

## Two Exceptional Patterns of Helical SBUs Found in MOF Structures.

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### Supplementary Information

Standard simplification of two three-way rod MOFs leads to complicated underlying net that called 4,4,4,4T73(Fig.S1).

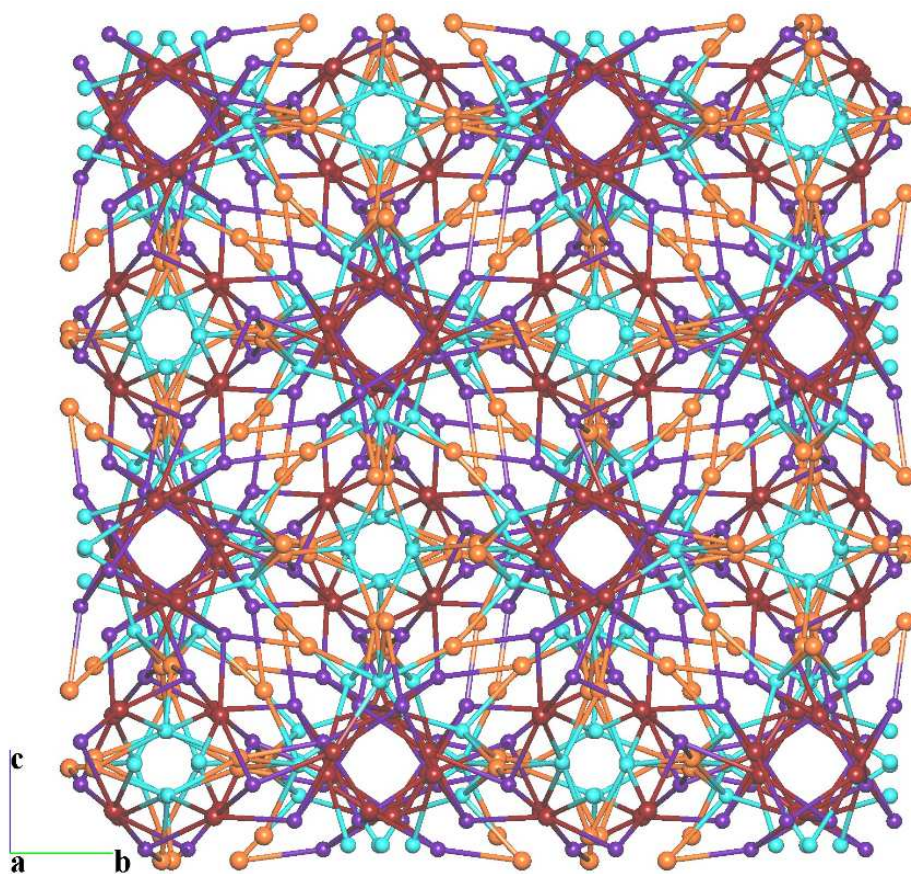


Figure S1. The four-nodal 4-c underlying net of the standard representation for isorecticular JONKEE and YIKJUJ. Metals (Ag or Cu) cyan and violet, ligand center of mass orange and brown.

Alternative representations of the underlying nets are possible and can be used to identify isorecticular compounds.

- a) If we consider as nodes the 4-c metal atoms inside the helices of edge sharing tetrahedra and the 3-c point of extension we get a 6-nodal 3,4- c underlying net with point symbol  $(4.9.10)(4.9^2)_3(4^2.9^2.10^2)(4^2.9^3.10)$  (figure S2b).
- b) If we exclude the nodes at the center of the tetrahedra and we use only the vertices of them, we get the representation using only the *point of extensions*, that is now 4-nodal 6-c  $(3^6.4^4.6^3.7^2)(3^6.4^4.6^4.7)$  (figure S2d).
- c) Further simplification of the tetrahedra to their centers leads to the simplest 3-nodal 4-c underlying net of a new topology with point symbol  $(6^4.8^2)(6^5.8)_3$  (Figure S2f).
- d) Last representation<sup>1</sup> (Figure S2h) shows only the isolated rods and below the packing of the rods: each of the three perpendicular sets pack as square lattices, giving the projection in the figure.

The coordinates of the four nets illustrated in figures S1 and S2 are collected in the Systre file “Nets\_3-way\_structures.cgd”

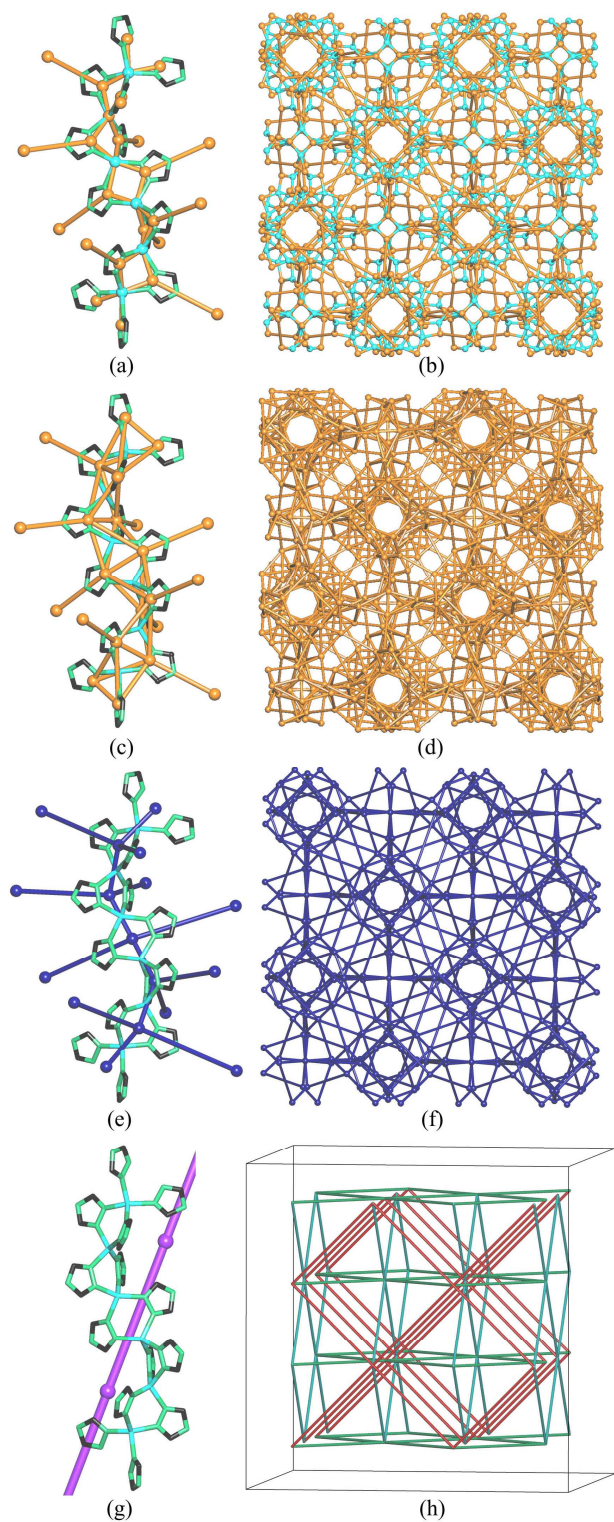


Figure S2. The merged fragments of rods and 6-nodal 3,4-c net (a), 4-nodal 6-c net (c), 3-nodal 4-c net (e), rod axis (g). The views of the appropriate underlying nets (b, d and f) and of three intersected square layer (**sql**) projections for each set of parallel rods (h).

Standard simplification of two-way rod MOF (HOWPOA) gives the 4-nodal 4- c underlying net with point symbol  $(4^2.6^2.8^2)_3(4^2.6^3.8)_2(4^2.6^4)$  (Fig. S3).

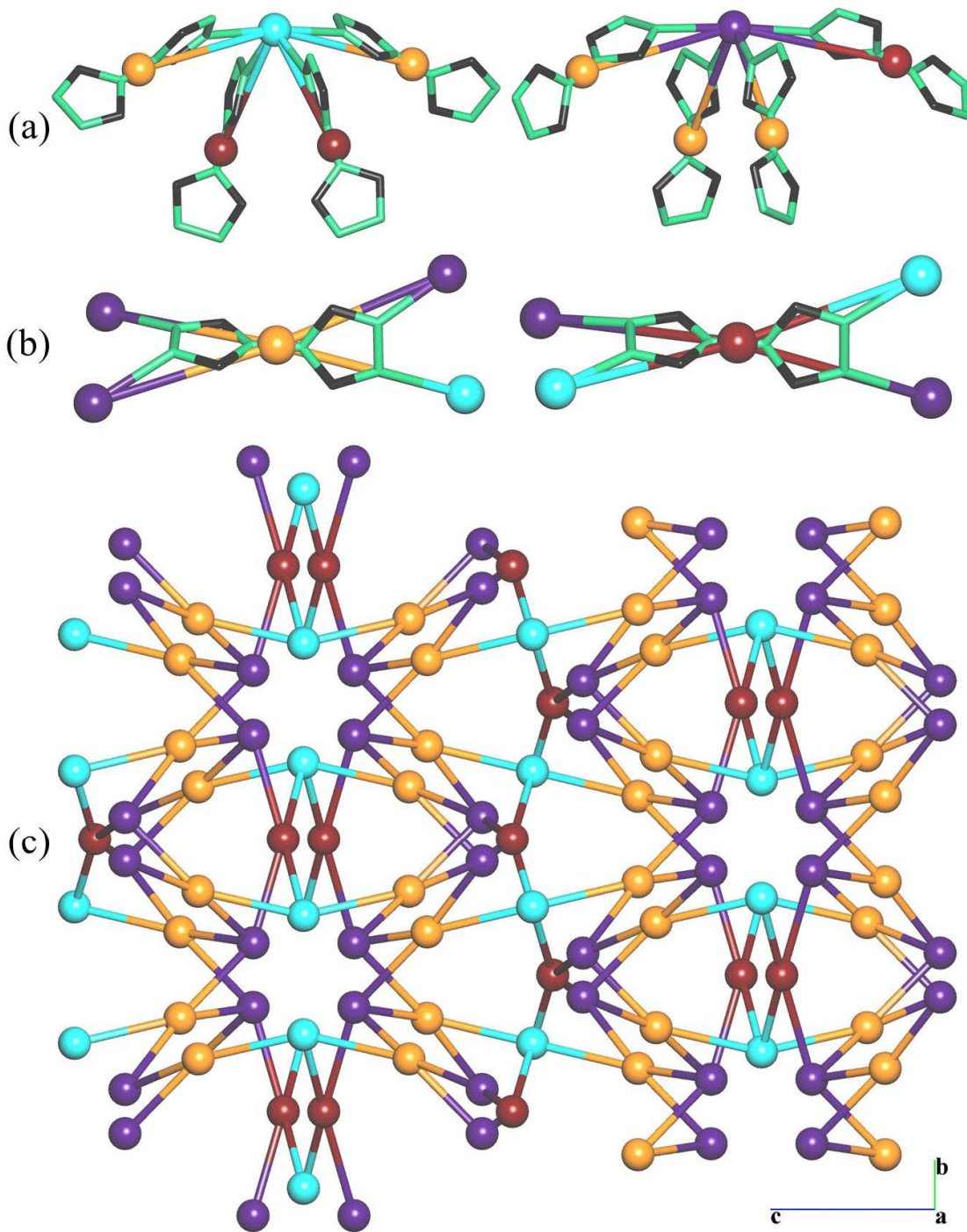


Figure S3. Coordination environments for symmetry distinct silver atoms (a) and btr linkers (b) in HOWPOA. The [100] view for 4-nodal 4- c 4,4,4,4T79 underlying net.

The same procedure of alternative simplification was performed for HOWPOA. The resulting underlying nets consists of:

- a) Four-coordinated metal atoms inside the tetrahedra and the 3-coordinated point of extension. 5-nodal 3,4-c underlying net with point symbol  $(4.9^2)_2(4^2.9^2.11^2)$  is presented in figure S4b;
- b) Only 6-coordinated *point of extensions*, the 3-nodal 6- c underlying net with point symbol  $(3^6.4^4.6^3.7^2)$  is obtained (figure S4d);
- c) Four- coordinated centers of tetrahedra, that forms the 2-nodal 4- c underlying net with point symbol  $(5^3.8^3)(5^5.8)_2$  (Figure S4f);
- d) Rod projections onto (hkl) planes: each of the two perpendicular sets pack as hexagonal lattices (Fig S4h).

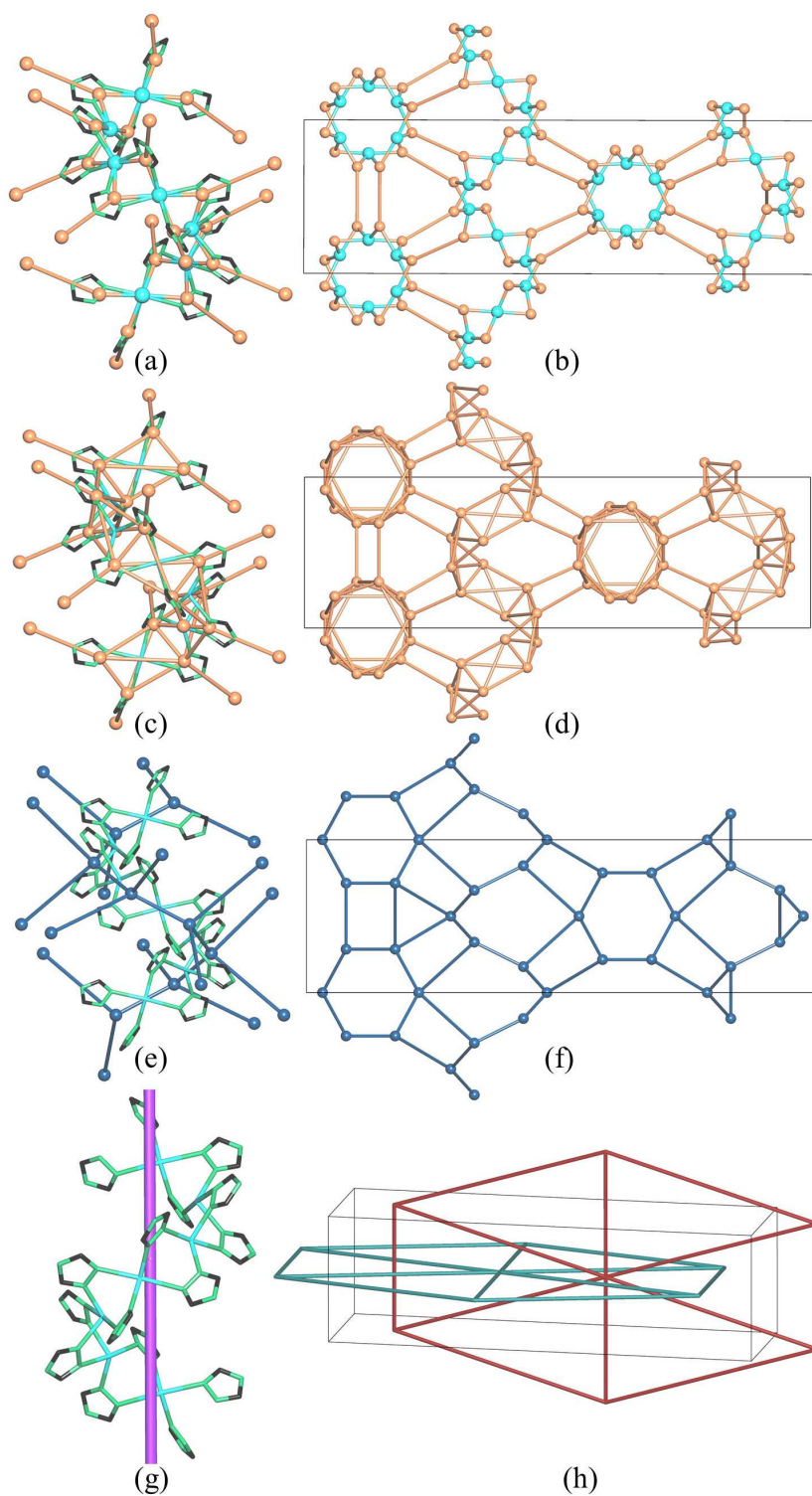


Figure S4. Rods are merged with fragments of underlying nets and their overall views down  $[100]$ : 5-nodal 3,4-c (a,b), 3-nodal 6-c (c,d), 2-nodal 4-c net (e,f). The rod twines its axis (g). The hexagonal (**hxl**) projections for different set of parallel rods intersect (h).

In determining the net of linked points of extension for HOWPOA we note that the tetrahedra in rods are very flat and perhaps better considered as quadrangles. One then obtains the elegant trinodal 4-c net **lxx** shown in figure S5. The symmetry is  $I-42d$  as in the crystal. The pattern of rod axes is the invariant 4-layer tetragonal packing with symmetry  $I4_1/amd$ ; however, to accommodate the  $6_1$  and  $6_3$  helices, the mirror symmetry elements normal to these axes must be removed in the net and the crystal.

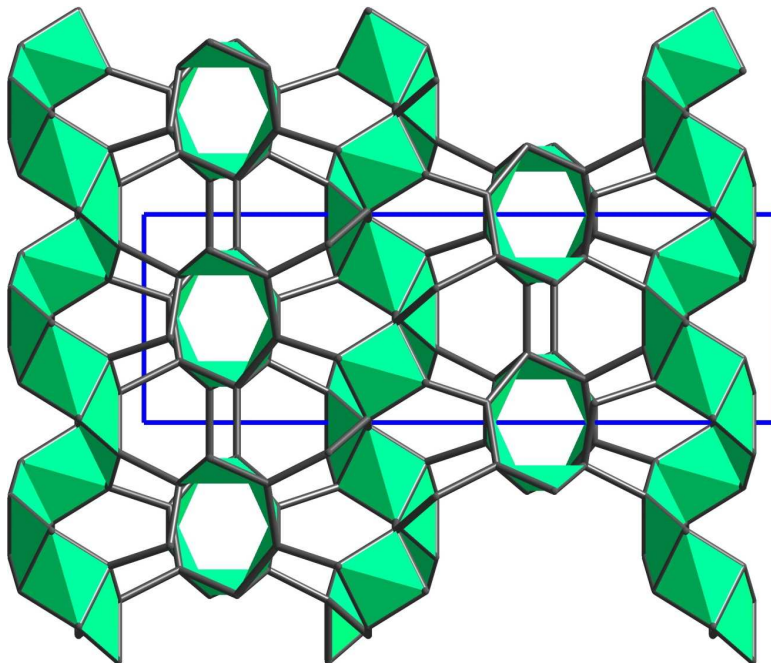


Fig. S5. The 3-nodal 4-c net **lxx** for the HOWPOA projected down [100] with **c** horizontal on the page.

The coordinates of nets, which are presented in figures S4 and S5, are collected in the Systre file “Nets\_HOWPOA.cgd”

## Recommendations for design of the three-way helical rod MOFs

The ratio Metal:Ligand in the three rod MOFs is 1:1 and all have the pores filled by counterions and solvent molecules. If the ratio is different only finite SBUs are observed (Table S1). Counterion and solvent molecules also affect the network topology. Thus, coordination of additional terminal ligands ( $\text{NO}_3^-$  in HOWPIU<sup>2</sup> and  $\text{H}_2\text{O}$  in HOWPEQ<sup>2</sup>) in complexes with ratio Metal:btr = 1:1 prevent formation of rods and leads to dimeric and tetrameric SBUs (Fig. S6).

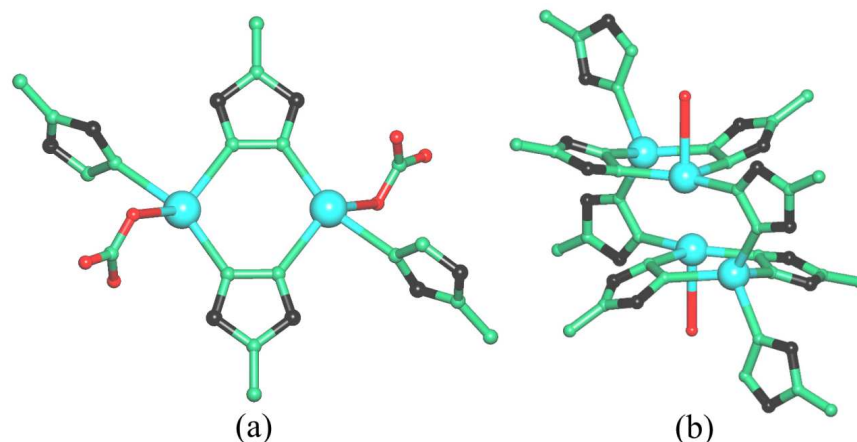


Figure S6. Dimeric (a) and tetrameric (b) SBUs from HOWPIU and HOWPEQ structures.

From this analysis it can be concluded, that to obtain rod MOFs with bisazole ligands the ratio Metal:bisazole = 1:1 should be used, and the coordination of additional ligands (counterion or solvent) should be avoided.

To explore the possibility to obtain other helical rod MOFs, we extracted from CSD all 3-periodic coordination polymers with rods “of  $\text{MN}_4$  tetrahedra linked by N-N bonds” and a ratio M:bisazole = 1:1 (Table S2). The analysis of the conformation of the bisazole ligands shows four groups illustrated in figure S7.



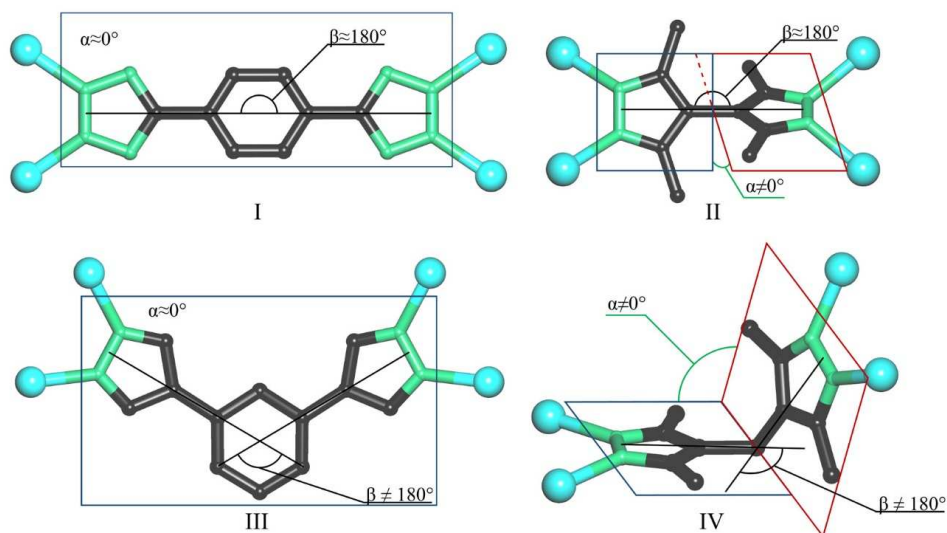


Figure S7. Four types of bisazole-containing ligands: (I) flat linear; (II) twisted linear; (III) flat angular, twisted angular (IV).

The conformation of 4,4'-bi-1,2,4-triazole ligand in the three helical rod MOFs (HOWPOA, JONKEE, YIKJUZ) belongs to type II (with  $\alpha$  in range 65-90°). Therefore, we can assume that the twisted linear conformation of bisazole ligand favors formation of helical rods. From the resulting sample of 36 structures, we found three more helical rod MOFs:

[Cd(Me<sub>4</sub>bpz)] (HIQPAA<sup>3</sup>; H<sub>2</sub>Me<sub>4</sub>bpz=3,3',5,5'-tetramethyl-4,4'-bipyrazole),

Co(1,3-bdp)·DEF·0.5H<sub>2</sub>O (LUQGAG<sup>4</sup>; 1,3-H<sub>2</sub>bdp=1,3-benzenedi(4-pyrazolyl)), and

[Co<sup>II</sup>(bdpm)] (DUKXEO<sup>5</sup>; bdpm=bis(3,5-dimethyl-4-pyrazolato)methane), which frameworks are neutral (Fig. S7).

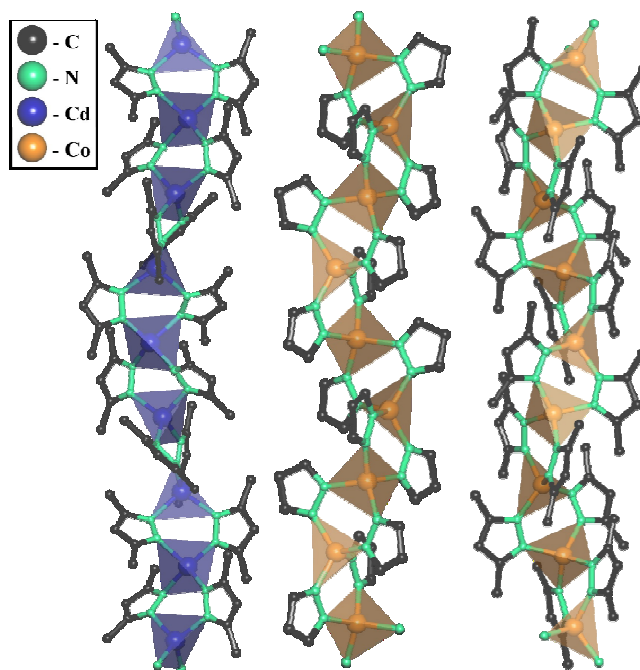


Figure S7. Isolated helices from structures of HIQPAA (left), LUQGAG (middle), DUKXEO (right).

From the six helical MOF structures four (JONKEE, YIKJUZ, HOWPOA, HIQPAA) contains bisazole ligand in conformation of type II ( $\alpha$  varies in range 23-90°), one in conformation of type III (LUQGAG), and one in conformation of type IV (DUKXEO). Linear rods (23 MOFs) in general (22 structures) are constructed from flat linear ligands (type I), and zigzag rods (7 MOFs) can be obtained with a bisazole with conformation of type I (2), II (1), combination of I and II (1), or IV (3). Thereby, the design of helical rod MOFs isoreticular to JONKEE and YIKJUZ is seen to be possible with elongation of bisazole ligand, but the ligand should keep twisted linear shape with  $\alpha$  in range 65-90°. In addition, the effect of counterion and solvent should be taken into account.

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