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Halide Coordination to Zinc Porphyrin Sensitizers Anchored to Nanocrystalline TiO_2

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The coordination of halide ions to 5-(3,5-dicarboxyphenyl)-10,15,20-tri-*p*-tolylporphinatozinc(II) anchored to mesoporous nanocrystalline (anatase) TiO_2 thin films (TiO_2/ZnP) immersed in propylene carbonate was quantified. The addition of tetrabutylammonium halide salts to the external propylene carbonate electrolyte resulted in a red shift in the absorption spectrum with the maintenance of five isosbestic points. The absorption spectra were within experimental error the same for ZnP and ZnP−X^- compared to TiO_2/ZnP and TiO_2/ZnP−X^-: A_{Soret}ZnP = 427 nm (ε = 574 000 M^{-1} cm^{-1}), A_{Soret}ZnP−Cl^- = 435 nm (ε = 905 000 ± 12 000 M^{-1} cm^{-1}), A_{Soret}ZnP−Br^- = 436 nm (ε = 776 000 ± 30 000 M^{-1} cm^{-1}), and A_{Soret}ZnP−I^- = 437 nm (ε = 620 000 ± 56 000 M^{-1} cm^{-1}). Titration studies with the halides revealed sharp isosbestic points consistent with formation of a 1:1 halide/porphyrin adduct. Equilibrium constants for ZnP were found to be 1670 M^{-1} for Cl^-, 96 M^{-1} for Br^-, and 5.5 M^{-1} for I^-, and the corresponding values for TiO_2/ZnP were significantly smaller, 780 M^{-1}, 70 M^{-1} and 3.4 M^{-1}. A quasi-reversible wave was observed by cyclic voltammetry of TiO_2/ZnP, $E_{1/2}(ZnP^{+/0})$ = +790 mV vs Ag/AgCl, that was shifted 160 mV after addition of excess chloride, $E_{1/2}(ZnP{-}Cl^{0/-})$ = +630 mV. In regenerative solar cells with quinone/hydroquinone redox mediators, TiO_2/ZnP and TiO_2/ZnP−X^-, where X is Cl, Br, or I, were found to convert light into electrical power. The photocurrent action spectrum demonstrated that energy conversion was initiated by light absorption of ZnP and/or the halide adduct.

Introduction

The most efficient sensitizers for dye sensitized (Grätzel) solar cells are Ru^{II} polypyridyl compounds such as *cis*-$Ru(dcb)_2(NCS)_2$, where dcb is 4,4′-$(COOH)_2$-2,2′-bipyridine, which is often referred to as the N3 sensitizer. There is considerable interest in identifying alternative sensitizers that do not require ruthenium. Less expensive organic pigments, such as porphyrins, have received much attention in this regard.[1–4] In fact, a 5.6% global efficiency was recently reported with a zinc-porphyrin sensitized Grätzel cell, and high efficiencies have also been reported with other organic sensitizers.[4,5] These values are getting very close to the ∼11% global efficiencies that have been confirmed with the N3 sensitizer.[6]

Porphyrin sensitizers provide some opportunities for solar energy conversion that could not be readily achieved with Ru(II) polypyridyl compounds. For example, porphyrins typically have an order of magnitude higher extinction coefficient and can be incorporated into linear arrays that undergo rapid energy transfer for sensitization of low surface area semiconductors.[7] Metallo-porphyrins have axial coordination sites while Ru(II) polypyridyl compounds are coordinatively saturated. The presence of open coordination sites could be exploited for small molecule activation and photocatalysis in photoelectrosynthetic dye sensitized solar

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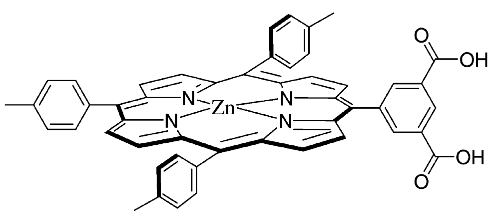
Scheme 1



cells. Ligand coordination can also be used to tune the porphyrin's redox potentials and light harvesting properties.[8–12] For first row transition metal porphyrins, coordinated ligands can exchange rapidly with other ligands in the environment. Such dynamic equilibria have been exhaustively studied and are now well understood in fluid solution and biological media.[13–15] The same is not true for porphyrins anchored to semiconductor surfaces where the interface could significantly influence the equilibrium.

Here we report studies of the equilibrium between halide ions and 5-(3,5-dicarboxyphenyl)-10,15,20-tri-*p*-tolylporphinatozinc(II), abbreviated ZnP, anchored to high surface area, mesoporous, nanocrystalline (anatase) thin films of TiO_2, Scheme 1. Comparative studies in fluid solution and on the semiconductor surface revealed small but significant differences in the coordination equilibrium. There was strong experimental evidence for photoinduced charge injection from the zinc porphyrin-iodide adduct to nanocrystalline TiO_2 with a yield comparable to that of the ZnP sensitizer. Consequences of adduct formation on the light harvesting efficiency and redox properties of the porphyrin sensitizers are discussed.

Experimental Section

Materials. The following reagents were used as received: propylene carbonate, anhydrous (Aldrich, 99.7%), tetrabutylammonium iodide (TBAI) (Sigma Aldrich, 99%), tetrabutylammonium bromide (TBABr) (Aldrich, 99%), tetrabutylammonium chloride (TBACl) (Sigma Aldrich, 98%), tetrabutylammonium hexafluorophosphate (TBAH) (Fluka, ≥99%), lithium perchlorate ($LiClO_4$) (Aldrich, 99.99%), hydroquinone (H_2Q) (Aldrich, 99+%), lithium iodide (LiI), anhydrous (Aldrich, 99.99%), titanium isopropoxide (Aldrich, 97%), microscope slides (Fisher Scientific), and fluorine-doped tin oxide (FTO) (Pilkington, 7 Ω/square). 1-4 benzoquinone (Q) (Aldrich, 98%) was freshly recrystallized from ethanol before use.

Sensitized TiO_2 Preparation. Mesoporous nanocrystalline (anatase) thin films of TiO_2 on glass slides or fluorine doped tin oxide (FTO) were prepared as described previously.[16] The synthesis and characterization of the porphyrin sensitizer 5-(3,5-dicarboxyphenyl)-10,15,20-tri-*p*-tolylporphinatozinc(II) (ZnP) was also previously described.[17] The porphyrins were anchored to the thin films by overnight reactions in toluene. The TiO_2/ZnP films were then rinsed and stored in neat toluene until use.

Spectroscopy. UV−vis Absorbance. Steady-state absorption measurements were performed at room temperature in a Varian Cary 50 UV−vis spectrophotometer in a 1 cm path length quartz cuvette. The TiO_2/ZnP thin films were placed diagonally in the cuvette with the solvents or electrolytes of interest. An unsensitized TiO_2 thin film was used as a reference.

Electrochemistry. Cyclic voltammetry of TiO_2/ZnP electrodes were performed in a standard three-electrode configuration with a saturated Ag/AgCl reference electrode and a Pt mesh counter electrode. The electrolyte consisted of 0.1 M TBAH in propylene carbonate. The effects of halide ions on the reduction potentials were quantified by the addition of TBAX (X = Cl, Br, and I) to a 0.1 M TBAH propylene carbonate electrolyte. Potentials were scanned at 200 mV/s between 400 mV and 1000 mV versus saturated Ag/AgCl. Care was taken to avoid anodic excursions into the second porphyrin oxidation.

Photocurrent action spectra were measured in a two-electrode configuration at room temperature. The ZnP surface coverage was kept between 9.0×10^{-9} and 2.6×10^{-9} mol/cm^2. A known area of a TiO_2/ZnP electrode was immersed in an electrolyte with a Pt mesh counter electrode. The TiO_2/ZnP was illuminated through the FTO support with a PhotoMax 100 W Xe lamp coupled to a $^1/_4$ m Oriel Cornerstone monochromator. Incident irradiances were measured using a Graesby Optronics S370 optometer with a calibrated silicon diode from UDT. Photocurrents were measured with a Keithley 617 electrometer. Incident photon-to-current (IPCE) values were calculated using eq 1. The photocurrent was the total current measured under illumination minus the dark current.

$$\mathrm{IPCE} = \frac{1240(\mathrm{eV\ nm})}{\lambda(\mathrm{nm})} \times \frac{\mathrm{Photocurrent(A)} \times \mathrm{Photodioderesponsivity}(\mathrm{V}^{-1})}{\mathrm{Photodiode\ Photocurrent(A)}} \qquad (1)$$

The electrolyte for incident photon-to-current efficiency (IPCE) measurements, 0.5 M hydroquinone, 25 mM 1,4- benzoquinone, and 0.1 M $LiClO_4$ in propylene carbonate, was prepared shortly before photoelectrochemical measurements. To quantify halide effects, 0.6 M TBACl, 0.6 M TBABr, or saturated TBAI were included in the electrolyte. In some experiments, the iodide concentration was varied by adding known amounts of 0.5 M LiI and 0.05 M I_2 propylene carbonate solution.

Results

The preparation of mesoporous nanocrystalline TiO_2 thin films with surface anchored 5-(3,5-dicarboxyphenyl)-10,15,20-tri-*p*-tolylporphinatozinc(II) (ZnP), abbreviated ZnP/TiO_2, was recently reported.[18] Carboxylic acid groups are the most well studied linkers for TiO_2 surfaces.[19] The visible absorp-

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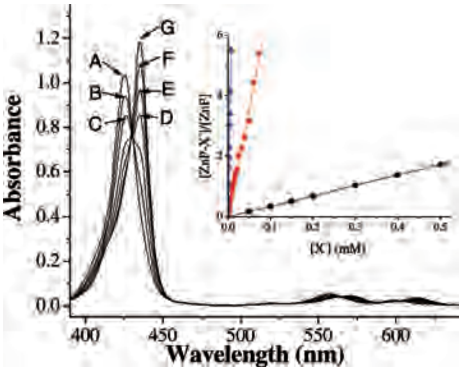

Figure 1. Room-temperature absorption spectra of TiO_2/ZnP in 0.5 M TBAH propylene carbonate with 0 M TBACl (A), 0.51 mM TBACl (B), 1.02 mM TBACl (C), 1.52 mM TBACl (D), 2.51 mM TBACl (E), 5.82 mM TBACl (F), 121 mM TBACl (G). The inset shows the plot of $[ZnP-X^-]/[ZnP]$ vs $[Cl^-]$ (blue triangles), $[Br^-]$ (red circles), $[I^-]$ (black squares).

tion spectrum of a TiO_2/ZnP thin film immersed in a 0.5 M TBAH propylene carbonate solution was within experimental error and the same as that observed for ZnP dissolved in the same electrolyte. The addition of tetrabutylammonium halide salts to the external propylene carbonate electrolyte resulted in a red shift in the absorption spectrum with the maintenance of five isosbestic points. Typical data for chloride coordination to TiO_2/ZnP is shown in Figure 1. Qualitatively similar behavior was observed for ZnP in fluid propylene carbonate. The magnitude of the red shift induced for each halide was quantified at the Soret absorption maximum, Table 1.

The extinction coefficient of ZnP was taken from that reported for Zn tetraphenylporphyrin, ($\varepsilon_{422} = 5.74 \times 10^5$ $M^{-1}cm^{-1}$) and was assumed to be unchanged on the TiO_2 surface.[20] The absorption spectra and extinction coefficient of ZnP halide adducts, $ZnP-X^-$, were determined from titration studies like that shown in Figure 1. With such data, the relative concentrations of TiO_2/ZnP and $TiO_2/ZnP-X^-$ were calculated at known halide concentrations by deconvolution of the composite absorption spectra. The $[ZnP-X^-]/[ZnP]$ ratio as a function of the halide ion concentration is shown as an inset in Figure 1. The data was found to be linear, and equilibrium constants were abstracted from the slopes, Table 2.

Cyclic voltammetry measurements were performed in standard three electrode configurations with a TiO_2/ZnP working electrode in 0.1 M TBAH propylene carbonate. A quasi-reversible wave for the surface bound porphyrin was observed $E_{1/2}(ZnP^{+/0}) = +790$ mV versus Ag/AgCl, Table 2. The redox chemistry is termed quasi-reversible because the peak anodic and cathodic currents were the same; however, the magnitude of the peak-to-peak separation was greater than 80 mV. The addition of TBACl resulted in spectroscopic changes consistent with the formation of $TiO_2/ZnP-Cl^-$, and a new quasi-reversible wave assigned to $E_{1/2}(ZnP-Cl^{0/-}) = +630$ mV versus Ag/AgCl, Figure 2. The addition of 2 mM Br^- or I^- resulted in large anodic currents due to the direct oxidation of the halides that obscured the porphyrin redox chemistry.

The incident photon-to-current efficiency (IPCE) was measured as a function of excitation wavelength in a sandwich cell arrangement with a TiO_2/ZnP photoelectrode, a Pt counter electrode, and a 0.5 M hydroquinone (H_2Q), 25 mM 1,4-benzoquinone (Q), 0.1 M $LiClO_4$ propylene carbonate electrolyte. With 0.6 M TBACl (or 0.6 M TBABr) present in the electrolyte a ~10 nm red shift in the spectrum resulted. At this halide concentration, complete conversion of TiO_2/ZnP to $TiO_2/ZnP-X^-$ was expected, Table 2, and indeed sensitized photocurrents were observed for $TiO_2/ZnP-X^-$. Under such conditions, a very small photocurrent (IPCE $\ll$ 1% maximum, typical 0.3%) was observed. The photocurrent action spectrum observed with saturated tetrabutyl ammonium iodide (>1 M iodide) showed contributions from both TiO_2/ZnP and $TiO_2/ZnP-I^-$. The IPCE at the absorption maximum for $TiO_2/ZnP-I^-$ was 0.15%. A concentration study was conducted by controlled addition of 0.5 M LiI and 0.05 M I_2 (LiI/I_2) to the quinone/hydroquinone (H_2Q/Q) solution, Figure 3. Addition of LiI/I_2 to the H_2Q/Q propylene carbonate electrolyte resulted in the appearance of a photocurrent response at longer wavelengths consistent with sensitization by $TiO_2/ZnP-I^-$. Comparison of photocurrent action and absorptance spectra of mixed TiO_2/ZnP, $ZnP-I^-$ samples indicated that the maximum photocurrent efficiency after light absorption by ZnP was within experimental error the same as that observed for $ZnP-I^-$, $IPCE_{max} = 0.9 \pm 0.4\%$. Light excitation into the Q-bands was also found to give rise to a sensitized photocurrent with IPCE < 0.02% for H_2Q/Q that increased to ~0.1% in LiI/I_2 electrolyte.

Discussion

The coordination chemistry of synthetic and naturally occurring metalloporphyrins is extremely well documented.[13–15] Zinc(II) metalloporphyrins have been of particular interest for solar energy conversion as the filled d-shell does not quench the porphyrin singlet excited state.[21] The d^{10} electronic configuration also precludes complications from metal centered redox chemistry. The results presented here support previous findings that an equilibrium between halide ions and Zn porphyrins exists in fluid solution.[11,22,23] Here we find that a similar equilibrium exists when the porphyrin was anchored to high surface area, mesoporous TiO_2 thin films immersed in propylene carbonate, eq 2.

$$TiO_2/ZnP + X^- \overset{K_{eq}}{\rightleftharpoons} TiO_2/ZnP-X^- \qquad (2)$$

The maintenance of isosbestic points through the titration of TiO_2/ZnP with halides is consistent with a 1:1 Lewis acid−base adduct between ZnP and the halide ion.[22] The equilibrium constants were largest for chloride (780 M^{-1}) and decreased with bromide (70 M^{-1}) and even more for

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Table 1. Spectroscopic Properties of ZnP and ZnP−X$^-$ Adducts in Propylene Carbonate[a]

		ZnP	ZnP−Cl$^-$	ZnP−Br$^-$	ZnP−I$^-$
A_{Soret}[b] (nm)	solution	425	434	435	436
	TiO$_2$	427	435	436	437
ΔA_{Soret}[c] (nm)	solution		9.4 ± 0.4	10.6 ± 0.3	10.8 ± 0.1
	TiO$_2$		8.0 ± 0.1	9.0 ± 0.5	10.0 ± 0.4
ΔA_{Soret}[d] (cm^{-1})	solution		509	572	583
	TiO$_2$		429	486	535
ε_{ZnP-X}−(M^{-1} cm^{-1})[e]		574 000[d]	905 000 ± 12 000	776 000 ± 30 000	620 000 ± 56 000

[a] All measurements collected at room temperature. [b] Wavelength at the Soret maximum absorption. [c] Calculated change in Soret maximum absorption, $A_{Soret,\ ZnP-Halide}$(nm) − $A_{Soret,\ ZnP}$(nm). [d] Calculated change in Soret maximum absorption, $A_{Soret,\ ZnP-Halide}$(cm^{-1}) − $A_{Soret,\ ZnP}$(cm^{-1}). [e] Extinction coefficient from ref 21.

Table 2. Thermodynamic Properties of ZnP−X$^-$ adducts in Propylene Carbonate

		K_{eq}[a] (M^{-1})	$-\Delta G_{rxn}$[b] (kJ/mol)	ΔE_{rxn}[c] (mV)	E_{rxn} (ZnP−X$^{0/-}$)[d] (mV vs Ag/AgCl)
ZnP−Cl	solution	1670 ± 30	18 400	190	
	TiO$_2$	780 ± 40	16 000	170	+620[e]
ZnP−Br	solution	96 ± 4	11 000	120	
	TiO$_2$	70 ± 4	10 800	110	+680
ZnP−I	solution	5.5 ± 0.7	4100	42	
	TiO$_2$	3.4 ± 0.1	3300	34	+760

[a] K_{eq} calculated from eq 1 measured at room temperature in propylene carbonate. [b] Gibbs free energy change, ΔG_{rxn}, in kJ/mol. [c] Change in electromotive force, ΔE_{rxn}. [d] Reduction potential calculated for ZnP−X + e$^-$ → [ZnP−X]$^-$ vs a Ag/AgCl reference by E_{rxn} (ZnP−X$^{0/-}$) = $E_{1/2}$ (ZnP$^{+/0}$) − ΔE, where $E_{1/2}$ (ZnP$^{+/0}$) is the $^1/_2$ wave potential measured by cyclic voltammetry in the absence of halide. [e] Measured value was +630 mV vs Ag$^+$/Ag.

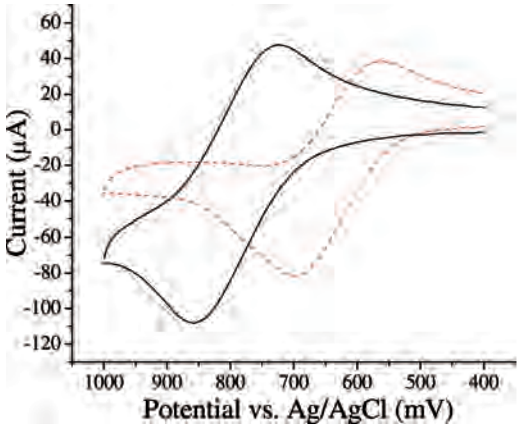

Figure 2. Cyclic voltamograms of TiO$_2$/ZnP collected at a scan rate of 200 mV/s before and after the addition of 2 mM TBACl to 0.1 M TBAH propylene carbonate electrolyte, attributed to TiO$_2$/ZnP (solid black line) and TiO$_2$/ZnP−Cl$^-$ (dashed red line), respectively.

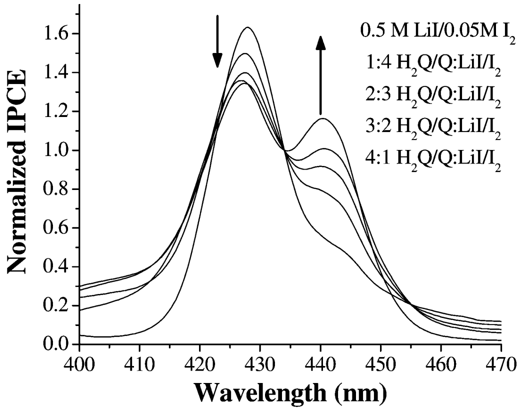

Figure 3. Photocurrent action spectra of a TiO$_2$/ZnP sample with the indicated redox mediators in 0.1 M LiClO$_4$ propylene carbonate electrolytes. The IPCE is the incident photon-to-current efficiency that was calculated with eq 1. The spectra were normalized at the absorption isosbestic point (434 nm). The arrows indicate the influence of increased iodide concentration.

iodide (3.4 M^{-1}). Zn(II) is considered a hard Lewis acid and clearly prefers the hard chloride base relative to the softer iodide. The trend in equilibrium constants also tracks the known gas phase stability of metal halides.[24] Interestingly, the equilibrium constants were smaller by factors of 0.8 to 0.4 when ZnP was anchored to the anatase TiO$_2$ surface relative to fluid solution, Table 2. The polar TiO$_2$ surface and mesoporous structure significantly disfavors halide coordination relative to fluid propylene carbonate solution. While halide coordination to ZnP was suppressed in the mesoporous semiconductor film, high concentrations of Br$^-$ or Cl$^-$ resulted in complete conversion of TiO$_2$/ZnP to TiO$_2$/ZnP−X$^-$, indicating that the equilibrium depicted in eq 2 could be shifted completely to the right and that all the porphyrins bound to TiO$_2$ were coordinated to a halide ion.

A significant bathochromic (red) shift was observed to accompany ZnP−X$^-$ adduct formation, the magnitude of which was not correlated with the measured equilibrium constants. In fact, the most stable chloride adduct resulted in the smallest spectral shift. Previous workers have attempted to correlate Zn(II) porphyrin spectroscopy with halide polarizability, that is, the degree to which the halide transfers negative charge to the porphyrin ring.[25] Indeed Fajer's early experimental studies showed hyperfine coupling between the halide ion and the oxidized porphyrin ring.[22] Here we found that TiO$_2$/ZnP−Cl$^-$ was more easily oxidized than TiO$_2$/ZnP by 160 mV. Similar behavior has been reported for ZnTPP, where TPP is tetraphenylporphyrin, in fluid solution,[22] indicating that the halide imparts a significant inductive effect on the porphryin ring. Interestingly, the chloride equilibrium constant measured spectroscopically corresponds to ΔE_{rxn} = 170 mV at room temperature, which is in excellent agreement with the difference in reduction potential, $E_{1/2}$ (ZnP$^{+/0}$) − E_{rxn} (ZnP−X$^{0/-}$), measured electrochemically. This finding allowed us to estimate the reduction potentials of the bromide and iodide adducts that could not be determined experimentally, Table 2.

The visible absorption spectrum of the halide adducts is better suited for terrestrial solar light harvesting than is the uncomplexed ZnP. The bathochromic shift moves the intense

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Soret band closer to the maximum solar photon flux. The light harvesting efficiency of a monolayer on a flat surface is defined as the fraction of light absorbed and can be related to the molar extinction coefficient and the area occupied on the electrode, that is, the "footprint", eq 3.[18]

$$\mathrm{LHE} = 3.82 \times 10^{-5} \cdot \varepsilon/\mathrm{footprint} \qquad (3)$$

Previous studies revealed that a 115 Å^2 footprint was appropriate for porphyrins bound by a single CO_2H group.[18] With this footprint, a monolayer of the ZnP−Cl would harvest 0.22% of the AM 1.5 spectrum while the uncomplexed ZnP harvests only 0.14%. The enhanced LHE results from both an increased extinction coefficient and a more favorable absorption spectrum. The Br^- and I^- adducts have slightly better overlap with the AM 1.5 spectrum than does the ZnP−Cl^-; however, this is offset by lower extinction coefficients resulting in poor LHEs, 0.13% and 0.11%, respectively. It is interesting to note that butyl thiolate coordination to ZnTPP results in a much more dramatic red shift in the porphyrin absorption spectrum similar to that known for cytochrome P450.[23] Here too, however, the red shift is apparently accompanied by a significant decrease in the extinction coefficient. Nevertheless, the LHE of a ZnTPP monolayer on a flat surface is doubled by thiolate coordination from 0.04% to 0.08%. In reviewing the spectral properties of a large number of metalloporphyrins, it seems that a factor of 2 is about the maximum increase in solar harvesting of air mass 1.5 solar photons that one could reasonably expect to achieve through axial ligation of metalloporphyrins.[13–15,23]

The photocurrent action spectrum of TiO_2/ZnP thin films in regenerative solar cells with quinone/hydroquinone redox mediators was that expected for light absorption by ZnP. The addition of excess bromide or chloride, resulted in a ~10 nm red shift in the photocurrent action spectrum consistent with excited-state electron injection by the ZnP−X^- adducts. The photocurrent efficiency under these conditions was very small, <1%. The addition of iodide to the electrolyte resulted in photocurrent action spectrum consistent with sensitization by ZnP and ZnP−I^-. The improved efficiency, $\mathrm{IPCE}_{\mathrm{max}} = 1.2 \pm 0.4\%$, presumably results from more favorable sensitizer regeneration by iodide relative to hydroquinone. For a large number of samples, the sensitized photocurrent efficiency of ZnP and ZnP−I^- were approximately the same. Therefore, if iodide oxidation by ZnP−I occurs through an inner-sphere mechanism, this is not reflected by an enhanced photocurrent efficiency. We note that while TiO_2/ZnP−I is expected to be a weaker oxidant than TiO_2/ZnP^+ by about 30 mV, a comparison with reduction potentials of efficient Ru(II) sensitizers indicates that all the ZnP halide adducts are expected to rapidly oxidize iodide after excited state injection into TiO_2.[19]

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