Supporting Information

Tridentate Cobalt complexes as alternate redox couples for high efficiency Dye Sensitized Solar Cells

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Materials

All chemicals and solvents were purchased from commercial sources and used without further purification. Sodium tetracyanoborate was purchased from SelectLab Chemicals GmbH, Germany.

Synthesis of Cobalt complexes

A solution of $CoCl_2$ (0.25 g, 1.05mmol) in water is added drop wise to a methanolic solution of (3.15 mmol) ligand (terpy), and the solution turns yellow immediately. To this solution added LiTFSI excess in 10ml water and immediately got the precipitate. Filtered the complex and washed with water and dried under vacuum to get $[Co^{II}(Cl\text{-}terpy)_2](TFSI)_2$.

A solution of $CoCl_2$ (0.25 g, 1.05mmol) in water is added drop wise to a methanolic solution of (3.15 mmol) ligand (terpy), and the solution turns yellow immediately. To this solution add a methanolic bromine solution and immediately get some precipitate. Separate the precipitate and to the filtrate added excess of LiTFSI dissolved in 15 ml of water to get the precipitate of oxidized form of the cobalt complex. Collected the precipitate and washed with water and dried under vacuum to isolate $[Co^{III}(Cl\text{-}terpy)_2](TFSI)_3$.

$[Co^{II}(terpy)_2](B(CN)_4)_2$ / $[Co^{III}(terpy)_2](B(CN)_4)_3$ complexes were synthesized as explained above but instead of using LiTFSI salt, $Na(BCN)_4$ was used.

Table S1 Characterization of the diffusion coefficient of the Co^{3+} complex in the electrolytes

Electrolyte	$Co^{III}(terpy)_2](B(CN)_4)_3$	$Co^{II}(terpy)_2](B(CN)_4)_2$	$D_{Co}{}^{3+}$ [cm^2/s]
E_2	0.04	0.2	$5.1x10^{-6}$
E_3	0.07	0.2	$6.2x10^{-6}$
E_4	0.10	0.2	$5.7x10^{-6}$
E_7	0.07	0.2	$2.9x10^{-6}$

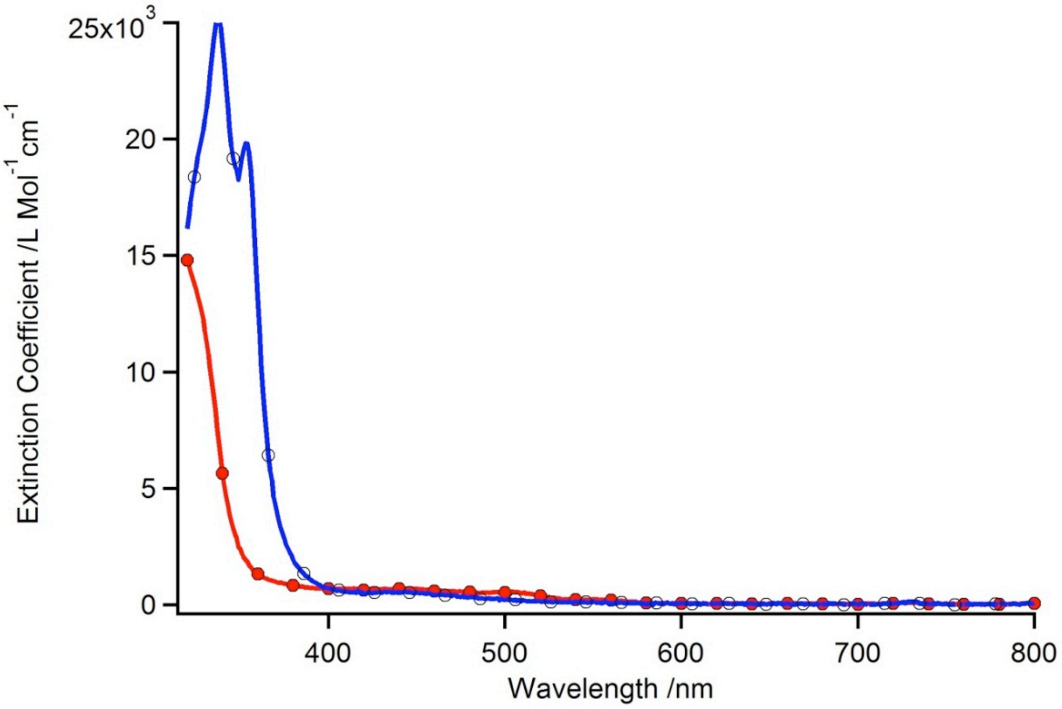

Figure S 1 UV-Vis absorption spectra of $[Co^{II}/^{III}(terpy)_2]$ $(TFSI)_{2\ /3}$ (red line for the reduced form and blue for the oxidized form).

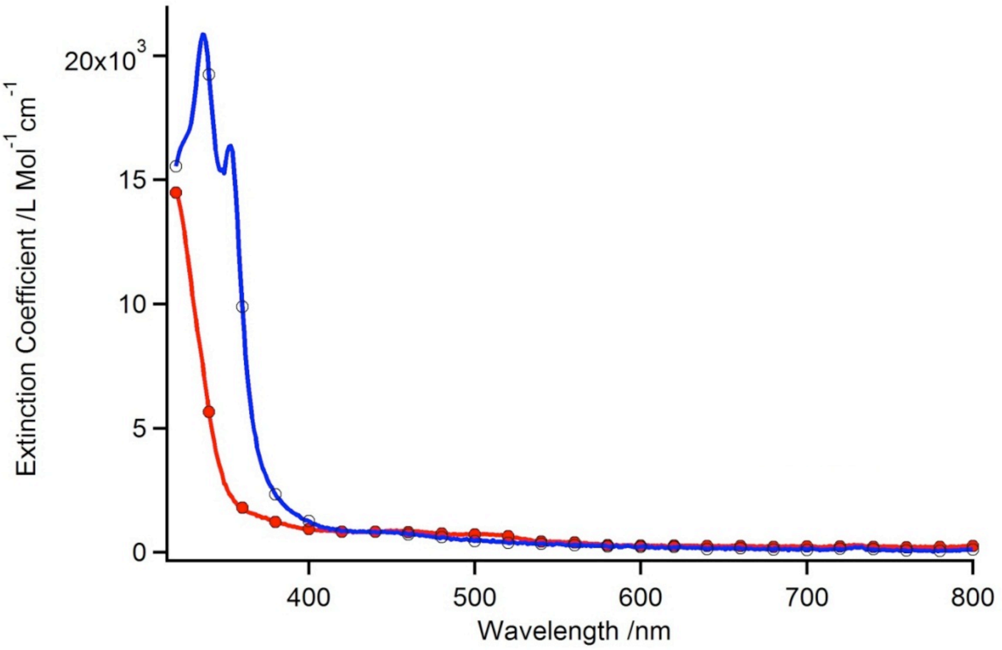

Figure S 2 UV-Vis absorption spectra of $[Co^{II}/^{III}(Cl\text{-}terpy)_2]$ $(TFSI)_{2\ /3}$ (red for the reduced form and blue for the oxidized form).

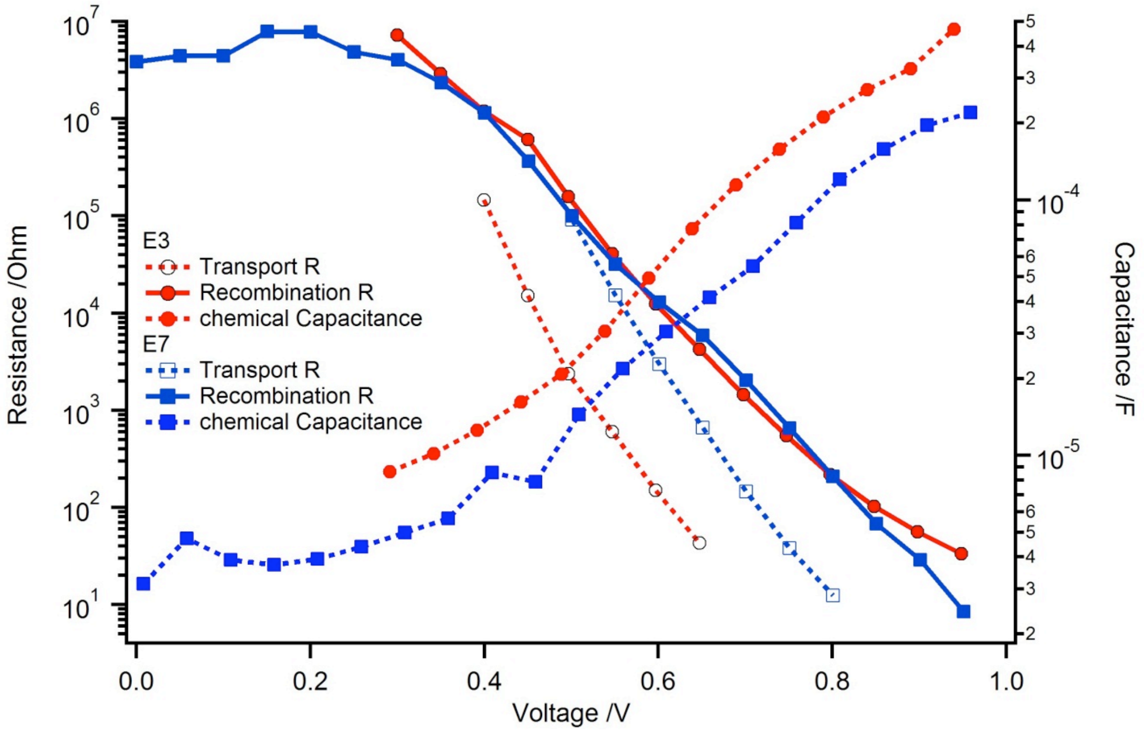

Figure S 3 Transport and recombination resistance and the chemical capacitance determined for devices with E3 and E7 electrolytes.

Depending on the composition of redox electrolyte the conduction band of TiO_2 can vary and the relative position between the devices can be determined using EIS and transient photovoltage and charge extraction measurements. The main characteristic parameters like charge transfer resistance, transport resistance and chemical capacitance for the comparison between the chloro-terpyridine Cobalt complex and the iodine-based devices extracted from the EIS analysis are presented in the Figure S4. As shown in Figure S5, the DOS extracted from EIS exhibits a difference of about 200 mV (in case of the charge extraction measurements the difference is also about 200 mV between the two electrolytes (see Figure S6)). This comparison clearly shows that the use of a higher redox potential electrolyte (E7) can confer a salient V_{OC} enhancement (between the E7 and the iodine based DSC devices the difference in V_{OC} is about 170mV). As there is a shift of ~20 mV in the conduction band position of TiO_2 between the two devices this observation implies also a shorter electron lifetime for E7 electrolyte at a given voltage (or rather E_F). This leads to a further reduction of the maximum achievable V_{OC} difference between the I^-/I_3^--based and the E7 based device.

To compare the electron recombination characteristics the electron lifetimes of an E7 and an I^-/I_3^--based device are plotted vs. the DOS in Figure S7 (similar results can be observed with transient photovoltage decay measurements, see also the Figure S8). The shift in conduction band of the TiO_2 and the lower electron lifetime give a clear explanation for the lower than expected V_{OC} with the E7 electrolyte based device.

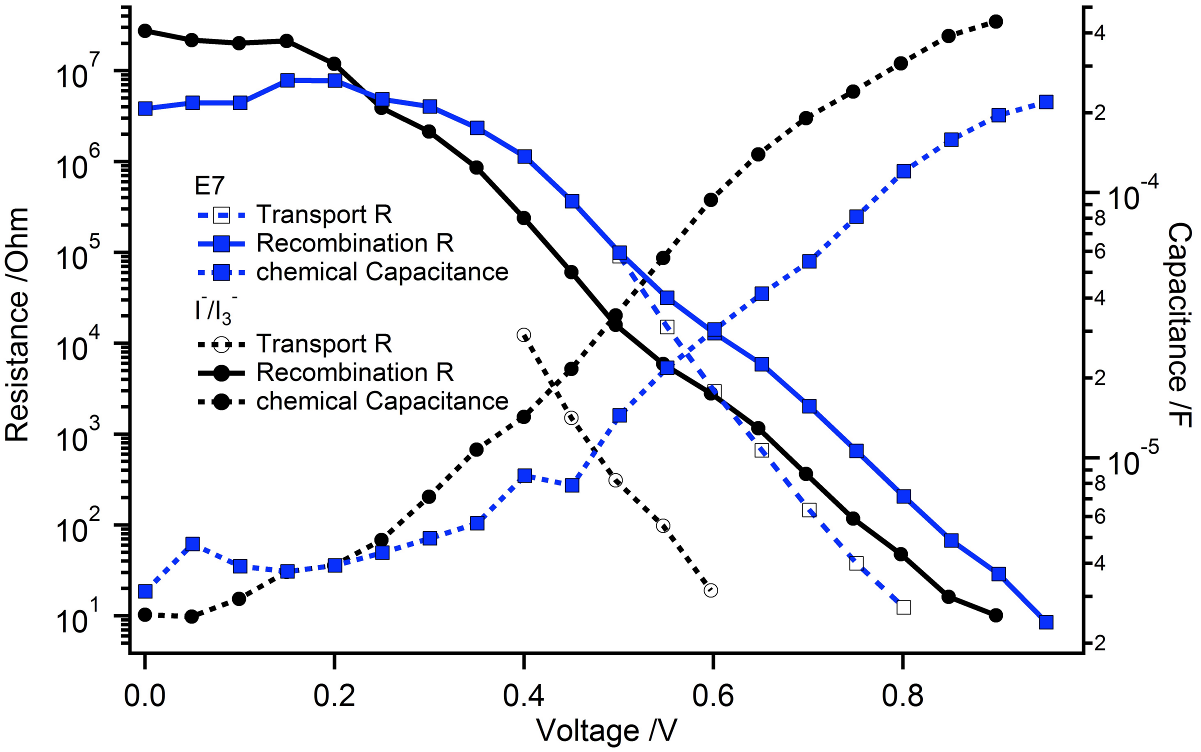

Figure S 4 Transport and recombination resistance and the chemical capacitance determined for devices with E7 and the iodide/triiodide based electrolyte.

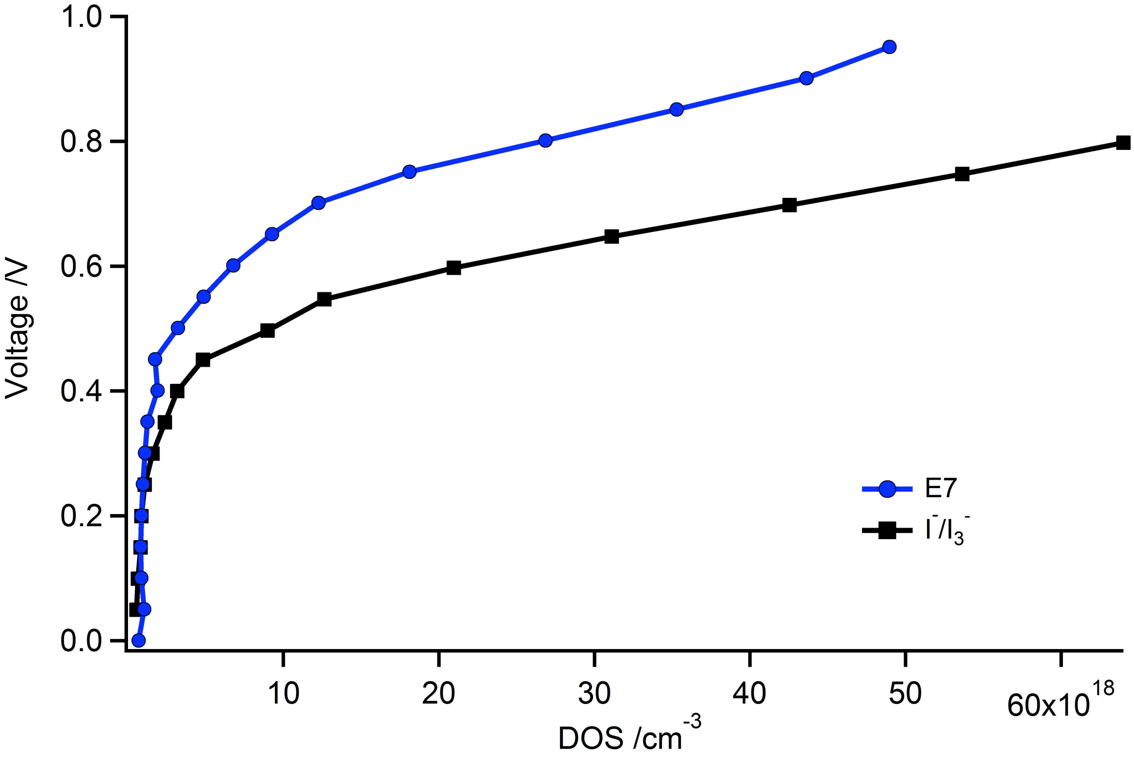

Figure S 5 DOS of the E7 and Iodine redox mediators based devices determined by EIS.

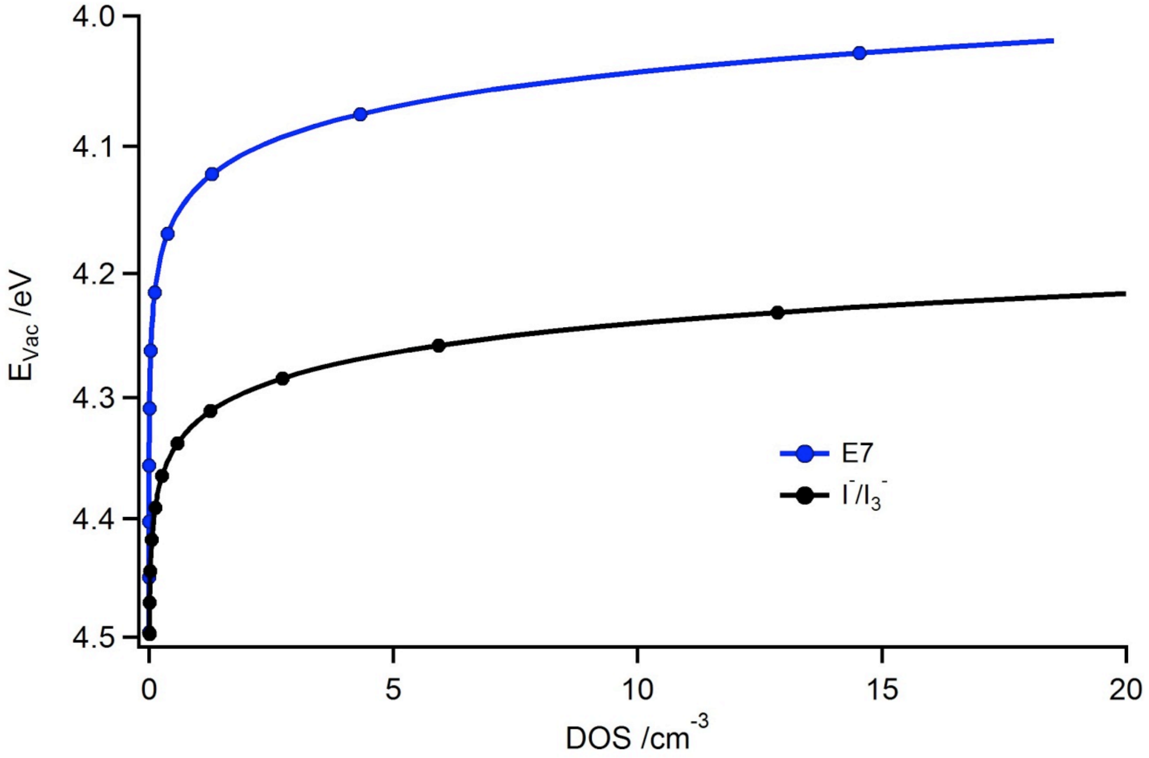

Figure S 6 DOS determined by charge extraction measurements of the E7 and Iodine redox mediators based devices.

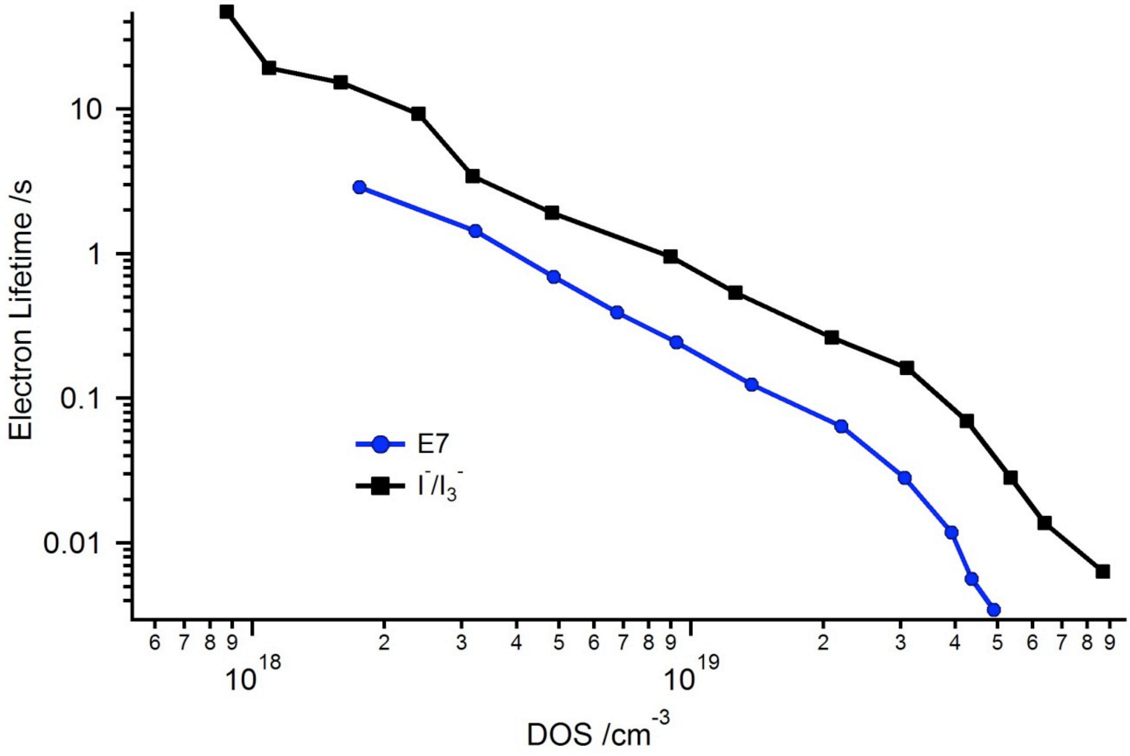

Figure S 7 Electron lifetime vs. DOS of the E7 and Iodine redox mediators based devices determined by EIS.

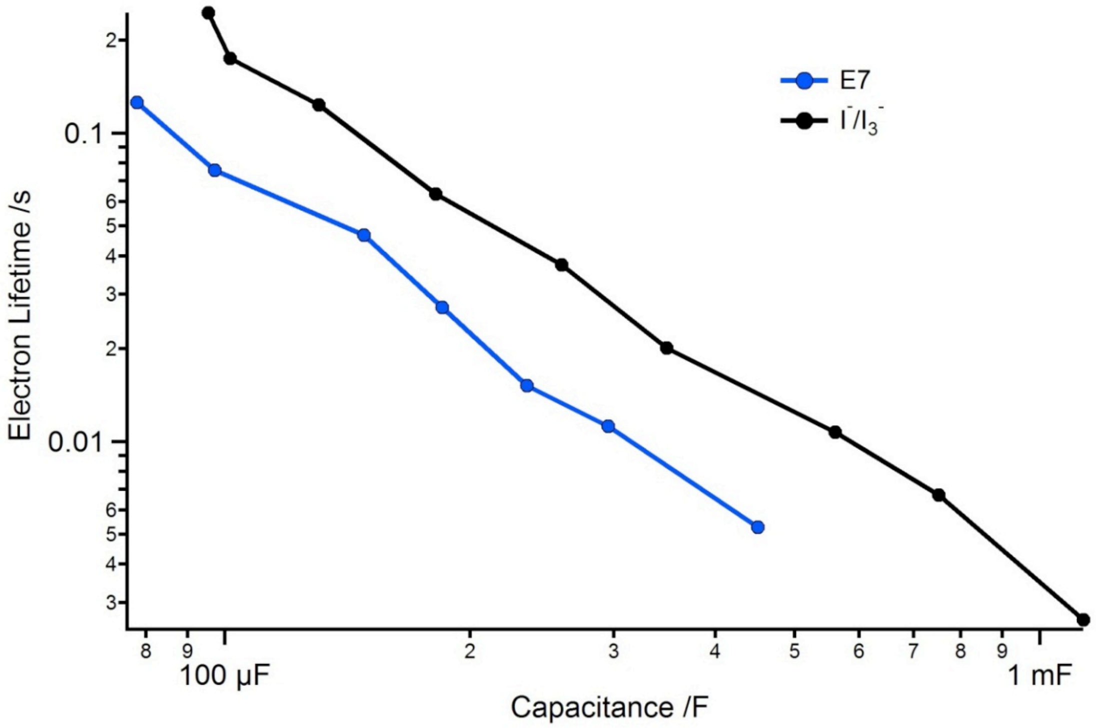

Figure S 8 Electron lifetime vs capacitance of the E7 and Iodine redox mediators based devices determined by transient photovoltage decay measurements.