Formation of large confined spherical space with small aperture using flexible hexa-substituted sumanene

As represented by Metal Organic Frameworks (MOFs) and Covalent Organic Framework (COFs), network compounds having pores are of great interest due to their high potential as functional materials in, for example, selective molecular sorption, separation, and catalytic reaction. Additionally, discrete caged materials are also of interest due to the unusual regioselectivity of the reactions within and the ability to trap large molecules such as proteins. In view of these properties, aperture (or open window) size of the pores or the cages strongly influence their utilizations. Especially, the ones with small aperture work as the useful molecular hosts to embed functional guests such as polyoxometalates, which eventually serve Lewis acidic heterogeneous catalytic ability. In addition, such porous materials with confined space are promising to protect the interactive species to enable unimolecular-analysis.

Sumanene (**1**) is one of the representative curved-π conjugated molecules, which possesses a partial structure of fullerene C_{60} (Fig. 1(a)) [1]. Its three-dimensionally curved structure has attracted the interest of many researchers and is also a promising building block for the preparation of porous materials. However, so far curved-π conjugated molecules exclusively formed non-porous layered network structures rather than with spherical pores despite their curved skeletons. This is strongly due to their intrinsic nature to easily stack each other. Meanwhile, **1** is known to show the dynamic bowl inversion, which requires the structural flexibility [2]. In addition, further structural flexibility at the peripheral moiety of sumanene skeleton is afforded by hexa-substitution of **1**, which also brings high structural symmetry [3]. Such properties of hexa-substituted sumanene give rise to the expectation that they will also meet the criteria for the formation of confined space by proper introduction of metal coordination.

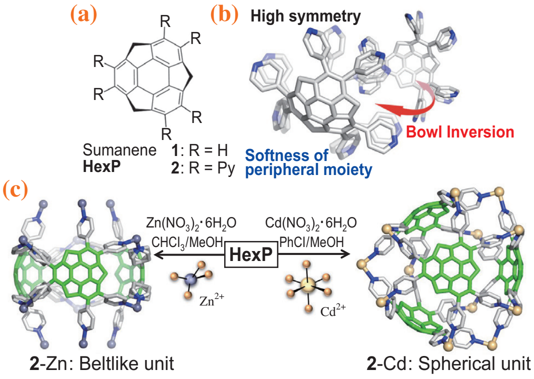

Fig. 1. **(a)** Molecular structures of sumanene **1** and **HexP 2**. **(b)** Structural features of hexa-substituted sumanene as the building block of spherical confined space. **(c)** Schematic models of the formation of **2**-Zn and **2**-Cd.

In this work, we show the preparation of porous coordination networks with effective use of the sumanene skeleton to form large confined space exclusively with small apertures (Fig. 1(b)) [4]. For the ligand, we used hexapyridylsumanene (**2**: **HexP**) having a γ-pyridyl group at the periphery of **1** [5]. The obtained network systems contained a belt-like trimer unit and a spherical tetramer unit, which beautifully reflected the curved structure of **1** skeleton, resulted in possessing large confined spaces with small open window.

Both of the single crystals of $[Zn_2\mathbf{2}Cl_2](NO_3^-)_n(solv)_m$ (**2**-Zn) and $[Cd_{1.5}\mathbf{2}(CH_3OH)(H_2O)_2](NO_3^-)_3(solv)_n$ (**2**-Cd) were prepared by layer diffusion method. X-ray diffraction data was obtained using SPring-8 **BL02B1** (for **2**-Zn) and **BL40XU** (for **2**-Cd). X-ray single crystal structure analysis revealed that **2**-Zn possessed a highly symmetrical packing pattern with a $P6_3/m$ space group reflecting the C_3 symmetric structure of **2**. All six pyridine moieties of the ligand **2** connected to Zn atoms having tetrahedral geometry with typical N-Zn^{2+} distances. The unique feature of this system is that large voids with the diameter of 10.3 Å, which can even hold C_{60}, were formed by the connection of three **HexP** moieties via total six Zn atoms forming the belt-like repeating units (Fig. 2(a)).

All Zn atoms had tetrahedral coordination geometry and the two bonds of the four were used for the formation of the belt-like repeating unit (Fig. 2(b)). The remaining two were used for the formation of Zn^{2+}-Cl bond and further connection among the belt-like units resulted in the three-dimensional network with the channels along the *c* axis, in which crystallin solvents and counter anions were severely disordered (Fig. 2(c)).

Meanwhile, highly symmetrical structure with $P4_2/n$ space group were confirmed for **2**-Cd crystal (Fig. 3). In the crystal structure, all six pyridine rings of **2** connected to Cd atom having octahedral geometry with typical N-Cd^{2+} distances. As a result of the combination of octahedral coordination environment of Cd^{2+} and the curved structure of **2**, the unique spherical repeating unit composed of four **HexP** ligands and 12 Cd atoms was formed instead of the belt-like unit found in **2**-Zn. The diameter of the spherical unit was 13.7 Å. The unit had two types of the open windows with different size of the apertures (Fig. 3(b), pink and light blue parts) and the inner space of the void was filled with severely disordered crystalline solvents as observed in **2**-Zn.

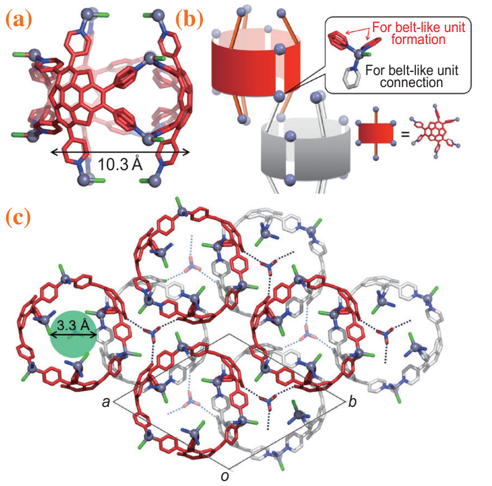

Fig. 2. **(a)** The belt-like trimer unit. **(b)** The schematic model of the connection mode between the two belt-like units in a unit cell viewed from the *a** axis. The red model is corresponding to the belt-like unit in figure (a). **(c)** the *c* axis projection of the packing pattern in **2**-Zn. The same colored units are in the same plane. Blue, N; pale blue, Zn; bright green, Cl. Hydrogen atoms and disordered molecules are omitted for clarity.

These apertures were covered by forming the packing structure to eventually construct 1D channel along the *c* axis with very small open window (2.1 Å×2.1 Å). This indicated that all the spherical units in the **2**-Cd network work as almost isolated spaces.

To Investigate the detailed structural information of **HexP** moiety in both of the networks, we focused on how the sumanene bowl structure changed and how the peripheral pyridine rings distorted (Fig. 4). In **2**-Zn, the sumanene bowl became deeper than the pristine one. On the other hand, sumanene bowl became shallower in **2**-Cd. In addition, the peripheral pyridine ring distortion in the networks were characteristic based on the packing structures. In **2**-Zn, two types of the tendencies were observed; the four pink-colored peripheral pyridine rings that contributed to the formation of the trimer unit distorted to the endo direction of the sumanene skeleton, while the remaining orange-colored peripheral pyridine rings involved in the formation of 1D channels went to the exo direction. Meanwhile, all the peripheral pyridine rings in **2**-Cd went to the exo direction of the sumanene bowl. These different structural parameters clearly indicated that **HexP** moiety in both of the porous networks provided high flexibility. Eventually, the central angles of the skeleton of **2** in **2**-Zn and **2**-Cd, which extends from the center of the hexagonal ring at the bottom of the sumanene skeleton to almost all the diagonal directions were nicely arranged to form 3D network structures with beautiful spherical components by coordinate both tetrahedral and octahedral metal ions (125.13°, 135.63° in **2**-Zn, 145.58°~149.26° in **2**-Cd).

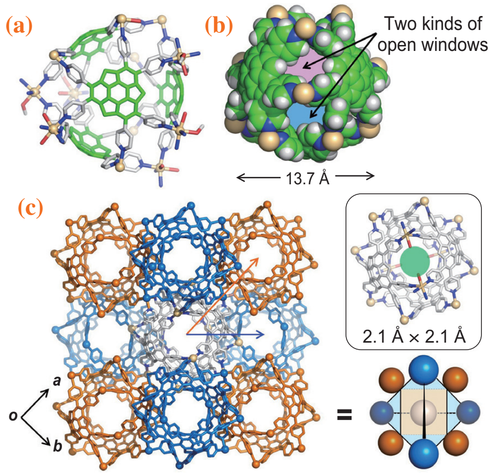

Fig. 3. **(a)** The spherical repeating unit. **(b)** Two types of open windows. Pink: surrounded by two Cd^{2+}s; Light blue: surrounded by three Cd^{2+}s. **(c)** The *c* axis projection of the packing structure in **2**-Cd. Marine blue and orange parts are corresponding to the same colored spheres in the inset model.

These network materials having large confined spaces with small apertures might be useful to isolate the reactive species, which may facilitate the investigation of the properties of single molecule or the control of the assembled properties such as magnetism.

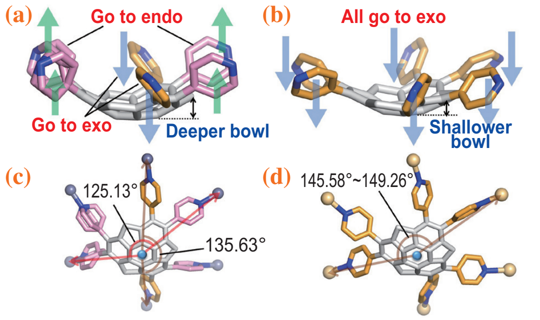

Fig. 4. **(a)** Peripheral distortion angles of the skeleton of **2** in **2**-Zn. **(b)** Peripheral distortion angles of the skeleton of **2** in **2**-Cd. **(c)** Central angles of the skeleton of **2** in **2**-Zn. **(d)** Central angles of the skeleton of **2** in **2**-Cd.

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