



Interfacial charge transfer in a functionalized polyoxotitanate cluster



Jie Hou^a, Qun Zhang^b, Yufei Wu^a, Yuliang Liu^a, Lin Du^{b,*}, Chen-Ho Tung^a, Yifeng Wang^{a,*}

^a Key Lab for Colloid and Interface Science of Ministry of Education, School of Chemistry and Chemical Engineering, Shandong University, Ji'nan 250199, PR China

^b Environment Research Institute, Shandong University, Ji'nan 250199, PR China

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ABSTRACT

Understanding the charge transfer processes at the dye/TiO₂ interface is often modeled using catechol/TiO₂ systems. However, it indeed require precise structural information. In order to simulate the dye/TiO₂ systems at a molecular level, herein we report the synthesis and structure of a novel titanium oxo-cluster [Ti₄O(OⁱPr)₆(DTBC)₄] (**1**) functionalized with 3,5-di-tert-butylcatechol (DTBC). UV–Vis spectroscopy, electron spin resonance (ESR), X-ray photoelectron spectroscopy (XPS) and density functional theory (DFT) calculations show that **1** exhibits property of Ti(III) which is caused by substantial charge transfer from the π electrons of the benzene rings to Ti3d orbitals. The present precise structure and charge transfer mechanism help to better understand chromophore binding to semiconductor surfaces and charge transfer at the dye/TiO₂ interfaces.

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1. Introduction

Charge transfer at the dye/TiO₂ interface is a fundamental process that is involved in dye-sensitized solar cells [1] and photosensitized dye degradation [2]. Recently, it has been demonstrated that phenol-derivatives, especially pyrocatechol-derivatives can bind to TiO₂ surfaces and endow the nanoparticles with strong visible-light absorption and properties of Ti(III) [3–6]. In these systems, photo-induced electron injection is strongly affected by the binding modes of the ligands on the semiconductor surfaces. Importantly, the catechol moiety (and similar structures) is not only the functional group of many artificial dyes but also found common in many naturally occurred chromophores [7–9]. While density functional theory (DFT) calculation [10,11], and other methods like transient spectra [4,5], STM [11], ESR [8], vibration spectra and electrochemistry [12] have been applied extensively to understand the structure and charge-transfer, precise structural information has been indeed unavailable or experimentally inaccessible [11,12].

In recent years, polyoxotitanates [13,14] functionalized with ligands like catechol, isonicotinate and phosphonate have been reported by several groups [15–19]. These precise structures obtained by X-ray diffraction possessing similar binding modes of the ligands at the ligand/TiO₂ interfaces have provided

opportunities to study the interfacial electron transfer at a molecular level [13,20].

In this study, we present the synthesis, structure, spectroscopy and theoretical studies of a novel titanium oxo-cluster [Ti₄O(OⁱPr)₆(DTBC)₄] (**1**) bonded with 3,5-di-tert-butylcatechol (DTBC). The model ligand DTBC and the polyoxotitanate framework are both colorless while the cluster compounds absorb substantially in the visible region, suggesting a similar charge transfer process to that in pyrocatechol/TiO₂ systems. While the binding mode of DTBC to the titanium-oxo framework is inspiring for catechol binding to TiO₂, compound **1** exhibits properties of Ti(III)—also similar to catechol-functionalized TiO₂ nanoparticles. The charge transfer can be further enhanced by visible-light irradiation. Hence compound **1** can be used to simulate the charge transfer in dye/TiO₂ systems at a molecular level. Based on the experimental and theoretical results, it becomes clearer now that the charge transfer occurs between π orbitals in the benzene rings and the Ti3d orbitals in the titanium-oxo framework.

2. Experimental

2.1. Chemicals

Titanium tetraisopropoxide (TTIP) was purchased from Sigma–Aldrich. 3,5-Di-tert-butylcatechol (DTBC) was obtained from Alfa-Aesar. Isopropanol was obtained from Fisher. All the solvents were dried by distillation with CaO before use.

* Corresponding authors.

E-mail addresses: lindu@sdu.edu.cn (L. Du), yifeng@sdu.edu.cn (Y. Wang).

2.2. Instruments

All the water-sensitive materials were handled in a glovebox (Mikrouna China Co. Ltd). Elemental analyses (C, H) were obtained by a FLASH EA1112 elemental analyzer. UV–Vis absorption spectra were measured on Agilent Cary 60 spectrophotometer. X-ray photoelectron spectroscopy (XPS) spectra were recorded using the Omicron (ESCA+) spectrometer using an Al K α source (1486.6 eV). Electron spin resonance (ESR) measurements were performed on a Bruker ESR E500 instrument.

2.3. Synthesis of [Ti₄O(OⁱPr)₆(DTBC)₄] (**1**)

To a 25 mL Teflon-lined Parr bomb a mixture of TTIP (1.00 g; 3.50 mmol), DTBC (0.366 g; 1.60 mmol) and isopropanol (16.0 mL) were added. The bomb was sealed and then maintained 100 °C for 3 days. After slow cooling (2 °C h⁻¹), a dark-red solution was obtained and allowed to stand. After several days, dark-red crystals of **1** appeared which were collected by filtration, washed with isopropanol and stored in the glove box. Yield: 328 mg (57.5% based on DTBC). Elemental Anal. Calc.: C, 61.58; H, 8.52. Found: C, 60.52; H, 8.59%. IR was provided as Fig. S1 in the Supporting Information. ¹³C NMR: (CD₂Cl₂, δ ppm; Fig. S2): 110.31, 113.24, 131.19, 143.57, 151.78, 156.59 (4C₆H₆); 24.24, 25.36, 25.50, 29.79, 31.71, 34.29 (8 C(CH₃)₃ and 12 CH₃); 77.24, 81.34 (6 OCH₂CH₃).

2.4. X-ray crystallography

A crystal was mounted with an optical microscope under cryo-N₂ steam. Data were collected at 173 K using a Bruker SMART APEX II diffractometer with a CCD area detector using Mo K α radiation ($\lambda = 0.71073$ Å). Indexing was made with APEX2, data integration and reduction were performed using SaintPlus 6.01 [21], and absorption correction was made using SADABS [22]. Structure solution and refinement were performed using the Olex2 v1.2 software [23], the SHELX package and the least-square method. Hydrogen atoms were added as riding atoms theoretically. The crystallographic data are shown in Table 1.

Table 1
Crystallographic data of **1**.

Formula	Ti ₄ O ₁₅ C ₇₄ H ₁₂₂
Formula weight	1443.31
Crystal system	monoclinic
Space group	P21/C
T (K)	173
a (Å)	17.229(3)
b (Å)	22.147(4)
c (Å)	22.196(4)
α (°)	90
β (°)	101.626(2)
γ (°)	90
V (Å ³)	8296(3)
Z	4
D _{calc} (g/cm ³)	1.156
Abs. Coeff. μ (mm ⁻¹)	0.427
Total reflections	60286
Min–max θ (°)	4.85–55.204
Unique reflections	59525
Calculated reflection ($I > 4\sigma$)	11594
R ₁ [$I \geq 2\sigma$]	0.0886
wR ₂ (all data)	0.2569
R _{int}	0.0758
Goodness of fit (GOF) on F ²	1.075
Parameters	883
Restraints	50
Largest difference peak/hole (e Å ⁻³)	1.45/–0.73

2.5. ESR measurements

Experiments were conducted at ambient temperature and the settings were: central field, 3480.00 G; sweep width, 300 G; microwave frequency, ca. 9.73 GHz; modulation frequency, 5.00 kHz; microwave power, 10.11 mW. 532 nm laser was used to irradiate the samples. The ESR signals were simulated with Hyperfine Spectrum program within the Biomolecular EPR Spectroscopy package.

2.6. Density functional theory (DFT) calculations

Density of states (DOS) and time-dependent DFT (TDDFT) calculations were performed in the Gaussian 09 package at the B3LYP/6-31G level of theory. The experimentally determined geometric parameters of compound **1** were used for calculations. The density of states (DOS) diagram was obtained using the Multiwfn software. The UV–Vis spectrum was calculated using time-dependent DFT (TDDFT) method. For this, Self-Consistent Reaction Field (SCRF) calculation with Polarizable Continuum Model (PCM) was used to define the solvent as isopropanol, and 200 lowest-energy states were computed to cover the visible and UV region of the electronic spectrum.

3. Results and discussion

3.1. Synthesis and structure

Synthesis of **1** involves the solvothermal treatment of TTIP in anhydrous isopropanol in the presence of DTBC. Isopropyl ether

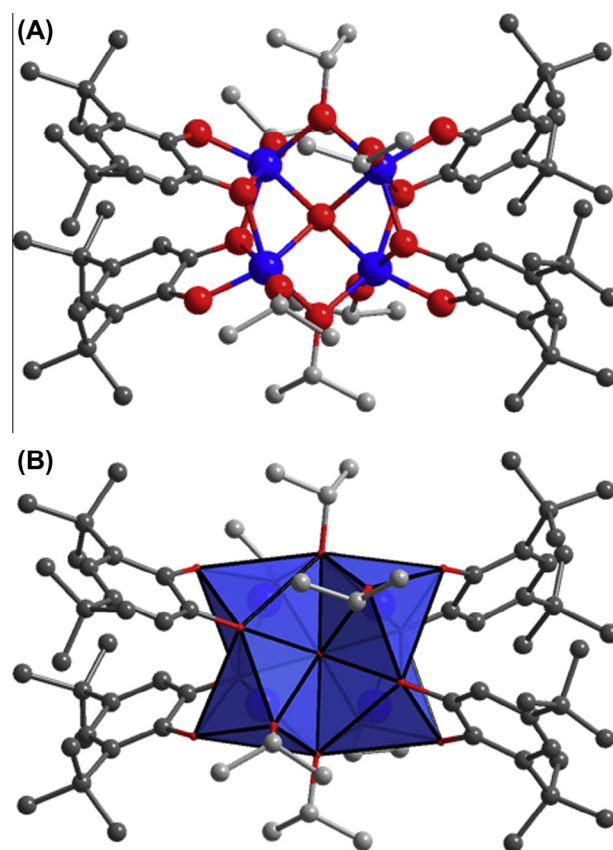


Fig. 1. (A) ball-and-stick and (B) combined ball-and-stick and polyhedral views of cluster compound **1**. Color scheme: Ti, blue; O, red; C, gray. The TiO₆ moieties are drawn into octahedrons with Ti at the center. For clarity, hydrogen atoms are omitted. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

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