Development of high efficiency 100% aqueous cobalt electrolyte dye-sensitised solar cells

-- Supporting Information --

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SI-1  Electrochemical and optical characterisation

Fig. S1 Molar extinction coefficients of the water soluble redox couples compared to [Co(bpy)$_3$](PF$_6$)$_2$ and [Co(bpy)$_3$](PF$_6$)$_3$ in acetonitrile. 1 mM of each redox species was dissolved in water (for the water soluble redox couples) or in acetonitrile.

Fig. S2 Cyclic Voltammogram of [Co(bpy)$_3$]Cl$_2$ in water. Electrolyte: 1 mM [Co(bpy)$_3$]Cl$_2$, 1 M KCl in water, WE: glassy carbon, CE: graphite rod, Ref: Ag|AgCl.

Fig. S3 Cyclic Voltammogram of [Co(phen)$_3$]Cl$_2$ in water. Electrolyte: 1 mM [Co(phen)$_3$]Cl$_2$, 1 M KCl in water, WE: glassy carbon, CE: graphite rod, Ref: Ag|AgCl.
Fig. S4 Cyclic Voltammogram of D51 sensitised on a TiO$_2$ film measured in water. Electrolyte: 0.1 M LiTFSI, 0.05 M Triton in water, WE: dye-sensitised TiO$_2$ film on FTO glass, CE: graphite rod, Ref: Ag|AgCl.

Fig. S5 Cyclic Voltammogram of LEG4 sensitised on a TiO$_2$ film measured in water. Electrolyte: 0.1 M LiTFSI, 0.05 M Triton in water, WE: dye-sensitised TiO$_2$ film on FTO glass, CE: graphite rod, Ref: Ag|AgCl.

Fig. S6 Determining the diffusion coefficient of K$_3$[Fe(CN)$_6$] in water. A: Cyclic voltammograms were measured at different scanning speeds. Electrolyte: 10 mM K$_3$[Fe(CN)$_6$], 0.5 M KCl in water, WE: glassy carbon, CE: carbon rod, Ref: Ag|AgCl. B: The peak currents plotted versus the square root of the scan speeds.
Fig. S7 Determining the diffusion coefficient of [Co(bpy)$_3$]Cl$_2$ in water in water. A: Cyclic voltammograms were measured at different scanning speeds. Electrolyte: 5 mM [Co(bpy)$_3$]Cl$_2$, 0.5 M KCl in water, WE: glassy carbon, CE: carbon rod, Ref: Ag|AgCl. B: The peak currents plotted versus the square root of the scan speeds.

Fig. S8 Determining the diffusion coefficient of [Co(phen)$_3$]Cl$_2$ in water in water. A: Cyclic voltammograms were measured at different scanning speeds. Electrolyte: 5 mM [Co(phen)$_3$]Cl$_2$, 0.5 M KCl in water, WE: glassy carbon, CE: carbon rod, Ref: Ag|AgCl. B: The peak currents plotted versus the square root of the scan speeds.
Fig. S9 Contact angles measured of deionised water (top), 0.8 M MBI in deionised water (middle) and 0.13 M [Co(phen)_3]Cl_2 and 0.8 M MBI in deionised water (bottom) on LEG4 (left column) or D51 (right column) sensitised TiO_2 surfaces.
SI-2 DSC characterisation

Fig. S10 J-V curves measured at 1 sun of solar cells assembled with the organic dyes D51 or LEG4 in combination with Co(bpy)$_3$, Co(phen)$_3$ or I/I$_3$ based electrolytes. The electrolytes were the following: Co(bpy)$_3$ (0.13 M [Co(bpy)$_3$]Cl$_2$, 0.04 M [Co(bpy)$_3$]Cl, 0.8 M MBI in water), Co(phen)$_3$ (0.13 M [Co(phen)$_3$]Cl$_2$, 0.04 M [Co(phen)$_3$]Cl, 0.8 M MBI in water) and I/I$_3$ (4 M KI, 20 mM I$_2$ in water).

Fig. S11 J-V curves measured at in dark of solar cells assembled with the organic dyes D51 or LEG4 in combination with Co(bpy)$_3$, Co(phen)$_3$ or I/I$_3$ based electrolytes. The electrolytes were the following Co(bpy)$_3$ (0.13 M [Co(bpy)$_3$]Cl$_2$, 0.04 M [Co(bpy)$_3$]Cl, 0.8 M MBI in water), Co(phen)$_3$ (0.13 M [Co(phen)$_3$]Cl$_2$, 0.04 M [Co(phen)$_3$]Cl, 0.8 M MBI in water) and I/I$_3$ (4 M KI, 20 mM I$_2$ in water).
**SI-3  Kinetics and mass transport**

Fig. S12 Transient absorption measurements. Measurements are done on LEG4 sensitised TiO$_2$ films in contact with stock solution (0.2 M TBP and 0.1 M LiClO$_4$ in acetonitrile) shown as blue trace and redox species in stock solution (0.22 M $[\text{Co(bpy)}_3]\text{Cl}_2$, 0.2 M TBP, 0.1 M LiClO$_4$ in acetonitrile) as red trace. Fitting to data is shown as black line.

Fig. S13 Transient absorption measurements. Measurements are done on D51-sensitised TiO$_2$ films in contact with 1 M KNO$_3$ in water, shown as blue trace and 0.13 M $[\text{Co(phen)}_3]\text{Cl}_2$ in water, shown as red trace. Fitting to data is shown as black line.

Fig. S14 Transient absorption measurements. Measurements are done on LEG4-sensitised TiO$_2$ films in contact with 1 M KNO$_3$ in water, shown as blue trace and 0.13 M $[\text{Co(phen)}_3]\text{Cl}_2$ in water, shown as red trace. Fitting to data is shown as black line.
Fig. S15 Photocurrent transient measurements with extracted $J_{\text{peak}}$ plotted versus biased light. Red = 0.04 M, yellow = 0.05 M, green = 0.06 M [Co(phen)$_3$]Cl$_3$.

Fig. S16 Photocurrent transient measurements with extracted $J_{\text{peak}}$ plotted versus biased light. yellow = S90 = 15 $\mu$m, green = S60 = 18 $\mu$m and blue = S30 = 20 $\mu$m thickness of spacer between working electrode and counter electrode.
### SI-4 Stability measurements

**Fig. S17** J-V curves measured every 6 hour, at 1 sun, at MPP, of solar cells assembled with the organic dye D51 and 0.13 M [Co(phen)$_3$]Cl$_2$, 0.04 M [Co(phen)$_3$]Cl$_3$, 0.8 M MBI in water as electrolyte.

**Fig. S18** Evolution of the PCE obtained by J-V measurements every 5 hours, during 200 hours, 1 sun illumination at MPP.

**Fig. S19** Evolution of the $V_{oc}$ during 200 hours, 1 sun illumination at MPP.
After approximately 120 hours, some zig-zagging can be observed in the PCE trends (calculated from MPP tracking) seen in Figure 8. However, this trend is not observed for the PCE trends calculated from J-Vs (Figure S18). This was due to a change in the J-V scanning range, which was implemented at approximately 120 hours due to the increasing $V_{oc}$, the forward scan bias range increased from 1 V to 1.2 V. This led to some insignificant transient hysteresis when MPP tracking after each J-V, observable as zig-zags; the overall stability trend was unchanged.
SI-5 Increasing the $V_{oc}$

Fig. S22 Cyclic Voltammogram of $[\text{Co(bpy-pz)}_3\text{Cl}_2$ in water. Electrolyte: 1 mM $[\text{Co(bpy-pz)}_3\text{Cl}_2$, 1 M KCl in water, WE: glassy carbon, CE: graphite rod, Ref: Ag/AgCl.

Fig. S23 Determining the diffusion coefficient of $[\text{Co(bpy)}_3\text{Cl}_2$ in water. A: Cyclic voltammograms were measured at different scanning speeds. Electrolyte: 5 mM $[\text{Co(bpy)}_3\text{Cl}_2$, 0.5 M KCl in water, WE: glassy carbon, CE: carbon rod, Ref: Ag/AgCl. B: The peak currents plotted versus the square root of the scan speeds.
Fig. S24 JV curve measured at 1 sun of solar cells assembled with the organic dyes D51 in combination with Co(bpy-pz)$_3$ electrolyte. The electrolyte consisted of: 0.13 M [Co(bpy-pz)$_3$]Cl$_2$, 0.06 M [Co(bpy-pz)$_3$]Cl$_3$ and 0.8 M MBI in water.

Fig. S25 Photocurrent linearity, $J_{sc}$ plotted versus biased light. The Co(phen)$_3$ and Co(bpy-pz)$_3$ electrolytes have the same weak mass transport limitation. Measurements performed on solar cells with D51 dye and Co(phen)$_3$ and Co(bpy-pz)$_3$ electrolytes (0.13 M [Co(phen/bpy-pz)$_3$]Cl$_2$, 0.06 M [Co(phen/bpy-pz)$_3$]Cl$_3$ and 0.8 M MBI in water).