Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics

Supporting Information

Regeneration and Recombination kinetics in Cobalt Polypyridine based Dye-Sensitized Solar Cells, explained using Marcus theory

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Synthesis of redox shuttles

Materials. Cobalt chloride hexahydrate was purchased from Fluka. All solvents were used as pa grade. 4-(tert-Butyl)-2-(1H-3,5-dimethylpyrazol-1-yl)pyridine was synthesized in a similar fashion to the recently published synthesis of 4-(tert-butyl)-2-(1H-pyrazol-1-yl)pyridine.[1] H NMR spectra were recorded using a Bruker AV 400 MHz spectrometer. Chemical shifts δ (in ppm) are referenced to residual solvent peaks. For ^{1}H NMR: acetone-D6, 2.05 ppm. ^{19}F and ^{31}P NMR were recorded using a Bruker AV 200 MHz spectrometer. Coupling constants are expressed in hertz (Hz). High-resolution mass spectra (HRMS) were obtained with a Waters Q-TOF-MS instrument using electrospray ionisation (ESI).

4-Methyl-2-(1*H*-pyrazol-1-yl)pyridine. 0.95 g (14.0 mmol, 2 eq) of Pyrazole was dissolved in 20 mL of DMSO at room temperature and 1.57 g (14.0 mmol, 2 eq) of KO^tBu was added. The mixture was heated to 40 ˚C for 20 min. and then 0.78 g (7.0 mmol, 1 eq) of 2-Fluoro-4-picoline (2-Fluoro-4-methyl-pyridine) was added and the mixture was heated to 110 ˚C overnight. After cooling to room temperature the mixture was diluted with water and extracted with Et_2O (3x). The combined colourless organic layers were washed with water, dried over $MgSO_4$ and concentrated. The yellow oil was purified by column chromatography using CH_2Cl_2/EtOAc = 6/1 as solvent mixture. The pure product was obtained as colourless liquid in 99% yield (1.11 g, 6.9 mmol).

$[Co(Mepy\text{-}pz)_3](PF_6)_2$. 478 mg (3.0 mmol, 3.0 eq) of 4-Methyl-2-(1*H*-pyrazol-1-yl)pyridine ligand were dissolved in a 2:1 mixture of water and MeOH (20 mL/10 mL) and then heated to 70 °C. 238 mg (1.0 mmol, 1 eq) of $CoCl_2*6H_2O$ were added as a solid. The mixture was stirred at 70 °C for 10 min and then 0.92 g KPF_6 dissolved in 20 mL of hot water were added. After cooling to r. t. the precipitate was collected on a sintered glass frit, washed with water and Et_2O and dried in vacuo. The pure *fac*-Isomer was obtained as pale orange solid. Yield: 668 mg (0.81 mmol, 81%). HRMS (ESI-TOF) m/z (%): calcd. for $C_{27}H_{27}CoN_9$. 268.0861; found 268.0860 (100) $[(M - 2PF_6)^{2+}]$. Anal. Calcd. for $C_{27}H_{27}CoF_{12}N_9P_2$ (826.43): C 39.24, H 3.23, N 15.25; found: C 39.23, H 3.35, N 14.84%.

$[Co(Mepy\text{-}pz)_3](PF_6)_3$. 380 mg (2.4 mmol, 3.0 eq) of 4-Methyl-2-(1*H*-pyrazol-1-yl)pyridine ligand were dissolved in a 2:1 mixture of water and MeOH (20 mL/10 mL) and then heated to 70 °C. 190 mg (0.8 mmol, 1 eq) of $CoCl_2*6H_2O$ were added as a solid. The mixture was stired at 70 °C for 10 min and then 2 mL of H_2O_2 (30%) and 2 mL of HCl (25%) were added and the mixture was stirred at 70 °C for further 30 min. 0.92 g KPF_6 dissolved in 20 mL of hot water were added. After cooling to r. t. the precipitate was collected on a sintered glass frit, washed with water and Et_2O and dried in vacuo. The pure *fac*-Isomer was obtained as orange solid. Yield: 287 mg (0.3 mmol, 38%). ^{1}H NMR (400 MHz, acetone-D6): δ 9.49-9.46 (m, 3H, ArH), 8.56 (s, 3H, ArH), 7.94 (d, J = 30.2 Hz, 3H, ArH), 7.73-7.71 (m, 3H, ArH), 7.68-7.60 (m, 3H, ArH), 7.25-7.21 (m, 3H, ArH), 2.73 (s, 9H, CH_3) ppm. HRMS (ESI-TOF) m/z (%): calcd. for $C_{27}H_{27}CoN_9P_2F_{12}$ 826.1005; found 826.1021 (35) $[(M - PF_6)^+]$, calcd. for $C_{27}H_{27}CoN_9PF_6$ 340.5682; found 340.5704 (63) $[(M - 2PF_6)^{2+}]$.

$[Co(Me_2pz\text{-}py\text{-}pzMe_2)_2](TFSI)_2$. 802 mg (3.0 mmol, 2.0 eq) of Me_2pz-py-$pzMe_2$ ligand was dissolved in 100 mL of acetonitrile and 500 mg (2.1 mmol, 1.4 eq) of $CoCl_2*6H_2O$ dissolved in 20 mL of water was added. The mixture was stirred at room temperature for 30 min. and then 1.72 g (6.0 mmol, 4 eq) of Lithium trifluoromethansulfonimid (LiTFSI) was added as aqueous solution. The mixture was stirred for another 30 min. and then the mixture was concentrated until the solution turned colourless and a orange to red precipitate had formed. The precipitate was collected, washed with water and Et_2O and dried in vacuo to obtain the product as orange solid. Yield: 1.70 g (1.47 mmol, 98 %). MS (ESI-TOF) m/z (%): calcd. 873.15; found 873.18 (86) $[(M - TFSI)^+]$; calcd. 296.61; found 296.62 (61) $[(M - 2TFSI)^{2+}]$.

$[Co(Me_2pz\text{-}py\text{-}pzMe_2)_2](TFSI)_3$. 535 mg (2.0 mmol, 2.0 eq) of Me_2pz-py-$pzMe_2$ ligand was dissolved in 100 mL of acetonitrile and 333 mg (1.4 mmol, 1.4 eq) of $CoCl_2*6H_2O$ dissolved in

20 mL of water was added. After 30 min. at room temperature 768 mg (1.4 mmol, 1.4 eq) of $Ce(NH_4)_2(NO_3)_6$ was added as aqueous solution to oxidize the cobalt. The mixture was stirred overnight at room temperature and then concentrated to approximately half of the total volume. The remaining solution was allowed to stand at room temperature for 72 h and the dark precipitated formed was filtered off. To the solution 1.5 g (5.2 mmol, 5.2 eq) of Lithium trifluoromethansulfonimid (LiTFSI) was added and the solution was diluted with methanol and stirred at room temperature. After 2h the mixture was concentrated and water was added to force precipitation of the product. The precipitate was collected, washed with water and Et_2O and dried in vacuo overnight. The product was obtained as ochre solid. Yield: 700 mg (0.49 mmol, 35%).

1. N. M. Shavaleev, R. Scopelliti, E. Baranoff, M. Grätzel and M. K. Nazeeruddin, *Inorg. Chim. Acta.*, 2012, **383**, 316-319.

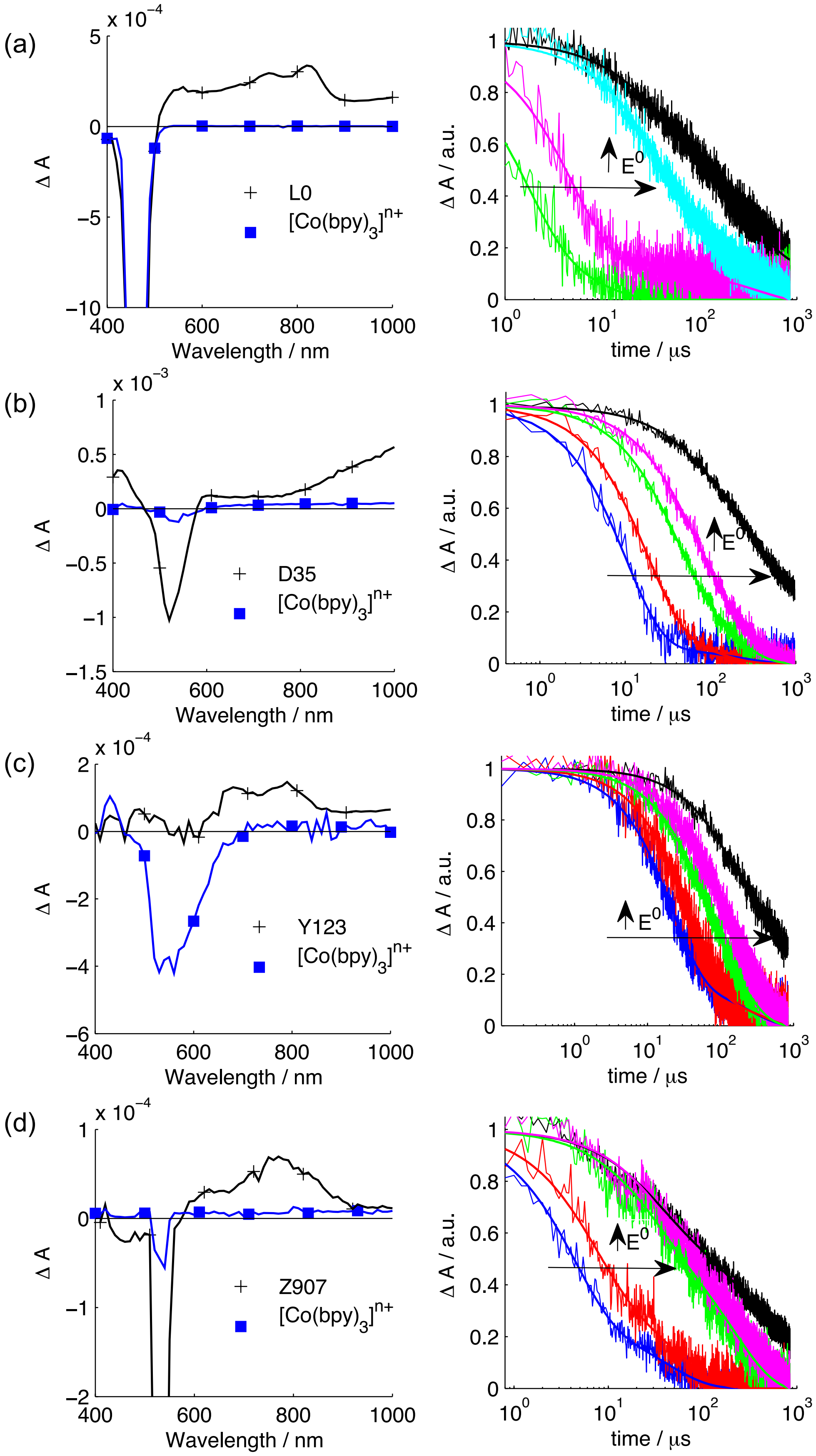

Figure S1. PIA spectrum and transient absorption kinetics measurements for (a) L0, (b) D35, (c) Y123 and (d) Z907 sensitized TiO_2 films.

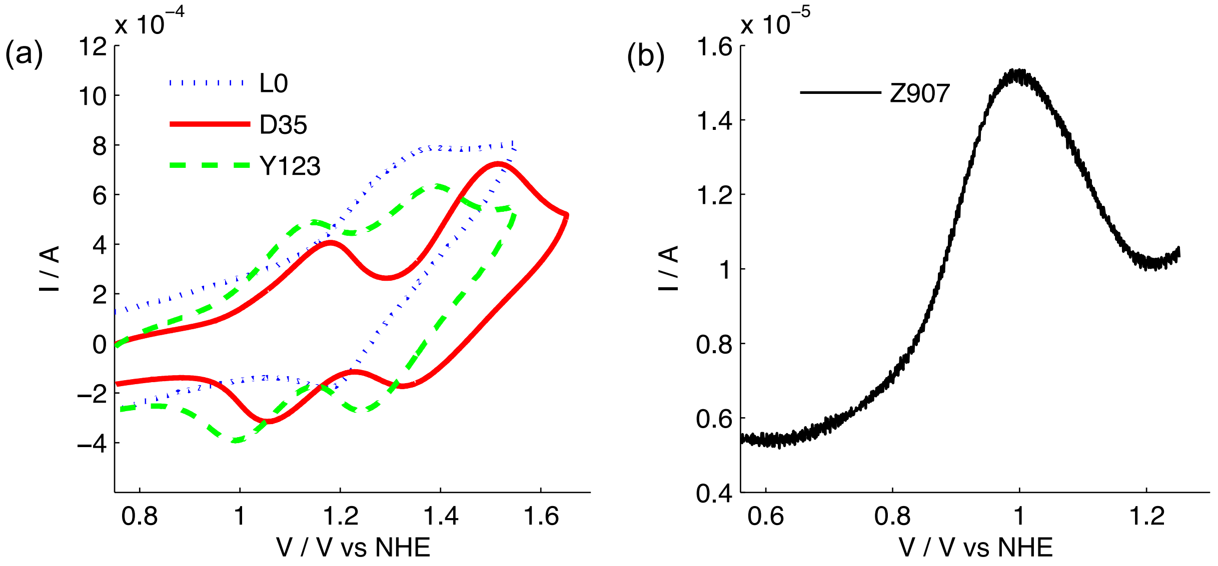

Figure S2. (a) Cyclic voltammogram measured at a scan rate of 0.1 Vs^{-1} for L0, D35 and Y123 sensitized TiO_2 films. (b) Square wave voltammogram for Z907 sensitized FTO glass, measured with a pulse amplitude of 10 mV and a frequency of 80 Hz.

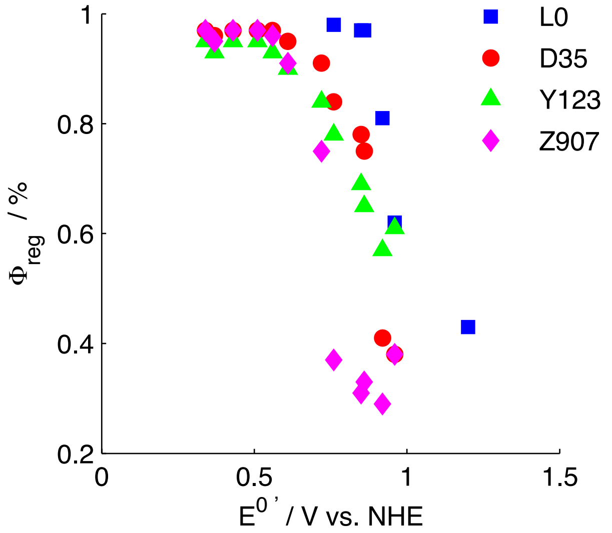

Figure S3. Regeneration efficiencies for the different dyes versus the formal potential of the cobalt complexes.

Table S2. Current-Voltage characteristics for D35 sensitized DSCs.

Redox couple	V_{OC} *(V)*	$E_{F,\,OC}$ *(V vs NHE)*[a]	J_{SC} *(mAcm*$^{-2}$*)*	*FF*	*η (%)*
$[Co(bpy)_3]^{n+}$	0.89	-0.37	9.4	0.57	4.8
$[Co(phen)_3]^{n+}$	0.91	-0.33	8.2	0.51	3.8
$[Co(Me_2bpy\text{-}pz)_2]^{n+}$	1.02	-0.30	6.1	0.61	3.7
$[Co(bpy\text{-}pz)_2]^{n+}$	1.02	-0.20	5.3	0.68	3.6
$[Co(py\text{-}pz)_3]^{n+}$	0.90	-0.02	2.5	0.66	1.5
$[Co(Mepy\text{-}pz)_3]^{n+}$	0.88	0.04	0.78	0.58	0.4

[a] The electrochemical potential in the TiO_2 under open circuit conditions is calculated as follows $E_{F,OC} = E_{redox} - V_{OC}$, where E_{redox} is determined using the Nernst equation.

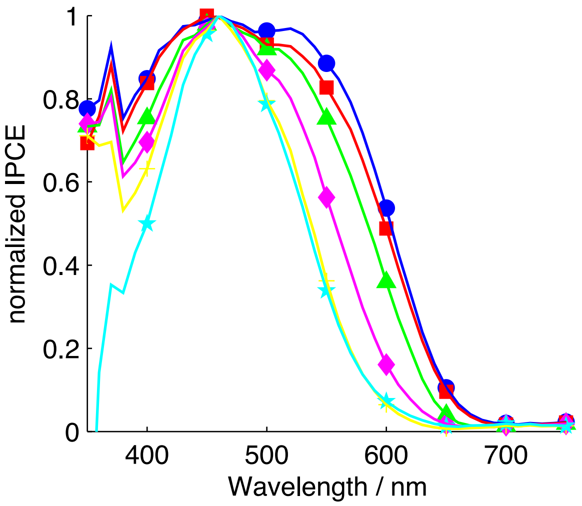

Figure S4. Normalized spectra of incident photon to current efficiency (IPCE) for D35 sensitized DSCs.

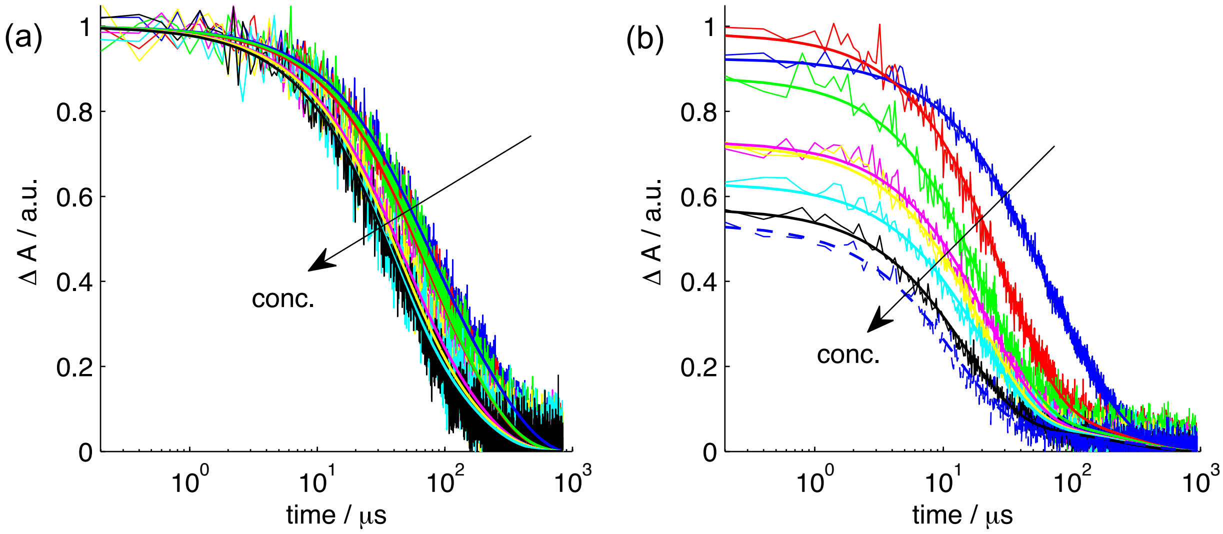

Figure S5. Transient absorption kinetics dependence on concentration for D35 sensitized TiO_2 using (a) $[Co(Cl\text{-}phen)_3]^{2+}$ and (b) $[Co(bpy\text{-}pz)_2]^{2+}$ electrolyte. The amplitude of the absorbance signal for $[Co(Cl\text{-}phen)_3]^{2+}$ decreased when the redox electrolyte was added and the signal was therefore normalized versus the signal for the D35 sensitized TiO_2 film in inert electrolyte before the addition of the redox electrolyte. 20 % was added to the signal to correct for scattering losses from the electrolyte.

The observed regeneration rate constants (k'_{reg}) in Figure 6 were described by a sum of two exponential functions, from which an average rate constant was calculated, equations 1, 2.[2]

$$\Delta Abs = A_0 + A_1 \exp(-k_1 t) + A_2 \exp(-k_2 t) \tag{1}$$

$$k'_{reg} = \frac{A_1/k_1 + A_2/k_2}{A_1/k_1^2 + A_2/k_2^2} \tag{2}$$

The slopes from the linear fits of k'_{reg} versus the concentration of Co(II) provided the second-order rate constants for dye regeneration.

2. K. C. D. Robson, K. Hu, G. J. Meyer and C. P. Berlinguette, *J. Am. Chem. Soc.*, 2013, **135**, 1961-1971.

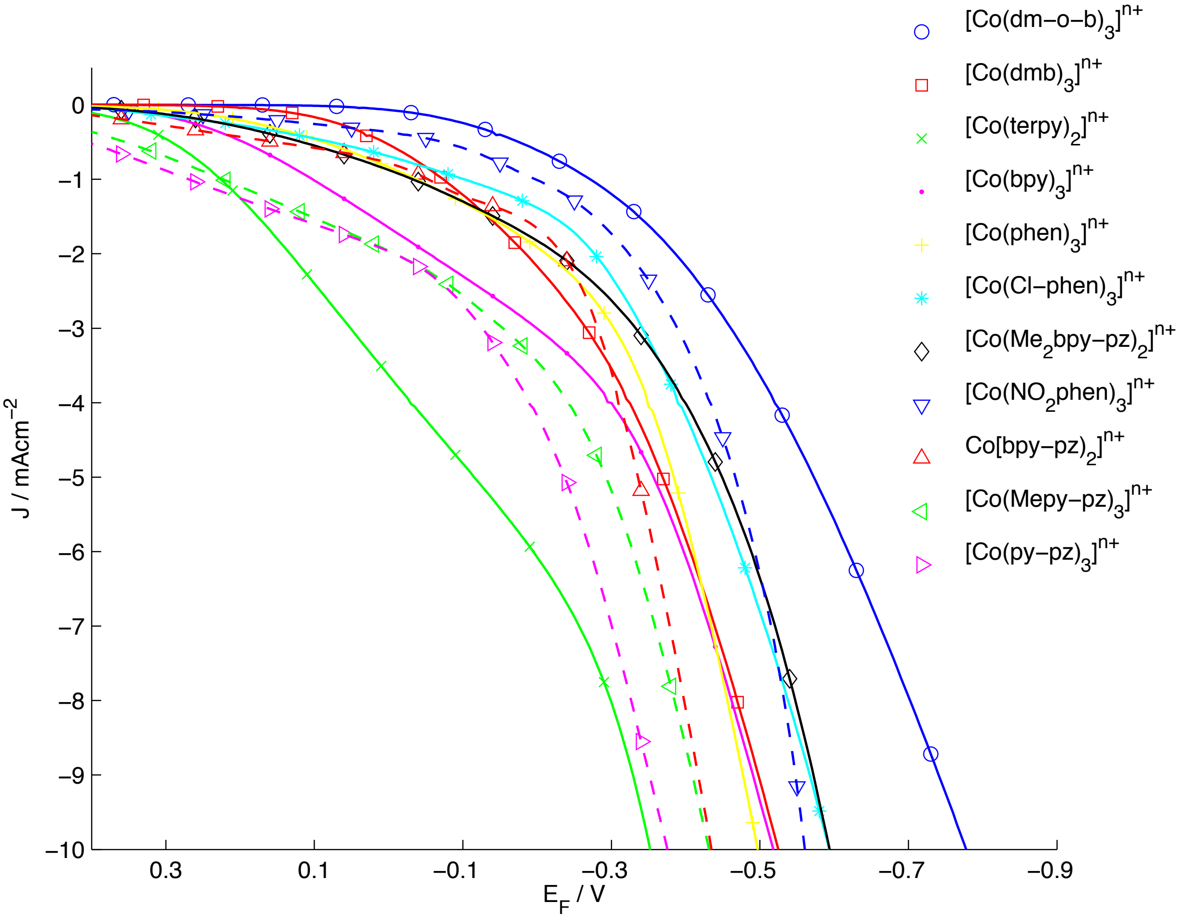

Figure S6. Dark current densities versus the *quasi*-Fermi level of the TiO_2 for D35-sensitized DSCs prepared using $TiCl_4$ pre- and post treatment.