

Supporting Materials

Relating structure and photoelectrochemical properties: electron injection by structurally and theoretically characterized transition metal-doped phenanthroline-polyoxotitanate nanoparticles

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1S. Synthesis of $Ti_{17}O_{28}(O^iPr)_{16}(Fe^{II}Phen)_2$ and crystallization

All of the reagents and solvents were purchased from commercial sources and used without further purification. Titanium(IV) isopropoxide (99.999%) and iron(II) acetate ($\geq 99.99\%$) were purchased from Sigma-Aldrich, 1,10-phenanthroline monohydrate ($\geq 99\%$) from Acros Organics, whereas 2-propanol (anhydrous, $\geq 99.5\%$) was purchased from Alfa Aesar. Compounds containing titanium were stored and handled in a nitrogen glove-box atmosphere.

Titanium(IV) isopropoxide (0.2 ml, 0.67 mmol), iron(II) acetate (11.7 mg, 0.067 mmol), 1,10-phenanthroline monohydrate (13.3 mg, 0.067 mmol) and 0.5 ml of 2-propanol were mixed together in a Pyrex glass tube (15 cm in length, 8.14 mm in inner diameter and 11.14 mm in outer diameter) in a standard glove-box under nitrogen atmosphere. Once the tube was taken outside the glove-box, it was sealed immediately using a torch. Subsequently, it was heated in an oven at 150°C for 96 hours and then cooled to 40°C and left for 72 hours. When the oven was cooled to room temperature, the brown mother liquor was left standing for several days. Within that time brownish block-shaped crystals of $Ti_{17}O_{28}(O^iPr)_{16}(Fe^{II}Phen)_2$ were formed. They were collected by filtration, washed with 2-propanol and dried in a nitrogen atmosphere. Yield: 9.0 mg (10.0% based on iron(II) acetate).

2S. X-ray data collection and refinement

Measurements were carried out on a Bruker AXS Kappa APEX II Ultra diffractometer equipped with a TXS rotating anode (Mo- K_{α} radiation, $\lambda = 0.71073 \text{ \AA}$), Helios optics and a 700 Series Cryostream Oxford Instruments device. The single crystal was at 40 mm distance from the CCD camera and cooled to 90 K. Data were collected with ω scans (with 0.5° rotation increment) and analyzed with the APEX2 diffractometer software.¹ The program the SORTAV²⁻⁵ was used for the multi-scan absorption correction, frame-to-frame scaling and merging of the reflections. The crystal structure was solved using the charge flipping method⁶⁻⁸ implemented in the SUPERFLIP program,⁹ and refined on F with the JANA package. Analytical scattering factors as tabulated in the International Tables for Crystallography¹⁰ were used. The O^iPr groups were treated as rigid bodies with standard

C–O and C–C bond distances ($d_{c-o} = 1.45 \text{ \AA}$, $d_{c-c} = 1.52 \text{ \AA}$).¹¹ All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were located in the idealized positions ($d_{c-H} = 0.96 \text{ \AA}$), their APDs were constrained to ride on the parent carbon atom ($U_{iso}^H = 1.2 \cdot U_{eq}^C$). Final refinement parameters are listed in the CIF file which is available at the Cambridge Structural Database¹² (deposition number: CCDC 977542).

3S. Preparation of the working electrode

Crystals were washed with 2-propanol and weighed before being dissolved. In the case of sample **1**, about 9 mg of $Ti_{17}O_{28}(O^iPr)_{16}(Fe^{II}Phen)_2$ was dissolved in a mixture of anhydrous isopropanol (about 0.5 ml), anhydrous toluene (about 0.5 ml) and anhydrous dichloromethane (about 2 ml). Samples **2** and **3** were both prepared by dissolving about 5–10 mg of $Ti_{17}O_{28}(O^iPr)_{16}(Fe^{II}Phen)_2$ in about 2 ml of anhydrous dichloromethane.

The solutions were deposited onto fluorine doped tin oxide FTO-coated glass (12 – 14 Ω /square), spread with a pipette over a selected area of the working electrode and left to evaporate. The layer of the first sample was translucent brownish. $Ti_{17}O_{28}(O^iPr)_{16}(Fe^{II}Phen)_2$ was better soluble in pure dichloromethane and thus the films of samples **2** and **3** were more uniform and thicker. The layer of sample **3** was the thickest one and dark brown in colour. Due to the sample sensitivity to moisture and air, it was difficult to measure the exact film thickness. To avoid cluster hydrolysis or any other kind of decomposition, all actions were carried out under inert conditions in a glove-box.

4S. Photoelectrochemistry

Short-circuit photocurrent action spectra were collected as described elsewhere.^{13, 14} A custom-made 500- μ L Teflon cell with a sensitized-FTO/ $Ti_{17}O_{28}(O^iPr)_{16}(Fe^{II}Phen)_2$ working electrode and a Pt mesh counter-electrode was used. The electrolyte solution consisted of 0.05 M I_2 and 0.5 M LiI in CH_3CN . In a typical photoelectrochemical experiment, five shortcircuit photocurrent action spectra were acquired over the course of approximately 10 minutes for a given Ti-cluster-functionalized electrode. Initial and final values of incident photon-to-current efficiency (IPCE) differed by about 5% over the course of these experiments (values of IPCE were at the level of 1.4 % at maximum).

Photoelectrochemical measurements were made using a wavelength-calibrated 75 W Xe arc lamp (Newport Photomax) coupled to a monochromator (Newport Cornerstone 260 1/4m). The resulting beam illuminated a 0.47 cm² area on the backside of the working electrode. Short-circuit measurements were conducted with a source meter (Keithley 2400). Experimental parameters were analyzed with a Lab View program. The resulting current vs. wavelength curves are shown in the main paper. The corresponding IPCE curves are illustrated in Fig. 1S. The density of state for the Ti17 cluster, which is not photoactive in the 400-460 nm region is shown in Fig. 2S.

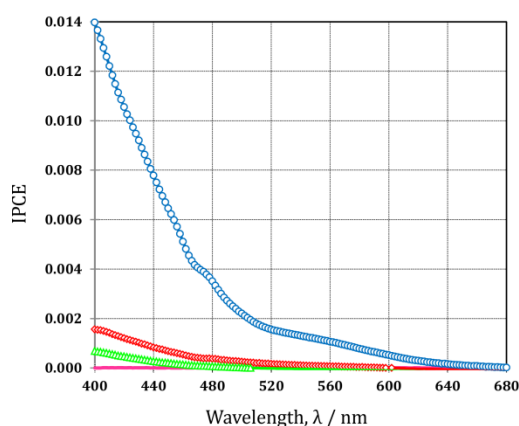


Figure 1S. The Incident Photon to Current Efficiency (IPCE) ratio for the experiments shown in Figure 3.

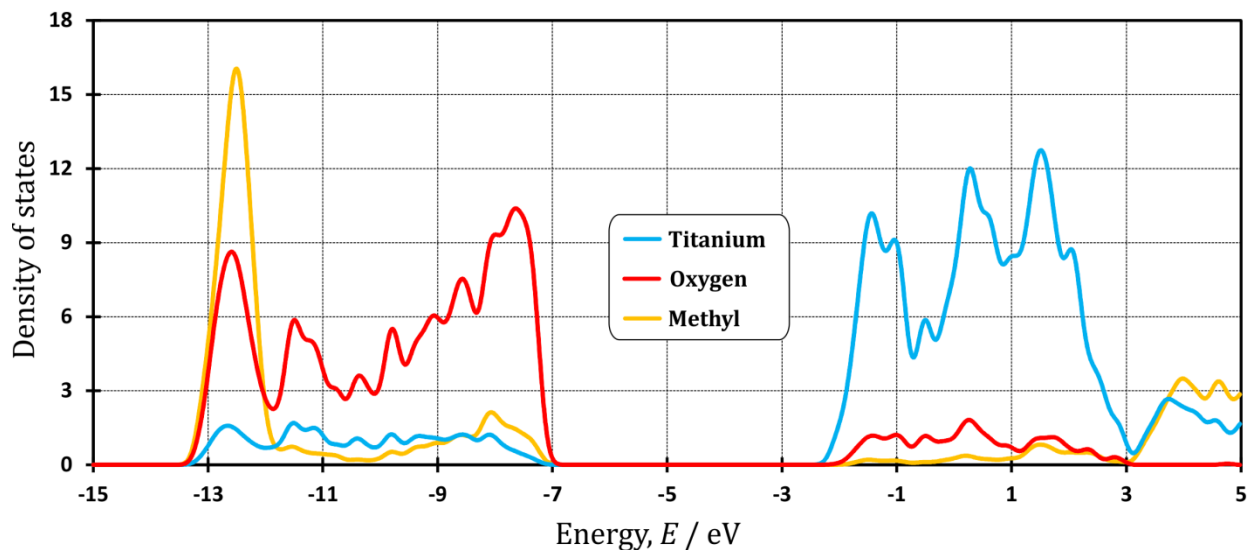
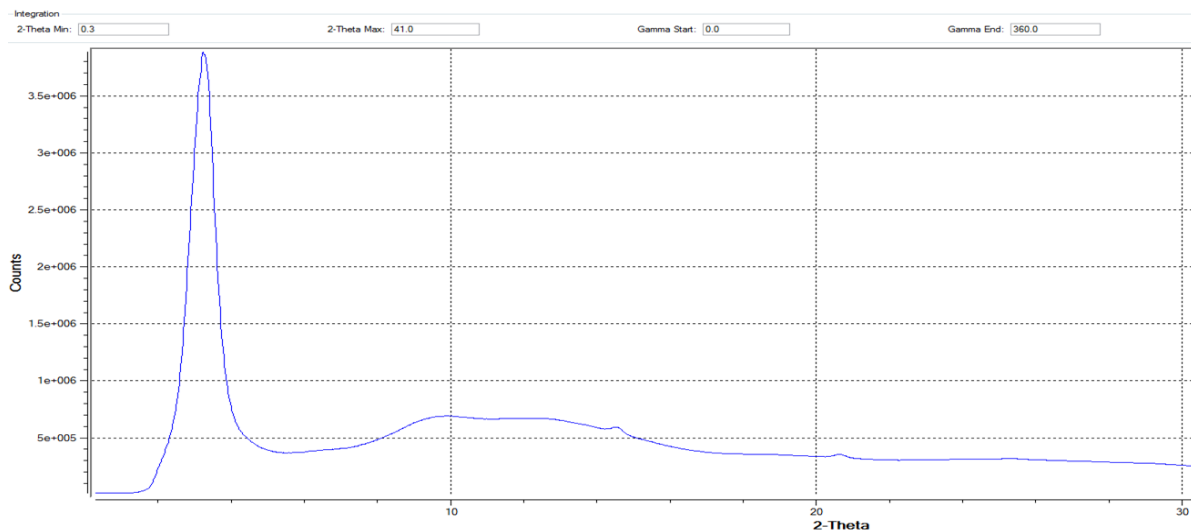
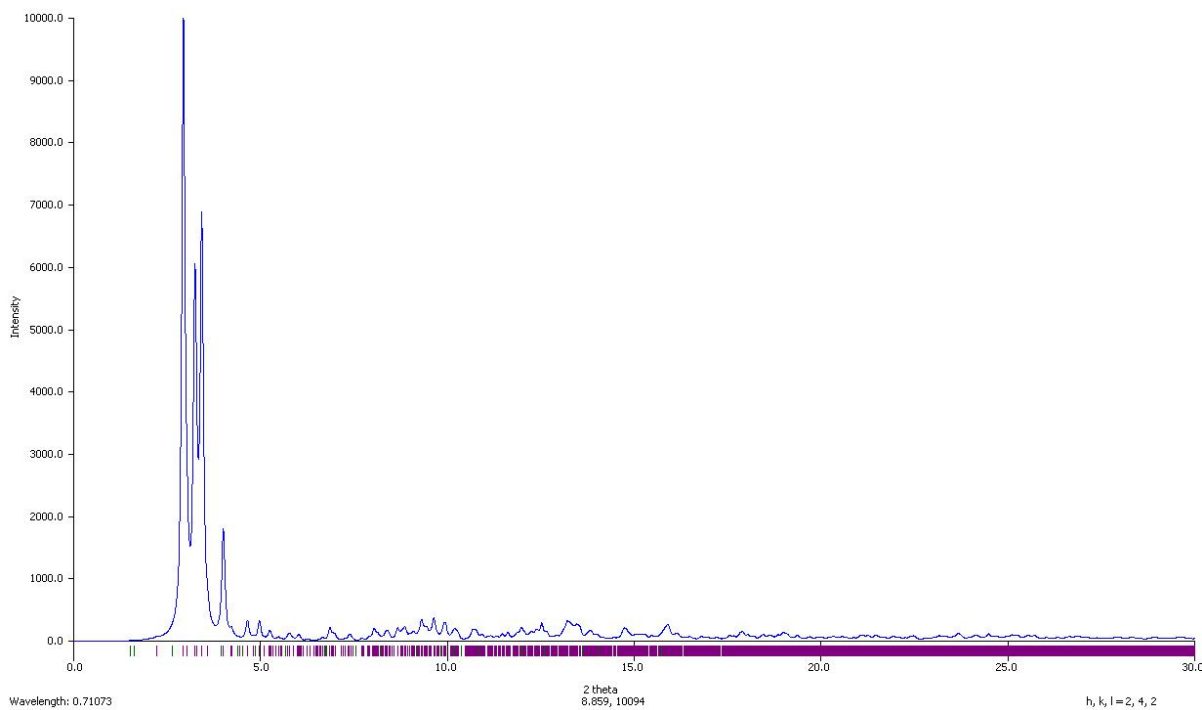


Figure 2S. Calculated density of states for the [Ti₁₇O₂₄(OPri)₂₀] cluster.

5S. Powder diffraction patterns



(a)



(b)

Figure 3S. (a) X-ray powder diffraction pattern of a $Ti_{17}O_{28}(O^iPr)_{16}(Fe^{II}Phen)_2$ film covering the FTO working electrode. (b) Calculated powder diffraction pattern based on the known crystal structure.

6S. Solid-state absorption

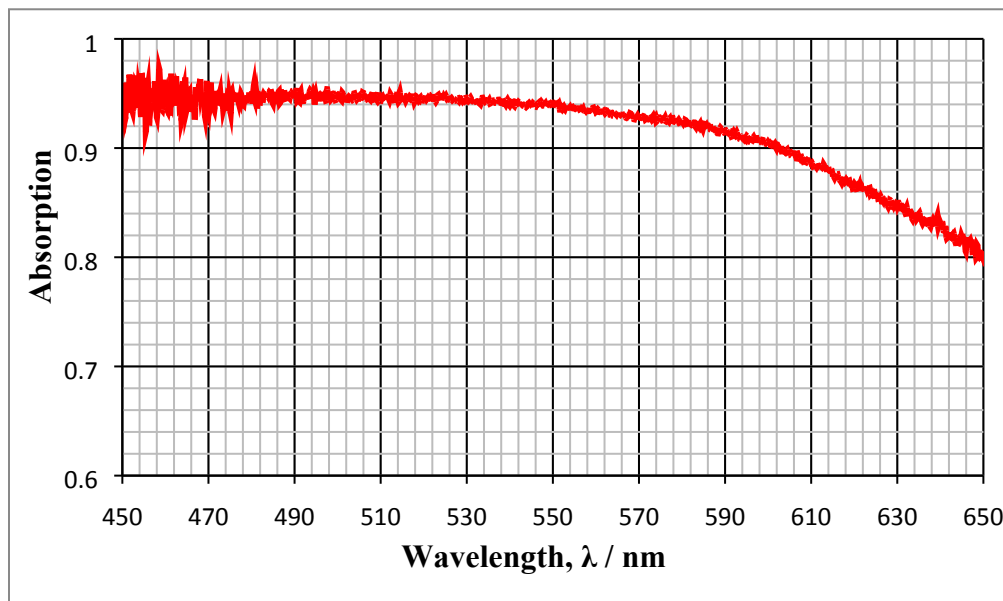


Figure 4S. Absorption spectrum of a $\sim 20 \mu\text{m}$ thick single crystal of $\text{Ti}_{17}\text{O}_{28}(\text{O}^i\text{Pr})_{16}(\text{Fe}^{\text{II}}\text{Phen})_2$

7S. Theoretical calculations

TDDFT calculations were performed in the *GAUSSIAN09* package¹⁵ at the PBE0/LANL2DZ level of theory. 50 lowest-energy transitions were evaluated, what covers the visible region of the electronic spectrum. For the purpose of this study the experimental geometry of the oxotitanate cluster was used, in which the isopropoxy groups were substituted with methoxy substituents (any disorder was removed), while all the X-H distances were set to neutron-normalized values.¹⁶

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