Cluster Chemistry

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Bandgap Engineering of Titanium–Oxo Clusters: Labile Surface Sites Used for Ligand Substitution and Metal Incorporation

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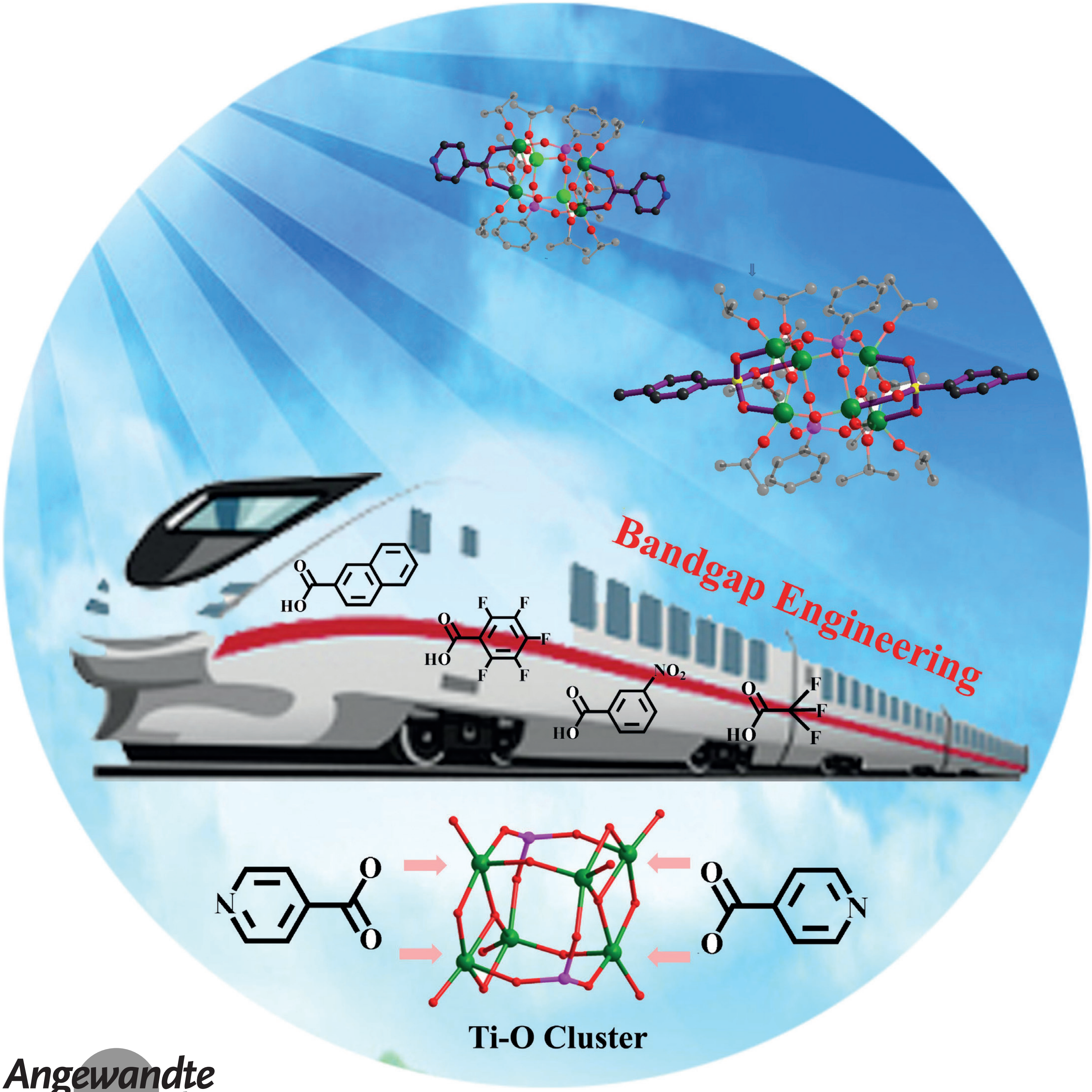

Abstract: *Through the labile coordination sites of a robust phosphonate-stabilized titanium–oxo cluster, 14 O-donor ligands have been successfully introduced without changing the cluster core. The increasing electron-withdrawing effect of the organic species allows the gradual reduction of the bandgaps of the {Ti_6} complexes. Transition-metal ions are then incorporated by the use of bifunctional O/N-donor ligands, organizing these {Ti_6} clusters into polymeric structures. The coordination environments of the applied metal ions show significant influence on their visible-light adsorption. Both the above structural functionalizations also tune the photocatalytic H_2 production activities of these clusters. This work provides a systematic bandgap engineering study of titanium–oxo clusters, which is important not only for their future photocatalytic applications, also for the better understanding of the structure–property relationships.*

Titanium dioxide (TiO_2) has been a technologically important and widely used photocatalyst for solar energy conversion and degradation of environmental pollutants.[1–3] However, most of the applications of TiO_2 have been limited to the UV-light range (< 5 % of the solar spectrum) because of its large bandgap. Lots of effective approaches have been developed to modify the electronic band structure of TiO_2 and to improve its photocatalytic performances, such as metal/nonmetal doping, dye sensitization, crystal structure, and morphology modification.[4–10] As the structure and reactivity model compounds of bulk nanoscale TiO_2, titanium–oxo clusters (TOCs) have recently attracted many research interests.[11–18] Moreover, TOCs are usually crystalline materials and can provide precise structural information by X-ray diffraction studies which are necessary to do theoretical calculations.[19] Therefore, investigation on the bandgap engineering of TOCs will not only be beneficial for their photocatalytic behavior, but also can help to elucidate the mechanisms of TiO_2 modification.[20,21]

Although many TOCs with various structure types have been reported, the systemic studies on regulating their bandgaps are still very rare. Few examples are reported by Wright and Coppens which mainly focus on the influence of binding models of ligands and doping of metal ions, respectively.[19,21–23] However, most of these studies are carried out on TOCs with different nuclearities, except for the investigation on metal–halogen doping of a series of {Ti_{11}} clusters.[24] It still remains a great challenge to investigate how the bandgap of a confirmed TOC can be tuned without changing its Ti−O core structure. To realize this research idea, a robust TOC is necessary but not sufficient. Surface activity that can allow ligand exchange and metal incorporation is another key point to conduct such bandgap engineering study.

Based on our former research on polymetallic manganese complexes, organophosphonate-bridging clusters often present labile coordination sites in their outer faces.[25,26] So phosphonate-stabilized titanium clusters (PTC) can have the potential to do ligand substitution and then serve as proper candidates for bandgap adjustment investigation. Schubert has recently reported a stable {Ti_6} cluster core, [Ti_6O_4-($OiPr)_{10}(O_3PR)_2(OAc)_2$] (OAc = acetate), that can be formed with different bridging phosphonate ligands.[27] By carefully analyzing the structure of this {Ti_6} cluster core, we find that it does present 3 × 2 = 6 labile coordination sites from its two {$Ti_3(\mu_3\text{-}O)$} outer faces (Figure 1). Therefore, we decide to use this {Ti_6} cluster as a platform to investigate the bandgap modulations of TOCs. 14 O-donor ligands, including carboxylates, phosphonates, and sulfonates, have been successfully introduced to the active coordination sites of the {Ti_6} cluster core (Figure 2 a). Solid-state diffuse reflectance spectra studies indicate that high electron-withdrawing organic species can significantly reduce the bandgaps of these {Ti_6} complexes. Interestingly, when bifunctional O/N ligands are applied, transition-metal ions can be incorporated and further organize the {Ti_6} clusters into extended structures, efficiently increasing the adsorptions in the visible-light range. Moreover, the photocatalytic water-splitting hydrogen-evolution activities of these complexes are investigated, which are also influenced by the ligands substitution and metal incorporation.

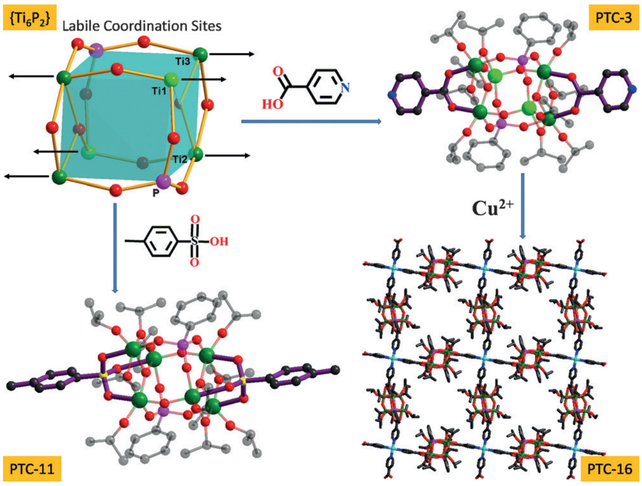

Figure 1. Illustration of the structural evolution (ligand substitution and metal incorporation) of the {Ti_6P_2} cluster core, through the labile coordination sites. The five-coordinated Ti1 atoms are highlighted in light-green color.

The solvothermal reaction between $Ti(OiPr)_4$, phenolphosphonate and acetate in isopropyl alcohol produces large, colorless crystals of [$Ti_6O_4(OiPr)_{10}(O_3P\text{-}Phen)_2(OAc)_2$] (**PTC-1**) in good yields. Single-crystal X-ray analysis reveals that **PTC-1** has similar core structure as those {Ti_6} clusters reported by Schubert, except that phenolphosphonate is firstly applied to stabilize this {Ti_6} complex. The {Ti_6} core

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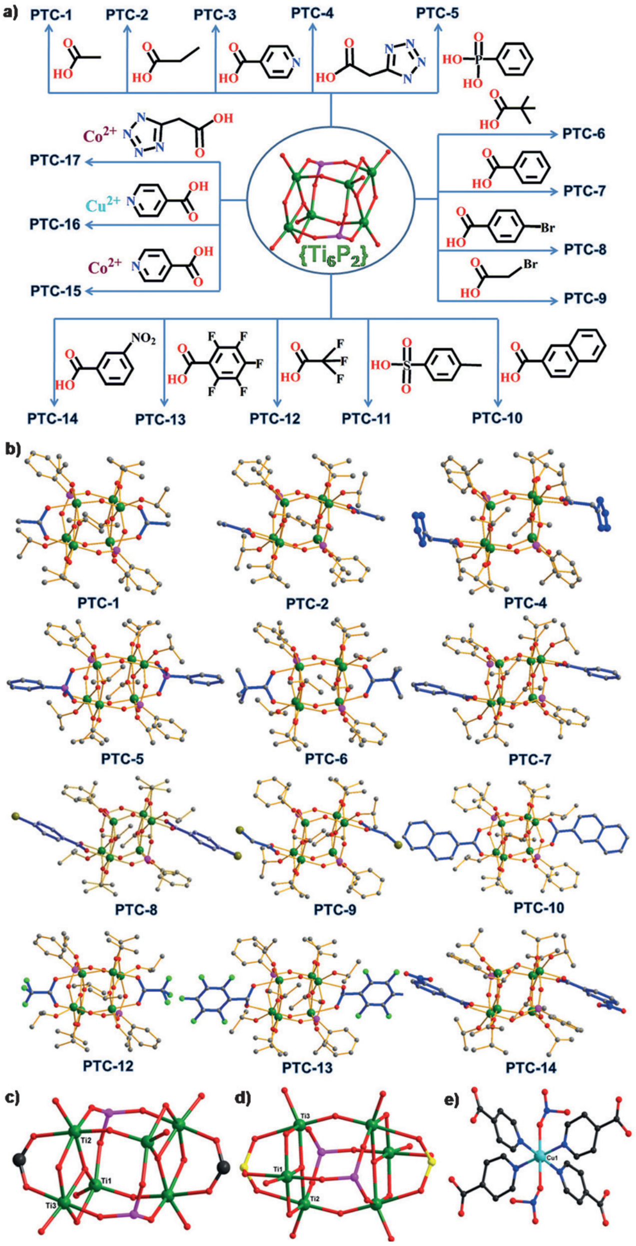

Figure 2. a) Illustration of the assembly of **PTC-1-17**. b) Crystal structures of the $\{Ti_6\}$ cluster family, with the functionalized ligands highlighted in blue color. c,d) Representative coordination modes of $\{Ti_6\}$ in **PTC-1** and **PTC-11**. e) Coordination environment of the Cu ions in **PTC-16**.

consists of two triangular $\{Ti_3(\mu_3\text{-}O)\}$ subunits which are held together by two μ_2-O^{2-} ions and two bridging phenolphosphonate ligands. It is worth noting that Ti2, Ti3 atoms bridged by acetates are in six-coordinated octahedral environments, whilst Ti1 is only five-coordinated which should have the possibility to capture one more terminal ligand to fulfil an octahedral coordination. Moreover, the Ti−O bond length between acetate and Ti2, Ti3 are 2.145 and 2.074 Å, respectively, which are longer than other Ti−O bonds. Therefore, considering the uncompleted coordination sphere of Ti1 and also the weak bonding between Ti2, Ti3, and acetate, the $\{Ti_3(\mu_3\text{-}O)\}$ subunit should have three potential active sites that can be used for ligand substitution by other O-donor species. This would give us an opportunity to investigate the ligand-dependent bandgap engineering of TOCs.

As shown in Figure 2, by introducing different carboxylate ligands instead of acetate into the reaction system, similar $\{Ti_6\}$ cluster structures can be readily obtained, indicating that the acetate sites are rather active and can be easily used for ligand exchange. The calculated bandgap of **PTC-1** from the absorption spectrum is about 3.70 eV. When propanoic acid and pivalic acid are applied, the corresponding bandgaps of **PTC-2** and **PTC-6** are reduced to 3.60 and 3.45 eV, respectively, confirming that the ligand substitution indeed can tune the bandgaps of TOCs. Interestingly, when halide-functionalized acetates, bromoacetic acid, and trifluoroacetic acid are introduced to the $\{Ti_6\}$ clusters, the obtained **PTC-9** and **PTC-12** present even lower bandgaps of 3.39 and 3.31 eV. These results suggest that the introduction of electron-withdrawing organic species can reduce the bandgaps of TOCs. To further verify this observation, aromatic carboxylic acids are applied. Absorption spectra studies confirm that benzoic acid-functionalized **PTC-7** and 2-naphthalenecarboxylic acid-functionalized **PTC-10** both have significantly lower bandgaps than acetate-functionalized **PTC-1**. The introduction of 4-bromobenzene carboxylic acid and pentafluorobenzoic acid give rise to the formation of **PTC-8** and **PTC-13**. Similar to the electron-withdrawing effect observed in the fatty acid family, here the bandgaps also present a sequence of **PTC-7** > **PTC-8** > **PTC-13**. Most significantly, **PTC-14** with *m*-nitrobenzoic acid as ligand displays the lowest bandgap of 3.21 eV, which is about 0.5 eV lower than that of **PTC-1**. This should be attributed to the strong electron-withdrawing behavior of nitro groups.

The above ligand substitutions only involve the two coordination active sites on Ti2 and Ti3. To further investigate the labile activity on the Ti1 site, two tridentate O-donor ligands, phenolphosphonate and *p*-toluenesulfonic acid, are selected giving rise to **PTC-5** and **PTC-11**. Interestingly, compared to benzoic acid-functionalized **PTC-7**, **PTC-5** has a higher bandgap while **PTC-11** has a lower bandgap. Therefore, the functional groups themselves also have influence on the bandgaps of the TOCs.

However, the adsorptions of the above TOCs are all located in the UV light area (Figure 3). It still needs a new method to further reduce the bandgaps of these $\{Ti_6\}$ clusters. It has been well established that the bandgaps of titanium–oxo clusters can be modified by metal doping.[28,29] If we can incorporate some transition-metal ions into the outer space of the $\{Ti_6\}$ cluster, but without changing its core structure, adsorptions in the visible-light range will be generated. The precise complex structure will allow us to study the influence of metal doping on bandgaps at molecular level.

The labile coordination sites of this $\{Ti_6\}$ cluster give us an idea that they might be functionalized into cluster-based ligands if bifunctional O/N-donor ligands are introduced. For this aim, isonicotinic acid is selected to prepare **PTC-3** (Figure 1). As expected, two isonicotinic acids take the positions of acetates in $\{Ti_6\}$ to form a Ti_6-(isonicotinic)$_2$ cluster ligand, the two pyridine groups of which remain

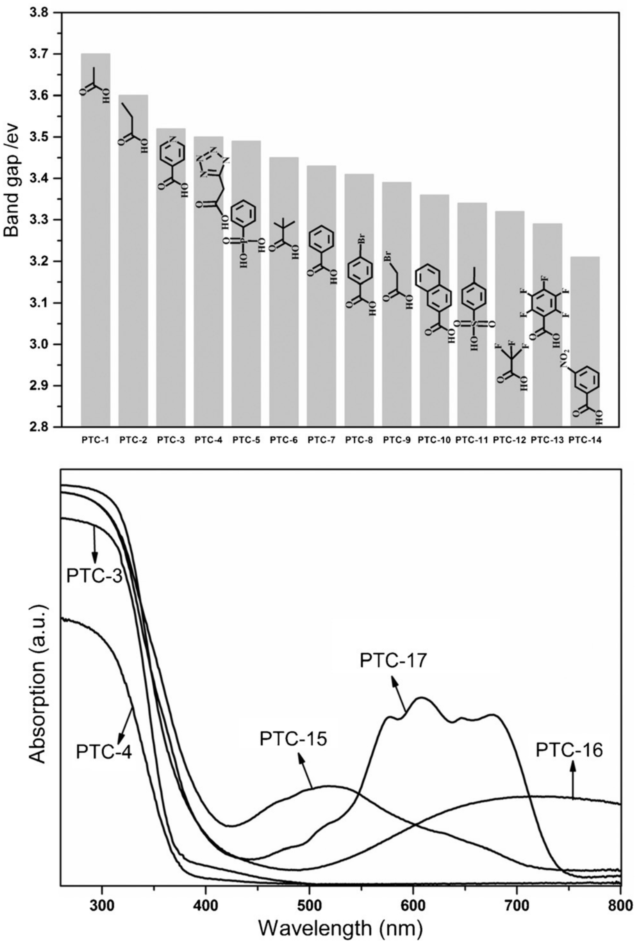

Figure 3. Upper panel: Bandgap summary of **PTC-1** to **PTC-14**. Lower panel: Adsorption spectra of the {Ti_6}-based cluster ligands and the corresponding transition-metal-incorporated coordination polymers.

uncoordinated and point outside from two sides. These free pyridine groups of the {Ti_6} cluster-based ligands should have good potential to coordinate with other transition metals. Therefore, $Co(NO_3)_2$ was added to the synthetic reaction of **PTC-3**, giving rise to the formation of pink crystals of **PTC-15**. As shown in Figures 4 and S15, in the structure of **PTC-15**, the Ti_6-(isonicotinic)$_2$ cluster ligands are coordinated to Co^{2+} ions and then extended into ordered arrays. Each Ti_6-(isonicotinic)$_2$ cluster connects two Co ions through its two pyridine groups. From the point of view of coordination chemistry, Ti_6-(isonicotinic)$_2$ can be seen as a functionalized “bipyridine-type” ligand which is similar to 4,4′-bipyridine. Meanwhile, each Co atom is coordinated by three different Ti_6-(isonicotinic)$_2$ clusters in a “T” connection model, giving rise to the onedimensional ladder-type structure of **PTC-15**. To the best of our knowledge, this is for the first time that nanoscopic, organophosphonate-bridged titanium–oxo clusters are applied as building units for the construction of coordination polymers. As indicated by the absorption spectra studies (Figure 3), the adsorption of **PTC-3** is still in the UV light area (bandgap = 3.52 eV), whist **PTC-15** presents a new adsorption band between 450 and 750 nm because of the d–d transitions of Co^{2+}. This is in agreement with the pink color of **PTC-15**.

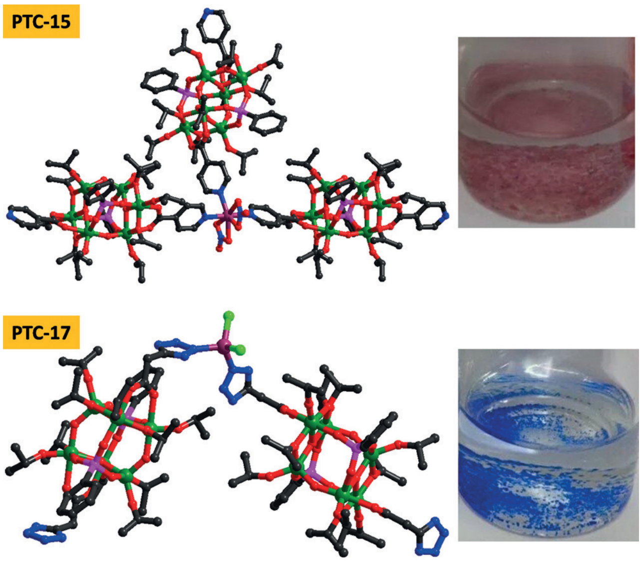

Figure 4. Crystal structures and colors of Co-incorporated **PTC-15** and **PTC-17** with seven- and four-coordinated Co ions, respectively.

Interestingly, the adsorption can be further moved to a high-wavelength area when Cu^{2+} is applied instead of Co^{2+}, through the formation of blue crystals of **PTC-16**. In the structure of **PTC-16**, the Ti_6-(isonicotinic)$_2$ cluster also acts as a linear “bipyridine-type” ligand and links two Cu atoms, whilst here the Cu^{2+} ion is bound to four Ti_6-(isonicotinic)$_2$ clusters in a planar form, organizing the {Ti_6} clusters into a four-connected network (Figures 1 and S16). Compared to **PTC-3**, **PTC-16** produces a new, broad visible-light adsorption band starting from 500 nm, corresponding to $^2T_{2g} \rightarrow {}^2E_g$ transitions of Cu^{2+} (Figure 3).

To illustrate the influence of the coordination environments of incorporated metal ions on the bandgaps of such {Ti_6} cluster family, tetrazolyl acetic acid that has different coordination behaviors from isonicotinic acid, is selected. Similarly, this ligand can also occupy the labile active sites of the {Ti_6} cluster, giving the formation of a tetrazolyl-functionalized titanium–oxo complex **PTC-4**. When $CoCl_2$ is added to the synthetic reaction of **PTC-4**, blue crystals of **PTC-17** form. In the structure of **PTC-17**, the Ti_6-(tetrazolyl)$_2$ clusters are linked by Co^{2+} ions into a 1D polymer (Figures 4 and S17). It is worth of noting that the adsorption behavior of **PTC-17** is quite different from another Co-doping 1D polymer **PTC-15**. Although **PTC-4** almost presents the same bandgap as **PTC-3** (3.50 vs. 3.52 eV), the visible-light adsorption band of **PTC-17** not only moves to higher wavelength area but also displays significantly higher intensity than that of **PTC-15**. We think these differences might arise from the different coordination behaviors of Co^{2+} ions. In **PTC-15**, each Co is seven coodrinate, with three nitrogen atoms from three Ti_6-(isonicotinic)$_2$ cluster ligands and four oxygen atoms from two nitrates; whilst in **PTC-17**, each Co is tetrahedrally coordinated by two Ti_6-(tetrazolyl)$_2$ cluster ligands and two chloride anions. The $^4A_2 \rightarrow {}^4T$ transitions of tetrahedral Co^{2+} attribute

Table 1: Summary of the UV-light photocatalytic H_2 production using the {Ti_6} complexes as catalysts (PTC = phosphonate-stabilized titanium clusters).

Complex	PTC-1	PTC-3	PTC-4	PTC-5	PTC-6	PTC-7	PTC-10	PTC-11	PTC-12	PTC-14	PTC-15	PTC-16	PTC-17
H_2 production ($\mu mol\,g^{-1}h^{-1}$)	0	47.61	28.88	16.67	0	14.42	16.42	3.08	54.52	0	12.08	9.45	23.20

to the visible-light adsorption of **PTC-17**.[28] Therefore, the coordination environments of the doped metal ions can also significantly tune the bandgaps of TOCs.

Much of the research interest on titanium–oxo clusters originates from modulating the photocatalytic TiO_2 materials. However, although many different TOC structures have been reported, their applications in photocatalytic water splitting still remain very rare.[30] To evaluate the photocatalytic performances of this series of {Ti_6}-based hybrid complexes, the UV-light photocatalytic hydrogen production studies were carried out. Interestingly, although the archetype cluster **TPC-1** does not show any H_2 evolution activity, the functionalization by some organic species enables the {Ti_6} clusters to be efficient catalysts (Table 1, Figure S68). Thereinto, the trifluoroacetic functionalized **PTC-12** gives the highest H_2 production of 54.52 $\mu mol\,g^{-1}h^{-1}$. The stationary H_2 production rate during the test time also indicates that these {Ti_6}-based photocatalysts are quite stable. These obtained results confirm that TOC complexes can also present efficient photocatalytic water-splitting activity, which are highly dependent on the structural functionalization.

In summary, we have presented one systemic study on the bandgap engineering of nanoscopic titanium–oxo clusters. Through the use of the labile coordination sites of a robust phosphonate-stabilized {Ti_6} cluster, a variety of O-donor ligands, including carboxylates, phosphonates, and sulfonates, have been applied as functional organic species. Moreover, the introduction of bifunctional O/N-donor ligands allows us to incorporate a second transition metal and organize these {Ti_6} clusters into extended structures. Absorption spectra studies confirm that both the electron-withdrawing effect of organic ligands and the coordination environments of the incorporated metal ions can significantly influence the bandgap structures of TOCs. The photocatalytic water-splitting hydrogen evolution by these TOCs has also been investigated. Our work not only presents a powerful approach for the bandgap adjustment of TOCs, also provides a perfect model library for related theoretical studies.

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Keywords: bandgaps · cluster compounds · labile coordination sites · ligand effects · titanium

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