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# Dynamic covalent organic frameworks

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Covalent organic frameworks (COFs) have emerged as one of the most promising classes of crystalline and porous materials as they offer precise control over structural, catalytic, and optical properties via the design of monomers and their connectivity. While most COFs are rigid materials with fixed geometry, porosity, and properties, recently developed dynamic COFs can change these properties in response to external stimuli such as solvents, vapours, temperature, or light. This research field is rapidly developing and new generations of both 2D and 3D dynamic COFs now offer large and fully reversible changes of unit cell volumes and porosities as well as full control over the expansion/contraction along pre-defined crystal directions. They hold great promise for various applications ranging from economically important uses in gas separation and monomer purification to future technologies including adaptive sensing and spin-optoelectronics. While the design, synthesis and applications of rigid COFs have been the subject of several recent reviews, a comprehensive summary of the current state of the art, challenges and opportunities of dynamic COFs has remained elusive. In this review, we provide an overview of the dynamic COFs reported to date and analyse their structures and underlying design principles. We discuss the different origins of structural flexibility, and summarise first applications and future challenges and opportunities of these intriguing materials.

## 1. Introduction

Covalent organic frameworks (COFs) are an emerging class of crystalline porous polymers that are constructed by interconnecting rigid or semi-rigid organic building blocks.<sup>1–5</sup> Since

their initial reports by Yaghi and co-workers,<sup>6–8</sup> COFs have sparked an enormous surge in scientific interest due to their modular design, structural predictability, tuneable porosity and wide range of bespoke chemical and electronic functionalities.<sup>9–19</sup>

COFs can be covalently linked in all three dimensions (3D COFs),<sup>20–25</sup> or they can be composed of covalently linked layers (2D COFs)<sup>26–32</sup> or ribbons (1D COFs)<sup>33–36</sup> that are held together by

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and synthesis of framework materials with tailored opto- and spin-electronic properties.

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non-covalent interactions (Fig. 1). The framework topology, geometry and porosity are primarily determined by the selection of the building blocks<sup>37–41</sup> and can be tuned further *via* the synthesis conditions employed during the COF polymerisation.<sup>42–46</sup>

The exceptional crystallinity of COFs compared to conventional polymers is primarily due to the monomer design<sup>47–51</sup> and the linkage chemistry.<sup>52–56</sup> COFs are typically constructed from two building blocks equipped with complementary functional groups for polymerisation, and extensive research has gone into optimising monomer geometries.<sup>57–60</sup> The covalent linkages between building blocks are chosen such that they are slightly reversible, allowing bonds to be formed, broken and re-formed during the synthesis.<sup>61–63</sup> This provides an effective error correction mechanism, enabling the materials to approach their thermodynamically stable, long-range ordered state.

A wide range of functional monomers has been developed, giving rise to bespoke frameworks with well-defined structural, catalytic, optical and electronic properties. The resulting functional COFs are highly promising for future applications in gas storage and separation, catalysis, energy storage, optoelectronics and sensing.<sup>64–78</sup>

While most COFs are rigid frameworks with permanent porosity, an increasing number of COFs have now been found to switch their geometry or porosity reversibly when exposed to

gases or solvent vapours.<sup>79–81</sup> This intriguing behaviour is known from several classes of metal–organic frameworks (MOFs) and the respective materials are referred to as soft porous crystals or dynamic frameworks.<sup>82,83</sup> Here, well-engineered flexibility along selected crystal directions enables these materials to switch cooperatively between two or more crystalline phases with the same topology but different unit cell parameters, symmetries and porosities.<sup>84,85</sup> Framework dynamics is predominantly triggered by the introduction or extraction of guest molecules, but can also be induced by applied electric fields, temperature or light irradiation.<sup>86–92</sup> Potential applications of dynamic frameworks have focused predominantly on selective adsorption and separation,<sup>93,94</sup> but these materials could also provide new opportunities for manipulating optoelectronic and spin-electronic properties,<sup>95,96</sup> highlighting their potential impact across multiple research fields and disciplines.

In this review article, we aim to provide a comprehensive overview of dynamic COFs, with an emphasis on the COF designs and underlying principles to generate structural flexibility. We will begin with a summary of known dynamic COFs with various 3D and 2D topologies, followed by an in-depth analysis of the factors that govern framework flexibility and dynamics. We will also explore how framework dynamics influences emerging applications, and outline current

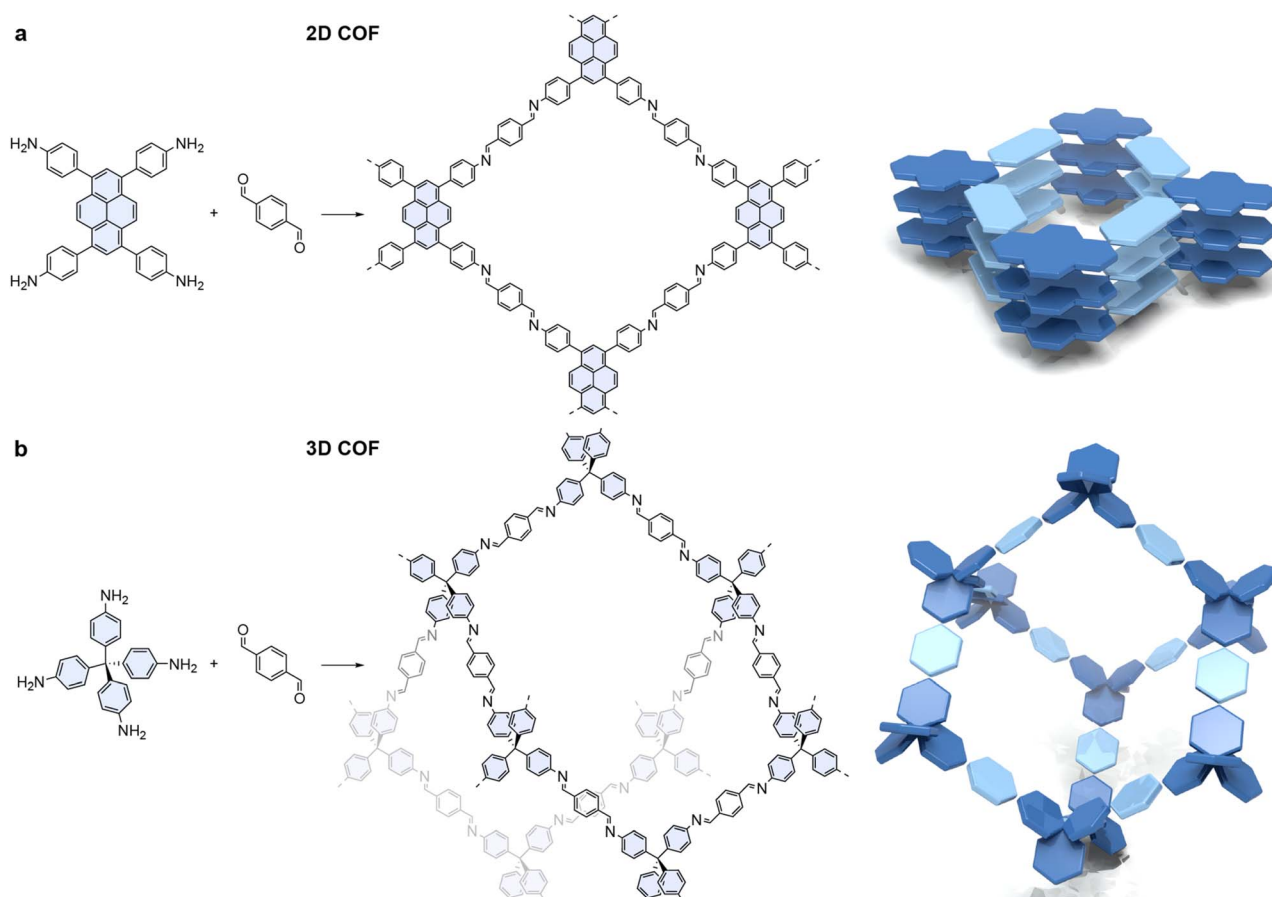


Fig. 1 Representative examples of (a) 2D and (b) 3D COFs.<sup>20,58</sup>



challenges and opportunities in designing next-generation COFs with adaptive, multifunctional capabilities.

## 2. Covalent organic frameworks

COFs combine the traits of organic polymers and framework materials. Chemically, COFs are polymers formed through covalent linkages. Structurally, COFs share characteristics with MOFs and other frameworks, *i.e.*, their geometry being primarily determined by the shape of the building blocks. This unique combination opens the door to a plethora of tailor-made materials with customizable structural, chemical, and electronic properties.

The general design of COFs as well as their synthesis and applications have been reviewed in a number of recent articles.<sup>97–122</sup> We will thus provide only a brief overview before focusing on dynamic COFs.

### 2.1. Monomer and framework design

Analogous to DNA and proteins, COFs can be described by a primary, secondary, and tertiary structure. COF monomers are generally selected to be sufficiently rigid with a predictable molecular geometry. Additionally, for generating interconnected networks, at least one of the monomers must be able to form more than two bonds with neighbouring building blocks. These multitopic building blocks are often referred to as “nodes”. 3- and 4-connected nodes are most common,<sup>123–132</sup> but also 6-, 8-, and 16-connected variants have been employed successfully.<sup>133–137</sup> The other monomer(s) can be ditopic (often referred to as “linkers”) or multitopic.

Polymerisation of these building blocks generates the primary structure of the framework. If the monomer geometries and synthesis conditions are chosen appropriately, this process simultaneously creates a periodic secondary structure with a predictable topology. For example, the combination of (pseudo)tetragonal tetratopic and angled ditopic monomers generates 1D ribbons,<sup>36</sup> while the combination of the same nodes with linear counterparts generates extended 2D sheets with **sql** topology (Fig. 1a).<sup>27,58</sup> Non-planar multitopic monomers can give rise to 3D secondary structures such as the diamond-like (**dia**) and quartz (**qtz**) frameworks generated by (pseudo) tetrahedral units (Fig. 1b)<sup>20,44</sup> and **pts** networks composed of tetrahedral and square planar nodes.<sup>24,138</sup>

These covalently linked objects form periodic tertiary structures *via* non-covalent interactions. 2D COF layers stack *via* electrostatic and dispersive forces. This is often referred to as  $\pi$ -stacking although the attraction between aromatic molecules can be due to a combination of several different mechanisms.<sup>139,140</sup> Likewise, the ribbons of 1D COFs are typically  $\pi$ -stacked. Additionally, they are geometrically interlocked or postsynthetically crosslinked along the third dimension.<sup>33</sup>

3D COFs can in some cases be realised as non-interpenetrated frameworks without a tertiary structure.<sup>141,142</sup> However, most 3D COF lattices are highly porous with void fractions often ranging between 50 and 90%. Thus, the formation of interpenetrated lattices is favoured, leading to more

densely packed frameworks with altered symmetries and reduced porosities. The number of interpenetrated lattices can range between 2-fold interpenetration for most **pts** networks<sup>138</sup> up to 15-fold for **dia** COFs comprising large building blocks.<sup>143</sup>

### 2.2. Linkage chemistry

The realisation of crystalline covalently interconnected networks imposes substantial challenges to the polymerisation processes that need to be overcome by careful selection and optimisation of the linkage chemistry. Monomers need to attach in the correct orientation and must form all bonds with the correct partners in order to avoid lattice strain and defects in the growing COF crystals.<sup>144</sup> High crystallinity thus requires an effective error correction mechanism, *i.e.*, sufficient reversibility to allow bonds to be formed, broken and re-formed during the synthesis. This dynamic covalent chemistry enables the frameworks to approach their thermodynamically stable, long-range ordered geometry rather than becoming trapped in an amorphous state. Suitable building block designs or pre-organisation of the monomers using surfactants or micelles can reduce the number of error correction cycles necessary to obtain high crystallinity.<sup>57,145,146</sup> but there is a general trend that more reversible linkages afford more crystalline COFs.<sup>52</sup>

While the first COFs were constructed from boroxines or boronate esters,<sup>6,8</sup> imines have evolved into the most widely used COF linkages.<sup>20,26</sup> Generated *via* acid-catalysed condensation of primary amines and aldehydes, they represent an excellent trade-off between crystallinity and stability and are compatible with a large variety of functional monomers. Single-crystalline imine-linked COFs have recently become accessible through modulator strategies, in which monofunctional reagents such as aniline are used to suppress rapid nucleation and polymerisation.<sup>22,55</sup>

Linkages that provide enhanced stability at the expense of reduced crystallinity include phenazines<sup>147–149</sup> and imides.<sup>150–152</sup> Enhanced chemical stability can also be obtained *via* multistep reactions, where the initial reversible condensation provides crystalline pre-organisation of the framework, while subsequent irreversible reactions generate more stable bonds. Typical examples include imidazoles,<sup>153</sup> thiazoles<sup>154,155</sup> and  $\beta$ -ketoenamines.<sup>156,157</sup>

Vinylene linkages, formed *via* base-catalysed Knoevenagel condensation or acid- or base-catalysed aldol condensation,<sup>54,158–160</sup> can endow the frameworks with improved chemical stability and enhanced electronic conjugation. For improved crystallinity, linker exchange strategies have opened up viable routes for converting imine-linked COF single crystals into vinylene-linked single-crystalline COFs.<sup>56,161</sup>

### 2.3. Dynamic COFs

Dynamic behaviour describes the ability of some frameworks to undergo fully reversible crystal-to-crystal transformations under preservation of the framework topology, *i.e.*, no chemical bonds are formed or broken.



Since their structure is predominantly defined by the geometry and connectivity of the building blocks, COFs are almost always porous with void fractions often above 50% and much lower densities than molecular crystals or linear polymers.<sup>50,142</sup> These voids do not only create accessible pores, but can also alter the mechanical properties of the frameworks as they allow subunits to rotate, bend and slide without substantially compressing/straining chemical bonds or  $\pi$ - $\pi$  contacts. Depending on the COF geometry and topology, this can result in structural flexibility at low activation energies.

Dynamic transformations typically involve two or more crystalline phases of different porosities that are commonly referred to as contracted-pore (cp), open-pore (op), and (if applicable) intermediate-pore (ip) phases. Phase transitions can be step-wise or continuous, and are categorised as 'gate opening' if an initially contracted framework expands upon guest uptake, or 'breathing' if the framework contracts upon initial guest uptake and re-opens when guest loading is increased.<sup>83,162</sup>

Constructing dynamic COFs requires careful engineering of the framework flexibility along selected crystal directions, as well as optimising the delicate balance between flexibility and stability. Ideally, a well-designed dynamic COF should respond to an external trigger with a pre-defined cooperative geometry change and return to its initial state when the stimulus is removed. At the same time, sufficient robustness is required to ensure that the COF can be toggled between its phases without degradation or loss of long-range order.

Framework dynamics in COFs has so far mostly been induced by the uptake or release of guest molecules. Other triggers that have been employed include temperature changes, external pressure, and the light-induced photoisomerisation of photoswitch moieties.

Framework dynamics in COFs can take different forms, depending on the combination of rigid and flexible elements in the COF design. In the simplest case, frameworks are rigid in

two dimensions and can expand or contract along the third (Fig. 2a). "Wine rack" type COFs are flexible along two dimensions, but rigid along the third (Fig. 2b). This concept can be realised for instance with **sql** lattice 2D COFs or their 3D COF counterparts with **scu** topology.<sup>71,81,163</sup>

Conversely, most dynamic 3D COFs show framework flexibility along all three dimensions (Fig. 2c). This is for example the case with **dia** frameworks where expansion along two dimensions upon guest uptake causes contraction along the third, and *vice versa*.<sup>164</sup>

In 2D COFs, guest uptake can also result in altered stacking of the COF layers (Fig. 2d).<sup>165</sup> COFs can also exhibit local flexibility upon guest uptake without macroscopic changes of the unit cell parameters or porosity (thus strictly speaking not counted as dynamic frameworks) (Fig. 2e). This type of flexibility has been observed for "woven" COFs.<sup>166</sup> In addition to guest-induced framework dynamics, some photoswitch-modified COFs can display small unit cell changes upon photoisomerisation (Fig. 2f). For instance, dithienylethene-bridged 2D COFs contract along the stacking direction upon photoisomerisation from the open to the more planar closed configuration.<sup>167</sup>

### 3. Dynamic 3D COFs

3D COFs can be very porous materials depending on their framework topology, size and geometry of building blocks, and interpenetration. This provides a wide design space for dynamic frameworks with tuneable host-guest interactions. An overview of the most important 3D COF topologies and the nodes used for constructing dynamic 3D COFs is shown in Fig. 3.

#### 3.1. COFs with **dia** topology

COFs with **dia** topology, constructed from tetrahedral and linear or two complementary tetrahedral building blocks such as

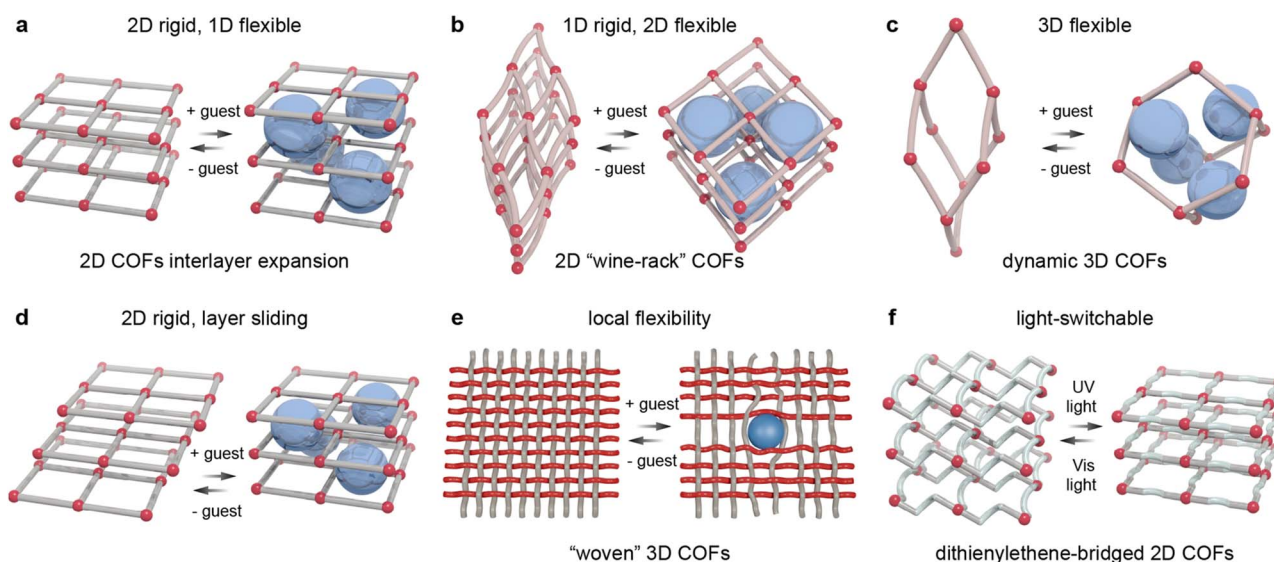


Fig. 2 Overview of dynamic frameworks and other flexible COFs. (a–c) Frameworks with flexibility in one, two, or three dimensions. (d) Guest uptake can change the layer stacking in 2D COFs. (e) Local flexibility. (f) Photoswitch-modified COFs.



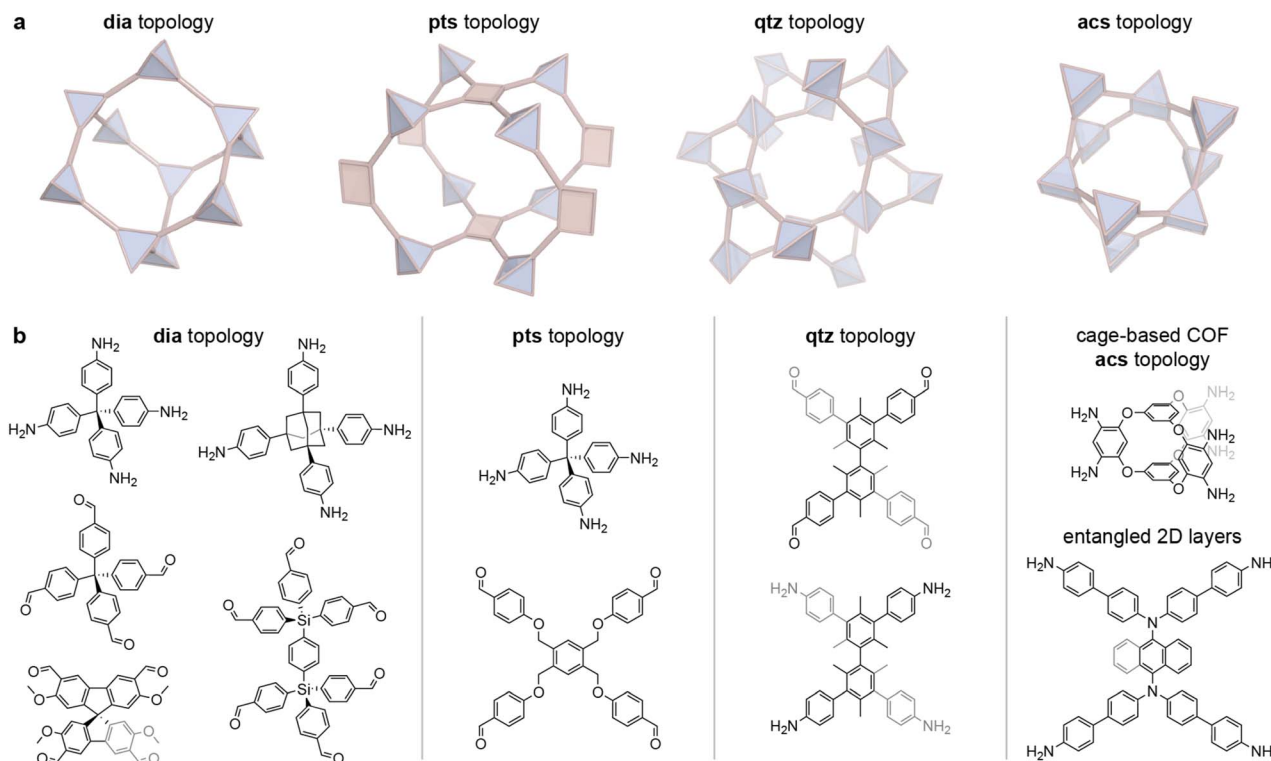


Fig. 3 (a) Illustrations of the most important topologies of 3D COFs. (b) Chemical structures of the node-forming tetratopic and 6-connected monomers used for constructing dynamic 3D COFs.

functionalised tetraphenylmethanes (TPMs), are among the most common 3D COFs. **dia** COFs can be described as a quasi-infinite lattice of edge-sharing adamantane-like cages (Fig. 3a). Due to the very high void fraction of a single lattice, most **dia** COFs crystallise with interpenetrated lattices.<sup>168</sup>

The first imine-linked 3D COF (COF-300) was realised *via* co-condensation of tetrakis(4-aminophenyl)methane (TAM) with terephthalaldehyde.<sup>20</sup> This COF was microporous due to a 5-fold interpenetrated structure, but unlike previously reported COFs, the Ar sorption isotherm displayed a pronounced hysteresis and a step around  $p/p_0 = 0.1$ . This feature was explained by the dynamic response of the framework, specifically a gate-opening process where higher pressure is required to activate the pores. Similar gate-opening was observed for the larger homologue, the biphenyl-linked COF-320.<sup>21</sup> Additionally, the structure of this COF was found to be temperature-dependent. At room temperature, the COF had pores with a square cross-section, while at 89 K the framework was significantly contracted with rectangular pores.

Dynamic COFs were first described in more detail by Wang and colleagues, who studied LZU-301, a COF-320 analogue with a 3,3'-bipyridine linker.<sup>79</sup> Exposure of this material to solvents such as tetrahydrofuran (THF) led to a shift and splitting of the main reflections in the powder X-ray diffraction (PXRD) patterns, indicating a symmetry-breaking lattice expansion with up to 35% increase in unit cell volume. The observed phase transformations were fully reversible upon drying. The framework dynamics were further investigated using variable temperature <sup>129</sup>Xe NMR. At room temperature, the COF adopted

its contracted phase with low Xe loading due to the small pore size. Upon cooling to 193 K, an increasing amount of Xe was adsorbed by the COF, resulting in framework expansion. This was accompanied by a downfield shift of the <sup>129</sup>Xe NMR signals caused by stronger Xe–Xe interactions of the densely packed Xe atoms.

To date, COF-300 remains one of the most widely studied dynamic 3D COFs. Crystals suitable for single crystal X-ray diffraction (SC-XRD) have been achieved *via* modulators that control the nucleation and growth.<sup>22,55</sup> Depending on the synthesis conditions, this COF can crystallise in two isomers with 5- and 7-fold interpenetration, respectively.<sup>168</sup> In the 5-fold interpenetrated variant, the conformation of the TAM nodes is close to ideal tetrahedral geometry. This isomer has a pore diameter of about 8 Å, while the 7-fold interpenetrated COF-300 is elongated along the *c*-axis and features very narrow pores with only 4 Å diameter.

Upon guest uptake, the 7-fold interpenetrated COF-300 expands and the initially distorted adamantane-like cages assume a less elongated geometry (Fig. 4, right).<sup>164</sup> Notably, this guest-loaded COF is very similar to the 5-fold interpenetrated COF-300 isomer discussed above. This study also revealed that the geometry of the solvated framework is almost identical for a broad range of solvents, including THF, toluene, xylenes and acetonitrile.<sup>164</sup> Moreover, *in situ* PXRD conducted during CO<sub>2</sub> adsorption and desorption confirmed that the COF undergoes well-defined transitions between crystalline phases, as opposed to swelling that would manifest as gradual shifts of the PXRD reflections.



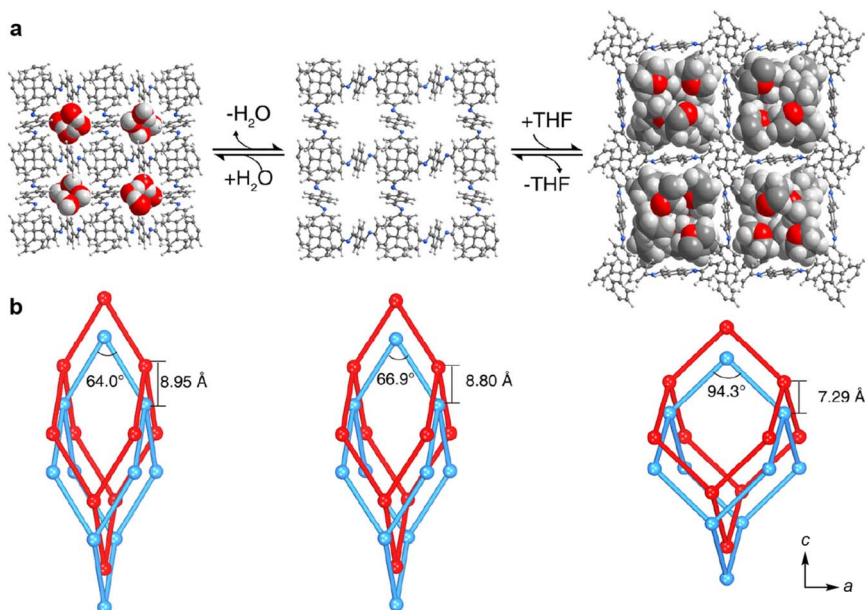


Fig. 4 Guest-triggered structural deformations of COF-300. (a) The COF expands upon THF uptake, but contracts when water is adsorbed in the pores due to strong host–guest interactions. (b) Guest-induced distortion of the adamantane-like cages. Reproduced with permission from ref. 164. Copyright 2019 American Chemical Society.

While the uptake of most guest molecules causes dynamic COFs to expand, strongly interacting guests can also trigger a framework contraction. SC-XRD and cryo-electron diffraction tomography studies on 7-fold interpenetrated COF-300 revealed that water molecules can form hydrogen bonds with the imine linkages, causing a substantial contraction of the hydrated framework (Fig. 4, left).<sup>22,164,169</sup>

Another key aspect for understanding dynamic COFs is the arrangement of the guest molecules within the pores. Zhang and co-workers employed COF-300 single crystals grown *via* a diffusion gradient transimination protocol to study the adsorption of various guests *via* SC-XRD and *in situ* PXRD during solvent vapour adsorption (Fig. 5).<sup>86</sup> The adsorption of BuOH caused phase transitions from the guest free tetragonal cp phase to an orthorhombic ip phase at low BuOH loading and a tetragonal op phase at higher BuOH loading. SC-XRD revealed that the phases correspond to the adsorption of two and four BuOH molecules, respectively, per pore and COF repeat unit. A comparison of a variety of linear, branched, and aromatic solvents revealed that the guest molecules assume specific periodic arrangements in the COF pores depending on their shape, size, and interactions with the COF host.

Host–guest interactions were further illustrated by a recent study of extended aromatic guests, including anthracene, pyrene and perylene in the pores of COF-300.<sup>87</sup> It was found that the COF adapts its symmetry and pore size to match the steric requirements and preferred packing of the guests. These dynamic transformations can result in expansion or contraction of whole COF crystals. Optical dark-field microscopy revealed that exposure of COF-300 single crystals to chloroform triggered observable shape changes within 60–80 s.<sup>170</sup>

While COF-300 is synthesised from an amine-functionalised tetrahedral node, the structurally related COF-303 is obtained

by reacting tetrakis(4-formylphenyl)methane with 1,4-phenylenediamine.<sup>55</sup> This COF was found to display similar dynamic behaviour when exposed to solvents, transforming from cp and ip phases with rectangular pore cross-sections to an op phase with square prismatic pores.

Replacing terephthalaldehyde in COF-300 with biphenyl-4,4'-dicarbaldehyde generates the larger COF-320.<sup>21</sup> However, this COF can exist in different isomeric forms depending on the synthesis conditions. Solvothermal synthesis at 120 °C resulted in the more rigid COF-320 with permanent porosity, whereas low-temperature synthesis at 65 °C led to the strongly contracted COF-320-A.<sup>171</sup> While both frameworks share the same chemical composition, they differ in their crystal structure. Notably, COF-320-A was found to be dynamic when exposed to gases like C<sub>2</sub>H<sub>4</sub>, C<sub>2</sub>H<sub>2</sub>, or CO<sub>2</sub>. Structural analysis using continuous rotation electron diffraction (cRED) revealed that the imine bonds in COF-320-A adopt a *cis* configuration, enabling the rotation and bending of the biphenyl bridge unit at low activation energies. In contrast, the *trans* configuration of the imines in standard COF-320 restricts this rotation, rendering it more rigid.

Preparation of this COF *via* a ventilation-vial synthetic protocol produced COF-320-V, which had a similarly contracted geometry in its guest-free cp phase.<sup>172</sup> Upon exposure to 1,4-dioxane, this COF expanded substantially with a volume change of 78%. Butane adsorption at 298 K revealed the existence of two ip phases with two and four butane molecules per pore and unit cell, respectively. In the fully expanded op phase, five butane molecules were adsorbed, resulting in a volume expansion of 65% relative to the cp phase.

TAM-based COFs provide ample opportunities for tailoring chemical, structural, and electronic properties *via* functionalisation of the linear linkers.<sup>173</sup> Especially the hydroxy-



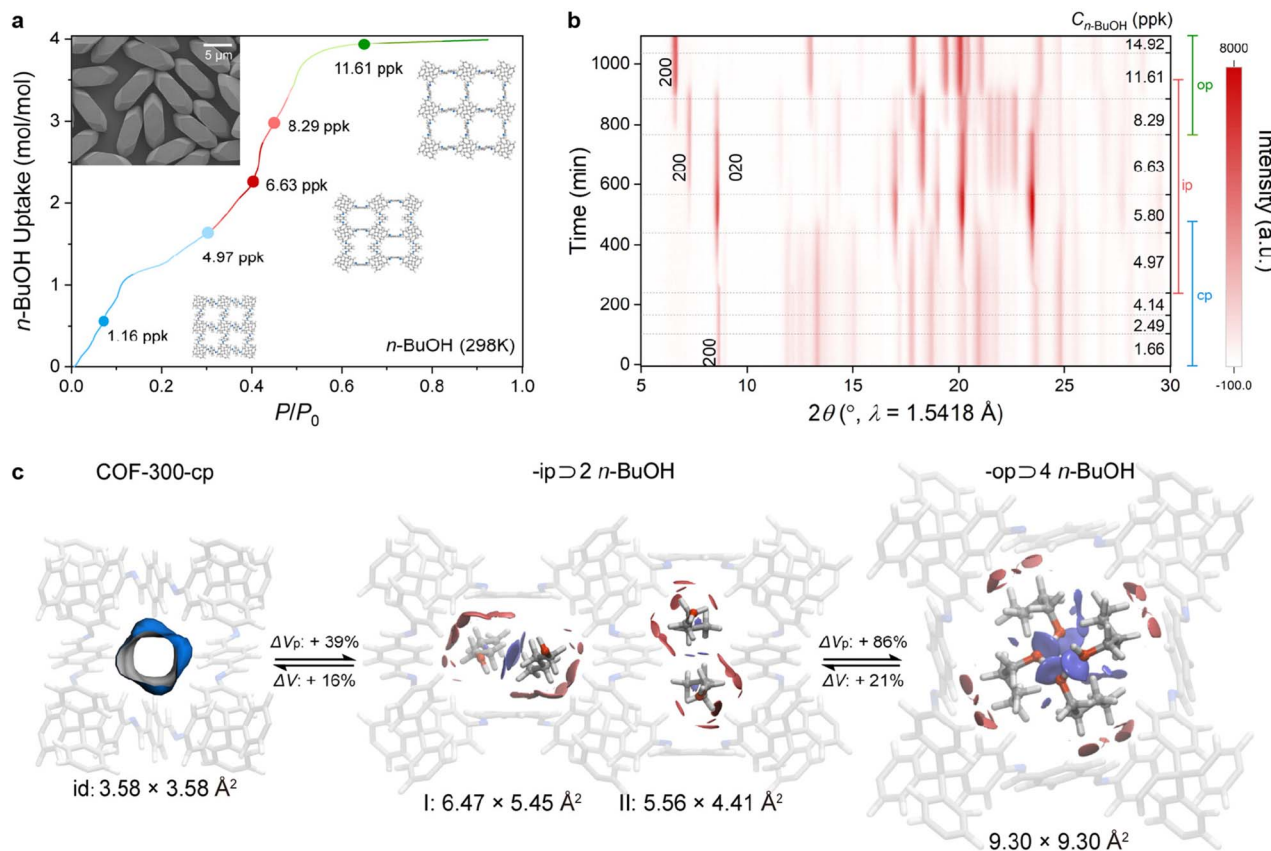


Fig. 5 Guest alignment in the pores of COF-300. (a) *n*-BuOH adsorption isotherm. The colours indicate the cp, ip and op phases, respectively. (b) Corresponding *in situ* PXRD patterns recorded during BuOH adsorption. (c) Single crystal structures of the three COF phases, highlighting the alignment of the *n*-BuOH guest molecules. Reproduced from ref. 86. CC-BY-NC-ND 4.0.

functionalised aldehyde monomers allow for combining electronic and structural changes. COF-301, synthesised by co-condensation of TAM with 2,5-dihydroxyterephthalaldehyde, was found to change its colour from yellow to light brown when the framework contracts upon desolvation.<sup>95,146</sup> When the COF was exposed to water, its colour changed further to dark brown. This effect was explained by an enolimine–ketoenamine tautomerism, where the solvated COF supports the enolimine form, but contraction stabilises the *cis*-ketoenamine. Similar behaviour was also observed for COF-310, which is constructed from a 2,6-dihydroxynaphthalene-1,5-dicarbaldehyde linker.<sup>77</sup>

Combining TAM with an anthracene-based linker yielded the dynamic COF-330 with the photoactive acene moieties in an acceptor–donor–acceptor configuration.<sup>78</sup> The guest-free COF was highly contracted, causing effective fluorescence quenching due to close contacts between the chromophores. Uptake of acetone vapour led to a step-wise expansion of the COF with three observed phases, corresponding to 2, 16, and 20 solvent molecules per unit cell, respectively. These phase changes were accompanied by fluorescence turn-on due to increased anthracene distances and distinct emission spectra for each phase.

Frameworks with **dia** topology can also be realised with other tetrahedral building blocks. Fang *et al.* employed a methoxy-functionalised spiro-bifluorene tetraaldehyde monomer in combination with benzidine-derived linear linkers to construct

a series of non-interpenetrated 3D COFs.<sup>174</sup> The framework dynamics was controlled *via* steric hindrance and the rigidity of the benzidine linkers. Unmodified benzidine proved too flexible and the guest-free COF assumed a contracted microporous structure. The 2,2',6,6'-tetramethylbiphenyl variant, on the other hand, was substantially more rigid and permanently mesoporous. Notably, the 2,2'-dimethylbiphenyl-bridged COF was semi-flexible and showed gate-opening dynamics.

Sun *et al.* constructed **dia** frameworks by incorporating the 6-connected 1,4-phenylenebis(tris(4-formylphenyl)silane) in place of two tetrahedral nodes.<sup>175</sup> The resulting COFs lost their long-range order upon drying, but their crystallinity was recovered by exposure to THF.

### 3.2. 3D COFs with pts topology

Frameworks with **pts** topology are generated by combining tetrahedral with square or rectangular building blocks.<sup>138</sup> Depending on the size and steric demands of the monomers, the COFs can be non-interpenetrated or interpenetrated.<sup>24,176</sup> Due to the combination of two tetratopic nodes of different geometry, **pts** COFs tend to be more rigid than **dia** frameworks and realising dynamic materials requires careful building block design.

Wang *et al.* used the co-condensation of rectangular 1,2,4,5-tetrakis[(4-formylphenoxy)methyl]benzene (TFMB) and



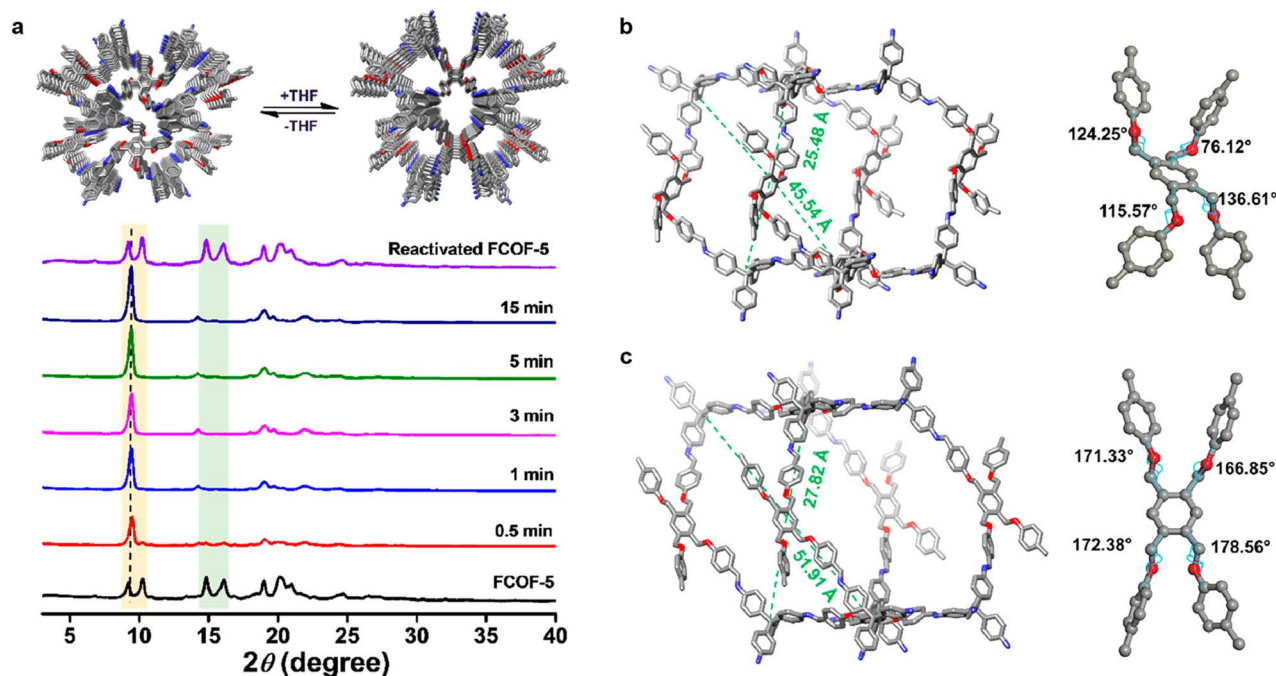


Fig. 6 Dynamics of FCOF-5 based on a flexible building block. (a) Phase transformation upon exposure to THF vapour. (b) Single-crystal structure of the guest-free COF showing the distorted geometry of the flexible moiety. (c) Structure of the expanded THF-filled COF. Reproduced with permission from ref. 80. Copyright 2021 American Chemical Society.

tetrahedral TAM to construct the dynamic FCOF-5 with a six-fold interpenetrated **pts** topology (Fig. 6).<sup>80,94</sup> The TFMB moiety is inherently flexible due to its four  $-\text{CH}_2-\text{O}-$  single bonds. The guest-free FCOF-5 was highly contracted, and single-crystal cRED data showed that this was due to buckling of the TFMB moiety. Upon solvation with THF, the TFMB expanded to a more planar geometry, allowing the COF to assume an *op* configuration. Analysis of the gas-triggered dynamics of this COF *via in situ* PXRD/gas adsorption revealed a single-step gate-opening step upon adsorption of  $\text{CO}_2$ ,  $\text{C}_2\text{H}_6$ , and other C2 and C3 hydrocarbons. Moreover, FCOF-5 was found to possess significantly higher affinity for  $\text{C}_3\text{H}_4$  over  $\text{C}_3\text{H}_6$ , enabling the selective removal of  $\text{C}_3\text{H}_4$  from binary gas mixtures.

### 3.3. 3D COFs with other topologies

While in most cases combining two tetrahedral building blocks yields COFs with **dia** topology, the hexagonal **qtz** topology can be accessible depending on synthesis conditions and building block flexibility.<sup>44–46</sup> Jiang *et al.* combined the pseudo-tetrahedral bimesityl tetra-aniline and bimesityl tetra-benzaldehyde to generate USTB-5 with a three-fold interpenetrated **qtz** topology.<sup>72</sup> This COF showed gate-opening type dynamics with contraction upon solvent removal and reversible expansion upon adsorption of solvents or  $\text{N}_2$ . Notably, the expansion was one-dimensional along the helical axis of the COF, accompanied by a contraction along the other two dimensions. While most **dia** COFs lose their dynamic behaviour upon linkage conversion (see Section 5.2), the imine linkages of USTB-5 could be reduced or oxidised and the framework dynamics was retained. This series of COFs also showed strong

temperature-dependent expansion by up to 8% upon heating from 100 to 300 K.

Dynamic COFs can also be constructed from higher-connectivity nodes. This was achieved by combining an amine-functionalised molecular cage with 2,5-dihydroxyterephthalaldehyde to produce 3D-CageCOF-1 with an interpenetrated **acs** topology.<sup>25</sup> In the dry state, this COF was contracted due to a rotation of the cage moieties, in conjunction with flexing of the linear bridges. Exposure to *N,N*-dimethylformamide (DMF) led to straightening of the bridges and reversible expansion of the framework.

In a different approach, a dynamic 3D COF was constructed from entangled 2D layers.<sup>177</sup> Here, the design strategy was to induce sufficient steric hindrance to prevent  $\pi$ -stacking of the 2D layers, while allowing two sets of layers to form an entangled structure. This COF showed dynamic framework expansion when exposed to THF vapour due to torsion between the entangled layers as well as multiple conformational changes within the 2D layers.

## 4. Dynamic 2D COFs

2D COFs are layered structures with covalent linkages within the 2D sheets and non-covalent interlayer interactions (Fig. 7). Framework dynamics can affect both the in-plane and out-of-plane geometries.

### 4.1. 2D COFs with hcb topology

Honeycomb-like (**hcb**) COFs are typically generated by combination of trigonal and linear or two complementary trigonal



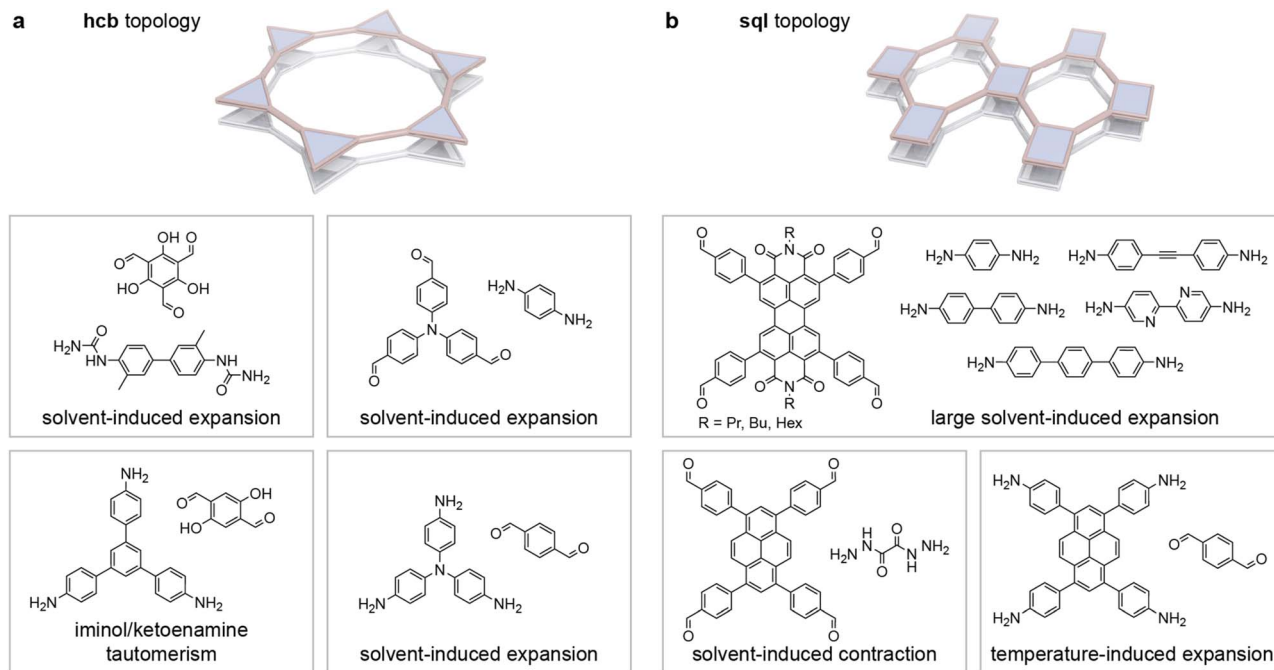


Fig. 7 Illustrations of the topologies of dynamic 2D COFs (top) and the combinations of monomers used for constructing these frameworks (bottom). (a) Hexagonal frameworks with **hcb** topology, (b) rectangular **sql** frameworks.

building blocks. They are mostly low-density materials with close to eclipsed (AA) stacking (alternating AB and ABC layer sequences are less common) and very high porosities.<sup>40,178</sup> While most **hcb** COFs are rigid, there are a few examples of dynamic COFs.

Semi-flexible urea-linked COFs displayed very high crystallinity when immersed in MeCN.<sup>179</sup> Unlike the smaller-pore COF-117, the biphenyl-bridged COF-118 retained its crystallinity upon desolvation. Its unit cell, however, contracted from 36.1 Å to 35.3 Å along *a* and *b*, and expanded from 3.4 Å to 3.8 Å along the stacking direction (*c* axis). These changes were fully reversible upon exposure to MeCN or MeOH vapour.

Similar contraction upon solvent removal was also observed for triphenylamine-based COFs.<sup>180</sup> A comparison of two structural isomers with different orientation of the imine linkages revealed more pronounced dynamics for the tris(4-formylphenyl)amine-based IISERP-COF2, which was attributed to its slightly different geometry and less polarised imines.

Like the hydroxy-functionalised 3D COFs discussed in Section 3.1, the 2,5-dihydroxyterephthalaldehyde-based TAPB-PDA-OH COF showed reversible iminol-to-ketoenamine tautomerism when exposed to water.<sup>181</sup> In this case, however, the re-arrangement of the in-plane linkages led to an expansion of the framework from 28 Å to 32 Å, which, as the COF dried, relaxed to its original position.

#### 4.2. 2D COFs with **sql** topology

Square lattice (**sql**) COFs are obtained by combining square or rectangular nodes with linear linkers, or by polymerising two geometrically compatible square or rectangular nodes. Layer stacking in **sql** COFs follows typically a slightly inclined AA

sequence, leading to straight and accessible pores with a rhombic cross-section.<sup>58,63</sup>

While most pyrene-based COFs are rigid frameworks with very high porosity, linker exchange of an imine-linked tetakis(4-formylphenyl)pyrene/*p*-phenylenediamine COF using oxalylhydrazide afforded the semi-flexible SF-COF.<sup>182</sup> Unlike the parent framework, this COF contracted by about 2 Å along *a* and *b* when immersed in THF.

Dynamic 2D COFs that can be reversibly switched between a non-porous *cp* phase and porous *ip* and *op* phases were realised *via* a “wine rack” COF design (Fig. 8).<sup>81</sup> These COFs consisted of rigid columns of  $\pi$ -stacked PDIs that were interconnected by flexible imine-linked bridges, allowing the frameworks to expand and contract like foldable wine racks. For example, upon exposure to toluene vapour, the *bu*PDI-1P COF achieved up to 40% expansion relative to its *cp* phase. These substantial geometry changes were found to affect also the electronic coupling between the PDI columns, leading to a switch from h-aggregation in the *op* phase to ‘null-aggregates’ with monomer-like behaviour in the *cp* phase COF.

Isostructural extension of these frameworks using longer biphenyl and terphenyl linkers produced a series of strongly dynamic COFs with very large solvent-induced framework expansion.<sup>163</sup> Upon loading with cyclohexane, the PDI-3P COF exhibited an elongation of its *a* axis from 20.4 Å to 35.7 Å, which translated into a record-high volume change of 85% relative to the *cp* phase.

While the above COFs show in-plane expansion or contraction upon guest uptake, their layer-to-layer distances remain relatively unaffected. In contrast, polyhedral crystal films of tetraphenylpyrene-based COFs exhibited pronounced



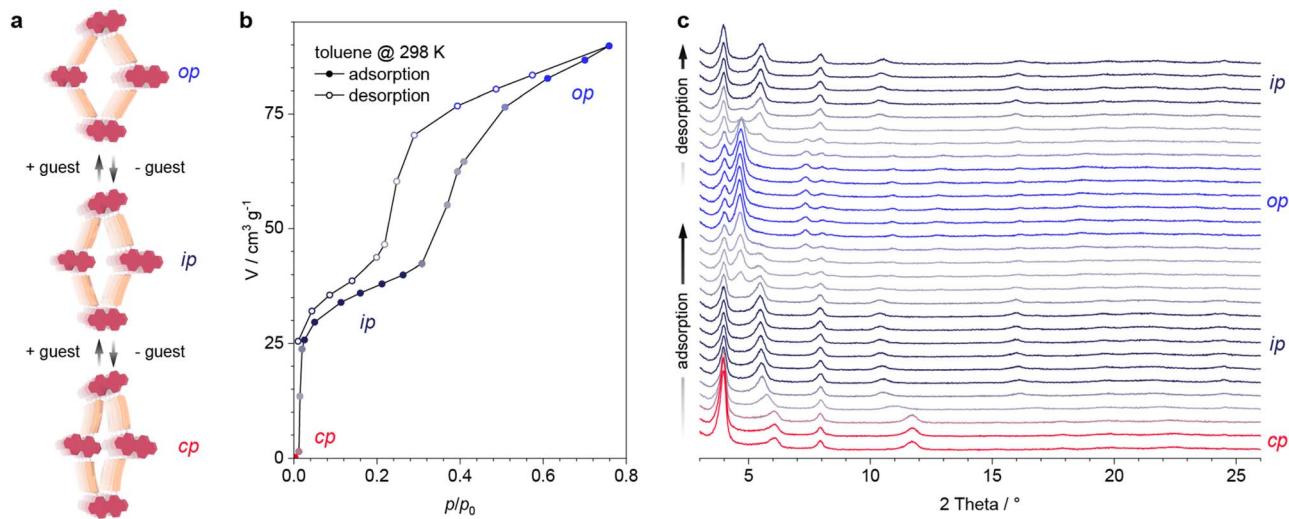


Fig. 8 (a) 2D "wine rack" type dynamic COFs display step-wise pore opening upon guest uptake.<sup>165</sup> (b and c) Toluene vapour adsorption and corresponding *in situ* PXRD patterns of the dynamic *bu*PDI-1P COF.<sup>81</sup> Toluene uptake triggers two phase transformations that appear as steps in the sorption isotherms, accompanied by a shift of the 110 reflection from 6.1° (cp phase) to 5.5° (ip phase) to 4.6° (op phase). Copyright 2024 the authors of ref. 81, under exclusive license to Springer Nature.

temperature-induced and fully reversible expansion of the interlayer distances from 3.76 Å at 50 °C to 3.99 Å at 350 °C.<sup>183</sup> Notably, this temperature-induced dynamics was uniaxial, leaving the in-plane geometry unchanged during the temperature cycles.

#### 4.3. Interlayer sliding

A unique type of framework dynamics found in 2D COFs is the solvent-induced layer sliding. Here, the in-plane geometry and layer-to-layer distances remain largely unchanged, but the stacking pattern changes, typically between eclipsed and inclined (slip-stacked) or serrated configurations.

Studies of triphenylbenzene-based COFs with various linear linkers revealed that the frameworks can lose their long-range order upon solvent treatment, but this can be largely restored by annealing in supercritical CO<sub>2</sub>.<sup>184</sup>

Layer sliding transformations between two crystalline COF phases were first observed for the tetrathiafulvalene-based TTF-DMTA COF.<sup>165</sup> In its guest-free state, this material assumed a slip-stacked arrangement with narrow pores. Solvent uptake led to a re-arrangement of the layers to approximate an eclipsed configuration with increased pore diameter.

On the other hand, solvent-induced interlayer shifting has also been reported for examples where the guest-free COF assumes an AA stacking sequence.<sup>185,186</sup> Here, solvent or gas uptake causes in these cases a reversible phase transformation to a staggered AB configuration.

#### 4.4. Photoswitchable COFs

Photoswitches, *i.e.*, moieties that can be toggled between two isomers with different geometries by light irradiation could be a facile solution for achieving remote control over COF geometries. While most photoswitch-modified COFs reported to date are rigid frameworks in which the photoswitches can be used to

control their porosity,<sup>187,188</sup> small changes of the layer spacing have been achieved in some frameworks.

Dithienylethenes are capable of reversible photocyclization when exposed to UV light. This functionality was successfully incorporated in a dithienylethene-bridged COF.<sup>167</sup> Irradiation with 365 nm light led to cyclisation of the photoswitch from its open to the closed form, concomitant with an increase in electrical conductivity. Since the closed form is more planar, this led to a contraction of the framework along the stacking direction from 6.6 Å to 6.3 Å. This process could be reversed by illumination with 550 nm visible light.

In a different study, an azobenzene-modified COF was found to expand slightly when the photoswitches isomerised to their more bulky *Z* configuration.<sup>189</sup>

## 5. Origins of the framework dynamics

Most COFs are rigid frameworks with permanent porosity, which can adsorb and release guests without changing their crystal structures. The ability of dynamic COFs to adapt their geometries to guest molecules reversibly while fully retaining their crystallinity requires well-engineered framework flexibility. Dynamic COFs must be sufficiently flexible to respond to external triggers with well-defined structural changes, but at the same time robust enough to avoid collapse of the pores and amorphization upon desolvation. This carefully balanced flexibility is usually achieved with a combination of factors, which we will discuss in the following.

### 5.1. Distortion of tetraphenylmethane (TPM) nodes

TPM-based building blocks are the most prominent monomers for constructing dynamic *dia* net COFs such as COF-300. These frameworks are composed of interconnected adamantane-like cages with 10 TPM moieties located at the corners (Fig. 9a).



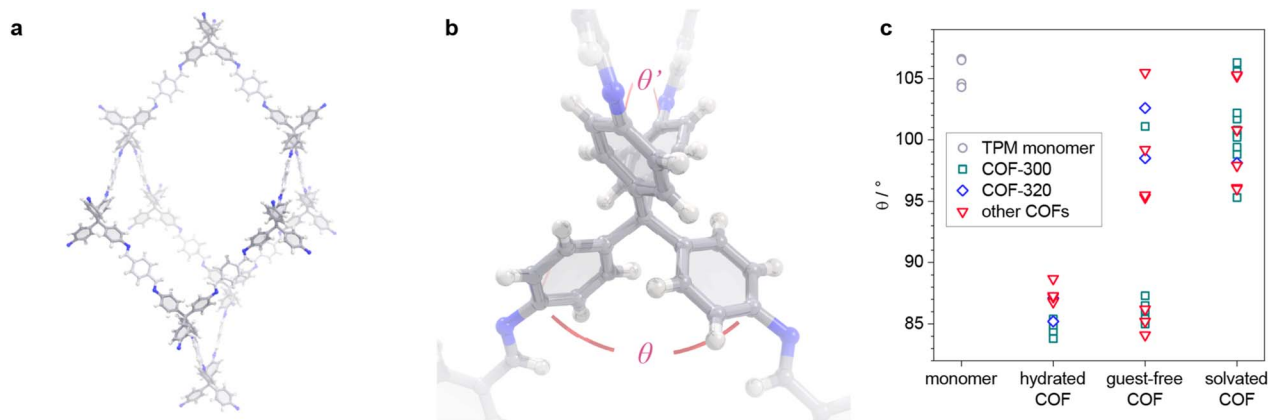


Fig. 9 (a) Adamantane-like cage of COF-300 with ten TPMs at the corners. Interpenetrated lattices are omitted for clarity. (b) Magnified view of the TPM moiety and illustration of the node angle  $\theta$ , measured between the outermost carbon atoms. (c) Node angle  $\theta$ , extracted from crystal structures of TPM-based dynamic COFs (green, blue, red) and molecular crystals (grey).

A key feature of the TPM moiety is its flexibility about the central  $sp^3$  carbon atom. The four  $\sigma$  bonds allow not only for a semi-confined rotation of the phenyl rings, but also for considerable distortion of the local geometry.

Studies of COF-300 synthesised under different conditions revealed an interpenetration isomerism with 5-fold and 7-fold interpenetrated lattices.<sup>168</sup> Interestingly, the number of interpenetrated lattices had a stark effect on the geometry of the TPM nodes and the adamantane cages. In **dia-c5** COF-300, the angles of the adamantane cages were 103.4° and 112.6° for the smaller and larger angle, respectively, which is close to ideal tetrahedral geometry of 109.5°. The adamantane cages of **dia-c7** COF-300, on the other hand, are highly distorted to 66.9° and 134.1°, respectively, which has been attributed to decreasing nonbond energy and van der Waals forces.

Single crystal structures of various solvated and hydrated COF-300 samples showed very similar geometries, where the solvent-loaded COFs approximate ideal tetrahedral geometry, whereas the water-containing COFs feature highly distorted adamantane cages (Fig. 4).<sup>22,164,169</sup> These observations are not limited to COF-300. The adamantane cages in isostructural frameworks such as the biphenyl-bridged COF-320 or functionalized COFs such as COF-301 exhibit very similar angles.

The angles measured between the nodes of the adamantane cages, however, are influenced by at least two factors, that is the geometry of the TPM moieties as well as the orientation and angles of the interconnecting imine bonds (see discussion below). We analysed the reported crystal structures of 12 TPM-based dynamic COFs and determined the node angles  $\theta$  and  $\theta'$ , measured between the outermost carbon atoms of the approximately face-to-face oriented phenyls (Fig. 9b and c).<sup>21,22,77–79,86,87,95,164,168,169,172</sup> In most highly symmetric COFs  $\theta = \theta'$ , but there are some exceptions.<sup>95,172</sup> In molecular crystals of TPM or TAM, the deviation from ideal tetrahedral geometry is small with  $\theta \approx 105^\circ$ .<sup>190,191</sup> The TPM moieties in fully solvated or gas-loaded COFs adopt similar geometries with  $\theta$  ranging from 95° to 106°, depending on the specific COF and guest. In hydrated COFs, on the other hand, the TPM nodes adopt

a heavily distorted geometry with  $\theta$  around 85° for all reported structures. TPMs in the guest-free, activated COFs can adopt two different geometries with  $\theta$  either being around 85° like in the hydrated COFs, or  $\theta$  ranging from 95° to 105°, like in the solvated COFs. Interestingly, which of these two TPM configurations is present depends not only on the chemical structure of the respective COFs, but can be synthesis-dependent. In particular for COF-300, both geometries have been found in guest-free single crystals (Fig. 9c, green squares). Synthesis *via* a ventilation-vial protocol at 65 °C furnished COFs with strongly distorted TPM nodes, while the modulator-aided crystallisation at room temperature resulted in more tetrahedral TPM geometries with  $\theta = 101^\circ$ .<sup>22,164</sup>

## 5.2. Imine bond rotation

In imine-linked dynamic COFs, the conformational changes of the imine bonds provide a key contribution to the framework flexibility and dynamics. Rotation of the  $-C=N-$  moiety leads to a pedal-like motion that can narrow or widen the COF pores depending on the imine orientation.<sup>79</sup> Systematic studies on COF-300 single crystals revealed that the terephthalic diimine bridge units can toggle between *anti*-periplanar, *syn*-periplanar, and anticlinal configurations, leading to crystallographic symmetry-breaking along with framework expansion or contraction.<sup>86</sup> Throughout the conformational transition, the dominant interaction within the framework changed from node–edge to both node–node and edge–node interactions, demonstrating the flexibility of the moieties within the dynamic framework. In the larger homologue, COF-320, framework contraction is facilitated by a bridge geometry where both imines share almost the same orientation with a small torsion angle of 38° (Fig. 10), leading to buckling of the biphenyl unit.<sup>172</sup> The very large solvent-induced expansion of this COF is achieved by rotation of the imines to a torsion angle of 113°, causing the biphenyl to straighten and increasing the node-to-node distances from 21.8 to 23.2 Å.

Imine rotation requires sufficient space between interpenetrated lattices or COF layers. The interpenetrated lattices of



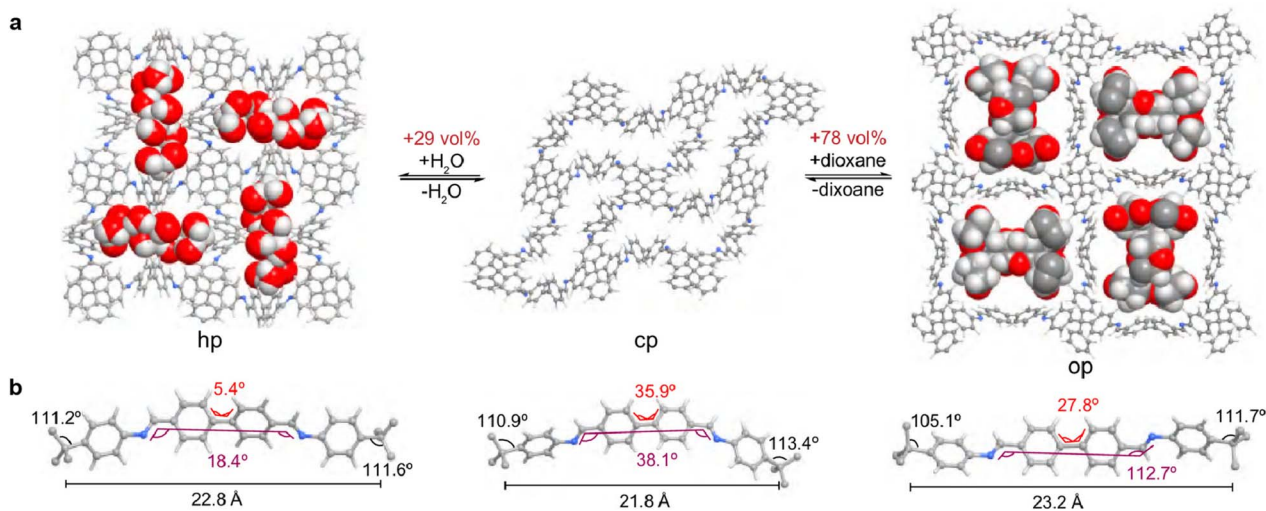


Fig. 10 (a) Water- and solvent-induced geometry changes of COF-320-V. (b) Guest-induced conformational changes of the imine bonds and biphenyl linker. Reproduced from ref. 172. CC BY-NC-ND 4.0.

dia net 3D COFs are typically displaced by about 8 Å along the crystallographic *c* axis, allowing for relatively unimpeded imine rotation. Most 2D COFs, however, are closely  $\pi$ -stacked with layer-to-layer distances around 3.5 Å and only small (if any) lateral offsets below 1.5 Å.<sup>40,58</sup> Hence, 2D COFs are usually rigid with permanent porosity.

An exception to this is the recently developed family of PDI-based dynamic 2D COFs, where a substantial lateral offset provides the  $-\text{Ph}-\text{C}=\text{N}-(\text{Ph})_n-\text{N}=\text{C}-\text{Ph}-$  ( $n = 1-3$ ) bridge units with sufficient flexibility to enable the imine rotation (Fig. 11).<sup>81,163</sup> Consequently, these COFs are highly dynamic with two-step pore opening and solvent-induced expansions of up to 85% relative to the cp phase.

The importance of revolving imine bonds for the framework dynamics is further highlighted by studies where imine bonds

were reduced to amines and formamides. It would be expected that the greater flexibility of the secondary amine linkages would translate into highly flexible COFs. However, integrating amine linkages into otherwise rigid COFs did not produce dynamic frameworks.<sup>192,193</sup> Imine reduction starting from the dynamic COF-300 furnished the similarly dynamic COF-300-AR.<sup>194</sup> But the further conversion into formamides caused a rigidification of the COF despite their otherwise almost identical structure.

In two further studies, reduction or oxidation of the imine linkages both resulted in a rigidification of the respective COFs, which was ascribed to the hindered rotation of the amines or amides.<sup>72,170</sup>

### 5.3. Flexible building blocks

Additional flexibility can be introduced *via* suitably designed flexible building blocks. While pts COFs are typically rigid with permanent porosity, the introduction of a flexible 1,2,4,5-tetra(phenoxymethyl)benzene (TFMB) building block comprising four  $\sigma$ -bonded  $-\text{CH}_2-\text{O}-$  moieties yielded the dynamic FCOF-5 (Fig. 6).<sup>80,94</sup> Here, the framework dynamics is due to buckling/stretching of the TFMB unit.

In a similar approach, Cooper *et al.* used an organic cage as a triangular prism node to construct a cage-based 3D COF (Fig. 12).<sup>25</sup> This COF crystallised with a 2-fold interpenetrated acs topology. Owing to its slightly flexible ether-linked cage node and conformational changes of the imine linkages, it exhibited reversible dynamic behaviour, switching between a contracted small-pore and a large-pore structure upon exposure to solvents such as DMF.

### 5.4. Framework topology and symmetry

Besides the precise control of the local or short-range flexibility *via* the strategies discussed above, the second key component

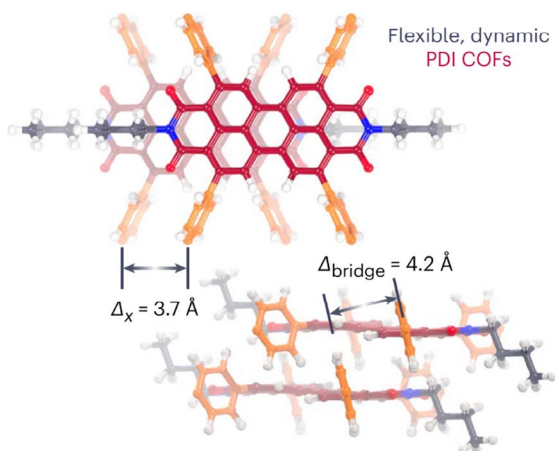


Fig. 11 Lateral offset between COF layers generates dynamic 2D COFs. PDI moieties are strongly slip-stacked, breaking the  $\pi$ - $\pi$  interactions between adjacent linear bridge units (highlighted in orange). Copyright 2024 the authors of ref. 81, under exclusive license to Springer Nature.



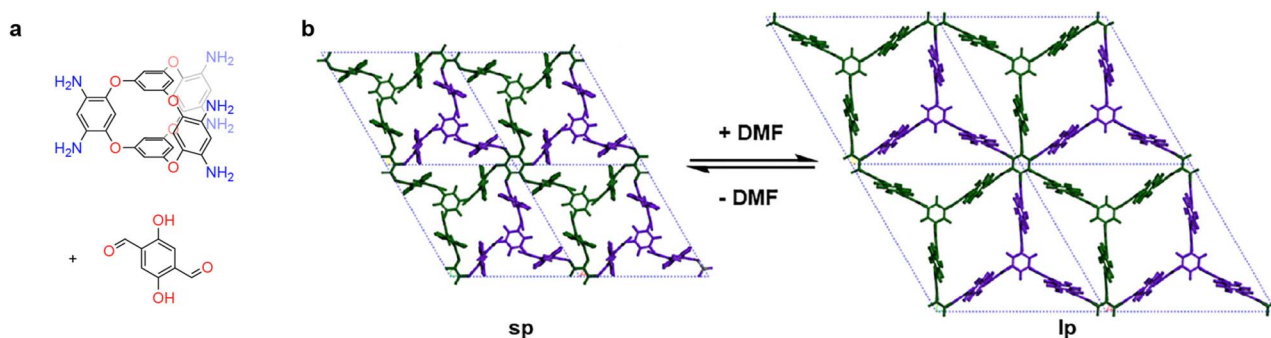


Fig. 12 (a) Chemical structures of the cage monomer with flexible ether moieties (red) and the linear 2,5-dihydroxyterephthalaldehyde linker. (b) The cage-based 3D-CageCOF-1 can be toggled between its small-pore (sp) and large-pore (lp) structural isomers by loading and removal of DMF, respectively. Adapted from ref. 25. CC-BY.

for designing dynamic COFs is the framework topology and symmetry.

Chemical bonds possess very high resistance towards compression or elongation, whereas the energy barriers for bending or twisting deformations are much lower. Thus, dynamic COFs require topologies that allow for volume changes solely *via* bending of flexible moieties without substantial compression or elongation.

In 2D COFs, these criteria are met by the **hcb** and **sql** topologies (Fig. 13a), but not by Kagome (**kgm**) nets,<sup>28,57</sup> whose triangular components translate any shear stress into compressive forces. Accordingly, several examples of dynamic 2D COFs with **sql** and **hcb** structure have been reported, but no dynamic **kgm** COFs.

The same considerations also apply to 3D COFs. This field is dominated by **dia** frameworks, where the main mode of framework dynamics is the distortion of the adamantane cages (Fig. 4). In contrast, the more interconnected **pts** networks require highly flexible building blocks to exhibit framework dynamics, and the dynamic volume changes are significantly smaller (Fig. 13b, purple). Truss-like topologies such as **bor** or **scu** nets have so far only produced rigid frameworks.<sup>8,135</sup>

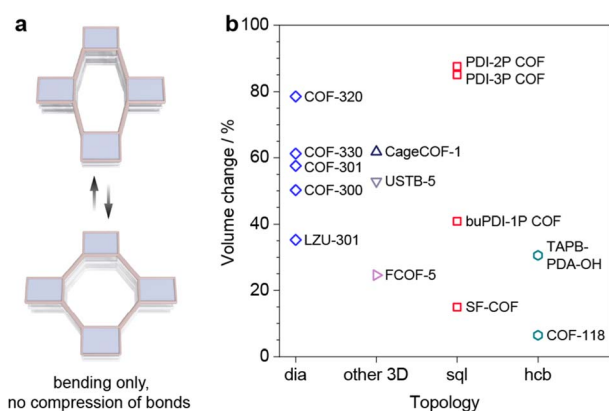


Fig. 13 (a) Pore expansion of an **sql** framework can be achieved by bending of the bridge units, without compression or elongation. (b) Dependence of dynamic framework expansion, calculated relative to the volume of the respective cp phase, on the COF topology.

The influence of the topology is further illustrated by comparing COFs with isostructural lattices but different interpenetration patterns. Deng *et al.* constructed COF-308, a COF-300 analogue from TAM and 2,3-dimethoxyterephthalaldehyde.<sup>195</sup> The interpenetrated **dia** lattices of COF-300 share the same orientation and are stacked along the *c* axis, allowing for synchronous distortion of all adamantane cages. Conversely, COF-308 crystallises with an uncommon [4 + 2] interpenetration, where two lattices were rotated by 180°. This was found to hinder the simultaneous adamantane cage distortion, rendering COF-308 rigid and permanently porous.

Framework dynamics requires the concerted motion of all flexible moieties within a crystal domain, and effective synchronisation could be supported (or hindered) by the framework geometry. In order to derive design rules for highly dynamic COFs, we compared the most dynamic COFs reported to date with different topologies and symmetries.<sup>25,72,78–81,86,95,163,164,172,179,181,182</sup> We found that both the majority of examples and the strongest unit-cell changes were associated with two topologies – the 3D **dia** and the 2D **sql** lattices (Fig. 13b). It is noteworthy that the node monomers employed in constructing these COFs exhibit only two-fold rotational symmetry (Fig. 3b and 7), and all nodes share the same orientation in the respective frameworks. This reduces the crystal symmetry, resulting in a preferred direction for guest-triggered distortions of flexible moieties and thereby the desired synchronisation. Indeed, the highly dynamic PDI-based **sql** COFs expand along the *a* axis, whereas the *b* axis remains relatively unaffected upon guest uptake. Likewise, the adamantane cages of **dia** COFs deviate from tetrahedral symmetry (Fig. 4 and 9), causing a preferred contraction along *c*, accompanied by expansion along the other two dimensions.

In contrast, **hcb** lattices have three-fold or six-fold rotational symmetry, resulting in multiple possible directions for guest-induced expansion/contraction, which could hinder the concerted geometry changes. This could be one of the reasons for the small guest-induced volume changes of these frameworks despite their very large void fractions. The importance of concerted framework flexibility is further corroborated by the



observation that **hcb** COFs based on flexible building blocks can be rigid and highly porous.<sup>196</sup>

### 5.5. Local flexibility of woven and entangled COFs

COFs containing metal complex nodes can form interwoven or entangled networks of low-dimensional threads.<sup>23,197</sup> These frameworks can be subsequently demetalated and remetalated to change their mechanical properties and porosities.

In the demetalated state, these materials are held together solely by the mechanical interlaced threads and non-covalent interactions. This enables substantial local flexibility and thereby the “adaptive inclusion” of larger guest molecules.<sup>166</sup>

In another work, Yaghi *et al.* constructed 3D COFs from interlocking 1D square ribbon.<sup>198</sup> In the demetalated form, the individual 1D ribbons are held together only by mechanical interlocking of rings, which allows their collective movement to produce a narrow-pore form. Adsorption of THF vapour resulted in a gradual re-opening of the COF pores and the COF adopted a geometry that was close to the structure of the metalated COF.

## 6. Applications of dynamic COFs

Dynamic COFs are an intriguing materials platform that can be tailored towards applications in several different fields. Emerging applications as adsorbents or membrane materials utilize their adaptive pore size and shape, whereas future applications as sensor materials make use of geometry-dependent electronic coupling within the frameworks and host-guest interactions.

### 6.1. Adsorption and separation

Dynamic COFs can be high-capacity sponges for the adsorption of pollutants. A COF constructed from an extended adamantane-based tetrahedral node was employed as a high-capacity adsorbent for iodine vapour.<sup>199</sup> At 75 °C, 1 g of this COF was able to adsorb 4.7 g I<sub>2</sub>. The high capacity was ascribed to the formation of a charge transfer complex between the iodine and the pore walls as well as the structural flexibility, allowing the COF to adapt its pore geometry to the iodine guest while fully retaining its connectivity. Extension of this concept to acetylene- and diacetylene-bridged 3D COFs yielded materials with adsorption capacities of up to 0.59 g g<sup>-1</sup>.<sup>200</sup>

The selective adsorption capacity of dynamic COFs has also been applied for the separation of mixtures of solvents or gases. COF-300 variants with multiple functionalised linkers have been employed in the separation of benzene and cyclohexane vapours.<sup>173</sup> In breakthrough experiments benzene was retained by the COFs with selectivity coefficients of up to 8.3 due to its stronger adsorption. COF-300 showed also preferential adsorption of C<sub>2</sub>H<sub>2</sub> over C<sub>2</sub>H<sub>4</sub>, suggesting a potential for application in gas separation.<sup>194</sup>

The technologically relevant separation of trace amounts of C<sub>3</sub>H<sub>4</sub> from C<sub>3</sub>H<sub>6</sub> was successfully demonstrated with the **pts** net FCOF-5.<sup>94</sup> This process is a key step in the production of polymer-grade C<sub>3</sub>H<sub>6</sub> and adsorption-based separation could be an energy-efficient alternative to current technology. Here, the

different gate-opening behaviours in response to the two gases despite their similar size and kinetic diameters led to a high adsorption selectivity of 11.6 for C<sub>3</sub>H<sub>4</sub> and thus efficient retention in breakthrough experiments.

### 6.2. Photocatalysis

The conformational flexibility of dynamic COFs can also be employed to fine-tune their photocatalytic activity. This concept has been illustrated for the photocatalytic oxidation of iodine.<sup>201</sup> Single crystals of COF-300 were treated with various solvents to obtain a series of COF geometries with differently twisted diimine linkers, allowing for optimisation of the singlet-triplet energy gap to boost the intersystem crossing. The resulting better charge carrier separation led to improved iodine oxidation performance.

### 6.3. Optoelectronic properties and sensing

Taking advantages of the structural dynamics of 3D COFs, Zhang *et al.* reported the synthesis of an anthracene-modified dynamic 3D COF with interpenetrated **dia** topology (Fig. 14).<sup>78</sup> In the guest-free state, this COF was strongly contracted, leading to efficient fluorescence quenching of the anthracene moieties. Upon exposure to acetone and dioxane vapours or butane gas, the material showed a step-wise expansion and adaptive guest inclusion, accompanied by fluorescence turn-on. Owing to host-guest interactions, the emission spectra were sensitive to the specific guests and their concentration.

Interactions between semiconductor moieties in solids can lead to h-type or j-type aggregation or mixed forms, depending on the intermolecular geometries. While this is generally dictated by the crystal structure, dynamic COFs are capable of substantial geometry changes. Indeed, the switchable geometry of 2D PDI COFs with molecular displacements of up to 10 Å upon toggling between the respective cp to op phases gives rise to geometry-dependent absorption and emission spectra.<sup>81</sup> While the op COFs are strongly h-aggregated due to their closely-packed PDI columns, this effect is compensated by interactions between these columns in the cp COFs due to the shortened distances. As a result, the cp phase COFs approximate “null-aggregates” with monomer-like absorption and emission spectra. These findings highlight the potential impact of dynamic frameworks across multiple research fields.

Fang *et al.* developed a piezochromic 3D COF with donor-acceptor moieties composed of a twisted electron-rich triphenylamine rotor linked to an electron-deficient benzimidazole.<sup>202</sup> Due to constrained vibrations, this material showed aggregation-induced emission (AIE) under mild pressure below 1 GPa, followed by aggregation-caused quenching (ACQ) at higher pressures. This was accompanied by a continuous and reversible red-shift of the emission maximum from 500 nm to 687 nm. Similar piezochromic fluorescence behaviour has also been observed for bicarbazole-based 3D COFs.<sup>45</sup>

Hydroxy-modified dynamic 2D and 3D COFs have been found to exhibit fully reversible colour changes upon water adsorption.<sup>77,95,181</sup> This behaviour has been attributed to an enolimine-ketoenamine tautomerism that is facilitated by the



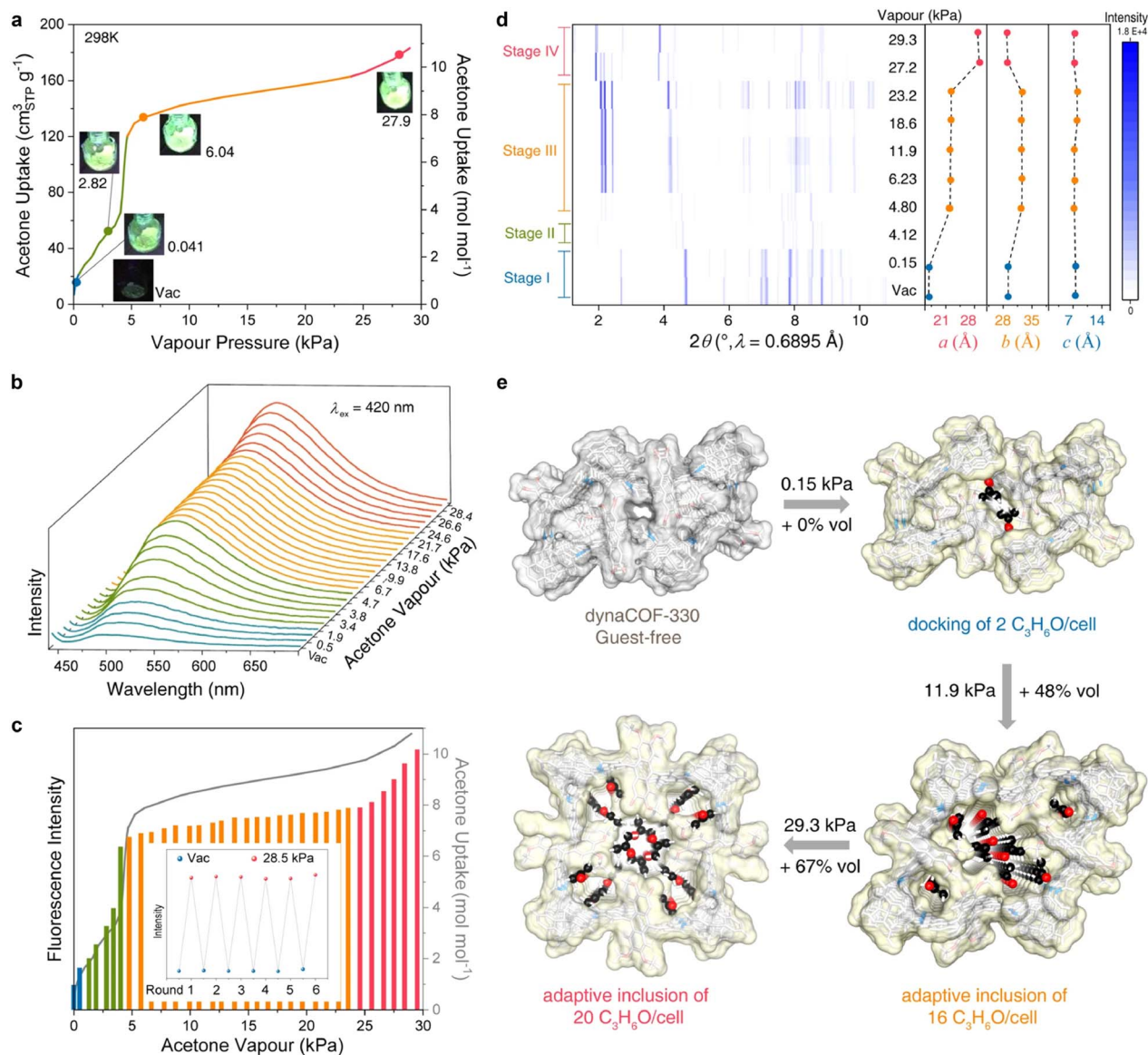


Fig. 14 (a) Acetone adsorption triggers a fluorescence turn-on in the anthracene-containing COF-330. (b) Evolution of the fluorescence spectra. (c) Correlation between emission intensity and acetone uptake. (d) Synchrotron PXRD data and extracted lattice parameters showing four different COF phases. (e) Evolution of the crystal structure during adaptive inclusion of various numbers of acetone molecules per unit cell. Reproduced from ref. 78. CC-BY-NC-ND 4.0.

structural contraction of the COFs. As this process is selective to water and distinct from the solvatochromic colour changes induced by adsorption of other solvent vapours,<sup>16,181</sup> these COFs can act as colorimetric water sensors.

#### 6.4. Mechanochemical actuation

Dynamic COFs could serve as mechanochemical actuators that translate the geometry changes of individual crystallites into macroscopic displacements. This concept was first demonstrated using particles of the flexible FCOF-5 dispersed in a polyvinylidene fluoride (PVDF) matrix.<sup>80</sup> The as-prepared film was rolled up due to the contraction of the guest-free COF, but straightened reversibly and repeatably when exposed to THF vapour.

This concept was further extended to light-operated actuation by embedding a photoresponsive acylhydrazone-linked COF into a polyethyleneglycol (PEG) matrix.<sup>203</sup> Illumination of the COF/PEG film with UV light triggered the  $E \rightarrow Z$  isomerisation of the photoswitches, resulting in a contraction of the COF. Since most light was absorbed close to the illuminated surface, the contraction was stronger on that side, causing the bending of the composite film. This process was fully reversible upon illumination with blue light or treatment at 100 °C.

## 7. Conclusion and outlook

Dynamic COFs are a fascinating family of soft porous crystals that have emerged from being a chance find to a class of COFs



with carefully engineered flexibility and designed structural, catalytic, and electronic properties. While most dynamic COFs to date are based on diamond-like topologies, the design space for soft porous COFs is rapidly expanding to a multitude of 3D and 2D topologies. The discovery of new dynamic COFs so far has predominantly been driven by experimental studies, but future theoretical models could allow for identifying the most promising framework candidates *in silico*, thus significantly accelerating the materials development. In particular, quantitative metrics such as the energy barriers for expansion/contraction and a detailed understanding of the interactions between framework and guest molecules could provide important guidelines for designing new dynamic COFs. With a rapidly expanding materials basis and the recent insights into their atomic structure and origins of the framework dynamics in hand, new materials can be tailored for diverse applications. Potential impact of the new material ranges from economically important uses in gas separation and monomer purification to future technologies including the topochemical control of chemical reactions, adaptive sensing, spin-optoelectronics, and soft robotics.

## Author contributions

LZ and FA performed the literature review and data analysis, and wrote the manuscript. FA supervised the project.

## Conflicts of interest

There are no conflicts to declare.

## Data availability

No primary research results have been included and no new data were generated or analysed as part of this review.

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