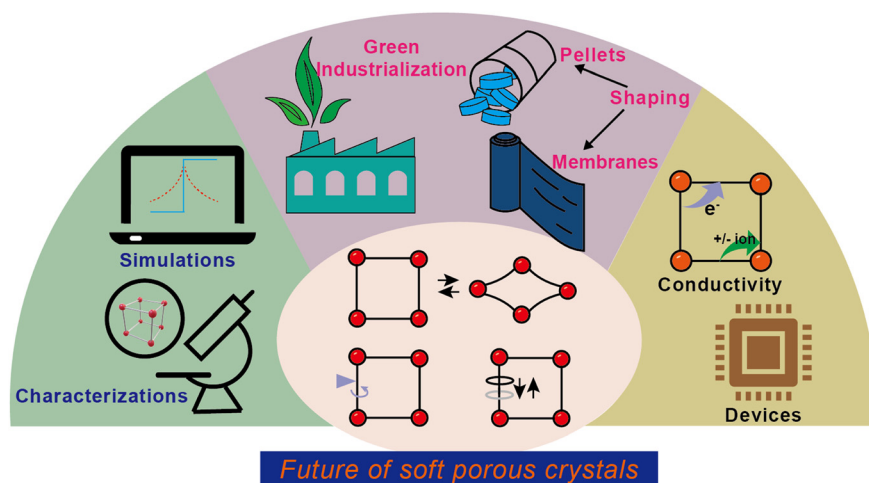

Fig. 13 Future opportunities and potential of SPCs in industrialization and shaping, conductivity and devices, and characterizations and simulations.

4.1 Industrialization and shaping of SPCs

To date, more than 100 000 MOFs with different structures have been published during the last three decades, whereas frameworks with structural flexibility are limited, remaining a relatively blank field to be explored. Besides, the research on soft MOFs remains predominantly in the laboratory development stage despite significant scientific breakthroughs and innovative achievements to date. Researchers focus on the exploration of soft MOF design, synthesis, structural manipulation, performance characterization, and application development. Despite the theoretical promise and initial experimental validation of soft MOFs, several challenges hinder their transition from the laboratory to industrial-scale production. First, laboratory-scale synthesis methods are often limited in scale and necessitate the development of efficient, cost-effective, and scalable manufacturing processes. Second, maintaining structural integrity and consistent performance of soft MOFs during upscaling is a major challenge, requiring stringent quality control standards and advanced characterization techniques. Furthermore, practical applications may involve post-processing, encapsulation, or integration of MOFs with other components, which need to be addressed outside the confines of the laboratory.

Recently, some companies have begun to convert MOFs from academia to industry, indicating this field is about to enter a new era. The German chemical giant BASF was the earliest company to use MOFs for natural gas fuel storage of heavy-duty trucks. Following this successful prototype, TruPick, the first commercial product based on MOF adsorbent, was launched. This MOF adsorbent has the capability to delay the ripening of fruits and vegetables by storing and releasing 1-methylcyclopropene. Another commercial product designed shortly thereafter was the ION-X gas storage and delivery system by NuMat, which was used for harmful gas storage such as hydrogen arsenide, phosphine, and boron trifluoride used in the electronics industry.[135] Atomis has worked with Japanese companies to commercialize three products: MOFs with a longer lifespan for fluorine coatings, MOF membranes with extremely high deodorizing performance, and MOFs for recovering fluorine refrigerants such as CFCs. Currently, there are many MOF-related companies which successfully upgraded from start-ups to commercial companies that can realize mass production of many MOFs. By using solid/semisolid synthetic methods, the cost of more than 10 kinds of MOFs can be reduced to less than 10 USD per kg. In a recent study, a catalytic proton exchange technology utilizing MIL-101(Cr) significantly enhanced the cleanup efficiency of tritiated water, overcoming the limitations of traditional water distillation. Through this approach, effective treatment of tritiated water is achieved, providing new insights for industrial applications.[136]

Factors such as the surge in industrial gas production, increasing government support, rising urbanization and development of artificial intelligence (AI) have driven exponential growth in the MOF market in recent years. According to a forecast, the market is expected to grow from $0.48 billion in 2024 to $0.63 billion in 2025, at a compound annual growth rate (CAGR) of 30.8%. It is further projected to reach $1.55 billion by 2029, with a CAGR of 25.2%.[137] A key subset of this growth is driven by flexible sorbents, particularly soft MOFs, which are now transitioning from lab-scale research to practical applications. Zinc-based, copper-based, iron-based, aluminum-based, and magnesium-based MOFs are among the most promising candidates for commercialization of soft MOFs due to their high accessibility.[138] Zinc-based MOFs, such as CALF-20, have undergone industrial testing for CO_2 capture in cement plants, with BASF scaling production to hundreds of tons annually.[139] ZIF-8 has already been produced using a continuous hydrothermal system at a rate of 810 g h^{-1} (pilot scale), and several companies are now capable of producing it at the kilogram scale and beyond.[140] The hydrophilic aluminum-based MOF-303 exhibits highly efficient water-harvesting capabilities, making it an excellent candidate for extracting water from desert air. It has demonstrated a water collection capacity of 0.7 liters per kilogram per day under real-world conditions in the Mojave Desert. A water-assisted synthesis approach was subsequently developed, enabling the production of 3.5 kg per batch with a high yield of 94%.[47]

Despite the above achievements, developing effective and versatile large-scale synthesis methods for SPCs remains a challenge and most available technologies do not meet the requirements for green and sustainable development. In most cases, SPCs are synthesized in the form of powder, and shaping these materials into thin films, pellets or membranes will be of importance to practical application.[109,141] Hybridizing SPCs with other materials, such as polymers, may be a facile strategy to realize the production of SPC-based membranes for separation, leveraging a synergistic effect.

The structural dynamics of SPCs—specifically, their ability to expand or contract in response to external stimuli—pose tremendous challenges from an engineering perspective. When such structural changes occur during the expansion and shrinkage cycles of an adsorbent, adaptive tanks would need to be deliberately designed to accommodate these volume fluctuations in some cases. However, in standard equipment, which usually has a fixed size standard, a common strategy involves two aspects: incorporating sufficient spatial tolerance through internal structural design, and employing adhesives for granulation to counteract flexibility-induced collapse.

One major challenge arises when SPCs are deposited onto rigid substrates such as metals, ceramics, or silicon wafers. Cyclic expansion and contraction can induce interfacial stress, potentially leading to delamination or peeling. To mitigate this, strategies such as surface pretreatment of the substrate, controlled film thickness, and anisotropic crystal growth have shown promise in enhancing interfacial

adhesion and delaying film failure. For example, increasing substrate roughness can promote mechanical interlocking and improve adhesion strength. Additionally, promoting the infiltration of the matrix into the substrate has been demonstrated to effectively enhance the stability of composite membranes.[142] In the context of shaped SPC pellets, similar issues arise. Some pellets have been found unable to withstand the mechanical stress induced by phase transitions during adsorption–desorption cycles, leading to disintegration after exposure to high-pressure gas adsorption.[143] Therefore, the selection and innovation of shaping processes and binders (such as polyvinyl alcohol, sodium alginate, and methyl cellulose) play a crucial role in improving pellet stability. A representative case involves the use of methyl cellulose as a binder in extrusion processes, which significantly enhanced the mechanical stability of MIL-53(Al) pellets while preserving their flexibility, making them suitable for industrial applications.[144] Moreover, from the perspective of material design, using SPCs with localized flexibility as functional components could help avoid the negative impacts associated with volume changes.[145]

Crystal size has a multidimensional impact on material performance.[84] Small-sized crystals (<100 nm) offer shorter diffusion paths, which can enhance adsorption and desorption kinetics; however, their high surface-to-volume ratio may amplify the effects of surface defects—for example, exposed active sites can lead to reduced stability. In contrast, large-sized crystals (>1 μm) exhibit significantly increased diffusion resistance, particularly in fast-cycling applications such as pressure swing adsorption (PSA), which may result in a decrease in effective capacity. On the other hand, larger crystals typically have fewer internal defects and greater structural rigidity. In terms of deformation behavior, small crystals may display size-dependent deformation mechanisms due to quantum confinement effects or surface-energy dominance. Therefore, it is essential to precisely control crystal size through tailored synthesis conditions—such as adjusting additives or temperature in solvothermal methods—to strike an optimal balance between mass transport efficiency and mechanical stability.

Looking ahead, future research could focus on the development of dynamically responsive composite materials, such as those featuring self-healing interfaces or adaptive pore structures, to enhance the robustness of materials under real-world operating conditions. Such innovations will be key to enabling the practical deployment of SPCs in energy-efficient and sustainable separation and storage technologies. Collaborative efforts from scientists, engineers, and investors will accelerate the transition from the laboratory to the marketplace.

4.2 Conductive SPCs

Despite their wide applications in multiple areas, especially gas adsorption and separation, the research for soft MOFs with conductivity is rare, which limits their utilization in electronic devices, and electrochemical and photo-electrochemical catalysis. Although several strategies such as doping, and hybridization have been proposed to endow these materials with conductivity,[146] the intrinsic electronic conductivity should be further improved through the design of conjugated linkers with flexibility. The design and preparation of conductive soft MOFs with stimulus conformational transformation is expected to construct multifunctional devices. For instance, the structural alterations between *op* to *cp* may cause reversible changes in material conductivity (semiconductor/metal/insulator), endowing application in memristive devices where the conductive modulation between high and low resistance is desired; the sensitivity of a chemiresistor gas sensor is expected to achieve significant improvement accompanied along the crystalline-to-crystalline phase transitions upon exposed to target compounds; unconventional electrical phenomena are expected to be established on the synergistic interface of SPCs. Although fabrication methods for free-standing or substrate-supported nano-scale MOF thin films have been well established, developing convenient, rapid, and energy-saving techniques to realize the control fabrication of high-quality thin films is urgently needed.[147] Besides, research on heterogeneous SPCs thin film growth is an emergency due to the lattice mismatching facts.

4.3 Characterizations and theoretical calculations of SPCs

Understanding the influencing factors of dynamic behavior (gate opening pressure) of SPCs is of significance to finely tune the switching behavior and meet targeted application demands. Material characterization plays a vital role in revealing a material's intrinsic properties, optimizing its performance, guiding the design of new materials, and ensuring reliability and effectiveness in practical applications. Due to SPCs' unique structural tunability, rich porous architecture, and wide-ranging potential applications, there are new challenges and demands for characterization techniques. In recent years, characterization technologies targeting soft MOFs have steadily evolved, with the aim of precisely and comprehensively revealing their structural attributes, dynamic behavior, and performance in practical applications. In addition to being analyzed through routine characterization methods such as XRD, TEM, SEM, AFM,[148,149] FTIR, XPS, TGA, Raman spectroscopy, NMR, *etc.*, some advanced *in situ* methods have been developed to observe the dynamic transition of SPCs directly[150–152] although flexible characters could be confirmed by the presence of steps in the isotherm indirectly. *In situ* characterization techniques for soft MOFs refer to the methods that monitor and analyze the physicochemical properties and dynamic responses of these materials to external stimuli (such as temperature, pressure, gas environment, and electric or magnetic fields) while maintaining their native structure and environmental conditions. In most cases, soft MOFs serve in complex working environments, and the *operando* technology holds significant

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value due to its ability to unveil the dynamic behavior, structural evolution, and functional mechanisms of these materials under actual operating conditions, such as gas adsorption, catalytic reactions, and electrochemical processes.[88,152] Additionally, the development of high-resolution transmission electron microscopy, ultrafast spectroscopy and multimodal coupling also boost the development of soft MOFs. Quantum mechanical calculations (*e.g.*, density functional theory, DFT) and molecular simulations (*e.g.*, molecular dynamics, Monte Carlo) are essential for understanding the energetics and mechanistic details of structural transitions in soft MOFs.[145,153–156] These methods can predict equilibrium structures, transition pathways, and activation energies, guiding experimental investigations and facilitating the rational design of new soft MOF systems. These technological advancements not only deepen our fundamental understanding of the scientific questions surrounding soft MOFs but also provide robust support for their design, fabrication, and practical application optimization.

Looking forward, the development of SPCs holds immense promise for the future, as their unique properties and tunable characteristics open new avenues for innovative applications and scientific breakthroughs. Although a breakthrough with SPCs is not currently foreseeable based on existing research, the discovery of new, unpredicted functionalities remains difficult but possible.

Data availability

No new data were created or analyzed in this study. Data sharing is not applicable to this article.

Conflicts of interest

The authors declare no conflict of interest.

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References

1 S. Horike, S. Shimomura and S. Kitagawa, Soft porous crystals, *Nat. Chem.*, 2009, **1**, 695–704.

2 S. Kitagawa, Future porous materials, *Acc. Chem. Res.*, 2017, **50**, 514–516.

3 C. Kang, Z. Zhang, S. Kusaka, K. Negita, A. K. Usadi, D. C. Calabro, L. S. Baugh, Y. Wang, X. Zou, Z. Huang, R. Matsuda and D. Zhao, Covalent organic framework atropisomers with multiple gas-triggered structural flexibilities, *Nat. Mater.*, 2023, **22**, 636–643.

4 X. Liu, J. Li, B. Gui, G. Lin, Q. Fu, S. Yin, X. Liu, J. Sun and C. Wang, A crystalline three-dimensional covalent organic framework with flexible building blocks, *J. Am. Chem. Soc.*, 2021, **143**, 2123–2129.

5 Z. B. Zhou, H. H. Sun, Q. Y. Qi and X. Zhao, Gradually tuning the flexibility of two-dimensional covalent organic frameworks via stepwise structural transformation and their flexibility-dependent properties, *Angew. Chem., Int. Ed.*, 2023, **62**, e202305131.

6 Y. Chen, Z. L. Shi, L. Wei, B. Zhou, J. Tan, H. L. Zhou and Y. B. Zhang, Guest-dependent dynamics in a 3D covalent organic framework, *J. Am. Chem. Soc.*, 2019, **141**, 3298–3303.

7 X. Tang, J. Pang, J. Dong, Y. Liu, X.-H. Bu and Y. Cui, Supramolecular assembly frameworks (SAFs): Shaping the future of functional materials, *Angew. Chem., Int. Ed.*, 2024, **63**, e202406956.

8 X. Yu Gao, Y. Wang, E. Wu, C. Wang, B. Li, Y. Zhou, B. Chen and P. Li, Multivariate hydrogen-bonded organic frameworks with tunable permanent porosities for capture of a mustard gas simulant, *Angew. Chem., Int. Ed.*, 2023, **62**, e202312393.

9 H. Wang, B. Li, H. Wu, T. L. Hu, Z. Yao, W. Zhou, S. Xiang and B. Chen, A flexible microporous hydrogen-bonded organic framework for gas sorption and separation, *J. Am. Chem. Soc.*, 2015, **137**, 9963–9970.

10 Y. Gu, J. J. Zheng, K. I. Otake, S. Sakaki, H. Ashitani, Y. Kubota, S. Kawaguchi, M. S. Yao, P. Wang, Y. Wang, F. Li and S. Kitagawa, Soft corrugated channel with synergistic exclusive discrimination gating for CO_2 recognition in gas mixture, *Nat. Commun.*, 2023, **14**, 4245.

11 S. Ainiwaner, H. Huang, J.-J. Zheng, F. Li, X.-T. Yang, Y.-Y. Guo, F. Yuan, M.-S. Yao and Y. Gu, Boosting C_2H_6/C_2H_4 separation via the precise electrostatic modulation of synthetic 1D channel at atomic level, *Nano Res.*, 2024, **17**, 10083–10087.

12 Q. Ju, J. Zheng, L. Xu, H. Jiang, Z. Xue, L. Bai, Y. Guo, M. Yao and T. Zhu, Enhanced carbon capture with motif-rich amino acid loaded defective robust metal-organic frameworks, *Nano Res.*, 2023, **17**, 2004–2010.

13 E. Velasco, S. Xian, H. Wang, S. J. Teat, D. H. Olson, K. Tan, S. Ullah, T. M. Osborn Popp, A. D. Bernstein, K. A. Oyekan, A. J. Nieuwkoop, T. Thonhauser and J. Li, Flexible Zn-MOF with rare underlying scu topology for effective separation of C6 alkane isomers, *ACS Appl. Mater. Interfaces*, 2021, **13**, 51997–52005.

14 J. Wang, Y. Zhang, Y. Su, X. Liu, P. Zhang, R. B. Lin, S. Chen, Q. Deng, Z. Zeng, S. Deng and B. Chen, Fine pore engineering in a series of isoreticular metal-organic

frameworks for efficient C_2H_2/CO_2 separation, *Nat. Commun.*, 2022, **13**, 200.

15 Z. Ju, E. M. El-Sayed and D. Yuan, Dynamic metal-organic frameworks for the separation of hydrogen isotopes, *Dalton Trans.*, 2020, **49**, 16617–16622.

16 Y. Li, J. Xiao, Y. Guo, N. Han, F. Yuan, Y. Chen and M.-S. Yao, Dynamic apertures with diffusion-regulatory functionality in soft porous crystals: A key to solving the century puzzle on isotopologues separation, *Nano Res.*, 2023, **16**, 3254–3255.

17 S. Krause, V. Bon, I. Senkovska, U. Stoeck, D. Wallacher, D. M. Többens, S. Zander, R. S. Pillai, G. Maurin, F. X. Coudert and S. Kaskel, A pressure-amplifying framework material with negative gas adsorption transitions, *Nature*, 2016, **532**, 348–352.

18 N. Li, J. Pang, F. Lang and X. H. Bu, Flexible metal-organic frameworks: From local structural design to functional realization, *Acc. Chem. Res.*, 2024, **57**, 2279–2292.

19 J. Li and B. Chen, Flexible hydrogen-bonded organic frameworks (HOFs): Opportunities and challenges, *Chem. Sci.*, 2024, **15**, 9874–9892.

20 X. Zhao, Y. Wang, D. S. Li, X. Bu and P. Feng, Metal-organic frameworks for separation, *Adv. Mater.*, 2018, **30**, e1705189.

21 H. Zhang, K. Zhao, W. Guo, K. Liang, J. Li, X. Li, Q. Deng, X. Xu, H. Chao, H. Xi and C. Duan, Room-temperature rapid synthesis of hierarchically porous ZIF-93 for effective adsorption of volatile organic compounds, *Ind. Chem. Mater.*, 2024, **3**, 109–121.

22 S. B. Peh, A. Karmakar and D. Zhao, Multiscale design of flexible metal-organic frameworks, *Trends Chem.*, 2020, **2**, 199–213.

23 Z. Liu, L. Zhang and D. Sun, Stimuli-responsive structural changes in metal-organic frameworks, *Chem. Commun.*, 2020, **56**, 9416–9432.

24 F. Bigdeli, C. T. Lollar, A. Morsali and H. C. Zhou, Switching in metal-organic frameworks, *Angew. Chem., Int. Ed.*, 2020, **59**, 4652–4669.

25 L. E. Kreno, K. Leong, O. K. Farha, M. Allendorf, R. P. Van Duyne and J. T. Hupp, Metal-organic framework materials as chemical sensors, *Chem. Rev.*, 2012, **112**, 1105–1125.

26 X. Wang, H. Wang, J. Zhang, N. Han, W. Ma, D. Zhang, M. Yao, X. Wang and Y. Chen, Peroxidase-like active Cu-ZIF-8 with rich copper(I)-nitrogen sites for excellent antibacterial performances toward drug-resistant bacteria, *Nano Res.*, 2024, **17**, 7427–7435.

27 Y. He, Z. Wang, H. Wang, Z. Wang, G. Zeng, P. Xu, D. Huang, M. Chen, B. Song, H. Qin and Y. Zhao, Metal-organic framework-derived nanomaterials in environment related fields: Fundamentals, properties and applications, *Coord. Chem. Rev.*, 2021, **429**, 213618.

28 L. Zou, C. C. Hou, Z. Liu, H. Pang and Q. Xu, Superlong single-crystal metal-organic framework nanotubes, *J. Am. Chem. Soc.*, 2018, **140**, 15393–15401.

29 W. Yao, C. Hu, Y. Zhang, H. Li, F. Wang, K. Shen, L. Chen and Y. Li, Hierarchically ordered porous carbon with

atomically dispersed cobalt for oxidative esterification of furfural, *Ind. Chem. Mater.*, 2023, **1**, 106–116.

30 Z. Yu, L. Tang, N. Ma, S. Horike and W. Chen, Recent progress of amorphous and glassy coordination polymers, *Coord. Chem. Rev.*, 2022, **469**, 214646.

31 Y. Wang, H. Jin, Q. Ma, K. Mo, H. Mao, A. Feldhoff, X. Cao, Y. Li, F. Pan and Z. Jiang, A MOF glass membrane for gas separation, *Angew. Chem., Int. Ed.*, 2020, **59**, 4365–4369.

32 Y. Zhong, P. Liao, J. Kang, Q. Liu, S. Wang, S. Li, X. Liu and G. Li, Locking effect in metal@MOF with superior stability for highly chemoselective catalysis, *J. Am. Chem. Soc.*, 2023, **145**, 4659–4666.

33 Z. Yan, X. Liu, B. Ding, J. Yu and Y. Si, Interfacial engineered superelastic metal-organic framework aerogels with van-der-Waals barrier channels for nerve agents decomposition, *Nat. Commun.*, 2023, **14**, 2116.

34 S. Horike, S. S. Nagarkar, T. Ogawa and S. Kitagawa, A new dimension for coordination polymers and metal-organic frameworks: Towards functional glasses and liquids, *Angew. Chem., Int. Ed.*, 2020, **59**, 6652–6664.

35 M. Kondo, T. Yoshitomi, K. Seki, H. Matsuzaka and S. Kitagawa, Three-dimensional framework with channeling cavities for small molecules: $\{M_2(4,4'\text{-bpy})_3(NO_3)_4 \cdot xH_2O\}_n$ (M = Co, Ni, Zn), *Angew. Chem., Int. Ed. Engl.*, 1997, **36**, 1725–1727.

36 H. Sakamoto, K.-i. Otake and S. Kitagawa, Progressive gas adsorption squeezing through the narrow channel of a soft porous crystal of $[Co_2(4,4'\text{-bipyridine})_3(NO_3)_4]$, *Commun. Mater.*, 2024, **5**, 171.

37 B. Zhang, H. Chen, Q. Hu, L. Jiang, Y. Shen, D. Zhao and Z. Zhou, CelluMOFs: Green, facile, and flexible metal-organic frameworks for versatile applications, *Adv. Funct. Mater.*, 2021, **31**, 2105395.

38 S. Yuan, L. Feng, K. Wang, J. Pang, M. Bosch, C. Lollar, Y. Sun, J. Qin, X. Yang, P. Zhang, Q. Wang, L. Zou, Y. Zhang, L. Zhang, Y. Fang, J. Li and H. C. Zhou, Stable metal-organic frameworks: Design, synthesis, and applications, *Adv. Mater.*, 2018, **30**, 1704303.

39 W. L. Teo, W. Zhou, C. Qian and Y. Zhao, Industrializing metal-organic frameworks: Scalable synthetic means and their transformation into functional materials, *Mater. Today*, 2021, **47**, 170–186.

40 Q. M. Sun, J. H. He and J. M. Lu, Recent advances and potential applications of flexible adsorption and separation materials: A review, *Energy Sci. Eng.*, 2022, **11**, 952–973.

41 Y. Su, K. I. Otake, J. J. Zheng, S. Horike, S. Kitagawa and C. Gu, Separating water isotopologues using diffusion-regulatory porous materials, *Nature*, 2022, **611**, 289–294.

42 L. Bondorf, J. L. Fiorio, V. Bon, L. D. Zhang, M. Maliuta, S. Ehrling, I. Senkovska, J. D. Evans, J. O. Joswig, S. Kaskel, T. Heine and M. Hirscher, Isotope-selective pore opening in a flexible metal-organic framework, *Sci. Adv.*, 2022, **8**, eabn7035.

43 D.-W. Lim, J. Ha, Y. Oruganti and H. R. Moon, Hydrogen separation and purification with MOF-based materials, *Mater. Chem. Front.*, 2021, **5**, 4022–4041.

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Ind. Chem. Mater., 2025, **3**, 651–680 | **675**

44 J. Park, A. Adhikary and H. R. Moon, Progress in the development of flexible metal-organic frameworks for hydrogen storage and selective separation of its isotopes, *Coord. Chem. Rev.*, 2023, **497**, 215402.

45 A. Halder, R. A. Klein, S. Shulda, G. A. McCarver, P. A. Parilla, H. Furukawa, C. M. Brown and C. M. McGuirk, Multivariate flexible framework with high usable hydrogen capacity in a reduced pressure swing process, *J. Am. Chem. Soc.*, 2023, **145**, 8033–8042.

46 H. Song, Y. Peng, C. Wang, L. Shu, C. Zhu, Y. Wang, H. He and W. Yang, Structure regulation of mof nanosheet membrane for accurate H_2/CO_2 separation, *Angew. Chem., Int. Ed.*, 2023, **62**, e202218472.

47 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 and G. K. H. Shimizu, A scalable metal-organic framework as a durable physisorbent for carbon dioxide capture, *Science*, 2021, **374**, 1464–1469.

48 R. Oktavian, R. Goeminne, L. T. Glasby, P. Song, R. Huynh, O. T. Qazvini, O. Ghaffari-Nik, N. Masoumifard, J. L. Cordiner, P. Hovington, V. Van Speybroeck and P. Z. Moghadam, Gas adsorption and framework flexibility of CALF-20 explored via experiments and simulations, *Nat. Commun.*, 2024, **15**, 3898.

49 Y. Yan, D. I. Kolokolov, I. da Silva, A. G. Stepanov, A. J. Blake, A. Dailly, P. Manuel, C. C. Tang, S. Yang and M. Schroder, Porous metal-organic polyhedral frameworks with optimal molecular dynamics and pore geometry for methane storage, *J. Am. Chem. Soc.*, 2017, **139**, 13349–13360.

50 T. Kundu, M. Wahiduzzaman, B. B. Shah, G. Maurin and D. Zhao, Solvent-induced control over breathing behavior in flexible metal-organic frameworks for natural-gas delivery, *Angew. Chem., Int. Ed.*, 2019, **58**, 8073–8077.

51 H.-Y. Jiang, Z.-M. Wang, X.-Q. Sun, S.-J. Zeng, Y.-Y. Guo, L. Bai, M.-S. Yao and X.-P. Zhang, Advanced materials for NH_3 capture: Interaction sites and transport pathways, *Nano-Micro Lett.*, 2024, **16**, 228.

52 H. Jiang, L. Xu, K. Peng, X. Zhang, S. Zeng, Y. Guo, L. Bai, M.-S. Yao and X. Zhang, Confined dual functionalized ionic liquids in metal-organic frameworks for selective NH_3 adsorption, *Chem. Eng. J.*, 2024, **497**, 154543.

53 Y. Chen, B. Shan, C. Yang, J. Yang, J. Li and B. Mu, Environmentally friendly synthesis of flexible MOFs $M(NA)_2(M = Zn, Co, Cu, Cd)$ with large and regenerable ammonia capacity, *J. Mater. Chem. A*, 2018, **6**, 9922–9929.

54 Y. Zhang, L. Wang, W. Sun, Y. Hu and H. Tang, Membrane technologies for Li^+/Mg^{2+} separation from salt-lake brines and seawater: A comprehensive review, *J. Ind. Eng. Chem.*, 2020, **81**, 7–23.

55 Y. Lu, R. Zhou, N. Wang, Y. Yang, Z. Zheng, M. Zhang, Q. F. An and J. Yuan, Engineer nanoscale defects into selective channels: MOF-enhanced Li^+ separation by porous layered double hydroxide membrane, *Nano-Micro Lett.*, 2023, **15**, 147.

56 R. Xu, Y. Kang, W. Zhang, X. Zhang and B. Pan, Oriented UiO-67 metal-organic framework membrane with fast and selective lithium-ion transport, *Angew. Chem., Int. Ed.*, 2022, **61**, e202115443.

57 M. Abdollahzadeh, M. Chai, E. Hosseini, M. Zakertabrizi, M. Mohammad, H. Ahmadi, J. Hou, S. Lim, A. Habibnejad Korayem, V. Chen, M. Asadnia and A. Razmjou, Designing angstrom-scale asymmetric MOF-on-MOF cavities for high monovalent ion selectivity, *Adv. Mater.*, 2022, **34**, e2107878.

58 M. Bonneau, C. Lavenn, J. J. Zheng, A. Legrand, T. Ogawa, K. Sugimoto, F. X. Coudert, R. Reau, S. Sakaki, K. I. Otake and S. Kitagawa, Tunable acetylene sorption by flexible catenated metal-organic frameworks, *Nat. Chem.*, 2022, **14**, 816–822.

59 A. X. Zhu, Q. Y. Yang, S. Mukherjee, A. Kumar, C. H. Deng, A. A. Bezrukov, M. Shivanna and M. J. Zaworotko, Tuning the gate-opening pressure in a switching pcu coordination network, X-pcu-5-Zn, by pillar-ligand substitution, *Angew. Chem., Int. Ed.*, 2019, **58**, 18212–18217.

60 J. Pang, Z. Di, J. S. Qin, S. Yuan, C. T. Lollar, J. Li, P. Zhang, M. Wu, D. Yuan, M. Hong and H. C. Zhou, Precisely embedding active sites into a mesoporous Zr-framework through linker installation for high-efficiency photocatalysis, *J. Am. Chem. Soc.*, 2020, **142**, 15020–15026.

61 L. L. Zhuo, P. Chen, K. Zheng, X. W. Zhang, J. X. Wu, D. Y. Lin, S. Y. Liu, Z. S. Wang, J. Y. Liu, D. D. Zhou and J. P. Zhang, Flexible cuprous triazolate frameworks as highly stable and efficient electrocatalysts for CO_2 reduction with tunable C_2H_4/CH_4 selectivity, *Angew. Chem., Int. Ed.*, 2022, **61**, e202204967.

62 S. Yuan, L. Zou, H. Li, Y.-P. Chen, J. Qin, Q. Zhang, W. Lu, M. B. Hall and H.-C. Zhou, Flexible zirconium metal-organic frameworks as bioinspired switchable catalysts, *Angew. Chem., Int. Ed.*, 2016, **55**, 10776–10780.

63 J. Pang, S. Yuan, D. Du, C. Lollar, L. Zhang, M. Wu, D. Yuan, H. C. Zhou and M. Hong, Flexible zirconium MOFs as bromine-nanocontainers for bromination reactions under ambient conditions, *Angew. Chem., Int. Ed.*, 2017, **56**, 14622–14626.

64 P. Wu, Y. Li, J. J. Zheng, N. Hosono, K. I. Otake, J. Wang, Y. Liu, L. Xia, M. Jiang, S. Sakaki and S. Kitagawa, Carbon dioxide capture and efficient fixation in a dynamic porous coordination polymer, *Nat. Commun.*, 2019, **10**, 4362.

65 T. Luo, H. S. Jeppesen, A. Schoekel, N. Bonisch, F. Xu, R. Zhuang, Q. Huang, I. Senkovska, V. Bon, T. Heine, A. Kuc and S. Kaskel, Photocatalytic dehalogenation of aryl halides mediated by the flexible metal-organic framework MIL-53(Cr), *Angew. Chem., Int. Ed.*, 2025, **64**, e202422776.

66 C. Li, H. Zhang, M. Liu, F.-F. Lang, J. Pang and X.-H. Bu, Recent progress in metal–organic frameworks (MOFs) for electrocatalysis, *Ind. Chem. Mater.*, 2023, **1**, 9–38.

67 A. E. Baumann, D. A. Burns, B. Liu and V. S. Thoi, Metal-organic framework functionalization and design strategies for advanced electrochemical energy storage devices, *Commun. Chem.*, 2019, **2**, 86.

68 S. Nagappan, M. Duraivel, V. Elayappan, N. Muthuchamy, B. Mohan, A. Dhakshinamoorthy, K. Prabakar, J.-M. Lee and K. H. Park, Metal-organic frameworks-based cathode materials for energy storage applications: A review, *Energy Technol.*, 2023, **11**, 2201200.

69 R. Kumar, M. Mooste, Z. Ahmed, S. Akula, I. Zekker, M. Marandi, M. Käärik, J. Leis, A. Kikas, A. Treshchalov, M. Otsus, J. Aruväli, V. Kisand, A. Tamm and K. Tammeveski, Highly active ZIF-8@CNT composite catalysts as cathode materials for anion exchange membrane fuel cells, *Ind. Chem. Mater.*, 2023, **1**, 526–541.

70 T. Zhao, H. Wu, X. Wen, J. Zhang, H. Tang, Y. Deng, S. Liao and X. Tian, Recent advances in MOFs/MOF derived nanomaterials toward high-efficiency aqueous zinc ion batteries, *Coord. Chem. Rev.*, 2022, **468**, 214642.

71 P. Dong, X. Zhang, W. Hiscox, J. Liu, J. Zamora, X. Li, M. Su, Q. Zhang, X. Guo, J. McCloy and M. K. Song, Toward high-performance metal-organic-framework-based quasi-solid-state electrolytes: Tunable structures and electrochemical properties, *Adv. Mater.*, 2023, **35**, e2211841.

72 X. Song, X. Xu and J. Liu, Application of metal/covalent organic frameworks in separators for metal-ion batteries, *ChemNanoMat*, 2023, **9**, e202300246.

73 Z. H. Li, H. Zeng, G. Zeng, C. Ru, G. Li, W. Yan, Z. Shi and S. Feng, Multivariate synergistic flexible metal-organic frameworks with superproton conductivity for direct methanol fuel cells, *Angew. Chem., Int. Ed.*, 2021, **60**, 26577–26581.

74 D. Sheberla, J. C. Bachman, J. S. Elias, C. J. Sun, Y. Shao-Horn and M. Dinca, Conductive MOF electrodes for stable supercapacitors with high areal capacitance, *Nat. Mater.*, 2017, **16**, 220–224.

75 K. Jayaramulu, M. Horn, A. Schneemann, H. Saini, A. Bakandritsos, V. Ranc, M. Petr, V. Stavila, C. Narayana, B. Scheibe, S. Kment, M. Otyepka, N. Motta, D. Dubal, R. Zboril and R. A. Fischer, Covalent graphene-MOF hybrids for high-performance asymmetric supercapacitors, *Adv. Mater.*, 2021, **33**, e2004560.

76 C. Huang, W. Sun, Y. Jin, Q. Guo, D. Mucke, X. Chu, Z. Liao, N. Chandrasekhar, X. Huang, Y. Lu, G. Chen, M. Wang, J. Liu, G. Zhang, M. Yu, H. Qi, U. Kaiser, G. Xu, X. Feng and R. Dong, A general synthesis of nanostructured conductive metal-organic frameworks from insulating MOF precursors for supercapacitors and chemiresistive sensors, *Angew. Chem., Int. Ed.*, 2024, **63**, e202313591.

77 L.-A. Cao, Y.-Q. Li, Y.-F. Huo, L. Sun, X.-Q. Li, L. Chen, X.-T. Yang, F.-L. Yuan and M.-S. Yao, Volatolomics in fritillarias and their identification by orientation controlled cMOF thin film chemiresistors, *Chin. J. Chem.*, 2024, **43**, 371–377.

78 P. Velusamy, C.-H. Su, P. Ramasamy, V. Arun, N. Rajnish, P. Raman, V. Baskaralingam, S. M. Senthil Kumar and S. C. Gopinath, Volatile organic compounds as potential biomarkers for noninvasive disease detection by nanosensors: A comprehensive review, *Crit. Rev. Anal. Chem.*, 2022, **53**, 1828–1839.

79 W. Hu, W. Wu, Y. Jian, H. Haick, G. Zhang, Y. Qian, M. Yuan and M. Yao, Volatolomics in healthcare and its advanced detection technology, *Nano Res.*, 2022, **15**, 8185–8213.

80 L. S. Xie, G. Skorupskii and M. Dinca, Electrically conductive metal-organic frameworks, *Chem. Rev.*, 2020, **120**, 8536–8580.

81 Y. Jian, W. Hu, Z. Zhao, P. Cheng, H. Haick, M. Yao and W. Wu, Gas sensors based on chemi-resistive hybrid functional nanomaterials, *Nano-Micro Lett.*, 2020, **12**, 71.

82 B. Zhong, X. Qin, H. Xu, L. Liu, L. Li, Z. Li, L. Cao, Z. Lou, J. A. Jackman, N.-J. Cho and L. Wang, Interindividual- and blood-correlated sweat phenylalanine multimodal analytical biochips for tracking exercise metabolism, *Nat. Commun.*, 2024, **15**, 624.

83 G. Ding, J. Zhao, K. Zhou, Q. Zheng, S. T. Han, X. Peng and Y. Zhou, Porous crystalline materials for memories and neuromorphic computing systems, *Chem. Soc. Rev.*, 2023, **52**, 7071–7136.

84 S. Ehrling, H. Miura, I. Senkovska and S. Kaskel, From macro- to nanoscale: Finite size effects on metal-organic framework switchability, *Trends Chem.*, 2021, **3**, 291–304.

85 S. Sakaida, K. Otsubo, O. Sakata, C. Song, A. Fujiwara, M. Takata and H. Kitagawa, Crystalline coordination framework endowed with dynamic gate-opening behaviour by being downsized to a thin film, *Nat. Chem.*, 2016, **8**, 377–383.

86 Y. Sakata, S. Furukawa, M. Kondo, K. Hirai, N. Horike, Y. Takashima, H. Uehara, N. Louvain, M. Meilikhov, T. Tsuruoka, S. Isoda, W. Kosaka, O. Sakata and S. Kitagawa, Shape-memory nanopores induced in coordination frameworks by crystal downsizing, *Science*, 2013, **339**, 193–196.

87 F. Yang, G. Xu, Y. Dou, B. Wang, H. Zhang, H. Wu, W. Zhou, J.-R. Li and B. Chen, A flexible metal–organic framework with a high density of sulfonic acid sites for proton conduction, *Nat. Energy*, 2017, **2**, 877–883.

88 M. S. Yao, K. I. Otake, T. Koganezawa, M. Ogasawara, H. Asakawa, M. Tsujimoto, Z. Q. Xue, Y. H. Li, N. C. Flanders, P. Wang, Y. F. Gu, T. Honma, S. Kawaguchi, Y. Kubota and S. Kitagawa, Growth mechanisms and anisotropic softness-dependent conductivity of orientation-controllable metal-organic framework nanofilms, *Proc. Natl. Acad. Sci. U. S. A.*, 2023, **120**, e2305125120.

89 M. S. Yao, K. I. Otake, J. Zheng, M. Tsujimoto, Y. F. Gu, L. Zheng, P. Wang, S. Mohana, M. Bonneau, T. Koganezawa, T. Honma, H. Ashitani, S. Kawaguchi, Y. Kubota and S. Kitagawa, Integrated soft porosity and electrical properties of conductive-on-insulating metal-organic framework nanocrystals, *Angew. Chem., Int. Ed.*, 2023, **62**, e202303903.

90 C. Z. Wang, J. Chen, Q. H. Li, G. E. Wang, X. L. Ye, J. Lv and G. Xu, Pore size modulation in flexible metal-organic framework enabling high performance gas sensing, *Angew. Chem., Int. Ed.*, 2023, **62**, e202302996.

91 H. Chen, Z. You, X. Wang, Q. Qiu, Y. Ying and Y. Wang, An artificial olfactory sensor based on flexible metal-organic

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Ind. Chem. Mater., 2025, **3**, 651–680 | **677**

frameworks for sensing VOCs, *Chem. Eng. J.*, 2022, **446**, 137098.

92 N. Yanai, K. Kitayama, Y. Hijikata, H. Sato, R. Matsuda, Y. Kubota, M. Takata, M. Mizuno, T. Uemura and S. Kitagawa, Gas detection by structural variations of fluorescent guest molecules in a flexible porous coordination polymer, *Nat. Mater.*, 2011, **10**, 787–793.

93 S. Wannapaiboon, A. Schneemann, I. Hante, M. Tu, K. Epp, A. L. Semrau, C. Sternemann, M. Paulus, S. J. Baxter, G. Kieslich and R. A. Fischer, Control of structural flexibility of layered-pillared metal-organic frameworks anchored at surfaces, *Nat. Commun.*, 2019, **10**, 346.

94 L. Wang, Metal-organic frameworks for QCM-based gas sensors: A review, *Sens. Actuators, A*, 2020, **307**, 111984.

95 X. Yan, X. Su, J. Chen, C. Jin and L. Chen, Two-dimensional metal-organic frameworks towards spintronics, *Angew. Chem., Int. Ed.*, 2023, **62**, e202305408.

96 R. Dong, Z. Zhang, D. C. Tranca, S. Zhou, M. Wang, P. Adler, Z. Liao, F. Liu, Y. Sun, W. Shi, Z. Zhang, E. Zschech, S. C. B. Mannsfeld, C. Felser and X. Feng, A coronene-based semiconducting two-dimensional metal-organic framework with ferromagnetic behavior, *Nat. Commun.*, 2018, **9**, 2637.

97 X. Li and J. Yang, Realizing two-dimensional magnetic semiconductors with enhanced curie temperature by antiaromatic ring based organometallic frameworks, *J. Am. Chem. Soc.*, 2019, **141**, 109–112.

98 C. Yang, R. Dong, M. Wang, P. S. Petkov, Z. Zhang, M. Wang, P. Han, M. Ballabio, S. A. Brauninger, Z. Liao, J. Zhang, F. Schwotzer, E. Zschech, H. H. Klauss, E. Canovas, S. Kaskel, M. Bonn, S. Zhou, T. Heine and X. Feng, A semiconducting layered metal-organic framework magnet, *Nat. Commun.*, 2019, **10**, 3260.

99 X. Song, X. Wang, Y. Li, C. Zheng, B. Zhang, C. A. Di, F. Li, C. Jin, W. Mi, L. Chen and W. Hu, 2D semiconducting metal-organic framework thin films for organic spin valves, *Angew. Chem., Int. Ed.*, 2020, **59**, 1118–1123.

100 X. Song, C. Jin, H. Chen, S. Ding, Z. Liu, Y. Li, X. Yan, W. Mi, L. Chen and W. Hu, Two-dimensional conductive metal-organic framework reinforced spinterface in organic spin valves, *CCS Chem.*, 2024, **6**, 208–217.

101 P. Wang, X. Jiang, J. Hu, B. Wang, T. Zhou, H. Yuan and J. Zhao, Robust spin manipulation in 2D organometallic Kagome lattices: A first-principles study, *Phys. Chem. Chem. Phys.*, 2020, **22**, 11045–11052.

102 Z. Shan, J. Z. Xiao, M. Wu, J. Wang, J. Su, M. S. Yao, M. Lu, R. Wang and G. Zhang, Topologically tunable conjugated metal-organic frameworks for modulating conductivity and chemiresistive properties for NH_3 sensing, *Angew. Chem., Int. Ed.*, 2024, **63**, e202401679.

103 L. Y. Zhan, Y. Zhou, N. Li, L. J. Zhang, X. J. Xi, Z. Q. Yao, J. P. Zhao and X. H. Bu, A high working temperature multiferroic induced by inverse temperature symmetry breaking, *J. Am. Chem. Soc.*, 2024, **146**, 5414–5422.

104 Y. Liu, H. Wang, W. Shi, W. Zhang, J. Yu, B. K. Chandran, C. Cui, B. Zhu, Z. Liu, B. Li, C. Xu, Z. Xu, S. Li, W. Huang, F. Huo and X. Chen, Alcohol-mediated resistance-switching behavior in metal-organic framework-based electronic devices, *Angew. Chem., Int. Ed.*, 2016, **55**, 8884–8888.

105 L. Pan, Z. Ji, X. Yi, X. Zhu, X. Chen, J. Shang, G. Liu and R. W. Li, Metal-organic framework nanofilm for mechanically flexible information storage applications, *Adv. Funct. Mater.*, 2015, **25**, 2677–2685.

106 G. Ding, Y. Wang, G. Zhang, K. Zhou, K. Zeng, Z. Li, Y. Zhou, C. Zhang, X. Chen and S. T. Han, 2D metal-organic framework nanosheets with time-dependent and multilevel memristive switching, *Adv. Funct. Mater.*, 2018, **29**, 1806637.

107 C. K. Liu, V. Piradi, J. Song, Z. Wang, L. W. Wong, E. H. Tan, J. Zhao, X. Zhu and F. Yan, 2D metal-organic framework $Cu_3(HHTT)_2$ films for broadband photodetectors from ultraviolet to mid-infrared, *Adv. Mater.*, 2022, **34**, e2204140.

108 J.-S. M. Lee, K.-i. Otake and S. Kitagawa, Transport properties in porous coordination polymers, *Coord. Chem. Rev.*, 2020, **421**, 213447.

109 M.-S. Yao, K.-i. Otake and S. Kitagawa, Interface chemistry of conductive crystalline porous thin films, *Trends Chem.*, 2023, **5**, 588–604.

110 A. Wang, M. Walden, R. Ettlinger, F. Kiessling, J. J. Gassensmith, T. Lammers, S. Wuttke and Q. Peña, Biomedical metal-organic framework materials: Perspectives and challenges, *Adv. Funct. Mater.*, 2024, **34**, 2308589.

111 X. Qin, B. Zhong, S. Lv, X. Long, H. Xu, L. Li, K. Xu, Z. Lou, Q. Luo and L. Wang, A zero-voltage-writing artificial nervous system based on biosensor integrated on ferroelectric tunnel junction, *Adv. Mater.*, 2024, **36**, 2404026.

112 P. Horcajada, T. Chalati, C. Serre, B. Gillet, C. Sebrie, T. Baati, J. F. Eubank, D. Heurtaux, P. Clayette, C. Kreuz, J. S. Chang, Y. K. Hwang, V. Marsaud, P. N. Bories, L. Cynober, S. Gil, G. Ferey, P. Couvreur and R. Gref, Porous metal-organic-framework nanoscale carriers as a potential platform for drug delivery and imaging, *Nat. Mater.*, 2010, **9**, 172–178.

113 P. Horcajada, C. Serre, G. Maurin, N. A. Ramsahye, F. Balas, M. Vallet-Regi, M. Sebban, F. Taulelle and G. Ferey, Flexible porous metal-organic frameworks for a controlled drug delivery, *J. Am. Chem. Soc.*, 2008, **130**, 6774–6780.

114 X. G. Wang, L. Xu, M. J. Li and X. Z. Zhang, Construction of flexible-on-rigid hybrid-phase metal-organic frameworks for controllable multi-drug delivery, *Angew. Chem., Int. Ed.*, 2020, **59**, 18078–18086.

115 T. Kitao, Y. Zhang, S. Kitagawa, B. Wang and T. Uemura, Hybridization of MOFs and polymers, *Chem. Soc. Rev.*, 2017, **46**, 3108–3133.

116 B. Liu, X. Chen, N. Huang, S. Liu, Y. Wang, X. Lan, F. Wei and T. Wang, Imaging the dynamic influence of functional groups on metal-organic frameworks, *Nat. Commun.*, 2023, **14**, 4835.

117 Z. Zhong, Y. Huang and W. Yang, Toward a low-cost uranium-adsorbing material based on nonwoven fabrics

and photografting technology, *Ind. Chem. Mater.*, 2025, **3**, 57–68.

118 Y. Xie, Z. Liu, Y. Geng, H. Li, N. Wang, Y. Song, X. Wang, J. Chen, J. Wang, S. Ma and G. Ye, Uranium extraction from seawater: Material design, emerging technologies and marine engineering, *Chem. Soc. Rev.*, 2023, **52**, 97–162.

119 L. Li, W. Ma, S. Shen, H. Huang, Y. Bai and H. Liu, A combined experimental and theoretical study on the extraction of uranium by amino-derived metal-organic frameworks through post-synthetic strategy, *ACS Appl. Mater. Interfaces*, 2016, **8**, 31032–31041.

120 B. Zhao, L. Yuan, Y. Wang, T. Duan and W. Shi, Carboxylated UiO-66 tailored for U(VI) and Eu(III) trapping: From batch adsorption to dynamic column separation, *ACS Appl. Mater. Interfaces*, 2021, **13**, 16300–16308.

121 D. Mei, L. Liu and B. Yan, Adsorption of uranium (VI) by metal-organic frameworks and covalent-organic frameworks from water, *Coord. Chem. Rev.*, 2023, **475**, 214917.

122 S. E. Gilson, M. Fairley, S. L. Hanna, J. E. S. Szymanowski, P. Julien, Z. Chen, O. K. Farha, J. A. LaVerne and P. C. Burns, Unusual metal-organic framework topology and radiation resistance through neptunyl coordination chemistry, *J. Am. Chem. Soc.*, 2021, **143**, 17354–17359.

123 S. E. Gilson, M. Fairley, P. Julien, A. G. Oliver, S. L. Hanna, G. Arntz, O. K. Farha, J. A. LaVerne and P. C. Burns, Unprecedented radiation resistant thorium-binaphthol metal-organic framework, *J. Am. Chem. Soc.*, 2020, **142**, 13299–13304.

124 L. Chen, Z. Bai, L. Zhu, L. Zhang, Y. Cai, Y. Li, W. Liu, Y. Wang, L. Chen, J. Diwu, J. Wang, Z. Chai and S. Wang, Ultrafast and efficient extraction of uranium from seawater using an amidoxime appended metal-organic framework, *ACS Appl. Mater. Interfaces*, 2017, **9**, 32446–32451.

125 D. Mei, L. Liu, H. Li, Y. Wang, F. Ma, C. Zhang and H. Dong, Efficient uranium adsorbent with antimicrobial function constructed by grafting amidoxime groups on ZIF-90 via malononitrile intermediate, *J. Hazard. Mater.*, 2022, **422**, 126872.

126 G. Zhang, Y. Fang, Y. Wang, L. Liu, D. Mei, F. Ma, Y. Meng, H. Dong and C. Zhang, Synthesis of amino acid modified MIL-101 and efficient uranium adsorption from water, *J. Mol. Liq.*, 2022, **349**, 118095.

127 Z. H. Zhang, J. H. Lan, L. Y. Yuan, P. P. Sheng, M. Y. He, L. R. Zheng, Q. Chen, Z. F. Chai, J. K. Gibson and W. Q. Shi, Rational construction of porous metal-organic frameworks for uranium(VI) extraction: The strong periodic tendency with a metal node, *ACS Appl. Mater. Interfaces*, 2020, **12**, 14087–14094.

128 S. M. Sheta, M. A. Hamouda, O. I. Ali, A. T. Kandil, R. R. Sheha and S. M. El-Sheikh, Recent progress in high-performance environmental impacts of the removal of radionuclides from wastewater based on metal-organic frameworks: A review, *RSC Adv.*, 2023, **13**, 25182–25208.

129 J. Liu, X. Wang, Y. Zhao, Y. Xu, Y. Pan, S. Feng, J. Liu, X. Huang and H. Wang, NH_3 plasma functionalization of UiO-66-NH_2 for highly enhanced selective fluorescence detection of U(VI) in water, *Anal. Chem.*, 2022, **94**, 10091–10100.

130 X. Cao, Y. Sun, Y. Wang, Z. Zhang, Y. Dai, Y. Liu, Y. Wang and Y. Liu, PtRu bimetallic nanoparticles embedded in MOF-derived porous carbons for efficiently electrochemical sensing of uranium, *J. Solid State Electrochem.*, 2020, **25**, 425–433.

131 H. Liu, T. Fu and Y. Mao, Metal-organic framework-based materials for adsorption and detection of uranium(VI) from aqueous solution, *ACS Omega*, 2022, **7**, 14430–14456.

132 H.-B. Peng, H.-R. Nan, S.-Q. Li, Y.-Q. Wang, Z.-M. Dong, Z.-B. Zhang, X.-H. Cao and Y.-H. Liu, Covalently construction of C-GSH-AuNCs@UiO-66-NH_2 composites as an efficient turn-on fluorescence sensor for UO_2^{2+}, *J. Solid State Chem.*, 2024, **334**, 124650.

133 V. Bon, N. Kavoosi, I. Senkovska and S. Kaskel, Tolerance of flexible MOFs toward repeated adsorption stress, *ACS Appl. Mater. Interfaces*, 2015, **7**, 22292–22300.

134 S. Ghojavand, E. Dib and S. Mintova, Flexibility in zeolites: Origin, limits, and evaluation, *Chem. Sci.*, 2023, **14**, 12430–12446.

135 Frameworks for commercial success, *Nat. Chem.*, 2016, **8**, 987–987.

136 H. Liu, Q. Yang, N. Luan, L. Chen, S. Zhang, X. Dai, A. Jin, T. Wang, J. Shu, N. Shen, J. Xu, J. Li, H. He, Z. Xu, G. Zhang, C. Gu, H. Yang, J. Chai, L. Mao, S. Guo, K. Liu, P. Lin, X. Liu, X. Ouyang, Y. Pan, X. Zhang, Z. Chai and S. Wang, Catalytic proton exchange in water distillation for efficient tritiated water clean-up, *Nat. Sustain.*, 2025, **8**, 553–561.

137 Metal-organic framework global market report 2025–by product type (zinc-based, copper-based, iron-based, aluminum-based, magnesium-based, and other types), by application (gas storage, gas and liquid adsorption, catalysis, drug delivery, other applications)–market size, trends, and global forecast 2025–2034, **https://www.thebusinessresearchcompany.com/report/metal-organic-framework-global-market-report**.

138 Metal organic framework market-by product, by synthetic method, by application, by region-global forecast, 2025–2034, **https://www.gminsights.com/industry-analysis/metal-organic-frameworks-market**.

139 A market for metal-organic frameworks, *Nat. Mater.*, 2025, **24**, 157.

140 D. Chakraborty, A. Yurdusen, G. Mouchaham, F. Nouar and C. Serre, Large-scale production of metal-organic frameworks, *Adv. Funct. Mater.*, 2023, **34**, 216919.

141 M. Kalaj, K. C. Bentz, S. Ayala Jr, J. M. Palomba, K. S. Barcus, Y. Katayama and S. M. Cohen, MOF-polymer hybrid materials: From simple composites to tailored architectures, *Chem. Rev.*, 2020, **120**, 8267–8302.

142 X. L. Liu, Y. S. Li, G. Q. Zhu, Y. J. Ban, L. Y. Xu and W. S. Yang, An organophilic pervaporation membrane derived from metal-organic framework nanoparticles for efficient recovery of bio-alcohols, *Angew. Chem., Int. Ed.*, 2011, **50**, 10636–10639.

143 T. Kundu, B. B. Shah, L. Bolinois and D. Zhao, Functionalization-induced breathing control in metal-organic frameworks for methane storage with high deliverable capacity, *Chem. Mater.*, 2019, **31**, 2842–2847.

144 M. Kriesten, J. Vargas Schmitz, J. Siegel, C. E. Smith, M. Kaspereit and M. Hartmann, Shaping of flexible metal-organic frameworks: Combining macroscopic stability and framework flexibility, *Eur. J. Inorg. Chem.*, 2019, **43**, 4700–4709.

145 S. Krause, N. Hosono and S. Kitagawa, Chemistry of soft porous crystals: Structural dynamics and gas adsorption properties, *Angew. Chem., Int. Ed.*, 2020, **59**, 15325–15341.

146 N. H. Kwon, S. Han, J. Kim and E. S. Cho, Super proton conductivity through control of hydrogen-bonding networks in flexible metal-organic frameworks, *Small*, 2023, **19**, e2301122.

147 T. Zhang, S. Chen, P. S. Petkov, P. Zhang, H. Qi, N. N. Nguyen, W. Zhang, J. Yoon, P. Li, T. Brumme, A. Alfonsov, Z. Liao, M. Hambsch, S. Xu, L. Mester, V. Kataev, B. Buchner, S. C. B. Mannsfeld, E. Zschech, S. S. P. Parkin, U. Kaiser, T. Heine, R. Dong, R. Hillenbrand and X. Feng, Two-dimensional polyaniline crystal with metallic out-of-plane conductivity, *Nature*, 2025, **638**, 411–417.

148 N. Hosono and S. Kitagawa, Direct observation of porous coordination polymer surfaces by atomic force microscopy, *Jpn. J. Appl. Phys.*, 2022, **61**, SL0802.

149 N. Hosono, A. Terashima, S. Kusaka, R. Matsuda and S. Kitagawa, Highly responsive nature of porous coordination polymer surfaces imaged by in situ atomic force microscopy, *Nat. Chem.*, 2019, **11**, 109–116.

150 V. Bon, E. Brunner, A. Pöppl and S. Kaskel, Unraveling structure and dynamics in porous frameworks via advanced in situ characterization techniques, *Adv. Funct. Mater.*, 2020, **30**, 1907847.

151 L. R. Parent, C. H. Pham, J. P. Patterson, M. S. Denny, Jr., S. M. Cohen, N. C. Gianneschi and F. Paesani, Pore breathing of metal-organic frameworks by environmental transmission electron microscopy, *J. Am. Chem. Soc.*, 2017, **139**, 13973–13976.

152 Y. Fu, A. C. Forse, Z. Kang, M. J. Cliffe, W. Cao, J. Yin, L. Gao, Z. Pang, T. He, Q. Chen, Q. Wang, J. R. Long, J. A. Reimer and X. Kong, One-dimensional alignment of defects in a flexible metal-organic framework, *Sci. Adv.*, 2023, **9**, eade6975.

153 F. Salles, A. Ghoufi, G. Maurin, R. G. Bell, C. Mellot-Draznieks and G. Ferey, Molecular dynamics simulations of breathing MOFs: Structural transformations of MIL-53(Cr) upon thermal activation and CO_2 adsorption, *Angew. Chem., Int. Ed.*, 2008, **47**, 8487–8491.

154 A. K. Cheetham, G. Kieslich and H. H. Yeung, Thermodynamic and kinetic effects in the crystallization of metal-organic frameworks, *Acc. Chem. Res.*, 2018, **51**, 659–667.

155 S. Kitagawa, *Flexible metal-organic frameworks: Structural design, synthesis and properties*, Royal Society of Chemistry, 2024.

156 J. D. Evans and F.-X. Coudert, Challenges and opportunities of molecular simulations for negative gas adsorption, *Acc. Mater. Res.*, 2024, **5**, 640–647.