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First example of *ete* topology: Construction and characterizations of 4-fold interpenetrating 3D silver(I) coordination polymer with bis(4-pyridyl)cyclotetramethylsilane

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ABSTRACT

Self-assembly of $AgClO_4$ with bis(4-pyridyl)cyclotetramethylsilane (L) produces a 4-fold interpenetrating 3D coordination polymeric framework consisting of $[Ag_5(L)_7(CH_3CN)_2](ClO_4)_5{\cdot}2CH_3CN$ (**1**). The topological analysis indicates that the compound is the first example of a binodal 3,3-connected $(8^2{\cdot}10)_2$-**ete** net topology. Its thermal behavior and photoluminescent properties have been investigated.

One hot issue in the field of crystal engineering and supramolecular chemistry is to design and construct novel topology preferably with task-specific functions [1,2]. In particular, interpenetrated metal–organic frameworks have attracted great attention owing to both a variety of stable intriguing topological architectures [3–10] and high performance functions in various specific areas of gas-storage, adsorption and separation, catalysis, molecular and ion sensing, nonlinear optics, biomedical imaging, and drug delivery [11–17]. Such interpenetrated structures were generally induced by appropriate long spacer ligands [18–20]. Over the past decade, we have demonstrated that various silicon-containing pyridyl compounds are remarkable nitrogen donor ligands for desirable functional coordination molecular materials [21–26]. These silicon-containing pyridyl ligands take advantage of easy adjustable length and Lewis basicity, flexible angles around silicon atom(s), and conformational non-rigidity in construction of various coordination polymers. However, it is unusual to obtain new topology via the reaction of metal ions with the silicon containing ligands. In this communication, we report an unprecedented 4-fold interpenetrating **ete** net topology from the reaction of $AgClO_4$ with a new tectonic ligand, bis(4-pyridyl) cyclotetramethylsilane (L), along with its related properties including thermal behavior and photoluminescence.

The reaction of $AgClO_4$ with L in a mixture of methanol and ethanol produced crude solid product. Recrystallization of the crude product from a mixture of acetonitrile and diethyl ether formed colorless block crystals consisting of $[Ag_5(L)_7(CH_3CN)_2](ClO_4)_5{\cdot}2CH_3CN$ (**1**) (Supplementary material) suitable for single crystal X-ray diffraction [27]. The crystalline product is insoluble in water and common organic solvents such as acetone, acetonitrile, benzene, chloroform, diethyl ether, and tetrahydrofuran, but is easily dissociated in dimethyl sulfoxide and *N,N*-dimethylformamide. The compound is stable in aerobic condition.

The crystal structure reveals a 4-fold interpenetrating 3D framework in the trigonal unit cell with the space group $P3_221$ (No. 154) [28]. As shown in Fig. 1, the skeletal structure of the 3D framework consists of five silver(I) ions and seven ligands, in which three crystallographically different silver(I) ions (2Ag(1), 2Ag(2), and Ag(3)) exist in the asymmetric unit. L is employed as a bidentate bridging ligand in the structure. Ag(1) ion has a pseudo trigonal bipyramidal geometry with three nitrogen donors from three ligands (Ag–N = 2.274(7)–2.307(7) Å) in a basal plane and a nitrogen and an oxygen donor from coordinated acetonitrile molecules (Ag–N = 2.511(8) Å) and ClO_4^- anion (Ag···O = 3.117(7) Å; N–Ag···O = 178.0(3)°, Fig. S1), respectively, in *trans* positions. The local geometry around Ag(2) ion approximates to a pseudo trigonal bipyramidal arrangement with three nitrogen donors from three ligands (Ag–N = 2.227(7)–2.262(8) Å) and two oxygen donors (Ag···O = 2.846(8), 2.849(7) Å) from two ClO_4^- anions in *trans* positions. Ag(3) ion has a distorted tetrahedral arrangement with two nitrogen donors from two ligands (Ag–N = 2.146(7) Å; N–Ag–N = 158.8(4)°) and two oxygen donors (Ag···O = 2.92(1) Å) from a bidentate ClO_4^- anion (Fig. S1). There are two kinds of 80- and 100-membered metallamacrocyclic rings (Fig. S2) in the 3D coordination polymer, as will be discussed in detail.

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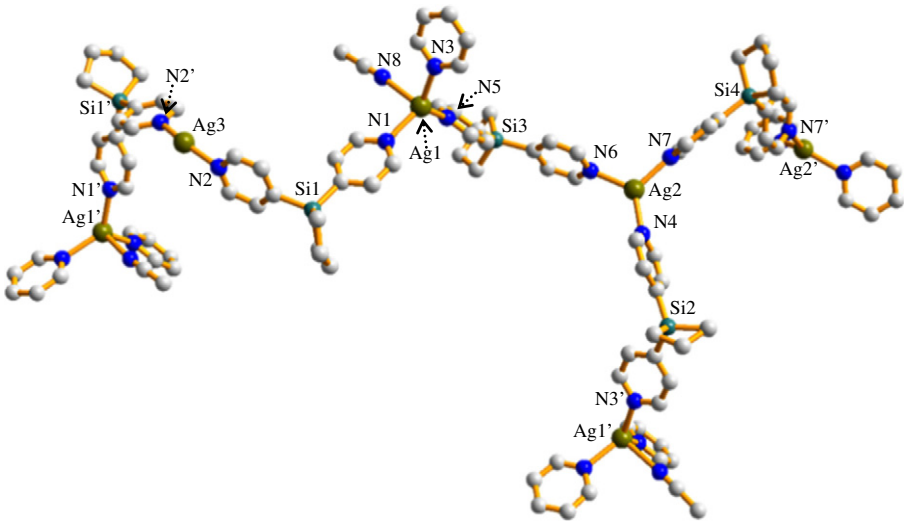

Fig. 1. An asymmetric unit including atom-labeling for **1**. The hydrogen atoms, anions, and solvate acetonitrile molecules were omitted for clarity.

As illustrated in Fig. 2, from the topological point of view, the combination of 3-connected Ag(1) and Ag(2) centers resulted in 3D network with a binodal 3,3-connected **ete** net topology (point symbol $(8^2{\cdot}10)_2$) [29]. This 3D network contains three kinds of helices with different chirality, which can be distinguished as small, medium, and large helices in a 2: 1: 1 ratio (Fig. 2(b)). The left-handed small helices consist of three

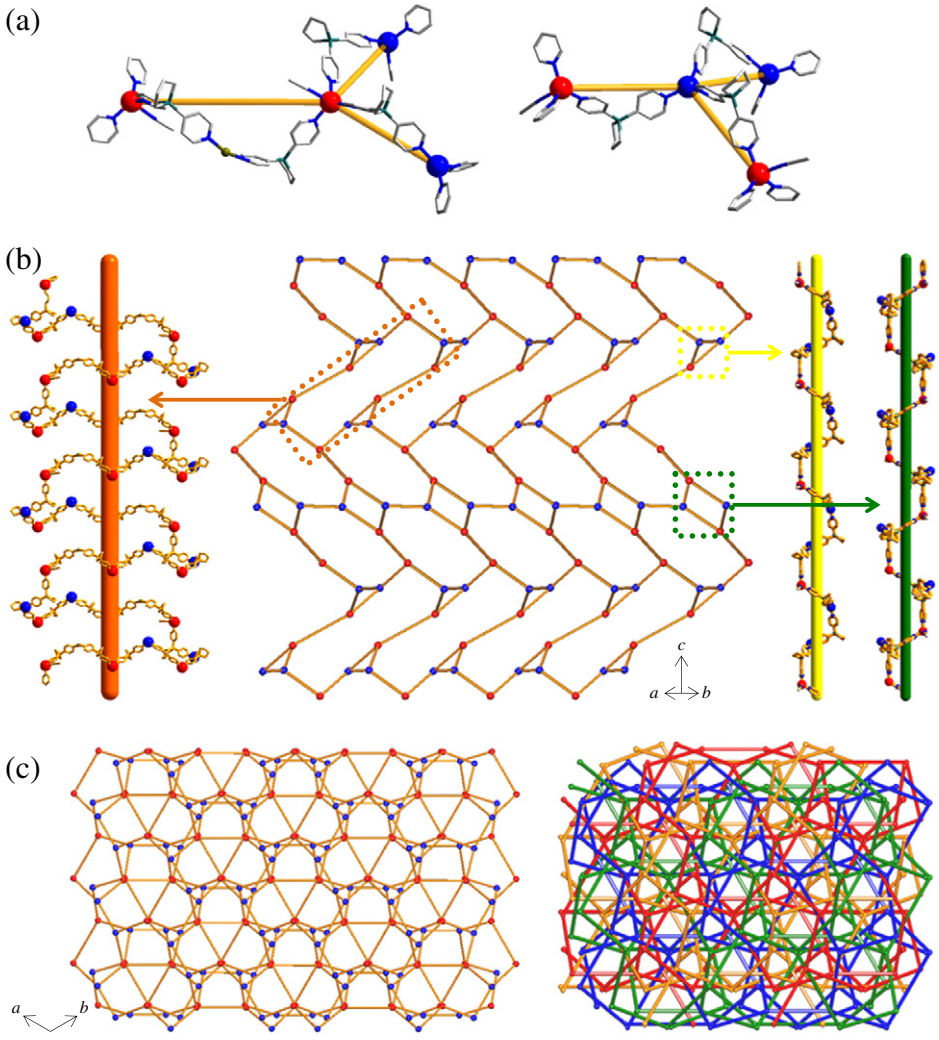

Fig. 2. Topological representation of **1**. (a) Wireframe diagrams of 3-connected silver(I) ions with schematic connectivity to centers of three neighboring silver(I) ions (red, Ag(1); blue, Ag(2)). (b) Side view of schematic drawings of one 3D **ete** net with the left- and right-handed helical chains. (c) Top views of one 3D substructure and 4-interpenetrating frameworks.