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Construction of molecular rectangles with titanium–oxo clusters and rigid aromatic carboxylate ligands†

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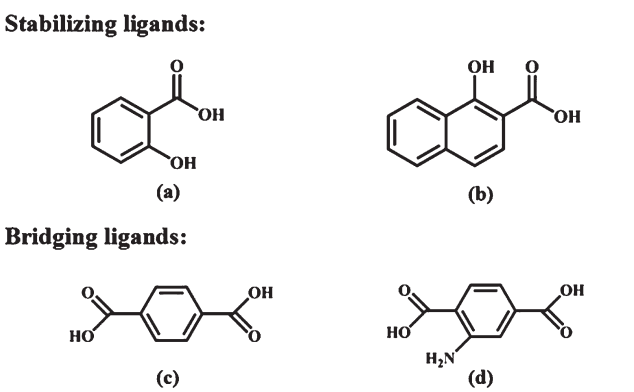
Four rectangular molecular architectures have been successfully constructed using $\{Ti_5O_7\}$ clusters as inorganic vertical edges and bridging aromatic carboxylates as horizontal edges. The introduced organic ligands show a strong influence on the light absorption behaviors of the obtained hybrid complexes.

Regular-shape coordination complexes are an important class of advanced molecular materials because of their numerous and diverse applications in probes,[1] host–guest chemistry,[2] catalysis,[3,4] molecular devices,[5,6] and photocatalysis.[7] The fabrication of various nanoscale molecular architectures such as triangles, squares, pentagons, hexagons, cages, and boxes has been well reported so far.[8–11] But the structures of molecular rectangles are relatively difficult to assemble and very few reports are known to date.[12] Stang and co-workers successfully synthesized a nanoscopic molecular rectangle by the self-assembly of a pre-designed Pt-based molecular clip and symmetrical dipyridyl ligands.[13] Furthermore, it still remains a challenge to prepare polymetallic components containing molecular rectangles.

As an important raw material, titanium dioxide (TiO_2) has found wide application in pigments, sunscreens and toothpaste[14,15] and has also shown great potential in the global renewable energy arena with regard to environmental and solar energy applications.[16–18] Along this line, polyoxo–titanium clusters (PTCs) have been attracting much research attention in recent years, because they possess well-defined structures and can be used as reactivity model compounds of TiO_2 nanoparticles.[19–25]

Another major advantage of PTCs is that they can be easily functionalized by organic ligands.[26] In the course of our research on titanium–oxo clusters, recently, we successfully applied a variety of bridging ligands to organize the 0D $\{Ti_6\}$ clusters[27,28] into 1D, 2D, and 3D materials with polynuclear copper halides.[29] Furthermore, we also prepared some molecular cluster series with metal–oxo subunits and bridging organic ligands.[30] But there are not yet any reports on the crystal structures of PTCs with rectangle shaped architectures.

In this work, we report four polyoxo–titanium molecular clusters, namely $Ti_{10}(\mu_2\text{-}O)_2(\mu_3\text{-}O)_2(\mu_2\text{-}O^iPr)_6(sac)_4$ $(bdc)_2(O^iPr)_{14}$ (**PTC-121**; H_2sac = salicylic acid; H_2bdc = terephthalic acid; HO^iPr = isopropanol), $Ti_{10}(\mu_2\text{-}O)_2(\mu_3\text{-}O)_2(\mu_2\text{-}O^iPr)_6(sac)_4(2\text{-}NH_2\text{-}bdc)_2(O^iPr)_{14}$ (**PTC-122**; 2-NH_2-H_2bdc = 2-aminoterephthalic acid), $Ti_{10}(\mu_2\text{-}O)_2(\mu_3\text{-}O)_2(\mu_2\text{-}O^iPr)_6(npc)_4$ $(bdc)_2(O^iPr)_{14}$ (**PTC-123**; H_2npc = 1-hydroxy-2-naphthoic acid), $Ti_{10}(\mu_2\text{-}O)_2(\mu_3\text{-}O)_2(\mu_2\text{-}O^iPr)_6(npc)_4(2\text{-}NH_2\text{-}bdc)_2(O^iPr)_{14}$ (**PTC-124**) with such kinds of rectangle shaped architectures. Salicylic acid and 1-hydroxy-2-naphthoic acid (Scheme 1a and b) were chosen as stabilizing ligands and terephthalic acid and 2-aminoterephthalic acid were employed as bridging ligands (Scheme 1c and d) to form these new molecular clusters. The crystal structure arrange-



Scheme 1 Illustration of the applied stabilizing and bridging ligands: (a) salicylic acid (H_2sac); (b) 1-hydroxy-2-naphthoic acid (H_2npc); (c) terephthalic acid (H_2bdc); (d) 2-amino terephthalic acid (2-NH_2-H_2bdc).

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†Electronic supplementary information (ESI) available: Materials, synthesis, physical measurements and Cif files. CCDC 1572540 (**PTC-121**), 1572541 (**PTC-122**), 1572542 (**PTC-123**), and 1572543 (**PTC-124**). For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c7dt03470a

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ments of metal–oxo building units and their bonding patterns with different ligands are discussed in brief. To the best of our knowledge, these are the first example of PTCs with crystal structures having rectangle like architectures. Moreover, the light absorption behaviors of these four molecular clusters are well investigated and the influence of organic ligands is explained in detail.

Through the solvothermal reaction of salicylic acid, terephthalic acid and $Ti(O^iPr)_4$ in isopropanol at 80 °C for three days, colorless crystals of **PTC-121** were obtained with a high yield. **PTC-122** to **PTC-124** are also synthesized under similar reaction conditions by changing the combinations of bridging and stabilizing ligands (experimental details in the ESI†). All of these reactions produced four pairwise isomorphic structural analogues that can be categorized into two pairs (**PTC-121** & **PTC-122**: Pair-I; **PTC-123** & **PTC-124**: Pair-II) of molecular clusters. X-ray crystallography analysis reveals that **PTC-121** and **PTC-122** are crystallized in the monoclinic $P2_1/c$ space group, while **PTC-123** and **PTC-124** are crystallized in trigonal $R\bar{3}$ space group. In all four compounds, a common metal–oxo building unit (Ti_3) is observed that has been reported earlier in many molecular clusters (Fig. 1a and 2a).[26] As shown in Fig. 1a, the trinuclear unit is formed by the combination of three titanium atoms and one μ_3-O atom, one μ_2-O atom and one μ_2-O^{i}Pr atom. Each of these three titaniums is further terminally bonded with one isopropanol group. These trinuclear units are extended on both sides with additional titaniums to form a pentanuclear moiety. The additional titanium atoms are attached through the stabilizing ligands and μ_2-O^{i}Pr atoms. All the titaniums in this building unit are six coordinated, exhibiting slightly distorted octahedral coordination geometries. The Ti–O distances are in the range from 1.751(3) to 2.208(3) Å and are all in reasonable ranges (Table S2†). The flipping of combinations of stabilizing ligands produced two types of pentanuclear moieties with decorated H_2sac and H_2npc ligands at their corners, respectively. Furthermore, the bridging ligands are attached on the upper and lower parts of these pentanuclear moieties by bonding each carboxylic acid to two titanium atoms. Two such kinds of bridging ligands are involved in bonding to form the decanuclear molecular clusters with four stabilizing ligands in total (Fig. 1b). Similar kinds of structural arrangements are observed in all the four molecular clusters synthesized in this work.

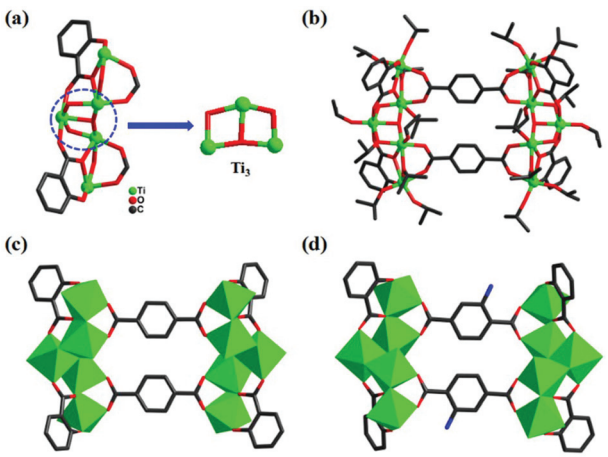


Fig. 1 The sac-{Ti_5} unit in **PTC-121** (a) and molecular structures of **PTC-121** (b, c) and **PTC-122** (d).

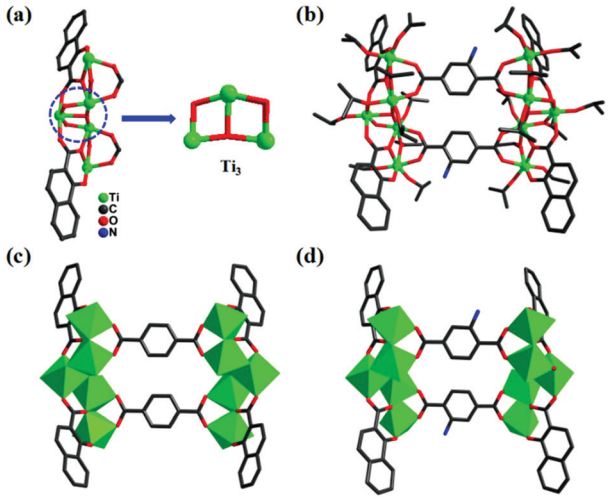


Fig. 2 The npc-{Ti_5} unit in **PTC-124** (a) and molecular structures of **PTC-124** (b, d) and **PTC-123** (c).

To easily understand the rectangular shapes of these molecular clusters, the pentanuclear building units decorated with stabilizing ligands are regarded as vertical edges and the bridging ligands as horizontal edges (Fig. 1c). When the horizontal bridging bdc ligand was replaced by 2-NH_2-bdc, **PTC-122** was prepared (Fig. 1d), which also has similar bonding and coordination arrangements as **PTC-121**. Interestingly, through the substitution of the stabilizing sac ligands by npc, the second pair of molecular clusters (**PTC-123** and **PTC-124**) are obtained with bdc and NH_2-bdc, respectively (Fig. 2c and d).

According to the above results, a novel and efficient synthetic strategy is employed to assemble the {Ti_5} subunits with a series of different functional ligands to form four related molecular clusters with rectangular shapes. The structural characteristics of the {Ti_5} units might be advantageous for accessing all functional Ti^{4+} sites for different applications. It is also important to mention that the stabilizing ligands (sac and npc) have two functional groups at neighboring positions and will assist the easy formation of pre-nucleation clusters in the reaction solutions. Such an effective cluster formation could enhance the chances of constructing symmetrical structures. Additionally, the bridging ligands (bdc and 2-NH_2-bdc) have their coordinating groups at symmetrical positions to assist the bonding of two subunits on both sides of the rectangle. The successful synthesis of these molecular clusters with rectangle like architectures has proved that employing both asymmetrical and symmetrical ligands in a single pot reaction can form highly symmetrical crystal structures.

Diffuse reflectance spectroscopic measurements were carried out on four compounds to understand their optical

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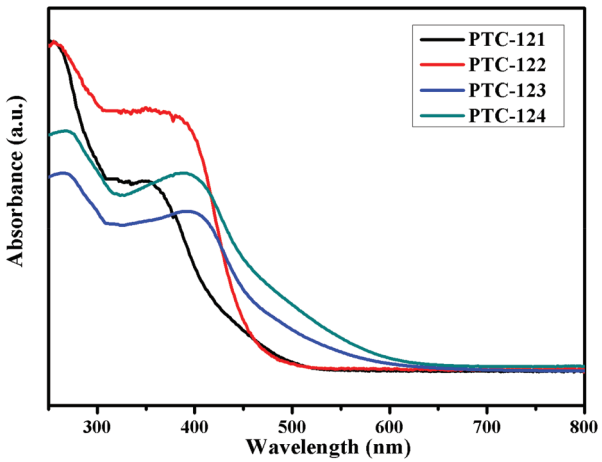


Fig. 3 The solid-state UV-vis absorption spectra of **PTC-121** to **PTC-124**.

absorption properties (Fig. 3). The optical bandgaps calculated for **PTC-121** to **PTC-124** were 2.84 eV, 2.71 eV, 2.55 eV, and 2.43 eV, respectively. It is interesting to find that the higher wavelength absorption (300–450 nm) by **PTC-122** is much stronger than that for **PTC-121**. The same tendency is also observed between **PTC-124** and **PTC-123**. This is believed to be due to the additional $-NH_2$ group in the bridging 2-NH_2-bdc ligand for **PTC-122** and **PTC-124**.[31] It is also interesting to learn that there is a big bandgap reduction of 0.29 eV between **PTC-121** and **PTC-123** with the same bridging bdc ligands. Similarly, the reduction between **PTC-122** and **PTC-124** is 0.28 eV. Such bandgap reduction might be attributed to the naphthalene group in **PTC-123** and **PTC-124**. Due to the presence of both naphthalene in the stabilizing ligands and $-NH_2$ group in the bridging ligands, the largest bandgap reduction between **PTC-121** and **PTC-124** is found to be 0.41 eV.

In summary, two pairs of molecular rectangles containing similar inorganic Ti–O building units and rigid organic ligands have been successfully synthesized. By the crossed combination of two pairs of stabilizing and bridging ligands, the $\{Ti_5\}$ subunits can be readily formed and linked into rectangular structures. Moreover, these molecular clusters display diverse ligand dependent light absorption characteristics. Our results provide an intriguing and effective concept of using titanium–oxo clusters as building blocks for the construction of beautiful rectangular architectures.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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