Connecting Titanium-Oxo Clusters by Nitrogen Heterocyclic Ligands to Produce Multiple Cluster-Series with Photocatalytic H₂ Evolution Activities

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ABSTRACT: We herein demonstrated the ability of nitrogen heterocyclic ligands in connecting polyoxotitanium complexes into crystalline multiple cluster-series. Moreover, their bandgap and photocatalytic water-splitting behaviors were studied. The highest H₂ evolution activity reaches up to 42.80 $\mu\text{mol g}^{-1} \text{h}^{-1}$ for PTC-46.

Nowadays the exploration of synthesis and structures of crystalline polyoxotitanium materials has increasingly turned into a worldwide hot research topic.^{1, 2} The motivation comes from mimicking and substituting titanium dioxide (TiO₂), which has been widely used as a technologically important photocatalyst for production of solar fuels like hydrogen.³⁻⁵ However, the photocatalytic behaviors of TiO₂ are highly determined by the HOMO–LUMO spacing between the occupied and unoccupied energy levels, which can be referred to the bandgaps of semiconductors.² A general consensus gives a relatively high bandgap of 3.20 eV for TiO₂ (anatase).⁶ Hence, materials with tunable bandgaps are favorable. In terms of readily tailored and post modification, the bandgap adjustment can be realized through the introduction of crystalline polyoxotitanium materials. In addition, their accurate structural information provides reference substance for theoretical calculation and possibility to the clarification of reaction mechanism.

With the development of characterization approach of crystalline materials and the diverse synthetic methods, family of polyoxotitanium clusters (PTCs) has been largely expanded.⁷⁻²² Breakthroughs have been achieved not only in structural types but also the cluster nuclearities. So far, the largest molecular polyoxotitanium cluster contains 52 Ti atoms.²³ Even though far less than the 368 atoms in polyoxometalates, there is still great potential. Nevertheless, the majority of reported PTCs are based on O-donor ligands, those with direct Ti–N bonds are also of particular interest. It is reported that N-doping of TiO₂ has great impacts on its properties, but it is still a challenge to synthesize such N-containing crystalline materials.²⁴⁻²⁷ Recently, azole ligands have been extensively confirmed to be effective in synthesis of polyoxotitanium clusters.²⁸ Therein, a series of tetranuclear and hexanuclear titanium-oxo clusters have been prepared. As a continuation of this work, we herein demonstrate how nitrogen heterocyclic ligands work in the further connection of these building blocks to form multiple cluster-series.

Moreover, UV-light driven H₂ evolution studies confirm that they are stable photocatalysts.

Scheme 1 The illustration of the influence of phenylphosphonic acid /azole molar ratios on the nuclearities of PTCs with direct Ti–N bonds.

In this text, nitrogen heterocyclic ligands were widely studied including piperazine (PIP), Adenine (ADN), aminopyrazine (APZ), and 2-aminoisonicotinic acid (ANA). In recent work with azole ligand, the reaction of phenylphosphonic acid (PPA), imidazolate (Im), and Ti(OiPr)₄ in isopropanol led to the formation of PTC-40, [Ti₄(μ₃-O)(μ₂-OiPr)₃(OiPr)₅(PPA)₃(Im)]. By using similar methods, we have modified the molar ratio of PPA:azole and obtained [Ti₄(μ₃-O)(PPA)₃(OⁱPr)₈]₂(PIP)·2HOⁱPr (PTC-43), [Ti₄(μ₃-O)(PPA)₃(OⁱPr)₈]₂(ADN) (PTC-44), [Ti₄(μ₃-O)(PPA)₃(OⁱPr)₈]₂(APZ) (PTC-45), and [Ti₄(μ₃-O)(PPA)₃(OiPr)₈]₂[Ti₆(μ₃-O)₂(μ₂-O)₂(PPA)₂(OiPr)₁₀](ANA)₂ (PTC-46). Apart from the difference among ligands, we found that the nuclearities of these PTCs strongly depend on the dosage ratio of phenylphosphonic acid to

azole (Scheme 1, Table S5). It reveals that the increment of the phenylphosphonic acid may allow the higher concentration of tetranuclear subunits to form higher nuclearity. With the increment of such molar ratio from 0.43 in PTC-40 to 3.10 in PTC-46, the cluster nuclearity undergoes a change from tetranuclear to tetradecanuclear. Their phase purity was confirmed by comparison of the measured powder X-ray diffraction (PXRD) pattern with the simulated one from the crystal structure (Figures S1–S4). Their crystal structures were characterized by single-crystal X-ray diffraction analysis.

Figure 1 The dumbbell like structures of duple $\text{Ti}_4\text{-Ti}_4$ cluster-series PTC-43 to PTC-45. Colour code: Green Ti; Red O; Black C; Pink P; Blue N.

One prominent structure feature of PTC-43, PTC-44, and PTC-45 is that they are composed of dimeric tetranuclear subunits appeared in PTC-40. The structure of PTC-40 can be described as a distorted tetrahedral with μ_3 -oxygen bridged trinuclear cluster as basal and the fourth titanium atom as vertex.²⁸ The imidazole ligand is attached to the fourth titanium atom with direct Ti–N bonds, leaving the other N atom uncoordinated. However in PTC-43, PTC-44, and PTC-45 the two opposite N atoms of the heterocyclic ligands linked the two vertices of tetrahedral subunits to form a dumbbell like octahedral cluster (Figure 1). The diameter of these clusters is in the range of 1.4–1.5 nm. All of the titanium atoms exhibit octahedral coordination geometry. Each basal Ti atom is coordinated by one μ_3 -oxygen, two oxo bridges from two adjacent PPA ligands, two bridging and one terminal oxygen atoms from three isopropanol molecules. While the TiO_5N octahedral geometry of the fourth titanium atom of each subunit is surrounded by three oxo bridges from three PPA ligands, two isopropanol molecules and one N atom from PIP in PTC-43, ADN in PTC-44 and APZ in PTC-45, respectively. The Ti–N bonds range from 2.24 to 2.29 Å, which are consistent with the literatures.²⁹ The remarkable structure feature of PTC-46 is the presence of two basic organophosphonate-

bridging building blocks. One is the above mentioned tetrahedral cluster and the other is the literature documented hexanuclear $\{\text{Ti}_6\text{P}_2\}$ core.^{18,30} Through the use of the labile coordination sites of the robust phosphonate-stabilized hexanuclear core, diverse O-donor ligands have been applied as functional organic species. In addition, we have demonstrated the effectiveness of azole ligands in the construction of direct Ti–N bonds. Herein, through the combination of N and O-donor in 2-aminoisonicotinic acid, an interesting nanoscale triple cluster series forms in PTC-46, whose diameter reaches as long as 2.8 nm (Figure 2).

Figure 2 The structure of the triple $\text{Ti}_4\text{-Ti}_6\text{-Ti}_4$ cluster-series PTC-46. Colour code: Green Ti; Red O; Black C; Pink P; Blue N.

The solid state UV-vis absorption spectra of these four compounds are shown in Figure 3a. According to the Kubelka–Munk function,³¹ the optical bandgaps of them are estimated to be 3.58, 3.47, 3.16 and 3.19 eV for PTC-43, PTC-44, PTC-45 and PTC-46, respectively. The bandgap differential between them is likely the result of the different supporting ligand, nuclearity and coordination environment within their cluster cores. Despite clusters of PTC-43 to PTC-45 possess the same nuclearity, the observed differences in their absorption edges suggest that complicated factors especially the applied organic linkers are at work in determining the bandgaps of these materials.

To evaluate the photocatalytic performances of these compounds, the UV-light driven photocatalytic hydrogen production studies were carried out. Typically, 100 mg solid sample of was dispersed in 90 mL H_2O with 10 mL methanol as the sacrifice agent. A 300 W Xe lamp was used as the UV-visible light source. The evolved hydrogen was monitored by online gas chromatography (GC) analysis with an interval of two hours. The H_2 production of these compounds is presented in Figure 3b. Thereinto, the triple cluster series PTC-46 gives the highest H_2 production of 42.80 $\mu\text{mol g}^{-1} \text{h}^{-1}$. Although presenting the same nuclearity, PTC-43, PTC-44, and PTC-45 display varied H_2 production activities. Nevertheless, the

stationary H₂ generation rate during the test also indicates that these photocatalysts are quite stable. To confirm their photocatalytic stability, recycling experiments were performed under the same conditions. Similar H₂ evolution behaviors were observed within 3 cycles. The PXRD patterns of the collected solids after photocatalysis also preserved most of their characteristic signals (Figures S11–14). All these results confirm that these PTCs are quite stable photocatalysts.

Figure 3 (a) Solid-state absorption spectra of the four samples. (b) Hydrogen evolution plots catalyzed by different complexes.

In summary, by the application of nitrogen heterocyclic ligands, we have developed an unprecedented approach for connecting robust titanium-oxo units into multiple cluster-series. Duple Ti₄-Ti₄ and triple Ti₄-Ti₆-Ti₄ complexes are successfully prepared and display various bandgaps and photocatalytic H₂ evolution properties. These results not only reveal the potential ability of nitrogen heterocyclic ligands in constructing polyoxotitanium complexes, but also indicate their underlying applications as photocatalysts.

Supporting Information. Materials, synthesis and physical measurements, and CIF file (CCDC 1534751 (PTC-43), 1524240 (PTC-44), 1524242 (PTC-45), 1524243 (PTC-46)). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Duple Ti₄-Ti₄ and triple Ti₄-Ti₆-Ti₄ cluster-series are constructed using nitrogen heterocyclic ligands as linkers, representing good and stable H₂ evolution activities.

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