

Adaptive metal–organic frameworks with crystalline dynamicity for durable gas separation

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Dynamic chemistry offers opportunities for the design of smart materials that can self adapt or self repair to mediate their functionality. However, achieving anti-crack toughness using dynamic covalent bonds is often overlooked in crystalline porous solids such as metal–organic frameworks. Here we propose that crystalline dynamicity can be derived from bio-inspired disulfide metathesis, as demonstrated by a dynamic combinatorial library of isomeric metal–organic frameworks (LIFM-105, LIFM-105i, and LIFM-105a). Sulfur–sulfur bond breakage and regeneration facilitate stimuli-responsive interconversion between two-dimensional and three-dimensional frameworks, involving simultaneous layer rotation, component shift and linkage reorganization. The disulfide exchange-based crystal dynamics provides these porous solids with gas-induced adaptiveness and the gate effect, enabling pore tuning for efficient removal of C_2H_2 from C_2H_4 . Additionally, the guest-adaptation-motivated restoration and reorganization of the ‘damaged’ frameworks afford a promising protocol to apply radical-mediated dynamic solids as adaptive porous materials for durable separation and other applications.

The separation and purification of gas mixtures with similar physicochemical properties is industrially relevant, offering high-grade raw chemicals for the production of various commodities. Typically, these processes are realized through distillation and solvent extraction technologies¹, which account for substantial industrial energy consumption. Therefore, it is necessary to pursue energy- and cost-efficient alternatives, and enormous efforts have been made to develop new separation methods. Non-thermal-driven adsorptive separation technologies using porous solid materials, such as customizable metal–organic frameworks (MOFs), offer a promising solution for discriminating

similar gas mixtures like acetylene and ethylene (C_2H_2/C_2H_4) due to their tunable pore structures and functionalities^{2–4}.

As MOFs are crystalline solids prone to fragility during repeated adsorption–desorption processes, circumvention of their mechanical vulnerability for prolonged usage without performance deterioration remains a challenge⁵. Much effort has been made to enhance their chemical and thermal stability⁶, but the mechanical anti-crack robustness against structural damage for long-term application has been largely overlooked. Flexible and dynamic MOFs that can undergo structural changes in response or adaptation to gas adsorption and

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desorption stimuli have drawn intense attention^{4,7,8}. They either show flexibility via bond or angle variations while maintaining the connectivity with a breathing or swelling effect (gate effect) for improved gas separation^{9–11} or exhibit flexibility via bond breaking and reforming for pore optimization to reinforce gas selectivity^{8,12,13}. However, little progress has been made in designing guest-adaptive MOFs with autonomous bond regeneration and exchange to in situ restore or reshuffle frameworks for the sake of anti-fatigue performance.

The progress of dynamic covalent chemistry^{14–20} has deepened our understanding of the physical world by leveraging dynamic and reversible nature of chemical bonds, enabling the precise construction of more advanced and smart materials featuring adaptable, restorable or self-healing characteristics^{20–22}. In nature, S–S bonds are crucial for the structural stability and chemical activity of disulfide-containing proteins²³. The structural units impart stability to the resident proteins to prolong the service time, whereas the redox-active units bestow dynamic activity on the proteins to benefit adaptive regulation of the structure for selective recognition of substrates, which is pivotal to many specific and effective functions^{24,25}. Thiyl radicals, known for their ease of formation, viable reactivity and good reversibility, are widely utilized in various biological processes^{26,27}. Inspired by these natural systems, biomimetic studies have emerged to design various intelligent materials^{28,29}, albeit mainly focusing on soft materials of low crystallinity^{30,31}. We envisage that the dynamic covalent S–S bonds with reversible breakage and recombination properties in response to external stimuli may act in a dual role to introduce toughness and adaptiveness into crystalline porous solids^{28,32,33}, thereby generating disulfide-based MOF crystals combining robusticity, dynamicity and flexibility to achieve durability against crystal brittleness and self-adaptive capacity for selective gas separation^{19,34–36}.

Here, we report a radical-mediated dynamic remedial strategy, based on bio-inspired disulfide metathesis¹⁵, for designing adaptive MOFs with crystalline dynamicity. Three isomeric MOFs of $[\text{Zn}(\text{dpds})_2](\text{SiF}_6)_2$, namely LIFM-105, LIFM-105i, and LIFM-105a, have been identified to form a dynamic combinatorial library undergoing guest-driven structural transformations (Fig. 1). We note that the conversion of three isomers occurs in the solid state by S–S exchange, accompanied by bond breakage, layer rotation, component shift and linkage reorganization. This is confirmed by in situ electron paramagnetic resonance (EPR), in situ single-crystal X-ray diffraction (SCXRD), in situ powder X-ray diffraction (PXRD) and in situ variable temperature Raman (VT-Raman), as well as theoretical calculations. This adaptive MOF system displays selective absorption of C_2H_2 over C_2H_4 , where LIFM-105 is the guest-favoured state (T_{guest}), while LIFM-105a is preferred as the guest-free state (T_{free}). The interconversion between them takes place with ease through in situ disulfide exchange during recycling processes without collapse of the crystalline porosity. This enables efficient and prolonged usage of $\text{C}_2\text{H}_2/\text{C}_2\text{H}_4$ separation, which is confirmed by the multiple transient breakthrough experiments in combination with consecutive C_2H_2 adsorption–desorption experiments. These results suggest the potential of disulfide metathesis to restore or reorganize the ‘damaged’ framework during repeated back-and-forth adsorption–desorption, endowing the soft MOFs with robust porosity for durable gas-adaptive separation. The adsorption mechanism has been elucidated by in situ SCXRD, in situ infrared (IR) and theoretical calculations.

Results and discussion

Synthesis and crystal structures

The reaction of the 4,4′-dipyridyl disulfide (dpds) ligand with $\text{ZnSiF}_6 \cdot x\text{H}_2\text{O}$ in methanol at room temperature produced colourless crystals of LIFM-105 ($[\text{Zn}(\text{dpds})_2](\text{SiF}_6)_2 \cdot 3\text{MeOH}$; Fig. 1), which crystallizes in the $C2/c$ space group and features a three-dimensional (3D) porous framework of *cds* topology (Fig. 2a–d, see details in Supplementary Figs. 1–88 and Supplementary Tables 1–4). The framework is constructed with the looped chains composed of $\text{Zn}_2(\text{dpds})_2$ rings, which

are interconnected by the pillared SiF_6^{2-} anions. The one-dimensional (1D) looped chains are staggered in a plane, while they are rotated by an angle of 68.06° between adjacent layers (Supplementary Fig. 7). The zig-zag channels are formed across the $\text{Zn}_2(\text{dpds})_2$ cavities with a necked aperture of approximately $2.1 \times 3.8 \text{ \AA}^2$ (considering the van der Waals (vdW) radii of the atoms, Fig. 2b,i). We note that LIFM-105, accommodating methanol guests (T_{guest} state), can transform into intermediate LIFM-105i (T_{int} state) and then empty LIFM-105a (T_{free} state) via a potential transient LIFM-105ii (T_{trans} state), by heating crystals under N_2 gas blowing for different times to partially or completely remove methanol molecules, and can be restored to LIFM-105 by soaking in methanol (Fig. 1 and Supplementary Figs. 24–26). SCXRD analyses show that LIFM-105i keeps the same *cds* topology, whereas LIFM-105a changes to a two-dimensional (2D) *sql* network (Fig. 2e–h). Compared with the prototypical LIFM-105 (*proto*-LIFM-105), LIFM-105i can be formed through slight layer rotation by 6.69° . However, conversion into LIFM-105a seems to necessitate a dramatic back rotation of 68.06° , which is hard to achieve in the solid state. Instead, structural transformation between LIFM-105 and LIFM-105a can be easily realized through local S–S bond cleavage and rearrangement (Fig. 1). LIFM-105i presents similar zig-zag channels to LIFM-105, while LIFM-105a features linear gourd-shaped channels with an aperture of $2.6 \times 3.3 \text{ \AA}^2$ (Fig. 2f,i). The structural comparison of three isomeric MOFs suggests that their porosity and flexibility are influenced by the orientations of pyridyl rings in the $\text{Zn}_2(\text{dpds})_2$ loops and their rotations contribute a gate effect to gas separation performance. Evidence for this is provided by in situ SCXRD analysis of the C_2H_2 -loaded LIFM-105· C_2H_2 crystal that shows pore deformation upon C_2H_2 adsorption (Fig. 2c, see details in Supplementary Figs. 11, 16, 17, 20, 23, 68 and 74).

Radical-mediated solid-state dynamics

To track the reversible 3D–2D framework transitions between LIFM-105 and LIFM-105a, in situ variable temperature powder X-ray diffraction (VT-PXRD) patterns were recorded and compared with those of pristine MOFs (Fig. 3a). A phase change of LIFM-105 occurred above 40°C and this evolved to a new LIFM-105a structure at 60°C , which was maintained up to 160°C . A more detailed transformation process was observed using time-dependent in situ PXRD experiments under N_2 blowing at 35°C (Fig. 3b). A transient phase appeared and this gradually transformed into LIFM-105i within 20 min, persisting for 90 min before converting into methanol-free LIFM-105a after 150 min. The whole process occurred in a single-crystal-to-single-crystal (SC-SC) fashion as seen by in situ SCXRD measurements (Fig. 3c). The single-crystal data collected at room temperature and 35°C without N_2 blowing showed that it retained the LIFM-105 structure (Supplementary Table 1), while the data collected under continuous heating and N_2 blowing at 35°C confirmed conversion into LIFM-105a via LIFM-105i. This SC-SC transformation phenomenon unambiguously showed that S–S bond exchange did occur in the solid state as demonstrated in Fig. 1, readily driven by methanol-guest removal. To understand the reshuffling behaviour of the S–S bonds in the solid state, variable-temperature electron paramagnetic resonance (VT-EPR) experiments were performed separately for the dpds ligand and LIFM-105 (Fig. 3d–f and Supplementary Fig. 28). No EPR signal was observed for the ligand alone from 25 to 120°C , whereas LIFM-105 exhibited strong EPR peaks characteristic of the ‘sulfur pattern’³⁷. This corresponds to spin–orbit coupling of the unpaired electron on the S atoms, thus confirming pyridyl-sulfanyl radical (pys·) formation via S–S bond cleavage. The in situ VT-EPR experiments further showed that the radical signal slightly increased from 20 to 50°C (Fig. 3d), suggesting ongoing disulfide metathesis for structural conversion. However, the signal gradually decreased from 50 to 120°C and left it alone afterwards, indicating prominent S–S bond reshuffling around 50°C (Fig. 3e,f).

To confirm the presence of pys· radicals in LIFM-105 at room temperature, time-dependent EPR spectra were recorded under 370 nm

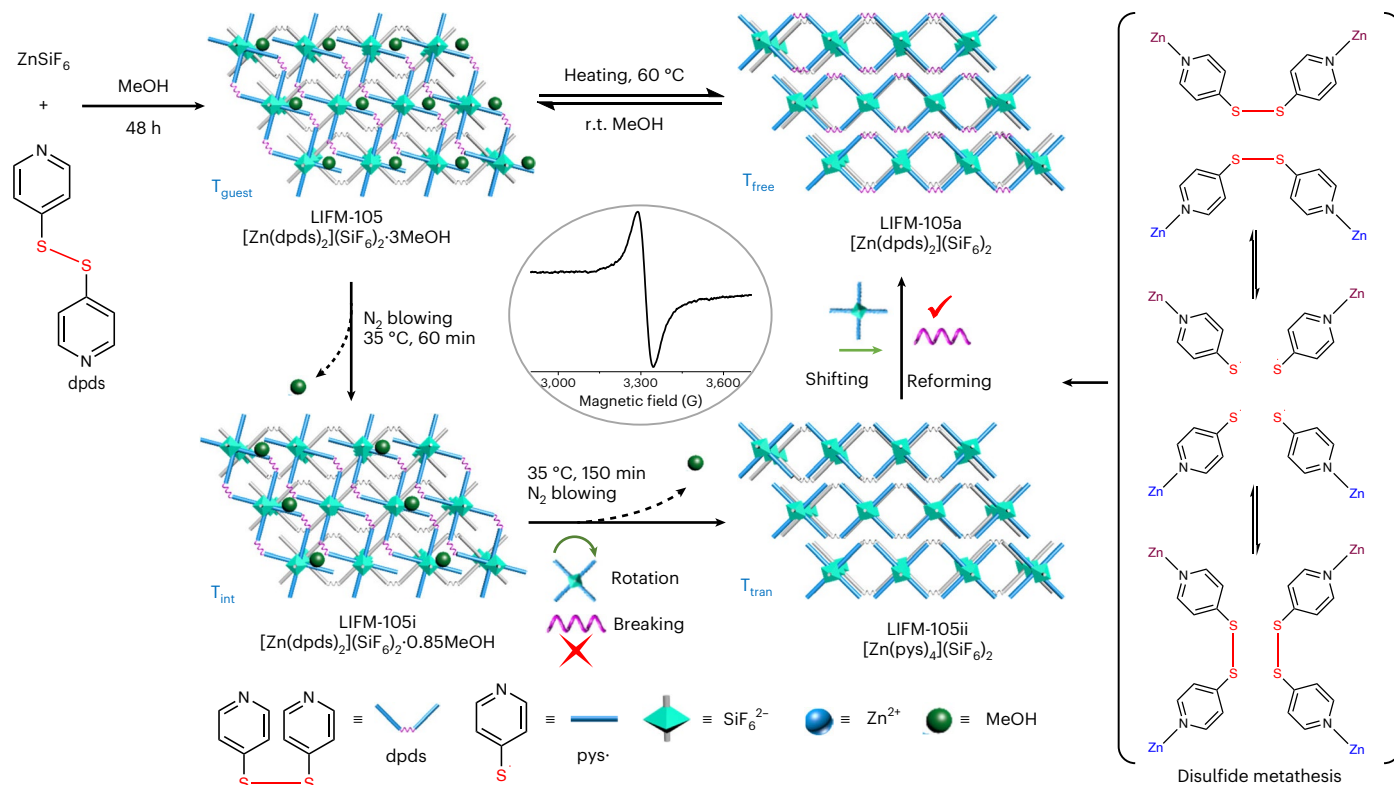


Fig. 1 | Disulfide metathesis-mediated dynamic combinatorial library of MOFs. Structural transformation from LIFM-105 (T_{guest} state) to LIFM-105i (T_{int} state) and LIFM-105a (T_{free} state) through LIFM-105ii (T_{tran} state) driven by gentle heating and guest removal, accompanied by the rotation and shift of building units and the

breaking and reforming of S-S bonds. The transient state of LIFM-105ii is shown for understanding of local S-S bond reshuffling processes. The inset picture in the centre shows a representative EPR spectrum of the pyridyl-sulfanyl radical. MeOH, methanol; r.t., room temperature.

light irradiation (Supplementary Fig. 28). As expected, the signal intensity increased with exposure time but it was gradually restored to its original state in the dark, indicating accelerated $\text{pys}\cdot$ radical formation via S-S bond cleavage under light irradiation and reformation in the dark. Moreover, PXRD analysis showed that the LIFM-105 structure remained intact under light alone at room temperature, but transformed into LIFM-105a under simultaneous light irradiation and N₂ blowing (35°C) or vacuum treatment (Supplementary Fig. 29). This suggests that S-S cleavage alone imparted minimal influence on the crystallinity, while the structural change through S-S bond reshuffling needed a driving force from methanol-guest removal, where S-S bond cleavage and reorganization was inevitable for the dramatic 3D→2D framework conversion. Furthermore, the differential scanning calorimetry (DSC) measurements confirmed the phase transition between 40 and 60°C as indicated by in situ VT-EPR and VT-PXRD (Supplementary Fig. 27). The DSC trajectory displayed a gradual endothermic curving trend from room temperature to 43°C and then an abrupt exothermic peak immediately followed by an endothermic peak before 60°C . These observations suggested that S-S bond breakage and reformation constantly happened in the solid state³⁸, where the bond breaking was sped up by heating, and a massive breaking and reforming took place in the range 40 – 60°C . The overall thermal effect should be partially counteracted by the enthalpy required for rotation/shift of building blocks and escape of methanol guests. An apparent energy of 9.13 kJ mol^{-1} was estimated to be required to surpass the transition states for structural transformation, which is indicative of a facile process assisted by radicals to start with ease³⁹. In situ VT-Raman spectra further confirmed structural transformation with noticeable variations in signal profile and intensity from 40 to 50°C , involving the characteristic S-S bond peak at $\sim 542\text{ cm}^{-1}$ (ref. 40), proving that the structural transformation accompanied by cleavage and regeneration of S-S bonds is able to

reshuffle $\text{pys}\cdot$ radical units in different conformations (Supplementary Figs. 16–19 and 30)⁴¹. These findings supported by in situ VT-PXRD, SCXRD, VT-Raman, DSC and in situ VT-EPR results, show a crystalline dynamicity mediated by disulfide metathesis, enabling the 3D→2D topological interconversion via radical-based rearrangement that is otherwise unachievable in the solid state.

It has been well understood theoretically and experimentally that S-S bonds with low bond dissociation energy, especially in aromatic disulfides, could autonomously exchange under mild conditions even without needing any catalyst or external intervention^{38,39,42,43}. From the above results, it is reasonable to expect that three isomeric MOFs constructed with the twisted dpds ligands tend to form a dynamic combinatorial library (DCL), where S-S bonds are in constant exchange³⁸ with the breakage and reformation instantaneously sped up in response to environmental stimuli, allowing linkage reorganization for facile conversions among LIFM-105, LIFM-105i and LIFM-105a via disulfide metathesis. This is largely owing to the distorted and strained conformations⁴¹ of dpds ligands in the looped $[\text{Zn}_2(\text{dpds})_2]_n$ chains, which are pillared by SiF_6^{2-} anions to fix the neighbouring $\text{pys}\cdot$ radicals in close proximity to ensure S-S bond reshuffling with ease (Fig. 1), similar to the reported effect contributed by hydrogen-bonding interactions^{38,39}. It is also reasonable that the porosity in LIFM-105 is adaptive to guests to form the T_{guest} state with preferential guest-framework interactions, while guest removal provokes structural transformation accompanied by slight rotation of interlayer $\text{Zn}_2(\text{pys})_4$ and SiF_6^{2-} components released by S-S breaking (Fig. 1). LIFM-105i represents the intermediate T_{int} state stabilized by partially loaded guests, and evacuation of all guests results in conversion into LIFM-105a as a stable T_{free} state, which has to occur through linkage reorganization. Additionally, LIFM-105a can transform back into the original LIFM-105 after methanol uptake, further confirming the guest-adaptive

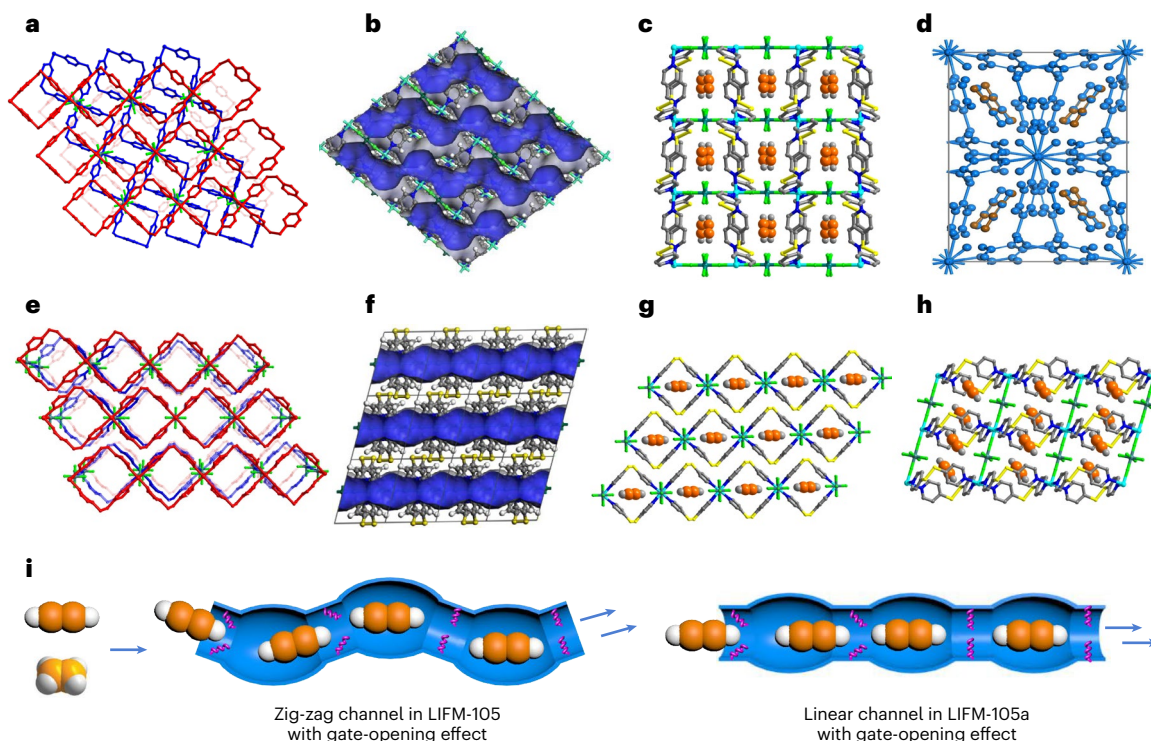


Fig. 2 | Structural comparison of LIFM-105, LIFM-105a and LIFM-105-C₂H₂.

a, Crystal structure of LIFM-105 showing the lattice arrangement viewed in the *c*-axis direction. **b**, Zig-zag channels extending along the *c*-axis in LIFM-105. **c**, Crystal structure of LIFM-105-C₂H₂ adsorbing C₂H₂ molecules in the pores viewed in the *a*-axis direction. **d**, Comparison of the C₂H₂-loaded structure of LIFM-105-C₂H₂ resolved by SCXRD (brown) with the simulated one obtained using DFT calculations (blue). **e**, Crystal structure of LIFM-105a showing the lattice arrangement viewed in the *a*-axis direction. **f**, Linear channels extending along

the *a*-axis in LIFM-105a. **g, h**, Simulated structures of LIFM-105a adsorbing C₂H₂ molecules in the pores viewed in the *a*- and *b*-axis directions. **i**, Channels in LIFM-105 and LIFM-105a with a gate-opening effect imposed by rotation of the pyridyl rings, showing selective adsorption of C₂H₂ from the C₂H₂/C₂H₄ mixture. Atom colour scheme for C₂H₂ and C₂H₄, C atoms are orange and H are light grey. Atom colour scheme for the framework of LIFM-105 and LIFM-105a, C atoms are grey, N atoms are blue, S atoms are yellow, F atoms are bright green, Zn atoms are cyan and Si atoms are teal. H atoms are omitted for clarity.

character (Supplementary Figs. 31 and 32). The disulfide exchange enables dynamic conversions among these states with concomitant rotation of pyridyl rings, providing the MOF pores with a guest-inducible gate effect (Fig. 2) for selective gas adsorption^{44,45}. Meanwhile, the swift S–S bond breaking/reforming renders MOFs with excellent restoring or restructuring capability, promising for prolonged and durable processes, which is unprecedentedly found in crystalline disulfide-containing MOFs^{35–37,46}.

Gas adsorption and separation

The phase-pure MOF samples have been identified by PXRD patterns, IR spectra and thermo-gravimetric analysis (TGA) (Supplementary Figs. 33–37). TGA combined with VT-PXRD confirmed the thermal stability of the MOFs up to 160 °C. Similar to the methanol removal process by heating, LIFM-105 transformed into LIFM-105a under high vacuum activation. However, the empty framework of LIFM-105 could be obtained via a supercritical CO₂ activation process (Supplementary Fig. 33).

The activated LIFM-105 and LIFM-105a showed minimal adsorption of N₂ (77 K), so their porosity was evaluated by CO₂ adsorption isotherms at 195 K (Supplementary Figs. 38–41). Both MOFs exhibit type I patterns, with CO₂ saturated amounts of 59.4 and 67.7 cm³ g^{−1}, Brunauer–Emmett–Teller (BET) surface areas of 190.1 and 182.1 m² g^{−1} and total pore volumes of 0.11 and 0.12 cm³ g^{−1} for LIFM-105 and LIFM-105a, respectively (Supplementary Table 5). Based on their suitable pore apertures, the adsorption of C₂H₂ and C₂H₄ was measured at 273, 298, and 313 K to evaluate their potential for separating C₂H₂/C₂H₄ (Fig. 4a and Supplementary Figs. 42–45). Both LIFM-105 and LIFM-105a showed steeper C₂H₂ isotherms than C₂H₄, especially at

low pressure, indicating stronger C₂H₂–framework interactions. At 273 K and 1 bar, C₂H₂ uptakes were 68.0 (3.03 mmol g^{−1}) and 52.3 cm³ g^{−1} (2.33 mmol g^{−1}), while C₂H₄ uptakes were 25.6 (1.14 mmol g^{−1}) and 20.9 cm³ g^{−1} (0.93 mmol g^{−1}), corresponding to C₂H₂/C₂H₄ uptake ratios of 2.65 and 2.51 for LIFM-105 and LIFM-105a (Fig. 4a), respectively, indicative of competent C₂H₂/C₂H₄ separation ability. We note that both LIFM-105 and LIFM-105a present stepwise C₂H₂ adsorption behaviours, suggesting a C₂H₂-induced gate effect stemming from pyridyl ring rotation prompted by C₂H₂ loading to break the metastable state via a gate-opening behaviour. Such a gate effect may drive S–S bond reshuffling to lead to structural conversion between LIFM-105 and LIFM-105a during repeated adsorbing–desorbing processes, tuning the adaptive pores for selective C₂H₂ adsorption.

To get more insight into the gate effect and structural transformations, in situ gas-loading-dependent PXRD patterns for LIFM-105 and LIFM-105a were collected at various C₂H₂ pressures at 298 K (Supplementary Figs. 46 and 47). For LIFM-105, the C₂H₂-loading PXRD patterns showed slight shifts of the (110), (020), (002), (130), and (201) peaks along with increasing C₂H₂ pressure from 0.18 to 90 kPa, indicative of minor expansion of pore windows and consistent with the SCXRD analysis of the C₂H₂-loaded crystal structure (Supplementary Figs. 11 and 23). For comparison, LIFM-105a showed obvious shifts of the (010), (01–1), (100), (011), and (02–1) peaks around 13 kPa, clearly indicating a structural change with pore deformation. We note that the C₂H₂ pressure that promotes peak shifting is in close accordance with the C₂H₂ adsorption isotherms, confirming that the stepwise C₂H₂ adsorption arises from a gate effect accompanying structural transformation. Comparison of the gas-loading-dependent PXRD patterns with those of LIFM-105 and LIFM-105a shows that C₂H₂ adsorption drives conversion

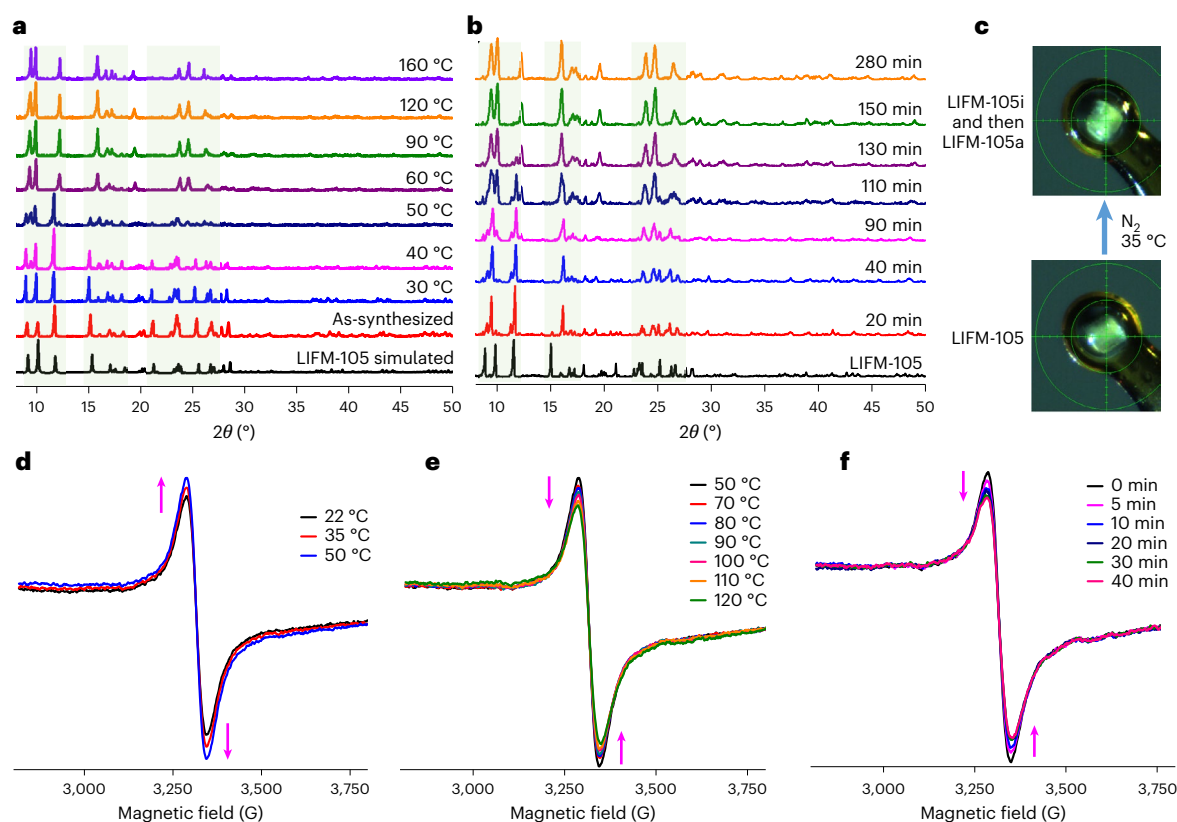


Fig. 3 | Structural transformation and radical identification. **a**, In situ VT-PXRD patterns of LIFM-105. **b**, Time-dependent in situ PXRD monitoring of LIFM-105 under N_2 blowing at 35 °C. Grey shading in **a** and **b** represents the changes in the diffraction peaks, which indicates a transformation of the structure. **c**, SC-SC

structural transformations from LIFM-105 into LIFM-105i and then LIFM-105a.

d–f, In situ EPR spectra of LIFM-105 at different temperatures and times: 22–50 °C (**d**), 50–120 °C (**e**) and leaving it alone after heating to 120 °C (**f**).

of LIFM-105a towards LIFM-105, while release of C_2H_2 leads to recovery of LIFM-105a (Supplementary Figs. 46–49 and Supplementary Table 2). These results confirm that the disulfide metathesis-mediated structural interconversions indeed take place during the C_2H_2 adsorption–desorption process, with LIFM-105 acting as the gas-adapted state (T_{guest}) while LIFM-105a acts as the stable gas-free state (T_{free}). This deduction is made by the similarity of the SCXRD-determined space groups of LIFM-105 loading methanol guests and LIFM-105- C_2H_2 loading C_2H_2 guests (Supplementary Table 1).

The isosteric heat of adsorption (Q_{st}) was calculated using the Clausius–Clapeyron equation. This gave Q_{st} values of 60.0 and 60.1 kJ mol $^{-1}$ for C_2H_2 and 39.0 and 37.2 kJ mol $^{-1}$ for C_2H_4 for LIFM-105 and LIFM-105a, respectively, at near zero coverage (Supplementary Figs. 50–53), further confirming stronger C_2H_2 –framework interactions. Multi-cycle C_2H_2 adsorption–desorption experiments at 298 K showed that LIFM-105 initially experienced a slight drop in C_2H_2 uptake over the beginning three rounds, coinciding with the PXRD analyses that the empty LIFM-105 tends to transform into more stable guest-free LIFM-105a for repeated loading of C_2H_2 (Fig. 4b and Supplementary Figs. 33 and 54). Afterwards, almost constant C_2H_2 uptakes as for pristine LIFM-105a for an additional fifty rounds of adsorption–desorption cycles were observed (Fig. 4c), confirming its excellent reusability and durability. These recycling adsorption–desorption processes indicate that the empty LIFM-105 actually exists as a metastable state, showing a strong propensity to convert into LIFM-105a as a guest-adaptive adsorbent. Impressively, the damaged LIFM-105/105a frameworks are able to regenerate or reorganize through S–S exchange along with structural deformation or conversion without loss of crystallinity. This indicates a potential restoring and reconstructing capability for repeated back-and-forth gas uptakes and releases through disulfide

metathesis, clearly observed from the in situ C_2H_2 -loading-dependent PXRD patterns (Supplementary Figs. 46 and 47). This unique crystalline dynamicity provides a smart protocol to resist deterioration and fracture, thus generating robust crystalline porous materials adequate for sustained gas separation.

The C_2H_2/C_2H_4 separation performance was evaluated using the ideal adsorbed solution theory (IAST) (Supplementary Figs. 55–58 and Supplementary Table 6)^{47,48}. LIFM-105a exhibited good C_2H_2/C_2H_4 selectivities ranging from 13.0 to 35.8 for gas mixtures with varying C_2H_2/C_2H_4 ratios, less than those of empty LIFM-105 but comparable with those of some well-performing MOFs (Supplementary Fig. S9 and Supplementary Table 7)^{49–54}. For a 1:99 (v:v) C_2H_2/C_2H_4 mixture, the predicted selectivity of LIFM-105a was 21.7 at 0.1 bar and 298 K (Supplementary Fig. 60), which is satisfactory owing to stronger C_2H_2 –framework interactions for a high C_2H_2 uptake at low pressure. We note that the C_2H_2/C_2H_4 (1:99, v:v) selectivities of LIFM-105 (16.4) and LIFM-105a (13.1) at 298 K and 1.0 bar are comparable with those of many well-performing MOFs, but lower than that for CuSnF $_6$ -dpds-sql (36.6)⁴⁶, CuSnF $_6$ -dpds-cds (62.9)⁴⁶, SIFSIX-2-Cu-i (44.5)⁴⁴, ZNU-11 (20.73)⁵⁵ and so on (Fig. 4d and Supplementary Table 7). Given the flexible nature of LIFM-105/105a, the IAST selectivity may just represent a qualitative prediction of C_2H_2/C_2H_4 separation potential.

To evaluate the practical separation performance, transient breakthrough experiments were conducted for a C_2H_2/C_2H_4 (1:99, v:v) gas mixture at 298 K (Fig. 4e–g and Supplementary Figs. 61–65). LIFM-105a achieved a C_2H_2 breakthrough at 136.7 min g $^{-1}$, capturing 238.3 mmol l $^{-1}$ of C_2H_2 , which is comparable to well-performing MOFs such as SIFSIX-1-Cu (265.3 mmol l $^{-1}$)⁴⁴, Fe-MOF-74 (100.7 mmol l $^{-1}$)⁴⁹ and NOTT-300 (68.3 mmol l $^{-1}$)⁵¹. Moreover, the C_2H_4 productivity with >99.99% purity was 11.5 mmol g $^{-1}$ based on a single breakthrough curve

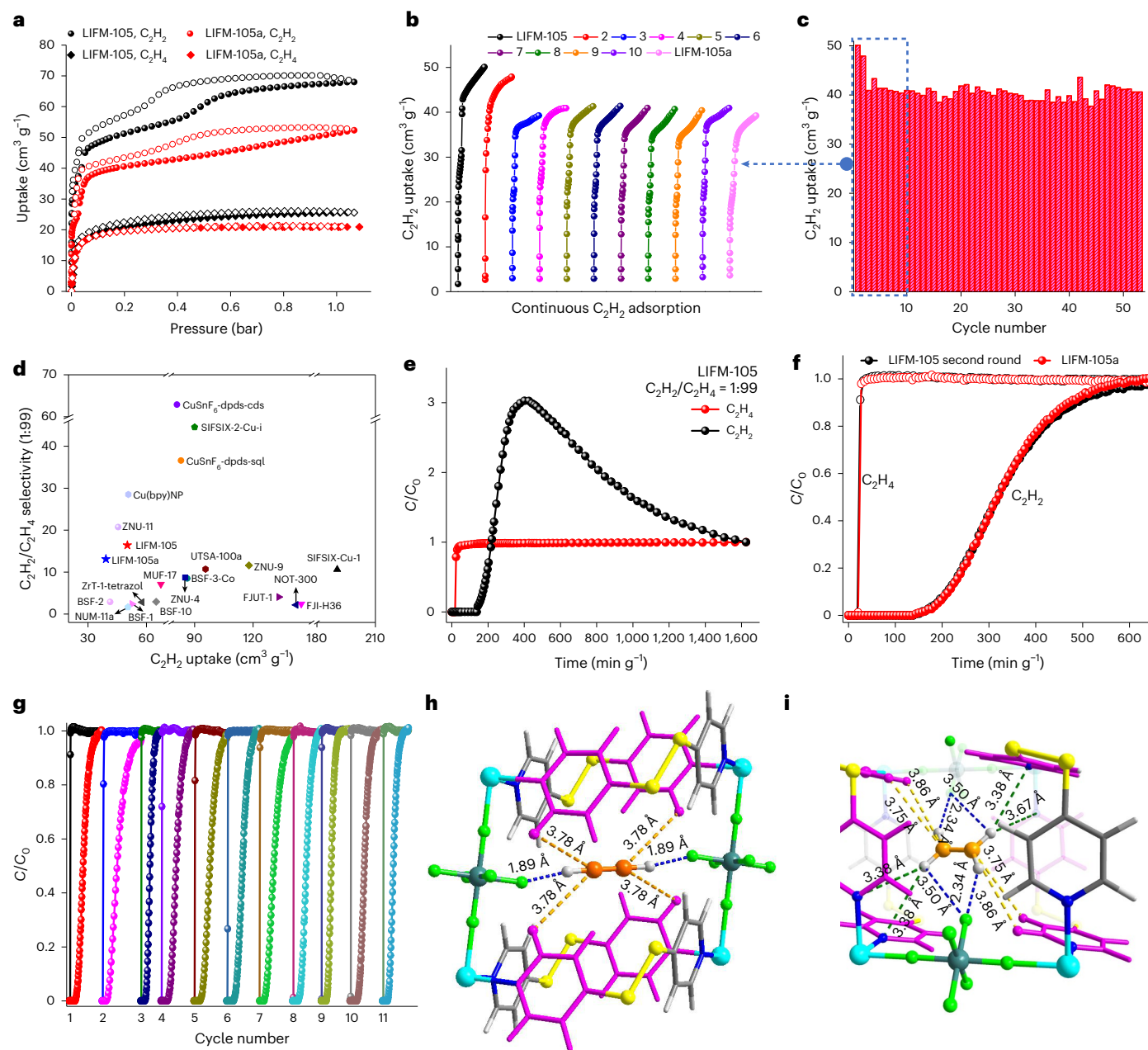
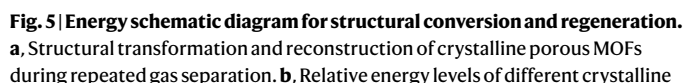


Fig. 4 | Gas adsorption and separation study. **a**, C_2H_2 and C_2H_4 adsorption isotherms of LIFM-105 and LIFM-105a at 273 K. **b**, Ten continuous rounds of C_2H_2 adsorption on LIFM-105 at 298 K. **c**, A total of 53 rounds of C_2H_2 adsorption performed consecutively at 298 K. **d**, Comparison of C_2H_2 uptake capacity and $\text{C}_2\text{H}_2/\text{C}_2\text{H}_4$ (1:99, v/v) IAST selectivity of LIFM-105 and LIFM-105a with those of reported MOFs at 298 K and 1 bar. **e, f**, Breakthrough curves of LIFM-105 and LIFM-105a for a 1:99 $\text{C}_2\text{H}_2/\text{C}_2\text{H}_4$ mixture at 298 K and 1 bar with a constant flow rate of 2.0 ml min^{-1} . C_0 represents the original concentration of C_2H_2 or C_2H_4 in a $\text{C}_2\text{H}_2/\text{C}_2\text{H}_4$ (1:99, v/v) gas mixture. C represents the concentration of C_2H_2 or C_2H_4 in the

gas that has flowed out at any given time t . C/C_0 represents the ratio of the C_2H_2 or C_2H_4 concentration in the gas that has flowed out at any given time t to the C_2H_2 or C_2H_4 concentration in the feed gas mixture. **g**, Eleven continuous rounds of breakthrough curves after the first breakthrough experiment of LIFM-105. **h**, The preferred binding sites for C_2H_2 (site I) in LIFM-105a. **i**, The binding site for C_2H_4 in LIFM-105a. Atom colour scheme for C_2H_2 and C_2H_4 , C atoms are orange and H are light grey. Atom colour scheme for the framework of LIFM-105 and LIFM-105a, C atoms are grey, N atoms are blue, S atoms are yellow, F atoms are bright green, Zn atoms are cyan and Si atoms are teal. H atoms are omitted for clarity.

with a flow rate of 2 ml min^{-1} . This is comparable to many reported MOFs such as SIFSIX-1-Cu (12.4 mmol g^{-1})⁴⁴, FJUT-1 ($13.94 \text{ mmol g}^{-1}$)⁵⁶, ZJU-74a (12.2 mmol g^{-1})⁵⁷ and $\text{CuSnF}_6\text{-dpds-sql}$ (14.5 mmol g^{-1})⁴⁶ (Supplementary Table 7). LIFM-105a also exhibited good separation performance at higher flow rates (3 and 5 ml min^{-1}) (Supplementary Figs. 62 and 63). For comparison, LIFM-105 also showed effective $\text{C}_2\text{H}_2/\text{C}_2\text{H}_4$ separation initially but released captured C_2H_2 molecules quickly after

137.9 min g^{-1} (Fig. 4e), implying the instability of empty LIFM-105 and transformation into LIFM-105a for steady separation performance. PXRD confirmed that LIFM-105 transformed into LIFM-105a after the first round of breakthrough experiments, as verified by almost identical breakthrough curves for its second round and the first round of LIFM-105a (Fig. 4f and Supplementary Fig. 66). The transformed LIFM-105a showed excellent and persistent separation capacity over the



The guest-induced dynamics may be understood from plentiful hydrogen bonds and vdW forces, including O···H, F···H, and N···H interactions, formed among methanol, SiF₆²⁻ and pyridyl rings (Fig. 5, Supplementary Figs. 82–86 and Supplementary Tables 3 and 4), adequately consolidating the framework of LIFM-105. It has been reported that

SiF_6^{2-} anions can rotate in SIFSIX materials^{44,61,62}, triggering pyridyl ring rotation via F...H hydrogen bonding. Methanol escape from LIFM-105 weakens the methanol–framework interactions, especially releasing constraints on SiF_6^{2-} to trigger its rotation. This consequently induces pyridyl ring rotation owing to F...H interactions between SiF_6^{2-} and the pyridyl rings. Therefore, S–S exchange will be promoted to result in structural conversions from LIFM-105 into intermediate LIFM-105i and finally LIFM-105a, which is the most stable guest-free state (Fig. 1).

GCMC and DFT calculations provide deeper insight into crystalline dynamicity during structural transformations (Fig. 5). MOF isomers, including methanol-adsorbed LIFM-105 (3 MeOH) and LIFM-105i (0.85 MeOH) and guest-free LIFM-105 and LIFM-105a, were first optimized using DFT simulations, and calculated under the generalized gradient approximation (GGA) together with the Perdew–Burke–Ernzerhof (PBE) exchange–correlation functional. The much lower energy level of methanol-loaded LIFM-105 ($T_{\text{guest-1}}$) than empty LIFM-105 ($T_{\text{free-1}}$) corresponds to the strong tendency to stabilize the framework with methanol guests via host–guest interactions (Fig. 5b and Supplementary Tables 3 and 4). Moreover, the slightly lower energy level of the guest-free LIFM-105a than the empty LIFM-105 ($\Delta E = 7.17 \text{ kJ mol}^{-1}$) confirms it as the more stable guest-free state ($T_{\text{free-2}}$), with easy interconversion between states. This is consistent with the DSC observation, underpinning the C_2H_2 -induced transformation of empty LIFM-105 into LIFM-105a after two C_2H_2 adsorption rounds and just one breakthrough experiment (Fig. 4b,c and Supplementary Figs. 33 and 66). Similar to the methanol-induced reversible conversion between methanol-adsorbed LIFM-105 and guest-free LIFM-105a via the T_{int} state of LIFM-105i, C_2H_2 full loading is expected to induce the structural transformation of LIFM-105a into LIFM-105- C_2H_2 , a C_2H_2 -adapted state ($T_{\text{guest-2}}$).

Therefore, a dynamic equilibrium mechanism mediated by disulfide metathesis enables structural interconversion and regeneration of crystalline MOFs, supporting repeated gas adsorption–desorption cycles (Fig. 5a), which accounts for persistent $\text{C}_2\text{H}_2/\text{C}_2\text{H}_4$ separation performance with robustness and adaptiveness over 53 rounds of adsorption and 11 rounds of breakthrough experiments (Fig. 4c,g). The regeneration and reconstruction capability of MOFs has been further validated by restoring completely deteriorated amorphous LIFM-105 crystals (heated at 175°C or ground and then heated at 175°C) via methanol soaking, as seen by PXRD and SCXRD analyses (Supplementary Fig. 87). Moreover, the LIFM-105 crystals retained structural integrity and high crystallinity under high pressure (40 MPa), demonstrating outstanding mechanical robustness (Supplementary Fig. 88). Comparable with the repairing and healing effect of disulfide metathesis in soft materials and biological processes,^{26–33,38–43} the autonomous S–S bond exchange in the crystalline state offers a biomimetic approach to manoeuvre internal structural stress and distortion, enabling large amplitude motion of building units without compromising overall connectivity and reconstructing the locally and transiently damaged structure to avoid brittle failure. This mechanism also allows instant microenvironmental restoration or reorganization of the deteriorated framework during back-and-forth gas uptake cycles, thereby ensuring prolonged usability. Such adaptive anti-crack and anti-fatigue properties mediated by disulfide metathesis show the potential of crystal dynamics to achieve toughness of MOF materials via softness. Rather than relying on conventional synthetic strategies to stiffen and solidify the rigid MOF structures that are intrinsically prone to brittleness and vulnerability, this methodology aligns with the natural philosophy of overcoming hardness with softness.

Conclusions

Bio-inspired disulfide metathesis has been demonstrated as a viable strategy for achieving radical-directed dynamics in the solid state within adaptive crystalline MOFs. The reversible structural transformation and guest-adaptive behaviour mediated by S–S bond cleavage and reformation allow the rotation and shifting of building components to

reorganize framework linkages for gas-adaptation and the gate effect, consequently fine tuning the porosity for preferable C_2H_2 adsorption over C_2H_4 . Crucially, these adaptive MOFs leverage facile S–S bond reshuffling to restore and restructure the transiently damaged framework during repeated adsorption–desorption processes, ensuring efficient and long-term $\text{C}_2\text{H}_2/\text{C}_2\text{H}_4$ separation. This work presents a feasible pathway to address the durability-against-fragility challenge in crystalline MOFs by synergizing toughness and robustness with softness and adaptiveness.

Methods

All the reagents and solvents were purchased from commercial sources and utilized without further purification. dpds was purchased from Aladdin. Solid-state IR spectra were recorded using a Nicolet/Nexus-670 Fourier transform infrared spectrometer with KBr pellets in the region $4,000\text{--}400 \text{ cm}^{-1}$. Single-crystal X-ray diffraction data were collected using a Rigaku Oxford SuperNova X-ray diffractometer equipped with a Cu sealed tube ($\lambda = 1.54178 \text{ \AA}$) at 50 kV and 0.80 mA. PXRD was carried out using a Rigaku SmartLab diffractometer with Cu $\text{K}\alpha 1$ radiation ($\lambda = 1.54056 \text{ \AA}$) in Bragg–Brentano geometry. TGA was conducted on a NETZSCH TG209 system in nitrogen at 1 bar with a heating rate of $10^\circ\text{C min}^{-1}$. Gas adsorption isotherms were measured using a Micromeritics ASAP 2020 physisorption analyser by the volumetric method for pressures between 0 and 1.0 bar. Gas adsorption measurements used ultra-high purity N_2 , CO_2 , C_2H_2 and C_2H_4 gas. EPR spectra were recorded using a Varian E-109 spectrometer with a cavity resonator. All continuous wave (CW) EPR spectra were acquired at 200 mW observed power, 100 kHz modulation frequency and 1.0 G modulation amplitude. Raman spectra were collected using a Renishaw inVia Qontor confocal Raman microscope with 785 nm laser excitation. In situ gas-loading-dependent PXRD patterns were recorded using a PANalytical X'Pert³ powder diffractometer with a Cu tube ($\lambda = 1.54056 \text{ \AA}$) at 40 kV and 40 mA.

Synthesis of LIFM-105

A methanol solution (20 ml) of $\text{ZnSiF}_6 \cdot x\text{H}_2\text{O}$ (165.6 mg) was dropped into a pre-prepared methanol solution (40 ml) of dpds (392.0 mg) under stirring. The mixture was stirred for 48 h at room temperature. The obtained solid was exchanged with methanol three times, giving LIFM-105 in 68.8% yield (269.2 mg). To grow single crystals of LIFM-105, 2 ml methanol was layered over 2 ml methanol solution containing dpds (19.6 mg) in a tube. A 2 ml methanol solution of $\text{ZnSiF}_6 \cdot x\text{H}_2\text{O}$ (8.3 mg) was carefully layered over the buffer layer. The tube was sealed and left undisturbed at room temperature. After three days, colourless block crystals were obtained.

Synthesis of LIFM-105i

A round-bottom flask containing the as-synthesized LIFM-105 was heated at 35°C and a slow stream of nitrogen was introduced. After 40 min, LIFM-105i was obtained.

Synthesis of LIFM-105a

A round-bottom flask containing the as-synthesized LIFM-105 was heated at 35°C and a slow stream of nitrogen was introduced. After 150 min, LIFM-105a was obtained.

Data availability

Crystallographic data for the structures in this Article have been deposited at the Cambridge Crystallographic Data Centre under deposition numbers CCDC 1919410 (LIFM-105-100 K), 2440073 (LIFM-105-298 K), 2440074 (LIFM-105-308 K), 2373234 (LIFM-105i), 1919412 (LIFM-105a) and 1919414 (LIFM-105 C_2H_2). Copies of the data can be obtained free of charge via <https://www.ccdc.cam.ac.uk/structures/>. The data that support the conclusions in the paper are present in the Article or its Supplementary Information. Source data are provided with this paper.

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Author contributions

C.-Y.S. conceived and coordinated the project. C.-X.C. and S.M. designed the experiments. C.-X.C. carried out the syntheses and measurements. C.-X.C. and K.T. performed the in situ IR experiments. C.-Y.S., S.M. and C.-X.C. wrote the manuscript. P.C.L., Z.-W.W. and Y.Y.X. helped in experiments. X.C. and L.Y. performed the theoretical calculation. C.-X.C., Z.N., Z.-W.W. and C.S. performed the crystal analyses.

Competing interests

The authors declare no competing interests.

Additional information

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