

Electronic Supporting Information

5 Enhanced photocurrents via redox modulation by fluoride binding to oxoporphyrinogen in a zinc porphyrin-oxoporphyrinogen surface modified TiO₂ supramolecular solar cell^s

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Experimental

Chemicals and materials. Chemicals and reagents used in the synthesis of the dyad were purchased from Tokyo Kasei Chemical Co. (TCI), Wako Chemical Co. or Aldrich Chemical Co. (Milwaukee, WI) while tetra-*n*-butylammonium perchlorate (TBA)ClO₄, and tetra-*n*-butylammonium
15 iodide, (TBA)I, used as supporting electrolytes in photoelectrochemical studies, were from Fluka Chemicals. Fluorine doped ITO glass (tec7) electrodes were from Pilkington North America Inc. (Toledo, OH). Nanocrystalline TiO₂ (ST21, 20 nm average particle size) was kindly provided by Ishihara Corporation (San Francisco, CA).

Instrumentation and procedure. Electronic absorption spectra were obtained using a
20 Shimadzu (Kyoto, Japan) Model 1600 UV-vis spectrophotometer. Photocurrent-photovoltage characteristics of the solar cells were measured using a Keithley Instruments, Inc. (Cleveland, OH) Model 2400 Current/Voltage Source Meter under illumination with an AM 1.5 simulated light source (Newport Corporation (Irvine, CA) Solar Simulator Model 9600 of 150-W). A 340-nm filter was introduced in the light path to eliminate UV radiation. Light intensity was monitored by using an
25 Optical Model 1916-C Power Meter of Newport. The solar simulator was calibrated according to a literature method.¹ Incident photon-to-current efficiency (IPCE) of conversion measurements were

performed under conditions of $\sim 2.5\text{-mW cm}^{-2}$ monochromatic light illumination using a setup comprising a 450-W Xe lamp and monochromator. Thin films of TiO_2 on FTO were prepared using the Doctorblade technique according to a literature procedure.² Photoelectrochemical cells were constructed using platinized ITO as counter electrode in non-coordinating DCB containing 0.5 M (*n*-Bu)₄NI and 0.03 M I_2 as redox mediator.

For the photoelectrochemical cell construction, a thin non-crystalline TiO_2 film coated fluorine doped indium tin oxide (FTO) electrode ($\sim 10\text{-}12$ microns, tec7 grade from Pilkington) was surface modified by placing the electrode in an ethanolic solution of 4-carboxyphenyl-imidazole (0.20 M) overnight, according to our earlier published method.⁶ After removal of unbound material (2-3 ethanol washings), the TiO_2 electrode was immersed in DCB solution containing ZnP-OxP for about 30 min. After this, the electrode was rinsed with DCB to remove excess of uncoordinated dyad. Photoelectrochemical cell assembly was completed using platinized FTO as counter electrode in noncoordinating DCB containing 0.50 M (*n*-Bu)₄NI and 0.030 M I_2 as redox mediator.

- 15 1. S. Ito, H. Matsui, K. Okada, S. Kusano, T. Kitamura, Y. Wada and S. Yanagida, *Solar Energy Materials & Solar Cells*, 2004, **82**, 421.
2. S. Ito, P. Chen, P. Comte, M. K. Nazeeruddin, P. Liska, P. Péchy and M. Grätzel, *Prog. Photovoltaics: Res. Appl.*, 2007, **15**, 603.

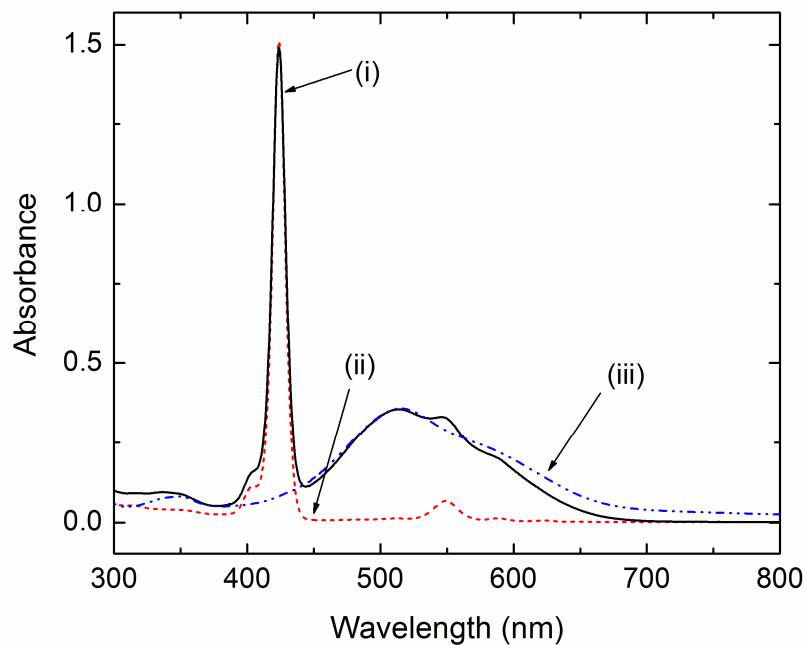


Fig. S1. Normalized absorption spectra of (i) ZnP-OxP dyad, (ii) ZnTPP and (iii) OxP in DCB.

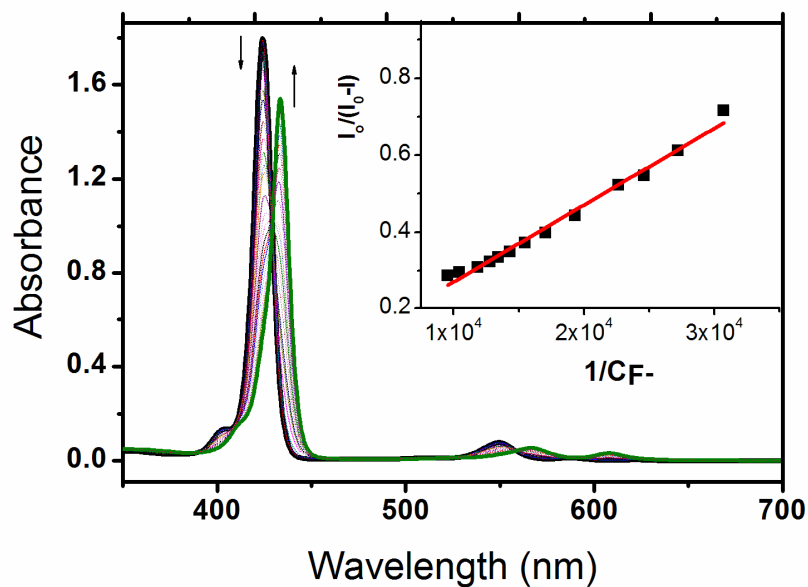


Fig. S2. Spectral changes observed during titration of F^- into a solution of zinc tetraphenylporphyrin (ZnTPP) in DCB. The figure inset shows Benesi-Hildebrand plot constructed to calculate the binding constant.

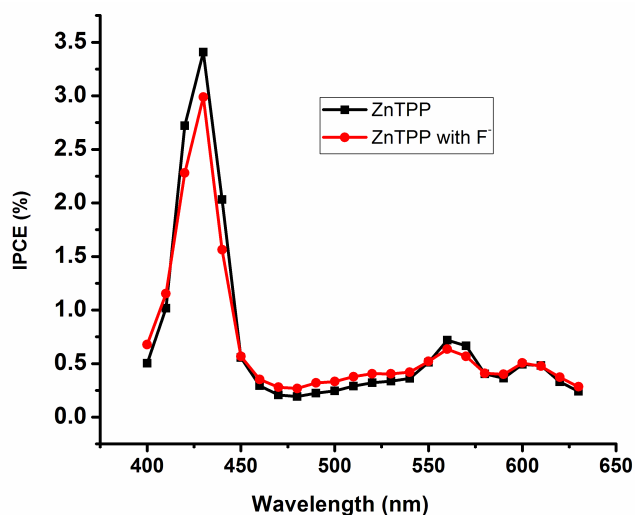


Fig. S3. IPCE(%) characteristics revealing the effect of F^- binding to ZnP (black line in the absence and red line the presence of F^- (the electrode was dipped in a 1.5 mM F^- solution for 1 min prior measurements). The $I-V$ curves were generated in DCB containing I_3^-/Γ^- (0.50 M / 0.030 M) redox mediator using an AM 1.5 simulated light source with a 340 nm UV-cut off filter.