Net-Clipping: An Approach to Deduce the Topology of Metal– Organic Frameworks Built with Zigzag Ligands

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ABSTRACT: Herein we propose a new approach for deducing the topology of metal−organic frameworks (MOFs) assembled from organic ligands of low symmetry, which we call *net-clipping*. It is based on the construction of nets by rational deconstruction of edge- transitive nets comprising higher-connected molecular building blocks (MBBs). We have applied net-clipping to predict the topologies of MOFs containing zigzag ligands. To this end, we derived 2-connected (2-c) zigzag ligands from 4-c square-like MBBs by first splitting the 4-c nodes into two 3-c nodes and then clipping their two diagonally connecting groups. We demonstrate that, when this approach is applied to the 17 edge-transitive nets containing square-like 4-c MBBs, net-clipping leads to generation of 10 nets with different underlying topologies. Moreover, we report that literature and experimental research corroborate successful implementation of our approach. As proof-of-concept, we employed net-clipping to form three new MOFs built with zigzag ligands, each of which exhibits the deduced topology.

Reticular chemistry, defined as the "process of assembling judiciously designed rigid molecular building blocks (MBBs) into predetermined ordered structures (networks), which are held together by strong bonding",[1,2] has become essential in the design and synthesis of porous metal−organic frameworks (MOFs). Its success lies in precise analysis of the geometry and connectivity of the MBBs as well as in classification of their assemblies into different topologies.[3] Thus, over the past two decades, application of the mathematics discipline of topology to MBBs[4,5] [or secondary building units (SBUs)][2,6] has enabled synthesis of myriad MOFs based on reticulation of edge-transitive nets or their derived nets. Complementarily to these approaches, research- ers have recently devised new design strategies to further expand rational design of MOFs, including supermolecular building blocks (SBBs)[7−9] and supermolecular building layers (SBLs).[9,10] These strategies also include the merged-net approach, which is based on merging two edge-transitive nets into one minimal edge-transitive net, a useful strategy for rational design of mixed-linker MOFs.[11]

Herein we report a new design approach that, unlike the rational, bottom-up construction of edge-transitive nets, is based on the top-down deconstruction of edge-transitive nets. Our group recently reported that the combination of certain building blocks can induce structural irregularity (known as geometry mismatch)[12] that complicates rational design of MOFs, as has been observed with use of less-symmetric, 2- connected (2-c) groups such as bent,[13] twisted,[14] or zigzag ligands/MBBs.[15] In addition, the various possibilities of orientation of nonlinear ligands around inorganic MBBs lead to a high number of theoretical possibilities for polymorphism and, therefore, a low structural predictability (Figure S1).[16,17] However, as high symmetry would likely be mostly favored, we reasoned that less-symmetric ligands could be derived from more-symmetric MBBs of higher connectivity by simply reducing the connectivity of the latter. For example, a zigzag ligand can be formed by removing the two diagonally connecting groups of the two 3-c nodes derived from a 4-c MBB (Figure 1a). Accordingly, we reasoned that MOF structures made of less-symmetric ligands could be anticipated via rational clipping of the connecting groups of more- symmetric MBBs in edge-transitive nets. This new approach, which we have called net-clipping, provides further insights to our recent works on transversal reticular chemistry[15] and geometry mismatch[12] and can facilitate rational design of MOFs built up from less-symmetric MBBs.

We propose the use of net-clipping to rationalize/anticipate the MOFs that could be built from zigzag ligands. To this end, among the 54 edge-transitive nets (with D-symbol size ≤32) reported by O'Keeffe et al.,[18] we first selected the 17 nets assembled from 4-c square-like MBBs. These nets are formed by combining a 4-c MBB with other polygonal and polyhedral MBBs (Table 1). Next, we derived these nets by splitting the 4-c nodes into two 3-c nodes (Figure 1).[19] This node splitting step is important to reduce the symmetry of the 4-c MBBs and convert them into rectangular shapes, from which the two zigzag ligands can be originated by clipping the two diagonally connecting groups (Figure 1).[20] Notably, this process led to 39 derived nets.[21] Importantly, reducing the symmetry of some of the initial edge-transitive nets (nbo, ssb, pts, scu, and ftw) leads to two symmetrically different 4-c planar nodes. In these cases, as the two types of nodes can be split distinctly, more than two derived nets can be formed.

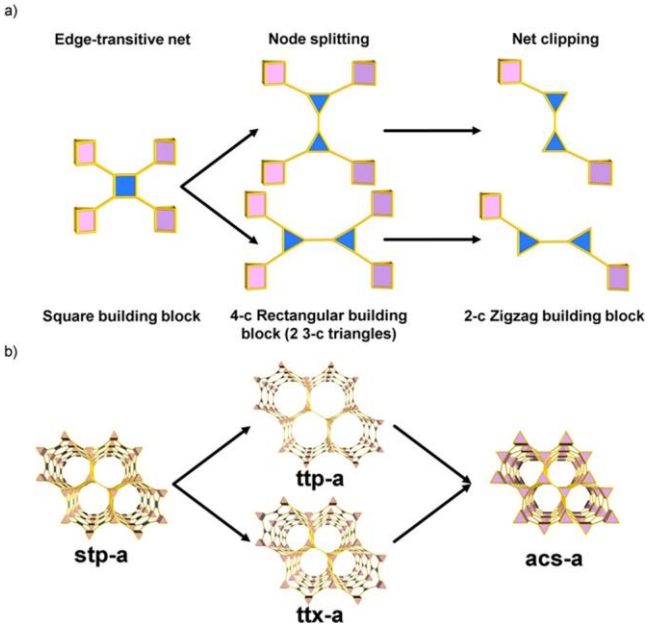

Figure 1. (a) Schematic of the deconstruction of a 4-c square MBB in a zigzag building block by splitting the node into two 3-c triangles in different axes (node splitting) and then removing two diagonally connections (net-clipping). (b) Schematic showing an example of our approach (node splitting + net clipping) applied to an edge-transitive net built from 4-c and 6-c triangular prism MBBs.

We then applied net-clipping to the derived nets by erasing the two diagonally connecting groups to mimic the presence of zigzag-shaped MBBs (Figure 1b; Figures S4–S20). The 10 resultant nets are summarized in Table 1. We concluded that most 3D nets (pto, ssb, pts, pth, she, soc, stp, scu, and ftw) are clipped into other 3D nets (srs, lvt, dia, qtz, hxg, crs, acs, bcu, and fcu, respectively); that some 3D nets (nbo, lvt, and ssb) are clipped into the 2D sql net; and that the remaining nets (tbo, rhr, ssa, sqc, csq, and shp) cannot be clipped into other nets. Interestingly, we found a common feature among all these latter edge-transitive nets: the presence of a 6-cycle[22] that comprises three 3-c nodes (derived from three 4-c nodes) and three other MBBs and that frustrates the net clipping in a fully zigzag fashion (Figures S21 and S22).

Once we had theoretically deduced the MOF structures that could be formed using zigzag ligands, we experimentally assessed our net-clipping approach. To this end, we chose two types of MOFs assembled from combining a 4-c MBB with a 4-c square-like MBB or a 12-c cuboctahedral MBB. Then, we combined the zigzag ligand analogs (derived from the 4-c MBB) with the corresponding polyhedral MBBs to synthesize two new MOFs, whose topologies we compared with those that we had deduced by net-clipping. Note that, in two other cases, to further support the net-clipping approach, we used MOF structures already reported in the literature (MOFs made by combining a 4-c MBB with 4-c tetrahedral or 8-c cubic MBBs).

We began with the nbo MOF PCN-10 (derived net: fof), which is built by connecting 4-c square-like Cu(II) paddle- wheel MBBs through 4-c 3,3′,5,5′-azobenzene-tetracarboxylate (3,3′,5,5′-ABTC) ligands.[23] In this case, net-clipping induced the formation of a 2D sql MOF (Table 1). Remarkably, replacing 3,3′,5,5′-ABTC with the corresponding zigzag 3,3′- azobenzene-dicarboxylate (3,3′-ABDC) ligand afforded the expected 2D sql MOF (Figure 2a, top). This entailed reaction of copper(II) nitrate salt and H_2(3,3′-ABDC) in *N,N*-dimethylformamide (DMF) under solvothermal conditions, which yielded green needle-shaped crystals of Cu-sql-3,3′- ABDC. Single-crystal X-ray diffraction (SCXRD) revealed formation of an ABCD packing of a 2D network of formula Cu_2(3,3′-ABDC)$_2$(H_2O)$_2$, which crystallizes in the $C2/m$ space group (Figure 2). As expected, the building unit in Cu-sql-3,3′-ABDC is the Cu(II) paddle-wheel unit. In this framework, each of these units is connected to four others through four bridging zigzag 3,3′-ABDC ligands, adopting a 4-c sql underlying topology (Figure 2a, top).

Table 1. Net-Clipping of All the Derived Nets from 4-c Square Nodes in the 17 Selected Edge-Transitive Nets[a]

MBB	Main Topology	Derived Net	Clipped Net
	tbo	tbd xaa	
	pto	ptd	srs
	nbo	fof fog tfb	sql
	rhr	ucp sqc12288*	
	lvt	lil lim	sql
	ssa	sty Initial structure; Bond sets: 1,3:bbp**	
	ssb	stu stw	sql
		stj stx	lvt
	pts	dmd dmg dmh tfi	dia
	pth	hst 3,4T45***	qtz
	she	sqc12215*	hxg
	soc	cdj edq	crs
	stp	ttp ttx	acs
	scu	tty cut 3,3,8T132***	bcu
	sqc	sqc3520* sqc3782*	
	csq	xly xlz	
	ftw	kle kxe ttv	fcu
	shp	ced cec	

[a]For the derived nets, asterisks indicate the following: *topologies corresponding to the Systre code in the Epinet database; **topology corresponding to the subnet transformation symbols nomenclature; and ***topologies corresponding to the TOPOS symbols nomenclature.

Interestingly, our net-clipping approach is further corrobo- rated by the fact that an isostructural sql MOF made by linking Zn(II) paddle-wheel units by 3,3′-ABDC ligands had previously been described by Liang et al.[24] Similarly, two other independently, previously reported structures reinforce our approach: NOTT-204,[25] a pts MOF (derived net: tfi) built by linking the 4-c 3,3′,5,5′-biphenyl-tetracarboxylate (3,3′,5,5′-BPTC) ligand and the 4-c tetrahedral In(III)-based MBB; and InOF-4,[26] a dia-MOF made by connecting the same 4-c tetrahedral In(III)-based MBBs through the zigzag 3,3′- biphenyl-

dicarboxylate (3,3′-BPDC) ligand. Interestingly, both of these MOF structures are related by net-clipping, which induced formation of a clipped dia topology from a pts topology (Table 1 and Figure 2b, top).

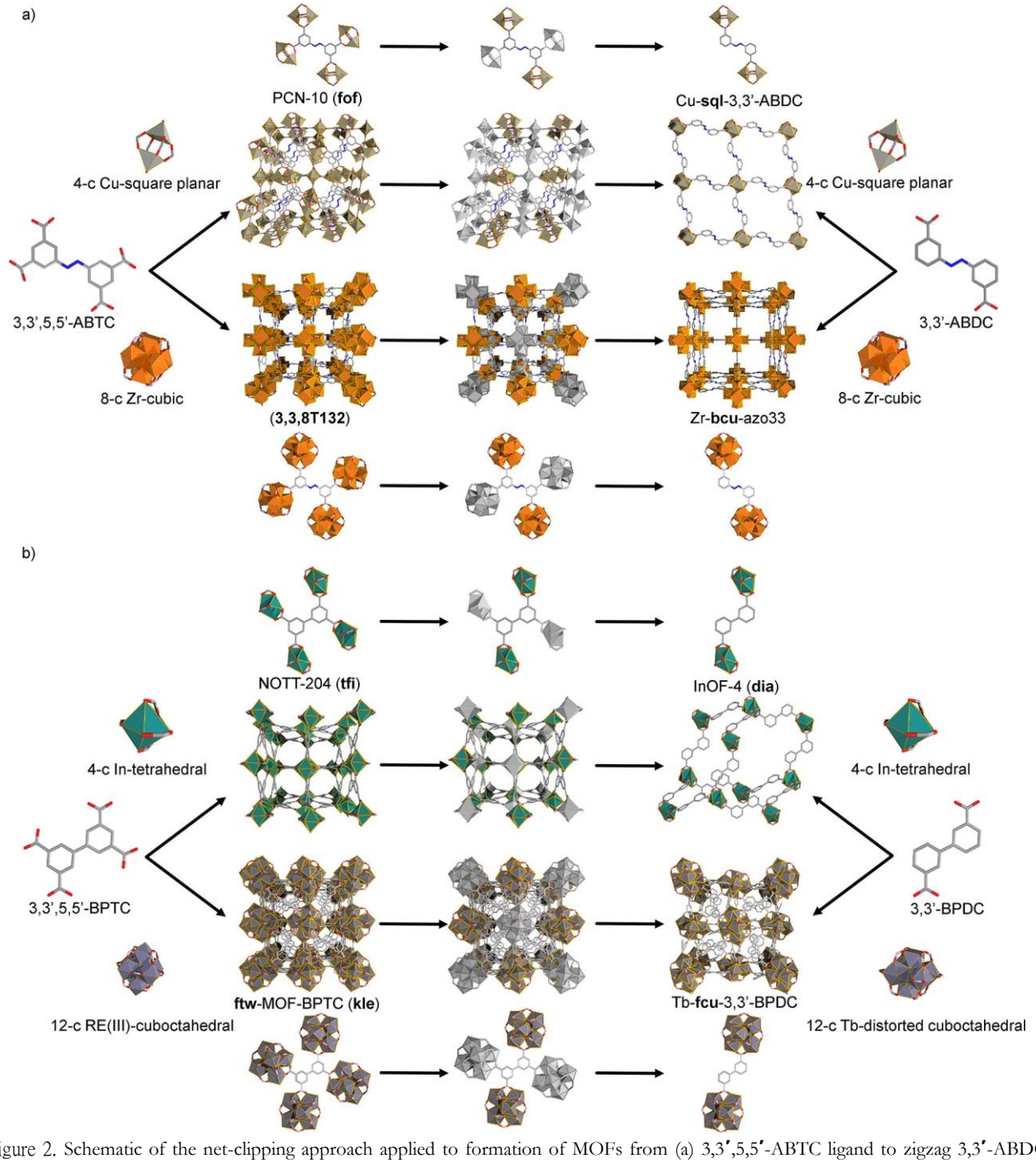

Figure 2. Schematic of the net-clipping approach applied to formation of MOFs from (a) 3,3′,5,5′-ABTC ligand to zigzag 3,3′-ABDC combined with (top) 4-c paddle-wheel Cu(II) MBBs and (bottom) 8-c cubic Zr(IV)-based MBBs, and from (b) 3,3′,5,5′-BPTC to 3,3′-BPDC ligand combined with (top) 4-c tetrahedral In(III)-based MBBs and (bottom) 12-c cuboctahedral Tb(III)-based MBBs.

Next, we shifted our attention to another MOF assembled from the 4-c 3,3′,5,5′-ABTC ligand and a higher-connected MBB, the 8-c cubic $Zr_6O_4(OH)_4(OOC\text{-}R)_8(H_2O)_4(OH)_4$ hexanuclear MBB.[27] This MOF shows the scu topology, in which we reasoned that replacement of 3,3′,5,5′-ABTC with 3,3′-ABDC would generate a clipped bcu MOF (Table 1). Interestingly, our group recently reported that combination of this 8-c MBB with a series of zigzag ligands, including 3,3′- ABDC, leads to formation of MOFs with the bcu topology (Figure 2a, bottom), which further supports net-clipping.[15]

Recently, Eddaoudi et al. reported that combining 4-c ligands (e.g., 3,3′,5,5′-ABTC or 3,3′,5,5′-BPTC) with 12-c cuboctahedral

rare earth metal (RE) MBBs affords RE-ftw- MOFs (derived net: kle).[28] From this topology, net-clipping predicts formation of a MOF with the fcu underlying topology. To investigate this, we used the zigzag 3,3′-BPDC ligand as a substitute for the 4-c 3,3′,5,5′-BPTC ligand. Reaction of terbium(III) nitrate salt and H_2(3,3′-BPDC) in the presence of 2-fluorobenzoic acid in DMF under solvothermal conditions yielded transparent octahedral crystals of Tb-fcu-3,3′-BPDC. SCXRD revealed formation of a 3D net with formula $[(CH_3)_2NH_2]_2[Tb_6(\mu_3\text{-}OH)_8(3,3'\text{-BPDC})_6(H_2O)_4]$, which crystallizes in the $P2_1/n$ space group. As we had expected, the presence of 2-fluorobenzoic acid as modulator[29] enabled formation of the hexanuclear RE MBB in Tb-fcu-3,3′-BPDC. In this framework, each of these MBBs is connected to 12 others, through 12 bridging zigzag 3,3′-BPDC groups, adopting overall a 12-c fcu topology (Figure 2b, bottom). Note that, compared to the archetypical 12-c Zr-fcu-4,4′-BPDC (known as UiO-67),[30] Tb-fcu-3,3′-BPDC shows a less-symmetric, distorted structure. We attributed this feature to the transversal parameter of the zigzag ligand as well as to the different metal-based MBBs, in which Zr(IV) ions had been replaced with Tb(III) ions, thereby providing a slightly different coordination environment (Figures S30 and S31.Once we had confirmed the feasibility of our net-clipping approach, we applied it to synthesize a new acs-MOF built with a zigzag ligand. To this end, we synthesized a rigid zigzag 1,5-naphthalenedicarboxylate (1,5-NDC) ligand and selected the well-known [Fe(III)]$_3$O trimeric unit as the trigonal prism MBB.[31] We synthesized this zigzag ligand because, to our knowledge, an stp MOF assembled from the corresponding 4-c 1,4,5,8-naphthalenetetracarboxylate ligand and a 6-c trigonal prism MBB for which net-clipping induced formation of an acs topology has never previously been reported. First, H_2(1,5-NDC) was synthesized from the corresponding diamine derivative via several functional group interconver- sions (see SI). Then, the Fe(III) trimeric unit was synthesized in an acetic acid solution, according to a literature protocol.[32] Finally, the pre-formed Fe(III) unit was reacted with H_2(1,5- NDC) and acetic acid in DMF under solvothermal conditions for 48 h. After this period, orange hexagonal crystals suitable for SCXRD were collected. SCXRD revealed formation of a 3D structure with formula $Fe_3(\mu_3\text{-}O)(1,5\text{-NDC})_3\text{-}(H_2O)_2(OH)$, which crystallizes in the $P\text{-}6_3m$ space group. In Fe-acs-1,5-NDC, each trimer is connected to six others through six zigzag 1,5-NDC ligands, adopting the 6-c acs underlying topology (Figure 3). Note that the structure of Fe- acs-1,5-NDC, although slightly distorted, is similar to that of MOF-235/MIL-88B,[33,34] which also exhibits an underlying acs topology.

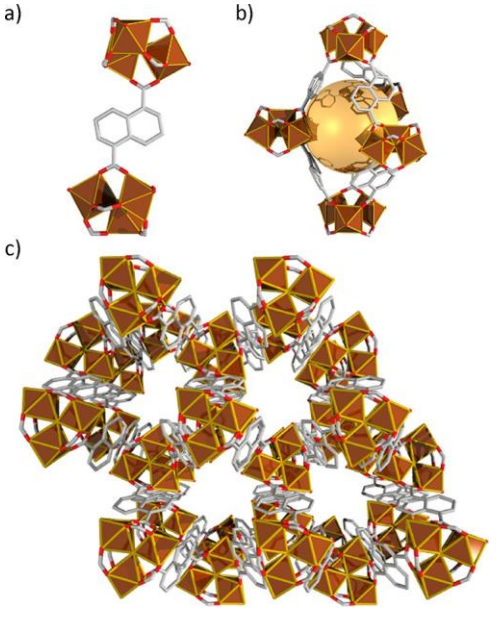

Figure 3. Crystal structure of Fe-acs-1,5-NDC, showing (a) the zigzag connection between the Fe trimers, (b) the trigonal bipyramid cage, and (c) the channels formed through the *c* axis.

In summary, we have proposed and validated a new approach, net-clipping, for rational design of MOFs made of zigzag ligands. First, we demonstrated the relationship between these ligands and more symmetric 4-c ligands. Next, we studied the edge-transitive nets with 4-c nodes with an associated square vertex figure, and their derived nets, to identify the possible outcomes. Then, we applied our net-clipping approach to deduce the different topologies that should be accessible upon assembly of zigzag ligands with different polyhedral MBBs. Finally, we demonstrated the feasibility of net-clipping through the successful design and assembly of three novel MOFs based on MBBs with different connectiv- ities: Cu-sql-3,3′-ABDC (4-c, paddle-wheel), Fe-acs-1,5-NDC (6-c, trimer), and Tb-fcu-3,3′-BPDC (12-c, hexamer). Our approach enriches the repertoire for topological predictions, and we anticipate the application of net-clipping to bent ligands, via clipping of 4-c MBBs in other ways, as well as its eventual use with MBBs of other connectivity.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/jacs.0c03404.

Chemicals, instrumentation, net-clipping approach and synthetic procedures, schemes of the topologies resulting from the net-clipping, PXRD, crystallographic data, structural details, and ^{1}H NMR spectra, including Figures S1−S31 (PDF)
X-ray crystallographic data for Cu-sql-3,3′-ABDC (CIF) X-ray crystallographic data for Fe-acs-1.5-NDC (CIF) X-ray crystallographic data for Tb-fcu-3,3′-BPDC (CIF)

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Notes

The authors declare no competing financial interest.

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