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Coordination and supramolecular assembly of $\{Cd_2Ge_8V_{12}O_{48}\}$ building block and Cucurbit[6] to form rotaxane-shaped hybrids

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Assembly of cucurbit[6] and $\{Cd_2Ge_8V_{12}O_{48}\}$ cluster produced two rotaxane-shaped and polyrotaxane-shaped solids by changing the ratio of starting precursors in the system. High oxygen density of polyoxoanion surface provides active sites to extend a single rotaxane-shaped hybrid 1 to a 1D polyrotaxane-shaped hybrid 2. This construction strategy may afford an entirely new methodology for polyoxometalate-based hybrid chemistry.

Supramolecular architectures and materials built by large subunits have attracted great interest because they not only open the way for obtaining a wide variety of fascinating structures but also have the potential applications in molecular separation, devices, sensors, catalysis, storage, and so on.[1] Cucurbit[n]urils (Q[n]s or CB[n]s),[2] which are a family of macrocyclic compounds features pumpkin-like shape with a characteristic rigid hydrophobic cavity of low polarity and two identical opening carbonyl fringed portals that have a wide range of applications in molecular recognition,[2b] catalysis,[2a] sensing,[3] drug delivery,[4] and can coordinate to alkali and alkali-earth metal cations,[5] have become a hot topic in supramolecular chemistry. Of particular interest, cucurbit[n]urils have now been considered as a new class of ideal building blocks in ration design of supramolecular hybrids.[6] Herein, it is interesting in the realm of designing and constructing rotaxane-shaped inorganic-organic hybrids using The flexible assembly of cucurbit[n]urils with other building blocks may provide a new way to construct novel structural hybrids.

Polyoxometalates (POMs), a wide class of metal oxide clusters generally featured as large molecular structures, have discrete and coordination-adjustable structures and potentially employed in redox catalysis, magnetism, photochemistry.[7] Importantly, they are used as outstanding nanoscale inorganic secondary building units (SBUs) for the design and construction of functional hybrid materials.[8] Therefore, POMs can form either supramolecular assemblies with organic or metal-organic moieties through weak interactions such as van der Waals and H-bonding interaction,[9] or coordination complexes with metal ions. Whereas, one straightforward yet challenging strategy would be the introduction of nanoscale inorganic-organic entities into coordination and supramolecular assemblies taking advantage of the SBU concept[10].

Confronted with this formidable challenge, we have made great efforts to construct nanoscale inorganic-organic complex by using simple, readily available building blocks-polyoxometalates. Although POMs are generally too large to be included by CB[n] molecules as normal guests, their interaction with the back of CB[n]s has drawn intensive attention. The first example of inorganic-organic hybrid complexes based on CB[n] and POMs has been reported by Kögerler *et al*., in which complementary CB[6]/CB[8] cucurbituril and $\{V_{18}\}$ iso-polyoxovanadate clusters are generated *via* supramolecular interactions.[11] Cao and coworkers, as well as other groups, prepared a series of hybrid complexes of CB[n]-POM, such as $(HO)_{10}CB[5]\text{-}\{PMo_{12}O_{40}\}^{3-}$, $(Me)_{10}CB[5]\text{-}\{V_{10}O_{28}\}^{6-}$, $CB[6]\text{-}\{SiW_{12}O_{40}\}^{4-}$, $(Me)_{10}CB[5]\text{-}\{Mo_8O_{26}\}^{4-}$, $(Me)_{10}CB[5]\text{-}\{SiW_{12}O_{40}\}^{4-}$, $(Me)_{10}CB[5]\text{-}\{H_2V_{10}O_{28}\}^{4-}$, $(Me)_{10}CB[5]\text{-}\{P_2W_{18}O_{62}\}^{6-}$ and $(Me)_{10}CB[5]\text{-}\{PMo_{12}O_{40}\}^{3-}$.[12] Since the hybrids are expected to display interesting physical and chemical properties that origin from the unique supramolecular structure. Among these hybrid complexes, co-assembly of $Me_{10}CB[5]$ and CB[6] with POMs show moderate photocatalytic activity for the degradation of dyes under visible light irradiation.[12a, 12b] Up to date, there have rarely been reports about cucurbituril interacting with POMs through coordination bonds to form supramolecular assemblies, so it is a fansicinating scientific study for supramolecular chemistry.

Herein, we report the assembly of CB[6] with POM anions under different conditions to form a single rotaxane-shaped inorganic-organic hybrid materials (compound **1**) and further an extended 1D polyrotaxane-shaped inorganic-organic hybrid solid (compound **2**) as illustrated in scheme 1. The composition of the compounds were evidenced by combination of X-ray single crystal data, TGA and elemental analysis: $\{[(Cd(en)_2)(Cden)_2Ge_8V_{12}O_{40}(OH)_8]_2[(Cden)_2en]CB[6]\}\cdot 20H_2O$(**1**) $\{[(Cden)_2Ge_8V_{12}O_{40}(OH)_8][(Cden)_2en]CB[6]\}\cdot 7H_2O$(**2**) (en=ethylenediamine). We believe that this work gave a hint for the assembly of a macrocycle and POM building blocks as well as a new way to build up a 1D polyrotaxane-shaped hybrid materials from a single rotaxane-shaped solid.

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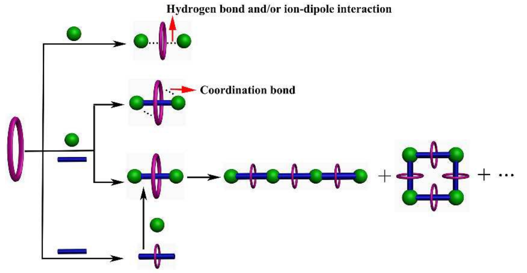

Scheme 1 A visual combinational library of POMs-cucurbituril frameworks. The ball in green represents the metal or POMs; the rod in blue represents the ligand; the loop in purple represents the cucurbituril.

Reddish brown crystals of **1** and **2** were readily synthesized by one-pot synthesis of NH_4VO_3, GeO_2, $CdCl_2 \cdot 2.5H_2O$, H_3BO_3 and CB[6] in ethylenediamine(en) aqueous solution at 170 °C for 4 days. When we did not add CB[6] in solution, a 3D polymer of POM will form, having the en ligand as a linker, which had been previously reported by Yang and co-workers[6g]. The as-synthesized crystals were characterized by elemental analysis, IR spectroscopy, powder X-ray diffraction (PXRD) and thermogravimetric analysis (TGA) (see ESI †for details). The experimental PXRD patterns of **1** and **2** are in good agreement with the simulated PXRD patterns from the single-crystal X-ray diffraction, which indicates the phase purity of the synthesized samples (Figure. S1 and S2). Thermogravimetric analyses were performed in air to investigate stability of compounds (Figure S4 and S5). The TGA curves of 1 and 2 show a three-step weight loss with the overall weight loss of 30.29% and 37.35% between 30 and 720 °C, respectively, which can be attributed to the loss of water molecules, en ligands and CB[6] ligands (cal. 29.44% and 37.05%). The experimental values match well with the calculated values.

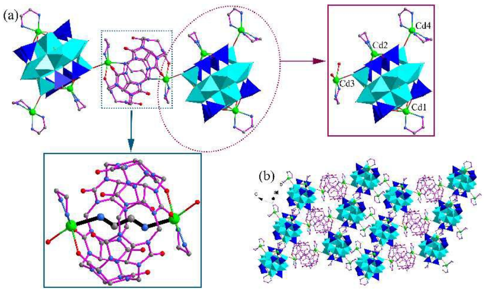

Fig. 1 (a) The assembly of CB[6] and capped polyoxoanion $\{Cd_2Ge_8V_{12}O_{48}\}$ leads to compound **1;** (b) The packing diagram of 2D supramolecular matrix of compound **1**. Color codes: C, gray; N, pink; O, red; V, turquiose; Ge, blue; Cd, green, (c) Topological alignments between inorganic aggregates and organic macrocycles.

Single-crystal X-ray diffraction analysis reveals that compound **1** crystallizes in the triclinic space group $P\bar{1}$ and features a single rotaxane-shaped unit, which is built by $\{Cd_2Ge_8V_{12}O_{48}\}$ clusters, and $[(Cden)_2en]$CB[6] component (Fig. 1). The rotaxane-shaped unit is end-capped by two $\{Cd_2Ge_8V_{12}O_{48}\}$ clusters with an en molecule threading through the CB[6] ring and each $Cd_2Ge_8V_{12}$ is further decorated by one $[Cd(en)_2]^{2+}$ units to generate a unique cluster. The terminal oxygen O29 from the V=O is bound to a Cd ion, with the Cd3-O29 distance being 2.432(8) Å. The Cd3 ion is coordinated to one en molecule *via* Cd-N bonds, two oxygen atoms of the carbonyl groups from a CB[6] ring and half of the en molecule threading through the CB[6]. Four unique Cd sites display three different coordination environments: N-Cd(1,2)-O trigonal prisms, O-Cd(3)-N trigonal prisms and O-Cd(4)-N square pyramids. The Cd center with a trigonal prism is composed of two N atoms of one en ligand and four bridging O atoms of two adjacent VO_5 groups, while the Cd center with a square pyramid is defined by four N atoms of two en ligands with the distances of Cd-N varying from 2.271(1) to 2.384(9) Å and one O atom from the VO_5 group with Cd-O distance being 2.432(8) Å. All V centers have a distorted VO_5 square-pyramidal environment with the V-O distances ranging from 1.577(7) to 2.018(6) Å and the V-V distances range from 2.793(3) to 3.038(2) Å. In the Ge_2O_7 units, the Ge-O distances vary from 1.708(7) to 1.782(7) Å. Two en molecules employ two different coordination models: one en molecule chelates with the Cd3 ion; while the other coordinates to Cd3 ion with one N atom. The latter one plays an important role with the en molecule threading through CB[6], the other N atom is coordinated to another Cd3 ion and Cd3 ion is connecting with the terminal oxygen O29 from $\{Cd_2Ge_8V_{12}O_{48}\}$ cluster to construct the rotaxane-shaped solid structure.

We suppose that high density of oxygen surface might provide active sites to connect with additional $[(Cden)_2en]$CB[6] units so that 1D polyrotaxane-shaped solid could be built. In the synthesis of compounds, we tried to construct different dimensional rotaxane-shaped solid structures, however, the Cd4 ion was fully occupied by en molecules, while ratio of en to the Cd ion is 556:1, and so we reduced the amount of the en solution to adjust the coordination model of the Cd ion, while ratio of en to the Cd ion is 546:1. Luckily, a 1D polyrotaxane-shaped solid (compound **2**) was successfully synthesized. This molecule crystallizes in the monoclinic space group $C2/c$ and features a one-dimensional chain structure (Fig. 2). The coordination mode between Cd3 ions and POM anions plays an important role in forming 1D polyrotaxane-shaped solid. The high oxygen density on the surface of POMs provides active sites for Cd cations to extend the framework. This one-dimensional zigzag chain is formed by $\{Cd_2Ge_8V_{12}O_{48}\}$ clusters, $Cd3^{3+}$ ions, en and CB[6] ligands. The oxygen O22 from the $\{Cd_2Ge_8V_{12}O_{48}\}$ cluster is connecting with the $Cd3^{2+}$ ion, while $Cd3^{2+}$ ion is coordinated to two en molecules and two oxygen atoms of the carbonyl groups from CB[6]. One en molecule threaded through CB[6] and two terminal N atoms are linked to two different $Cd3^{3+}$ ions. Then, the $Cd3^{3+}$ ions bind with O atoms from a $\{Cd_2Ge_8V_{12}O_{48}\}$ cluster to build one-dimensional polyrotaxane-shaped solid chains.

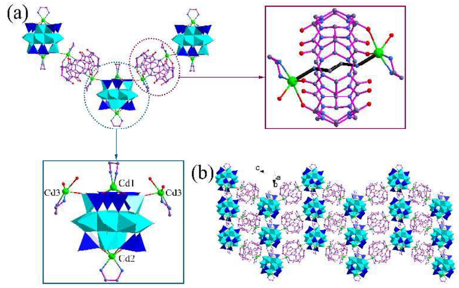

Fig. 2 (a) The assembly of CB[6] and polyoxoanion $\{Cd_2Ge_8V_{12}O_{48}\}$ leads to compound **2** and the connection between basic building blocks in compound **2**; (b) The infinite 1D chains formed a 2D supramolecular network. Color codes: C, gray; N, pink; O, red; V, turquiose; Ge, blue; Cd, green, (c) Topological alignments between inorganic aggregates and organic macrocycles.

The variable-temperature magnetic susceptibility for **1** and **2** have been measured in the range of 2-300K in an applied field of 1 k Oe (Fig.3 and Fig.4). The x_MT for **1** is 3.38 $cm^{-3}mol^{-1}$ K at room temperature, which is lower than the theoretical value of 4.5 cm^{-3} mol^{-1} K for 12 noninteracting V (S=1/2) cations considering g=2. The x_MT for **2** is 4.98 $cm^{-3}mol^{-1}K$ at room temperature, which is higher than the theoretical value. When the temperature cools down, the x_MT value decreases gradually to reach a value of 1.424 $cm^{-3}mol^{-1}K$ for **1** and 1.566 cm^{-3} mol^{-1} K for **2** at 30 K and declines rapidly to reach a minimum of 0.38 $cm^{-3}mol^{-1}K$ for **1** and 0.16 $cm^{-3}mol^{-1}K$ for **2** at 2K, respectively. The decrease of x_MT upon cooling is the signature of an antiferromagnetic exchange coupling between the V^{IV} through oxygen bridges. The x_M^{-1} versus T is in correspondence with Curie-Weiss law in the range of 150-300 K with C=6.78 $cm^{-3}\cdot mol^{-1}\cdot K$ and θ=-309.50 K for **1**, and C=12.87 $cm^{-3}\cdot mol^{-1}\cdot K$ and θ=-482.88 K for **2**, respectively, which further indicate the antiferromagnetic couplings.

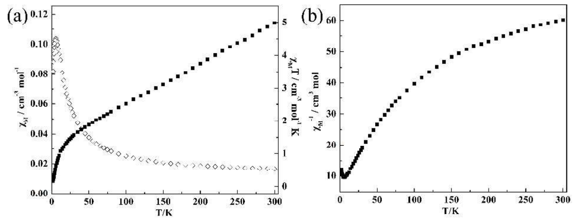

Fig. 3 (a)Plot of x_M and x_MT versus T for compounds **1** between 2 and 300K in an applied field of 5 k Oe. (b) Plot of x_M^{-1} versus T for **1**.

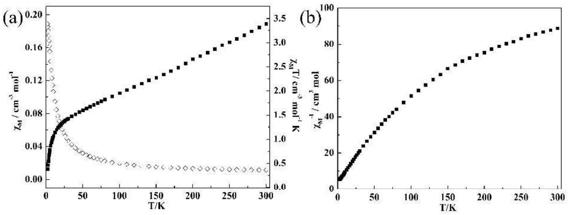

Fig. 4 (a)Plot of x_M and x_MT versus T for compounds **2** between 2 and 300K in an applied field of 5 k Oe. (b) Plot of x_M^{-1} versus T for **2**.

In summary, we have successfully constructed a single rotaxane-shaped solid and a 1D polyrotaxane-shaped solid, employing CB[n], Cd^{2+} and $\{Cd_2Ge_8V_{12}O_{48}\}$ polyoxoanions. It is the first time to realize the construction of POM-based 1D polyrotaxane-shaped solid based on a single rotaxane-shaped solid . The high oxygen density of POM surfaces provides active sites to extend a single rotaxane-shaped solid to a 1D polyrotaxane-shaped solid. The magnetism of the two compounds was investigated due to the existence of V^{IV} clusters and they both exhibited antiferromagnetic phenomenon. This method offers a new way to construct multifunctional rotaxane-shaped solids as well as 1D polyrotaxane-shaped solids and enrich the family of POM-based inorganic-organic hybrids. Work is in progress to further adjust the magnetism of these CB[n]-POM *via* external stimuli and study other hybrids between CB[n] and POMs.

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Notes and references

†Electronic supplementary information (ESI) available: Details of measurements, experimental and theoretical calculated details, additional structural figure and characterization data.

1 (a) C. J. Brown, F. D. Toste, R. G. Bergman and K. N. Raymond, *Chem. Rev.*, 2015, **115**, 3012-3015; (b) M. R. Hansen, R. Graf and H. W. Spiess, *Chem. Rev.*, 2016, **116**, 1272-1308; (c) F. Huang and E. V. Anslyn, *Chem. Rev.*, 2015, **115**, 6999-7000; (d) L. Yang, X. Tan, Z. Wang and X. Zhang, *Chem. Rev.*, 2015, 115, 7196-7239; (e) M. T. Albelda, J. C. Frias, E. Garcia-Espana and H. J. Schneider, *Chem. Soc. Rev.*, 2012, **41**, 3859-3877; (f) L. Cera and C. A. Schalley, *Chem. Soc. Rev.*, 2014, **43**, 1800-1812. (g) H. Yang, B. Yuan X. Zhang and O. A. Scherman, *Acc. Chem. Res.*, 2014, **47**, 2106-2115. (h) P. F. Wei, X. Z. Yan and F. H. Huang, *Chem. Soc. Rev.*, 2015, **44**, 815-832. (i) Z. F. He, W. Jiang and C. A. Schalley, *Chem. Soc. Rev.*, 2015, **44**, 779-789.

2 (a) K. I. Assaf and W. M. Nau, *Chem. Soc. Rev.*, 2015, **44**, 394-418; (b) L. Isaacs, *Acc. Chem. Res.*, 2014, **47**, 2052-2062; (c) J. Kim, I. S. Jung, S. Y. Kim, E. Lee, J. K. Kang, S. Sakamoto, K. Yamaguchi and K. Kim, *J. Am. Chem. Soc.*, 2000, **122**, 540-541. (d) A. E. Kaifer, *Acc. Chem. Res.*, 2014, **47**, 2160-2167.

3 G. Ghale, V. Ramalingam, A. R. Urbach and W. M. Nau, *J. Am. Chem. Soc.*, 2011, **133**, 7528-7535.

4 G. Hettiarachchi, D. Nguyen, J. Wu, D. Lucas, D. Ma, L. Isaacs and V. Briken, *PloS one,* 2010, **5**, No. e10514.

5 (a) J. Lü, J.-X.Lin, M.-N. Cao and R. Cao, *Coord. Chem. Rev.*, 2013, **257**, 1334-1356. (b) X. L. Ni, X. Xiao, H. Cong, Q. J. Zhu, S. F. Xue and Z. Tao, *Acc. Chem. Res.*, 2014, **47**, 1386-1395.

6 (a) J. W. Lee, S. Samal, N. Selvapalam, H. J. Kim, *Acc. Chem. Res.*, 2013, **36**, 621-630. (b) K. Kim, *Chem. Soc. Rev.*, 2002, **31**, 96-107. (c) X. L. Ni, X. Xiao, H. Cong, L. L. Liang, K. Cheng, X. J. Cheng, N. N. Ji, Q. J. Zhu, S. F. Xue and Z. Tao, *Chem. Soc. Rev.*, 2013, **42**, 9480-9508.

7 (a) A. Dolbecq, E. Dumas, C. d. R. Mayer and P. Mialane, *Chem. Rev.*, 2010, **110**, 6009-6048; (b) X. Fang, L. Hansen, F. Haso, P. Yin, A. Pandey, L. Engelhardt, I. Slowing, T. Li, T. Liu, M. Luban and D. C. Johnston, *Angew. Chem., Int. Ed.*, 2013, **52**, 10500-10504; (c) T. Liu, M. L. Langston, D. Li, J. M. Pigga, C. Pichon, A. M. Todea and A. Muller, *Science*, 2011, **331**, 1590-1592; (d) M. D. Symes and L. Cronin, *Nat. chem.*, 2013, **5**, 403-409; (e) S. S. Wang and G. Y. Yang, *Chem. Rev.*, 2015, **115**, 4893-4962; (f) T. Yamase, *Chem. Rev.*, 1998, **98**, 307-326; (g) J. Zhou, J. W. Zhao, Q. Wei, J. Zhang and G. Y. Yang, *J. Am. Chem. Soc.*, 2014, **136**, 5065-5071; (f) J. Zhou, J. Zhang, W. H. Fang and G. Y. Yang, *Chem. - Eur. J.* 2010, **16**, 13253-13261.

8 S. Taleghani, M. Mirzaei, H. Eshtiagh-Hosseini and A. Frontera, *Coord. Chem. Rev.*, 2016, **309**, 84-106.

9 D. Gatteshi, A. Ganeschi, L. Pardi and R. Sessoli, *Science*, 1994, **265**, 1054.

10 (a) N. C. Kasuga, M. Umeda, H. Kidokoro, K. Ueda, K. Hattori and K. Yamaguchi, *Cryst. Growth Des.*, 2009, **9**, 1494-1498; (b) X. L. Ni, X. Xiao, H. Cong, Q. J. Zhu, S. F. Xue and Z. Tao, *Acc. Chem. Res.*, 2014, **47**, 1386-1395; (c) Y. Xu, Y. Gao, W. Wei, Z. Wang, S. Li and C. Hu, *Dalton Trans.*, 2013, **42**, 5228-5231; (d) C. Aronica, G. Chastanet, E. Zueva, S. A. Borshch, J. M. Clemente-Juan and D. Luneau, *J. Am. Chem. Soc.*, 2008, **130**, 2365-2371.

11 X. Fang, P. Kögerler, L. Isaacs, S. Uchida and N. Mizuno, *J. Am. Chem. Soc.*, 2009, **131**, 432-433.

12 (a) M. Cao, J. Lin, J. Lü, Y. You, T. Liu and R. Cao, *J. Hazard. Mater.*, 2011, **186**, 948-951; (b) J. Lü, J. X. Lin, X. L. Zhao and R. Cao, *Chem. Commun.*, 2012, **48**, 669-671; (c) B. X. Han, C. Z. Wang, K. Chen, X. Xiao, Z. Tao, S. F. Xue, Y. Q. Zhang and Q. J. Zhu, *CrystEngComm*, 2014, **16**, 1615-1619; (d) B. X. Han, C. Z. Wang, Y. Zhao, K. Chen, Q. J. Zhu, S. F. Xue, Y. Q. Zhang and Z. Tao, *Eur. J. Inorg. Chem.*, 2014, **2014**, 831-835; (e) J. Lin, J. Lü, M. Cao and R. Cao, *Cryst. Growth Des.*, 2011, **11**, 778-783. (f) J. X. Lin, J. Lü, R. Cao, J. T. Chen and C.Y. Su, *Dalton Trans.*, 2009, 1101-1103; (g) J. X. Lin, J. Lü, H. X. Yang and R. Cao, *Cryst. Growth Des.*, 2010, **10**, 1966-1970; (h) L. W. Han, J. X. Lin, J. Lü and R. Cao, *Dalton Trans.*, 2012, **41**, 10080-10084; (i) N. C. Kasuga, M. Umeda, H. Kidokoro, K. Ueda, K. Hattori and K. Yamaguchi, *Cryst. Growth Des.*, 2009, **9**, 1494-1498; (j) D. G. Samsonenko, O. A. Gerasko, A. V. Virovets and V. P. Fedin, *Izv. Akad. Nauk. Ser. Khim.*, 2005, **7**, 1513-1517.