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# Mesoporous zirconium based metal-organic frameworks, a topological review

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Through the gathering of metals and clusters with organic linkers, the metal—organic frameworks (MOFs) family emerges, representing highly applicable class of porous and crystalline materials in the world of chemistry. This class has the potential to shape the future of this field of science. The remarkable stability of zirconium and carboxylate ligands, coupled with the possibility of creating highly porous structures with a variety of arrangements, has led the authors to compile this review. In this study, we will investigate ten topologies that appeared in reported mesoporous Zr-Based MOFs and discuss their special properties. The applications of these structures are strongly influenced by their topologies, and the authors have concluded that understanding the topology and, more generally, the structure of MOFs helps to find the most optimal MOF for the intended application of researchers in each project.

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## 1. Introduction

Zirconium can be categorized as an infrequent element, making up around 0.023% of the Earth's crust.¹ This element is found in two forms: (1) white, suggesting its crystalline structure. (2) Blue-black powder form, suggesting that it is amorphous. Zirconium has many advantages over other transition metals, such as high mechanical and chemical stability of its products,

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spherical electron orbitals, low ionic radius, and electron pair acceptance capacity.<sup>2-4</sup> Zr ions are used as a metal to remove contaminants from the aqueous surroundings. Zr-based adsorbents are hard Lewis acids. They have properties such as high affinity for electronegative ligands, abundance in nature due to high production, low production cost, non-toxicity, environmental compatibility, low solubility in water, and inertness in redox and acid-based reactions.<sup>1,5</sup>

The growing interest in metal-organic frameworks (MOFs) stems from their structural versatility and the ability to tailor their chemical and physical properties by adjusting



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acterization of MOF- and ZIF-based nanocomposites for antibacterial applications, drug delivery systems, and water purification. He has published several articles in the field of porous materials. Driven by a passion for sustainable technologies, he continues to explore materials that contribute to clean energy, pollutant removal, and advanced sensing platforms.



Pooria Refah

Pourya Refah graduated with a bachelor's degree in Chemistry from the University of Tehran in 2023. He is a chemist, and his research and studies focus on metal-organic frameworks (MOFs), including their structures, green and optimized synthesis methods for specific MOFs, as well as their applications in pharmaceuticals and drug delivery.

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components such as metal nodes, organic linkers and overall topologies. Thus, manipulation of one of these parameters in their synthetic pathway will show completely different chemical and physical properties for them.<sup>6,7</sup> MOFs have opened up a fascinating new field of research into coordination compounds, with applications including catalysts, 8-10 electrochemical and chemical sensing11-13 encapsulation of macromolecular compounds14 and enzymes,15,16 fuel cells,17 gas storage,18-20 removal of hazardous materials (such as heavy metals,21,22 organic dyes,23 greenhouse gases24 and toxins25), water splitting,26 anti-bacterial and bacteriostatic,27-30 anticancer activities, 31-35 semi-conductors, 36 molecular reactors 37,38 chromatography,39 drug delivery40-42 and etc. The effectiveness of these metal frameworks is restricted in numerous critical applications due to the combination of two factors: the low stability of MOFs and the small sizes of their pores, especially when subjected to harsh conditions. 43 The primary condition to expand the efficiency of MOFs is to increase their chemical stability. According to Pearson's hard and soft acid and base principle (HSAB theory),44 chemically stable MOFs can be obtained by using carboxylate ligands with low-capacity metal ions such as Zr<sup>4+</sup>, Al<sup>3+</sup>, Cr<sup>3+</sup>, etc or produced low-capacity metal ions using azolate ligands such as Ni<sup>2+</sup>, Zn<sup>2+</sup>, Co<sup>2+</sup>, etc.<sup>45</sup> As a case in point, Zr4+ carboxylate MOFs have improved research efforts since the discovery of UiO-66.46 Despite the good stability of these MOFs compared to most reported MOFs, Zr-MOFs exhibit poor resistance against strong Lewis bases. Meanwhile, alkaline/nucleophilic conditions are prevalent in experimental applications, such as many catalytic coupling reactions. 43,47 The other group of stable MOFs comprises azolate ligands and lowtransfer-capacity metal ions, which exhibit higher stability compared to their carboxylate counterparts under gaseous



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current research focuses on the crystal engineering of coordination polymers and supramolecular compounds, metal-organic frameworks (MOFs) and their potential applications in energy storage materials, separation, drug delivery and catalysis. He also researches in synthesis and characterization of nano-scale materials. In 2013, he won the second place in the Khwarizmi Young Award for his work in the field of modulating methane storage in nanoporous anionic MOFs via post synthetic cation exchange process.

conditions.<sup>48</sup> Another method to enhance the stability of MOFs involves selecting nodes composed of relatively mild Lewis acidic species such as Zn<sup>2+</sup> or Cu<sup>2+</sup>. However, their weak coordination bonds make them susceptible to chemical attacks. To address this issue, clusters made of harder Lewis acid metals should be chosen as nodes. For instance, porphyrin Zr-MOFs demonstrate exceptionally high chemical stability.<sup>49</sup>

To overcome the limitations associated with small pore sizes and limited accessibility in many conventional MOFs, especially when dealing with large molecules or catalytic systems, the development of mesoporous structures has become increasingly important. According to IUPAC, mesoporous materials are defined as those possessing pore diameters between 2 and 50 nm, and various strategies have been developed to achieve this structure. Liu et al. classified these synthetic strategies into categories which can be listed like this. These strategies include incorporation of defects via ligand doping, the use of elongated organic linkers, stepwise assembly protocols, gelation, micro to meso conversion processes and topological control. Among these, topology directed design offers a unique route to introducing intrinsic microporosity without relying heavily on postsynthetic modifications or templating agents. This topological approach enables the creation of open, hierarchical and highly connected networks that maintain structural robustness while enhancing mass transport properties. Thus, understanding and controlling MOF topology is not only essential for improving stability, but also for rationally designing frameworks with mesoporous characteristics suited for advanced applications. 49 Guan and co-workers have elucidated reproducible and reliable methods to produce mesoporous and highly stable MOFs for future applications such as adsorption of large molecules, drug delivery, and size-selective catalysis. The reported methods include templating methods, with two subgroups: the single templating agent method and the cooperative template system; gelation process; methods that do not use templates; supercritical fluid synthesis, with two subgroups: CO2-directed assembly method and ionic liquid/supercritical CO2 emulsion technique; post-synthetic strategy, with two subgroups: hydrolytic post-synthetic methods and stepwise exchange of ligands; co-assembly of metal and ligand fragments; modulator-induced defect-formation strategy (which became very popular in recent years<sup>50</sup>) and encapsulation and etching method.<sup>51</sup> As a result, Albolkany et al. reported a new method for converting microporous materials to mesoporous ones through molecular surgery.52 Creating clusters instead of simple metal ions was a turning point in the construction of MOFs. So far, zirconiumbased clusters containing three to twelve metal atoms have been reported; however, in this context of MOFs, the most commonly observed nodes are Zr-based/oxo-cluster such as ZrO6, ZrO7 and Zr<sub>6</sub>O<sub>8</sub>. Notably, rare examples of larger cluster have been reported, including Zr<sub>8</sub>O<sub>6</sub> in PCN-221 (ref. 53) and Zr<sub>12</sub> clusters in CAU-45.54 Among these, the Zr<sub>6</sub>O<sub>8</sub> which often formulated as  $[Zr_6(OH)_4(O)_6]$ , is the most prevalent motif found in Zr-MOFs.55,56 Zirconium-based MOFs represent a significant subclass that has garnered considerable attention since the first reported Zr-based MOF, UiO-66, where Zr<sub>6</sub> clusters and 12connected inorganic linkers are connected.46 Great efforts have

been dedicated to developing this subclass of MOFs based on edge-transitive nets, owing to the increasing interest in reticular chemistry and the versatility of Zr-cluster connectivity. Therefore, due to the unique properties of Zr-based MOFs and their widespread applications as adsorbents, it is necessary to develop their behavioral and functional properties for further exploration. According to Scopus (Fig. 1), there has been a growing trend in technical work on MOFs over the past decades, with each year witnessing a greater percentage of studies conducted on their zirconium-based subgroup. Zr-based materials show a great range of applications in drug delivery and water treatment. Although there are only a few review articles on zirconium, they all focus on the investigation of Zr-MOFs. 57-60

Moreover, Zr-based MOFs have served as templates to achieve mesoporous materials in many studies, such as K-ZrO<sub>2</sub>,

which was designed using the **UiO-66** template, as reported by Wang *et al.*<sup>61</sup> or synthesis of yttria-stabilized zirconia (YSZ) with the same template reported by Yue *et al.*<sup>62</sup> A comprehensive review on the conversion of MOFs and coordination polymers into functional materials with nanostructures, such as metal oxides, carbon nanoparticles, porous carbons, and composites, has been published by Lee *et al.* They place particular emphasis on understanding the connection between the nature of the parent frameworks and the resulting nanomaterials. They discuss various experimental approaches based on mechanistic perception.<sup>63</sup>

In this study, 10 topologies that appear in published mesoporous Zr-based MOFs will be investigated, and we will discuss their special properties. The applications of these structures are strongly influenced by their topologies, and the authors have concluded that knowing the topology and, more generally, the

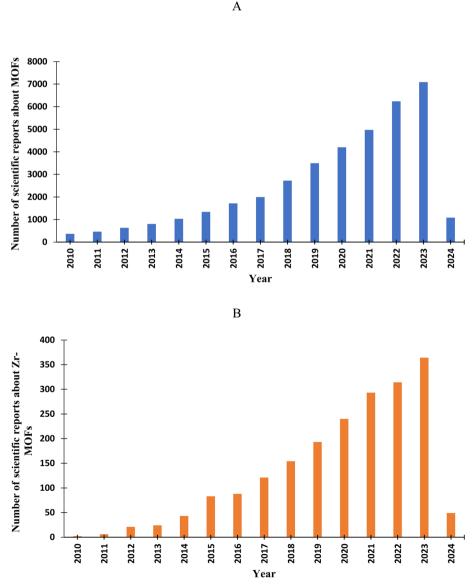


Fig. 1 Bibliometric analysis database of Scopus, showing published articles between 2010 to 2024. (A) About MOFs and (B) about Zr-based MOFs.

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**Table 1** Overview of Zr-based MOFs discussed in this review, including their structural features, topologies, and key properties<sup>d</sup>

	MOF	Linker	Cluster/core	Surface area $(m^2 g^{-1})$	Topology	Thermal stability (°C)	Pore size (Å)	Ref.
1	BUT-12	$\mathrm{CTTA}^{3-}$	$\mathrm{Zr_6O_4(OH)_8(H_2O)_4}$	3387	the, (3,8 connected)	320	13 and 21	77
7	BUT-13	$TTNA^{3-}$	$\operatorname{Zr}_6\mathrm{O}_4(\mathrm{OH})_8(\mathrm{H}_2\mathrm{O})_4$	3948	the, (3,8 connected)	430	14 and 28	77
·0	CAU-45	5-Acetamidoisophthalic acid	$Z\Gamma_6(\mu_3-O)_4(\mu_3-OH)_4, \ Z\Gamma_{1,2}(\mu_3-O)_8(\mu_3-OH)_8(\mu-OH)_6]^b$	NK"	NK"	330	17-22	54
4	Ce/Zr-DUT-67-pzd	TDC_	$[Zr_6O_6(OH)_2(tdc)_4(CH_3COO)_2]$	781.8	reo, (8,4 connected)	350	10	78
								and 79
2	Ce/Zr-MOF-808	$\mathrm{BTC}^{3-}$	$\mathrm{Zr}_6(\mu_3\text{-}\mathrm{O})_4(\mu_3\text{-}\mathrm{OH})_4$	2060	spn, (3,6 connected)	550	7–10	79
								and 80
9	Ce/Zr-UiO-66	$\mathrm{BDC}^{2-}$	$\left[\mathrm{Zr}_{6}(\mu_{3}\text{-}\mathrm{O})_{4}(\mu_{3}\text{-}\mathrm{OH})_{4}\right]$	1187	fcu, (12-connected)	450–600	9	79
								and 81
7	c- $(4,12)$ MTBC-M6	MTBC	$\mathrm{Zr_6O_4(OH)_4}$	$NR^a$	(4,12) connected	$\mathbf{NR}^a$	$\mathbf{NR}^a$	82
8	DUT-126	$\mathrm{TDC}^{2-}$	$\mathrm{Zr_6O_4(OH)_4}$	1297	hbr, (8,8-connected)	250	22.8, 11.8, 5.3	75
6	$Meso\ UiO-66-(OH)_2$	$\mathrm{BDC} ext{-}\mathrm{(OH)}_2^{2-}$	$\mathrm{Zr}_{6}(\mu_{3} ext{-}\mathrm{O})_{4}(\mu_{3} ext{-}\mathrm{OH})_{4})$	940	fcu, (12-connected)	300-500	26	83
10	Meso ${ m UiO-66-NH}_2$	$\mathrm{BDC\text{-}NH}_2^{2-}$	$\mathrm{Zr_6}(\mu_3\text{-O})_4(\mu_3\text{-OH})_4)$	1410	fcu, (12-connected)	300-500	28	83
11	MIP-206	$\mathrm{IPA}^{z-}$	$\mathrm{Zr}_6(\mu_3 ext{-}\mathrm{OH})_4(\mu_3 ext{-}\mathrm{OH})_4, \ \mathrm{Zr}_6(\mu_3 ext{-}\mathrm{OH})_6(\mu_3 ext{-}\mathrm{OH})_{1b}$	${ m NR}^a$	$\mathrm{NR}^a$	450	25–27°	84
12	MOF-545	${ m MTCPp^{4-}}$	$Z_{112}(\mu_3 - O_1)_8(\mu_3 - O_1)_8(\mu - O_1)_6] = Z_1 \epsilon [\mu_3 - O_1]_6$	2220	csa. (4.8 connected)	300	13. 37	85
13	MMU	$ m BDC^{2-}$	$NR^a$	453.8	$NR^a$	$NR^a$	35-70	98
14	MOF-526	TCBPP	$[\mathrm{Zr}_6(\mathrm{OH})_4\mathrm{O}_4(\mathrm{CO}_2)_{12}]$	4260	ftw, (4,12 connected)	400	25.5	87
15	MOF-527	TCTPP	$\left[\mathrm{Zr_6(OH)_4O_4(CO_2)_{12}}\right]$	2000	ftw, (4,12 connected)	400	31.4	87
16	MOF-528	TCTTPP	$[\operatorname{Zr}_6(\operatorname{OH})_4\operatorname{O}_4(\operatorname{CO}_2)_{12}]$	3550	ftw, (4,12 connected)	400	37.6	87
17	MOF-808	$\mathrm{BTC}^{3-}$	$\mathrm{Zr_6}(\mu_3 ext{-O})_4(\mu_3 ext{-OH})_4$	2060	spn, (3,6 connected)	550	7–10, 18.4	80
18	NU-1000	$\mathrm{TBAPy}^{4-}$	$\mathrm{Zr_6}(\mu_3\text{-OH})_8$	2320	csq, (4,8-connected)	200	14, 30	88
19	NU-1003	${ m TNAPy}^{4-}$	$\mathrm{Zr_6(\mu_3\text{-}OH)_8}$	2700	csq, (4,8-connected)	$NR^a$	38–45	68
20	NU-1008	${ m TCPB-Br}_2^{4-}$	$Zr_6(\mu_3-O)_4(\mu_3-O_{11})$ (11.0)	${f NR}^a$	csq, (4,8-connected)	$\mathrm{NR}^a$	13, 30	06
5	NIT-1010	TDCB4-	$OH_J_4(HCOO)_4(OH)_{3.5}(H_2O)_{3.5}$	07070	osa (4 8-oonnooted)	005	$ND^a$	6
22	NU-1105	$ m py-Fp^{4-}$	$Z_{\Gamma \in \{\Pi_3, \Omega_1\}_8}$ $Z_{\Gamma \in \{\Pi_3, \Omega_1\}_4}$	5645	fix. (4.12-connected)	470	$NR^a$	92
23	NU-1200	$ m TMTB^{4-}$	$Zr_6(\mu_3-OH)_8(OH)_8$	2400	the, (3,8-connected)	300	14, 20	99
24	NU-1601	$ m PET-2^{6-}$	$Zr_{6}(\mu_{3}-O)2(\mu_{3}-OH)$	3970	alb, (6,12-connected)	500	14, 22	74
25	NU-1602	PET-3 <sup>6-</sup>	$g(HCOO)(OH)(H_2O)$ $Zr_6(\mu_3-O)2(\mu_3-OH)$ g(HCOO)(OH)(HOO)	4500	alb, (6,12-connected)	480	17, 27	74
26	NU-500	${\rm TCPB\text{-}Br_2}^{4-}$	$2(\mu_3-0)_4(\mu_3-0)_4(\mu_3-0)_4(\mu_3-0)_4(\mu_3-0)_4(\mu_3-0)_4(\mu_3-0)_4(\mu_3-0)_4(\mu_3-0)_4(\mu_3-0)_4(\mu_3-0)_4(\mu_3-0)_4(\mu_3-0)_4(\mu_3-0)_4(\mu_3-0)_4(\mu_3-0)_4(\mu_3-0)_4(\mu_3-0)_4(\mu_3-0)_4(\mu_3-0)_4(\mu_3-0)_4(\mu_3-0)_4(\mu_3-0)_4(\mu_3-0)_4(\mu_3-0)_4(\mu_3-0)_4(\mu_3-0)_4(\mu_3-0)_4(\mu_3-0)_4(\mu_3-0)_4(\mu_3-0)_4(\mu_3-0)_4(\mu_3-0)_4(\mu_3-0)_4(\mu_3-0)_4(\mu_3-0)_4(\mu_3-0)_4(\mu_3-0)_4(\mu_3-0)_4(\mu_3-0)_4(\mu_3-0)_4(\mu_3-0)_4(\mu_3-0)_4(\mu_3-0)_4(\mu_3-0)_4(\mu_3-0)_4(\mu_3-0)_4(\mu_3-0)_4(\mu_3-0)_4(\mu_3-0)_4(\mu_3-0)_4(\mu_3-0)_4(\mu_3-0)_4(\mu_3-0)_4(\mu_3-0)_4(\mu_3-0)_4(\mu_3-0)_4(\mu_3-0)_4(\mu_3-0)_4(\mu_3-0)_4(\mu_3-0)_4(\mu_3-0)_4(\mu_3-0)_4(\mu_3-0)_4(\mu_3-0)_4(\mu_3-0)_4(\mu_3-0)_4(\mu_3-0)_4(\mu_3-0)_4(\mu_3-0)_4(\mu_3-0)_4(\mu_3-0)_4(\mu_3-0)_4(\mu_3-0)_4(\mu_3-0)_4(\mu_3-0)_4(\mu_3-0)_4(\mu_3-0)_4(\mu_3-0)_4(\mu_3-0)_4(\mu_3-0)_4(\mu_3-0)_4(\mu_3-0)_4(\mu_3-0)_4(\mu_3-0)_4(\mu_3-0)_4(\mu_3-0)_4(\mu_3-0)_4(\mu_3-0)_4(\mu_3-0)_4(\mu_3-0)_4(\mu_3-0)_4(\mu_3-0)_4(\mu_3-0)_4(\mu_3-0)_4(\mu_3-0)_4(\mu_3-0)_4(\mu_3-0)_4(\mu_3-0)_5(\mu_3-0)_5(\mu_3-0)_5(\mu_3-0)_5(\mu_3-0)_5(\mu_3-0)_5(\mu_3-0)_5(\mu_3-0)_5(\mu_3-0)_5(\mu_3-0)_5(\mu_3-0)_5(\mu_3-0)_5(\mu_3-0)_5(\mu_3-0)_5(\mu_3-0)_5(\mu_3-0)_5(\mu_3-0)_5(\mu_3-0)_5(\mu_3-0)_5(\mu_3-0)_5(\mu_3-0)_5(\mu_3-0)_5(\mu_3-0)_5(\mu_3-0)_5(\mu_3-0)_5(\mu_3-0)_5(\mu_3-0)_5(\mu_3-0)_5(\mu_3-0)_5(\mu_3-0)_5(\mu_3-0)_5(\mu_3-0)_5(\mu_3-0)_5(\mu_3-0)_5(\mu_3-0)_5(\mu_3-0)_5(\mu_3-0)_5(\mu_3-0)_5(\mu_3-0)_5(\mu_3-0)_5(\mu_3-0)_5(\mu_3-0)_5(\mu_3-0)_5(\mu_3-0)_5(\mu_3-0)_5(\mu_3-0)_5(\mu_3-0)_5(\mu_3-0)_5(\mu_3-0)_5(\mu_3-0)_5(\mu_3-0)_5(\mu_3-0)_5(\mu_3-0)_5(\mu_3-0)_5(\mu_3-0)_5(\mu_3-0)_5(\mu_3-0)_5(\mu_3-0)_5(\mu_3-0)_5(\mu_3-0)_5(\mu_3-0)_5(\mu_3-0)_5(\mu_3-0)_5(\mu_3-0)_5(\mu_3-0)_5(\mu_3-0)_5(\mu_3-0)_5(\mu_3-0)_5(\mu_3-0)_5(\mu_3-0)_5(\mu_3-0)_5(\mu_3-0)_5(\mu_3-0)_5(\mu_3-0)_5(\mu_3-0)_5(\mu_3-0)_5(\mu_3-0)_5(\mu_3-0)_5(\mu_3-0)_5(\mu_3-0)_5(\mu_3-0)_5(\mu_3-0)_5(\mu_3-0)_5(\mu_3-0)_5(\mu_3-0)_5(\mu_3-0)_5(\mu_3-0)_5(\mu_3-0)_5(\mu_3-0)_5(\mu_3-0)_5(\mu_3-0)_5(\mu_3-0)_5(\mu_3-0)_5(\mu_3-0)_5(\mu_3-0)_5(\mu_3-0)_5(\mu_3-0)_5(\mu_3-0)_5(\mu_3-0)_5(\mu_3-0)_5(\mu_3-0)_5(\mu_3-0)_5(\mu_3-0)_5(\mu_3-0)_5(\mu_3-0)_5(\mu_3-0)_5(\mu_3-0)_5(\mu_3-0)_5(\mu_3-0)_5(\mu_3-0)_5(\mu_3-0)_5(\mu_3-0)_5(\mu_3-0)_5(\mu_3-0)_5(\mu_3-0)_5(\mu_3-0)_5(\mu_3-0)_5(\mu_3-0)_5(\mu_3-0)_5(\mu_3-0)_5(\mu_3-0)_5(\mu_3-0)_5(\mu_3-0)_5(\mu_3-0)_5(\mu_3-0)_5(\mu_3-0)_5(\mu_3-0)_5(\mu_3-0)_5(\mu_3-0)_5$	$\mathbf{NR}^a$	(4,4,4,5-Connected net <sup>b</sup>	$\mathbf{NR}^a$	$9 \times 10$	9
			$OH)_4(HCOO)_4(OH)_{3.5}(H_2O)_{3.5}$		,	,		
27	NU-901	$\mathrm{TBAPy}^{4-}$	$\mathrm{Zr_{6}(\mu_{3} ext{-}OH)_{8}}$	1365	scu, (4,8-connected)	$\mathbf{NR}^a$		93
28	906-NN	${ m TCPB-Br}_2^{*-}$	$\mathrm{Zr_6}(\mu_3 ext{-}O_4(\mu_3 ext{-}O_4)$ . $\mathrm{(H_2O)}$ .	$NR^{x}$	scu, (4,8-connected)	$NR^{x}$	12  imes 27	9
29	NU-600	${ m TCPB-Br}_2^{4-}$	$Zr_6(\mu_3-O)_4(\mu_3-$	$\mathbf{NR}^a$	she,(4,6-connected)	NR	$13 \times 19$	9
		,	$OH)_4(HCOO)_4(OH)_{3.5}(H_2O)_{3.5}$	,				
30	NUPF-1 PCN 129	<i>с</i> Бүттүд	$Z_{\Gamma_6(\mu_3-O)_4(\mu_3-OH)_4}$	$NR^a$	scu, (4,8-connected)	450	23-51	94
16	1011-120	0113	Z16(H3-O11)8	7000	csy, (*,o-connected)	004	30/33, 13	60

ole 1 (Contd.)

	Thermal stability (°C)
	5,4-Connected 450 11, 20
	$^{4}$ , $^{4}$ , $^{8}$ ) connected NR $^{a}$ 12, 25–31
MTBC $Zr_6O_4(OH)_4$	$\mathrm{NR}^a$
$\mathrm{CC}^{2-}$ $\mathrm{Zr_6(\mu_3\text{-}O)_4(\mu_3\text{-}OH)_4}$	450–600
	$\mathrm{NR}^a$
	csq, (4,8-connected) 350 22.8
	cu, (4,8-connected) 400 13.7
$\Lambda  ext{e-TTFTB}^{4-}$ [Zr $_6 ext{O}_4( ext{OH})_4( ext{PhC})$	she. (4.6-connected) 400 12.6, 15.8, 20.7
	400

6,6′,6′′-(2,4,6-trimethylbenzene-1,3,5-triyl)tris(2-naphthoic acid). H<sub>2</sub>TDC: thiophene-2,5-dicarboxylate. H<sub>3</sub>BTC benzene 1,3,5-tricarboxylate. H<sub>2</sub>BDC: benzene 1,3-4-dicarboxylate. BA: isophthalic id. MTCPP: [5,10,15,20-tetrakis(4-carboxyphenyl)porphyrinato]-M (MTCPP (M = Mn(m), Fe(m) and Cu(n)) H<sub>4</sub>TBAPy: 1,3,6,8-tetrakis(p-benzoic acid)pyrene. H<sub>4</sub>TNAPy: 1,3,6,8-tetra(6-triangle-1) (BA) (MTCPP) (M = Mn(m), Fe(m) and Cu(n)) H<sub>4</sub>TBAPy: 1,3,6,8-tetrakis(p-benzoic acid)pyrene. H<sub>4</sub>TNAPy: 1,3,6,8-tetra(6-triangle-1) (BA) (MTCPP) (M = Mn(m), Fe(m) and Cu(n)) (MTCPP) (M = Mn(m), Fe(m) and Cu(n)) (MTCPP) (MTCPPP) (MTCPPP) (MTCPPP) (MTCPPP) (MTCPPP) (MTCPPP) (MTCPPP) (MTCPPP) (MTCPPP) (MTCPPPP) (MTCPPPP) (MTCPPPP) (MTCPPPP) (MTCPPPP) (MTCPPPP) (MTCPPPPP) (MTCPPPPP) (MTCPPPPP) (MTCPPPPPP) (MTCPPPPPPP) (MTCPPPPPPPP) ( carboxynaphthalen-2-yl)pyrene. TCPB-Br<sub>2</sub>: 1,4-dibromo-2,3,5,6-tetrakis(4-carboxyphenyl)benzene. TPCB: 3,3,5,5/-tetrakis(4-carboxyphenyl)-1,1'-bipheny. TMTB: 4,4',4"-(2,4,6-trimethylbenzene. 13,5-triyl)tribenzoic acid. H<sub>4</sub>ETTC: 4,4',4"-(ethene-1.1.2.2-tetrakis(4-carboxyphenyl)-1,1'-bipheny. TMTB: 4,4',4"-(2,4,6-trimethylbenzene. 13,5-triyl)tribenzoic acid. H<sub>4</sub>ETTC: 4,4',4"-(ethene-1.1.2.2-tetrakis(4-carboxyphenyl)-1,1'-bipheny. TMTB: 4,4',4"-(a,4,6-trimethylbenzene. NR: not reported. b New topology which were not named. A porphyrin carboxylate ligand. H3CTTA: 5′-(4-carboxyphenyl)-2′,4′,6′-trimethyl-[1,1′:3′,1″-terphenyl]-4,4″-dicarboxylic acid). H3TTNA Ni-TCPP: nickle-tetrakis(4-carboxyphenyl)-porphyrin. BDM: benzene1,3-dimesitylenic acid. 1,3,5-triyl)tribenzoic acid.  $H_4$ ETTC: 4,4',4'',4'''-(ethene-1,1,2,2-tetrayl)tetradiis [1,1':3',1'':4'',1''':3'',1'''-quinquephenyl]-4,4'''-dicarboxylate. Ni-TCPP: nickle-tetrakis(4 structure of MOFs helps to find the most optimal MOF for the intended application in each research project.

## 2. Discussion

## 2.1 Structure and topology

David Brown defined topology as the three-dimensional spatial arrangement of atoms in materials. The structural variety and topology of MOFs arise from various ways in which ligands and clusters connect. Topology in MOFs is influenced by ligands and their spatial orientation, clusters and their connectivity, and environmental conditions.<sup>64</sup> In many studies, researchers are trying to maintain the topology intact during ligand enlargement or reduction of connectivity by using modulators, which has shown the importance of topology.<sup>65</sup>

Topologies of Zr-based MOF include these topologies but as we know all topologies are not limited to these items:

csq (e.g., NU-1000 and PCN-222/MOF-545 (ref. 45 and 66)), scu (e.g., nu-902 (ref. 67)), spn (e.g., MOF-808 (ref. 68)), the (e.g., NU-1200 (ref. 69)/BUT-12 (ref. 70)), she (e.g., nu-600 (ref. 71)), ftw (e.g., MOF-1211 (ref. 72)), reo (e.g., DUT-51 (ref. 73)), flu (e.g., PCN-521 (ref. 74)), hbr (e.g., DUT-126 (ref. 75)) and alb (e.g., NU-1601 (ref. 76)) Table 1 shows that complete list of these topologies.

This review will focus on studies which are done from 2015 until 2021 that whose main research topics were mesoporous Zr-based MOFs.

Illuminating the dominating parameters of MOFs, such as topology, thermal and chemical stability, and porosity, is not simple. Since the first Zr and tetra-topic linker MOFs, numerous topologies have been reported, which can be attributed to the linker conformation and connectivity of clusters. These are influenced by various synthetic conditions such as modulating reagent and its concentration, metal salt as a precursor, temperature, solvent, and reagent concentration. The topologies of reported Zr-MOFs and their applications dependent on structure are discussed in the following sections.

## 2.2 csq topology

The **csq** topology is one of the most famous and frequently reported topologies among Zr-based MOFs. This topology provides two kinds of channels with different shapes and sizes, referred to as the hierarchical model; one central hexagonal channel is surrounded by six triangular channels.<sup>99</sup>

This topology was observed in **NU-1000**, first reported by Mondloch *et al.* They studied the post-synthesis metalation from the vapor phase (AIM) on **NU-1000**. When choosing a suitable MOF for the AIM process, three design criteria should be considered: 1. meso channels, 2. thermal and hydrolytic stability, and 3. spatially oriented functional groups. **NU-1000**, with 30 Å meso channels and the **csq** topology, a 4,8-connected topology with 8-connected  $Zr_6(\mu_3\text{-OH})_8$  clusters and 4-connected 1,3,6,8-tetrakis(p-benzoic acid)Pyreme linkers (see Fig. 2), maintains stability up to 500 °C, fulfilling all three criteria. This MOF provides the best template for demonstrating quantitative and self-limiting metalation by AIM. It consists of eight nodes,

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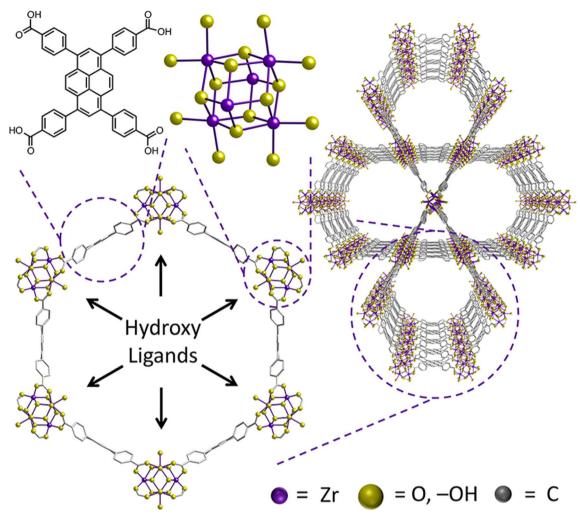


Fig. 2 Schematic of NU-1000, without hydrogen atoms which are hidden for better understanding.<sup>88</sup> From ref. 88 with permission. Copyright 2013, American Chemical Society.

each comprised of a  $Zr_6$  cluster in the shape of an octahedron, topped by eight  $\mu_3$ -OH ligands.<sup>88</sup>

Pankajakshan *et al.* described **NU-1000** as including 8-connected  $Zr_6(\mu_3\text{-O})_4(\mu_3\text{-OH})_4(H_2O)_4(OH)_4$  nodes interconnected with 1,3,6,8-(*p*-benzoate)-pyrene, also known as  $TBAPy^{4-}$  linkers. In contrast, **UiO-67** contains 12-connected  $Zr_6O_4(OH)_4$  cluster nodes and linear 4,4'-biphenyl dicarboxylic acid (BPDC) ligands, and both materials are water-stable. **NU-1000** exhibits a face-centered cubic organization of clusters with six Zr atoms and features both free and bridging –OH and  $H_2O$  groups. Additionally, **NU-1000** has wide mesoporous channels (31 Å), while **UiO-67** possesses two cages in the form of octahedral (16 Å) and tetrahedral (14 Å). Both materials are recognized as hierarchical structures<sup>100</sup> (in the next section, UiO-67's topology will be discussed).

These MOFs were employed for the removal of toxic glyphosate molecules from wastewater. It was demonstrated that the adsorption efficiency increases with the reduction in MOF size. In NU-1000, this effect was pronouncedly better compared to UiO-67. The relationship between MOF samples and glyphosate was observed in all experiments. It was found that all the

samples maintained their structural morphology after glyphosate adsorption. An increase in the amount of phosphorus resulted in a reduction in particle sizes. The stability of washed samples was assessed using powder XRD, which revealed that the structure of **NU-1000** remained stable even after washing. However, **UiO-67** samples were lost after washing, highlighting the advantage of **NU-1000** and its **csq**-net topology over **UiO-67**.

Topology not only influences applications but also can affect post-synthetic modifications. Choi *et al.* demonstrated a post-synthetic modification (PSM) that involved adding iron thio-late to **NU-1000**. They used this catalyst to convert  $\mathrm{NO}^{3-}$  to  $\mathrm{NH}^{4+}$ . Although this group studied the catalytic performance of the new material using the Brunauer–Emmett–Teller (BET) theory analysis, which revealed a reduction in surface area from 2260 m<sup>2</sup> g<sup>-1</sup> to 320 m<sup>2</sup> g<sup>-1</sup>, showing that the 1.2 nm triangular channel had completely disappeared and the meso channels remained unoccupied due to the presence of the FeSC12-AIM substrate inside the channels (Fig. 3).<sup>8</sup>

**Nu-1000** was used as a propane oxidizer at a low temperature by Li *et al.* They have used **NU-1000** as a supporter for heterogenic Co<sup>2+</sup> catalyst that reduces reaction temperature from 300–

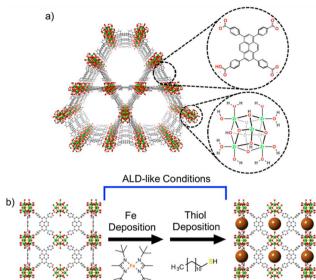


Fig. 3 (a) Structure of the NU-1000 and its 6 metal cluster and pyrene-based linker that includes the binding sites for iron thiolate precipitation and deposition, which are zoomed in (b) the ALD procedure of iron thiol cluster generation in the MOF.<sup>8</sup> From ref. 9 with permission. Copyright 2019, American Chemical Society.

350 °C (in case of  $VO_x$  to 200 °C). Their crystalline structure gives the opportunity to perform mechanism studies accurately. On its  $Zr_6$  nodes,  $Co^{2+}$  is present as a catalyst. Cobalt is located in MOF structure with two methods of SIM and AIM. The structure of **NU-1000** has a central hexagonal channel surrounded by hexagonal channels, and the product is called **Co-SIM-NU-1000** and **Co-AIM-NU-1000**. These two products have oxidized propane to propene at 230 °C in the presence of the

oxygen. They obtained that the best result occurs while using Co-SIM-NU-1000. The metalation process is associated with adding cobalt to the inside, which does not disrupt the structure. Ligand is pyrene based, and its long nature helps to stop the sintering process and keeps the surface area wide. The behaviors of Co-SIM-NU-1000 and Co-AIM-NU-1000 are different. When activated with oxygen, a new Co-Co bond is formed in Co-AIM that is not in Co-SIM. This reduces the surface of cobalt catalysts to be available in AIM.<sup>101</sup>

Li et al. synthesized a framework illustrating a pore size near 3.8–4.5 nm and the **ftw** topology to encapsulate and immobilize a nerve agent named OPAA. Unlike previous studies using micropore immobilizers, NU-1000 was utilized in this study, resulting in higher enzymatic activity compared to previous methods. Previous attempts to increase the pore size of NU-1000 by introducing single or triple C-C bonds in the connecting structure failed, leading to the creation of an isomorph MOF with the ftw topology each time. To address this issue, Li et al. utilized a tetra-carboxylate pyrene-based linker and DMF as a solvent, with trifluoroacetic acid as a modulator, to produce NU-1003 with the same csq topology as NU-1000. They reported two different pore sizes: 4.4 nm hexagonal and 1.7 nm triangular pores, as expected in the csq-net, which were slightly larger than the previous attempts by this team. Additionally, Li et al. used PCN-128 with csq topology and 4.2 nm hexagonal pores and 4 nm triangular pores. This MOF was first reported and characterized by Zhang et al.74 In both of Li's studies, OPAA was immobilized, and its enzymatic activity was measured. The csq topology proved to be particularly suitable for this study due to the hierarchical structure with a wide window between meso and micro cavities, allowing the enzyme to be in proximity to infiltrated reactants. The NU-1003 and PCN-128 windows

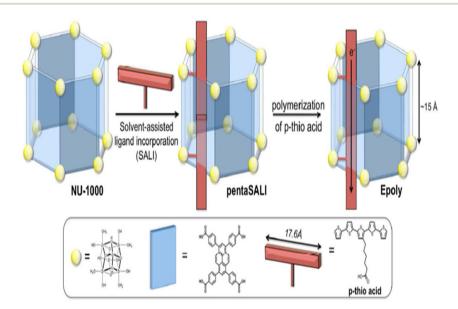


Fig. 4 Schematic illustration of the solvent-assisted ligand incorporation (SALI) process used to modify NU-1000 with a pentathiophene-based conductive polymer. The deprotonated p-thio acid molecules are selectively grafted onto the  $Zr_6$  nodes, forming conductive polymer strands within the larger channels of the hierarchical MOF structure. This post-synthetic modification preserves the framework's porosity and high surface area while enabling electrical conductivity. The schematic is conceptual and does not imply strict alignment of the polymer strands along the channel direction or their exclusive orientation.  $^{108}$  From ref. 108 with permission. Copyright 2017, American Chemical Society.

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measured 12  $\times$  13 Å and 9  $\times$  9 Å, respectively. To determine the capacity of OPAA to load into NU-1003, crystals of different sizes were placed in BTP (bis-tris-propane) buffer with a pH 7.2 solution of OPAA. After OPAA immobilization, the volume of triangular channels decreased from 0.20 to 0.15 cm<sup>3</sup> g<sup>-1</sup>, and hexagonal channels decreased from 0.45 to 0.14 cm<sup>3</sup> g<sup>-1</sup> in OPAA@NU-1003-size compared to NU-1003-size. This indicated that OPAA had filled the hexagonal channels while the micropores were relatively unoccupied. The study then investigated the enzyme activity after OPAA immobilization and the effect of

lation) and Samon (an actual nerve agent). The catalytic

performance of the immobilized OPAA in the mesoporous MOF

was improved compared to free OPAA in the BTP buffer. 65,102

Noh et al. reported the use of NU-1000 to immobilize molybdenum oxide as a cyclohexane oxidation catalyst. The resulting Mo-SIM is comparable to Mo-ZrO2 but avoids the inefficiency associated with the formation of Mo-ZrO<sub>2</sub>. NU-1000 was chosen due to its excellent crystal structure, distinct topology, and thermal stability. The hierarchical structure with pores ranging from 10 to 31 Å facilitates optimal diffusion and accessibility of active sites.103

As mentioned above, the csq topology with fully available metal nodes is one of the best candidates for the AIM process. Rimoldi et al. have introduced a new atomic layer deposition method using [AlMe<sub>2</sub>(oipr)]<sub>2</sub> instead of the classic [AlMe<sub>3</sub>] to deposit aluminum onto Zr clusters. This new material, Al-NU-1000, exhibits high thermal stability, with aluminum replacing hydrogen in terminal ligands such as OH- and H2O. The superiority of [AlMe<sub>2</sub>(oipr)]<sub>2</sub>, also known as "DAMI," lies in its ability to maintain a tetrahedral spatial configuration in the vapor phase, enabling its use in gas-phase electron diffraction. However, the use of DAMI results in self-limitation of the reaction and a reduction in the reaction rate, leaving some coordination sites unoccupied. The ratio of Al/Zr<sub>6</sub> is reported as 7.104

Chen et al. used MOFs as absorption cooling systems based on the absorption and desorption of propane and isobutane. They used two frameworks with csq topology, 8-connected Zr<sub>6</sub>O<sub>8</sub> cluster, and tetra topic linkers (NU-1003 TNAPy4- and NU-1000 TBAPy<sup>4-</sup>) display two kinds of pores: micro triangular channels and meso hexagonal channels. Its obvious larger ligand in NU-1003 results more extensive channels (4.7 nm for central hexagonal channel's diameter in NU-1003 towards 3.3 nm in NU-1000). They have shown the mechanism of absorption flows in two steps (type IV), in which micro channels are filled the same as meso channels consecutively. Also, they have established the relationship between absorber dimensions and cooling capacity when wider channels for NU-1003, saturation loadings of both absorbent components are significantly larger than in NU-1000, in their past studies using MIL-101 as an absorbing agent showed weaker performance because of the lower saturation loading (in NU-1000 is 1 g/1 g, in NU-1003 is 1.4 g/1 g and in MIL-101 is 0.5 g/1 g). They used these MOFs for refrigeration, ice-making, and also heat pumps because these applications were very common with raising adsorption pressures. According to Lange et al. cooling capacity is described as

the latent heat of the refrigerant at the working capacity multiplied by the evaporator temperature, which is the maximum amount of cooling compounds that can be desorbed from the MOFs surface upon heating.105 The working capacity could depend on the difference in the refrigerant uptake, like temperature and pressure.106

Wang et al. studied the unsaturated clusters in NU-1000 and its performance in PSM, attributing its effectiveness to its topology. Despite the wide range of applications of MOFs, progress has reached a bottleneck in areas such as fuel cells and supercapacitors, which require low energy charge transfer. Various methods have been explored to increase MOF conductivity, but they often result in a reduction of the BET surface area to less than 1000 m<sup>2</sup> g<sup>-1</sup> or a change in topology, leading to the formation of amorphous products. For example, Talian et al. proposed bridging the metal nodes with new guest molecules to create a suitable path for conducting electric charge. 107 The method used in this study involved solvent-assisted ligand incorporation (SALI), employing a pentathiophene molecule, which is the deprotonated form of p-thio acid. This molecule features a carboxylate group on a flexible carbon chain, allowing it to be grafted onto the nodes of NU-1000 in a self-limiting manner. This process only reduces the pore size from 31 Å to 27 Å, leaving approximately 73% of the MOF's space unoccupied. The resulting BET surface area is 1600 m<sup>2</sup> g<sup>-1</sup>, significantly higher than that of porous carbon. The conductivity of

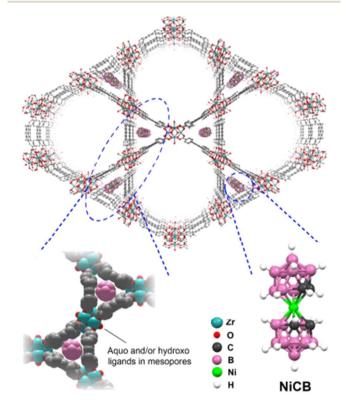


Fig. 5 The crystalline structure of NiCB@NU-1000 with occupied triangular channels and lack of hydrogen atoms. Triangular shaped channels of NiCB@NU-1000 are also demonstrated in below to illustrated the close interaction between NiCB and three neighbor pyrenes. Also there is presentation of NiCB. 109 From ref. 109 with permission. Copyright 2018, American Chemical Society.

the material varies depending on the thiophene doping level, ranging from 0 to  $1.7 \times 10^{-7} \, \mathrm{s \ cm^{-1}}$ . Strands of the conductive polymer formed post-synthetically on the inner surface of the wide channels of **NU-1000** are selectively positioned in the larger channels. The hierarchical nature of **NU-1000** provides both vacant channels and intact porosity, facilitating this process. <sup>108</sup> Fig. 4 shows the performance of modified MOF after *p*-thio acid addition.

High stability against water in a broad-ranging of pH values of zirconium-based MOFs is reputed, which is the reason why these MOFs are suitable to use in aqueous conditions like hydrogen progress catalysis and adsorption of water from air. Kung *et al.* tried to increase the electrical conductivity of MOFs by using metallacarboranes. In this way, they introduced

NiCB@NU-1000 and showed the potential of using these conductive metallacarboranes in electrochemical uses. To examine its redox activity, Mn-AIM-NiCB@NU-1000 was produced after manganese oxide was presented in NiCB@NU-1000. It can be seen in Fig. 5 that, NiCB existed in all the triangular shaped channels of NU-1000 at 100% occupancy. ICP-OES measurements of NiCB@NU-1000 samples in digested form showed a loading of  $0.74 \pm 0.07$  NiCB per each node. 109

Kung *et al.* also studied the rendering of mesoporous electroconductive MOFs and their chemical responsiveness. They utilized **NU-1000** and rendered it electronically conductive through a robust inorganic approach that preserved the material's structure and porosity. This approach relies on the condensed-phase bonding of tin species molecules onto MOF

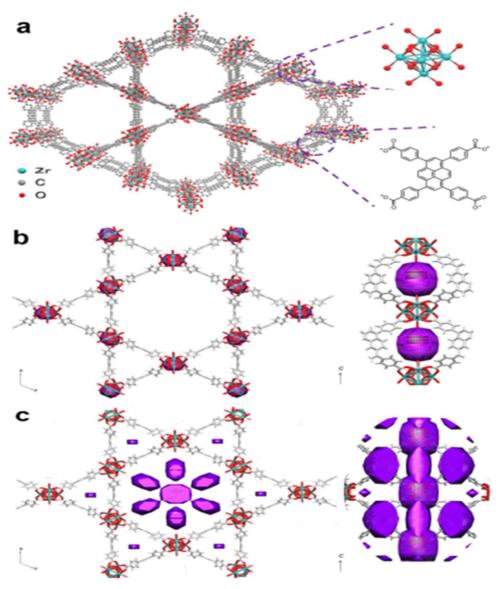


Fig. 6 Schematic representation of NU-1000 and the progression of the single-ion metathesis (SIM) process used to incorporate tin oxide into the framework. (a) Top-view of the NU-1000 crystal structure (hydrogen atoms omitted for clarity). (b) Electron density difference (EDD) map after one SIM cycle, showing initial incorporation of Sn(iv) species. (c) EDD map after three SIM cycles, indicating increased tin loading. The purple regions represent the electron density associated with tin oxide clusters bonded to the Zr<sub>6</sub> nodes. This post-synthetic modification preserves the mesoporous framework of NU-1000 while introducing electroconductivity *via* irreversible bonding between Sn species and node-bound hydroxyl and aqua ligands. From ref. 110 with permission. Copyright 2018, American Chemical Society.

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clusters. Specifically, this single-ion metathesis (SIM) method is employed to connect tin oxide clusters uniformly across 1D hexagonal and triangular meso- and microporous channels via irreversible reactions with hydroxyl and aqua ligands. These ligands are presented at the surface of the node with a ratio of 4.3, 9, and 14 tin(w) ions per Zr6 cluster after one, two, and three cycles of SIM, respectively.110 In this case before the increment of the metal index and also after that, this process can be compared with Fig. 6.

The target of Li and Gao et al. study was confined nano BiOI particles into NU-1000 with csq topology with two steps: first, be in the vicinity with Bi(NO<sub>3</sub>)<sub>3</sub>·5H<sub>2</sub>O to produce Bi<sup>3+</sup>@NU-1000 then, reacts with KI in ethylene glycol/H2O results in BiOI@NU-1000 used for valid photocatalytic hydrogen development in the presence of visible light.

Hierarchical structure, with pore widths of 31 and 10 Å, which makes NU-1000 a highly porous structure, high water, and weak acids stability, which was discussed in the first section, homogeneous distribution of Brønsted acids, -OH/-

OH<sub>2</sub> groups, at the Zr<sub>6</sub> clusters, which facilitated metalation and based on McGonigal and Deria et al. NU-1000 acts as a redoxtype photosensitizer and n-type semiconductor,92,111 all are reasons that according to that, Li et al. chose NU-1000 to merge the BiOI particle.112

The main focus of Kato et al.'s study revolves around the removal of pollutants and heavy metals utilizing Zr-based MOFs. They investigated the energetics of interactions between MOFs, specifically the well-known csq topology MOFs NU-1000, NU-1010, and PCN-608-OH, and toxic species. Within the csq topology, there are two unoccupied spaces for chemical absorption: smaller triangular channels and larger hexagonal channels. Their investigation considered both enthalpic and entropic parameters, revealing NU-1000's favorable enthalpic and entropic characteristics for absorption. In the absorption process of uremic toxins in mesopores, the primary driving force is entropic, while in other sites within smaller pores, referred to as cite one and cite two, absorption is driven by both enthalpic and entropic factors. Specifically, the adsorption of

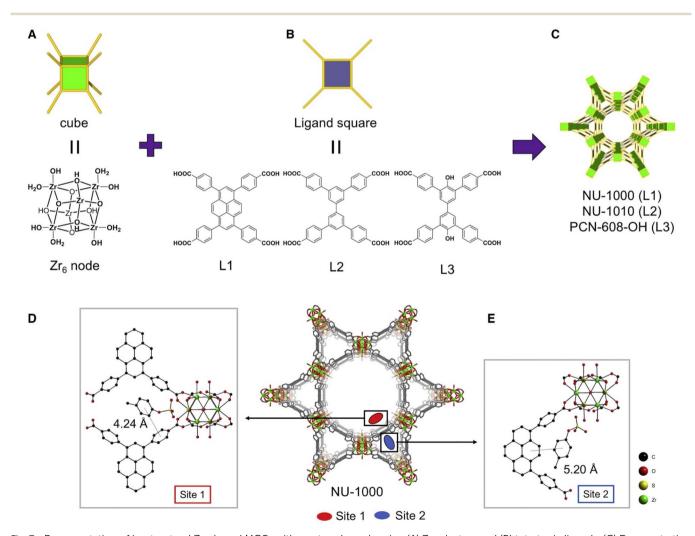


Fig. 7 Representation of isostructural Zr<sub>6</sub>-based MOFs with csq topology showing (A) Zr<sub>6</sub> clusters and (B) tetratopic ligands. (C) Demonstration of the  $\mathbf{csq}$  topology. Optimized geometries of p-cresyl sulfate (p-CS)-pyrene and  $\mathbf{Zr}_6$  clusters domains at both sites after p-CS adsorption at (D) site 1 and (E) site 2. Only one orientation of p-CS is depicted at each site for clarity, and potassium counter ions and hydrogens are not shown. From ref. 91 with permission. Copyright 2020, Cell Reports Physical Science.

potassium *p*-CS and potassium IS onto **NU-1010** exhibits noticeably greater increases in entropy compared to adsorption in **NU-1000**, indicating the significant role of hydrophobic interactions in the adsorption at site 1. The error bars represent the standard deviations of triplicate measurements (Fig. 7).<sup>91</sup>

Stability of Zr-MOF in a wide range of pH is one of the most important properties of them. This is the main reason for using highly stable porphyrin-based MOF called PCN-222 by Rezaei et al. for extract Hg2+ ions from fish samples with pipet tip method. Zhou et al. and Yaghi et al. first reported PCN-222 independently with csq, (4,8)-connected topology and 3.7 nm hexagonal channels and 2220 m<sup>2</sup> g<sup>-1</sup> BET surface.<sup>89,90</sup> The total pore volume of PCN-222 is reported to be 1.3 cm<sup>3</sup> g<sup>-1</sup>. It was using designed meso-tetrakis(4-carboxyphenyl)porphyrin  $(H_2TCPP)$  and  $Zr_6(\mu_3-OH)_8$  clusters. Rezaei et al. noted that the large pores of PCN-222 facilitate the diffusion process and enhance connectivity among guest sites, making it an excellent candidate for coordinating heavy metal absorbents. Li et al. also reported the production of PCN-222, known as MOF-545, using the solvothermal method with formic acid as a modulator. They utilized it as an absorbent for various anionic and cationic dyes, studying their adsorption kinetic parameters. These dyes were employed to investigate properties such as the kinetics of adsorption (which followed a pseudo-second-order model) and thermodynamics. The ideal Langmuir model suggested that adsorption occurs as a process of achieving monolayer coverage and is governed by an exothermic enthalpy effect. The remarkable adsorption capabilities of PCN-222 prompted researchers to develop a chromatography column for experimental use. Porphyrin frameworks, with or without metal ions, have been widely explored for various applications. Feng et al. reported PCN-222(Fe), which exhibits peroxidase activity, while Chen et al. reported PCN-222(Pd) as a fluorescent "turn on" sensor. 113 The method reported by Li, which is also documented by Zhou et al., involved two sonication steps and 80 hours of heating at 130 °C, in addition to the drying and activation processes. 114,115

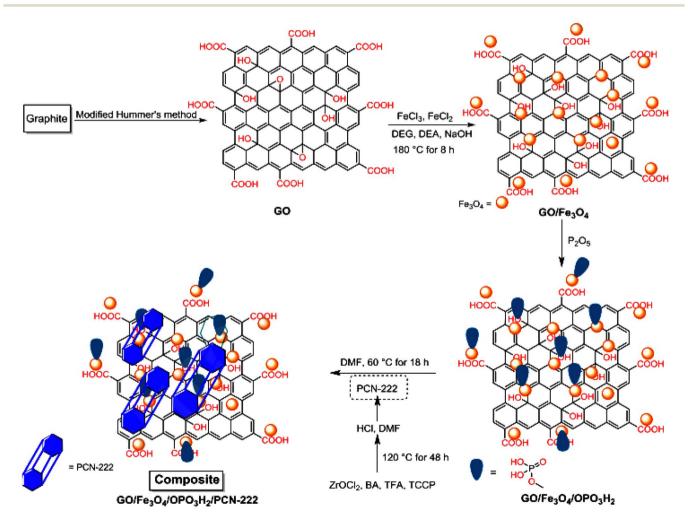
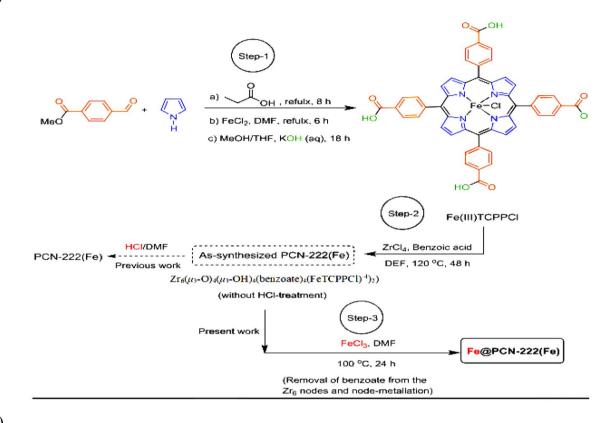


Fig. 8 Schematic representation of the synthesis pathway for the GO/Fe<sub>3</sub>O<sub>4</sub>/OPO<sub>3</sub>H<sub>2</sub>/PCN-222 composite. The process involves the stepwise functionalization of graphene oxide with iron oxide nanoparticles and phosphonic acid groups, followed by their incorporation onto the surface of the csq-topology Zr-based MOF, PCN-222. The resulting hybrid structure combines the high adsorption capacity of the functionalized nanomaterials with the porosity and selectivity of the MOF framework, enabling efficient uranium ion extraction from aqueous solutions.<sup>116</sup> From ref. 116 with permission. Copyright 2021, Elsevier.

a)



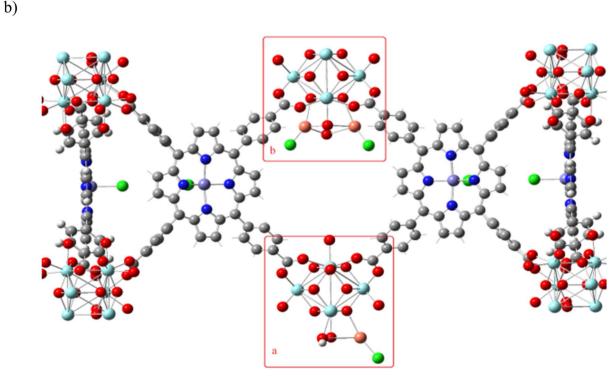


Fig. 9 Schematic representation of the incorporation of iron ions into the structure of PCN-222(Fe). (a) Stepwise synthesis of Fe@PCN-222(Fe), involving post-synthetic modification of PCN-222 with FeCl<sub>3</sub>, leading to dual incorporation of iron atoms both in the porphyrin centers (Fe- $TCPPCl \ linkers) \ and \ at the \ Zr_6 \ cluster \ nodes. (b) \ Proposed \ structural \ models \ of the \ resulting \ Zr_6Fe_2 \ node, \ illustrating \ the \ placement \ of \ iron(iii) \ ions \ descriptions \ description \$ around the metal clusters. Pink spheres represent Fe ions and green spheres represent Cl<sup>-</sup> counterions. This dual-metallic hierarchical MOF exhibits enhanced reactivity for visible-light photocatalysis and cooperative catalysis with earth-abundant metals.<sup>117</sup> From ref. 117 with permission. Copyright 2019, Elsevier.

Hariry et al. developed a new method for synthesizing PCN-222/MOF-545 based on ultrasound, which exhibited superiority due to lower temperature and significantly shorter synthesis duration. They dissolved ZrCl4 and MTCPP ligand in DMF with benzoic acid as a modulator under ultrasonic radiant power ranging from 600 W to 1200 W and temperatures between 40 °C to 120 °C for 120 minutes. Impurities were removed through a 24 hours washing process with acetone, followed by vacuum drying for 6 hours. Comparing the two methods, it was found that the crystals' morphology remained the same. Both methods demonstrated a type-IV absorb isotherm and a BET surface area of 2013.13 m<sup>2</sup> g<sup>-1</sup>. Samples synthesized with ultrasound exhibited two stages of weight loss: the first due to solvent elimination at 160 °C, followed by complete collapse between 300 °C to 600 °C. This data suggests that Hariry's method produces nearly identical results with significantly less energy and time. This newly synthesized MOF with porphyrin ligands can coordinate with different metals such as Mn3+, Fe3+, and Cu<sup>2+</sup>, providing additional coordination sites for absorbent materials. This prompted a comparison of their absorption properties, crystallization yields, and adsorption capacity for various organic dyes. The results indicate that PCN-222 with Cu<sup>2+</sup> exhibited a stronger correlation with MB similar to PCN-222-(Zr), while PCN-222-(Mn) demonstrated the highest adsorption capacity among different MOFs. However, Mn<sup>3+</sup> and Fe<sup>3+</sup> showed greater correlation with MO.<sup>85</sup>

Khajeh *et al.* successfully synthesized  $GO/Fe_3O_4/OPO_3H_2/PCN-222$  with a high-performance adsorbent on the surface of **csq**-topology Zr-based MOF in the way that showed in Fig. 8 presence of the  $GO/Fe_3O_4/OPO_3H_2$  results a reduce of the surface area from 2249 to 1350 m<sup>2</sup> g<sup>-1</sup>. This composite was

applied for distributive solid-phase uranium ions' extraction which dissolved in wastewater, based on critical parameters such as the amount of adsorbent, extraction and desorption times, pH of solution, and type and concentration of elution solvent that have been studied and optimized. Khajeh et~al. reported the highest adsorption capacity of the adsorbent was determined to be 416.7 mg g $^{-1}$ , much improved from what was reported with the individual components. The composite spectrum shows the characteristic adsorption bands related to the PCN-222 MOF and GO. The adsorption band is attributed to GO's existence from 220 nm to about 260 nm. Besides, the adsorption band from 410 nm to about 700 nm conforms to the porphyritic MOF. All received data emphasize that the metalorganic framework was perfectly linked to GO/Fe $_3$ O $_4$ /OPO $_3$ H $_2$  to achieve the formal hybrid material. $^{116}$ 

Khajeh et al. in another study, have reported zirconiumiron(III) porphyrin MOF with hierarchically structured called PCN-222(Fe). Post synthetically modification was applied on PCN-222 was with iron salts; this new modified MOF consists of  $Zr_6O_6(OH)_8(H_2O)_2(Fe)_2$  clusters connected by Fe-TCPPCl linkers (Fe2+ coordinated to central place of ligands) and used as an extra efficient forerunner, to result a MOF which has 2types of metals (Zr, Fe) named as Fe@PCN-222(Fe). Fe ions are present in both ligands and nodes. The apply of FeCl<sub>3</sub> can ensue in both eliminating the benzoic acids, potentially attributable to the in situ generations of HCl, and remained eight unsaturated terminals containing -OH//H2O ligands on the Zr6-clusters for the metalation. At the end, the iron(III) atoms were decorated around metal clusters of PCN-222(Fe), and a more reactive framework was obtained without using any post-treatment with a dilute hydrochloric acid solution as mentioned before. The

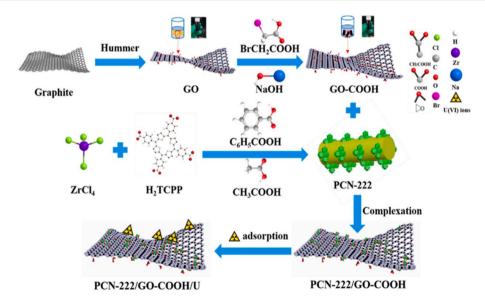


Fig. 10 Step-by-step schematic of the synthesis and assembly of the PCN-222/GO-COOH/U composite used for U(vi) adsorption. The process begins with the oxidation of graphite to graphene oxide (GO) via the Hummers' method, followed by functionalization with bromoacetic acid and subsequent carboxylation to yield GO-COOH. Separately, the Zr-based MOF PCN-222 is synthesized from ZrCl<sub>4</sub> and H<sub>2</sub>TCPP in the presence of benzoic and acetic acids. The PCN-222 framework is then anchored onto the GO-COOH surface via complexation to form the hybrid PCN-222/GO-COOH composite. This material is subsequently employed for the selective adsorption of U(vi) ions from aqueous solutions. The composite exhibits exceptional thermal, chemical, and structural stability, retaining the porphyrinic framework of PCN-222 while enabling efficient U(vi) recovery from real wastewater.<sup>118</sup> From ref. 118 with permission. Copyright 2021, Elsevier.

mesoporous MOF after modification could be used directly as (photo)-catalyst and not provide any damage to structure. This study exhibits the possible usage of multifunctional MOFs involve cooperative reactions that combine visible-light photocatalysis and earth-abundant metal catalysis. To be more understandable, an economically viable and environmentally benign process renders it more suitable for the continuous production of chemicals (Fig. 9).<sup>117</sup>

PCN-222/GO-COOH composites were subjected to boiling water, DMF, strong acid, or base at room temperature for 24 hours to check their stability. TGA results showed that PCN-222/ GO-COOH composites exhibited excellent thermal stability. These test results demonstrated the outstanding thermal, physical, and chemical stability of the composite. Bi et al. utilized this composite for U(v<sub>I</sub>) recovery from real U(v<sub>I</sub>)-containing wastewater, as discussed above by Khajeh et al. The distinguished selectivity, removal rate, and adsorption capacity of the PCN-222/GO-COOH composites make them suitable candidates for recovering U(vI) from real U(vI)-containing wastewater. TEM and TEM-EDS images captured from PCN-222 illustrate a normal tubular-like structure with a diameter of about 2.3 µm, exhibiting precise and uniform crystal lattices at higher magnification and uniform distributions of elements N, C, O, and Zr in the PCN-222. The step-by-step preparation of the absorbent is shown in Fig. 10. After complexing with GO-COOH, PCN-222 was successfully loaded onto the surface of GO-COOH, and the coating occurrence was observed at higher magnification, indicating that the original structure of PCN-222 was preserved in the complexation process.118

Modification of **PCN-222** once again has been chosen as the subject of the study of Khajeh *et al.* Thiol-functionalized **PCN-222** (**PCN-222-MBA**), was developed as an adsorbent using a SALI method, an acid-base reaction between molecule 4-mercaptobenzoic acid and terminal –OH/–H<sub>2</sub>O groups on Zr<sub>6</sub>-nodes of **PCN-222** to functionalize mesoporous **PCN-222** for gold ionic adsorption in the aqueous environment.<sup>119</sup>

He et al. focused on a modulator-based strategy for tuning the pore environment and mesoporous channels to achieve a structure with excellent catalytic activity, which serves as the gathering place of the MOF catalytic center. The size of the mesoporous channels is 2.8 nm, and although these long-range channels are not visible in the TEM image, they concluded that the environment around the cavity might vary. The mesoporous nature of the MOF, similar to PCN-222 (csq, (4,8)-connected), was determined by SAXS studies. The N2 adsorption isotherm is type IV, indicative of a mesoporous structure, with a range of 0.6 to 2.5 nm referred to as the hierarchical structure. NMR studies were conducted to understand the effect of modulators in the cavity environment, such as water and monocarboxylic acids. WM-MOFs, based on their design, exhibited excellent catalytic performance in the cycloaddition reaction of CO<sub>2</sub> and different epoxides, with high selectivity and conversion, and at low temperature and pressure. The effects of modulators (like water and monocarboxylic acids), as shown in this study, may explain why WM-MOFs exhibited higher weight loss and a lower decomposed temperature.84

It is evident that structures with csq topology have garnered considerable attention in research. However, it's essential not to overlook the fact that researchers are often drawn to working with structures that have been extensively studied rather than newer, less explored ones. The significance of this point can be carefully evaluated through subsequent studies conducted by various researchers and the conclusions drawn from these collective efforts. The csq structure renders the material suitable for applications requiring dual adsorptions of different molecules, as well as scenarios where the material needs to traverse units added to the MOF post-synthesis. The presence of two types of channels in the csq structure not only introduces new functional units but also makes it suitable for catalytic and absorption purposes. Nonetheless, the lack of uniform channels in the network has prompted researchers to explore other systems. It's worth noting that the realm of metal-organic frameworks (MOFs) is relatively new in scientific discussions, and comparative studies are common due to the variety of structures employed for similar applications.

## 2.3 scu topology

This topology provides uniform channels with 8 connected clusters and 4 connected organic nodes, so the same Zr precursor and same ligand which produced the  $\mathbf{csq}$  topology also could play a role in creating this topology (Fig. 11 and 22). The  $\mathbf{scu}$  topology, like the  $\mathbf{csq}$  topology, is among the most important and frequently observed topologies for zirconium-based metal-organic frameworks (MOFs). While these two topologies share many similarities, such as the hexanuclear zirconium cluster ([Zr<sub>6</sub>]) as the central metal node and their comparable high porosity, they also exhibit distinct differences. In  $\mathbf{csq}$ , the nodes are connected to linkers in a (4,8)-connected fashion, whereas in  $\mathbf{scu}$ , the connections follow a (6,6)-connected pattern. These simpler connections in the  $\mathbf{scu}$  structure result in more straightforward and homogeneous pores, as illustrated in Fig. 11. The  $\mathbf{csq}$  topology typically forms

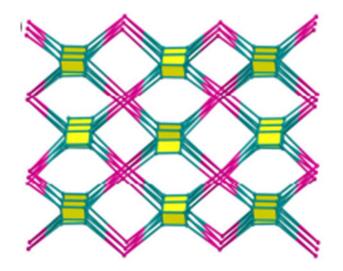


Fig. 11 Schematic of scu topology.<sup>137</sup> From ref. 137 with permission. Copyright 2018, American Chemical Society.

mesoporous channels with larger diameters, while **scu** channels are generally smaller and more uniform. This topology clearly creates more uniform cavities. **scu** MOFs are often utilized in applications requiring higher structural stability and more consistent diffusion properties.

NUPF-1 is one of the members of MPFs (metal porphyrin frameworks) with  $Zr_6(\mu_3-O)_4(\mu_3-OH)_4$  clusters similar to PCN-225 with scu, (4,8)-connected topology<sup>50,98</sup> reported by Xu et al. Until then this topology was unprecedented, they reported this MOF with doubly interpenetrations which has high thermal and chemical stability and undeniable flexibility. MPFs had wide application in optical perception systems, gas storage, and catalysts. Thus NUPF-1-RuCO was synthesized using  $[Ru_3(CO)_{12}]$  and the product was used for catalysis amination of alkanes with azides. Central metal in MPFs had a great effect on their property, for example, Wang et al. reported low catalytic activity toward epoxidation of trans-stilbene for MMPF-5(Cd) but changing Cd2+ to Cu2+ improved its catalytic performance.120 NUPF-1 has rod-shape purple crystals obtained by solvothermal reactions of a porphyrin ligand with ZrOCl<sub>2</sub>·8H<sub>2</sub>O in DMF and formic acid as a modulator. The porphyrin ligand is core-free and almost planar and also tetraphenyl porphyrin and benzoic acid moieties linked by amido units, with a span of 2.4 nm between the two neighboring carboxylate groups. Hence, the structure contains 8 connected octahedral nods and 4 connected D<sub>4</sub>h organic nods. Eventually, scu topology with 2.3  $\times$  5.1 nm was obtained. 73.6% of MOF was free space, and its large meso channel gives this opportunity for a twofold structure which was created and the only meso channel divided into 4 smaller channels with 2.66  $\times$  1.78 nm, 2  $\times$  0.72 nm, and 1.91 × 0.67 nm windows **NUPF-1** is strongly thermal and mechanical stable; TGA collapse temperature is 450 °C, and can tolerate pressure up to 12.5 Ton per cm<sup>2</sup>. It also showed high chemical stability; its pore volume didn't change in pH equal to 0.7 and 9. **NUPF-1** could absorb 107 cm<sup>3</sup> g<sup>-1</sup> of ethanol, 154 cm<sup>3</sup> g<sup>-1</sup> of methanol, and 182 cm3 g-1 of water in the vapor phase too, which clearly shows a high desire to absorb polar material. Another study talked about catalytic function of NUPF-1-RuCO and its size selective property in reactions.94

NU-1000, with the csq topology, emerged as a promising candidate for various absorption-based applications. Verma et al., while investigating the structural features of NU-1000, reported the existence of another scu-net polymorph, NU-901. This polymorph possesses a smaller average pore size and volume compared to NU-1000 and is not considered mesoporous, as also noted by Garibay et al. Its application in enhanced CO2 adsorption was investigated.121 Goswami et al. used time-resolved fluorescence imaging to identify this impurity as a structural isomer present at the center of the crystallites. They also mention that the type of modulator has an effect on the amount of this impurity. The scu-net structure of NU-901 features 1.2 nm diamond-shaped channels. In their study, they present some methods for limiting the production of NU-901, such as using biphenyl-4-carboxylic acid as a modulator or a comodulator like TFA.93 Although both NU-901 and NU-1000 are produced as impurities in another production process, phase-pure samples of both MOFs have been successfully

synthesized in bulk and investigated for electrocatalysis and separation membranes. Self-assembled monolayers and crystal engineering were utilized to control the polymorphism and orientation of NU-901/NU-1000 thin films, as shown in Fig. 12. The microspore width for both NU-901 and NU-1000 is almost balanced. However, owing to the presence of modulators occupying free sites of the cluster, the mesopores are smaller than reported. A washing step with HCl to remove modulators resulted in larger mesopores, approximately 30 Å. It was assumed that increasing the density of Zr-oxo clusters on the functionalized FTO can control the nucleation density of NU-1000. It can be inferred that the functionalized FTO possesses a surface coating of compact carboxyl groups (—COOH), mainly due to the ability of 16-PHDA to form a dense layer of carboxyl groups (—COOH) on the ITO surface.

As a different synthetic pathway from what was explained previously, presoaking the SAM-altered FTO substrate in the Zroxo cluster solution before the solvothermal synthesis enables a dense formation of Zr-oxo clusters on the substrate, leading to a high nucleation density in **NU-1000.**<sup>122</sup>

Using TTFTB (tetrathiafulvalene tetrabenzoate) and MeTTFTB (tetrathiafulvalene tetramethylbenzoate) ligands along with Zr<sub>6</sub> clusters, Su *et al.* reported two different MOFs with the following formulas:  $[\mathrm{Zr_6}(\mathrm{TTFTB})_2\mathrm{O_8}(\mathrm{OH}_2)_8]$  and  $[\mathrm{Zr_6}(\mathrm{MeTTFTB})_{1.5}\mathrm{O_4}(\mathrm{OH})_4(\mathrm{C_6H_5COO})_6]$ . Through steric tuning of the ligands, they achieved two distinct MOF structures. TTFTB leads to 4-connected square planar nodes, whereas Me-TTFTB results in 8-connected cubic nodes. This results in a 4,8-connected **scu** topology with TTFTB and a 4,6-connected she topology with Me-TTFTB.

**Zr-TTFTB**, which exhibited higher connectivity, showed micropores with a consistent pore size of about 12.7 Å. On the other hand, **Zr-MeTTFTB**, with lower connectivity, provided hierarchical pores with micropores measuring 12.6 and 15.8 Å, along with mesopores of 20.7 Å. The entire N<sub>2</sub> absorption and

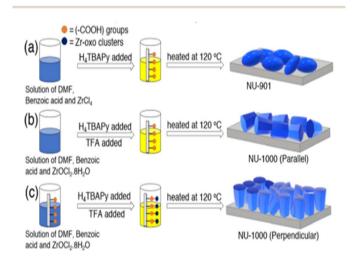


Fig. 12 Synthesis process to solvothermally produce films of three product (a) NU-901, (b) NU-1000 with parallel and (c) perpendicular orientation. 122 From ref. 122 with permission. Copyright 2021, American Chemical Society.

BET surface area reached 536 cm $^3$  g $^{-1}$  and 1932 m $^2$  g $^{-1}$ , respectively, with type-IV isotherms. However, **Zr-TTFTB** exhibited a type-I isotherm with an entire N $_2$  absorption of 393 cm $^3$  g $^{-1}$  and a BET surface area of 1353 m $^2$  g $^{-1}$ , indicative of a typical microporous structure.

Thus **scu** topology is another channel-oriented topology in which all channels are uniformly placed. In this topology, ligands and metal nodes are identified hypothetical cylinders within, making a good position for a flow of materials inside. In this topology, the channels can be square or rhombic, meaning that the vertical diameter and the horizontal diameter can be different or equal to each other. This topology has been studied more for absorption purposes, especially for gas absorption in the history of MOF uses. The lack of cages in the structure has made this topology inappropriate for loading applications or applications that require the fixation of a foreign substance inside the MOF.

#### 2.4 ftw topology

ftw topology is commonly produced when square/rectangular-shaped tetracarboxylates are coordinated to  $Zr_6$  clusters. Unlike previous topologies, here we have a cluster with more connectivity (12  $\nu s$ . 8), and regardless of the size of the ligand, we should see smaller cavities. A 12-connected  $Zr_6$  cluster ideally connected to a square or rectangular linker, and commonly did not provide mesoporous MOFs. 72

MMU is a Zr-based MOF based on BDC2- with 200 nm crystals in average, relatively low 453.8 m<sup>2</sup> g<sup>-1</sup> BET surface area, pore size between 3.5 to 7 nm, and ftw topology used by pang et al. for immobilizing laccase. They reported this MOF could accept 221.84 mg g<sup>-1</sup> of bovine serum albumin (BSA) in its pores. After that, the enzyme showed more stability in a wider range of pH and higher repeatability than the free enzyme. An interesting point about MMU is that its pores did not block in high concentration of enzyme; its structure allows the material to penetrate the pores structure after enzyme is encapsulated. For design of MMU, a surfactant-templating method that was previously used for silica gel to become mesopores was used. Chelating agent and surfactant added to the reaction caused developing of hierarchical structure. Pang et al. applied TFA as a modulator and CTAB (cetyltrimethylammonium bromide) as a chelating factor and small amount of hydrochloric acid.86

Li *et al.* proposed a novel MOF with a pore size ranging from 3.8 to 4.5 nm and **ftw** topology, utilizing it for encapsulating and immobilizing a nerve agent known as OPAA. Previous attempts to enlarge the pore and aperture size of **NU-1000** by introducing C–C single or triple bonds between adjacent phenyl rings resulted in the formation of an isomorphic zirconium MOF with the **ftw** topology. In response to this challenge, they developed a tetra-carboxylate pyrene-based linker, using DMF as the solvent and trifluoroacetic acid as a modulator to produce **NU-1003** with the same topology as **NU-1000**. Two types of pores were identified: 4.4 nm hexagonal and 1.7 nm triangular pores, showcasing an example of designing ligands to achieve the desired topology. This also demonstrates how altering and adding new lateral arms to ligands can impact the topology.<sup>102</sup>

Wang et al. during research on methods for separating ethylene gas from a mixture of gases, achieved new metalorganic frameworks called UPC-612 and UPC-613 that are modified version of ftw-based MOF-525 (first reported by Yaghi et al. in 2012 (ref. 123)) with Zr<sub>6</sub> clusters. Two new ligands called H<sub>4</sub>L-L and H<sub>4</sub>L-S has been used to product UPC-612 and UPC-613. These linkers were functionalized with a cyclopentadiene cobalt functional group which increases the host-guest interaction and achieves efficient ethylene purification. They reported BET surface area of UPC-612 and UPC-613 BET are 2016 and 853 m<sup>2</sup> g<sup>-1</sup>, respectively. The adsorption enthalpy order  $(Q_{\rm st})$  at zero coverage is  $C_2H_2$  (23.9 kJ mol<sup>-1</sup>) >  $C_2H_6$  $(22.4 \text{ kJ mol}^{-1}) > C_2H_4 (16.9 \text{ kJ mol}^{-1})$ ; in summary, UPC-612 separate C<sub>2</sub>H<sub>2</sub> and C<sub>2</sub>H<sub>6</sub> from C<sub>2</sub>H<sub>4</sub> compared to MOF-525 and the version that only modified by cobalt (MOF-525(Co)) uniquely, creates a substance with a purity percentage higher than 99.99%. Irregular cubes surrounded by six linkers presented in this MOF, have approximately 2 nm diameter of the cage and this feature enables modifications. Within a cage structure, the metal cluster is situated at the vertex, and the linker covers the surface of the cube, distinguished from the pore structure in which guest molecules cross through the cage; they need to enter through the cage window. Irregular movements are then made in the cavity and finally out of another cage window. They reported information on the mechanism and how to increase the separation capacity in their study.96

The orientation of  $\pi$ -interaction sites in a sequence of synthesized and evaluated MOFs, specifically MOF-526, MOF-527, and MOF-528, has been documented. These MOFs display a systematic increase in pore size, ranging from 1.9 nm in MOF-526 to 3.7 nm in MOF-528, as well as enhanced permanent porosity and capability to incorporate and subsequently release extended organic materials in water. The trapped organic material, which has a polycyclic structure, and the  $\pi$ -interaction between discrete porphyrin units in the MOF structure, contribute to remarkable reversibility. Additionally, the mesopores in these MOFs facilitate rapid adsorption kinetics. In particular, these MOFs, through their porphyrin units, enable the quantitative absorption of various large organic dyes (details provided below) in a 2:1 molar ratio, showcasing unique kinetic behavior for MOFs, such as a concentration of 4.54 imes105 mol L<sup>-1</sup> for rhodamine B (RhB) at very limited water concentrations of 10 ppm. Rotational-echo double-resonance (REDOR) NMR experiments exposed the interval between the entrapped molecules and the porphyrin units in the ligand, ranging from 3.24 to 3.37 Å, confirming the specific  $\pi$ -interaction. Ten complete inclusion-release cycles were successfully conducted in these MOFs, demonstrating their reversible and repeatable dynamics without any decomposition, making them highly suitable for recycling large polycyclic hazardous molecules from water. MOF-526, in particular, performs on par with leading-edge carbons and polymers. In contrast, this study introduces planar porphyrin-based linkers that are extended, with the largest organic linker spanning approximately 45 Å, effectively utilizing both sides of the flat porphyrin unit for interactions with organic guest molecules through specific  $\pi$ interactions. While a broad range of applications for porphyrin-

based MOFs, including catalysis and the absorption of gases and macromolecules, has been extensively explored, this is the inaugural study demonstrating their capability to quantitatively interact with prominent organic guest molecules using specific  $\pi$ -interactions for water and wastewater treatment. This characteristic, combined with their exceptional chemical stability, positions these MOFs as ideal candidates for kinetic recyclability and the removal of typical organic pollutants from water, challenging the latest advancements in carbons and polymers. Finally, the smallest member of this isoreticular group, MOF-525, is a chemically stable microporous MOF created by connecting 12-connected zirconium oxide clusters [Zr<sub>6</sub>(OH)<sub>4</sub>O<sub>4</sub>(- $(CO_2)_{12}$  with a porphyrin linker (tetrakis(4-carboxyphenyl) porphyrin), known as H2-TCPP, which has a square planar shape. To construct the larger members of this series, benzene or phenylene units are incorporated into the TCPP linker between the carboxylate and porphyrin  $\pi$ -interaction site. This

not only aids in purifying the linker during its synthesis but also ensures the reversibility necessary for the growth of the corresponding MOF crystals.108 Each extended MOF variant in this series maintained the fundamental cubic ftw topology. The strategic placement of the porphyrin unit at the center of each cubic lattice face ensured optimal separation of the  $\pi$ -interaction sites, facilitating dynamic and reversible interactions with guest molecules. The use of larger linkers led to an increase in the pore sizes of the MOFs from 2.0 to 4.5 nm, enhancing the efficacy of the  $\pi$ -interaction sites. This structural arrangement ensured that the porphyrin  $\pi$ -interaction sites were wellisolated within their crystal frameworks, allowing guest molecules complete access to the pores. The MOFs demonstrated type IV isotherms during N2 adsorption studies, with surface areas recorded at 4260, 2000, and 3550 m<sup>2</sup> g<sup>-1</sup>, respectively. Given their exceptional chemical stability, lasting porosity, and

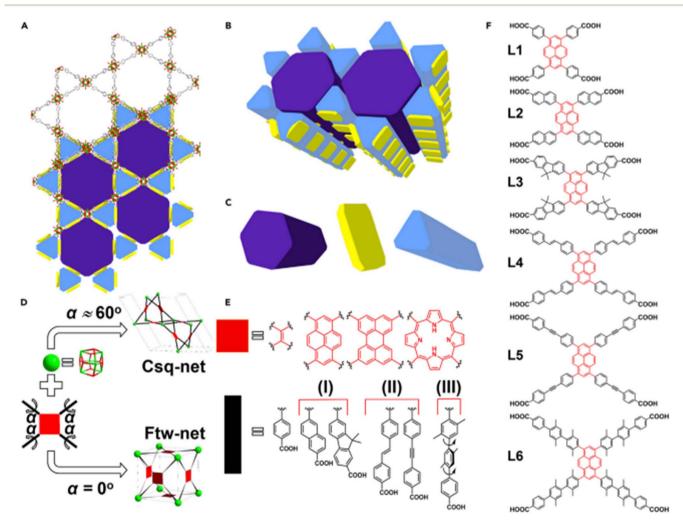


Fig. 13 Schematic presentation of csq-net topology and design of linkers for csq-net Zr-MOFs (A) Top view and (B) side view of interconnected hierarchical channels composed (C) channels structure shown by the geometric shapes marked in fig in csq-net Zr-MOFs. (D) Relationship between intramolecular torsion angles of the linkers and the topology of the resulting product ( $Zr_6$  clusters illustrated by green balls). (E) Existing and proposed chemical structures of the tetratopic linkers were composed of different backbones (red squares) and arms (black rods) used for constructing csq-net zirconium MOFs with varying carbon chain. (F) Chemical structures of linkers L1–L6 used for constructing NU-100x (x = 0, 3, 4, 5, 6, 7) series MOFs. 90 From ref. 90 with permission. Copyright 2019, Royal Society of Chemistry.

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substantial pore openings, these MOFs are perfectly suited for demonstrating consistent and reversible behavior in water.87

Lyu et al. reported another study on extending novel MOFs via linker functionalization. In this research, three distinct Zrbased MOFs were synthesized by controlling the steric aspects of the conformations of replaced tetratopic carboxylate linkers. They realized that topology could simply be related to the linker conformation adjustments. Factors affecting linker conformation is modulating reagent, concentration, metal precursor, environmental factors, and solvent. Using tetratopic linkers which provide high rotational freedom for their lateral arms like tetracarboxyphenylporphyrin (TCPP) may make various topologies.113,124 In recent studies by this group on the production of csq-net MOFs, they unexpectedly obtained MOFs with ftw topology instead of those with larger ligands. They proposed that a critical influence of the planar "backbone" and the arm's torsion angle was the reason for this observation. They suggested that when the torsion angle was close to 60°, the csq topology prevailed, while a torsion angle close to 0° resulted in the ftw topology (see Fig. 13). Density functional theory (DFT) calculations indicated that pyrene-aromatic systems tend to form 50-60° torsion angles around their minimal energy, providing insight into why researchers are encouraged to investigate linkers of this family to produce csq structures.66

Three linkers were designed to introduce to increase the rigidity of the structure (Fig. 13). With L1 linker NU-903 was formed (first reported with the name of CAU-24 by Stock et al. 125) with a scu topology. With L2, NU-904 is obtained, featuring ovalshaped crystals. The crystal properties of NU-904 reveal a unique reticular-merohedral twin configuration, where three distinct orientations are stacked along the b-axis, each rotated 60° relative to the others. This arrangement forms a rare 4,12-connected shp structure, representing the mean structure of the threefold twinned NU-904. The interplay of three scu-net components in the reticular twins contributes to the overall 6-fold symmetry observed in the structure. Notably, the presence of threefold twins in the ordered 4,8-connected scu structure results in a twinned version of the rare shp structure. This intrinsic connection between the two topological networks was previously undocumented before Lyu's investigation. Their findings also reveal channels with a triangular configuration, contrasting with the diamond-shaped channels identified in NU-903.90

ftw topology, like the other topologies mentioned before, is based on four connected linkers. Due to the higher connectivity of this topology compared to the previous ones, structures containing this topology are usually classified as microporous materials. Researchers enlarged the linkers, in order to reach mesoporous materials, and the use of peers usually leads to the creation of csq and scu topologies. Unlike the topologies before, ftw topology is based on cages and no channels are observed. As explained, this topology is mostly used for encapsulation or in reactions requiring, more and more frequent collisions; so we use them to stay for a longer time in the structure. Since the flow of molecules entering this structure must pass through one cage window and then leak from another window to the adjacent cage, such placement helps materials including this topology become very suitable for absorption and encapsulation

purposes. As discussed earlier, the ftw topology exhibits higher connectivity. This topology emerges when fewer modulators are used during synthesis. The high connectivity leads to the formation of smaller pores. Conventionally, employing smaller ligands in this topology results in non-mesoporous structures. The ftw topology also features higher symmetry and lacks a hierarchical structure. While scu and csq topologies are commonly used for applications such as gas adsorption and encapsulation, topologies like ftw and rtl are designed for more specialized applications or specific conditions.

#### 2.5 fcu topology

It is not wrong to mention that fcu was the first topology reported and investigated in Zr-based MOFs. The first reported Zrbased MOF was UiO-66, reported by Cavka in 2008.46 The UiO-66 structure consists of octahedral cages and tetrahedral cages, designed with slight triangular windows with a diameter near 0.6 nm (Fig. 14). UiO-66 is the first reported Zr-based MOF that has suitable stability and its and other derivatives of this compound's remarkable properties studied a lot even until now, 126 but it has tiny pores with low surface area. fcu topology includes a 12-connected Zr<sub>6</sub> cluster connected toward ditopic ligands like BDC in UiO-66, BPDC in UiO-67, and TPDC in UiO-68.127,128 Using UiO-66 and UiO-66-NH2 treated with C2F5 and CF<sub>4</sub> plasma is a novel approach to develop hierarchical MOF networks. One of the positive features of UiO-66 is its stability against moisture and acids, while its negative feature is the difficulty of electrical charge transfer. Additionally, its pore size is too small. Therefore, Decosta et al. developed a mesoporous MOF based on UiO-66 as a template. The results of the reaction with different powers of the ultrasonic systems are correlated with the duration of treatment: (1) reducing the power level to 75 W increased the N<sub>2</sub> uptake by achieving the highest etching efficiency, and (2) it increased the cavity size and BET surface area while using UiO-66. In this study, fluorocarbon radicals were used to break Zr-O bonds, providing an excellent method to achieve the fcu topology with larger pores with 4,4'-biphenyldicarboxylate (BPDC) and terphenyl dicarboxylate (TPDC) as a linker.129

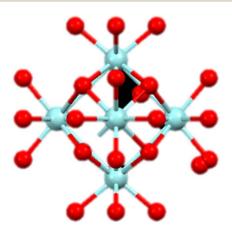


Fig. 14 Structure of UiO-66 node.

UiO-66, besides its importance as the first Zr-based also, plays a touchstone in comparisons, as we will see in the following. Kim et al. used three different absorbents (to separation of SF<sub>6</sub> gas from a mixture of SF<sub>6</sub> and N<sub>2</sub> UiO-66, UiO-67, and zeolite-13x). UiO-67 (first reported by Cavka et al. at 2008) is a mesoporous MOF that, for a smuch as its bigger pore size than UiO-66 showed better results in the separation process while both had fcu, 12-connected topology. UiO-67 has a bigger pore size that was confirmed by type (IV) BET adsorption and had the highest selectivity in high pressures. At low pressures, the order of selectivity for 50/50 and 10/90 compositions was as follows: UiO-66 > zeolite-13x > UiO-67 (contrary to what was said at high pressure). SF<sub>6</sub> uptake at low pressures is precisely the opposite correlated with the order of the smallest pore size of the adsorbents. Results clearly indicate the superior SF<sub>6</sub>/N<sub>2</sub> in 50/50 and 10/90 compositions separation performance of UiO-67 compared with UiO-66 and zeolite-13 under dynamic mixture flow conditions. 130

The topology of **Zr-UiO-66-PDC**, which is one of the precursor materials for the preparation of [**Zr-UiO-66-PDC-SO**<sub>3</sub>**H**]**Cl** that could be used for the preparation of dicyanomethylene pyridines *via* chemical and electrochemical methods, has been studied by Waitschat *et al.*<sup>131</sup> [**Zr-UiO-66-PDC-SO**<sub>3</sub>**H**]**Cl** contains 12-connected Zr clusters with **fcu** topological network. [Zr-UiO-66-PDC-SO<sub>3</sub>H]**Cl** is introduced as a mesoporous catalyst.

Lee et al. demonstrated an innovative method for converting microporous UiO-66 into an amorphous mesoporous absorbent resistant to extreme pH and intense nucleophile challenges. UiO-66 can function as an adsorbent in an acidic environment. It has been observed that it can absorb copper(II) and nucleophiles. However, its ability to maintain adsorption capacity despite the loss of its crystalline structure under the influence of nucleophiles at high or low pH indicates that its adsorption capacity does not depend solely on surface area or crystal structure. The disappearance of crystals occurs when it is immersed in acidic and nucleophilic conditions (0.1 M/1 M HCl/Cl<sup>-</sup>, HNO<sub>3</sub>/NO<sub>3</sub><sup>-</sup>, H<sub>2</sub>CO<sub>3</sub>/CO<sub>3</sub><sup>2-</sup>, H<sub>3</sub>PO<sub>4</sub>/PO<sub>4</sub><sup>3-</sup>, and HOAc/ OAc at pH 1, 7, and 12, as well as in 0.1 M NaOH). As part of this pivotal study, adsorption kinetic tests of Cu<sup>2+</sup> ions were conducted using pristine and modified UiO-66 with 4 mg mL<sup>-1</sup> adsorbents and an initial Cu<sup>2+</sup> concentration of 9.6 mg L<sup>-1</sup>,

Table 2 The BET surface area of anion-modified UiO-66 under different pH (ref. 132)

Sample	pH = 1	pH = 7	pH = 12
Pristine UiO-66	809.4		
0.1 M chloride	854.0	839.1	116.1
1 M chloride	479.2	349.1	6.5
0.1 M nitrate	737.6	527.3	727.3
1 M nitrate	400.4	281.2	18.5
0.1 M phosphate	9.7	12.3	28.8
1 M phosphate	5.3	3.6	9.9
0.1 M acetate	659.6	686.7	108.8
1 M acetate	428.7	31.8	33.3
0.1 M NaOH	148.0 (pH 13)		

shaken at 200 rpm and 25  $^{\circ}\mathrm{C}$  for 24 hours. Table 2 presents the effect of treatment.

The importance of the **fcu** topology is mostly summarized in its role in the history of zirconium-based MOFs. According to investigations and studies by various authors, this topology has been predominantly explored in the context of **UiO-66**. It is based on 2 and 12 connections, resulting in small pore sizes, yet a hierarchical structure is observed. Most studies have focused on **UiO-66** and its derivatives, as researchers aim to enhance this compound as the first zirconium-based MOF introduced.

## 2.6 spn topology

**MOF-808** which is reported by Furukawa and co-workers, is made of tetrahedral cages with inorganic SBUs at its vertices and the 1,3,5-BTC linkers at its faces.<sup>32</sup> In this MOF, six formate ligands complete the coordination of the Zr cluster, which causes a **spn** topology with an internal pore diameter of 1.8 nm for the **MOF-808**. Furthermore, it makes surface areas higher than  $2000 \text{ m}^2 \text{ g}^{-1}$ . According to the official description of IUPAC

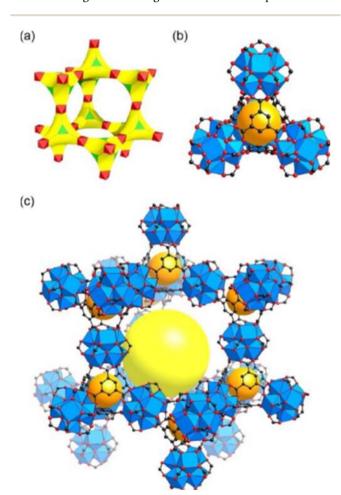


Fig. 15 Schematic of the spn topology (a) exhibited by MOF-808 with two kind of cages, first octahedral which indicate with red, and triangular which showed with green. (b) and large adamantane pores (c) atom color scheme: black for carbon, red for oxygen, blue for Zr. H atoms are hidden for better understanding. Large yellow and small orange balls showed the space in the framework.<sup>133</sup> From ref. 132 with permission. Copyright 2015, Wiley-VCH.

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TMTB

Zr<sub>e</sub> node

Fig. 16 Crystal structure and topology of the mesoporous Zr-based MOF NU-1200. The framework is constructed from 8-connected  $Zr_6$  nodes with the formula  $[Zr_6(\mu_3-O)_4(\mu_3-OH)_4]^{12+}$  and tritopic organic linkers, 4,4',4"-(2,4,6-trimethylbenzene-1,3,5-triyl)-tribenzoic acid (TMTB). NU-1200 exhibits a hierarchical pore architecture consisting of 1.4 nm sodalite-like cages and 2.2 nm interwoven mesoporous channels. Insets show the molecular structure of the TMTB linker and the  $Zr_6$  node. The presence of four terminal  $-OH/H_2O$  groups per cluster provides accessible metal grafting sites, making NU-1200 a suitable platform for post-synthetic metalation and catalytic applications. From ref. 139 with permission. Copyright 2021, American Chemical Society.

MOF-808, is not a mesoporous MOF, but because the very small distance between its dimensions and definition of mesoporous material and the fact that MOF-808 and PCN-777 are the only examples for **spn** topology, authors dealt with it very briefly.<sup>133</sup> The **spn** topology is distinct from the previously discussed topologies. In the **spn** topology, the nodes are connected in a (4,6)-fashion, resulting in small yet orderly channels. Unlike **csq**, there is no hierarchical structure observed here. Due to its small and uniform pores, the **spn** topology is well-suited for applications requiring the adsorption of small gases and material storage. Similar to **scu**, **spn** also exhibits high symmetry, in contrast to **csq** (Fig. 15).

## 2.7 reo topology

Nowadays, one of the most exciting fields of study involves the substitution of metals in synthesized MOFs, as explored in Gharevand et al.'s research. They introduced Ce metal into Zrbased nets of UiO-66 with fcu-12 connected topology, DUT-67 with reo-8-connected topology, and MOF-808 with spn-6-connected topology to create heterometal clusters. Their aim was to investigate the catalytic activity of these clusters in the conversion of diisopropylfluorophosphate to its alcohol derivative. The study revealed that increasing the Ce/Zr molar ratio and doping trace amounts of magnesium enhanced the catalytic rate of P-F bond cleavage. Previous studies by Plonka et al., Peterson et al., and Mondloch et al. have also investigated these MOFs, yielding promising results. 134-137 As we know, Zr4+ is a strong Lewis acid, which has been the main focus of attention in Zr-carboxylatebased MOFs. However, in many studies, Ce4+ has been found to be a more vital Lewis acid. The 4f orbital of Ce also exhibits stronger interaction with the P=O bond, thereby increasing the reaction rate. Due to the instability of Ce-based MOFs, investing in Zr/Ce-based MOFs could be a lucrative field. The molar ratios of incorporated Ce and Zr in mixed-metal MOFs are as follows: U01 (1Ce: 5Zr), U02 (2Ce: 4Zr), U03 (3Ce: 3Zr), D01 (2Ce: 4Zr), D02 (5Ce:1Zr), M01 (0.5Ce:5.5Zr), M02 (2Ce:4Zr), and M03

(5Ce:1Zr). In all the cases above, an increase in the Ce/Zr molar ratio resulted in an extended unit cell, which was logical due to the higher atomic radius of Ce. TGA reports have shown that the U series (U01, U02, U03) exhibited structural defects and a decrease in collapse temperature. N<sub>2</sub> absorption showed type I behavior, confirming their microporous nature. BET analysis revealed a decrease in surface area for the D series to 825 m<sup>2</sup> g<sup>-1</sup> according to Jacobson *et al.* MOF-808 with the **reo** topology provided better access for Ce substitution, a property that UiO-66 did not possess. Therefore, M01 and M02 exhibited higher BET surface areas, while M03 showed a lower surface area compared to MOF-808, likely due to its lower thermal stability.

In the second stage, the doping of magnesium was studied, which was first reported by Gil-San-Milan  $et\ al.$  They used  $[Mg(OMe)_2(MeOH)_2]_4$  for the metalation of the same MOFs. They reported that UiO-66 with ftw topology did not show any changes because Mg could not infiltrate into the micropores. However, in NU-1000 and MOF-808, Mg was added to the clusters, resulting in MgZr $_5(OH)_6$ . Comparing MOF-808 and NU-1000, MOF-808 exhibited better catalytic ability, indicating that since metalation only occurred in meso-sized pores, while nerve agent diffusion occurred in both meso and micro pores, the spn topology with unmixed pores showed better performance in nerve agent removal.

Garevand *et al.* reported merging Ce and Zr has an excellent effect on nerve agent removal, and also doping Mg in the system increases its catalytic performance. Y9,137 Nguyen *et al.* reported **reo**-net MOF termed **Reo-MOF-1**, synthesized with solvothermal method, using 4-sulfonaphthalene-2,6-dicarboxylate (HSNDC<sup>2-</sup>) as linkers and  $Zr_6O_8(H_2O)_8(CO_2)_8$  for clusters. they reported this MOF has **reo** structure with 23 Å central cages. As we expect from reo topology this MOF is also have eight 9 Å corner-shared octahedral cages too. The structure observed in **reo-MOF-1**, resembling that found in **DUT-52** (**fcu** topology), is distinguished by the absence of body-centered packing of the 12-connected  $Zr_6O_4(OH)_4(CO_2)_{12}$  clusters. This absence is

attributed to the subtle but crucial influence exerted by the bulkiness of functional groups on the linkers. The finding is supported by control experiments in which the ratio of H<sub>3</sub>SNDC/naphthalene-2,6-dicarboxylate linkers was varied. It is affirmed that bulky functionalities play a pivotal role in defectcontrolled synthesis. The reo-MOF-1<sub>A</sub> framework was obtained through linker exchange, resulting in a chemically and thermally stable material, despite its large pores. Remarkably, permanent porosity is exhibited by reo-MOF-1A (with BET and Langmuir SA values of 2104 m<sup>2</sup> g<sup>-1</sup> and 2203 m<sup>2</sup> g<sup>-1</sup>, respectively). Due to these remarkable structural features, a significant enhancement in the yield of Brønsted acid-catalyzed reactions is achieved by reo-MOF-1A. Upon analyzing the diffraction data of the as-synthesized reo-MOF-1 material, it is determined that the framework adopts a crystalline structure in the cubic space group  $Pm\bar{3}$  (no. 200), with a unit cell length measuring 23.6938 Å. This suggests that the Zr clusters within reo-MOF-1 are connected by SNDC3-/HSNDC2- linkers, mirroring the arrangement observed in DUT-52. Notably, the absence of 12-connected Zr<sub>6</sub>O<sub>4</sub>(OH)<sub>4</sub>(CO<sub>2</sub>)<sub>12</sub> clusters at the body-centered position in DUT-52 is confirmed in reo-MOF-1, as evidenced by the presence of reflections that would be forbidden in a body-centered unit cell. To refine the atomic positions within the lattice, a comprehensive Rietveld refinement is carried out on the proposed structure, resulting in successful refinement and low R-values. In their report they also mentioned high thermal stability and high BET surface area. 138 Same research group in another paper used this MOF for ultra-high removal of cationic malachite green dye from water. Topology of this product modified for this application as there is nearly 1 nm side cages which can absorb and stabilized dye in themselves. In their study, they investigated influence of pH and material content. They proposed, duo to SO<sub>3</sub>H groups which is present in reo-MOF-1 structure mechanism for adsorption, the adsorption mechanism of MG can be analyzed by examining various interactions, such as electrostatic forces and  $\pi$ - $\pi$  interactions. 139 As observed, the connectivity of this topology differs from that of the csq topology. The nodes are connected in

a (4,6)-fashion, resulting in a uniform, non-hierarchical, and three-dimensional network. The **reo** topology typically forms a three-dimensional structure that resembles a zeolitic network with symmetrical features. In the **reo** topology, the pores are generally smaller and more uniform. Structures with the **reo** topology are typically stable and resistant to temperature fluctuations and chemical conditions.

#### 2.8 the topology

the is one of the topologies that is suitable for PSM because in this topology, there are large sodalite-shaped cages that are surrounded by 12 channels. They are excellent for the penetration of guest molecules. NU-1200 is the first Zr-MOF designed with the topology and obtained by controlling the geometry of its constituent units. With 8 and 6 junction structures (in csp, bcu, and spn topologies), several coordination sites are covered with labial OH or H<sub>2</sub>O ligands and are suitable for substitution reactions or site limiting. The goal is to create some spatial constraints on the linker to create a triangular prism to reach the topology. This highly penetrating topology shows that Zr clusters are readily available for easy PSM execution. The ligand used is TMTB, which caused the carboxylates in this ligand to lock perpendicular in the benzoic plate. Although the structure remains D<sub>3</sub>h, but ligands are not in the same plane. For PSM: metal must react with OH<sup>-</sup> and H<sub>2</sub>O, the metal precursor must be solved by solvent but this solvent must not be coordinated, the acid from the modulator removal should not damage the MOF structure, and the ligand attached to the modulator causes rotation, destruction, and defect in the cluster.66

Chen *et al.* documented a robust heterogeneous molybdenum catalyst, constituted by  $-OH/H_2O$  metal grafting sites situated on the Zr<sub>6</sub> cluster of the mesoporous MOF **NU-1200**. This MOF possesses a mesoporous configuration, with terminal hydroxyl groups present on the Zr<sub>6</sub> cluster. **The** Zr-MOFs are comprised of 8-connected  $[Zr_6(\mu_3-O)_4(\mu_3-OH)_4]^{12+}$  clusters and three-topic 4,4',4"-(2,4,6-trimethylbenzene-1,3,5-triyl)-tribenzoic acid (TMTB) linkers, and they adopt a specific topology as illustrated in Fig. 16. The structure showcases 1.4 nm sodalite-like cages and

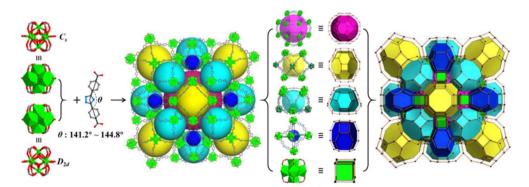


Fig. 17 Diagrammatic illustration of Zr-TZDB-bon-MOF: in the first column, zirconium-based inorganic MBBs with two  $C_s$  and  $D_2$ d symmetry group are accompanied by a bent organic linker ( $\theta$ , 141.2–144.8°) TZDB. Second column showing formation of 3D MOF with four different cages which magnified in the third column with pink color that showed rhombicuboctahedral, yellow color that showed cuboctahedral, aquamarine showed square antiprismatic and blue which represents octahedral cages. Resulting in the augmented bon natural tiling. Zr = green, C = gray, N = blue, and O = red. Hydrogen atoms are hidden for simplicity.<sup>141</sup> From ref. 140 with permission. Copyright 2020, Elsevier.

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additional interwoven mesoporous 2.2 nm channels, classified as mesopores. Given that each cluster is linked to eight linkers, a total of four unsaturated terminals with hydroxyl/aqua ( $-OH/H_2O$ ) groups are available, acting as grafting sites for active metal ions. These metal ions can be introduced through Solvothermal deposition In Metal–organic frameworks (SIM), a post-synthetic technique. In comparison to other 8-connected MOFs like NU-1000 and NU-1008, which demonstrate the csq topology and a characteristic c-pore, NU-1200 uniquely allows the anchoring of metal active species exclusively at the  $-OH/H_2O$  groups located in the mesopores. Additionally, the layered structure of NU-1200 enhances the diffusion of substrates, rendering it a promising heterogeneous base with the potential to provide consistently distributed active sites within its confined pore spaces.  $^{140}$ 

#### 2.9 bon topology

Two isometric Zr-based metal-organic frameworks (MOFs) with bon and reo topologies were synthesized solvothermally using ZrCl<sub>4</sub> and a bent ditopic carboxylate ligand. These MOFs are characterized by their mesoporous nature and exceptional stability. In contrast to the largest cage in MIL-101, the MOF which has bon topology consists of 24 metal clusters, equivalent to 144 zirconium atoms (as opposed to 126 in chromium), and 48 TZDB groups, which are novel in the context of MOFs. Cage which configured as rco shaped features twenty rectangular (approximately  $10.8 \times 20.2 \times 2$  Å), six square (approximately 15.5 Å), and eight triangular (approximately 8.8 Å) windows. This cage is encased by 12 sap, eight oct, and six cuo cages. By viewing the Metal Building Blocks (MBBs) as eight-connected quadrangular prismatic Secondary Building Units (SBUs), the ZrTZDB-bon-MOF can be described as a single-node net with a bon topology (refer to Fig. 17).

Single Crystal X-ray Diffraction (SCXRD) analysis highlights the distinctions between **Zr-TZDB-reo-MOF** and **Zr-TZDB-bon-MOF** in terms of unit cell parameters and space groups. **Zr-TZDB-reo-MOF** is composed of a crystallographically independent half TZDB linker and two zirconium ions. The reo topology

involves a combination of two  $Zr_1$  and four  $Zr_2$  ions with eight  $\mu_3$ -OH/O, eight terminal –OH/H<sub>2</sub>O groups, and eight distinct carboxylate groups, resulting in an identical MBB of  $[Zr_6O_4(-OH)_8(H_2O)_4(O_2C^-)_8]$ , albeit with  $D_{2h}$  symmetry (see Fig. 18). **Zr-TZDB-reo-MOF** is surrounded by cuo and oct cages with diameters of 25.3 Å and 20.2 Å, respectively.<sup>141</sup>

## 2.10 hbr topology

Darche *et al.* showed a modulator-based synthesis for a MOF named **DUT-126** with  $\rm Zr_6O_4(OH)_4$  cluster and  $\rm H_2TDC$  as a linker and trifluoroacetic acid as a modulator to produce **hbr** topology with (8,8)-connected SBU. Although the linker and cluster of **DUT-126** and **DUT-68** were completely the same, but their topology was different mainly because of the linkers place. This was the first **hbr** topology reported. **hbr** presents two kinds of micropores (0.58 nm) and middle-sized pores (1.18 nm) and one hexagonal meso channel (2.28 nm). The compound is stable in water and shows permanent porosity if activated from DMF in vacuum at temperatures lower than 180 °C. They reported BET surface area of 1297 m<sup>2</sup> g<sup>-1</sup> and 0.48 cm<sup>3</sup> g<sup>-1</sup> for total pore volume. Since the reduced connectivity of these MOF, functional groups could connect directly to metal clusters, and this property improves the catalytic capability of the system.<sup>75</sup>

#### 2.11 Other topologies

Recently a new MOF called CAU-45 was reported by Leubner et~al. This MOF has 6 and 12 metal nuclear ( $[\mathrm{Zr}_6(\mu_3\text{-O})_4(\mu_3\text{-OH})_4]^{12+}$  and  $[\mathrm{Zr}_{12}(\mu_3\text{-O})_8(\mu_3\text{-OH})_8(\mu\text{-OH})_6]^{18+}$ ) and 5-acetamidoisophthalic acid as ligand. Also Garai et~al. reported another 6 and 12 connected nods in MOF, MIP-206 that also synthesized with isophthalic acid and showed same 3-dimensional structure. They showed formic-acid-based chemical hydrogen storage when Pd-nano particles doped in MOF structure.  $^{84}$  CAU-45 exhibits a honeycomb structure with the  $[\mathrm{Zr}_{30}\mathrm{O}_{20}(\mathrm{OH})_{26}(\mathrm{OAc})_{18}\mathrm{L}_{18}]$  formula. Leubner et~al. reported zirconium acetate 5-acetamido isophthalic acid and acetic acid in a solvothermal reaction in two days achieved CAU-45 rode type crystals with the

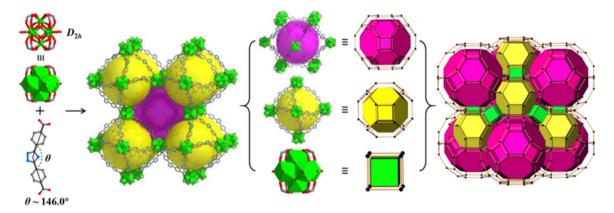


Fig. 18 Schematic representation of Zr-TZDB-reo-MOF: first column, zirconium-based hexanuclear inorganic MBB with  $D_{2h}$  symmetry group and bent organic linker ( $\theta \sim 146.0^{\circ}$ ) TZDB. Second column showing 3D MOF with two different cages which magnified in the third column with pink color for cuboctahedral and yellow which represented octahedral cages. Leading to the enhanced reo natural tiling. Zr is represented in green, C in gray, N in blue, and O in red. Hydrogen atoms are hidden for simplicity. From ref. 140 with permission. Copyright 2020, Elsevier.

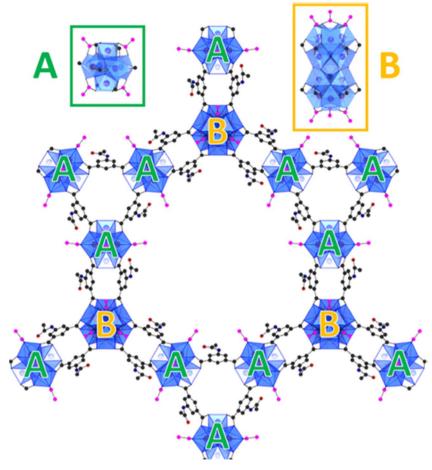


Fig. 19 Secondary building units (SBUs) of CAU-45 and their connection to a layer motif through 5-acetamido isophthalate ions. (A) Hexanuclear clusters. (B) Dodecanuclear clusters. Carbon atoms from the linker are shown in black, and acetate carbon atoms are in pink. Zirconium is depicted in bronze, oxygen in red, nitrogen in dark blue, and hydrogen is not displayed. Zirconium—oxygen clusters are highlighted in blue.<sup>54</sup> From ref. 54 with permission. Copyright 2020, American Chemical Society.

size of 0.3 to 3 µm. Stok et al. also reported a method that achieved low crystallized structure by using cRED crystal structure and unit cell determined. CAU-45 crystallizes in the hexagonal space group  $P6_3/mmc$  with a = 33.802(4) and c =29.096(5) Å, and the c-axis is arranged along the rod. This MOF has two different clusters, which is the first hexa- and dodecanuclear cluster reported. Before this, Zhang et al. reported a MOF with Zr<sub>8</sub> and Zr<sub>6</sub> clusters. The hexanuclear clusters show a presence of four acetate ligands per cluster, and in contrast, the dodecanuclear clusters display six acetate ligands per cluster. Each Zr<sub>12</sub> combined two other Zr<sub>12</sub> and make a thrimer connected by three linkers. Each unit-cell contains two trimers and two other free clusters. The description of the structure below assumes the inclusion of hydrogen atoms and hydrogen bonds that helps the layered structure of MOF gather together to be reinforced (Fig. 19).54

The synthesis of various MOFs with different topologies from the same materials was not an unprecedented research topic. Zhou *et al.* reported that by modifying the H<sub>4</sub>TPCB ligand at other sites, different topologies could be achieved. Additionally, numerous reports have documented the creation of different

MOFs with distinct topologies and connectivity using the same  ${\rm Zr_6}$  cluster and  ${\rm H_4TCPP}$  ligand.<sup>142</sup>

Chen *et al.* reported a significant study that showed how we could control topology by changing solvent or modulator. They used spatially restrained ligand  $H_4TCPB-Br_2$  and  $Zr_6$  clusters and achieved 4 completely anti-phase MOFs. Using DEF as the solvent and formic acid as modulator, they achieved to **NU-500** a novel MOF with extremely new (4,4,4,5) connected topology and  $[Zr_6(\mu-O)_4(\mu-OH)_4(HCOO)_4(OH)_{3.5}(H_2O)_{3.5}(TCPB-Br_2)(H_2-TCPBBr_2)_{0.25}]$  formula that was unprecedented. They reported that **NU-500** has block-shaped monoclinic crystals with  $9 \times 10$  Å foursquare pores in a microspore fashion. They also reported only under tightly controlled conditions, **NU-500** was formed, and is a kinetic driven product in the synthetic pathway of **NU-600** and **NU-1008**.

**NU-600** with **she** topology and  $[Zr_6(\mu-O)_4(\mu-OH)_4(CH_3-COO)_6(TCPB-Br_2)_{1.5}]$  formula formed using acetic acid as modulator and DEF as a solvent. It has 3 types of channels; 13 and 19 Å cubic channels along the *z*-axis and another tetragonal channel with size of  $13 \times 19 \text{ Å}^2$ , this one along the *x*-axis. **NU-906** crystals were oval-shaped with **scu** topology and  $[Zr_6(\mu-0)_4]_{1.5}$ 

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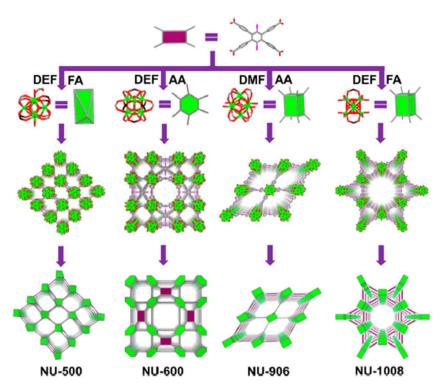


Fig. 20 This figure shows how the use of the same raw materials but different solvents and modulators can create different topologies in the product. Color scheme: C, gray; O, red; Br, pink; Zr, green. H atoms in the structures are omitted for clarity. Acetic acid is termed as AA and formic acid is termed as FA.6 From ref. 7 with permission. Copyright 2020, American Chemical Society.

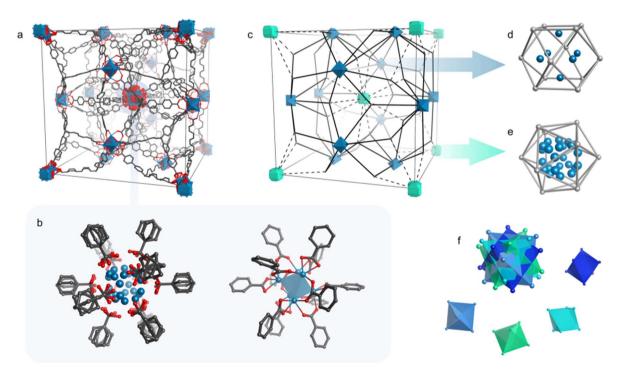


Fig. 21 The crystal structure of  $c-(4,12)MTBC-Zr_6$  is presented, depicting the complete unit cell (a) and emphasizing the modeled average disordered cluster site alongside one of its four potential local variants (b). The topological view (c) is provided, and the simplified representation of the ordered and disordered cluster sites (d) and (e) distinguishes Zr atoms in blue and the surrounding linker carboxylate carbons in silver. The superimposition of four Zr6 octahedra in the disordered cluster is highlighted by differentiating octahedra with various colors (f). For clarity, only the fraction of linkers within the unit cell is shown.<sup>82</sup> From ref. 82 with permission. Copyright 2023, American Chemical Society.

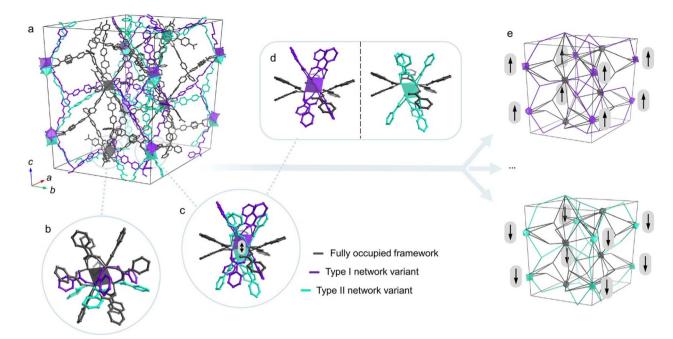


Fig. 22 Attributes of the intricate topology within the tr-(4,12)MTBC-Zr6 structure are outlined. The complete unit cell (a) is depicted, show-casing fully occupied clusters and linkers in gray (b), along with alternative framework fractions in violet and turquoise. Clusters positioned on the edges of the unit cell exhibit disorder in two alternative positions (c), either above or below the (1/4 0 0) site (d). The structures resulting from all "upshifted" or all "downshifted" clusters among all possible periodic or aperiodic networks are presented (e).<sup>82</sup> From ref. 82 with permission. Copyright 2020, American Chemical Society.

O)<sub>4</sub>(μ-OH)<sub>4</sub>(OH)<sub>4</sub>(TCPB-Br<sub>2</sub>)<sub>2</sub>] were manufactured using DMF solvent and acetic acid as the modulator. All channels are similarly 12  $\times$  27 Å and rhombic. Also, NU-1008 was synthesized using DMF as the solvent and formic acid as modulators and showed a familiar csq topology with 13 Å triangular channels and 30 Å hexagonal ones. Absorption behaviors of these MOFs were also investigated. Since there is no difference in materials, it could quickly understand that their different absorption behavior came from their different topology and spatial position of ligands. NU-500, NU-600, NU-906, and NU-1008 absorb *n*-hexane of 5.2 cm $^3$  g $^{-1}$ , 103.5 cm $^3$  g $^{-1}$ , 79,7 cm $^3$  g $^{-1}$ , and 167.7 cm<sup>3</sup> g<sup>-1</sup> respectively. They also studied the absorption of CEES and reported that NU-906, despite its smaller pores, showed higher absorption that is comes from higher interactions between ligands and CEES obtained for the special unique position of ligands (Fig. 20).6

In Lotsch study, the simultaneous synthesis of three distinct MOFs is documented, utilizing the same  $\rm Zr_6O_4(OH)_4$  clusters and methanetetrakis(p-biphenyl-carboxylate) (MTBC) linkers. Two novel structural models are introduced based on single-crystal diffraction analysis, specifically, cubic c-(4,12)MTBC-M<sub>6</sub> and trigonal tr-(4,12)MTBC-M<sub>6</sub>, encompassing 12-coordinated clusters and 4-coordinated tetrahedral linkers. Significantly, the cubic phase showcases a new architecture relying on orientational cluster disorder, crucial for its formation, and has been examined through a combination of average structure refinements and diffuse scattering analysis from both powder and single-crystal X-ray diffraction data. They believe varying of topology of Zr-based MOF are related to combinations of linkers

and clusters and limited by these factors. Enhancing the range of topologies in MOFs can be achieved by utilizing linker flexibility, which helps alleviate moderate geometric frustration in the structure. But on the other hand, ideal geometry of the building blocks limited this promised diversity. For c-(4,12) MTBC-Zr<sub>6</sub> they used benzoic acid as modulator to gain 2–5  $\mu m$  truncated octahedra crystals. This structure only had  $\rm Zr_6O_4(OH)_4$  SBUs. They detailed structure and place of SBUs to define this new topology. Fig. 21 schematically illustrate place of SBUs in crystal.

It was mentioned that synthesis of c-(4,12)MTBC-Zr<sub>6</sub> does not results in pure phase. They report two another phase of this structure. The initial discovery was made through single-crystal X-ray diffraction (SCXRD), identifying the tetragonal MOF **PCN-521** (4,8)-**flu** (which was previously reported by Zhang *et al.*<sup>143</sup>). The subsequent finding unveiled a previously unreported MTBC-Zr<sub>6</sub> framework with identical (4,12)MTBC-Zr<sub>6</sub> connectivity, albeit possessing a trigonal symmetry. called tr-(4,12) MTBC-Zr<sub>6</sub>.82 Structural detail of this new topology is discussed in Fig. 22.

## 3. Conclusions and outlook

Topology plays a central role in defining the chemical and physical properties of metal-organic frameworks (MOFs), directly influencing their pore size, stability and potential applications. Topologies with higher connectivity often result in smaller pore sizes and grater thermal and mechanical stability, making them advantageous for applications under harsh

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conditions. In contrast, the use of larger organic linkers can lead to frameworks with lower connectivity and larger mesopores, which are essential for applications requiring the diffusion of bulky molecules. This review investigates 10 famous topologies csq, scu, spn, the, she, ftw, reo, flu, hbr, alb and also some other and non-repetitive structures. We not only indicate which specific structures arise from each topology, but also highlighted the key properties of this frameworks. The review is an application-oriented review and as much as possible we have tried to mention all the applications that were reviewed for each framework and mention their strengths and weaknesses. We showed that the choice of structure can really help optimize a framework in an application. This review has shown how channel-based topologies (such as csq or ftw) are particularly suited for catalysis or sequential guest uptake, such as enzyme cascade systems, due to their directional pore architecture. On the other hand, cage-based topologies (such as flu or spn) offer isolated cavities ideals for drug encapsulation and controlled release. We also shown that how choosing wrong topologies for a project can reduced optimization in a project. The result of this review specifies achieving the best results in a scientific project is only possible with sufficient knowledge of the structure of the chemical we are dealing with. Although a project can be completed by choosing the wrong chemical structure, understanding the structures and their properties can save a research group money, time, and resources. We have also highlighted synthetic approaches and design principles that allow researchers to tailor topology through the choice of linkers, modulators and synthetic conditions. These two issues make our review a comprehensive resource for understanding, learning, and applying different topologies with an understanding of the advantages and disadvantages of these structures.

## **Author contributions**

All authors of this manuscript contributed equally to the process of ideation, research and data collection, and writing the final manuscript.

## Conflicts of interest

The authors declare no conflict of interest.

# Data availability

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

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