Cite this: Chem. Commun., 2011, 47, 5982-5984

www.rsc.org/chemcomm

COMMUNICATION

Interpenetrated metal-organic frameworks of self-catenated four-connected mok nets[†]

Yun Gong,^{ab} Yu-Chao Zhou,^b Tian-Fu Liu,^a Jian Lü,^{*a} Davide M. Proserpio^c and Rong Cao^{*a}

Received 21st January 2011, Accepted 29th March 2011 DOI: 10.1039/c1cc10411j

We describe two cobalt metal–organic frameworks built by amide derivative and organodicarboxyl co-ligands, displaying 3-fold interpenetration of 6^5 .8-mok nets which are 4-connected self-catenated nets described theoretically in the early nineties.

The contemporary explosion of research interest on coordination polymers (CPs) and metal-organic frameworks (MOFs) stems from not only from their promising practical applications¹ in several cutting-edge realms such as catalysis, magnetism, nonlinear optics, drug delivery, gas storage and separation, but also their intriguing variety of architectures and topologies.² In particular, topology focuses on the network connectivity generated via the reduction of periodic nets into node-and-linker/vertex-and-edge representations, which helps greatly the understanding of structural complexity, variety and entanglements of the coordination architectures.³ Crystal engineering of CPs/MOFs has thus been greatly accelerated along with the cumulative knowledge of the delicate correlations between structures and topology of nets.⁴ Nets such as dia, pcu, srs, and structures of known materials and minerals, have been frequently encountered in CPs/MOFs whereas some other nets have never been found.5 Molecular mimics of theoretically available nets are of interest in crystal chemistry and in mathematics, arousing open puzzles as well.

Four-connected (4-c) 3-periodic nets^{3d} captured special research attention both for their intrinsic interest (all zeolites are 4-c nets) and from a theoretical point of view: many 4-c nets have been deduced and summarized firstly by Wells^{3a} followed by several comprehensive discussions.⁶ O'Keffee collected some "dense and rare" 4-c nets in 1991,⁷ among which there is the first example of self-catenated 4-c net

- ^b College of Chemistry and Chemical Engineering,
- ChongQing University, ChongQing 400044, P. R. China
- ^c Università degli Studi di Milano, DCSSI, via Venezian 21, 20133 Milano, Italy

observed in a high-pressure polymorph of silica, coesite (**coe**) where the shortest 8-rings are catenated with other 8-rings (Fig. 1, left). In 2000, the only known example so far of coordination polymer with **coe** topology was isolated.⁸ O'Keeffe⁷ also created a new uninodal net by merging together pairs of the vertices of **coe** net, that still maintains the self-catenation property (Fig. 1, right). This new net was believed "not very likely to be found as a net in a crystal structure" because there was one distance between two nodes that was shorter than the edges.⁷ The self-catenated net has a vertex symbol⁹ of $6.6.6.6_{2.8_2}$ and named later as **mok** net (point symbol 6^{5} .8). It is as-yet an unrealized network topology in crystal structures of CPs/MOFs.¹⁰

Self-catenated framework structures represent one subclass of the most fascinating topological nets in the extraordinary family of entanglements, featuring one of the 'shortest rings' being catenated by other 'shortest rings' of the same net.^{3c,11} Though once only comes out serendipitously, deliberate synthesis of self-catenated CPs/MOFs has now been proven being rationally engineered by the combined use of long and bent organoamine and organocarboxylate ligands.¹² Herein we report two examples of MOF architectures featuring 3-fold interpenetration of the self-catenated 4-connected uninodal **mok** net, formulated as [Co(4,4'-BPIPA)(2,6-NDC)]·2DMF (1)‡ and [Co(4,4'-BPIPA)(4,4'-BPDC)]·2DMF (2) (4,4'-BPIPA = N,N'-bis-4-pyridyl-isophthalamide, 2,6-NDC = 2,6-naphthalenedicarboxylic acid, 4,4'-BPDC = 4,4'-biphenyldicarboxylic acid, Scheme 1).

Complex 1 crystallizes in monoclinic, space group C2/c§. In the structure of 1, the crystallographically independent cobalt center is bonded by two pyridyl N atoms from 4,4'-BPIPA and



Fig. 1 View of the ideal binodal coe (left) and uninodal mok (right) nets with catenated 8-ring (for coe) and 6-ring (for mok) highlighted.

^a State Key Laboratory of Structural Chemistry, Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences, Fujian, Fuzhou 350002, P. R. China. E-mail: rcao@fjirsm.ac.cn, lujian05@fjirsm.ac.cn; Fax: +8659183714946; Tel: +8659183796710

[†] Electronic supplementary information (ESI) available: Synthesis and general characterizations and additional structural figures. CCDC 764789, 764788 and 772375. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c1cc10411j



Scheme 1 Schematic view of the organic linkers.

four O atoms from two chelating carboxyl groups of 2,6-NDC (Fig. 2, top-left). The Co-N distances are 2.082(7) Å and 2.086(9) Å and the Co-O bonds are 2.091(7)/2.209(8) Å and 2.131(7)/2.155(7) A. Each Co atom connects to four neighboring ones through two 4.4'-BPIPA and two 2.6-NDC, both as linear linkers, to form an infinite three-dimensional threeperiodic network (3-D). There are three interpenetrated nets related by a single translational vector (Class Ia),¹³ with the shortest interpenetration vector [1/2, 1/2, 0] (and its symmetrically equivalent [1/2,-1/2,0]) of 15.11 Å. Topological analysis using TOPOS software¹⁴ identifies the net as **mok**. As mentioned earlier, another interesting aspect of the resulting mok net is that it is self-catenated as **coe**, but now the catenation happens among 6-rings (Fig. 1). Basic 6-membered cycles are observed in 1 formed by six Co, two 2,6-NDC and four 4,4'-BPIPA. The cycles have 'chair' configurations and build into a wavy hexagonal (hcb) sub-net (Fig. 2, top-right). A pair of the hcb sub-nets interpenetrates to each other by sharing the same average plane (Fig. 2, bottom) to give a 2-fold interpenetrated subunit. For the sake of clarity, we mark in a random sequence the six Co centers in a 6-membered cycle as Co1-Co6, although they are crystallographically identical, and the four hcb nets of the two neighbouring 2-fold layers (above and below a central one) as L1-L4. The interconnection among three 2-fold layers is achieved by Co1-L1, Co2-L2, Co3-L3, Co4-L4, Co5-L3, and Co6-L4. Thus an overall 3-D mok net is generated and the feature of interpenetration of the hcb



Fig. 2 View of the basic building blocks (top-left), individual **hcb** net (top-right), and the doubly interpenetrated **hcb** nets (top-right and bottom) in complex **1**. Color codes: C, black; N, blue; O, red; Co, green.

subunits is integrated into **mok** making it self-catenated (Fig. 3 top-left and top-right). Further complexity arises from the fact that there are three interpenetrated **mok** nets (Fig. 3 bottom and S3†). Uncoordinated DMF molecules fill in the voids of the network and are weakly coordinated *via* hydrogen bonds with the amide groups (N-H···O, 2.98 and 3.07 Å). Numbers of DMF molecules were determined mainly by elemental analysis and TGA analysis (Fig. S7†).

Complex 2 displays a similar network to complex 1 exhibiting 3-fold interpenetrated framework of **mok** nets. In fact, replacement of 2,6-NDC in 1 with longer 4,4'-BPDC result in 2. Thus, complexes 1 and 2 are topologically equivalent (Fig. S3[†]). However, complex 2 is less stable and loses solvent DMF faster than 1, possibly due to the larger solvent accessible voids induced by the longer 4,4'-BPDC linker in 2.

Calculations using *PLATON*¹⁵ indicate that complex **1** and complex **2** have solvent accessible volumes of 2688.7 Å³ (36.8%) and 3910.2 Å³ (44.1%), respectively, after the removal of guest solvent molecules. The permanent porosity was demonstrated by the N₂ adsorption isotherm of the activated samples (Fig. S4[†]). The BET surface area of **1** is calculated to be 116 m² g⁻¹ (langmuir surface area 169 m² g⁻¹) and the total pore volume is 0.07 cm³ g⁻¹. The former is smaller than the solvent-accessible surface area estimated from crystal structure which is probably caused by the incomplete removal of guest molecules or structural deformation during the thermal activation of **1** (indeed the heated samples lose crystallinity as seen from PXRD).¹⁶ The pore size obtained by applying the Horvath-Kawazoe¹⁷ (HK) equation to the N₂ sorption data is 5.03 Å which is consistent with the structure.



Fig. 3 Topological presentation the 3-D mok net derived from complex 1 by reducing the organic linkers as bold lines (top-left); The 4-connected mok net with highlighted a pair of self-catenated 6-rings. The piercing edges are the long, rigid dicarboxylic molecules (top-right); A view of the 3-fold interpenetrated mok nets (bottom).

Curiously, however, when the geometrically and chemically comparable (but shorter) terephthalic acid (TP) was used as a substitution of 2,6-NDC or 4,4'-BPDC, a new complex, [Co(4,4'-BPIPA)(TP)]·2DMF (3), was isolated. The Co centers in complex 3 are bonded by two pyridyl groups of 4,4'-BPIPA (Co-N 2.113(3) Å) and four oxygens of the two chelating carboxylate groups of TP (Co-O 2.070(2) and 2.254(2) Å). The metal centers are cross-linked by the two organic ligands (spacers) to give a 2-periodic sql layer. The layers are undulated and give rise to a 2-fold interpenetration sharing the same average plane (Fig. S5, ESI⁺). The 2-fold sql stacks along (010) in an ABAB sequence. The aromatic rings of the V-shaped 4,4'-BPIPA molecules point up- and downwards from the layers to form a multi-armed bilayer unit, which interdigitates with adjacent bilayers in a 'cross finger' way to give a 3-D supramolecular network (Fig. S6, ESI[†]). Guest DMF molecules reside into the interlayer regions through hydrogen bonds with the amide groups (N–H \cdots O, 2.889 Å).

The reason for the unexpected structure of complex 3 may be double: First, TP is considerably shorter than 2,6-NDC and 4,4'-BPDC that may not meet the requirement to realize the self-catenation. In fact, an intrinsic doubly interpenetrated hcb bilayer subunit is needed to realize **mok** topology. In the case of complex 3, instead we have doubly interpenetrated sql bilayer with 4-rings (with sides of 10.68, 14.31 Å), rather than the needed 6-rings hcb (with sides 12.92-16.95 for 1 and 15.02-16.98 for 2), The second difference is in the conformation of 4.4'-BPIPA observed for 3 (cis. defined by the two rotatable amido on a benzene ring of the 4,4'-BPIPA) versus 1 and 2 (trans), which may be responsible for the variety of the subunits (see Scheme S1^{\dagger}). Generally the N_{pvridvl} · · N_{pvridvl} distance of cis-4,4'-BPIPA (11.2 Å) is shorter than the N_{pyridyl} ···N_{pyridyl} distance of trans-4,4'-BPIPA (13.3 Å), thus the overall Co · · Co distances are much shorter in 3: the one bridged by 4,4'-BPIPA are 14.31 Å versus ca. 16.9 Å for 1 and 2. Moreover, the cis-/trans-configuration of 4,4'-BPIPA is somewhat controllable through the fine tuning of reaction temperature: the low temperature helps the formation of cis-configuration ligands (potentially result in 4-rings) whereas high temperature favors trans- configuration ligands (potentially result in 6-rings) which is consistent with our previous observations with some geometrically flexible ligands.¹⁸

In conclusion, two metal–organic frameworks with 6^{5} .8-mok topology have been synthesized and topologically characterized. The two MOFs reported in this work give beautiful examples showing a new type of topological nets and add first members in the inventory of 4-connected uninodal mok CPs/MOFs. A key to the successful isolation of the nets reported herein is the combined use of long and rigid dicarboxylate linkers with a flexible V-shaped pyridyl-amide derivative. It demonstrates again the theoretically anticipated topological nets can be accomplished in the area of CPs/MOFs.

Financial support from the 973 Program (2011CB932504, 2007CB815303), NSFC (20731005, 20821061, and 91022007), Fujian Key Laboratory of Nanomaterials (2006L2005), and the Key Project from CAS are gratefully acknowledged.

Notes and references

[‡] Syntheses. Red block crystals of complex **1** were originally obtained by solvothermal reaction of N,N'-bis-4-pyridinyl-isophthalamide, 2,6-naphthalenedicarboxylic acid, and Co(NO₃)2·6H₂O (1:1:1) in 8 mL DMF at 120 °C for 3 days. Red purple block crystals of complex **2** were synthesized at a higher temperature (150 °C) comparing with **1** and 4,4'-biphenyldicarboxylic acid was used instead of 2,6-naphthalenedicarboxylic acid. Red block crystals of complex **3** were synthesized with starting materials of N,N'-bis-4-pyridinylisophthalamide, terephthalic acid, and Co(NO₃)2·6H₂O (1:1:1) at a lower temperature of 105 °C. For details, see ESI[†] & Crystal data: see ESI for details[†].

- 1 See for example: C. Janiak and J. K. Vieth, *New J. Chem.*, 2010, **34**, 2366 and references therein.
- 2 See for example: E. V. Alexandrov, V. A. Blatov, A. V. Kochetkov and D. M. Proserpio, *CrystEngComm*, 2011, **13**, DOI: 10.1039/ C0CE00636J and references therein.
- 3 (a) A. F. Wells, *Three-dimensional Nets and Polyhedra*, Wiley-Interscience, New York, 1977; (b) S. R. Batten and R. Robson, *Angew. Chem., Int. Ed.*, 1998, **37**, 1460; (c) L. Carlucci, G. Ciani and D. M. Proserpio, *Coord. Chem. Rev.*, 2003, **246**, 247; (d) M. O'Keeffe, M. A. Peskov, S. J. Ramsden and O. M. Yaghi, *Acc. Chem. Res.*, 2008, **41**, 1782.
- 4 (a) B. Chen, M. Eddaoudi, S. T. Hyde, M. O'Keeffe and O. M. Yaghi, *Science*, 2001, **291**, 1021; (b) S. L. James, *Chem. Soc. Rev.*, 2003, **32**, 276; (c) S. Kitagawa, R. Kitaura and S. Noro, *Angew. Chem., Int. Ed.*, 2004, **43**, 2334.
- 5 (a) O. M. Yaghi, M. O'Keeffe, M. Eddaoudi, H. K. Chae, J. Kim and N. W. Ockwig, *Nature*, 2003, **423**, 705–714; (b) N. W. Ockwig, O. Delgado-Friedrichs, M. O'Keeffe and O. M. Yaghi, *Acc. Chem. Res.*, 2005, **38**, 176.
- 6 (a) M. O'Keeffe and N. E. Brese, Acta Crystallogr., Sect. A: Found. Crystallogr., 1992, A48, 663; (b) M. O'Keeffe, Acta Crystallogr., Sect. A: Found. Crystallogr., 1992, A48, 670; (c) M. O'Keeffe, Acta Crystallogr., Sect. A: Found. Crystallogr., 1995, A51, 916.
- 7 M. O'Keeffe, Z. Kristallogr., 1991, 196, 21.
- 8 L. Carlucci, G. Ciani, D. M. Proserpio and S. Rizzato, J. Chem. Soc., Dalton Trans., 2000, 3821.
- 9 V. A. Blatov, M. O'Keeffe and D. M. Proserpio, *CrystEngComm*, 2010, **12**, 44.
- 10 In the literature hunting for new topologies,² D. M. Proserpio with V. Blatov found the only other example of mok (also 3-fold interpenetrated of Class Ia) in an inorganic compound that never reached any database, and was not recognized as mok. It is the δ polymorph of Zn[Au(CN)₂]₂ reported in M. J. Katz, T. Ramnial, H.-Z. Yu and D. B. Leznoff, J. Am. Chem. Soc., 2008, 130, 10662.
- (a) B. F. Abrahamas, S. R. Batten, M. J. Grannas, H. Hamit, B. F. Hoskins and R. Robson, *Angew. Chem., Int. Ed.*, 1999, 38, 1475; (b) M. A. Withersby, A. J. Blake, N. R. Champness, P. A. Cooke, P. Hubberstey and M. Schroder, *J. Am. Chem. Soc.*, 2000, 122, 4044; (c) D. J. Price, S. R. Batten, B. Moubaraki and K. S. Murray, *Chem.-Eur. J.*, 2000, 6, 3186.
- 12 (a) X.-L. Wang, C. Qin, E.-B. Wang and Z.-M. Su, Chem.-Eur. J., 2006, 12, 2680–2691; (b) E. Shyu, R. M. Supkowski and R. L. LaDuca, Cryst. Growth Des., 2009, 9, 2481; (c) Y.-Q. Wang, J.-Y. Zhang, Q.-X. Jia, E.-Q. Gao and Cai-Ming Liu, Inorg. Chem., 2009, 48, 789.
- 13 (a) V. A. Blatov, L. Carlucci, G. Ciani and D. M. Proserpio, *CrystEngComm*, 2004, 6, 378; (b) I. A. Baburin, V. A. Blatov, L. Carlucci, G. Ciani and D. M. Proserpio, *J. Solid State Chem.*, 2005, **178**, 2452.
- 14 V. A. Blatov, *IUCr CompComm. Newsletter*, 2006, 7, 4; see also http://www.topos.ssu.samara.ru.
- 15 A. L. Spek, J. Appl. Crystallogr., 2003, 36, 7.
- 16 L.-L. Liang, J. Zhang, S.-B. Ren, G.-W. Ge, Y.-Z. Li, H.-B. Du and X.-Z. You, *CrystEngComm*, 2010, **12**, 2008.
- 17 G. Horvath and K. Kawazoe, J. Chem. Eng. Jpn., 1983, 16, 470.
- 18 W. Bi, R. Cao, D. Sun, D. Yuan, X. Li, Y. Wang, X. Li and M. Hong, *Chem. Commun.*, 2004, 2104; J. Lü, W.-H. Bi, F.-X. Xiao, S. R. Batten and R. Cao, *Chem.–Asian J.*, 2008, **3**, 542; J. Lü, W.-H. Bi and R. Cao, *CrystEngComm*, 2009, **11**, 2248.