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#### Introduction

The modular nature of metal-organic frameworks (MOFs) has been one of the main motivations behind the broad research interest in this class of solids in the past several decades.1-5 MOFs can be constructed with predetermined architectures by judiciously selecting molecular building blocks, *i.e.*, organic ligands and metal atoms or clusters of appropriate geometries. This approach, known as reticular chemistry, has been demonstrated powerfully by the construction of large families of isoreticular MOFs in which a single building block is substituted by others of the same connectivity and geometry, ultimately resulting in structures that share the same network topology, but show predictable differences in pore size and functionality.<sup>6-9</sup> However, in some cases, MOFs adopt different network topologies even though they are constructed using identical molecular building blocks. This phenomenon is known as framework isomerism<sup>10-12</sup> and is exemplified by groups of MOFs such as MIL-101 (mtn network) and MIL-88B (acs network),<sup>13,14</sup> UiO-66 (fcu) and EHU-30 (hex),<sup>15</sup> and MOF-177-mNH<sub>2</sub> (qom), MOF-155 (pyr), and MOF-156 (rtl).<sup>16</sup>

Typically, distinct framework isomers are favored under different crystallization conditions, and these differences are utilized in synthesizing phase pure isomeric frameworks. In the case of the **pcu** and **kag** framework isomers of the archetypal "pillar-layered" MOF, **DMOF-1**, the **kag** structure is favored

# Ligand cross-links as a design element in oligo- and polyMOFs†

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Metal–Organic Frameworks (MOFs) constructed using cross-linked oligomeric or polymeric ligands (oligoMOFs and polyMOFs respectively) have so far relied on a handful of canonical structural blueprints, in which the cross-links have not played a significant role in determining structure. In this study, we show that cross-links between terephthalate ligands in dabco-based Zn-MOFs (DMOFs) can exert control over the overall phase landscape of resulting oligo- and polyMOFs. We find that cross-links can direct the overall topology of the resulting MOF (**pcu** vs. **kag**) based on their length or rigidity, and can influence the phase transformation behavior of the **pcu** network. We also show the first example of tethered ligand dimers adopting a different MOF structure to the analogous trimer and polymer. Understanding the influence of cross-links on the formation of these MOFs will help guide the design of future MOF–polymer hybrid materials.

under kinetically controlled conditions, while the pcu structure is favored under thermodynamically forcing conditions. Following the discovery of each phase by Kim et al. and Chun et al.,<sup>17,18</sup> work by Kitagawa et al. has shown that the formation of the triangular structural subunits of the kag network is initially favored by the constituent Zn(II) paddlewheels and terephthalate (bdc<sup>2-</sup>) ligands over the **pcu** network due to steric considerations (Fig. 1(a-d)).19 Under kinetically controlled conditions, these triangular subunits act as nuclei for the growth of the kag framework. However, the extended pcu structure is energetically favored over kag, and is obtained upon the provision of sufficient thermal energy and reaction time. These differences were utilized by the groups of Verpoort and Walton to develop a rapid room temperature synthetic route to kag-DMOF-1, while also observing that the use of certain solvents instead favored the formation of pcu-DMOF-1 under the same conditions.<sup>20,21</sup> Additionally, Verpoort et al. have shown that solvents such as MeOH can mediate the transformation of kag-DMOF-1 to the thermodynamically favored pcu-DMOF-1 by simply soaking in the solvent at room temperature.22 Besides these isomeric structures, DMOF-1 also exhibits distinct phases of the pcu isomer through flexibility. These phases involve distortions of the framework induced by interactions with various guest molecules such as DMF, benzene, and isopropanol. The relationships between these phases and topologies is summarized in Fig. 1(e).

Numerous studies have explored the effect of introducing substituent groups to the terephthalic acid linker in **DMOF** analogues, especially with respect to modulation of the adsorption-induced phase change behavior of the resulting frameworks.<sup>23-30</sup> However, despite the variety of functional variants that have been made, the introduction of additional

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<sup>&</sup>lt;sup>†</sup> Electronic supplementary information (ESI) available: General experimental details, synthetic procedures for all ligands and MOFs, adsorption data, Pawley refinement data, <sup>1</sup>H digestion NMR data, Fig. S1–S60, and Tables S1–S4. See DOI: https://doi.org/10.1039/d4sc06109h



Fig. 1 Crystal structures of (a and b) pcu-DMOF-1 and (c and d) kag-DMOF-1; (e) schematic representation of the phases of DMOF-1 upon use of different synthetic conditions or other stimuli.

substituents to the H<sub>2</sub>bdc linker has not been reported to yield the kag structure, which Hungerford and Walton attribute to steric constraints.21

Recent work from the laboratories of Xiao, Johnson, He, Zhou, Cohen, and others, has explored the outcomes of incorporating flexible tethering groups between conventional ligands, resulting in oligomeric (oligoMOF) or polymeric (polyMOF) materials.<sup>31-42</sup> These tethers are sufficiently flexible to allow the retention of the overall network structure of the analogous untethered "parent" MOF, but can, in principle, impose constraints on the relative distance and orientation between the tethered bdc<sup>2-</sup> ligands. OligoMOF analogues of materials like IRMOF-1 (MOF-5), NOTT-101, and MOF-74 have been synthesized using this approach, which show modified properties owing to the incorporation of the tethering alkyl chains, such as modified sorbate uptake or exploitable surface functionality.<sup>31,32,41,43</sup> Notably, Xiao et al. showed that tether incorporation in an expanded MIL-53 analogue could modulate its phase change behavior. The tether stabilized the large-pore phase of the material, which is unfavored at low guest loadings in the untethered "parent" MOF.37

The use of ligands linked into polymers through repeating cross-links in a similar manner yields polyMOFs, which also typically adopt canonical MOF structures. Studies on systems such as IRMOF-1 and UiO-66 emphasize the versatility of these systems with respect to the polymer chains incorporated, without altering the overall crystalline lattice.31,32,44 In the examples reported so far, dimeric, trimeric, and polymeric tethers have adopted the same framework structure when combined with metal precursors under fixed conditions, and the number of repeating units has not been a factor in determining the structure adopted.

Despite some indications in previous studies that tether incorporation can result in unidentified phases, and that tether length can influence framework ordering relative to a single parent structure, the potential of tethers to influence the selection of competing structures has not been studied yet. In this work, we study the effects of joining terephthalic acid linkers with flexible alkyl chains and rigid xylyl spacers, in place of unmodified terephthalic acid in the synthesis of DMOF-1. We also study the impact of changing the number of repeating units on structure selection. The observed effect of ligand crosslinking on topology selection and phase transformations shows that flexible tethers may act as hitherto unstudied crystal engineering elements in the design and synthesis of MOFs, opening up a new chemical space for MOF discovery.

#### Results and discussion

Tethered oligomeric and polymeric H<sub>2</sub>bdc ligands were prepared according to reported procedures (see ESI<sup>†</sup>). These ligands feature H<sub>2</sub>bdc groups tethered using ether linkages by flexible *n*-alkyl chains of varying length, **butyl(bdc)**<sub>2</sub>, pentyl(bdc)<sub>2</sub>, hexyl(bdc)<sub>2</sub>, and heptyl(bdc)<sub>2</sub>; relatively rigid xylyl groups with similar numbers of carbon atoms between ether oxygens: o-xylyl(bdc)<sub>2</sub>, m-xylyl(bdc)<sub>2</sub>, and p-xylyl(bdc)<sub>2</sub>; a trimeric linker, pentyl<sub>2</sub>(bdc)<sub>3</sub>; and polymeric linkers with npentyl and *n*-heptyl spacers: **pbdc-5a** and **pbdc-7a** (Fig. 2). We use the above terms to refer to cross-linked ligands in both protonated and fully deprotonated states. Polymer formation in the cases of pbdc-5a and pbdc-7a was confirmed by MALDI-TOF MS (Fig. S1 and S2<sup>†</sup>). Oligomeric ligands were combined with zinc nitrate hexahydrate and 1,4-diazabicyclo[2.2.2]octane (dabco) in DMF and heated under solvothermal conditions using a procedure optimized for the synthesis of the parent pcu-DMOF-1 (ESI<sup>†</sup>). Previously reported synthetic difficulties associated with the synthesis of polyDMOFs were overcome by



Fig. 2 The cross-linked terephthalic acid ligands chosen for the construction of oligo- and poly-DMOFs.

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modifying the synthetic procedure, allowing a precipitate to form upon mixing reactants, and subjecting the suspension to solvothermal conditions without filtering the solids out.<sup>45</sup> The parent **kag-DMOF-1** was synthesized using the "rapid" procedure reported by Hungerford and Walton.<sup>21</sup> In order to keep the proportion of  $Zn^{2+}$ , dabco, and  $bdc^{2-}$  units identical across reactions with various tethered ligands, the number of moles of dimeric ligands (which contain two H<sub>2</sub>bdc units per formula mass) was halved relative to the procedure using untethered H<sub>2</sub>bdc, and the number of moles of pentyl<sub>2</sub>(bdc)<sub>3</sub> was reduced by a factor of three. The number of moles of polymer ligands was not changed, since they contain one bdc unit per formula unit.

Polycrystalline products were obtained from these reactions and were characterized by powder X-ray diffraction (PXRD), N<sub>2</sub> physisorption (at 77 K), and <sup>1</sup>H NMR (after digestion of the solid in acid). Upon comparison of the PXRD patterns obtained from the alkyl-tethered DMOFs, we find that although these reactions were carried out under identical conditions, the crystal structures adopted are clearly distinct (Fig. 3). The patterns shown by butyl(bdc)2-DMOF-1 and pentyl(bdc)2-DMOF-1 closely match the calculated pattern for kag-DMOF-1 with a characteristic  $2\theta$ peak at ca. 4.7°, whereas that shown by heptyl(bdc)<sub>2</sub>-DMOF-1 matches the calculated pattern for pcu-DMOF-1, with a characteristic  $2\theta$  peak at *ca.* 8.1°. The adoption of a phase pure kag structure by butyl(bdc)<sub>2</sub>-DMOF-1 and pentyl(bdc)<sub>2</sub>-DMOF-1, under conditions that yield the phase pure pcu structure using unfunctionalized terephthalic acid implies that the butyl and pentyl cross-links direct the adoption of the kag structure. This shows that the formation of the kag structure using functionalized bdc<sup>2-</sup> units is possible, but more importantly, that the cross-link between bdc<sup>2-</sup> units exerts a structure-directing influence under conditions that typically result in the pcu structure. The PXRD pattern of the putative hexyl(bdc)2-DMOF-1 does not correspond to either of these phases. The possibility of additional phases in the DMOF system was noted by Kitagawa

*et al.* in their study of framework isomerism in **DMOF-1**, and this material too may represent a novel structural arrangement.<sup>19</sup>

PXRD patterns obtained for *o*-xylyl(bdc)<sub>2</sub>-DMOF-1, *m*-xylyl(bdc)<sub>2</sub>-DMOF-1, and *p*-xylyl(bdc)<sub>2</sub>-DMOF-1 all match the calculated **pcu-DMOF-1** pattern (Fig. 4). This is notable because of the similarity in the number of carbon atoms between ether oxygens in each linker: four in *o*-xylyl(bdc)<sub>2</sub> and butyl(bdc)<sub>2</sub>, five in *m*-xylyl(bdc)<sub>2</sub> and pentyl(bdc)<sub>2</sub>, and six in *p*-xylyl(bdc)<sub>2</sub> and hexyl(bdc)<sub>2</sub>. None of the flexible alkyl-tethered linkers of corresponding lengths yielded pcu structures, implying that the rigidity of the xylyl tethers impose geometrical constraints incompatible with the formation of the kag structure.

The trimer-based **pentyl**<sub>2</sub>(**bdc**)<sub>3</sub>-**DMOF-1** and polymeric **pbdc-5a-DMOF-1** also adopted the **pcu** structure, in contrast to the dimeric **pentyl**(**bdc**)<sub>2</sub>-**DMOF-1** based on the same spacer (Fig. 5). This is the first observation of corresponding dimeric and trimeric oligoMOFs adopting distinct, isomeric framework structures, as well as the first example of isomerism between the framework structures of an oligoMOF and its exact polyMOF analogue. These results show the remarkable sensitivity of the DMOF system to subtle changes in the length, flexibility, and number of repeat units of tethered H<sub>2</sub>bdc ligands. Despite facile data collection on a laboratory source, Pawley refinement of the PXRD patterns of these MOFs showed good whole pattern fits, high phase purity, and minimal deviation of unit cell parameters from the reported single crystal structures of the parent **pcu-DMOF-1** and **kag-DMOF-1** (Table S1 and Fig. S3–S11<sup>†</sup>).

To better understand the role of the alkyl cross-link in directing the formation of isomeric networks, we conducted further experiments on **pentyl(bdc)**<sub>2</sub>-**DMOF-1** and **heptyl(bdc)**<sub>2</sub>-**DMOF-1**. When synthetic conditions were changed to the rapid method outlined by Hungerford and Walton, in which unfunctionalized terephthalate forms the **kag** network in the presence of triethylamine and DMF (see ESI Fig. S12†), the PXRD pattern of the product formed using **pentyl(bdc)**<sub>2</sub> is well-



Fig. 3 PXRD patterns of alkyl-tethered DMOFs in comparison with pcu-DMOF-1 and kag-DMOF-1.



Fig. 4 PXRD patterns of xylyl-tethered DMOFs in comparison with pcu-DMOF-1 and kag-DMOF-1.



Fig. 5 PXRD patterns of trimer- and polymer-based DMOFs in comparison with pcu-DMOF-1 and kag-DMOF-1.

defined and corresponds to the phase pure kag product. However, under the same conditions, the heptyl(bdc)<sub>2</sub> product shows poor crystallinity, only retaining the major peaks associated with the pcu structure. Therefore, although conditions that promote the formation of the kinetically favored kag structure do influence the reaction, the effect of the pentyl and heptyl cross-links remains the same as under solvothermal conditions. In addition, this observation shows that the heptyl cross-link also exerts its own structure directing effect on the product.

To investigate whether the pentyl cross-link permits the formation of the pcu structure under thermodynamically forcing conditions, we allowed solvothermal syntheses using pentyl(bdc)<sub>2</sub> to proceed for up to two weeks. PXRD patterns taken after one week and two weeks under these conditions showed the exclusive formation of the kag phase of pentyl(bdc)2-DMOF-1 with no discernible decrease of crystallinity, suggesting that the modulation of the landscape of available structures by the pentyl cross-link is indeed of a thermodynamic nature (Fig. S13<sup>†</sup>). This is consistent with observations from solvent soaking experiments, in which we observe that pentyl(bdc)2-DMOF-1 shows no change from its kag structure or decrease in crystallinity upon soaking for up to a week in solvents including MeOH, whereas unfunctionalized kag-DMOF-1 transforms to the pcu isomer in less than 72 hours under the same conditions, in agreement with Verpoort et al. (Fig. S14<sup>†</sup>).<sup>22</sup>

N2 physisorption experiments carried out on the tethered DMOFs showed the retention of appreciable BET surface areas in most materials, with characteristic Type I isotherms. Among alkyl-tethered DMOFs, BET surface area values varied from 841  $\pm$  60 and 1150  $\pm$  4  $m^2~g^{-1}$  for  $\textbf{butyl(bdc)_2-DMOF-1}$  and pentyl(bdc)<sub>2</sub>-DMOF-1, respectively to 962  $\pm$  1 m<sup>2</sup> g<sup>-1</sup> for heptyl(bdc)<sub>2</sub>-DMOF-1 (Fig. 6). These values are reduced relative to the values obtained for the parent pcu-DMOF-1 and kag-



Fig. 6 N<sub>2</sub> sorption isotherms (77 K) of alkyl-tethered DMOFs in comparison with pcu-DMOF-1 and kag-DMOF-1. Closed symbols represent adsorption and open symbols represent desorption.

**DMOF-1**, 1779  $\pm$  58 m<sup>2</sup> g<sup>-1</sup> and 1813  $\pm$  22 m<sup>2</sup> g<sup>-1</sup>, due to partial occlusion of pores by the flexible tethering moieties. Pore volumes were found to be 0.429  $\text{cm}^3 \text{g}^{-1}$  and 0.578  $\text{cm}^3 \text{g}^{-1}$  for butyl and pentyl tethered kag DMOFs, compared to 0.863 cm<sup>3</sup> g<sup>-1</sup> in the parent **kag-DMOF-1**. The pore volume of **heptyl(bdc)**-**DMOF-1** was found to be 0.443 cm<sup>3</sup> g<sup>-1</sup>, compared to 0.732 cm<sup>3</sup>  $g^{-1}$  in **pcu-DMOF-1**. These values confirm that large fractions of the parent pore volume are retained in oligo-DMOFs adopting both kag and pcu structures, despite the incorporation of tethering groups.

MOFs constructed using the xylyl-tethered H<sub>2</sub>bdc linkers showed BET surface areas of  $1093 \pm 84 \text{ m}^2 \text{ g}^{-1}$  for *o*-xylyl(bdc)<sub>2</sub>-**DMOF-1**, 892  $\pm$  1 m<sup>2</sup> g<sup>-1</sup> for *m*-xylyl(bdc)<sub>2</sub>-DMOF-1, and 892  $\pm$  1  $m^2 g^{-1}$  for *p*-xylyl(bdc)<sub>2</sub>-DMOF-1 (Fig. S15<sup>†</sup>). These three MOFs adopt the pcu structure, and the surface area available varies systematically with the increased centrality of the bulky phenyl ring in the tethered ligand molecule. This trend is also observed in pore volumes. The trimer-based pentyl2(bdc)3-DMOF-1 shows reduced porosity compared to its parent or dimer-based counterparts, and has a BET surface area of 448  $\pm$  88 m<sup>2</sup> g<sup>-1</sup>. The pentyl-spaced polyMOF, pbdc-5a-DMOF-1 shows minimal microporosity with a BET surface area of just  $100 \pm 6 \text{ m}^2 \text{ g}^{-1}$ . The heptyl-spaced polyMOF, pbdc-7a-DMOF-1, retains more of its microporosity in comparison, with a BET surface area of 251  $\pm$  5 m<sup>2</sup> g<sup>-1</sup> (Fig. S16<sup>†</sup>). The reduced porosity observed in poly-DMOFs compared to oligoDMOFs is consistent with the increased density of tethering units in polyDMOFs - 1 tethering unit per bdc unit in polymeric linkers, versus 0.5 tethering unit per bdc unit in dimer linkers - resulting in greatly diminished accessible void space in the ultramicroporous MOF structure.

The observation of varying degrees of crystallinity between oligo- and polyDMOFs bearing different tethering groups is found to correlate with the observation of varying degrees of macropore N<sub>2</sub> condensation in the high-pressure region of the respective isotherms. Materials with less crystalline PXRD patterns, such as p-xylyl(bdc)2-DMOF-1, pentyl2(bdc)3-DMOF-1, pbdc-5a-DMOF-1, and pbdc-7a-DMOF-1, show noticeably larger

steps due to macropore condensation, suggesting a relationship between crystal attributes such as size, morphology, defectivity, and  $N_2$  uptake.

Pore size distributions calculated from these isotherms by the Horvath-Kawazoe (HK) method provided corroborating structural insights (Table S2<sup>†</sup>). The parent pcu-DMOF-1 shows a sharp unimodal distribution of pore widths with a maximum at ca. 6.1 Å, whereas the parent kag-DMOF-1 shows a bimodal distribution of pore widths due to the presence of narrow triangular (ca. 6.3 Å) and broad hexagonal (ca. 11.3 Å) microporous channels (Fig. S17-S27<sup>†</sup>). We observe that tethered DMOFs adopting the kag structure, butyl(bdc)<sub>2</sub>-DMOF-1 and pentyl(bdc)<sub>2</sub>-DMOF-1, also show bimodal pore size distributions, while those that adopt the pcu structure show unimodal distributions. In contrast to the small deviations from the parent structures found in unit cell parameters, deviations from the pore size distribution maxima in the tethered material were found to be as large as ca. 1.0 Å. Pore contraction due to the incorporation of tethering groups can account for many of these deviations, but in some cases, such as the increase of the HK plot maximum associated with the micropore in o-xylyl(bdc)2-DMOF-1 and p-xylyl(bdc)<sub>2</sub>-DMOF-1, and the triangular micropore in butyl(bdc)2-DMOF-1 and pentyl(bdc)2-DMOF-1, distortion of framework components (e.g. torsion of phenyl rings) is suggested.

<sup>1</sup>H NMR experiments carried out on activated and aciddigested MOFs confirmed that cross-links in each ligand were intact and provided information on the composition of each material, by integration of proton signals corresponding to tethered H<sub>2</sub>bdc ligands and the single peak corresponding to dabco (Table S3 and Fig. S28-S39<sup>†</sup>). This method confirms that the parent MOFs show a H<sub>2</sub>bdc-to-dabco mole ratio of 2:1, corresponding to the expected formula of [Zn<sub>2</sub>(bdc)<sub>2</sub>(dabco)]. The dimeric oligoDMOFs in this study conform to a general formula of  $[Zn_2(tether(bdc)_2)(dabco)]$ , and the trimer-based pentyl<sub>2</sub>(bdc)<sub>3</sub>-DMOF-1 conforms to a formula of [Zn<sub>3</sub>(pentyl<sub>2</sub>( $bdc)_3$  (dabco)<sub>1.5</sub>]. The polyDMOFs have an expected H<sub>2</sub>bdc-todabco mole ratio of 2:1. However while pbdc-7a-DMOF-1 agrees with this ratio, the ratio found for pbdc-5a-DMOF-1 is nearly 3 : 1. Since <sup>1</sup>H NMR conducted on thoroughly washed but unactivated pbdc-5a-DMOF-1 (Fig. S40<sup>†</sup>) shows the expected H<sub>2</sub>bdc-to-dabco mole ratio of 2:1, the loss of dabco linkers can be attributed to degradation of the framework structure during activation. Finally, <sup>1</sup>H NMR of the as-synthesized hexyl(bdc)<sub>2</sub>-DMOF-1 material indeed conformed to the expected bdc: dabco mole ratio of 2:1, and may indicate a novel framework isomer of DMOF. Work to prepare single crystalline samples of hexyl(bdc)<sub>2</sub>-DMOF is ongoing.

FTIR spectra of the activated oligoDMOFs (Fig. S41–S49†) do not show any observable peaks in the region between 1720 cm<sup>-1</sup> and 1680 cm<sup>-1</sup>, which is associated with the C=O stretching vibration ( $v_{\rm s}$  C=O) of the free carboxylate groups in the respective tethered ligands. Instead, strong peaks associated with the asymmetric –COO<sup>-</sup> stretching mode ( $v_{\rm as}$  COO<sup>-</sup>) of coordinated carboxylates are observed in each case between 1640 cm<sup>-1</sup> and 1630 cm<sup>-1</sup>. This implies that uncoordinated carboxylate groups are not present in the oligo-MOFs in significant quantities. However, small shoulders are observed at *ca.* 1720 cm<sup>-1</sup> in the FTIR spectra of the polyDMOFs (Fig. S48 and S49†), suggesting that although the peak intensity and area corresponding to the  $v_s$  C=O stretch are greatly reduced, a notable fraction of carboxylate groups remain uncoordinated unlike in the oligoDMOFs, and that the additional constraints imposed by multiple repeating units hinder the efficient binding of all carboxylate groups in the **pcu** structure.

Examination of PXRD patterns of these materials before and after activation (Fig. 7) shows that the dimeric oligoDMOFs adopting **pcu** networks do not show noticeable structural changes upon activation, unlike **pcu-DMOF-1** which is known to undergo a phase transformation. Although cross-linked DMOFs adopt a **pcu** network, the incorporation of the heptyl cross-link results in clear phase differences from unfunctionalized **DMOF-1**. Whereas the flexibility of **DMOF-1** results in the adoption of a narrow pore DMF-loaded phase upon solvothermal synthesis, the structures of as synthesized **heptyl(bdc)<sub>2</sub>-DMOF-1** and **pbdc-7a-DMOF-1** closely resemble the large pore phase that corresponds to the guest-free **DMOF-1** structure.<sup>17</sup> This difference between phases is illustrated by a shift of the (100) peak from 8.25° (2 $\theta$ ) in the narrow pore phase to 8.10° (2 $\theta$ ) in the large pore phase.

Xylyl-tethered oligoDMOFs, **pentyl**<sub>2</sub>(**bdc**)<sub>3</sub>-**DMOF-1**, and **pbdc-5a-DMOF-1** which all adopt **pcu** networks similarly form the large pore phase directly upon synthesis in DMF. The assignment of phases in this manner is corroborated by Pawley refinement of PXRD data for all **pcu** oligoDMOFs against the large pore parent **pcu-DMOF-1** structure. We postulate this is due to the occupation of a large fraction of the pore volume of the structure by the cross-links, which may act as *de facto* guests and prevent pore contraction. Therefore, cross-links effectively "lock" each **pcu** structure into its large pore phase (Fig. S50†). To our knowledge, this is the second case of large pore phase stabilization upon cross-link incorporation, following the report



Fig. 7 PXRD patterns of as synthesized and activated DMOFs in comparison with **pcu-DMOF-1**. The red region highlights the (100) peak.

by Xiao *et al.*<sup>37</sup> However, the **pcu** structures obtained using pentyl cross-links, **pentyl**<sub>2</sub>(**bdc**)<sub>3</sub>-**DMOF-1** and **pbdc-5a-DMOF-1**, do show significant losses in crystallinity upon solvent removal at elevated temperature. This, taken together with the dabco linker vacancies seen in the NMR spectrum of digested **pbdc-5a-DMOF-1**, indicates that although increasing the number of repeating H<sub>2</sub>bdc units to three or greater directs the formation of **pcu** structures, these structures may be more strained and less robust than other **pcu** oligo- or polyDMOFs with better matches in cross-link length and framework dimensions.

Further insight into the stability of these materials is obtained from thermogravimetric analysis (TGA). After showing initial mass loss due to vaporization of interparticle and pore DMF below 200 °C, the kag oligoDMOFs based on butyl and pentyl cross-links show mass loss steps due to decomposition, with onsets at approximately 310 °C and 305 °C respectively, close to the reported value of 300 °C for the parent kag-DMOF-1 (Fig. S51 and S52<sup>†</sup>). Similarly, heptyl and xylyl-tethered pcu oligoDMOFs show decomposition steps between 325 °C and 335 °C, in agreement with reported values for pcu-DMOF-1 (Fig. S53-S56<sup>†</sup>). However, while pbdc-7a-DMOF-1 shows a similar decomposition temperature to the pcu oligo-DMOFs (325 °C), pentyl<sub>2</sub>(bdc)<sub>3</sub>-DMOF-1 and pbdc-5a-DMOF-1 show significantly lower decomposition temperatures (315 and 300  $^\circ$ C respectively), supporting the hypothesis that pentyl-tethered structures based on multiple repeating units show diminished stability (Fig. S57-S59†). We note that values for decomposition temperature are approximate due to the gradual slope of the mass loss steps, but provide helpful points of comparison between the materials in this study.

Scanning electron microscopy (SEM) conducted on selected tethered DMOFs reveals mixtures of discrete and intergrown crystals. Strikingly, the crystals of **pentyl(bdc)**<sub>2</sub>-**DMOF-1** show a distinct hexagonal morphology (Fig. 8(a)). In contrast, **pentyl**<sub>2</sub>(**bdc**)<sub>3</sub>-**DMOF-1** forms cuboidal rod-like crystals (Fig. 8(b)



Fig. 8 Scanning Electron Microscopy (SEM) images of (a) pentyl(bdc)<sub>2</sub>-DMOF-1, (b) pbdc-5a-DMOF-1, (c) heptyl(bdc)<sub>2</sub>-DMOF-1, and (d) pbdc-7a-DMOF-1.

and S60<sup>†</sup>), and pbdc-5a-DMOF-1 forms tapered cuboidal crystogether with smaller, intergrown nanocrystals. tals Heptyl(bdc)2-DMOF-1 and m-xylyl(bdc)2-DMOF-1 form mixtures of cuboidal and irregular block-shaped crystals (Fig. 8(c) and S61<sup>†</sup>), and pbdc-7a-DMOF forms a mixture of aggregated needle crystals and larger cuboidal crystals (Fig. 8(d)). Therefore, the kag structure of pentyl(bdc)2-DMOF-1 results in the adoption of crystals with hexagonal symmetry, whereas the cross-linked pcu DMOFs adopt morphologies with square cross-sections. These morphologies are consistent with the layer structure in each set of materials and with the morphologies shown by crystals of the parent MOFs.<sup>17,18</sup> Unlike some previously reported polyMOFs, pbdc-5a-DMOF-1 and pbdc-7a-DMOF-1 do not show significant hierarchical structuring of individual crystallites.46 While we cannot rule out the formation of amorphous polymer-only domains, the combination of FTIR, SEM, and digestion NMR data strongly suggests that such domains - implying larger fractions of uncoordinated carboxylate groups and ligand to dabco ratios than those observed - do not comprise more than ca. 10% of the final polyDMOF materials.

Observations from the various experiments detailed above can be rationalized from analysis of the parent **kag**- and **pcu-DMOF-1** structures. Both structures are based on pillared layers, with dinuclear Zn(n) paddlewheel SBUs providing their equatorial sites for layer formation through four ditopic  $bdc^{2-}$  ligands, and their axial sites for pillaring through neutral ditopic dabco ligands. The key difference between the structures is that the **pcu** network is constructed by the pillaring of **sql** sheets in which  $bdc^{2-}$  ligands make angles of *ca.* 90° with the paddlewheel axis, while the **kag** network consists of pillared **kgm** sheets in which  $bdc^{2-}$  ligands make angles of *ca.* 60° and *ca.* 120° with the paddlewheel axis (Fig. 9).

This results in structures that have approximately equal interlayer distances, governed by the size of the pillaring dabco ligand, but distinct pore architectures. pcu-DMOF-1 has uniform channels with a square cross section bounded by four bdc<sup>2-</sup> ligands. In contrast, kag-DMOF-1 has two types of channels, one narrow and triangular, and the other wide and hexagonal. Considering that tethering groups are bound to ether substituents on the bdc<sup>2-</sup> ligand, distances measured between aryl protons in the crystal structures of the parent frameworks provide an approximate measure of the space available for tether incorporation between pairs of bdc linkers. The interlayer distances in pcu-DMOF-1 (7.5 Å) and kag-DMOF-1 (7.4 Å) are very similar and do not provide a basis for structure directing effects upon tether incorporation. However, the distances between perpendicular (6.7 Å) and parallel (8.7 Å) pairs of bdc<sup>2-</sup> ligands in pcu-DMOF-1, and the narrow triangular channel in kag-DMOF-1 (5.9 Å) are in the appropriate range for the tethers studied here to exert an influence over framework formation.

Histograms were generated from the crystal structures deposited in the Cambridge Structural Database (CSD, see ESI for details<sup>†</sup>) of O···O distances between oxygen atoms bridged by alkyl and xylyl groups that are used as tethers in our study (Table S4 and Fig. S62<sup>†</sup>), to illustrate the typical range of distances shown by each tethering group in crystal structures.<sup>47</sup>



Fig. 9 Perspective views of the crystal structures of (a) pcu-DMOF-1 and (b) kag-DMOF-1, with highlighted inter-ligand distances and angles.

It was found that most butyl chains and a significant fraction of pentyl chains in reported structures adopt conformations resulting in O…O distance below the 5.9 Å value associated with the narrow pore in kag-DMOF-1. In contrast, histograms for the hexyl and heptyl tethers show distributions with no distances below 6.0 Å, which provides an empirical justification for the structure directing behavior observed. *m*-Xylyl and *p*-xylyl groups show distributions centered around ca. 6.5 Å and 7 Å respectively, compatible with the **pcu** structure they adopt. However, o-xylyl groups show distances only in the 4-6 Å range yet prefer the pcu structure. This suggests that additional factors such as tether rigidity play a role in structure selection. The narrow triangular pore in the kag structure may be accessible to the butyl tether of comparable length due to its flexibility and ability to contort into the confined space presented by the pore, while remaining inaccessible to the rigid o-xylyl tether.

Similar factors can explain the formation of the **kag** network by the dimeric pentyl-tethered ligand, and the **pcu** network by its trimeric and polymeric counterparts. Although the pentyl



**Fig. 10** Schematic representation of the DMOF phases accessible to (a) butyl- and pentyl-tethered dimeric bdc ligands; (b) heptyl-tethered dimeric, pentyl-tethered dimeric, and polymeric bdc ligands.

tether is short and flexible enough to bridge two  $bdc^{2-}$  groups in the triangular pore of the **kag** structure, any additional pentyl tether from the same  $bdc^{2-}$  unit would be required to traverse the hexagonal pore, in which parallel  $bdc^{2-}$  ligands are 19.9 Å apart, and adjacent ligands are 6.7 Å apart at a very obtuse angle. In these circumstances, we propose that the formation of a strained **pcu** structure becomes favored over **kag**, as seen in **pentyl**<sub>2</sub>(**bdc**)<sub>3</sub>-**DMOF-1** and **pbdc-5a-DMOF-1**. The modified relationships between phases and topologies upon tether incorporation are summarized in Fig. 10.

#### Conclusions

In this work, we have synthesized and characterized several new DMOFs based on oligomeric and polymeric linkers, with varying cross-link length, flexibility, and number of repeating ligand units. Our results show that although oligomeric and polymeric terephthalate-based ligands with dabco co-ligands adopt the canonical pcu-DMOF-1 structure in most cases, the ultimate structures are dictated by the length and flexibility of the tethering group. Specifically, we find that butyl- and pentyltethered dimers adopt an isomeric kag structure even under thermodynamically forcing conditions, whereas more rigid xylyl tethers of comparable length, or longer heptyl tethers adopt the parent pcu structure. Upon linking three or more terephthalate groups using pentyl spacers, we have found that ligands become incompatible with the kag structure and revert to pcu. Therefore, oligoMOFs based on dimeric ligands can form distinct structures from those based on trimers, or the corresponding polyMOFs under identical conditions, depending on the

specific framework structure. These results are the first example of flexible inter-ligand tethers acting as structure-directing elements in MOFs and show that the influences of these tethers on overall structure are more nuanced than previously realized.

Furthermore, we have shown that the phase transformations shown by the parent **pcu-DMOF-1** are altered upon cross-link incorporation, and the large pore phase is stabilized. The solvent-mediated transformation of **kag-DMOF-1** to **pcu-DMOF-1** is also rendered inaccessible upon cross-link incorporation. Therefore, the phase and topological landscapes of the **kag-** and **pcu-DMOF-1** structures have been shown to be highly sensitive to manipulation of the constraints over ligand geometry imposed by means of cross-linking moieties. The use of hexyltethered dimeric ligands further resulted in the formation of a possible new isomeric phase of DMOFs, showing that crosslinks may also provide a route to novel structures. Understanding the impact of ligand cross-links as design elements represents a step towards enhanced understanding of MOFpolymer compatibility.

#### Data availability

The data supporting this article have been included as part of the ESI.†

#### Author contributions

D. S. and S. M. C designed the materials and experimental strategy; D. S. conducted the experiments; D. S. and S. M. C wrote the manuscript. All authors have given approval to the final version of the manuscript.

#### Conflicts of interest

There are no conflicts to declare.

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