Electronic Supporting Information

Harnessing Molecular Photon Upconversion at Sub-Solar Irradiance Using Dual Sensitized Self-Assembled Trilayers

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Contents

Materials. 4,4'-(anthracene-9,10-diyl)bis(4,1-phenylene) diphosphonic acid (**A**)[1] $Co(phen)_3(PF_6)_2$ and $Co(phen)_3(PF_6)_3$ (**$Co^{3+/2+}$**)[2] were prepared by following previously published procedure. Zinc acetate dehydrate, H_2PtCl_6, nitrosyl tetrafluoroborate, cobalt (II) chloride, ammonium hexafluorophosphate (Sigma-Aldrich), 2,2' bipyridine (Oxchem), Pd(II) meso-tetra(4-carboxyphenyl)porphine (**PdP**), and Pt(II) meso-tetra(4-carboxyphenyl)porphine (**PtP**) (Frontier Scientific), were purchased from their respective suppliers, in parentheses, and used without further purification. All other reagents and solvents (analytical reagent grade) have been purchased and used without further purification from VWR. Fluorine-doped tin oxide (FTO) coated glass (sheet resistance 15 Ω $\square^{-1}$) was purchased from Hartford Glass Co. Meltonix film (1170-25) and Vac'n Fill Syringe (65209) were purchased from Solaronix. Micro glass cover slides (18 × 18mm) were obtained from VWR. ZrO_2 and TiO_2 sol-gel pastes were prepared following a previously reported procedure.[3-5]

Photophysical and Electrochemical Measurements.

Energy Transfer Measurements: The efficiency of interlayer energy transfer for ZrO_2-**A**-Zn-**PtP**, ZrO_2-**A**-Zn-**PdP** and ZrO_2-**PdP**-Zn-**PtP** were quantified using steady-state and and time-resolved emission experiments. **PtP** and **PdP** were excited at 510 nm and 525 nm, respectively, and emission was measured from 600-800 nm. Emission quenching was calculated using equation S1 where I_{SA} is the integrated emission intensity from 600-800 nm for ZrO_2-**A**-Zn-**PtP**, ZrO_2-**A**-Zn-**PdP** and ZrO_2-**PdP**-Zn-**PtP**, and I_S is the emission intensity for ZrO_2-**PtP** or ZrO_2-**PdP**. The concentration of sensitizer was the same in the monolayer and bilayer films so there was no need to correct for absorbance differences.

$$\% \, Quenching = \left(1 - \frac{\sum I_{SA}}{\sum I_S}\right) \times 100 \qquad \text{(Eq. S1)}$$

Incident Photon to Current Efficiency: IPCE was acquired every 5 nm (5 nm bandwidth) with excitation intensities measured at each wavelength (I_{ex}) to correct for variation throughout the spectrum. % IPCE was calculated using Equation S2.

$$\% \, IPCE = \frac{(J_{sc})(1240)}{(I_{ex})(\lambda)} \qquad \text{(Eq. S2)}$$

Amperometric $i-t$. Data were collected using a CH Instruments CHI630E electrochemical analyzer using a two-electrode configuration (TiO_2 working, Pt counter) held at 0 V applied potential. The samples were irradiated with either an AM1.5 solar simulator (Light Model 66181 oriel corrected with a standard air-mass filter) passing through a 375 nm (to prevent DPPA dimerization, blocks <5% of solar intensity) or 495 nm (to isolate the contribution due to upconversion) long pass filters, or with 532 nm from a Nd:YAG laser (Aixiz, AD-532-400T). The intensity of solar irradiance was controlled by varying the distance between the solar simulator source and sample. The laser light intensity was controlled using a neutral density filter as described above for the photophysical measurements. A Model T132 Shutter Driver/Timer (UniBlitz) coupled to a mechanical shutter (Vincent Associates, VS25) was placed between the light source and sample to control 10 s light-dark intervals over a 70 s time period.

Table S1. Performance characteristics of DSSCs containing dual sensitized bilayers and trilayer photoanodes under AM1.5 irradiation with 375nm and 495 nm long pass filters.

Sample	Filter (nm)	J_{sc} (μA/cm^2)	V_{oc} (mV)	η^a (%)
TiO_2-Zn-$PtP_{50\%}$	375	218	94	1.17×10^{-2}
	495	8.0	4.9	1.06×10^{-4}
TiO_2-Zn-$PdP_{50\%}$	375	201	113	7.36×10^{-3}
	495	7.8	7.0	$<1 \times 10^{-4}$
TiO_2-Zn-PtP/PdP	375	253	129	1.08×10^{-2}
	495	20.2	21	1.06×10^{-4}
TiO_2-Zn-PtP	375	316	96	8.98×10^{-3}
	495	37.3	17	1.54×10^{-4}
TiO_2-Zn-PdP	375	348	121	1.36×10^{-2}
	495	50.6	31	3.73×10^{-4}
TiO_2-Zn-PdP-Zn-PtP	375	402	160	2.22×10^{-2}
	495	74.1	58	1.16×10^{-3}

[a]η = (unflitered incident light power/electrical power output) ×100.

Table S2. Photophysical properties of A, PtP, and PdP.

	λ_{abs}[a] (nm) (ε,×10^4 M^{-1} cm^{-1})	λ_{em}[b] (nm)	τ[c] (μs)	Φ	k_r[d] (s^{-1})	k_{nr}[e] (s^{-1})	$E_{1/2}^{ox}$ (V vs NHE)	$E_{1/2}(S_1)$[f]	$E_{1/2}(T_1)$[g]
A	358 (0.77), 376 (1.27), 397 (1.20)	423	0.0021	0.527	2.6×10^8	2.3×10^8	1.33	-1.65	-0.45
PtP	405 (10.28), 510 (1.30), 540 (0.19)	669	41.1	0.016	3.9×10^2	2.4×10^4	0.99	-1.20	-0.86
PdP	419(14.63), 524 (1.41), 555(0.16)	693	412.8	0.005	1.3	2.4×10^3	0.95	-1.19	-0.84

[a] Measured in a DMSO solution. [b]Emission for **A**, **PtP**, and **PdP** on ZrO_2 in MeCN. [c]Lifetime from an exponential tail fit to the excited state decay (ex: 360 (A), 510 (PtP) nm, and 525 (PdP)). [d]$k_r = \Phi/\tau$. [e]$k_{nr} = (1-\Phi)/\tau$. [f]The singlet excited state reduction potential. [g]The triplet excited state reduction potential.

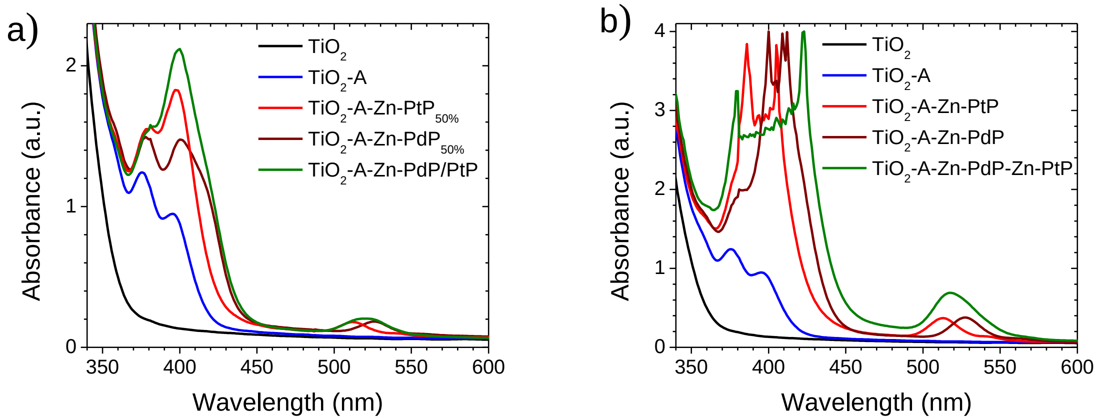

Figure S1. UV-vis absorption spectra for (a) the dual sensitized bilayer and components and (b) dual sensitized trilayer and components.

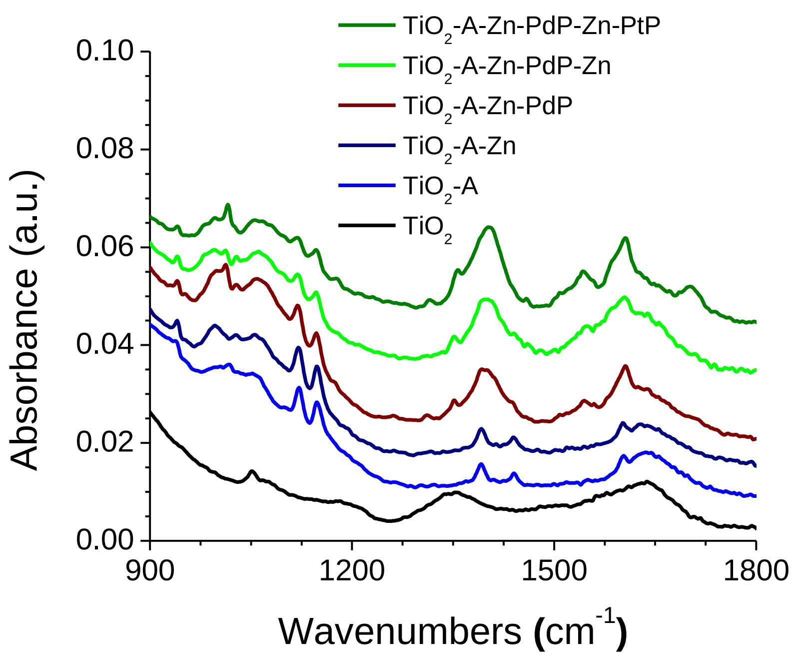

Figure S2. ATR-IR spectra throughout the formation of the dual sensitized trilayer (spectra are shifted in the y direction for clarity).

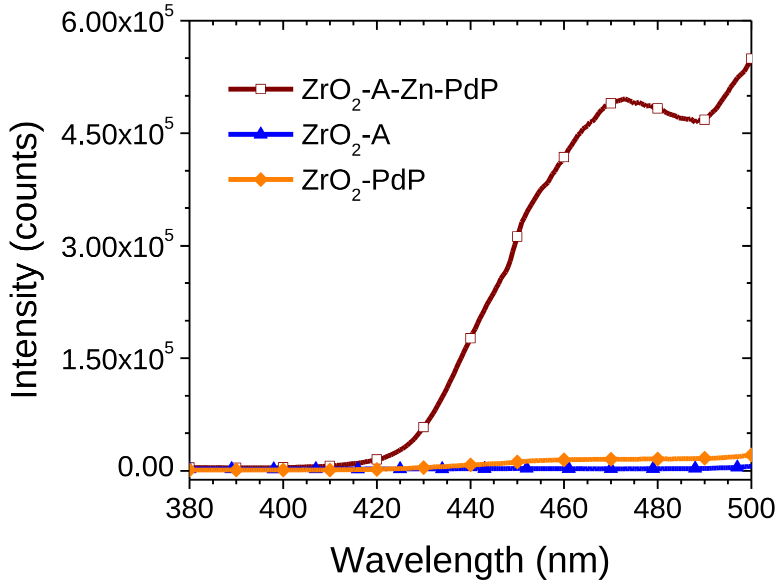

Figure S3. Emission spectra for ZrO_2-**A**-Zn-**PdP** (**A**:**PdP**, 10:1), ZrO_2-**A**, and ZrO_2-**PdP** in argon deaerated MeCN under 532 nm excitation (2.5 W/cm^2).

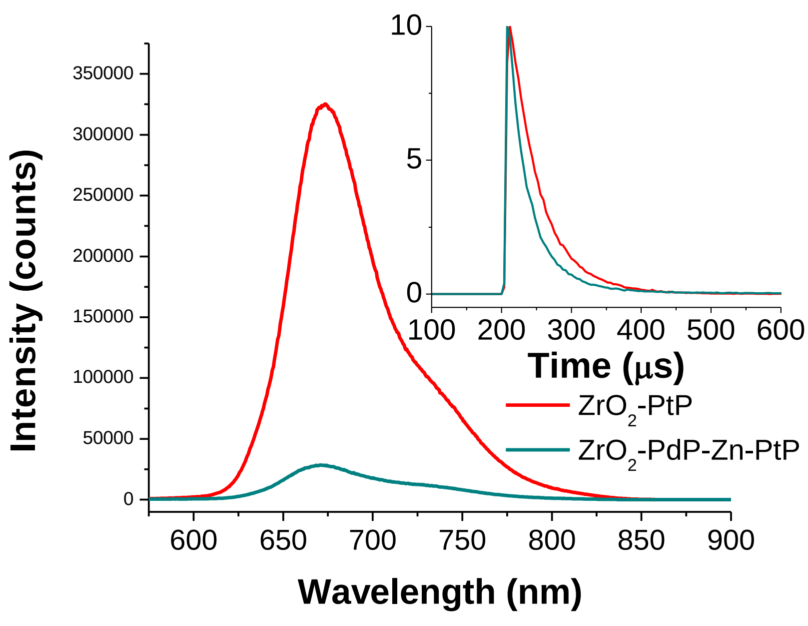

Figure S4. Emission spectra for ZrO_2-**PtP** and ZrO_2-**PdP**-Zn-**PtP** in MeCN excited at 505 nm (inset: time-resolved emission at 670 nm).

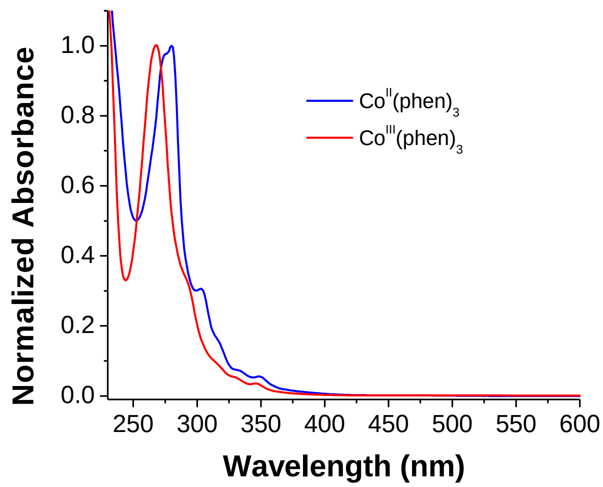

Figure S6. Normalized UV-vis absorption spectra for $Co^{II}(phen)_3$ $2PF_6$ and $Co^{III}(phen)_3$ $3PF_6$ in MeCN.

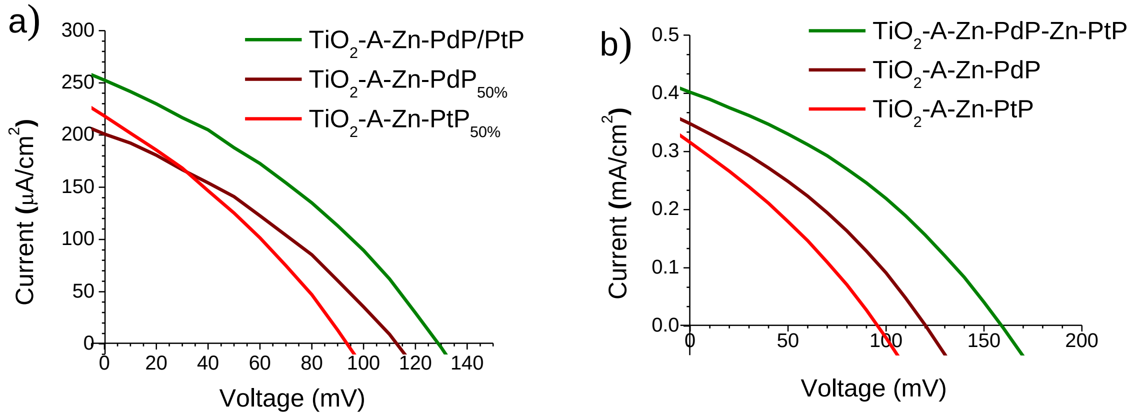

Figure S6. Photocurrent density-voltage characteristics for DSSCs with photoanodes composed of a) the dual sensitized bilayer and its comparable singly sensitized bilayers and b) the dual sensitized trilayer and its comparable singly sensitized bilayers all with $\mathbf{Co^{2+/3+}}$ redox mediator in MeCN under AM1.5 irradiation with a 375 nm long-pass filter.

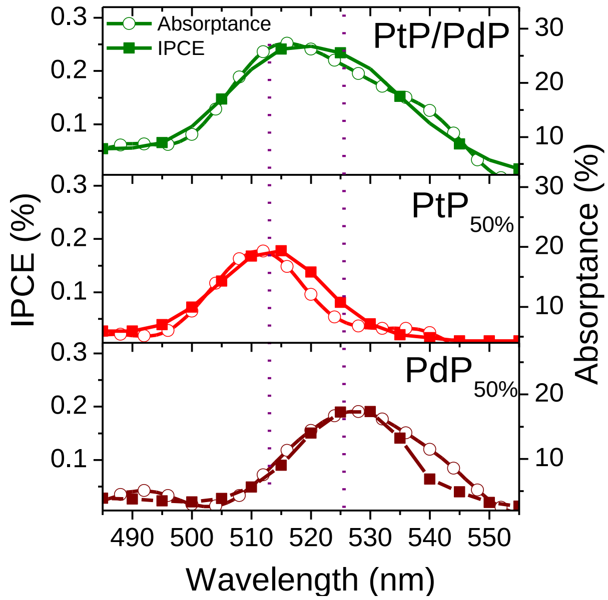

Figure S7. IPCE (filled squares) and absorptance (empty circles) for DSSCs composed of photoanodes of TiO_2-**A**-Zn-**X** where **X** is indicated in the top right corner of each spectrum.

References

1. S. P. Hill, T. Banerjee, T. Dilbeck and K. Hanson, *J. Phys. Chem. Lett.*, 2015, **6**, 4510-4517.
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