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

-- Supporting Information --

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SI-1 Electrochemical and optical characterisation

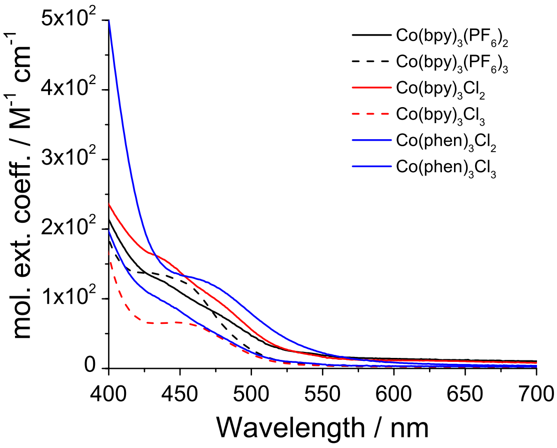


Fig. S1 Molar extinction coefficients of the water soluble redox couples compared to [$Co(bpy)_3$](PF_6)$_2$ and [$Co(bpy)_3$]](PF_6)$_3$ in acetonitrile. 1 mM of each redox species was dissolved in water (for the water soluble redox couples) or in acetonitrile.

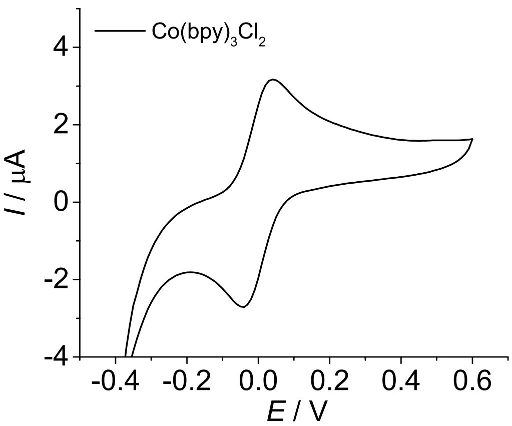


Fig. S2 Cyclic Voltammogram of [$Co(bpy)_3$]Cl_2 in water. Electrolyte: 1 mM [$Co(bpy)_3$]Cl_2, 1 M KCl in water, WE: glassy carbon, CE: graphite rod, Ref: Ag|AgCl.

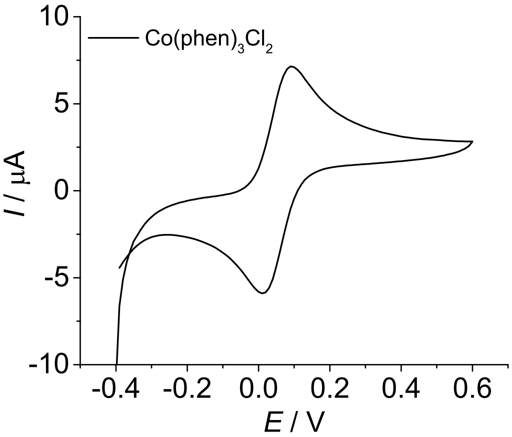


Fig. S3 Cyclic Voltammogram of [$Co(phen)_3$]Cl_2 in water. Electrolyte: 1 mM [$Co(phen)_3$]Cl_2, 1 M KCl in water, WE: glassy carbon, CE: graphite rod, Ref: Ag|AgCl.

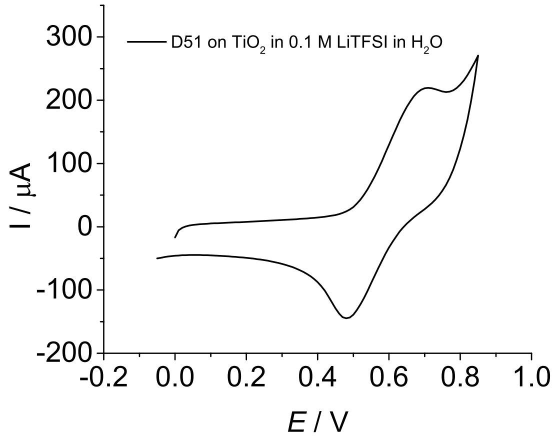


Fig. S4 Cyclic Voltammogram of D51 sensitised on a TiO_2 film measured in water. Electrolyte: 0.1 M LiTFSI, 0.05 M Triton in water, WE: dye-sensitised TiO_2 film on FTO glass, CE: graphite rod, Ref: Ag|AgCl.

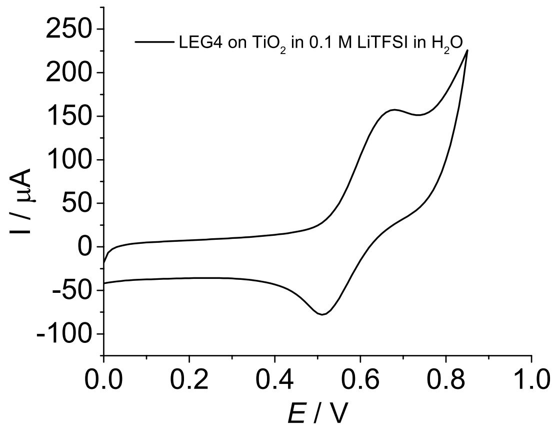


Fig. S5 Cyclic Voltammogram of LEG4 sensitised on a TiO_2 film measured in water. Electrolyte: 0.1 M LiTFSI, 0.05 M Triton in water, WE: dye-sensitised TiO_2 film on FTO glass, CE: graphite rod, Ref: Ag|AgCl.

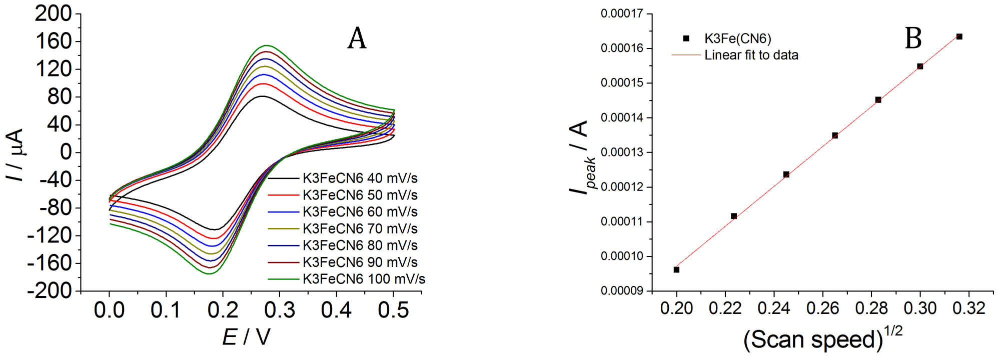


Fig. S6 Determining the diffusion coefficient of $K_3[Fe(CN_6)]$ in water. A: Cyclic voltammograms were measured at different scanning speeds. Electrolyte: 10 mM $K_3[Fe(CN_6)]$, 0.5 M KCl in water, WE: glassy carbon, CE: carbon rod, Ref: Ag|AgCl. B: The peak currents plotted versus the square root of the scan speeds.

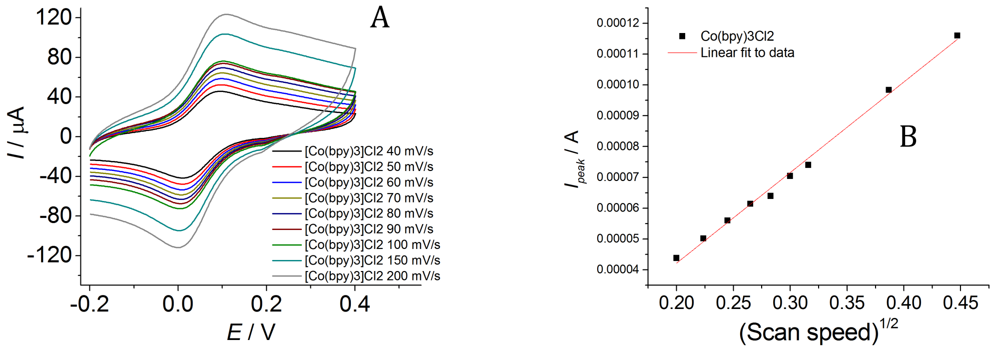


Fig. S7 Determining the diffusion coefficient of $[Co(bpy)_3]Cl_2$ in water in water. A: Cyclic voltammograms were measured at different scanning speeds. Electrolyte: 5 mM $[Co(bpy)_3]Cl_2$, 0.5 M KCl in water, WE: glassy carbon, CE: carbon rod, Ref: Ag|AgCl. B: The peak currents plotted versus the square root of the scan speeds.

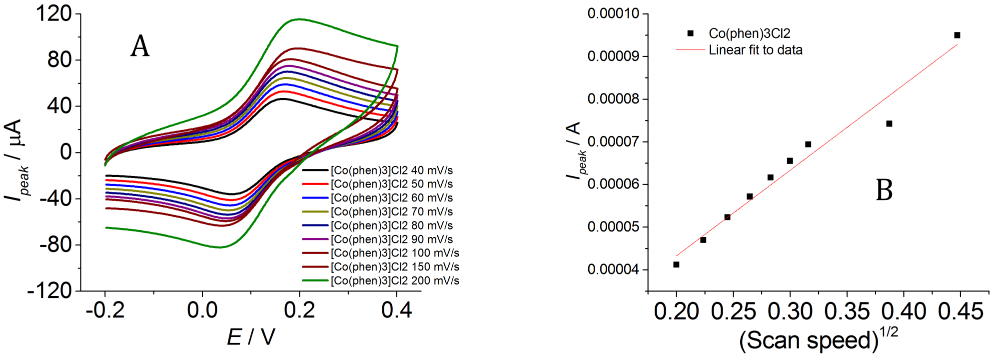
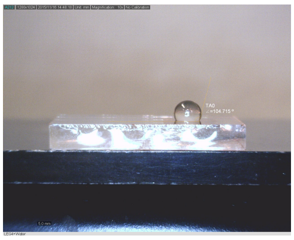
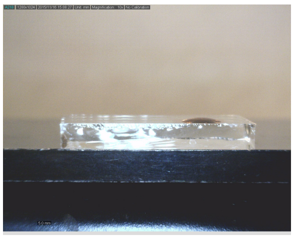


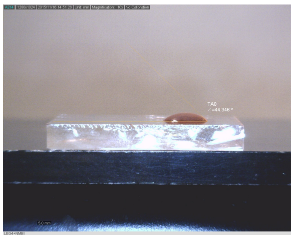
Fig. S8 Determining the diffusion coefficient of $[Co(phen)_3]Cl_2$ in water in water. A: Cyclic voltammograms were measured at different scanning speeds. Electrolyte: 5 mM $[Co(phen)_3]Cl_2$, 0.5 M KCl in water, WE: glassy carbon, CE: carbon rod, Ref: Ag|AgCl. B: The peak currents plotted versus the square root of the scan speeds.



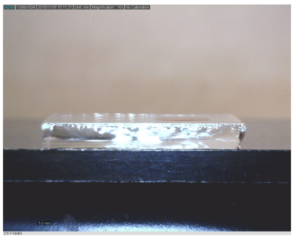
LEG4 + water



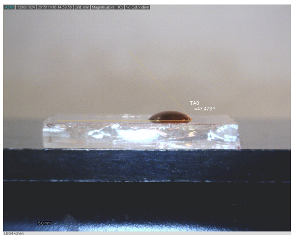
D51 + water



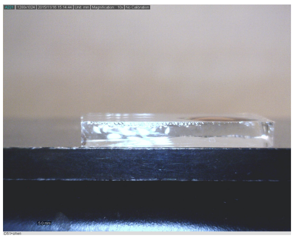
LEG4 + MBI



D51 + MBI



LEG4 + phen



D51 + phen

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

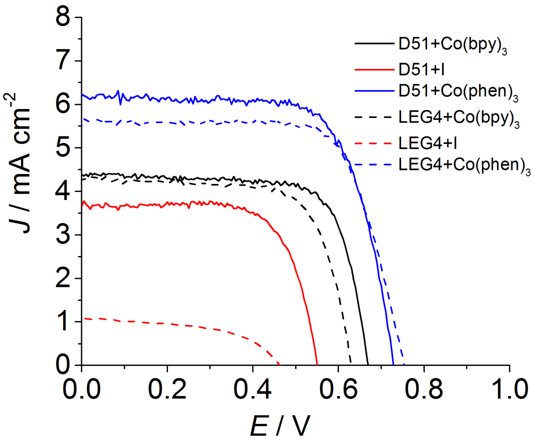


Fig. S10 J-V curves measured at 1 sun of solar cells assembled with the organic dyes D51 or LEG4 in combination with $Co(bpy)_3$, $Co(phen)_3$ or I^-/I_3^- based electrolytes. The electrolytes were the following: $Co(bpy)_3$ (0.13 M $[Co(bpy)_3]Cl_2$, 0.04 M $[Co(bpy)_3]Cl_3$, 0.8 M MBI in water), $Co(phen)_3$ (0.13 M $[Co(phen)_3]Cl_2$, 0.04 M $[Co(phen)_3]Cl_3$, 0.8 M MBI in water) and I^-/I_3^- (4 M KI, 20 mM I_2 in water).

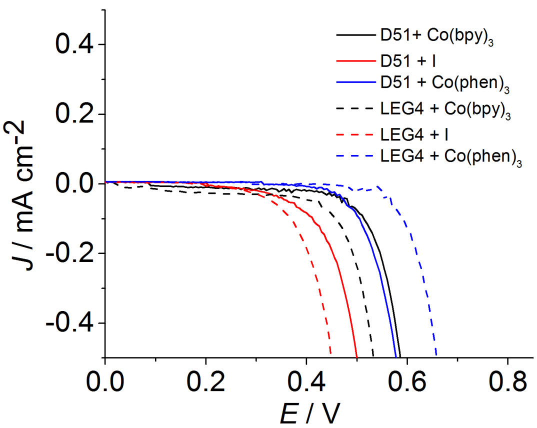


Fig. S11 J-V curves measured at in dark of solar cells assembled with the organic dyes D51 or LEG4 in combination with $Co(bpy)_3$, $Co(phen)_3$ or I^-/I_3^- based electrolytes. The electrolytes were the following $Co(bpy)_3$ (0.13 M $[Co(bpy)_3]Cl_2$, 0.04 M $[Co(bpy)_3]Cl_3$, 0.8 M MBI in water), $Co(phen)_3$ (0.13 M $[Co(phen)_3]Cl_2$, 0.04 M $[Co(phen)_3]Cl_3$, 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

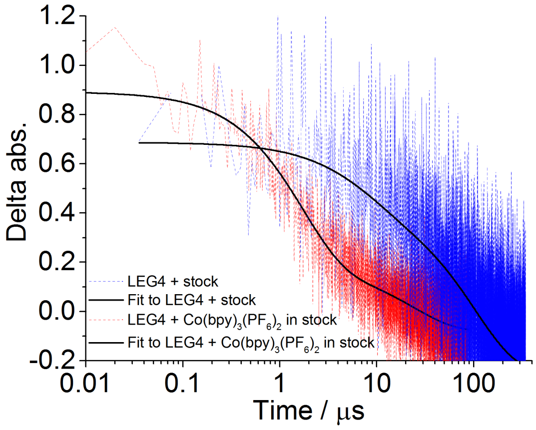


Fig. S12 Transient absorption measurements. Measurements are done on LEG4 sensitised TiO_2 films in contact with stock solution (0.2 M TBP and 0.1 M $LiClO_4$ in acetonitrile) shown as blue trace and redox species in stock solution (0. 22 M $[Co(bpy)_3]Cl_2$, 0.2 M TBP, 0.1 M $LiClO_4$ in acetontrile) as red trace. Fitting to data is shown as black line.

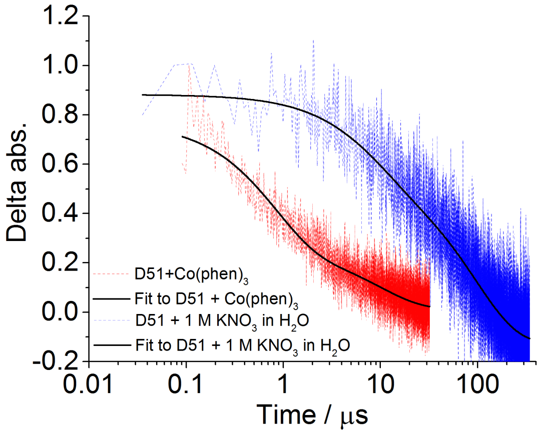


Fig. S13 Transient absorption measurements. Measurements are done on D51-sensitised TiO_2 films in contact with 1 M KNO_3 in water, shown as blue trace and 0.13 M $[Co(phen)3]Cl_2$ in water, shown as red trace. Fitting to data is shown as black line.

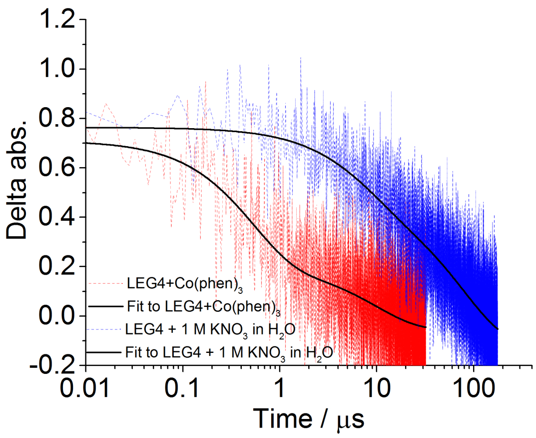


Fig. S14 Transient absorption measurements. Measurements are done on LEG4-sensitised TiO_2 films in contact with 1 M KNO_3 in water, shown as blue trace and 0.13 M $[Co(phen)3]Cl_2$ in water, shown as red trace. Fitting to data is shown as black line.

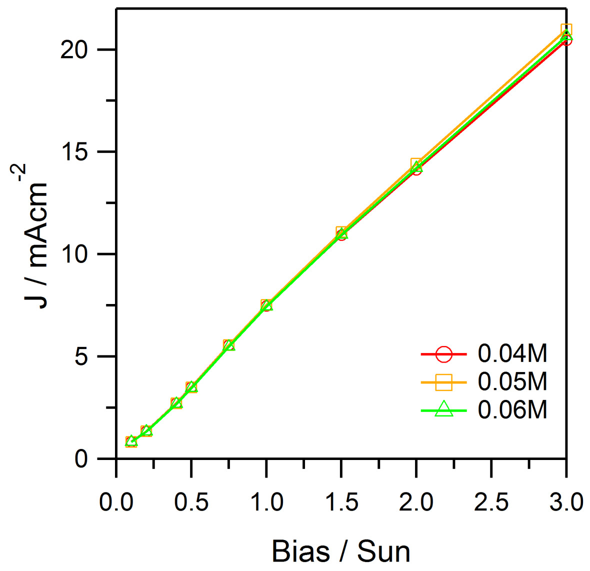


Fig. S15 Photocurrent transient measurements with extracted J_{peak} plotted versus biased light. Red = 0.04 M, yellow = 0.05 M, green = 0.06 M [Co(phen)$_3$]Cl$_3$.

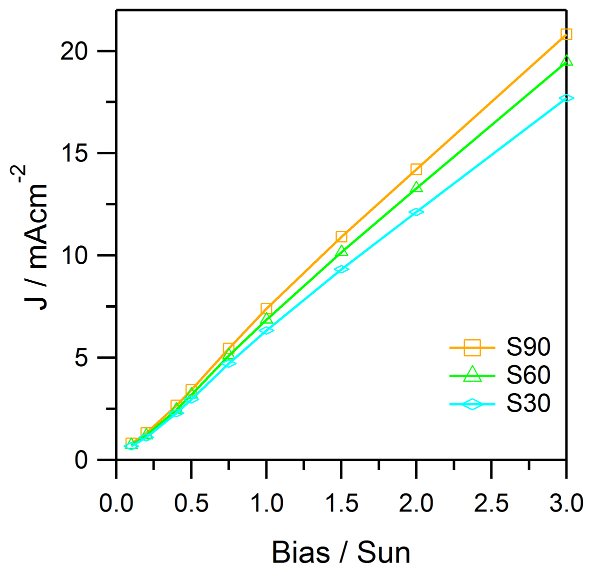


Fig. S16 Photocurrent transient measurements with extracted J_{peak} plotted versus biased light. yellow = S90 = 15 μm, green = S60 = 18 μm and blue = S30 = 20 μm thickness of spacer between working electrode and counter electrode.

SI-4 Stability measurements

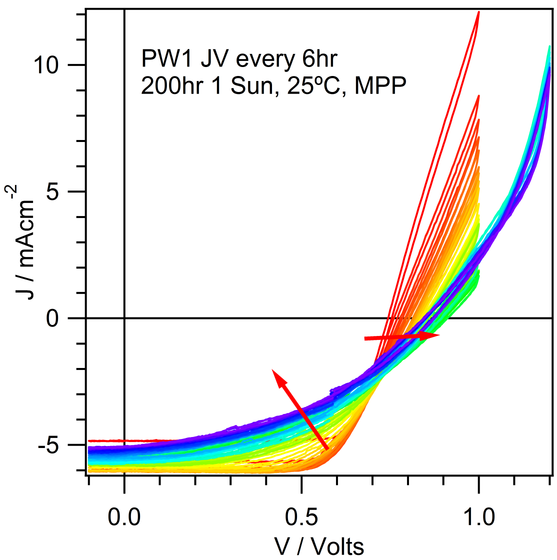


Fig. S17 J-V curves measured every 6 hour, at 1 sun, at MPP, of solar cells assembled with the organic dye D51 and 0.13 M $[Co(phen)_3]Cl_2$, 0.04 M $[Co(phen)_3]Cl_3$, 0.8 M MBI in water as electrolyte.

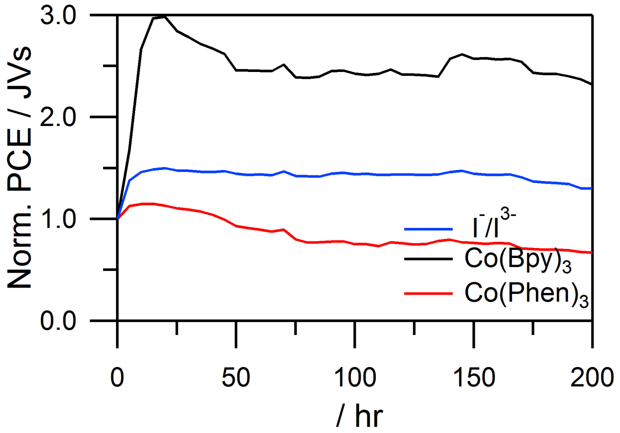


Fig. S18 Evolution of the PCE obtained by J-V measurements every 5 hours, during 200 hours, 1 sun illumination at MPP.

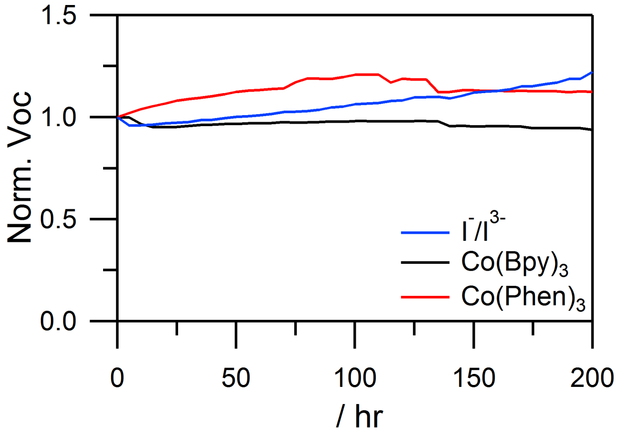


Fig. S19 Evolution of the V_{OC} during 200 hours, 1 sun illumination at MPP.

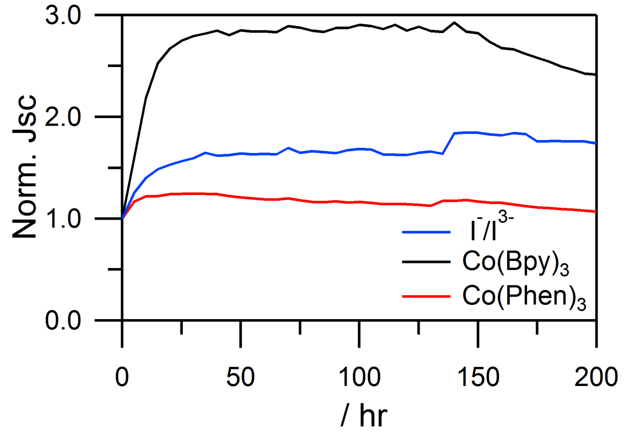


Fig. S20 Evolution of the J_{SC} during 200 hours, 1 sun illumination at MPP.

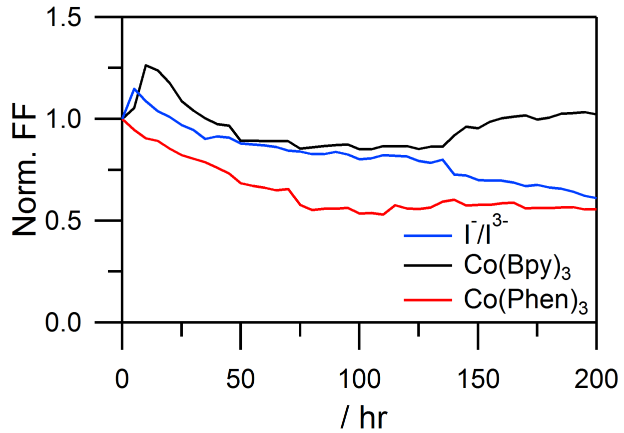


Fig. S21 Evolution of the FF during 200 hours, 1 sun illumination at MPP.

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}

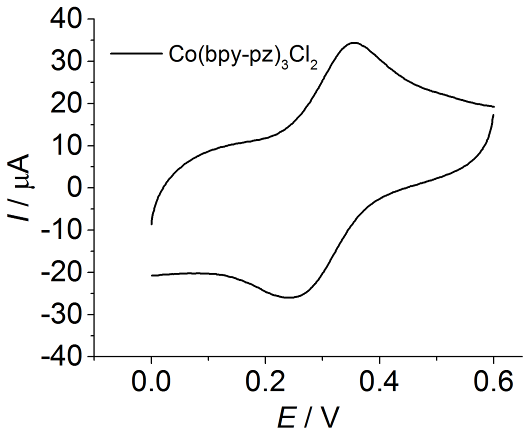


Fig. S22 Cyclic Voltammogram of $[Co(bpy\text{-}pz)_3]Cl_2$ in water. Electrolyte: 1 mM $[Co(bpy\text{-}pz)_3]Cl_2$, 1 M KCl in water, WE: glassy carbon, CE: graphite rod, Ref: Ag|AgCl.

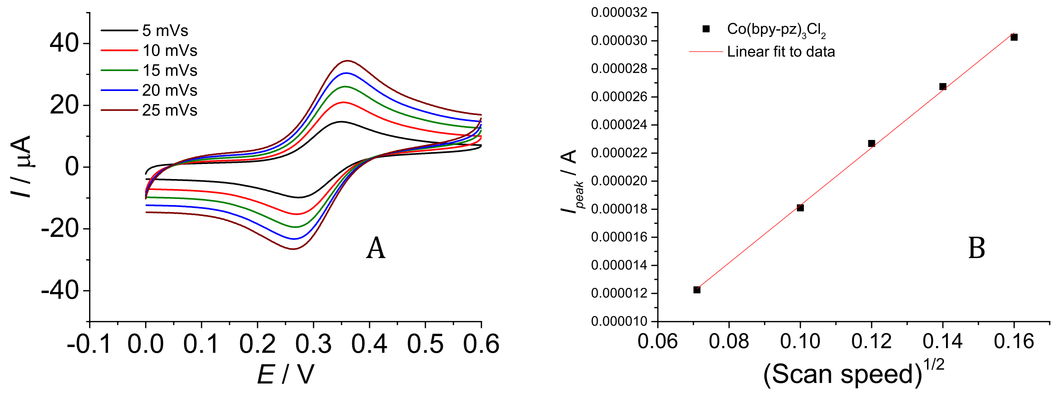


Fig. S23 Determining the diffusion coefficient of $[Co(bpy)_3]Cl_2$ in water. A: Cyclic voltammograms were measured at different scanning speeds. Electrolyte: 5 mM $[Co(bpy)_3]Cl_2$, 0.5 M KCl in water, WE: glassy carbon, CE: carbon rod, Ref: Ag|AgCl. B: The peak currents plotted versus the square root of the scan speeds.

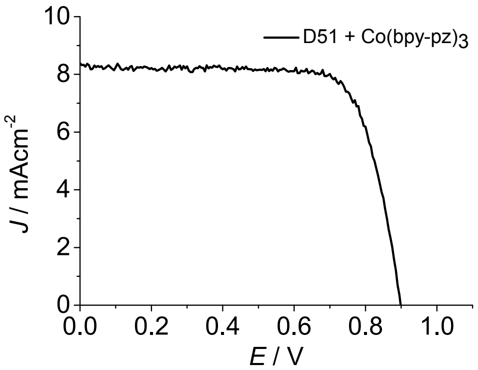


Fig. S24 JV curve measured at 1 sun of solar cells assembled with the organic dyes D51 in combination with $Co(bpy\text{-}pz)_3$ electrolyte. The electrolyte consisted of: 0.13 M $[Co(bpy\text{-}pz)_3]Cl_2$, 0.06 M $[Co(bpy\text{-}pz)_3]Cl_3$ and 0.8 M MBI in water.

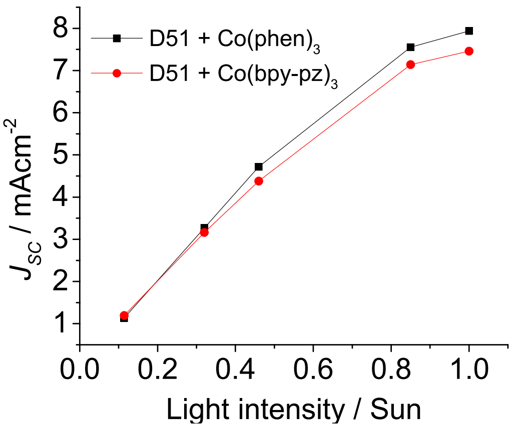


Fig. S25 Photocurrent linearity, J_{SC} plotted versus biased light. The $Co(phen)_3$ and $Co(bpy\text{-}pz)_3$ electrolytes have the same weak mass transport limitation. Measurements performed on solar cells with D51 dye and $Co(phen)_3$ and $Co(bpy\text{-}pz)_3$ electrolytes (0.13 M $[Co(phen/bpy\text{-}pz)_3]Cl_2$, 0.06 M $[Co(phen/bpy\text{-}pz)_3]Cl_3$ and 0.8 M MBI in water).