

Influence of Dye-Coordinated Metal Ions on Electron Transfer Dynamics at Dye-Semiconductor Interfaces

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EXPERIMENTAL DETAILS

Nanoparticle Paste Preparation

TiO₂ sol-gel preparation: 7.3 mL (11 wt%) of Tetraisopropyl Orthotitanate was added dropwise (110 mL/hr) to an ice cooled, rapidly stirring (300 rpm) 125 mL Erlenmeyer flask containing a solution of 0.42 mL nitric acid in 60 mL deionized water. The slurry was stirred for 15 min after which the flask was covered with aluminium foil and heated up to 95°C. The sample was held at this temperature until the volume was reduced, through evaporation, to 18 mL. The solution was placed in an acid digestion vessel (VWR, 25227-094) and heated in a box furnace (Thermo Scientific, BF51866A-1) at 200°C at 10.5 h. Upon cooling to room temperature, the solution was transferred to a glass vial. To the solution, 1g (5.3 wt%) of carbowax copolymer (ground to powder with a mortar and pestle) and the mixture was stirred for another 48 h.¹

[Co (phen)]^{2+/3+} synthesis: To a 50 mL flask, 300 mg (0.34 mmol) Co²⁺ phenantroline was added and dissolved completely in a minimal volume of acetonitrile solvent. To a second 50 mL flask, 78.8 mg (0.68 mmol) of NOBF₄ was dissolved completely in a minimum volume of acetonitrile solvent. In a 250 mL flask, 192.45 mg (1.19 mmol) of NH₄PF₆ was dissolved completely in minimum volume of acetonitrile solvent. The volume of acetonitrile used here was however much higher than the previous two. All three solutions were poured into a 500 mL flask and rotovaped to reduce overall volume. Ether solvent was added and the solution continuously swirled until no further cloudiness was observed. The solution was then placed in the freezer overnight to allow entire product to crash out. The precipitate was then vacuum filtered and washed with cold ether. The final product was left to dry and then collected to obtain [Co (phen)]³⁺ in 65% yield (227 mg, 0.22 mmol) as an orange solid.²

[Co(TTT)(NCS)₃]^{-1/0} synthesis: To a 50 mL flask, 50.0 mg (0.21 mmol) CoCl₂·(H₂O)₆ was added and dissolved completely in minimal volume of acetone solvent. 60.2 mg (0.15 mmol) of TTT ligand was weighed into a vial and added slowly as a suspension again using minimal volume of acetone to the stirring solution of CoCl₂·(H₂O)₆ over 10 min. The reaction mixture was stirred for another 10 minutes before TBANCS (378.7 mg, 1.26 mmol) was added in one portion. A green precipitate was readily formed but the suspension was allowed to stir for additional 10 minutes to ensure completion of the reaction. The suspension was purified with a Sephadex (LH-20) column using acetone as the solvent. Combined column fractions were reduced under vacuum to obtain [Co(TTT)(NCS)₃](TBA) in 60% yield (110 mg, 0.126 mmol) as a green solid. To perform ¹H NMR, the Co(II) complex was oxidized to Co(III) by using slight excess of NOBF₄ in CD₃CN.^{3, 4}

¹H NMR (400 MHz, CD₃CN) δ 9.02 (s, 2H), 8.62 (d, *J* = 1.8 Hz, 2H), 7.38 (dd, *J* = 6.3, 2.2 Hz, 2H), 7.08 (d, *J* = 5.9 Hz, 2H), 1.80 (s, 9H), 1.32 (s, 18H).

Nuclear Magnetic Resonance: The ¹H NMR spectrum for [Co³⁺(TTT)(NCS)₃]⁰ was recorded using Bruker 400 MHz spectrometer at room temperature. Chemical shifts for protons are reported in parts per million (ppm) relative to residual acetonitrile peak at 1.94 ppm. The NMR spectrum was processed using MNOVA.

Film and Device Characterization

Absorption spectroscopy: The UV–visible spectra were recorded using an Agilent 8453 UV–visible photodiode array spectrophotometer by placing the dry derivatized TiO₂/FTO slides perpendicular to the detection beam path.¹

Attenuated total reflectance infrared spectra: ATR-IR spectra were recorded using a Bruker Alpha FTIR spectrometer (SiC Glowbar source, DTGS detector) with a Platinum ATR

quickSnap sampling module (single reflection diamond crystal). Spectra were acquired from 800 to 3000 cm^{-1} at a resolution of 4 cm^{-1} . All ATR-IR spectra are reported in absorbance with a blank versus atmosphere.⁵

Nanosecond transient absorption measurements: Transient absorption (TA) measurements were carried out by inserting samples ($1 \times 4 \text{ cm}^2$ glass slides with a $1.5 \times 1 \text{ cm}^2$ TiO_2 active area) at a 45° angle into a 10 mm path length square cuvette containing 0.1 M TBP in MeCN. TA experiments were performed by using nanosecond laser pulses produced by a Continuum Surelite EX Nd:YAG laser combined with a Continuum Horizon OPO (532 nm, 5-7 ns, operated at 1 Hz, beam diameter $\sim 0.5 \text{ cm}$, 2.5 to 5 mJ/pulse) integrated into a commercially available Edinburgh LP980 laser flash photolysis spectrometer system. White light probe pulses generated by a pulsed 150 W Xe lamp were passed through the sample, focused into the spectrometer (5.5 nm bandwidth), then detected by intensified Andor iStar CCD camera. Detector outputs were processed using Edinburgh's L900 (version 8.2.3, build 0) software package.

Single wavelength kinetic absorption was detected by a photomultiplier tube with a 532 nm notch filter placed before the detector to reject unwanted scattered light. Detector outputs were processed using a Tektronix TDS3012C Digital Phosphor Oscilloscope interfaced to a PC running Edinburgh's L900 software package. Single wavelength kinetic data were the result of averaging 500 laser shots⁵ and were fit by using the bi-exponential function in equation 1. A weighted average of lifetime (τ) is calculated by using equation 2.

$$y = A_1 e^{-k_1 x} + A_2 e^{-k_2 x} + y_0 \quad (\text{eq 1})$$

$$\tau_i = 1/k_i; \langle \tau \rangle = \sum A_i \tau_i^2 / \sum A_i \tau \quad (\text{eq 2})$$

Photocurrent density-voltage Curves: The Power Conversion Efficiencies (PCE) of the DSSCs were measured by irradiating the devices with an AM1.5 Solar Spectrum generated from a 300 W xenon arc lamp (Ushio, UXL-302-O) enclosed in a Oriel Research Arc lamp Housing (Newport, 67005) with the light output passed through an AM 1.5 Global filter (Newport, 81094) and mechanical shutter (Newport, 71445). Current–voltage (J–V) relationship was measured using a Keithley Model 2400 Source Meter. The light intensity was measured using a calibrated reference cell and meter (Newport, 91150 V).^{1, 6}

Incident photon to current Efficiency: IPCE measurements were performed using light from the 300 W xenon lamp passed through a Cornerstone 260 monochromator (Newport, 74125) onto the cells and the light scanned from 300 to 800 nm in 5 nm intervals. Incident light intensity and photocurrent were measured using power meter (Newport, 2936-C) and Oriel 71580 Silicon Detector Head (Newport).^{1, 6}

Electrochemical impedance spectroscopy: EIS (Gamry Instruments, Interface 1000) was performed scanning from 10^6 Hz to 0.025 Hz with a perturbation amplitude of 10 mV after conditioning the cells for 15 s and allowing an initial delay of 50 s. Measurements were performed at open circuit voltage (OCV) under an AM 1.5 solar irradiation of 1 sun.^{1, 6}

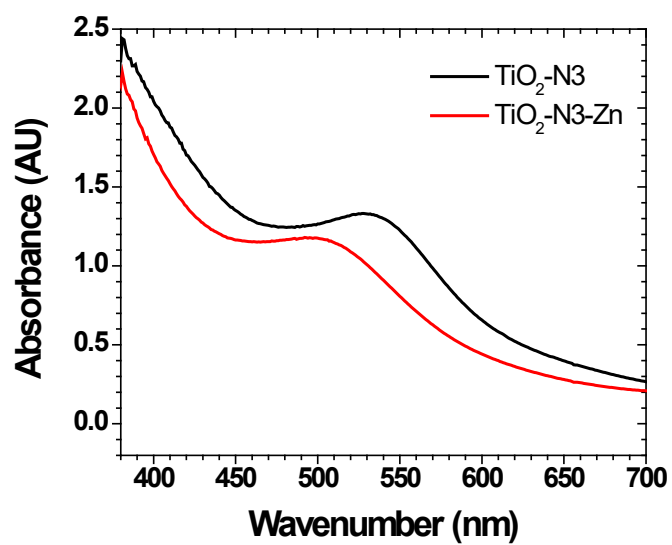


Figure S1. UV-vis absorption spectra for $\text{TiO}_2\text{-N3}$ and $\text{TiO}_2\text{-N3-Zn}$.

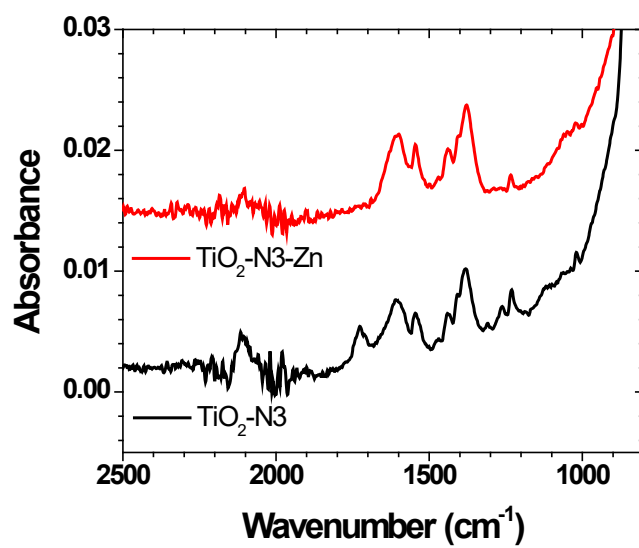


Figure S2. ATR-IR absorption spectra for $\text{TiO}_2\text{-N3}$ and $\text{TiO}_2\text{-N3-Zn}$.

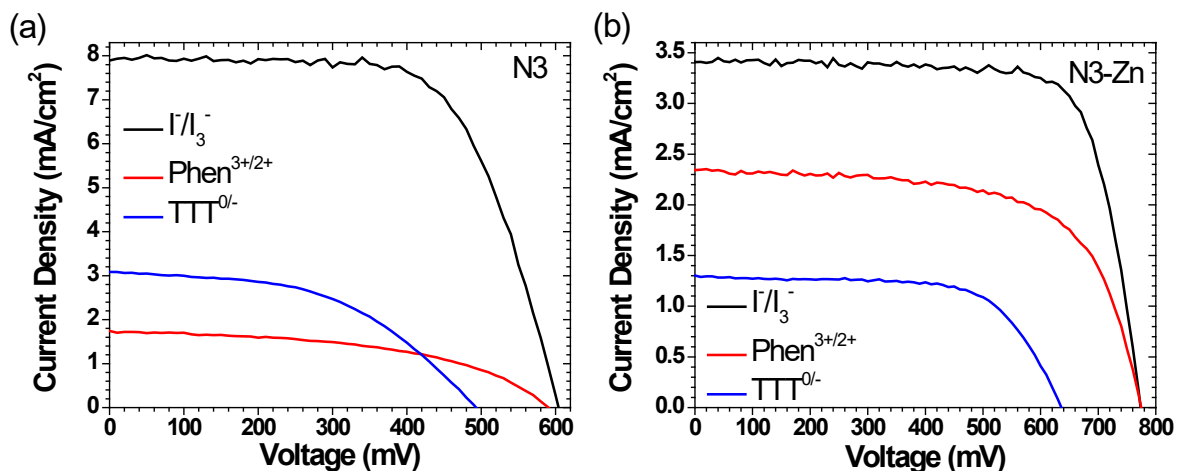


Figure S3. Photocurrent density-voltage (J-V) curves for DSSCs with photoanodes composed of a) TiO₂-N3 and b) TiO₂-N3-Zn with I⁻/I₃⁻, Phen^{3+/2+}, and TTT^{0/-} redox mediators.

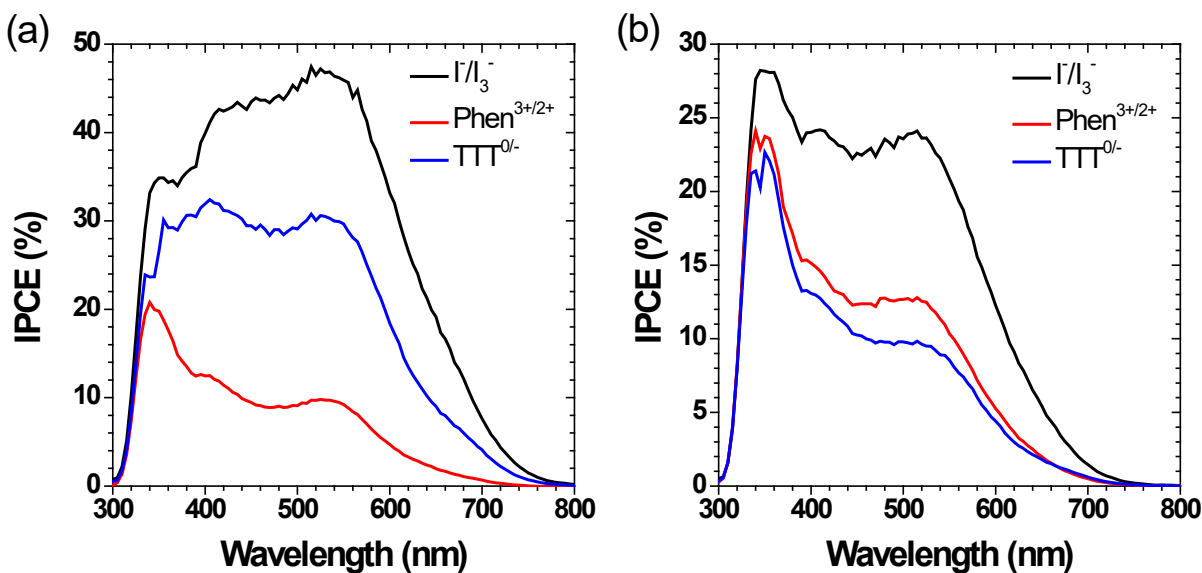


Figure S4. Incident photon-to-current efficiency spectra for DSSCs with photoanodes composed of a) TiO₂-N3 and b) TiO₂-N3-Zn with I⁻/I₃⁻, Phen^{3+/2+}, and TTT^{0/-} redox mediators.

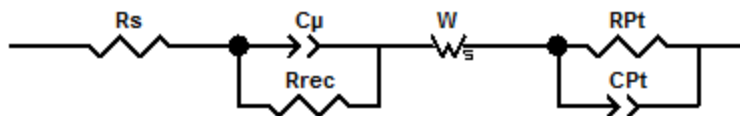


Figure S5. Equivalent circuit used to fit the electrochemical impedance spectroscopy data.

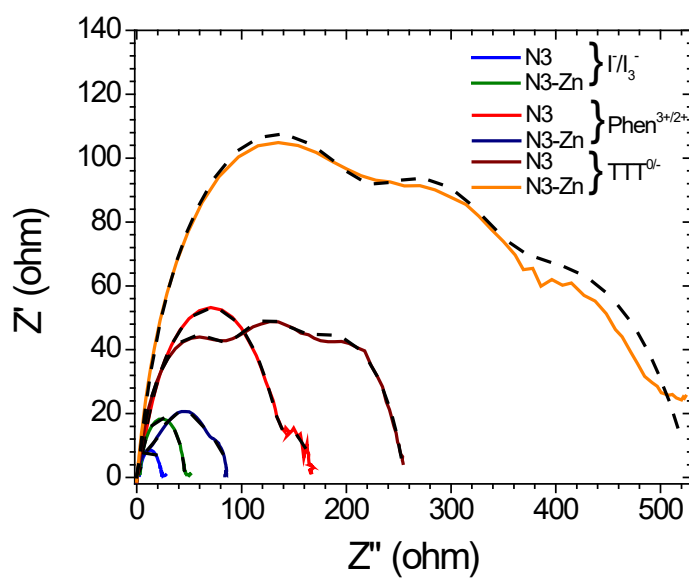


Figure S6. Nyquist plot for DSSCs with $\text{TiO}_2\text{-N3}$ and $\text{TiO}_2\text{-N3-Zn}$ photoanodes and I^-/I_3^- , $\text{Phen}^{3+/2+}$, and $\text{TTT}^{0/-}$ redox mediators. The fits for the data are shown as dashed black lines (Z' was normalized to correct for sheet resistance).

Table S1. EIS fitting parameters for the TiO₂-N3 and TiO₂-N3-Zn.

	TiO ₂ -N3 (I ⁻ /I ₃ ⁻)	TiO ₂ -N3 (Phen ^{3+/2+})	TiO ₂ -N3 (TTT ^{0/-})	TiO ₂ -N3-Zn ^{II} (I ⁻ /I ₃ ⁻)	TiO ₂ -N3-Zn ^{II} (Phen ^{3+/2+})	TiO ₂ -N3-Zn ^{II} (TTT ^{0/-})
R _{Pt} (Ω)	2.1	6.8	81.8	2.8	12.2	214.2
C _{Pt} (× 10 ⁻⁶ F)	2.4	0.1	12.3	8.9	6.5	3.7
R _k (Ω)	19.1	136.8	90.2	42.1	63.1	171.5
C _μ (× 10 ⁻⁴ F)	3.3	0.1	1.1	2.4	0.5	0.3
$k_{\text{eff}} = \omega_k (\times 10^2 / \text{s})^a$	1.6	9.9	1.0	1.0	3.1	0.8
$\tau_{\text{eff}} (\text{ms})^c$	6.4	1.0	10.1	10.1	3.2	12.8
R _w (Ω)	1.1	65.8	89.2	0.9	15.0	211.0
$\omega_d (\times 10^2 / \text{s})$	15.8	6.3	0.4	15.8	12.5	0.2
$n_s (\times 10^{17} / \text{cm}^3)^b$	4.0	0.1	1.4	2.9	0.6	0.9
$D_{\text{eff}} (\times 10^{-4} \text{ cm}^2 / \text{s})^d$	7.6	5.8	0.3	13.0	3.7	1.8
L _n (μm) ^e	22.1	7.6	5.3	36.2	10.9	4.8

a) $k_{\text{eff}} = 2\pi f$, b) $n_s = (k_B T L) / (q^2 A R_w D_{\text{eff}})$ where A is electrode area, T is temperature and L is film thickness, c) $k_{\text{eff}} = 1/\tau_{\text{eff}}$, d) $D_{\text{eff}} = (R_k/R_w) L^2 k_{\text{eff}}$, e) $L_n = (D_{\text{eff}} \times \tau_{\text{eff}})^{1/2}$.

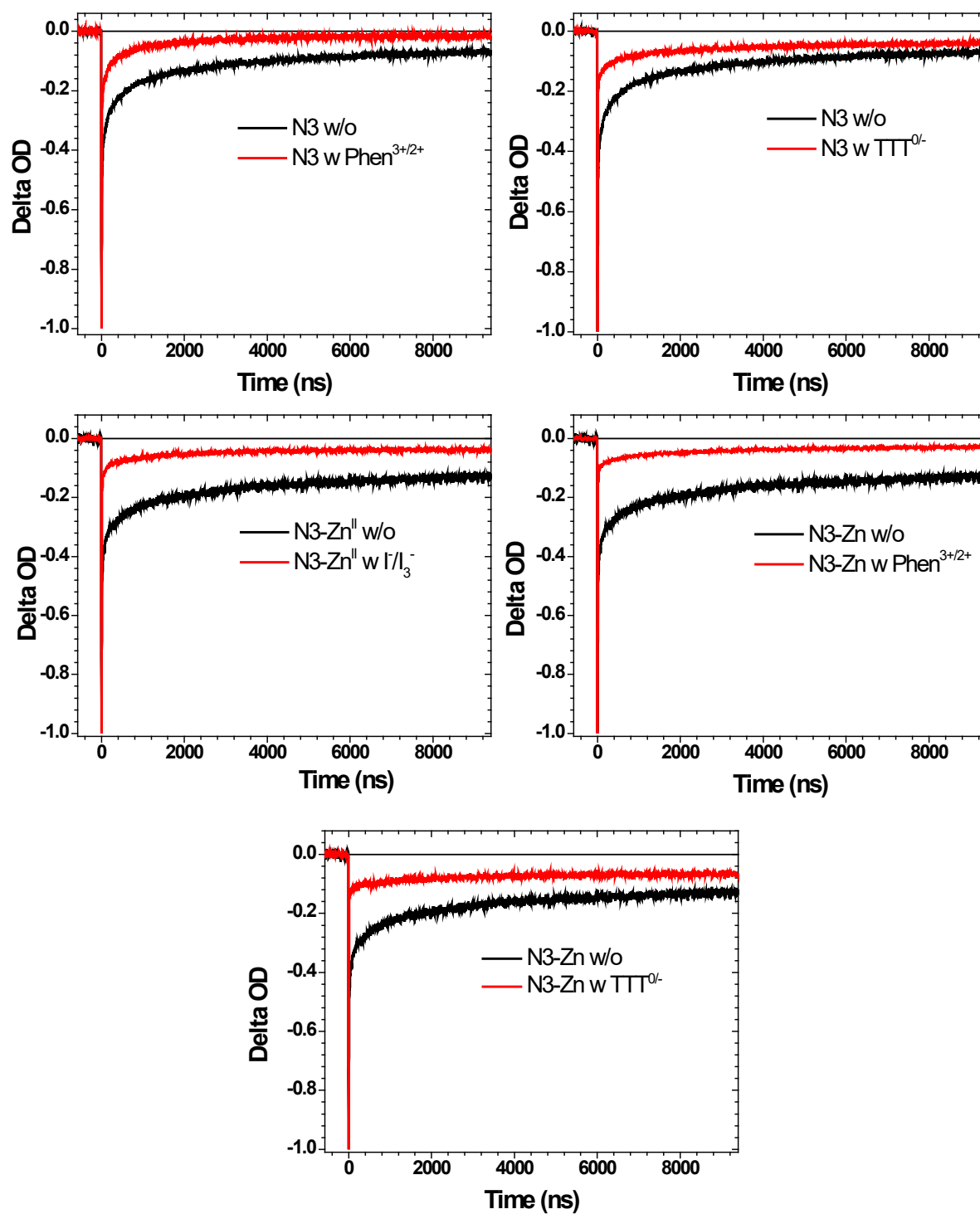


Figure S7. Transient absorption traces for TiO₂-N3 and TiO₂-N3-Zn with and without I⁻/I₃⁻, Phen^{3+/2+}, and TTT^{0/-} redox mediators.

Table S2. Parameters obtained from fitting the decay traces of TiO₂-N3 and TiO₂-N3-Zn from transient absorption measurements. ($\lambda_{\text{ex}} = 480 \text{ nm}$, 5 mJ/pulse, $\lambda_{\text{abs}} = 535 \text{ nm}$). All lifetimes are reported in nanoseconds.

		$\tau_1 (A_1)$	$\tau_2 (A_2)$	$\langle \tau \rangle$
TiO ₂ -N3	w/o	250 (0.11)	2740 (0.89)	2460
	I/I ₃ ⁻	90 (0.19)	900 (0.81)	740
	Phen ^{3+/2+}	160 (0.16)	1580 (0.84)	1360
	TTT ^{0/-}	190 (0.09)	2500 (0.91)	2300
TiO ₂ -N3-Zn	w/o	230 (0.07)	2870 (0.93)	2680
	I/I ₃ ⁻	110 (0.08)	1750 (0.92)	1620
	Phen ^{3+/2+}	150 (0.06)	2510 (0.94)	2360
	TTT ^{0/-}	160 (0.04)	2320 (0.96)	2220

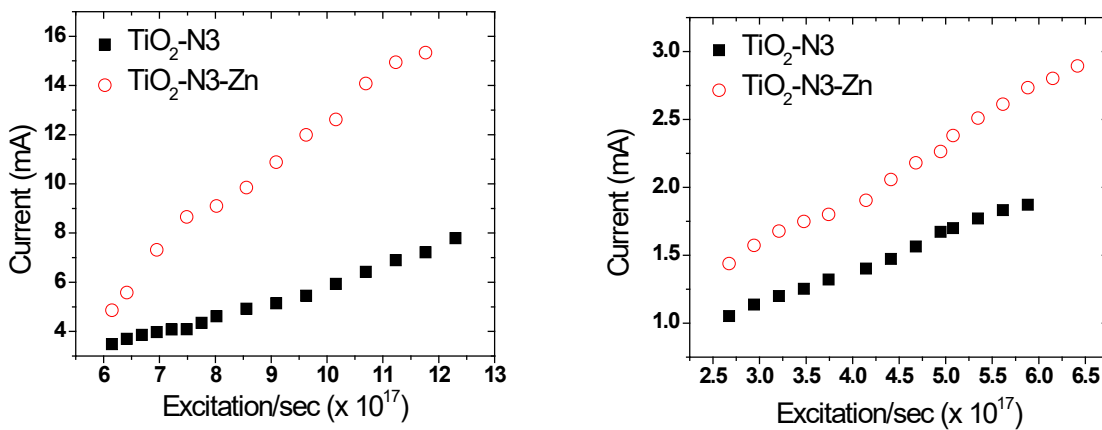


Figure S8. Photocurrent with respect to excitation rate for DSSCs containing TiO₂-N3 and TiO₂-N3-Zn anodes and a) I/I₃⁻ or b) Phen^{3+/2+} redox mediators in MeCN.

References

1. Ogunsolu, O. O.; Murphy, I. A.; Wang, J. C.; Das, A.; Hanson, K., Energy and Electron Transfer Cascade in Self-Assembled Bilayer Dye-Sensitized Solar Cells. *ACS Appl Mater Interfaces* **2016**, 8, 28633– 28640.
2. Feldt, S. M.; Gibson, E. A.; Gabrielsson, E.; Sun, L.; Boschloo, G.; Hagfeldt, A., Design of Organic Dyes and Cobalt Polypyridine Redox Mediators for High-Efficiency Dye-Sensitized Solar Cells. *J Am Chem Soc* **2010**, 132, 16714-16724.
3. Casarin, L.; Swords, W. B.; Caramori, S.; Bignozzi, C. A.; Meyer, G. J., Rapid Static Sensitizer Regeneration Enabled by Ion Pairing. *Inorg Chem* **2017**, 56, 7324-7327.
4. Benazzi, E.; Cristino, V.; Caramori, S.; Meda, L.; Boaretto, R.; Bignozzi, C. A., Electrochemical characterization of polypyridine iron(II) and cobalt(II) complexes for organic redox flow batteries. *Polyhedron* **2018**, 140, 99-108.
5. Ogunsolu, O. O.; Wang, J. C.; Hanson, K., Increasing the Open-Circuit Voltage of Dye-Sensitized Solar Cells via Metal-Ion Coordination. *Inorg Chem* **2017**, 56, 11168-11175.
6. Ogunsolu, O. O.; Wang, J. C.; Hanson, K., Inhibiting Interfacial Recombination Events in Dye-Sensitized Solar Cells using Self-Assembled Bilayers. *ACS Appl Mater Interfaces* **2015**, 7, 27730-4.