Electronic Supplementary Information

Significant performance improvement in dye-sensitized solar cells employing the cobalt(III/II) tris-bipyridyl redox mediator by co-grafting alkyl phosphonic acids with a ruthenium sensitizer

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Transient absorbance (ΔOD) decays following pulsed laser excitation for TiO_2 layers sensitized by Z907 dye (with or without coadsorbents) were recorded at λ = 680 nm, where the main contribution to ΔOD is from the oxidized dye (Fig. S1).[1] The absorbance decays were fitted with a stretched exponential function

$$\Delta\mathrm{OD} = \Delta\mathrm{OD}_0 \exp\left[-\left(\frac{t}{\tau_{\mathrm{KWW}}}\right)^{\alpha}\right] \quad \text{(S1)}$$

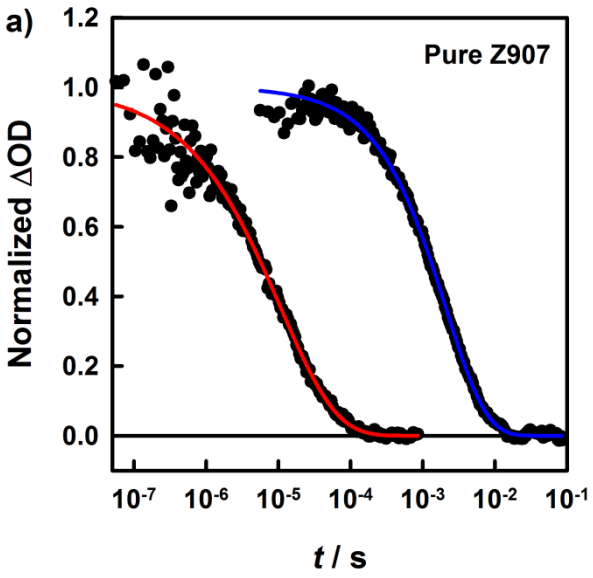
where $\Delta\mathrm{OD}_0$ is the absorbance change at t = 0, τ_{KWW} is a characteristic lifetime and α is the stretching exponent. Weighted-average lifetimes (τ_{obs}) appropriate for calculating the steady-state dye regeneration yield[2] were derived using

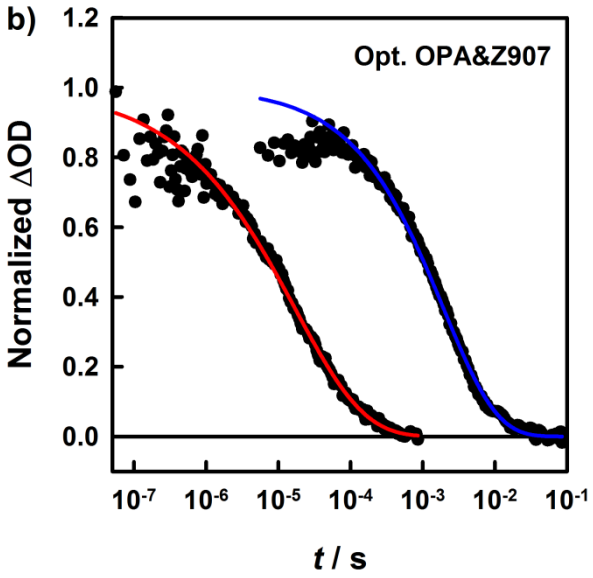
$$\tau_{\mathrm{obs}} = \frac{\tau_{\mathrm{KWW}}}{\alpha}\Gamma\left(\frac{1}{\alpha}\right) \quad \text{(S2)}$$

where Γ() is the gamma function. Dye regeneration yields (η_{reg}) were then estimated using

$$\eta_{\mathrm{reg}} = 1 - \frac{\tau_{\mathrm{obs}}}{\tau_{\mathrm{obs},0}} \quad \text{(S3)}$$

where τ_{obs} and $\tau_{obs,0}$ are the weighted-average lifetimes in the presence or absence of $[Co(bpy)_3]^{2+}$ (i.e. the electron donor which regenerates the oxidized dye), respectively. The results of this analysis are summarized in Table S1.





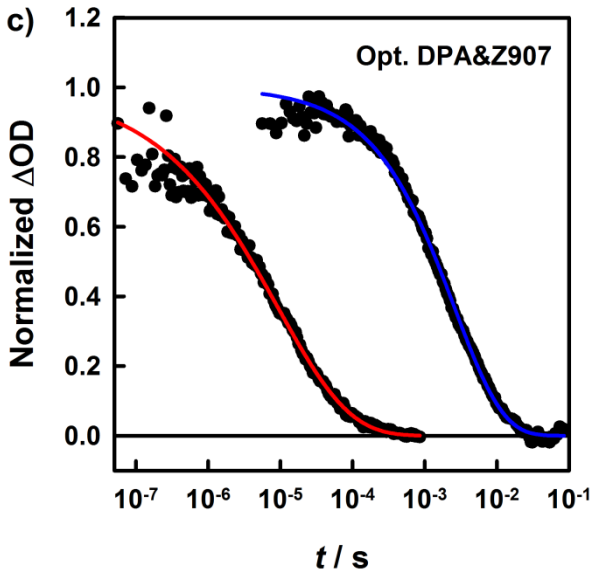


Fig. S1 Transient absorbance (ΔOD) decays at 680 nm following pulsed laser excitation (λ = 532 nm, pulse duration ~5 ns, pulse fluence ~10 μJ cm^{-2}) for a) Pure Z907, b) OPA:Z907 1:20 and c) DPA:Z907 1:40 in the presence (left trace) or absence (right trace) of $[Co(bpy)_3]^{2+}$. Red and blue solid lines are fits of eq. S1 to the data.

Table S1 Transient absorbance decay constants and regeneration efficiencies for TiO_2 films sensitized by Z907 with or without coadsorbents, calculated using eq. S2 and S3.

	τ_{obs} / μs	$\tau_{obs,0}$ / μs	η_{reg} / %
Pure Z907	17.6 ±0.8	2420 ±21.2	99.3 ±0.03
Opt. OPA&Z907	41.4 ±1.7	2982 ±37.1	98.6 ±0.06
Opt. DPA&Z907	24.3 ±1.1	3547 ±33.0	99.3 ±0.03

References:

(1) Zhang, Z. P.; Ito, S.; Moser, J. E.; Zakeeruddin, S. M.; Grätzel, M. *ChemPhysChem* **2009**, *10*, 1834-1838
(2) Anderson, A. Y.; Barnes, P. R. F.; Durrant, J. R.; O'Regan, B. C. *J. Phys. Chem. C* **2011**, *115*, 2439.