

Framework-Isomerism: Highly Augmented Copper(II) Paddlewheel-Based MOF With Unusual (3,4)-Net Topology

Nianyong Zhu,^{[a], [b]} Debobroto Sensharma,^[a] Paul Wix,^[a] Matthew J. Lennox,^[c] Tina Düren,^[d] Wai-Yeung Wong,^{[b], [e]} and Wolfgang Schmitt*^[a]

Abstract: The synthesis and structure of a new, highly augmented $\{Cu_2\}$ 'paddlewheel'-based metal-organic framework (MOF) that is stabilized by tritopic benzoate ligands is reported. The structure adopts an uncommon, less-symmetrical (3,4)-connected net topology and represents a rare framework isomer of the extensively studied $\{Cu_2\}$ -based **pto** and **tbo** analogues. The concomitant formation of three isomeric forms using $\{Cu\}_2$ -'paddlewheel' complexes and a single triangular, tri-functional ligand is unique and stems from the rotational flexibility of the benzoate moieties. Computational analyses support the structural studies and underline that this observed net topology can give rise to an exceptionally high surface area ($>3500\text{ m}^2/\text{g}$), despite the triple-interpenetrated nature of the compound.

Introduction

Metal-organic frameworks (MOFs) represent a unique class of coordination compounds whose structural, chemical and electronic characteristics promote applications in diverse areas of science.^[1,2] MOFs are regarded as potentially applicable materials for gas storage, gas separation, fuel gas conversion or catalysis.^[1,2a,b] Advantageous characteristics include porosity, exceptionally high surface areas (up to $7000\text{ m}^2/\text{g}$), high densities of active sites per volume and high diffusion coefficients.^[3] Also remarkable are their structural and constitutional diversities, their amenability to modification of both their organic and inorganic components and control over topology and cavity sizes.^[1,2] This latter preparative control distinguishes MOFs from many other classes of coordination compounds. Their assembly processes can be rationalized considering topological aspects of inorganic and organic nodes^[4] to produce 'default' nets that often relate to purely inorganic structure types (reticular synthesis concept).^[4a] Attention has recently also been directed to polymorphism or framework isomerism of MOFs,^[5] as compounds with identical framework composition give rise to distinctively different cavity geometries thus influencing the performances of the MOFs in diverse applications (i.e. catalysis whereby different pore geometries might give rise to shape-selectivity).^[6] MOFs composed of square and triangular nodal topologies are well-known to produce two edge-transitive topologies that can be described by the symbols **tbo** and **pto** according to the RCSR notation and relate to the purely inorganic, solid state structures of platinum oxide or the twisted boracite.^[7] Of particular interest in this context are $\{Cu\}_2$ -'paddlewheel'-based secondary building units whose **tbo/pto**-type MOFs provide one of the largest family of MOFs represented in scientific publications.^[8] Representative examples of MOFs with **tbo** topology are HKUST-1,^[9] PCN-6/6^[10] and MOF-399.^[7a] **pto**-Type networks occur for instance in MOF-14,^[11] MOF-143/DUT-34^[7a,12] and MOF-388.^[7a]

However, when considering the square and triangular geometries of organic and inorganic SBUs, one can expect that their assembly can lead to other 'default' nets. A topological consideration to classify and enumerate the special class of A_3X_4 -stoichiometric compounds in which each 3-connected node is connected to three 4-connected nodes and *vice-versa* (each 4-connected node to four 3-connected nodes), includes early approaches by Wells.^[13] However, considering the reported MOFs and considering current entries in the RCSR and EPINET databases, one can predict only a very limited number of augmented topological A_3X_4 -type MOF isomers composed of 4-connected square/rectangular and triangular tritopic linkers.^[12] Under this purview, Klein *et. al.* predicted the synthesis of a MOF which is classified by the EPINET notation as the sqc5590 net.^[12] However, paddlewheel-based MOFs of this topology, to the best of our knowledge, not been observed or isolated.

Results and Discussion

We previously used the trifunctional ligand 1,3,5-benzene-trisethynylbenzoic acid (BTEB) to prepare **pto**- and **tbo**-type MOFs, **TCM-4** and **TCM-8**, whose topologies give rise to exceptionally high surface areas.^[14] Here we demonstrate that the degree of rotational flexibility within the BTEB ligand results in the formation of a new third topological isomer $[Cu_3(BTEB)_2(H_2O)_2(DMF)]$, **TCM-10** (Figure 1). The concomitant formation of three topological isomeric MOFs using a single tritopic, triangular ligand is unique for the $\{Cu\}_2$ -'paddlewheel' reaction system.

TCM-10 co-crystallises reproducibly with **TCM-4** & **TCM-8** when BTEB and $Cu(NO_3)_2 \cdot 3H_2O$ are reacted in DMF in the presence

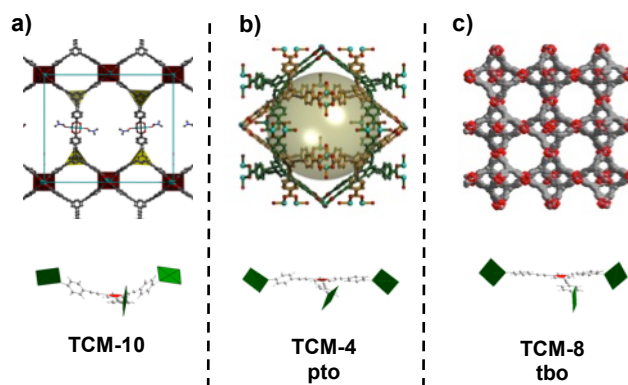


Figure 1. $\{Cu_2\}$ /BTEB framework isomers and binding mode of the BTEB ligand; a) **TCM-10** (representation of a single framework); b) **pto** network in **TCM-4** (representation of the dual interpenetrated structure); c) **tbo** structure **TCM-8** (representation of a single framework).

of 4,4'-bipyridine at 85°C. Whilst lower concentrations of the reactants favour the formation of **TCM-4**, higher concentrations (and longer reaction times) seemed to promote the formation of **TCM-10**. **TCM-10** forms blue, agglomerated block-shaped crystals that are distinctive from the green, polyhedron-type crystals of **TCM-4** and individual, light-blue crystals of **TCM-8**. Crystals of **TCM-10** were separated manually and single-crystal X-ray diffraction analysis demonstrates that the compound crystallises in the monoclinic space group $P2_1/c$. The phase-purity of the sample of **TCM-10** was confirmed by powder X-ray diffraction (Supporting Information). The results of the single-crystal structure analysis reveal that **TCM-10** is composed of triply interpenetrated frameworks which contrasts the dual framework structures of **TCM-4/8**. The analysis clearly underlines that **TCM-10** represents an isomeric form of the **pto** and **tbo** nets in **TCM-4/8**, however, one may note that the topology differs from that of the initially predicted sqc5590 net. The asymmetric unit of **TCM-10** contains two non-equivalent, fully deprotonated BTEB ligand molecules coordinated to three Cu(II) ions. The structural parameters of the symmetry-generated dinuclear $\{Cu_2\}$ SBUs in **TCM-10** closely relate to those observed in **TCM-4/8**. O-Donor atoms of *syn, syn* bidentate carboxylate groups provide the bases of the square pyramidal coordination polyhedra of each Cu^{II} centre (Cu-O bond lengths: 1.939(4) – 1.969(4) Å), and O donors of H₂O and DMF molecules bind in the apical positions (Cu-O bond lengths: 2.134(3) – 2.142(3) Å). The Cu–Cu distances in the dinuclear $\{Cu_2\}$ SBUs are ca. 2.6 Å. In agreement with the (3,4)-net topology, each $\{Cu_2\}$ SBU is coordinated by four tritopic BTEB ligands, and each BTEB moiety connects to three $\{Cu_2\}$ SBUs giving rise to a neutral network. It is observed that one of the squares defined by the $\{Cu_2\}$ SBUs is oriented perpendicular to the central benzene ring of the BTEB ligand, while the other two square SBUs adopt a conformation staggered by ca. 35° degrees relative to the central benzene ring. Adopting the former 90°-binding mode, the central phenyl and the outer benzoate ring systems are approximate co-planar whilst the 35°-binding mode results in a tilted conformation between central and outer phenyl rings. The two benzoate moieties that facilitate the 35° angles bridge in [010] parallel aligned $\{Cu_2\}$ SBUs units whereas the third benzoate links orthogonally aligned $\{Cu_2\}$ SBUs in the direction of the crystallographic *c*-axis. In the corresponding **pto** and **tbo** structures that are formed by BTEB and $\{Cu_2\}$ SBUs, the angles between the central phenyl and the square $\{Cu_2\}$ SBUs are identical, either ca. 55° for the **pto** or ca. 90° for the **tbo** structure (Figure 1). In both cases the organic ligands adopt C₃ symmetry. Thus, the here presented MOF is not isorecticular to HKUST-1 or MOF-14 and may be regarded as an isomeric 'intermediate' between the **tbo** and **pto** topologies.^{[8], [11]}

A more detailed topological consideration reflects the different binding arrangement of the benzoate groups of the BTEB ligands in **TCM-10** (Figure 2). The topological analysis

suggests that the net can indeed be described as a (3,4,4)-connected, 3-nodal net with two topologically distinguishable 4-connected nodes. The overall point symbol is $\{4.8^2\}_4\{4^2.8^2.10^2\}_2\{8^4.12^2\}$. The 4-connected vertex with the point symbol $\{4^2.8^2.10^2\}$ represents the $\{Cu_2\}$ SBUs in which the four adjacent terminal phenyl rings of the ligand are all tilted against their respective central ring. The 4-connected vertex with the point symbol $\{8^4.12^2\}$ represents the Cu^{II} dimer in the structure where the terminal phenyl rings of the ligand are coplanar to the respective central ring. Thus, the network in **TCM-10** represents a less-symmetrical (3,4)-connected net topology that is only once represented in the TTD database (3,4,4T84)^[15] and that distinctively differs from the nets in **TCM-4** and **-8**. The corresponding augmented analogue can be represented by the point symbol $\{3.16^2\}\{3.8.9\}_2\{4.16^2\}\{4.8.10\}_2$ (see Supporting Information). The simplified structural representations that highlight the binding modes of the organic ligands are shown in Figure 2a and 2b.

The observed triple-interweaving of the nets in **TCM-10** (Figure 3) can also be attributed to the extended and flexible nature of the BTEB ligand. π - π Stacking involving the phenyl rings from different sub-nets and bowing of the BTEB ligands stabilize the interwoven structure (Figures 3, 4 and SI). The observed type of interpenetration and connectivity results in cylindrical/hexagonal channels that extend in the direction of the crystallographic *c*-axis. Significantly sized openings can also be noticed in the [010]-direction. Packing diagrams that highlight the channels and the interpenetration of the three symmetry-equivalent networks are displayed along the unit cell directions in Figure 3d-f. Despite the interwoven nature, the unit cell of **TCM-10** has a solvent-accessible void volume of ca. 72% (corresponding to 11925 Å³). The significant solvent quantity in **TCM-10** is underlined by the thermogravimetric analysis carried out in a N₂ atmosphere. The thermogravimetric step associated with the loss of constitutional solvent molecules occurs up to 110 °C. The weight loss of ca. 5% above 110 °C is caused by the removal coordinated H₂O/DMF molecules before the oxidation of the

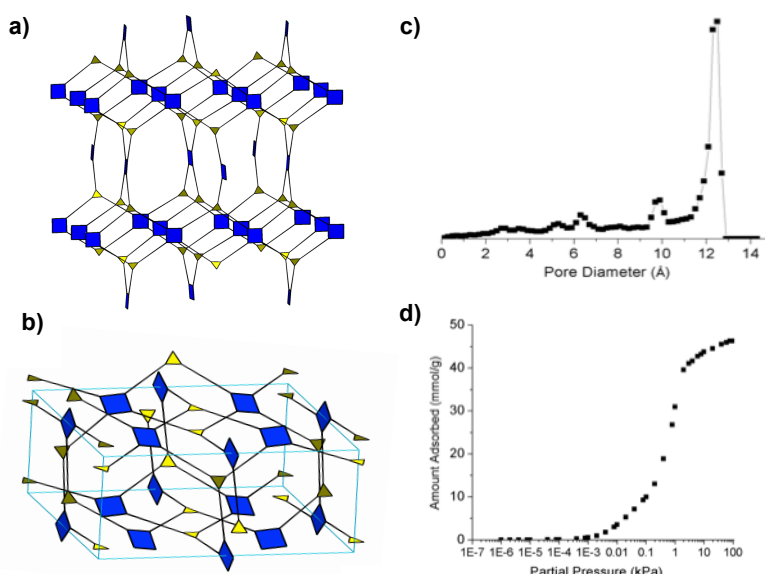


Figure 2. Augmented topological representations of a single net in **TCM-10** (a) and the triple interpenetrated net (b); (c) and (d) Calculated pore-size distribution and nitrogen adsorption isotherm of **TCM-10**.

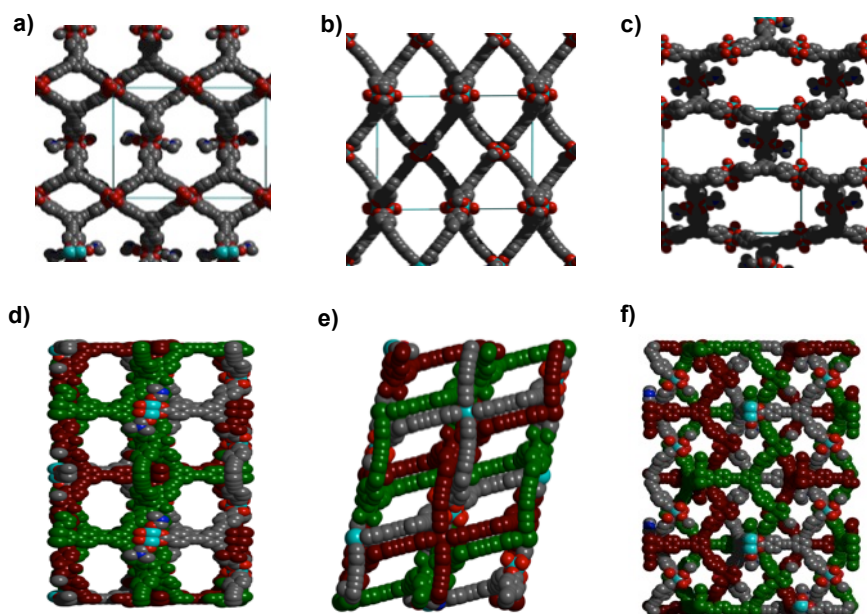


Figure 3. Space-filling representation of a single net in **TCM-10** with view in the [201]-direction (a), [010]-direction (b) and [10-1] direction (c). Triple interpenetration in **TCM-10** with view in the direction of the crystallographic *c*-axis (d), *b*-axis (e) and *a*-axis (f).

BTEB moieties destroys the network structure above ca. 280 °C (Supporting Information).

Considering that **TCM-10** forms in a product mixture, theoretical calculations were conducted to evaluate the possible surface areas and gas storage abilities of **TCM-10** and to compare these with **TCM-4/8**. A theoretical approach that calculates the largest solid sphere that can be inserted into the cavities whilst avoiding any overlap with framework atoms was used to determine the pore size distribution (PSD).^[16] This analysis confirmed that **TCM-10** contains well-defined micropores with cross-sectional diameters of ca. 12.3 Å and smaller, narrow cavities of ca. 9.8 Å in diameter (Figure 2c). This pore-size characteristic is distinctively different to that of the corresponding dual interpenetrated **pto** and **tbo** structures that contain either distinct micropores of 12.3, 14.5 and 18.5 Å in diameter (**TCM-8**) or larger defined pores with diameters > 20 Å (**TCM-4** or **TCM-4'**).^[14a,b] The accessible surface area for the fully desolvated structure of **TCM-10** of ca. 3850 m²/g was calculated by 'rolling' a nitrogen-sized sphere (diameter = 3.31 Å) along the surface of the framework atoms.^[17] The value is noteworthy considering the triple interpenetrated nature of the compound. It is in fact closely comparable with that of the dual interpenetrated **pto** structure,

achievable void volumes of the as yet hypothetical dual interpenetrated or single network structures are very large. Similarly, considering that the individual nets in **TCM-10**, **-8** and **-4** occupy closely comparable volumes, one can conclude that the observed type of topology gives rise to an intermediate intrinsic surface area which is larger than that of the corresponding **pto** network but lower than that of the **tbo** network.

Conclusions

In summary, we describe the synthesis and structure of a new highly augmented {Cu₂} 'paddlewheel'-based MOF that is stabilized by BTEB linkers. **TCM-10** reveals an uncommon, less-symmetrical (3,4)-connected net topology, thus represents a rare and new framework isomer to the extensively studied **pto** and **tbo** analogues.

The ethynyl moieties of the BTEB linkers not only result in an augmented structure, moreover, they impart rotational flexibility of the benzoate groups through the separation of the phenyl rings. The topological and structural analysis of **TCM-10** demonstrates that this flexibility is key for the structural diversity of this system allowing the concomitant formation of three distinct framework isomers using a single tri-topic, triangular ligand. Thus, the BTEB linker distinguishes itself from other smaller tritopic benzoates that have previously been used to prepare {Cu₂} based MOFs. For instance, in the geometrically restrained benzenetribenzoate (BTB) linker planarity of the phenyl rings is hampered by the close contacts of H-atoms, thus stabilizing the **pto**-topology in MOF-14.

Computational analyses suggest that the observed structure in **TCM-10** gives rise to a very high surface area, despite the triple

but significantly lower than the surface area of the corresponding **tbo** structure. The BET surface area of the fully de-solvated **TCM-10** was calculated to be 3904 m²/g (see Supporting Information). In-line with the calculated surface areas and He pore volume (1.65 cm³/g), the maximum nitrogen capacity of **TCM-10** is ca. 45 mmol/g (Figure 2d). The structure gives rise to a type-I adsorption isotherm whereby the low-pressure N₂ uptake is reduced in comparison to **TCM-4** or **TCM-8**.^[18, 14]

Table 1 compares the void volumes and calculated accessible theoretical surface areas of the three {Cu₂}/BTEB framework isomers. The variable BTEB connectivities result in closely related Cu/BTEB frameworks, each with its distinct pore sizes, surface areas and structural descriptors. One might remark that these Cu/BTEB framework isomers are not directly inter-convertible. In the triple interpenetrated **TCM-10** structure, each individual single net occupies ca. 10% of the entire unit cell volume, indicating the

Table 1. Comparison of the calculated surface areas and structural parameters of the isomeric {Cu₂}/BTEB frameworks.

	TCM-4	TCM-8	TCM-10
Interpenetration	Dual	Dual	Triple
Cell volume (Å³)/ Z	80939 /16	105620/16	16645/4
Void volume (%) / unit cell	78	84	72
Calc. surface area (m²/g)^[17]	3820	5441	3848

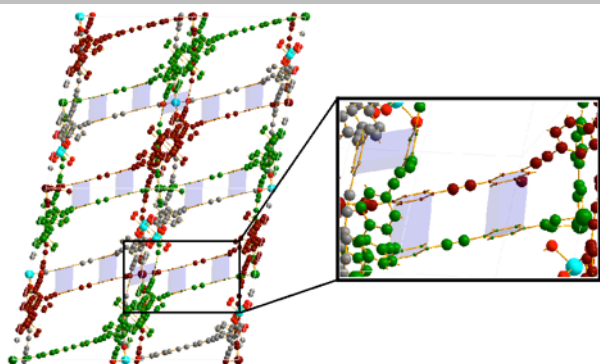


Figure 4. Stabilising π - π interactions between nets in **TCM-10**; structure with view in the direction of the crystallographic b -axis. The highlighted interactions are characterised by inter-plane distances between the aromatic rings systems of ca. 3.8 Å.

interpenetrated nature of the compound. The observed topology may be regarded as an 'intermediate' between the **tbo** and **pto** topologies resulting in higher intrinsic surface areas than the corresponding **pto** structures but lower surface areas than the **tbo** structures. **TCM-10** co-crystallizes with its isomers and future studies will focus development of synthetic strategies to produce phase-pure samples of this MOF.

Experimental Section

1,3,5-Benzene-tris-ethynylbenzoic acid (BTEB) was synthesized according to a literature method.^[19] The topology of **TCM-10** was determined with help of the program package ToposPro 5.0.^[20] Details of the computational and topological analyses are provided in the supporting information.

Preparation of [Cu₃(BTEB)₂(H₂O)₂(DMF)], **TCM-10:** To a solution of 0.065 g Cu(NO₃)₂·3H₂O in 2 mL DMF, 0.094 g BTEB was added. The resulting mixture was sonicated for 10 min. Then, a solution of 0.015 g 4,4'-bipyridine in 0.25 ml DMF was added. The resulting reaction mixture was reacted in a closed vial at 85°C in an oven for 48h. A mixture containing light-blue, plate-like crystals (**TCM-8**), greenish-blue polyhedron-type crystals (**TCM-4**) and aggregates of blue block-like crystals (**TCM-10**) was obtained. The latter crystals of **TCM-10** are distinguishable from the other crystals due to their color and morphology. **TCM-10** was isolated from the mixture manually. Yield: ca. 5-10%; Elemental analysis (%) of a dried sample of **TCM-10** {C₆₉H₄₁Cu₃NO₁₅}, with four non constitutional water molecules per formula unit: calcd. C 59.76, H 3.56, N 1.01; found C 59.76, H 3.39, N 1.40.

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Keywords: metal-organic frameworks • copper • topology • polymorphism • coordination chemistry

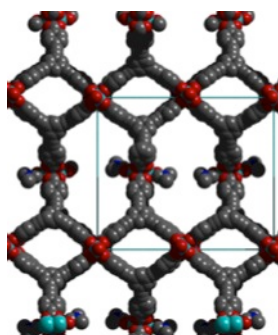
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Entry for the Table of Contents

SHORT COMMUNICATION

An uncommon, less-symmetrical (3,4)-connected net topology that represents a rare framework isomer of the extensively studied $\{Cu_2\}$ -based **pto** and **tbo** analogues is reported. Computational analyses suggests that the observed structure gives rise to a surface area of $> 3500 \text{ m}^2/\text{g}$, despite the triple interpenetrated nature of the compound.

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- [a] Prof. N. Zhu, D. Sensharma, P. Wix, Prof. W. Schmitt
School of Chemistry & CRANN Institute & AMBER Centre
Trinity College Dublin
University of Dublin
College Green, Dublin 2, Republic of Ireland
E-mail: schmittw@tcd.ie, Ph: 00353 1 896 3495
- [b] Prof. N. Zhu, Prof. W.-Y. Wong
Institute of Molecular Functional Materials & Department of
Chemistry
Hong Kong Baptist University
Waterloo Road, Hong Kong, HK
- [c] Dr. M. J. Lennox
School of Chemistry
University of Nottingham
Nottingham, NG7 2RD, UK
- [d] Prof. Tina Düren
Department of Chemical Engineering
University of Bath
Bath, BA2 7AY, UK
- [e] Prof. W.-Y. Wong
HKBU Institute of Research and Continuing Education, Shenzhen
Virtual University Park, Shenzhen 518057, China.

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