

# Dalton Transactions

Accepted Manuscript



This is an *Accepted Manuscript*, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

*Accepted Manuscripts* are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this *Accepted Manuscript* with the edited and formatted *Advance Article* as soon as it is available.

You can find more information about *Accepted Manuscripts* in the [Information for Authors](#).

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard [Terms & Conditions](#) and the [Ethical guidelines](#) still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this *Accepted Manuscript* or any consequences arising from the use of any information it contains.



Journal Name

ARTICLE

## A novel hexanuclear titanium(IV)-oxo-iminodiacetate cluster with $\text{Ti}_6\text{O}_9$ core: single-crystal structure and photocatalytic activities

Received 00th January 20xx,  
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

Lubin Ni,<sup>a</sup> Dashuai Liang,<sup>a</sup> Yin Cai,<sup>a</sup> Guowang Diao,<sup>\*a</sup> Zhaohui Zhou,<sup>\*b</sup>

A new family of hexanuclear titanium(IV)-oxo-carboxylate cluster  $\text{K}_7\text{H}[\text{Ti}_6\text{O}_9(\text{ida})_6]\text{Cl}_2 \cdot 15\text{H}_2\text{O}$  ( $\text{Ti}_6\text{O}_9$ ) has been synthesized via the  $\text{H}_2\text{O}_2$ -assisted reaction between  $\text{TiCl}_4$  and iminodiacetate ligands. This cluster was fully characterized by single-crystal X-ray diffraction and a wide range of analytical methods, including FT-IR, UV/vis spectroscopy as well as electrochemistry and thermogravimetric analysis. As a new type of carboxylate substituted Ti-oxo-cluster, the structural motif of  $\{\text{Ti}_6\text{O}_9\}$  cluster consists of one symmetric  $\{\text{Ti}_6\text{O}_6\}$  hexagonal prism with two staggered triangular  $\{\text{Ti}_3\text{O}_3\}$  subunits linked by three  $\mu_2\text{-O}$  bridges. The  $\{\text{Ti}_6\text{O}_9\}$  polyanions are linked by  $\text{K}^+$  cations to form a novel 3D architecture. The structural information and stability of  $\{\text{Ti}_6\text{O}_9\}$  polyanion in aqueous solution was thoroughly investigated by solid-state/solution NMR, ESI-MS spectroscopy. Moreover, this Ti-oxo cluster exhibits remarkable potential as a visible-light homogenous photocatalyst for degradation of the rhodamine B (RhB). Finally, a proposed peroxotitanium(IV)-mediated photocatalytic pathway involved is illustrated by spectroscopic data.

### Introduction

Titanium(IV)-oxo clusters (TOCs) are considered to be one of the most promising subclass of metal oxo-clusters (MOCs) for constructing nanostructural titanium dioxide at the atomic level.<sup>1</sup> Since the first crystal structure of a titanium-oxo-cluster  $[\text{Ti}_7\text{O}_{24}\text{Et}_{19}]$  was reported by Watenpaugh et al. in 1967,<sup>2</sup> TOCs have attracted worldwide research interest for decades owing to their promising applications, e.g. in the fields of catalysis, medicine, electro-optics, multifunctional materials, or nanotechnology.<sup>3</sup> Currently, TOCs are frequently used as photocatalysts for solar energy conversion and environmental applications due to their low toxicity, redox activity, high photostability, and high efficiency.<sup>4</sup> The development of TOCs photocatalysts for wastewater treatment and water splitting is a forefront topic in renewable energy and environmental research. However, two keys to unlocking the full potential of TOCs as prototype photocatalysts still remain to be found, namely predictive structural design over new motifs and comprehensive understanding of their catalytic mechanisms.<sup>5</sup> In this work, we thus present a new family of hexanuclear titanium(IV)-oxo-iminodiacetate complex, which shed new lights on the TOCs-based photocatalyst for varying mechanistic routes of dye degradation.

The whole TOCs family almost can be classified into three types based on their the different coordination modes of the ligands (O, OR, and L)<sup>1a</sup>: titanium(IV) oxo-alkoxides clusters  $[\text{Ti}_n\text{O}_m(\text{OR})_{4n-2m}]$ <sup>6,7</sup>, oxo-carboxo-alkoxides clusters  $[\text{Ti}_n\text{O}_{2n-x/2-y/2}(\text{OR})_x(\text{L})_y]$ <sup>8,9,10</sup>, and oxo-carboxo clusters  $[\text{Ti}_n\text{O}_m(\text{OOCR})_p]$ ,  $2m + p = 4n$ .<sup>11</sup> The hydrolytic stability of the carboxylate-substituted TOCs is higher than that of the titanium oxo-alkoxides clusters. In recent years, the direct utilization of carboxylate ligands has been verified as an effective method for the construction of new titanium(IV)-carboxo-clusters, owing to their versatile coordination modes, such as monodentate, bridging bidentate and bridging tridentate modes.<sup>12</sup> Therefore, numerous such titanium(IV) oxo-carboxo-alkoxides have been synthesized and structurally characterized with various core nuclearity ranging from 2 to 34. The largest TOC  $[\text{Ti}_{34}\text{O}_{50}(\text{OPr}^i)_{30}(\text{DMABA})_6]$  with  $\text{Ti}_{34}$  nuclearity has been observed by Sokolow et al.,<sup>10a</sup> followed by the Benedict et al.'s synthesis of  $\text{Ti}_{28}$ -containing TOC  $[\text{Ti}_{28}\text{O}_{40}(\text{OR})_{20}(\text{OOCR}')_{12}]$ .<sup>10b</sup> Nevertheless, only a few examples of purely titanium(IV)-carboxo-clusters  $[\text{Ti}_n\text{O}_m(\text{OOCR})_p]$  with  $\text{Ti}_2$ <sup>11a</sup>,  $\text{Ti}_4$ <sup>11b-d</sup> and  $\text{Ti}_8$ <sup>11e-h</sup> nuclearities, respectively, are known up to now. Representative examples for carboxylate-substituted polyoxotitanates include dinuclear polyanion  $[\text{Ti}_2(\text{O}_2)_2(\text{C}_6\text{H}_4\text{O}_7)_2]$ <sup>4, 11a</sup>, tetranuclear polyanion  $[\text{Ti}_4\text{O}_4(\text{nta})_4]$ <sup>4, 11b</sup>, octanuclear polyanion  $[(\text{Ti}_8\text{O}_8)(\text{dptaO})_4]$ <sup>4, 11c</sup>. The neutral clusters are illustrated by Kemmitt et al.'s citrate-substituted octamer  $[\text{Ti}_8\text{O}_{10}(\text{C}_6\text{H}_5\text{O}_7)_4(\text{H}_2\text{O})_{12}]$ <sup>11g</sup> and Sanchez et al.'s terephthalate-substituted octamer  $[\text{Ti}_8\text{O}_8(\text{OH})_4(\text{O}_2\text{CC}_6\text{H}_4\text{CO}_2)_6]$  (MIL-125),<sup>11h</sup> followed by Rozes et al.'s synthesis of octamers  $[\text{Ti}_8\text{O}_{10}(\text{OOCR})_{12}]$  and  $[\text{Ti}_8\text{O}_8(\text{OOCR})_{16}]$ .<sup>11f-11e</sup>

Iminodiacetic acid ( $\text{H}_2\text{ida}$ ) is a common dicarboxylate ligand widely employed as in coordination chemistry and immobilized metal affinity chromatography (IMAC) purification of proteins and nucleic acids.<sup>13</sup> To date, titanium-oxo-cluster substituted by iminodiacetate ligand has never been documented. Here, we

<sup>a</sup> College of Chemistry and Chemical Engineering, Yangzhou University, Yangzhou 225002, Jiangsu, People's Republic of China. Email: [gwdiao@yzu.edu.cn](mailto:gwdiao@yzu.edu.cn)

<sup>b</sup> State Key Laboratory for Physical Chemistry of Solid Surfaces, College of Chemistry and Chemical Engineering, Xiamen University, Xiamen 361005, People's Republic of China. Email: [zhzhou@xmu.edu.cn](mailto:zhzhou@xmu.edu.cn)

<sup>†</sup>Electronic Supplementary Information (ESI) available: X-ray crystallographic data in CIF format (CIF), crystallographic data, selected bond lengths and angles, X-ray powder diffraction pattern (XRPD), FT-IR, UV/vis, thermogravimetric analysis (TGA), electrospray ionization mass spectra (ESI-MS), cyclic voltammetry (CV) and photocatalytic properties. CCDC 1054148. For ESI and crystallographic data in CIF or other electronic format See DOI: 10.1039/x0xx00000x.

successfully introduced iminodiacetic acid (H<sub>2</sub>ida) into titanium-oxo clusters and first report the synthesis and characterization of a novel family of hexanuclear titanium(IV)-oxo-carboxylate complex K<sub>7</sub>H[Ti<sub>6</sub>O<sub>9</sub>(ida)<sub>6</sub>]Cl<sub>2</sub> · 15H<sub>2</sub>O, {Ti<sub>6</sub>O<sub>9</sub>}. To the best of our knowledge, the crystal structure of {Ti<sub>6</sub>O<sub>9</sub>} cluster has rarely been reported for carboxylate substituted titanium(IV)-oxo clusters family. These {Ti<sub>6</sub>O<sub>9</sub>} polyoxoanion moieties are further linked by K<sup>+</sup> cations into 3D open architectures in the solid-state. The structural stability of {Ti<sub>6</sub>O<sub>9</sub>} cluster in aqueous media was also investigated. Moreover, this Ti-oxo cluster exhibits remarkable potential as a visible-light homogenous photocatalyst for degradation of the rhodamine B (RhB). A proposed peroxotitanium(IV)-mediated photocatalytic pathway involved is illustrated by spectroscopic data.

## Experimental

### Materials and physical measurements.

Elemental analyses (C, H and N) were performed using EA 1110 elemental analyzer. Fourier transform infrared (FT-IR) spectra were recorded on a Bruker Optics Vertex 70 Spectrometer. Solution <sup>13</sup>C NMR spectra were measured on a Bruker Avance AV-400M H<sub>2</sub>O resonance spectrometer with D<sub>2</sub>O solvent using DSS (sodium 2,2-dimethyl-2-silapentane-5-sulfonate) as an internal reference at room temperature. Solid <sup>13</sup>C NMR spectra were recorded on a Bruker AV 400 NMR spectrometer using cross polarization, magic angle spinning (12 kHz) and Hexamethylbenzene (HMB) as the reference. The thermogravimetric analyses (TG) were collected with a Netzsch TG209 F1 instrument with a 10 °C min<sup>-1</sup> from 30 to 900 °C in flowing nitrogen atmosphere. UV/vis spectra were recorded on a Perkin-Elmer Lambda 650S spectrometer. The X-ray powder diffraction patterns (XRD) were recorded on a Philips X'Pert PRO diffractometer, operated at 40 kV and 30mA using a Cu-target tube. Cyclic voltammetry experiments were performed on a Metrohm Computrace Voltammetric Analyzer model 757 VA. The system was operated with 757 VA Computrace software (Metrohm). The three-electrode cell system consisted of a 2 mm glassy carbon working electrode (GCE, modified or unmodified), a saturated Ag/AgCl reference electrode and a Pt wire as the counter electrode. High mass accuracy ESI spectra were recorded on an ultrahigh-resolution ESI-Time-Of-Flight MS (Bruker Daltonik maxis (Bremen, Germany)). Spectra were obtained in negative-ion mode, with the capillary held at 4000 V. The drying gas flow rate was 4.0 L min<sup>-1</sup> with a temperature of 180 °C. The nebulizer gas was at a pressure of 0.4 bar. The m/z range detected was from 100 to 2500Da. A calibration tune mix (Agilent Technologies) was sprayed immediately prior to analysis, ensuring a high mass accuracy to assist in the identification of peaks. The flow rate of the solutions was 3L/min. {Ti<sub>6</sub>O<sub>9</sub>} cluster was dissolved in a H<sub>2</sub>O/MeCN mixture (80:20) to enhance peak intensity.

### Synthesis of K<sub>7</sub>H[Ti<sub>6</sub>O<sub>9</sub>(ida)<sub>6</sub>]Cl<sub>2</sub> · 15H<sub>2</sub>O {Ti<sub>6</sub>O<sub>9</sub>}.

2.00g (15mmol) of iminodiacetic acid was dissolved in 25 ml of deionized water with stirring. an aqueous solution of titanium(IV) tetrachloride (5mL, 5mmol, 1.0 M solution) was slowly added to the reaction mixture, and the mixture was left stirring for 30 min at pH values around 1.0. In a second step, 10 ml of 30% H<sub>2</sub>O<sub>2</sub> was dropwise introduced into the reaction mixture cooled with an ice

bath. The solution underwent a color change from colorless to dark red under stirring. Next, an additional amount of 5.0 M KOH solution was added to adjust pH value, followed by a color change to light yellow at pH values around 5.0 ~ 7.5. Slow evaporation of the solution afforded colorless single crystals of {Ti<sub>6</sub>O<sub>9</sub>} cluster after approx 10 d. Yield: 0.78g, 49% based on Ti. Ft-IR (cm<sup>-1</sup>): ν<sub>as</sub>(COO) 1657.1<sub>(vs)</sub>, 1622.5<sub>(vs)</sub>; ν<sub>s</sub>(COO) 1441.4<sub>(m)</sub>, 1386.7<sub>(s)</sub>, 1303.8<sub>(m)</sub>; ν(Ti-O-Ti) 826.2<sub>(s)</sub>; ν(Ti-O) 542.5<sub>(m)</sub>. <sup>13</sup>C NMR: δ<sub>c</sub> (D<sub>2</sub>O) ppm: 183.91(CO<sub>2</sub>); 59.67(CH<sub>2</sub>). Elemental analysis calcd. (found): C 5.03(14.90); H 3.42(3.78); N, 4.38(4.37).

### Photochemical Degradation of Dye.

The photocatalytic activity of the as-prepared {Ti<sub>6</sub>O<sub>9</sub>} compound was evaluated by monitoring the degradation of under visible-light irradiation (a solar-300 W Xe lamp, λ > 420 nm). The homogeneous photocatalytic system are prepared by addition of 50 mg water-soluble {Ti<sub>6</sub>O<sub>9</sub>} compound to 100 mL of RhB solution (10 μM), and then are added H<sub>2</sub>O<sub>2</sub> (2mL, 20mmol) before irradiation. During the photocatalytic tests, fixed amounts of the reaction solution were taken out at given time intervals. The concentrations of RhB during the degradation procedures were determined by UV-visible spectrophotometer at λ = 554 nm.

### X-ray crystallography.

Data collections of {Ti<sub>6</sub>O<sub>9</sub>} cluster was performed on an Oxford Gemini Sultra system with graphite mono-chromate (MoKα radiation, λ= 0.71073 Å) at 173K. Routine Lorentz and polarization corrections were applied, and an absorption correction was performed using the program *CrysAlis* (multi-scan).<sup>14</sup> The structures were solved using the WinGXpackage<sup>15</sup> and refined by full-matrix least-square procedures with anisotropic thermal parameters for all the non-hydrogen atoms using SHELXL-97.<sup>16</sup> Hydrogen atoms were included and located from difference Fourier maps but not refined anisotropically.

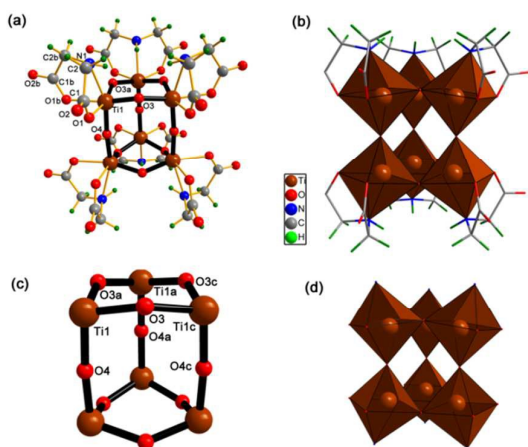
## Results and Discussion

### Synthesis and Crystal Structure.

The {Ti<sub>6</sub>O<sub>9</sub>} cluster was successfully isolated from the reaction of TiCl<sub>4</sub> and H<sub>2</sub>ida with a molar ratio of 1: 3.0 in the presence of excess hydrogen peroxide. The composition of {Ti<sub>6</sub>O<sub>9</sub>} cluster was determined from the combination of X-ray crystallography data with various additional analytical techniques (Table S1). Ball-stick plots of the structure are shown in Fig. 1, along with polyhedron views of the {Ti<sub>6</sub>O<sub>9</sub>} cluster structure. The symmetric and compact structure of [Ti<sub>6</sub>O<sub>9</sub>(ida)<sub>6</sub>]<sup>6-</sup> polyanion consists of two non-planar and staggered six-membered [Ti-(μ<sub>2</sub>-O)]<sub>3</sub> rings built by sharing vertices of the [TiO<sub>5</sub>N] octahedron (Figs. 1a-1b). Each [Ti-(μ<sub>2</sub>-O)]<sub>3</sub> ring is composed of three Ti(IV) atoms and three μ<sub>2</sub>-O ions. Two equivalent {Ti<sub>3</sub>O<sub>3</sub>} subunits are further linked each other by corner-sharing through three μ<sub>2</sub>-oxo bridges, thus leading to the formation of {Ti<sub>6</sub>O<sub>9</sub>} oxo-core. (Figs. 1c-1d). Each titanium center is surrounded by three oxygen atoms of μ<sub>2</sub>-O bridges, two oxygen atoms of carboxy groups and one imine nitrogen atom from iminodiacetate ligand (ida) in a distorted octahedron.

Additionally, the center of the hexameric cluster {Ti<sub>6</sub>O<sub>9</sub>} generates one void space with internal diameter ~3.54 Å [Ti1...O3c

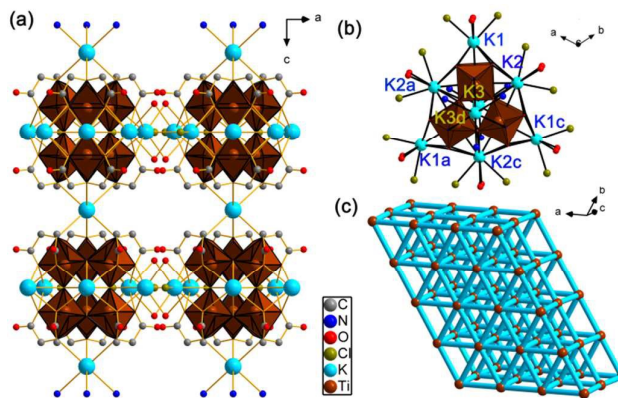
3.537(1) Å]. The distances between Ti and carboxylate O atoms [Ti1–O1 and Ti1–O1b distances: 2.096(2) Å; symmetry code:  $b, x-y, -y, z$ ] are relatively longer than the length of the Ti–( $\mu_2$ -O) bonds [Ti–O3 and Ti–O3a distances: 1.830(2) Å; Ti–O4 distance: 1.8121(7) Å; symmetry code:  $a, -y, x-y, z$ ]. Important Ti–O and Ti–N bond lengths and angles of  $\{\text{Ti}_6\text{O}_9\}$  cluster are listed in Tables S2. The average Ti–O and Ti–Ti bond distances observed for  $\{\text{Ti}_6\text{O}_9\}$  cluster are consistent with other reported titanium(IV)-oxo-carboxylate clusters (Table S3).<sup>11</sup> The  $\{\text{Ti}_6\text{O}_9\}$  cluster also displays strong N–H...O intramolecular hydrogen bonding between imine group from ida ligand and  $\mu_2$ -O3 bridges of  $[\text{Ti}_6\text{O}_9]^{6+}$  central core [N1...O3a 2.912(4) Å,  $\angle\text{N–H...O}$  130.35°], which contributes to the stabilization of hexanuclear Ti-oxo cluster.



**Fig. 1** (a) Ball-and-stick view of  $[\text{Ti}_6\text{O}_9(\text{ida})_6]^{6-}$  polyanion; (b) Combined polyhedral/ball-and-stick representation of  $[\text{Ti}_6\text{O}_9(\text{ida})_6]^{6-}$ ; (c) Ball-and-stick representation of  $[\text{Ti}_6\text{O}_9]^{6+}$  central core structure; (d) Polyhedral view of  $[\text{Ti}_6\text{O}_9]^{6+}$  core structure. (color code:  $[\text{TiO}_5\text{N}]$  octahedra: brown; Ti: brown; O: red; N: blue; C: black; H: gray. symmetry codes:  $a, -y, x-y, z$ ;  $b, x-y, -y, z$ ;  $c, -x+y, -x, z$ ).

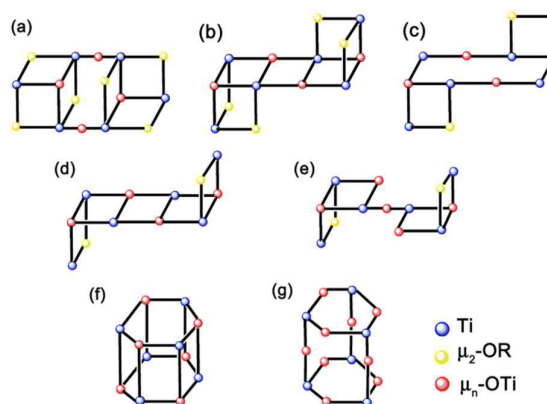
Interestingly, each  $\{\text{Ti}_6\text{O}_9\}$  polyanion furthermore coordinates with 8 potassium cations via 9  $\mu_2$ -O atoms of  $[\text{Ti}_6\text{O}_9]^{6+}$  structural core, 12 oxygen atoms of carboxy groups and 6 imine nitrogen atoms from ida ligands, which could be viewed as  $\mu_2$ -bridges to connect with adjacent  $\{\text{Ti}_6\text{O}_9\}$  polyanions forming 3D open-framework (Fig. 2a). K1 center is nine coordinated with four  $\mu_3$ -oxygen atoms (O1) of carboxy groups from ida ligands, one  $\mu_5$ -oxygen atom (O4) from  $[\text{Ti}_6\text{O}_9]^{6+}$  structural core, two bridging aqua-oxygen atom ( $\mu_2$ -O3W) and two bridging chloride atom ( $\mu_2$ -Cl1) (K1–O distances: 2.820(1)–3.206(5) Å, K1–Cl1 distances: 2.808(9) Å, Fig. 2b).<sup>17</sup> The coordination sphere of twelve-coordinated K2 cation is completed by four  $\mu_3$ -oxygen atoms (O1) of carboxy groups from ida ligands, two  $\mu_5$ -oxygen atoms (O4) and two  $\mu_3$ -oxygen atoms (O3) from  $[\text{Ti}_6\text{O}_9]^{6+}$  core, and two bridging aqua-oxygen atom ( $\mu_2$ -O3W) and two bridging chloride atom ( $\mu_2$ -Cl1) (K2–O distances: 3.089(3)–3.277(2) Å, K2–Cl1 distances: 2.891(10) Å, Fig. 2b). The octahedrally coordinated K3 cation is surrounded by six imine nitrogen atoms (N1) derived from six independent ida ligands (K3–N1 distances: 3.381(4) Å, Fig. 2b).

From the topological point of view, the  $[\text{Ti}_6\text{O}_9(\text{ida})_6]^{6-}$  clusters can be considered as 8-connecting nodes, the  $\text{K}^+$  cations can be assigned as bridging connector ligands between two clusters (Fig. 2c). Therefore, the 3D framework can be represented as a 8-connected “hex”<sup>18</sup> network with the Schläfli symbol  $[(3^6.4^{16}.5^2.6^4)]$ ; Fig. 2c) by TOPOS 4.0 analysis.<sup>19</sup> To the best of our knowledge, the topology of this framework has never been observed in TOCs chemistry before.



**Fig. 2** (a) Polyhedral/ball-and-stick representations of the 3D open framework in  $\{\text{Ti}_6\text{O}_9\}$  cluster along  $ac$  plane; (b) The coordination environments of K cations in  $\{\text{Ti}_6\text{O}_9\}$  cluster. symmetry codes:  $a, -y, x-y, z$ ;  $c, -x+y, -x, z$ ;  $d, x-y, x, 0.5+z$ ; (c) View of the topology of  $\{\text{Ti}_6\text{O}_9\}$  cluster ( $[\text{Ti}_6\text{O}_9(\text{ida})_6]^{6-}$  polyanions = brown node,  $\text{K}^+$  linkers = blue pillars).

Among the hexanuclear TOCs family, six different types of the hexamers have been reported to date (Figs. 3a–3f), and all titanium atoms are six-fold coordinated.<sup>1</sup> As shown in Figs. 3a–3e, the five basic skeletal arrangements of  $\text{Ti}_6$  oxo-clusters can be viewed as one or two corner-removed  $[\text{Ti–O}]_4$  cubes linked by oxo-bridge with a center of symmetry.<sup>20</sup> The sixth structural motif of  $[\text{Ti}_6\text{O}_6(\text{OR})_6(\text{OOCR}')_6]$ ,  $\{\text{Ti}_6\text{O}_6\}$ , consists of one symmetric  $\{\text{Ti}_6\text{O}_6\}$  hexagonal prism with two staggered triangular  $\{\text{Ti}_3\text{O}_3\}$  units (Fig. 3f).<sup>21</sup> The skeletal arrangement of new  $\{\text{Ti}_6\text{O}_9\}$  cluster is shown in Fig. 3g. There are two staggered triangular  $\{\text{Ti}_3\text{O}_3\}$  subunits bridged by three  $\mu_2$ -O in  $\{\text{Ti}_6\text{O}_9\}$  compound (Fig. 3g), but with different arrangement compared to  $\{\text{Ti}_6\text{O}_6\}$  cluster (Fig. 3f). To the best of our knowledge, the hexanuclear cluster found in new  $\{\text{Ti}_6\text{O}_9\}$  cluster has never been documented for titanium-oxo clusters.



**Fig. 3** Skeletal arrangements of the  $\text{Ti}_6$  carboxylate-substituted oxo clusters: (a–f) reported, (g)  $\{\text{Ti}_6\text{O}_9\}$  cluster.

Bond-valence-sum calculations (BVS)<sup>22</sup> (Table S4) revealed that the valences of all titanium (4.01) and oxygen atoms (1.74–2.22) in  $\{\text{Ti}_6\text{O}_9\}$  cluster are in agreement with their formal values, so none of the oxygen atoms of the TOC is protonated. In order to balance the charges of the  $\{\text{Ti}_6\text{O}_9\}$  polyanion,  $[\text{Ti}_6\text{O}_9(\text{ida})_6]^{6-}$ , we added one proton to  $\{\text{Ti}_6\text{O}_9\}$  cluster, because the product was isolated in acidic aqueous solution. This proton cannot be located crystallographically and are assumed to be delocalized over the entire structure, a commonly observed phenomenon in polyoxometalate chemistry.<sup>23</sup>

#### General Characterization.

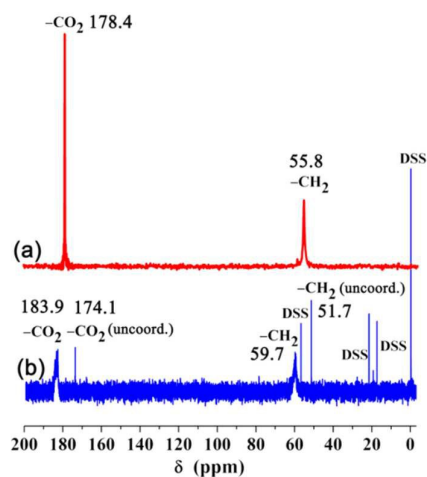
Phase purity of  $\{\text{Ti}_6\text{O}_9\}$  cluster was confirmed by comparison of experimental X-ray powder diffraction (PXRD) patterns with simulated patterns from single-crystal X-ray diffraction data (Fig. S2). Owing to the variation in the preferred orientation of the powder sample in the experimental PXRD, the intensities of the experimental and simulated PXRD patterns are different. The thermogravimetric (TG) curve of  $\{\text{Ti}_6\text{O}_9\}$  cluster displays continuous weight loss between 30 °C – 900 °C (Fig. S3). The weight loss of 24.5% is attributed to the loss of twenty lattice waters and two hydrogen chloride molecules in the temperature range of 30–355 °C (calcd 22.5%). From 400 °C to 870 °C, the  $\{\text{Ti}_6\text{O}_9\}$  cluster decomposes with stepwise loss of the organic ida ligands, leading to the collapse of Ti-oxo cluster. The residual weight may correspond to the final products of  $\text{K}_4\text{Ti}_3\text{O}_8$  (observed 44.3%, calcd 44.4%).

FT-IR spectra of  $\{\text{Ti}_6\text{O}_9\}$  cluster display the characteristic vibrations for the carboxy groups of ida (Fig. S4). The sharp absorption peaks at 1657(vs) and 1622(vs)  $\text{cm}^{-1}$  are attributed to the characteristic asymmetric stretching frequencies of the carboxy groups  $\nu_{\text{as}}(\text{COO})$ . The corresponding symmetric stretching vibrations  $\nu_{\text{s}}(\text{COO})$  appeared at 1441–1301  $\text{cm}^{-1}$ . They shift to lower values with respect to the carboxy groups of free ida ligand. The separation for the  $\nu_{\text{as}}(\text{COO})$  and  $\nu_{\text{s}}(\text{COO})$  peak positions is in the range 216 to 321  $\text{cm}^{-1}$ , suggesting the formation of the monodentate coordination of carboxylic acid to titanium via one oxygen atom.<sup>24</sup> Furthermore, the vibration bands for Ti-O and Ti-O-Ti bonds are present in 823 and 614  $\text{cm}^{-1}$ , respectively.<sup>25</sup> The FT-IR spectra agree with the results of X-ray structure determination. UV/vis diffuse reflectance spectra in the range between 190 and 700 nm (Fig. S5) display two absorption bands centered at 212 and 286 nm, respectively. Absorption bands at higher energies are assigned to the  $\pi_{\text{h}}^* \rightarrow d_{\sigma}^*$  LMCT transition involving framework titanium appears<sup>3d-3e</sup>, whereas the low energy bands arise from partially polymerized hexacoordinated Ti species, which contain Ti-O-Ti bonds in  $\{\text{Ti}_6\text{O}_9\}$  cluster<sup>26</sup>. The band gap of colorless  $\{\text{Ti}_6\text{O}_9\}$  cluster is around 3.7 eV, which corresponds to the onset energy of pure TOCs.<sup>3e</sup>

Cyclic voltammograms (CVs) are carried out to probe the redox stability of  $\{\text{Ti}_6\text{O}_9\}$  cluster in aqueous solutions (Fig. S6). The reduction process of Ti(IV) center of  $\{\text{Ti}_6\text{O}_9\}$  cluster in the negative potential region occur only at -0.675 V ( $E_{\text{pc}}$ ) via one electrochemically irreversible step.<sup>27</sup> However, no oxidation peaks were observed indicating that the initial oxidation state for the titanium centers is +4.<sup>28</sup>

#### The structural information of $\{\text{Ti}_6\text{O}_9\}$ cluster in aqueous solution.

Next, the structural information and stability of Ti-oxo cluster in aqueous media was investigated by solid/solution  $^{13}\text{C}$ -NMR spectroscopy and electrospray ionization mass spectra (ESI-MS). The solution  $^{13}\text{C}$  NMR spectra of  $\{\text{Ti}_6\text{O}_9\}$  cluster in  $\text{D}_2\text{O}$  revealed two set of resonances of carboxy ( $\delta$  183.91 and 174.07 ppm) and methylene carbons ( $\delta$  59.67 and 51.67 ppm), which might be attributed to the bound and decomposed free iminodiacetate (Fig. 4b). Compared with the corresponding carbons in  $\text{K}_2\text{ida}$  at the same pH 5.0 [ $\text{K}_2\text{ida}$ ,  $^{13}\text{C}$  NMR  $\delta_{\text{c}}(\text{D}_2\text{O}; \text{ppm})$ : 174.06 (COO) carboxy, 51.77 ( $\text{CH}_2$ ) methylene] (Fig. S7),  $\{\text{Ti}_6\text{O}_9\}$  cluster shows large downfield shifts of the carboxy carbon ( $\Delta\delta$  9.85 ppm) at 183.91 ppm and the methylene carbon ( $\Delta\delta$  7.90 ppm) at 59.67 ppm. This indicates that iminodiacetic acid groups are fully deprotonated and coordinated to the titanium cation simultaneously.<sup>29</sup> Moreover, the second set of  $^{13}\text{C}$  resonances [174.07 (COO) and 51.67 ( $\text{CH}_2$ ) ppm] in the highfield region are consistent with the shifts for free ida ligand ( $\Delta\delta$  0.01 and 0.1 ppm), which might demonstrate that ida ligands of  $\{\text{Ti}_6\text{O}_9\}$  cluster may undergo partial dissociation in aqueous solution. However, the solid state  $^{13}\text{C}$  NMR spectrum gives only one set of resonances of carboxy ( $\delta$  178.4 ppm) and methylene carbons ( $\delta$  55.8 ppm) without decomposition, which can be attributed to the coordinated ida ligand in a tridentate fashion (Fig. 4a). These results are in good agreement with solid-state structure from X-ray crystallography data. To gain further insight into the structural information of  $\{\text{Ti}_6\text{O}_9\}$  cluster in solution, we also investigated the ESI-MS spectrum of  $\{\text{Ti}_6\text{O}_9\}$  in a mixture of deionized water and acetonitrile (Fig. S8). The ESI-MS spectrum shows the entirety of  $[\text{Ti}_6\text{O}_9]^{6+}$  central core with various amounts of coordinated ida ligands, associated cations and water molecules (Fig. S8). All main distributions of peaks arise from doubly charged species. The mass peaks below  $m/z = 300$  clearly indicates the fragment of free ida ligands.

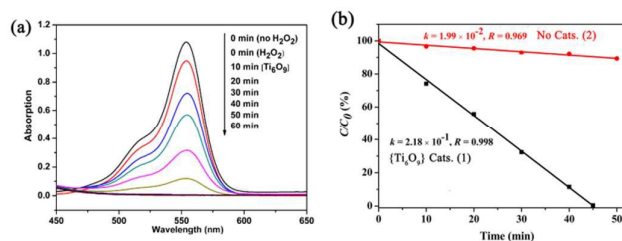


**Fig. 4** (a) Solid  $^{13}\text{C}$  NMR spectra of  $\{\text{Ti}_6\text{O}_9\}$  cluster; (b) Solution  $^{13}\text{C}$  NMR spectra of  $\{\text{Ti}_6\text{O}_9\}$  cluster.

#### Homogenous photodegradation of rhodamine B (RhB).

The homogeneous photocatalytic activity of  $\{\text{Ti}_6\text{O}_9\}$  cluster is evaluated by degradation of the rhodamine B (RhB) aqueous solution (10  $\mu\text{M}$ ) in the presence of hydrogen peroxide (20mmol, 2

mL) at room temperature.<sup>30</sup> The photocatalytic degradation process was monitored through the change in intensity of the characteristic absorption peak of RhB at 554 nm. Fig 5a displays that around 13% initial oxidation of RhB was observed by the addition of H<sub>2</sub>O<sub>2</sub> before visible light irradiation. As shown in Fig. 5a, it is noted that almost 99% decay of RhB is observed during 45 min in the system of {Ti<sub>6</sub>O<sub>9</sub>}/H<sub>2</sub>O<sub>2</sub> under the irradiation of visible light. However, no significant decrease of RhB concentrations after 50 min (only 22% decay) is observed in the presence of H<sub>2</sub>O<sub>2</sub> without {Ti<sub>6</sub>O<sub>9</sub>} catalyst (Fig. S9). The concentration of RhB ( $C/C_0$ ) decreases linearly with irradiation time via a zero-order process, and the coefficients  $R$  also show good linear dependent relation in Fig 5b. Obviously, the photodegradation rate constant  $k$  ( $2.18 \times 10^{-7} \text{ mol L}^{-1} \text{ min}^{-1}$ ) and half-life  $t_{1/2}$  (20 min) over {Ti<sub>6</sub>O<sub>9</sub>} cluster were much higher and shorter than  $k$  ( $1.99 \times 10^{-8} \text{ mol L}^{-1} \text{ min}^{-1}$ ) and  $t_{1/2}$  (219 min) in the absence of {Ti<sub>6</sub>O<sub>9</sub>} catalyst, respectively. These results indicate that {Ti<sub>6</sub>O<sub>9</sub>} catalyst exhibited excellent homogenous photocatalytic degradation efficiency for RhB. As the previously reported hexanuclear Ti-oxo cluster Ti<sub>6</sub>O<sub>3</sub>(o-BDC)<sub>2</sub>(OiPr)<sub>14</sub><sup>10h</sup>, {Ti<sub>6</sub>O<sub>3</sub>}, the photodegradation kinetics of dye displayed an exponential decay curve via a pseudo-first-order process in the system of {Ti<sub>6</sub>O<sub>3</sub>}/H<sub>2</sub>O<sub>2</sub>. Therefore, we speculate that the photocatalytic mechanism by new {Ti<sub>6</sub>O<sub>9</sub>} cluster is different from the pathway described for the known {Ti<sub>6</sub>O<sub>3</sub>} catalyst.<sup>10h</sup>

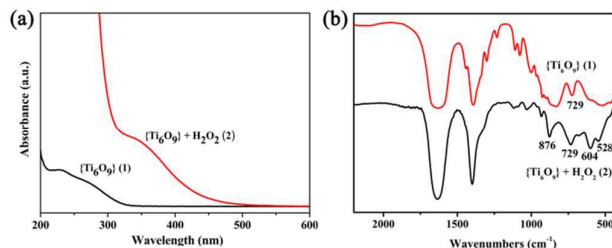


**Fig. 5** (a) Absorption spectra of RhB during the photocatalytic degradation under visible light in presence of {Ti<sub>6</sub>O<sub>9</sub>} cluster (50 mg) with H<sub>2</sub>O<sub>2</sub> (20 mmol, 2 mL); (b) Photodegradation of RhB illuminated by visible light versus irradiation time. [Reaction conditions: (1) 100 mL aqueous solution of RhB (10 μM) with 50 mg of {Ti<sub>6</sub>O<sub>9</sub>} cluster, H<sub>2</sub>O<sub>2</sub> (2 mL, 20 mmol); (2) 100 mL aqueous solution of RhB (10 μM), H<sub>2</sub>O<sub>2</sub> (2 mL, 20 mmol). Also shows the values of the photodegradation rate constant  $k$  ( $\times 10^{-6} \text{ mol L}^{-1} \text{ min}^{-1}$ ) and the linearly dependent coefficient  $R$ ].

#### Catalytic reaction pathways.

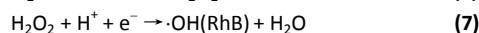
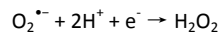
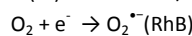
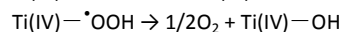
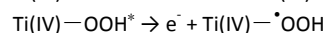
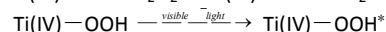
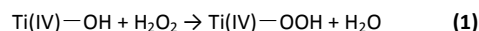
To gain further insight into the photocatalytic mechanism, we investigated the reactivity of {Ti<sub>6</sub>O<sub>9</sub>} photocatalyst towards hydrogen peroxide. Reference UV spectra of {Ti<sub>6</sub>O<sub>9</sub>} cluster in aqueous solution at pH 6.0 agree well with solid state spectra, which underlines the framework stability of the Ti-oxo cluster (Fig. 6a). UV spectra are altered after addition of hydrogen peroxide and the absorption edge shifts from 334 nm to 412 nm which indicates the formation of a characteristic yellow peroxotitanium species [Ti(O<sub>2</sub>)] (Fig. 6a)<sup>31</sup>. Moreover, addition of hydrogen peroxide to a {Ti<sub>6</sub>O<sub>9</sub>} cluster also leads to differences in the FT-IR spectra compared to {Ti<sub>6</sub>O<sub>9</sub>} cluster in the absence of hydrogen peroxide (Fig. 6b). A new weak band appears at 875 cm<sup>-1</sup> which arises from the stretching vibration ν(O-O) of the peroxy groups in {Ti<sub>6</sub>O<sub>9</sub>} cluster (Fig. 6b).<sup>32</sup> Two new bands appear at 604 and 528 cm<sup>-1</sup>,

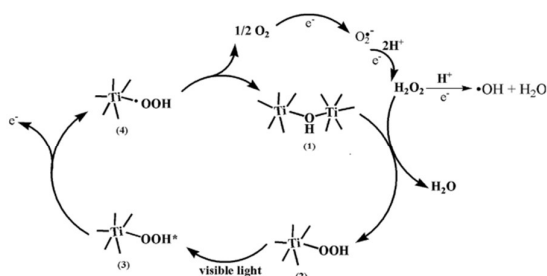
which can be assigned to characteristic stretching vibrations ν<sub>s</sub>[Ti(O<sub>2</sub>)] and ν<sub>as</sub>[Ti(O<sub>2</sub>)] of the peroxy structural unit [Ti(O<sub>2</sub>)] (Fig. 6b).<sup>33</sup> In addition, no photochromism is detected on {Ti<sub>6</sub>O<sub>9</sub>} cluster upon UV irradiation by a halogen lamp in the presence of alcohol, which further confirms that the absence of Ti(IV)/Ti(III) transfer in this system of {Ti<sub>6</sub>O<sub>9</sub>} cluster/H<sub>2</sub>O<sub>2</sub>.<sup>10h</sup>



**Fig. 6** (a) UV/vis spectra of {Ti<sub>6</sub>O<sub>9</sub>} cluster in solution (1), and {Ti<sub>6</sub>O<sub>9</sub>} cluster after treatment with excess of H<sub>2</sub>O<sub>2</sub> reaction (2); (b) FT-IR spectra of {Ti<sub>6</sub>O<sub>9</sub>} cluster in aqueous solution (1), and {Ti<sub>6</sub>O<sub>9</sub>} cluster after treatment with excess of H<sub>2</sub>O<sub>2</sub> reaction (2).

Based on these results, we propose a Ti(IV)-peroxy-mediated catalytic pathway for photocatalytic degradation of RhB with hydrogen peroxide in the presence of {Ti<sub>6</sub>O<sub>9</sub>} cluster (Fig. 7).<sup>34</sup> Initially, the protonated species Ti-OH (1) of {Ti<sub>6</sub>O<sub>9</sub>} cluster in acidic aqueous solutions (pH 3.2) reacts with hydrogen peroxide to form Ti-hydroperoxy complex (2) [Fig. 7, Eq. (1)], accompanied by the photo-response from UV region to visible light region (Fig. 6a). Next, Ti(IV)-hydroperoxy complex (2) serves as a photosensitizer and is excited by visible light from ground state to excited state of Ti-hydroperoxy species Ti-OOH\* (3) [Fig. 7, Eq. (2)]. In the meantime, an electron is ejected from the excited state complex (3) thereby generating Ti-hydroperoxy radical Ti-OOH• (4) [Fig. 7, Eq. (3)]. Ti-OOH• radical (4) is highly active and tends to self-react to resume the initial Ti-OH species (1) in association with releasing O<sub>2</sub> [Fig. 7, Eq. (4)]. Released O<sub>2</sub> captures an electron to generate superoxide radical O<sub>2</sub><sup>•-</sup> possessing strong oxidation ability thereby initiating the degradation of RhB [Eq. (5)]. The superoxide radical (O<sub>2</sub><sup>•-</sup>) can be further reduced by one electron to form hydrogen peroxide [Eq. (6)]. Hydroxyl radical •OH is produced from one-electron reduction of H<sub>2</sub>O<sub>2</sub> [Eq. (7)]. Both the hydroxyl radical •OH and superoxide radical O<sub>2</sub><sup>•-</sup> are the primary oxidizing species in the photocatalytic degradation of RhB.<sup>35</sup>





**Fig. 7** Proposed visible light photocatalytic degradation mechanism of RhB over  $\{Ti_6O_9\}$  photocatalyst.

## Conclusions

In summary, we have obtained a novel family of titanium-oxo clusters  $\{Ti_6O_9\}$  through incorporation of iminodiacetate ligands (ida) that the structure is identified by complementary crystallographic and analytical evidences. This compound consists of two staggered triangular  $\{Ti_3O_3\}$  subunits connected by three  $\mu_2$ -O bridges, leading to a new hexameric oxo core  $\{Ti_6O_9\}$  surrounded by six ida ligands. Seven alkali metal potassium cations were introduced into the  $\{Ti_6O_9\}$  system as bridging linkers to assemble a 8-connected network 3D network. Moreover,  $\{Ti_6O_9\}$  cluster exhibits remarkable visible-light photocatalytic activities for homogenous photodegradation of rhodamine B in the aqueous medium, and the complete removal of RhB was reached in 45 min. Pseudo-zero-order degradation rate constant was found from the batch experimental data. A Ti-peroxo-mediated catalytic pathway for photodegradation reaction was proposed and further suggested by spectroscopic investigations. Therefore, this well characterized new Ti-oxo cluster might bring forward the potential applications in photocatalysis and solar energy harvesting.

## Acknowledgements

This work was supported by the National Natural Science Foundation of China (Grant No. 21401162), the Natural Science Foundation of the Jiangsu Higher Education Institutions of China (Grant No. 14KJB430024), Jiangsu Provincial Postdoctoral Sustentation Fund (Grant No. 1402015B). Financial support from the Priority Academic Program Development of Jiangsu Higher Education Institutions and the Natural Science Foundation of Education Committee of Jiangsu Province (12KJB150023) is gratefully acknowledged. The authors also acknowledge the Testing Center of Yangzhou University for ESI-MS measurements.

## Notes and references

- (a) L. Rozes, C. Sanchez, *Chem. Soc. Rev.*, 2011, **40**, 1006; (b) L. Rozes, N. Steunou, G. Fornasieri, and C. Sanchez, *Monatsh. für Chemie*, 2006, **137**, 501; (c) D. Fattakhova-Rohlfing, A. Zaleska,

and T. Bein, *Chem. Rev.*, 2014, **114**, 9487; (d) P. Coppens, Y. Chen, E. Trzop, *Chem. Rev.*, 2014, **114**, 9645.

- K. Watenpau and C. N. Caughlan, *Chem. Commun.* 1967, 76.
- (a) S. Yuan, T.-F. Liu, D. Feng, J. Tian, K. Wang, J. Qin, Q. Zhang, Y.-P. Chen, M. Bosch, L. Zou, J. Teat, J. Dalgarnoc and H.-C. Zhou, *Chem. Sci.*, 2015, **6**, 3926; (b) J.-L. Hou, W. Luo, Y.-Y. Wu, H.-C. Su, G.-L. Zhang, Q.-Y. Zhu and J. Dai, *Dalton Trans.*, 2015, **44**, 19829; (c) F. Stehlin, F. Wieder, A. Spangenberg, J.-M. Le Meins, O. Soppera, *J. Mater. Chem. C*, 2014, **2**, 277; (d) J. -X. Yin, P. Huo, S. Wang, J. Wu, Q. -Y. Zhu and J. Dai, *J. Mater. Chem. C*, 2015, **3**, 409; (e) Y.-Y. Wu, P. Wang, Y.-H. Wang, J.-B. Jiang, G.-Q. Bian, Q.-Y. Zhu, J. Dai, *J. Mater. Chem. A*, 2013, **1**, 9862; (f) Z. Liu, J. Lei, M. Frascioni, X. Li, D. Cao, Z. Zhu, T. Schneebeli, C. Schatz, and J. Fraser Stoddart, *Angew. Chem. Int. Ed.* 2014, **53**, 9193.
- (a) X. Chen, S. S. Mao, *Chem. Rev.* 2007, **107**, 2891; (b) T. L. Thompson, J. T. Yates, *Chem. Rev.* 2006, **106**, 4428; (c) C. Chen, W. Ma, J. Zhao, *Chem. Soc. Rev.*, 2010, **39**, 4206; (d) G. Liu, L. Wang, H. G. Yang, H.-M. Cheng, G. Q. Lu, *J. Mater. Chem.* 2010, **20**, 831; (e) M. Gratzel, *Acc. Chem. Res.* 2009, **42**, 1788; (f) J. Yan, F. J. Zhou, *Mater. Chem.* 2011, **21**, 9406.
- (a) N. A. Mashayekhi, Y. Y. Wu, M. C. Kung and H. H. Kung, *Chem. Commun.*, 2012, **48**, 10096; (b) D. Feng, J. Tian, K. Wang, J. Qin, Q. Zhang, Y.-P. Chen, M. Bosch, L. Zou, S. Teat, S. Dalgarno, H. -C. Zhou, *Chem. Sci.*, 2015, **6**, 3926.
- (a) V. W. Day, T. A. Eberspacher, W. G. Klemperer, C. W. Park and F. S. Rosenberg, *J. Am. Chem. Soc.*, 1991, **113**, 8190; (b) G. Fornasieri, L. Rozes, S. Le Calve, B. Alonso, D. Massiot, M. N. Rager, M. Evain, K. Boubekeur and C. Sanchez, *J. Am. Chem. Soc.*, 2005, **127**, 4869; (c) V. W. Day, T. A. Eberspacher, W. G. Klemperer and C. W. Park, *J. Am. Chem. Soc.*, 1993, **115**, 8469; (d) S. Eslava, A. C. Papageorgiou, S. K. Beaumont, G. Kyriakou, D. S. Wright and R. M. Lambert, *Chem. Mater.*, 2010, **22**, 5174; (e) N. Steunou, G. Kickelbick, K. Boubekeur and C. M. Sanchez, *J. Chem. Soc., Dalton Trans.*, 1999, 3653; (f) C. F. Campana, Y. Chen, V. W. Day, W. G. Klemperer and R. A. Sparks, *J. Chem. Soc., Dalton Trans.*, 1996, 691.
- (a) A. Mosset and J. Galy, *C. R. Acad. Sci., Ser. II: Mec., Phys., Chim., Sci. Terre Univers*, 1988, **307**, 1747; (b) R. Schmid, A. Mosset and J. Galy, *J. Chem. Soc., Dalton Trans.*, 1991, 1999; (c) N. Steunou, F. Ribot, K. Boubekeur, J. Maquet and C. Sanchez, *New J. Chem.*, 1999, **23**, 1079; (d) F. Perineau, S. Pensec, C. Sassoie, F. Ribot, L. van Lokeren, R. Willem, L. Bouteiller, C. Sanchez, L. Rozes, *J. Mater. Chem.*, 2011, **21**, 4470.
- (a) A. Pandey, V. D. Gupta and H. Noth, *Eur. J. Inorg. Chem.*, 2000, 1351; (b) T. J. Boyle, R. P. Tyner, T. M. Alam, B. L. Scott, J. W. Ziller and B. G. Potter, *J. Am. Chem. Soc.*, 1999, **121**, 12104; (c) I. Mijatovic, G. Kickelbick, M. Puchberger and U. Schubert, *New J. Chem.*, 2003, **27**, 3; (d) A. Senouci, M. Yaakoub, C. Huguenard and M. Henry, *J. Mater. Chem.*, 2004, **14**, 3215; (e) B. Moraru, N. Husing, G. Kickelbick, U. Schubert, P. Fratzl and H. Peterlik, *Chem. Mater.*, 2002, **14**, 2732; (f) P. Piszczek, A. Radtke, T. Muzioł, M. Richert and J. Chojnacki, *Dalton Trans.*, 2012, **41**, 8261; (g) T. J. Boyle, T. M. Alam, C. J. Tafoya and B. L. Scott, *Inorg. Chem.*, 1998, **37**, 5588; (h) R. Ghosh, M. Nethaji and A. G. Samuelson, *Chem. Commun.*, 2003, 2556.
- (a) Y. Gao, F. R. Kogler, H. Peterlik and U. Schubert, *J. Mater. Chem.*, 2006, **16**, 3268; (b) G. Kickelbick, D. Holzinger, C. Brick, G. Trimmel and E. Moons, *Chem. Mater.*, 2002, **14**, 4382; (c) I. Mijatovic, G. Kickelbick and U. Schubert, *Eur. J. Inorg. Chem.*, 2001, 1933.
- (a) J. D. Sokolow, E. Trzop, Y. Chen, J.-J. Tang, L. J. Allen, R. H. Crabtree, J. B. Benedict and P. Coppens, *J. Am. Chem. Soc.* 2012, **134**, 11695; (b) J. B. Benedict, R. Freindorf, E. Trzop, J. Cogswell and P. Coppens, *J. Am. Chem. Soc.*, 2010, **132**, 13669; (c) K. Hong and H. Chun, *Inorg. Chem.*, 2013, **52**, 9705; (d) A. Radtke, P. Piszczek, T. Muzioł, A. Wojtczak, *Inorg. Chem.* 2014, **53**,

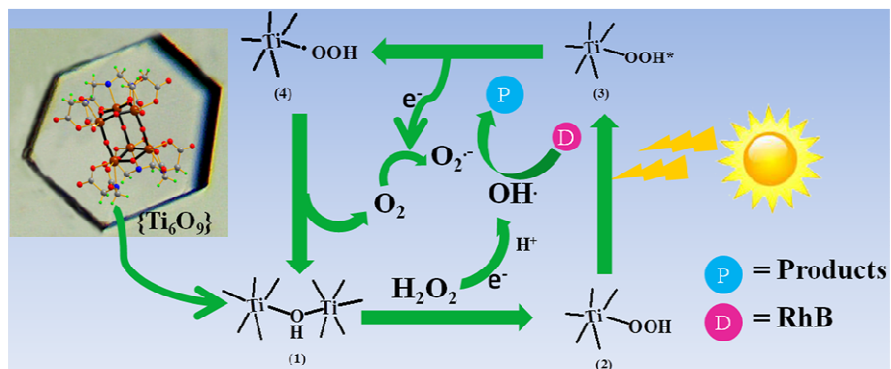
- 10803; (e) Y. -Y. Wu, X. -W. Lu, M. Qi, H. -C. Su, X. -W. Zhao, Q. -Y. Zhu, J. Dai, *Inorg. Chem.* 2014, **53**, 7233; (f) K. Hong, W. Bak, and H. Chun, *Inorg. Chem.* 2014, **53**, 7288; (g) K. Roztocki, D. Matoga, J. Szklarzewicz, *Inorg. Chem. Comm.* 2014, **40**, 22; (h) Y.-Y. Wu, W. Luo, Y.-H. Wang, Y.-Y. Pu, X. Zhang, L.-S. You, Q.-Y. Zhu and J. Dai, *Inorg. Chem.* 2012, **51**, 8982.
- 11 (a) M. Dakanali, E. T. Kefalas, C. P. Raptopoulou, A. Terzis, G. Voyiatzis; I. Kyrikou, T. Mavromoustakos, A. Salifoglou, *Inorg. Chem.* 2003, **42**, 4632; (b) K. Wiegardt, U. Quilitzsch, J. Weiss, B. Nuber, *Inorg. Chem.* 1980, **19**, 2514; (c) Y. Miyashita, M. M. Islam, N. Amir, K. Fujisawa, K. Okamoto, *Chem. Lett.*, 2004, **33**, 1516; (d) K. Hayashi, H. Murakami, and K. Nomiya, *Inorg. Chem.*, 2006, **45**, 8078; (e) T. Frot, S. Cochet, G. Laurent, C. Sassoie, M. Popall, C. Sanchez and L. Rozes, *Eur. J. Inorg. Chem.* 2010, 5650; (f) T. Frot, J. Marrot, C. Sanchez, L. Rozes, C. Sassoie, *Z. Anorg. Allg. Chem.* 2013, **639**, 2181; (g) T. Kemmitt, N. I. Al-Salim, G. J. Gainsford, A. Bubendorfer, M. Waterland, *Inorg. Chem.* 2004, **43**, 6300; (h) M. Dan-Hardi, C. Serre, T. Frot, L. Rozes, G. Maurin, C. Sanchez and G. Férey, /
- 12 Leading Edge Organometallic Chemistry Research (Eds.: M. A. Cato), Nova, New York, 2006.
- 13 (a) J. Porath, J. Carlsson, I. Olsson, G. Belfrage, *Nature*, 1975, **258**, 598; (b) T. Koike, S. Kajitani, I. Nakamura, E. Kimura, M. Shiro, *J. Am. Chem. Soc.* 1995, **117**, 1210.
- 14 Oxford Diffraction, CrysAlis CCD and CrysAlis RED, Oxford Diffraction Ltd., Abingdon, UK, 2005.
- 15 L. J. Farrugia, *J. Appl. Crystallogr.* 1999, **32**, 837.
- 16 G. M. Sheldrick, SHELX97, *Programs for Crystal Structure Analysis*; Release 97-2; University of Göttingen, Göttingen: Germany, 1997.
- 17 (a) I. V. Ogorodnyk, I. V. Zatovsky, N. S. Slobodyanik, *Acta Cryst. E*, 2009, **65**, i63; (b) I. V. Zatovsky, *Acta Cryst. E*, 2014, **70**, i41.
- 18 N. L. Rosi, J. Kim, M. Eddaoudi, B. Chen, M. O'Keeffe, O. M. Yaghi, *J. Am. Chem. Soc.* 2005, **127**, 1504.
- 19 V. A. Blatov and D. M. Proserpio, TOPOS 4.0, A program package for multipurpose crystallochemical analysis.
- 20 (a) N. Steunou, F. Robert, K. Boubekour, F. Ribot and C. Sanchez, *Inorg. Chim. Acta*, 1998, **279**, 144; (b) X. J. Lei, M. Y. Shang and T. P. Fehlnner, *Organometallics*, 1997, **16**, 5289; (c) X. J. Lei, M. Y. Shang and T. P. Fehlnner, *Organometallics*, 1996, **15**, 3779; (d) S. Doeuff, Y. Dromzee and C. Sanchez, *C. R. Acad. Sci., Ser. II: Mec., Phys., Chim., Sci. Terre Univers*, 1989, **308**, 1409.
- 21 (a) R. Papiernik, L. G. Hubert-Pfalzgraf, J. Vaissermann and M. Goncalves, *J. Chem. Soc., Dalton Trans.*, 1998, 2285; (b) G. A. Seisenbaeva, E. Ilina, S. Hakansson and V. G. Kessler, *J. Sol-Gel Sci. Technol.*, 2010, **55**, 1; (c) A. Rammal, F. Brisach and M. Henry, *C. R. Chim.*, 2002, **5**, 59; (d) P. Piszczek, A. Grodzicki, M. Richert and A. Wojtczak, *Inorg. Chim. Acta*, 2004, **357**, 2769; (e) P. Piszczek, M. Richert and A. Wojtczak, *Polyhedron*, 2008, **27**, 602.
- 22 (a) G. J. Palenik, *Inorg. Chem.* 1997, **36**, 3394; (b) I. D. Brown and D. Altermatt, *Acta Crystallogr. Sect. B.*, 1985, **41**, 244; (c) A. Trzesowska, R. Kruszynski and T. J. Bartczak, *Acta Crystallogr. Sect. B*, 2004, **60**, 174.
- 23 (a) P. Mialane, A. Dolbecq, L. Lisnard, A. Mallard, J. Marrot, F. Sécheresse, *Angew. Chem.* 2002, **114**, 2504; (b) V. A. Wright and D. P. Gates, *Angew. Chem. Int. Ed.* 2002, **41**, 2398; (c) H. Y. An, E. B. Wang, D. R. Xiao, Y. G. Li, Z. M. Su, L. Xu, *Angew. Chem.* 2006, **118**, 918; (d) Y. G. Li, Z. M. Su, L. Xu, *Angew. Chem. Int. Ed.* 2006, **45**, 904; (e) D. Y. Du, J. S. Qin, S. L. Li, Y. Q. Lan, X. L. Wang, Z. M. Su, *Aust. J. Chem.* 2010, **63**, 1398.
- 24 D. C. L. Vasconcelos, V. C. Costa, E. H. M. Nunes, A. C. S. Sabioni, M. Gasparon, W. L. Vasconcelos, *Mater. Sci. Appl*, 2011, **2**, 1375.
- 25 (a) R. Parra, M. S. Goes, M. S. Castro, E. Longo, P. R. Bueno, and J. A. Varela, *Chem. Mater.* 2008, **20**, 143; (b) Q. -X. Liu, Z.-H. Zhou, *Polyhedron*, 2012, **35**, 1.
- 26 (a) T. Blasco, M. A. Cambor, A. Corma and J. Perez-Pariente, *J. Am. Chem. Soc.* 1993, **115**, 11806; (b) G. Li, X. -S. Wang, X. -W. Guo, S. Liu, Q. Zhao, X. -H. Bao, L.-W. Lin, *Mater Chem Phys* 2001, **71**, 195.
- 27 (a) R. Uppal, C. D. Incarvito, K. V. Lakshmi, and A. M. Valentine, *Inorg. Chem.* 2006, **45**, 1795; (b) F. -F. Li, N. Chen, M. Mulet-Gas, V. Triana, J. Murillo, A. Rodriguez-Fortea, J. M. Poblet, L. Echegoyen, *Chem. Sci.*, 2013, **4**, 3404.
- 28 (a) P. Panagiotidis, E. T. Kefalas, C. P. Raptopoulou, A. Terzis, T. Mavromoustakos, A. Salifoglou, *Inorg Chim Acta*, 2008, **361**, 2210; (b) T. McGlone, L. Vila-Nadal, H. N. Miras, D.-L. Long, J. M. Poblet, L. Cronin, *Dalton Trans.*, 2010, **39**, 11599.
- 29 (a) G. Fornasieri, L. Rozes, S. Le Calvé, B. Alonso, D. Massiot, M. N. Rager, M. Evain, K. Boubekour, C. Sanchez, *J. Am. Chem. Soc.* 2005, **127**, 4869. (b) L.-B. Ni, R. -H. Zhang, Q. -X. Liu, W.-S. Xia, H. X. Wang, Z.-H. Zhou, *J. Solid State. Chem.* 2009, **182**, 2698; (c) Y.-F. Deng, Z. -H. Zhou, and H.-L. Wan, *Inorg. Chem.* 2004, **43**, 6266.
- 30 (a) Y. F. Rao, W. Chu, *Environ. Sci. Technol.* 2009, **43**, 6183. (b) C. C. Wang, W. Chu, *Environ. Sci. Technol.* 2003, **37**, 2310. (c) T. Hirakawa, Y. Nosaka, *Langmuir* 2002, **18**, 3247. (d) R. Selvin, H. Hsu, N. S. Arul, S. Mathew, *Sci. Adv. Mater.* 2010, **2**, 58.
- 31 (a) C. B. Allsopp, W. G. Leach, *Analyst*, 1941, **66**, 371; (b) W. A. Patrick and H. B. Wagner, *Anal. Chem.* 1949, **21**, 1279; (c) D. W. O'Sullivan, and M. Tyree, *Int J Chem Kinet*, 2007, **39**, 457.
- 32 F. Bonino, A. Damin, G. Ricchiardi, M. Ricci, G. Spanò, R. D'Aloisio, A. Zecchina, C. Lamberti, C. Prestipino, and S. Bordiga, *J. Phys. Chem. B*, 2004, **108**, 3573.
- 33 P. Jeske, G. Haselhorst, T. Weyhermueller, K. Wiegardt, B. Nuber, *Inorg. Chem.* 1994, **33**, 2462.
- 34 (a) Y. Wang, X.-J. Meng, X. -L. Yu, M. Zhang, J. -J. Yang, *Appl. Catal. B: Environ.* 2013, **138-139**, 326; (b) Y. Qiu and X. -J. Li, *Dalton Trans.*, 2014, **43**, 14537.
- 35 P. Pichat, *Photocatalysis and Water Purification: From Fundamentals to Recent Applications*, Wiley-VCH Verlag GmbH & Co. KGaA, Germany, Weinheim, 2013.



Graphical and textual abstract for the contents pages:

**A Novel Hexanuclear Titanium(IV)-oxo-iminodiacetate Cluster with  $\text{Ti}_6\text{O}_9$  Core: Single-Crystal Structure and Photocatalytic Activities.**

Lubin Ni<sup>a</sup>, Dashuai Liang<sup>a</sup>, Yin Cai<sup>a</sup>, Guowang Diao<sup>\*a</sup>, Zhaohui Zhou<sup>\*b</sup>



A new family of hexanuclear titanium(IV)-oxo-carboxylate cluster containing  $\{\text{Ti}_6\text{O}_9\}$  core exhibiting remarkable potential as a visible-light homogenous photocatalyst.