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# COMMUNICATION

# Cocrystal controlled solid-state synthesis of a rigid tetracarboxylate ligand that pillars both square grid and Kagomé lattice layers<sup>†</sup>

Jason A. Perman, Amy J. Cairns, Łukasz Wojtas, Mohamed Eddaoudi and Michael J. Zaworotko\*

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[Cu<sub>2</sub>(carboxylate)<sub>4</sub>] paddlewheel molecular building blocks, MBBs, are capable of generating square grid or Kagomé lattice supramolecular isomers when dicarboxylates such as 1,3-benzenedicarboxylate (1,3-bdc) and 1,4-benzenedicarboxylate (1,4-bdc) are exploited to link the paddlewheel MBBs. In this contribution we demonstrate that it is possible to use a solvent-free reaction (cocrystal controlled solid-state synthesis) to prepare a tetracarboxylic acid, H<sub>4</sub>BIPA-TC, formed by rigidly linking two 1,3-bdc moieties at the 5-position. BIPA-TC can pillar both square grid and Kagomé lattice supramolecular isomers, thereby generating nets that exhibit *lvt* or *nbo* topologies, respectively.

The continually evolving field of crystal engineering applies the concepts of supramolecular chemistry to facilitate bottom-up design of crystal structures. That molecular level control can be exerted over structure in turn affords diversity of composition and can even lead to control over properties as exemplified by two classes of compound: organic structures such as pharmaceutical cocrystals that enhance solubility or stability of a pharmaceutically active ingredient;1 metalorganic materials (MOMs) that use metals or metal clusters as nodes and multi-functional organic ligands as linkers.<sup>2-9</sup> Carboxylate sustained MOMs are particularly well studied and have furnished a number of prototypal structures based upon 1,3bdc,<sup>10-12</sup> 1,4-bdc,<sup>13-15</sup> and 1,3,5-benzenetricarboxylate.<sup>16,17</sup> We have been exploring green chemistry approaches for the synthesis of new imide based ligands via condensation of anhydrides and amines in the solid-state, *i.e.* cocrystal controlled solid-state synthesis (C3S3).18 C3S3 reactions are a subset of the much broader class of reactions encompassed by solid-state synthesis and are distinguished by the reactants that form in a cocrystal phase prior to reaction. Reduction or complete elimination of solvent and direct isolation of a pure product offers obvious advantages over solvent based approaches to synthesis.<sup>19-23</sup> In this contribution we demonstrate how

a tetracarboxylic acid 5,5'-(1,3,6,8-tetraoxobenzo[*Innn*][3,8] phenanthroline-2-7-diyl)bis-1,3-benzenedicarboxylic acid,  $H_4BIPA$ -TC, is prepared using C<sup>3</sup>S<sup>3</sup> and then used as a ligand to generate two isomeric nets that represent examples of "ligand-to-ligand" pillaring.

The 120° angle subtended by the carboxylate moieties of 1,3-bdc means that it can serve as an angular linker between the vertices of [M2(carboxylate)4] paddlewheel MBBs and sustain squares of squares (that in turn form undulating square grids)<sup>24</sup> or triangles of squares (that in turn form Kagomé lattices).25 1,3-bdc can also generate structures with both triangles and squares, the combination of which facilitates curvature and polyhedral structures that can exist within infinite nets (e.g. supermolecular building blocks, SBBs, as in HKUST-117 and rht-126) or as discrete molecules (e.g. small rhombihexahedra, faceted polyhedra that represents prototypal metalorganic polyhedra or nanoballs<sup>10,11</sup>) (Fig. 1). Rigidly linked pairs of 1,3-bdc ligands cannot link nanoballs because the only feasible 24connected net is binodal and requires a 3-connected node, e.g. a 24,3or rht topology.<sup>26-31</sup> However, flexibly linked pairs of 1,3-bdc moieties can engage in multiple links between the triangular or square windows of nanoballs and thereby reduce the nanoball to an 8-connected or 6-connected node.32-34 Flexibly linked 1,3-bdc



Fig. 1  $[M_2(carboxylate)_4]$  moieties (squares) linked at their vertices by 1,3-bdc ligands can generate three supramolecular isomers: square grids, Kagomé layers or discrete nanoballs.

Department of Chemistry, University of South Florida, 4202 East Fowler Avenue, CHE 205, Tampa, Florida, 33620-5250, USA. E-mail: xtal@ usf.edu; Tel: +1 813-974-3451

<sup>†</sup> Electronic supplementary information (ESI) available: FTIR, TGA, and NMR information is available for the ligand synthesis; a list of ligands used for pillaring Kagomé lattice and square grids is given in Fig. S5. CCDC reference numbers 789422–789424. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c0ce00542h



Fig. 2 Powder XRD and materials listed from bottom to top 5-NH<sub>2</sub>BDC, NTCDA, dry grind, DMF grind (cocrystal), and H<sub>4</sub>BIPA-TC.

moieties can also facilitate variants on Kagomé lattices.<sup>35</sup> We herein describe how a ligand based upon rigidly linked 1,3-bdc moieties can be prepared using  $C^3S^3$  and subsequently used to cross-link or pillar either of the 2D nets that are based upon  $[M_2(carboxylate)_4]$  paddlewheel MBBs.

### **Experimental and results**

Synthesis of H<sub>4</sub>BIPA-TC: 5-aminoisophthalic acid (5-NH<sub>2</sub>BDC) and 1,4,5,8-naphthalene tetracarboxylic dianhydride (NTCDA) were ground in a pestle and mortar in 2 : 1 stoichiometry with 100  $\mu$ L DMF resulting in the formation of a purple cocrystal. The cocrystal was heated for one hour at 180 °C to afford yellow H<sub>4</sub>BIPA-TC in yields of >95% (ESI†). Synthesis by refluxing in DMF has also been accomplished with yields of 85%.<sup>36</sup> Fig. 2 illustrates how this reaction can be monitored using powder X-ray diffraction. Dry grinding of the substrates affords a simple mixture of 5-NH<sub>2</sub>BDC and NTCDA. Similar behavior was seen with NTCDA and 3-aminobenzoic acid.<sup>18</sup> H<sub>4</sub>BIPA-TC is also isolated if the dry grind is heated. In both instances the isolated product is largely amorphous.

A mixture of  $Cu(NO_3)_2 \cdot 2.5H_2O$  (0.15 mmol), as prepared H<sub>4</sub>BIPA-TC (0.052 mmol), DMF (1 mL), chlorobenzene (1 mL) and

HNO<sub>3</sub> (0.45 mL, 3.5 M in DMF) was placed in a 20 mL scintillation vial. The solution was heated at 1.5 °C min-1 to 85 °C for 12 hours, heated at 105 °C for 23 hours and at 115 °C for 23 hours, affording single crystals of [Cu<sub>2</sub>(BIPA-TC)(H<sub>2</sub>O)<sub>2</sub>]<sub>n</sub>, 1 (ESI<sup>†</sup>).<sup>‡</sup> The crystal structure of 1 reveals that it is sustained by [Cu<sub>2</sub>(carboxylate)<sub>4</sub>] paddlewheel MBBs (Cu···Cu  $d_{avg} = 2.636(4)$  Å), the vertices of which are linked into Kagomé layers that are in turn pillared via ligand-toligand cross-linking (Fig. 3). Compound 1 therefore exhibits two types of 4-connected node (the paddlewheels and the BIPA-TC ligands) and their connectivity generates nbo topology. There are two types of windows and cavities in 1. One set of windows results from triangles of square paddlewheels and exhibits an effective diameter of ca. 5.0 Å. These windows lie above and below a cavity that results from cross-linking the remaining six vertices of the triangles of square paddlewheels by six BIPA-TC ligands. This cavity can accommodate an  $\sim$ 12.1 Å diameter sphere (Fig. S4<sup>+</sup>). The second cavity is connected through isosceles triangular windows with dimensions 12.25 Å by 3.94 Å ( $L \times W$ ). This small opening is due to the imide moiety rotating 82.2° and 79.2° with respect to the isophthalate plane, presumably because of steric repulsion between isophthalate C-H and imide C=O moieties. This cavity spans two layers with a length of  $\sim$ 32 Å and it exhibits a diameter of  $\sim$ 9 Å at its widest point (Fig. S4<sup>†</sup>). With axial ligands and solvent molecules removed, 1 exhibits 70% void space as calculated by Platon.<sup>37</sup>

A mixture of Cu(NO<sub>3</sub>)<sub>2</sub>·2.5H<sub>2</sub>O (0.052 mmol), H<sub>4</sub>BIPA-TC (0.05 mmol), DMA (1 mL), H<sub>2</sub>O (1 mL), and pyridine (0.1 mL, 1 M in DMF) was placed in a 20 mL scintillation vial. The solution was heated at 1.5°C min<sup>-1</sup> to 85°C for 12 hours, heated at 105°C for 23 hours and at 115 °C for 23 hours, affording single crystals of [Cu<sub>2</sub>(BIPA-TC)(DMA)<sub>2</sub>]<sub>n</sub>, 2a (ESI<sup>†</sup>).<sup>‡</sup> [Cu<sub>2</sub>(carboxylate)<sub>4</sub>] paddlewheels (Cu··· Cu d = 2.6620(7) Å) assemble into squares that adopt 1,2-alternate calixarene-like partial cone conformations and render 4,4-nets that possess an ~4.6 Å diameter window. Layers are cross-linked through **BIPA-TC** ligands, thereby generating zigzag channels of 10 Å by 13 Å and an lvt topology (Fig. 3). An ssb-like topology could also result with 4,4-layers if the squares of paddlewheels had adopted 1,3-alternate partial cone conformations, a situation which indeed occurred with another rigid tetracarboxylate ligand.38 With axial ligands and solvent molecules removed 2 exhibits 66% void space as calculated by Platon.<sup>37</sup> Cu(NO<sub>3</sub>)<sub>2</sub>·2.5H<sub>2</sub>O (0.1 mmol), H<sub>4</sub>BIPA-TC (0.05 mmol), DMF (1



Fig. 3 [Cu<sub>2</sub>(O<sub>2</sub>CR)<sub>4</sub>] linked by 1,3-bdc generates either Kagomé (above) or square grid (below) layers which can then be cross-linked by BIPA-TC<sup>4-</sup>.

mL), methanol (0.5 mL), 3,5-lutidine (11.3  $\mu$ L), HMTA (100  $\mu$ L, 1.4 M in H<sub>2</sub>O) and HNO<sub>3</sub> (0.4 mL, 2.8 M in DMF) heated at 1.5 °C min<sup>-1</sup> to 105 °C for 24 hours afforded single crystals of [Cu<sub>2</sub>(**BIPA-TC**)(3,5-lutidine)<sub>2</sub>]<sub>n</sub>, **2b** (ESI†).‡ Compound **2b** is isostructural with **2a** but 3,5-lutidine is coordinated to the paddlewheel moieties (Cu… Cu d = 2.6780(7) Å).

# Discussion

 $[Cu_2(BIPA-TC) \cdot solvent]_n$  exhibits supramolecular isomers that can be controlled by utilizing the appropriate conditions for their synthesis. The isostructural series NOTT-100 through 108, 110, 111 and PCN-14, 46 were also constructed through ligand-to-ligand cross-linking of 1,3-bdc moieties and exhibit the same topology as 1 whereas NOTT-109 exhibits ssb topology similar to 2. The NOTT and PCN nets use benzene, naphthalene, substituted benzene, and polyvne pillars (ESI<sup>+</sup>).<sup>38-41</sup> Until this study rigidly cross-linked 1,3bdc ligands had therefore afforded pillared Kagomé (nbo) nets with just one exception, NOTT-109. We herein report the first examples of ligand-to-ligand pillared square grid and Kagomé lattice structures which exhibit the same composition, *i.e.* supramolecular isomers. Very recently, Kitagawa et al. reported that metal-tometal pillaring using diamine pillars and [Zn<sub>2</sub>(carboxylate)<sub>4</sub>] paddlewheel MBBs can also afford such supramolecular isomers.<sup>42</sup> The NOTT series of compounds were evaluated in terms of porosity towards hydrogen and it was observed that smaller pore volume and smaller surface area afforded higher Qst at low loading. PCN-46 was also studied in terms of porosity towards hydrogen and was found to exhibit a higher Ost at low loading than NOTT-101, a compound with similar surface area.<sup>38,39</sup>

#### Conclusions

There is not yet a set of general rules that defines how subtle changes in reaction conditions afford one supramolecular isomer over another but herein we demonstrate that it is at least possible to exert control through reaction conditions. MOMs that are of the same composition but different in topology are not yet common but they could be of fundamental value since they will facilitate systematic study of binding affinity towards important guests such as small gas molecules (especially hydrogen and carbon dioxide). In particular, they will allow "apples with apples" comparisons of how pore size and surface area affect guest binding energies. Preliminary experiments suggest that 2a and 2b retain porosity following evacuation and in-depth studies are underway to determine its uptake behavior towards hydrogen and carbon dioxide. The synthesis of H<sub>4</sub>BIPA-TC reported herein requires little or no solvent and affords a product that is ready to use without cleanup. Such ligands might become attractive if and when practical applications for MOMs are developed.

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## Notes and references

‡ Crystal data for 1 at 100(2) K: Cu<sub>2</sub>C<sub>30</sub>H<sub>10</sub>N<sub>2</sub>O<sub>14</sub>, M = 749.48, monoclinic, C2/m; a = 32.461(12) Å, b = 18.024(6) Å, c = 19.748(7) Å,  $\beta = 119.964(9)^{\circ}$ , V = 10 010(6) Å<sup>3</sup>, Z = 6, D<sub>calcd</sub> = 0.746 Mg m<sup>-3</sup>,  $\mu =$ 0.672 mm<sup>-1</sup>, GOF = 0.951, final R<sub>1</sub> = 0.0819, wR2 = 0.1424 [for 5453 data I > 2 $\sigma$ (I)]. Crystal data for **2a** at 100(2) K: Cu<sub>2</sub>C<sub>38</sub>H<sub>28</sub>N<sub>4</sub>O<sub>14</sub>. 
$$\begin{split} M &= 891.72, \text{ orthorhombic } Imma; a = 15.2248(3) \text{ Å}, b = 36.4392(7) \text{ Å}, \\ c &= 10.3036(2) \text{ Å}, V = 5716.23(19) \text{ Å}^3, Z = 4, D_{\text{calcd}} = 1.036 \text{ Mg m}^{-3}, \mu = \\ 1.352^{-1}, \text{ GOF} &= 1.032, \text{ final } R_1 = 0.0375, \text{ w}R2 = 0.1018 \text{ [for 2594 data } I > \\ 2\sigma(I)\text{]}. Crystal data for$$
**2b** $at 183(2) K: Cu_2C_{44}H_{28}N_4O_{12}, M = 931.78, \\ \text{orthorhombic, } Imma; a = 14.981(21) \text{ Å}, b = 36.371(5) \text{ Å}, c = 10.922(2) \text{ Å}, \\ V &= 5951.1(16) \text{ Å}^3, Z = 4, D_{\text{calcd}} = 1.040 \text{ Mg m}^{-3}, \mu = 0.763 \text{ mm}^{-1}, \\ \text{GOF} &= 1.039, \text{final } R_1 = 0.0429, \text{ w}R2 = 0.1238 \text{ [for 2922 data } I > 2\sigma(I)\text{]}. \end{split}$ 

- 1 P. Vishweshwar, J. A. McMahon, J. A. Bis and M. J. Zaworotko, J. Pharm. Sci., 2006, 95, 499–516.
- 2 G. Ferey, Chem. Soc. Rev., 2008, 37, 191-214.
- 3 B. Moulton and M. J. Zaworotko, Chem. Rev., 2001, 101, 1629–1658.
- 4 M. Eddaoudi, D. B. Moler, H. L. Li, B. L. Chen, T. M. Reineke, M. O'Keeffe and O. M. Yaghi, Acc. Chem. Res., 2001, 34, 319–330.
- 5 M. Fujita, Chem. Soc. Rev., 1998, 27, 417–425. 6 S. Kitagawa, R. Kitaura and S. Noro, Angew. Chem., Int. Ed., 2004.
- **43**, 2334–2375.
- 7 M.-C. Hong and L. Chen, *Design and Construction of Coordination Polymers*, John Wiley & Sons, Inc., Hoboken, NJ, 2009.
- 8 L. R. MacGillivray, Metal–Organic Frameworks: Design and Application, John Wiley & Sons, Inc., Hoboken, NJ, 2010.
- S. R. Batten and R. Robson, *Angew. Chem., Int. Ed.*, 1998, **37**, 1460–1494.
  M. Eddaoudi, J. Kim, J. B. Wachter, H. K. Chae, M. O'Keeffe and O. M. Yaghi, *J. Am. Chem. Soc.*, 2001, **123**, 4368–4369.
- 11 B. Moulton, J. J. Lu, A. Mondal and M. J. Zaworotko, Chem. Commun. 2001, 863–864.
- 12 B. Moulton, J. J. Lu, R. Hajndl, S. Hariharan and M. J. Zaworotko, Angew. Chem., Int. Ed., 2002, 41, 2821–2824.
- 13 H. Li, M. Eddaoudi, T. L. Groy and O. M. Yaghi, J. Am. Chem. Soc., 1998, 120, 8571–8572.
- 14 H. Li, M. Eddaoudi, M. O'Keeffe and O. M. Yaghi, *Nature*, 1999, 402, 276–279.
- 15 G. Ferey, C. Mellot-Draznieks, C. Serre, F. Millange, J. Dutour, S. Surble and I. Margiolaki, *Science*, 2005, 309, 2040–2042.
- 16 J. J. Lu, A. Mondal, B. Moulton and M. J. Zaworotko, Angew. Chem., Int. Ed., 2001, 40, 2113–2116.
- 17 S. S. Y. Chui, S. M. F. Lo, J. P. H. Charmant, A. G. Orpen and I. D. Williams, *Science*, 1999, 283, 1148–1150.
- 18 M. L. Cheney, G. J. McManus, J. A. Perman, Z. Q. Wang and M. J. Zaworotko, *Cryst. Growth Des.*, 2007, 7, 616–617.
- 19 K. Tanaka and F. Toda, Chem. Rev., 2000, 100, 1025-1074.
- 20 F. Toda, in Organic Solid State Reactions, Springer-Verlag Berlin, Berlin, 2005, vol. 254, pp. 1–40.
- 21 G. Kaupp, in Organic Solid State Reactions, Springer-Verlag Berlin, Berlin, 2005, vol. 254, pp. 95–183.
- 22 A. V. Trask and W. Jones, in *Organic Solid State Reactions*, Springer-Verlag Berlin, Berlin, 2005, vol. 254, pp. 41–70.
- 23 F. Toda, Orgainic Solid-State-Reactions, Kluwer Academic Publisheers, 2002.
- 24 S. A. Bourne, J. J. Lu, A. Mondal, B. Moulton and M. J. Zaworotko, *Angew. Chem.*, *Int. Ed.*, 2001, **40**, 2111–2113.
- 25 J. J. Perry, G. J. McManus and M. J. Zaworotko, *Chem. Commun.*, 2004, 2534–2535.
- 26 F. Nouar, J. F. Eubank, T. Bousquet, L. Wojtas, M. J. Zaworotko and M. Eddaoudi, J. Am. Chem. Soc., 2008, 130, 1833–1835.
- 27 Y. Zou, M. Park, S. Hong and M. S. Lah, Chem. Commun., 2008, 2340–2342.
- 28 S. Hong, M. Oh, M. Park, J. W. Yoon, J. S. Chang and M. S. Lah, *Chem. Commun.*, 2009, 5397–5399.
- 29 Y. Yan, X. Lin, S. H. Yang, A. J. Blake, A. Dailly, N. R. Champness, P. Hubberstey and M. Schroder, *Chem. Commun.*, 2009, 1025–1027.
- 30 D. Zhao, D. Q. Yuan, D. F. Sun and H. C. Zhou, J. Am. Chem. Soc., 2009, 131, 9186–9188.
- 31 Y. Yan, I. Telepeni, S. H. Yang, X. Lin, W. Kockelmann, A. Dailly, A. J. Blake, W. Lewis, G. S. Walker, D. R. Allan, S. A. Barnett, N. R. Champness and M. Schroder, *J. Am. Chem. Soc.*, 2010, **132**, 4092–4094.
- 32 X. F. Liu, M. Park, S. Hong, M. Oh, J. W. Yoon, J. S. Chang and M. S. Lah, *Inorg. Chem.*, 2009, 48, 11507–11509.
- 33 J. J. Perry, V. C. Kravtsov, G. J. McManus and M. J. Zaworotko, J. Am. Chem. Soc., 2007, 129, 10076–10077.
- 34 X. S. Wang, S. Q. Ma, P. M. Forster, D. Q. Yuan, J. Eckert, J. J. Lopez, B. J. Murphy, J. B. Parise and H. C. Zhou, *Angew. Chem.*, *Int. Ed.*, 2008, 47, 7263–7266.

- 35 W. Qiu, J. A. Perman, L. Wojtas, M. Eddaoudi and M. J. Zaworotko, Chem. Commun., 2010, DOI: 10.1039/c0cc03270k.
- 36 D. Singh and J. B. Baruah, Tetrahedron Lett., 2008, 49, 4374-4377.
- A. L. Spek, J. Appl. Crystallogr., 2003, 36, 7–13.
  X. Lin, I. Telepeni, A. J. Blake, A. Dailly, C. M. Brown, J. M. Simmons, M. Zoppi, G. S. Walker, K. M. Thomas, T. J. Mays, P. Hubberstey, N. R. Champness and M. Schröder, J. Am. Chem. Soc., 2009, 131, 2159–2171.
- 39 D. Zhao, D. Q. Yuan, A. Yakovenko and H. C. Zhou, Chem. Commun., 2010, 46, 4196-4198.
- 40 S. Q. Ma, D. F. Sun, J. M. Simmons, C. D. Collier, D. Q. Yuan and H. C. Zhou, J. Am. Chem. Soc., 2008, 130, 1012-1016.
- 41 S. H. Yang, X. Lin, A. Dailly, A. J. Blake, P. Hubberstey, N. R. Champness and M. Schröder, *Chem.-Eur. J.*, 2009, **15**, 4829–4835.
- 42 M. Kondo, Y. Takashima, J. Seo, S. Kitagawa and S. Furukawa, CrystEngComm, 2010, 12, 2350-2353.