

Supplementary information

Long-Time Charge Separation in Porphyrin/KTa(Zr)O<sub>3</sub>  
as Water Splitting Photocatalyst

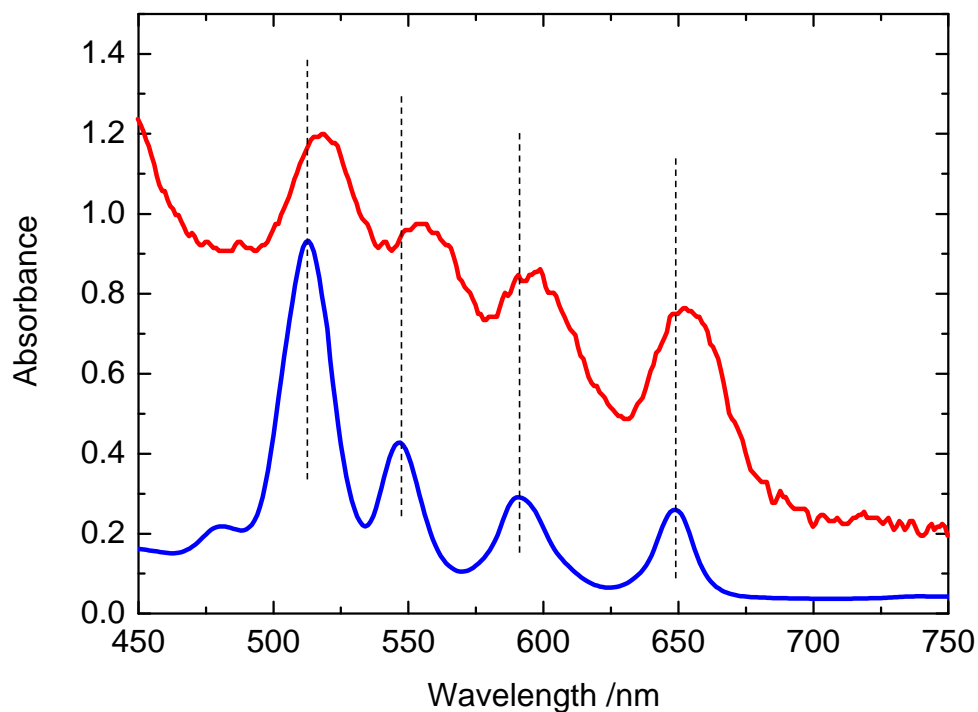
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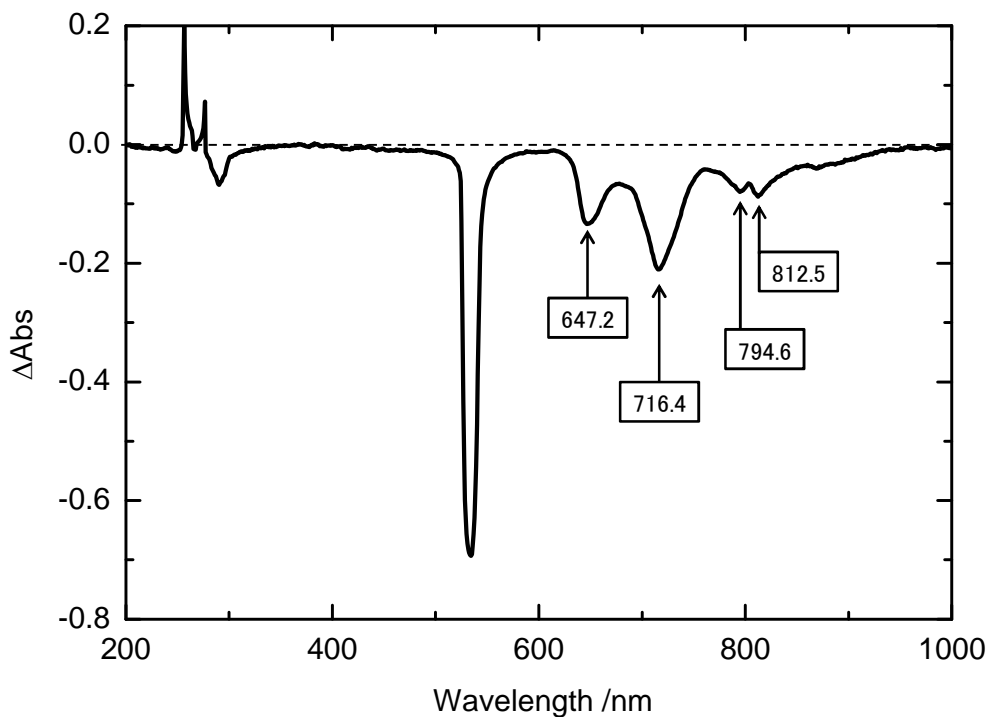
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S1



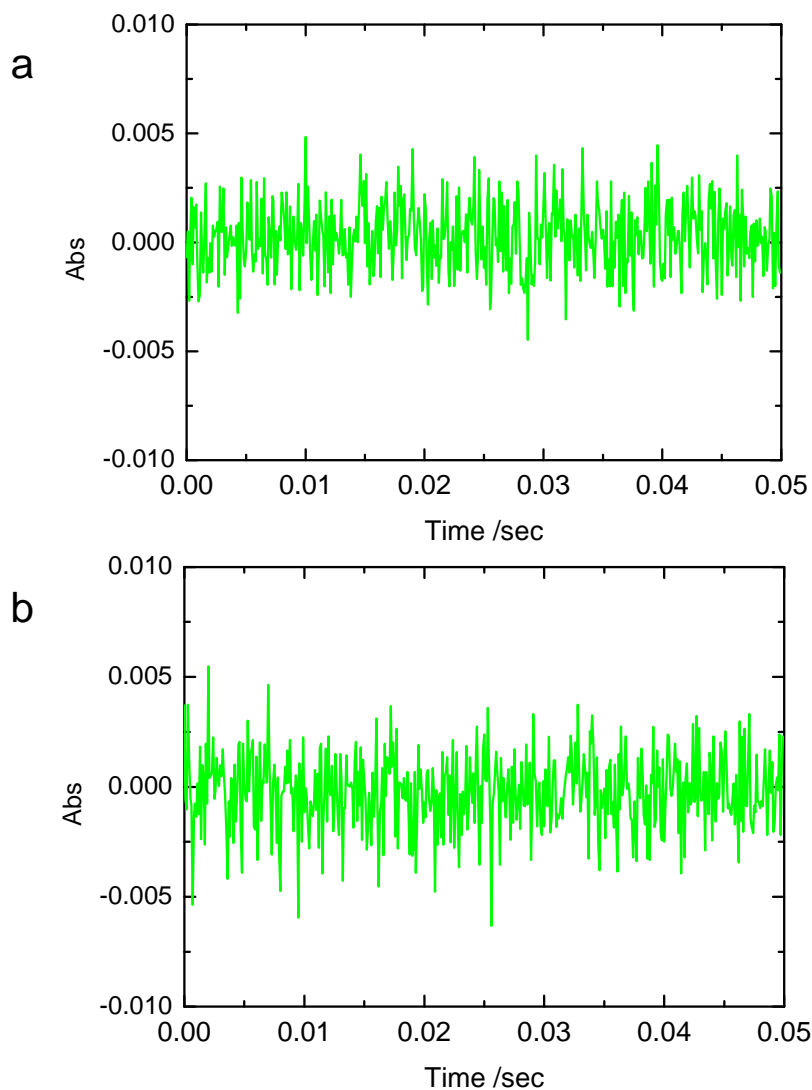
*Figure S1.* UV-vis spectra of Cr-TPP in tetrahydrofuran (THF) (blue line) and on KTa(Zr)O<sub>3</sub> surface (red line). Compared with the absorption spectrum of Cr-TPP monomer in THF, Q-band peaks (500–700 nm) of Cr-TPP/KTa(Zr)O<sub>3</sub> shifts to the long-wavelength side with an 8-10 nm. Red shift of absorption spectrum suggests the formation of Cr-TPP J-like aggregate over KTa(Zr)O<sub>3</sub>.

S2



*Figure S2.* Differential UV-vis spectra of Cr-TPP/KTa(Zr)O<sub>3</sub> disk irradiated with/without the fourth harmonic (266 nm) of Nd:YAG laser. 150 W Xe lamp was used for the probe light, and irradiation laser light was controlled by using optical shutter. Differential spectrum was detected with a photonic multichannel analyzer. Peaks of differential spectrum were observed at 647, 716, 795 and 813 nm by photoexcitation of KTa(Zr)O<sub>3</sub>. Along with the differential spectrum, the second harmonic of Nd:YAG laser was detected at 532 nm.

S3



*Figure S3.* Transient absorption decays of Cr-TPP/SiO<sub>2</sub> (b) and PtO<sub>x</sub>/Cr-TPP/SiO<sub>2</sub> observed at 650 nm. Measurements were carried out using the fourth beam (266 nm) from the Nd<sup>3+</sup>:YAG laser as the pump light source, operated by temporal control using a delay generator (DG535, Stanford Research Systems, Inc.). A screw cap quartz cell was used as the sample holder. The probe light from a 150 W Xe lamp (L11033, Hamamatsu Photonics K.K.) was collected with a focusing lens and detected with a photonic multichannel analyzer (PMA-12 C10029, Hamamatsu photonics K.K.). All experiments were performed at room temperature.

S4

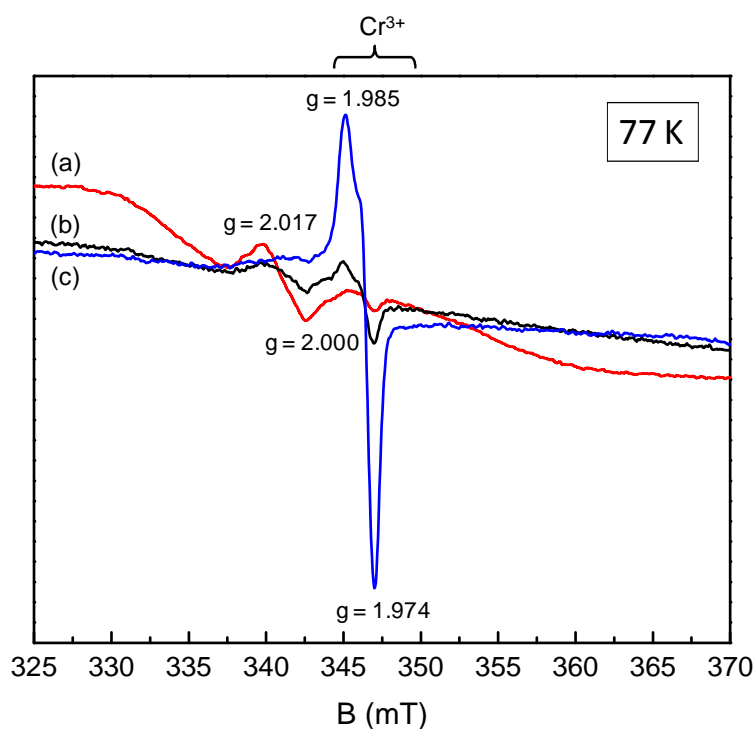


Figure S4. ESR spectra of (a) -1.2 V applied, (b) none, and (c) +1.5 V applied Cr-TPP in frozen *N,N*-dimethylformamide (DMF) at 77 K. Positive or negative voltage was applied using a potentiostat/galvanostat (HSV-100, Hokuto Denko Corp.) with a three-electrode configuration consisting of a Pt wire working electrode ( $\varphi = 0.3$  mm), a Pt wire counter electrode, and a commercially available Ag/AgCl electrode as the reference electrode. Porphyrin dyes were dissolved in DMF containing 0.1 M tetrabutylammonium perchlorate (Strem Chemicals, Inc.) as the supporting electrolyte. Sample solutions were presaturated with  $\text{N}_2$  and the voltage was applied under a  $\text{N}_2$  atmosphere. ESR spectra were measured in a quartz Dewar vessel filled with liquid nitrogen. As shown in Figure S-1, the electrochemical oxidation of Cr-TPP gave increase of the intensity of ESR signal at  $g = 1.985$  and  $g = 1.974$ . This  $g$ -value is well corresponding to  $g$ -value described in the literature edited by A. Abragam and B. Bleaney.<sup>1)</sup> Therefore, we assigned the observed ESR signal to the trivalent state of chromium ( $\text{Cr}^{3+}$ ).

#### Reference

1) A. Abragam and B. Bleaney, "Electron Paramagnetic Resonance of Transition Ions", Clarendon Press, Oxford (1970).