Supporting Information

Periodic molecular boxes in entagled enantiomorphic lcy nets

Yohei Takashima, Charlotte Bonneau, Shuhei Furukawa, Mio Kondo, Ryotaro Matsuda, and Susumu Kitagawa,

Contents:

1. Experimental Section

General. The chemicals and solvents used in the syntheses were of reagent grade and used without further purification. Thermogravimetric (TG) analysis were performed using a Rigaku Thermo plus TG-8120 apparatus in the temperature range between 298 K and 773 K in a N_2 atmosphere at a heating rate of 10 K min^{-1}. The powder X-ray diffraction (PXRD) were recorded with a Rigaku RINT-2000 Ultima diffractometer equipped with graphite monochromated Cu Kα radiation (λ = 1.54073 Å). The elemental analysis was carried out on a Flash EA 1112 series, Thermo Finnigan instrument. The adsorption isotherm was measured with automatic volumetric adsorption apparatus (BELSORP-max; Bel Japan Inc.). The *in-situ* XRPD/adsorption measurements were carried out using on a Rigaku UltimaIV with Cu Ka radiation connected with BELSORP-18 volumetric adsorption equipment (Bel Japan inc.).

Synthesis of 1. The mixture of $Zn(NO_3)_2 \cdot 6H_2O$ (149 mg, 0.5 mmol) and thiophene dicarboxylic acid (tda, 86 mg, 0.5 mmol) in DMF/MeOH (1:1, 50 mL) was heated for 48 h at 120 °C. White powders **1** were obtained (yield: 87.5 mg, 54%). The numbers of solvents in **1** was determined by elemental analysis and TG analysis (Fig. S1). Anal. Calcd (Found) for **1a•DMF•4H$_2$O**: $\{[Zn_4O(tda)_3(MeOH)](DMF)\bullet 4(H_2O)\}$ $[C_{22}H_{25}NO_{19}S_3Zn_4]$: C 27.4 (27.9); H 2.61 (2.60); N 1.45 (1.51). Crystals suitable for single-crystal X-ray diffraction structure analysis were obtained by the following procedure. The mixture of $Zn(NO_3)_2 \cdot 6H_2O$ (14.9 mg, 0.05 mmol), thiophene dicarboxylic acid (tda, 8.6 mg, 0.05 mmol) and pyridne (3.87 μl, 0.05 mmol) in DMF/MeOH (1:1, 5 mL) was heated for 48 h at 120 °C, resulting in colorless crystals (yield: 8.2 mg, 51%).

X-ray studies. A single crystal of **1a** was mounted in a loop. Measurements were made on a Rigaku AFC10 diffractometer with Rigaku Saturn CCD system equipped with a rotating-anode X-ray generator with confocal monochromated MoKα radiation and data was processed using Crystal Clear-SM 1.4.0(Rigaku). The structure was solved by direct methods and refined by full-matrix least-squares techniques on F^2 (SHELXL-97).[S1] All non-hydrogen atoms were anisotropically refined, while all hydrogen atoms were placed geometrically and refined with a riding model with U_{iso} constrained to be 1.2 times U_{eq} of the carrier atom. The diffused electron densities resulting from residual solvent molecules were removed from the data set using the SQUEEZE routine of PLATON and refined further using the data generated. The contents of the solvent region are not represented in the unit cell contents in crystal data.

S1 Sheldrick, G. M.; *Program for Crystal Structure Refinement*, University of Gottingen, Germany, 1997.

2. Thermogravimetric analysis of 1a

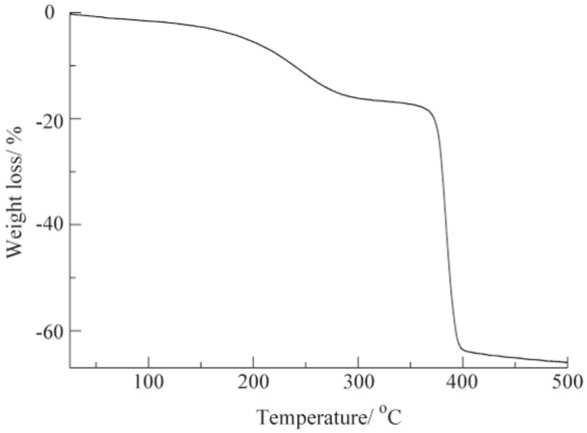

Fig.S1 TG analysis showing the weight loss in **1a**. The weight loss (16.8 %) is the weight of 1 MeOH, 1 DMF and 4 H_2O, which corresponds to the elemental analysis described above.

3. Topological studies

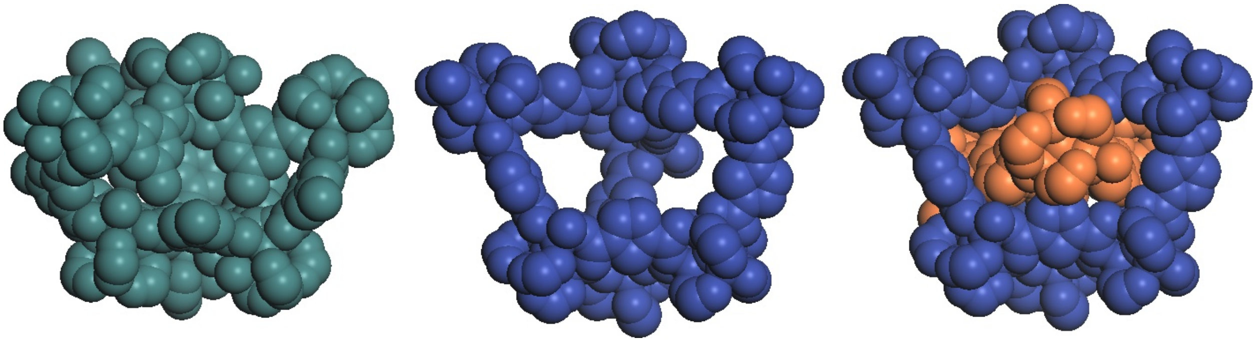

Fig. S2 Comparison of the volume available in the 3.5^3 cage in the compound reported by Chung *et al* (left) and one single component of Compound **1** (middle) in CPK representation. On the right, both interpenetrated components of compound **1** are represented.

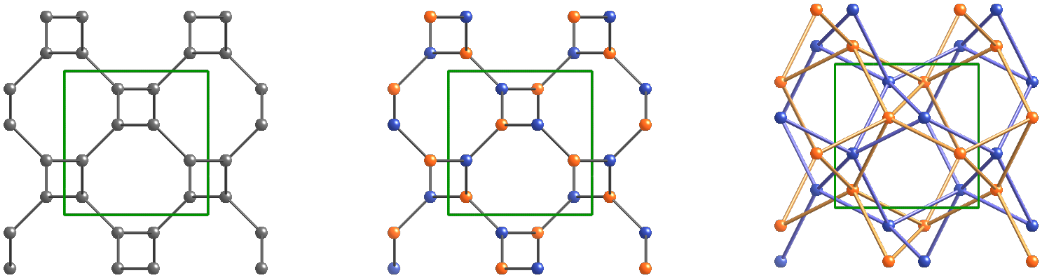

Fig. S3 The derivation **lcy** nets in *full* catenation from the **srs** net ($I4_132$) shows how the pair of enantiomorphors comes about. In view down the ***b***-axis: **srs** net (left), colouring of the **srs** net (middle) and last *fully* catenated **lcy** nets ($P4_132$ in blue, $P4_332$ in orange) obtained from drawing edges between same colour nodes. In this configuration, the three short distances between each nets which correspond to the edges of the **srs** net. *Full* catenation indicates that all rings of each net are catenated with the other net. All pictures are viewed down the ***b***-axis.

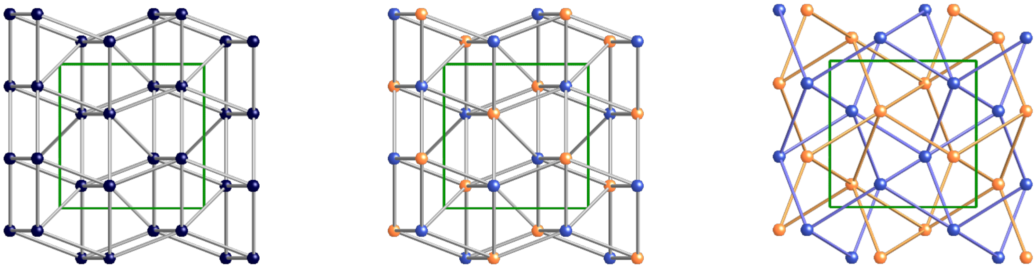

Fig. S4 Derivation and comparison of the **lcy-c*** net found in compound **1** (right) and the 7-coordinated sphere packing **svn** (left). Colouring the **svn** net and joining nodes of the same colour results in the **lcy-c*** net. All pictures are viewed down the ***b***-axis.

Identification of the highest symmetry embedding of the two interpenetrated components of compound 1 by Systre[1]. Notice that both nets are identical but of different handedness.

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Structure #1 - "Compound 1".

   Structure of dimension 3.
   Given space group is Pa-3.
   8 nodes and 24 edges in repeat unit as given.

   Structure is not connected.
   Processing components separately.

   ==========
   Processing component 1:
      multiplicity = 1
   Structure of dimension 3.
   Given space group is P1.
   4 nodes and 12 edges in repeat unit as given.

   Given repeat unit is accurate.
   Point group has 24 elements.
   1 kind of node.

   Equivalences for non-unique nodes:
      V2 --> V1
      V3 --> V1
      V4 --> V1

   Coordination sequences:
      Node V1:    6 24 48 86 138 192 260 348 432
530

   TD10 = 2065.0000

   Ideal space group is P4_132.
   Ideal group differs from given (P4_132 vs P1).

   Structure was found in builtin archive:
       Name:                   lcy

   Finished component 1.

   ==========
   Processing component 2:
      multiplicity = 1
   Structure of dimension 3.
   Given space group is P1.
   4 nodes and 12 edges in repeat unit as given.

   Given repeat unit is accurate.
   Point group has 24 elements.
   1 kind of node.

   Equivalences for non-unique nodes:
      V2 --> V1
      V3 --> V1
      V4 --> V1

   Coordination sequences:
      Node V1:    6 24 48 86 138 192 260 348 432
530

   TD10 = 2065.0000

   Ideal space group is P4_332.
   Ideal group differs from given (P4_332 vs P1).

   Structure was found in builtin archive:
       Name:                   lcy

   Finished component 2.

Finished structure #1 - "Compound 1".
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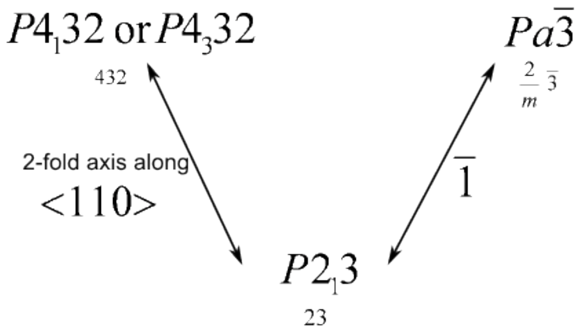
[1] Delgado-Friedrichs, O. & O'Keeffe, M. Identification and symmetry computation for crystal nets. Acta Crystallogr. A 59, 351–360 (2003).



Scheme S1

While it seems trivial that the maximum symmetry space group of a pair of interpenetrated nets belongs to a subgroup or supergroup of the single net, it is much less intuitive to understand how interpenatration can occur when this is not the case. As illustrated in scheme 1, we can see that both point groups of the space groups of the single lcy nets $P4_132$ (or $P4_332$) and the interpenetratd nets ($Pa\overline{3}$) originate from the 23 point group. Removing the 2-fold axis along the 110 direction transforms $P4_132$ (or $P4_332$) into $P2_13$, and adding a center of inversion results in $Pa\overline{3}$. Therefore, the catenation can be understood by recognising that the space group of the interpenetrated nets and the space group of the single net have the $P2_13$ subgroup in common.

4. Connolly surface simulation

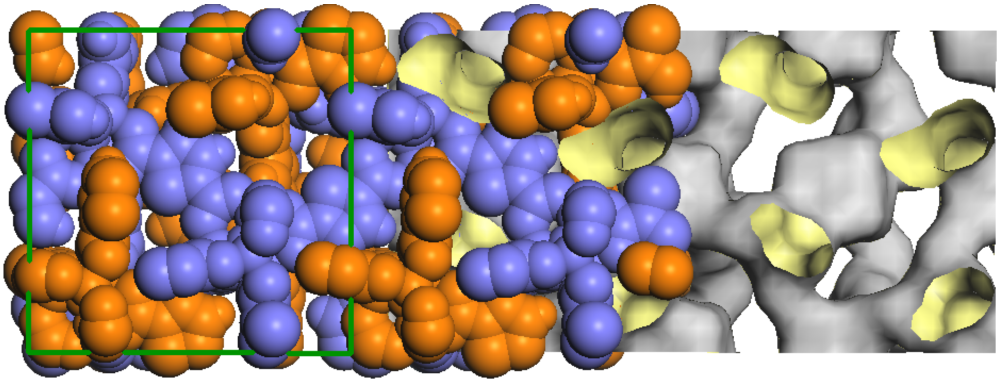


Fig. S5 Connolly surface simulated with a 1.4Å probe size revealed narrow short necks between boxes with approximate length of 1.1 Å and an aperture of 1.4 Å. CPK model with a 0.95 scaling factor. The yellow side of the Connolly surface represents the pore side.

5. Powder X-ray diffraction data of 1b

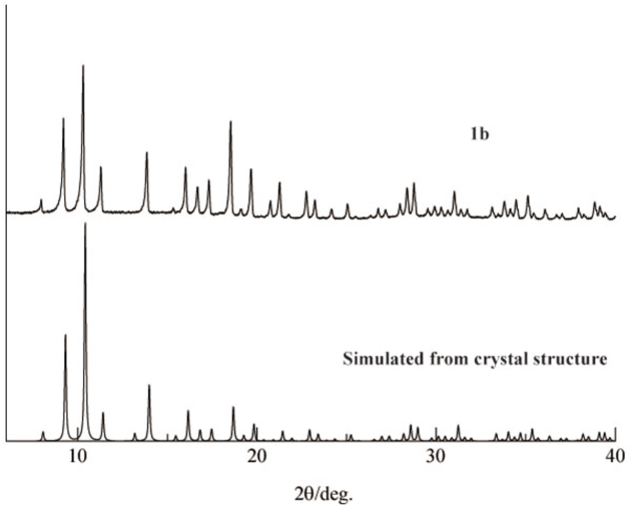


Fig. S6 PXRD patterns of the simulation from the crystal structure of **1a** and the experimental data of **1b**.

6. In-situ powder x-ray diffraction data on the 210 rection

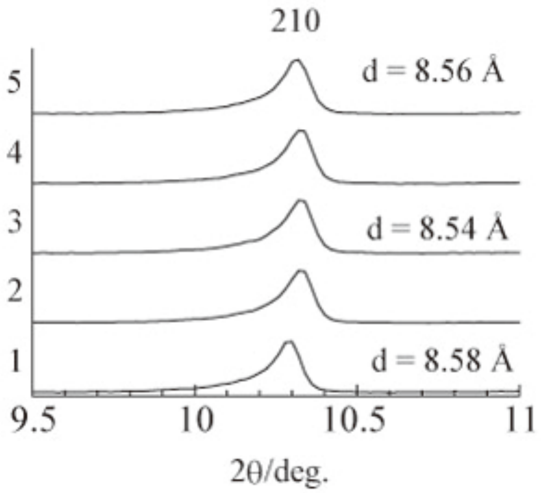


Fig. S7 Close-up on the 210 reflection with corresponding *d*-spacing at five points. These points correspond to those in Fig. 4.

7. Sorption isotherm of 1b with cm^3/g unit

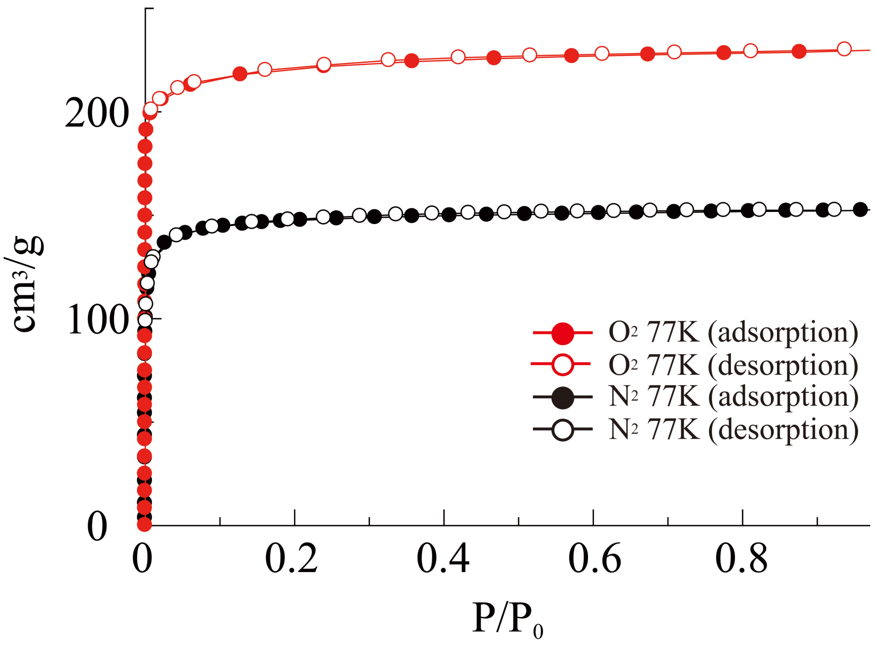


Fig. S8 Adsorption (filled circles) and desorption (open circles) isotherms for O_2 (red) and N_2 (black) of **1b** at 77 K

8. Thermogravimetric analysis of the sample after adsorption measurement.

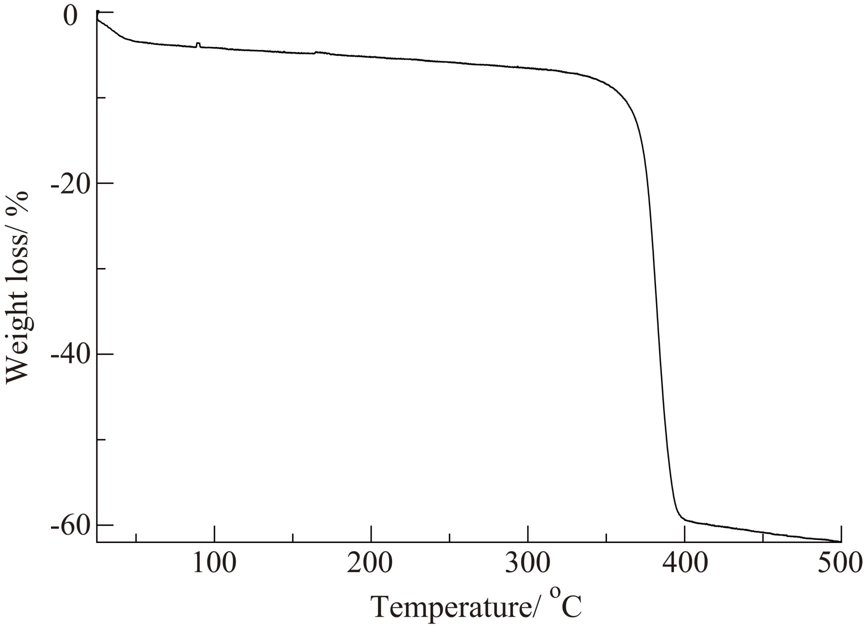


Fig. S9 TG analysis after gas sorption. Due to the presence of the open metal site, corresponding to the removal of the methanol molecule after the activation of the sample, the compound absorbs humidity readily after air exposure.