

Supplementary Information to:

Dye Regeneration and Charge Recombination in Dye-Sensitized Solar Cells with Ferrocene Derivatives as Redox Mediators

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SI-T1: Elemental analyses for ferrocenium TFSI salts.

Compound		%C	%H	%N	%S
FcTFSI	Found	30.3	2.31	2.99	14.0
	Calculated	30.9	2.16	3.00	13.7
FcEtTFSI	Found	32.9	3.01	2.75	12.5
	Calculated	34.0	2.86	2.83	13.0
FcEt ₂ TFSI	Found	35.4	3.81	2.65	12.0
	Calculated	36.8	3.47	2.68	12.3
FcMe ₁₀ TFSI	Found	45.1	5.07	2.14	10.2
	Calculated	43.6	4.99	2.31	10.6
FcBrTFSI	Found	26.5	1.64	2.72	12.0
	Calculated	26.4	1.66	2.57	11.8

Cyclic Voltammetry

SI-T2 Cyclic voltammetry in acetonitrile

	$I_{OX}(\mu A)$	$I_{RED}(\mu A)$	I_{OX}/I_{RED}	$E_{OX}(V)$	$E_{RED}(V)$	$E_{1/2}(V)$	$E_{OX} - E_{RED}(V)$	$D(\text{cm}^2 \cdot \text{s}^{-1})$
Et ₂ Fc	22	23	0.97	0.56	0.47	0.51	0.09	6.5E-06
EtFc	36	33	1.07	0.63	0.51	0.57	0.12	7.3E-06
Fc	45	44	1.03	0.69	0.57	0.63	0.12	1.9E-05
BrFc	24	24	0.99	0.84	0.75	0.80	0.09	7.9E-06
Br ₂ Fc	29	28	1.02	0.99	0.90	0.94	0.09	1.5E-05

CV measurements were made on 3 mM solution of the analyte in acetonitrile containing 0.1 M Bu₄NPF at a scan rate of 20 mVs⁻¹. The diffusion coefficient was calculated from CVs recorded at scan rates of 20, 50, 100, 150 and 200 mVs⁻¹. All potentials were measured vs. Ag / AgNO₃ and converted to the NHE scale using $E_{1/2} \text{Fc} = 0.63 \text{ V vs. NHE}$

SI-T3 Cyclic voltammetry in benzonitrile

	$I_{OX}(\mu A)$	$I_{RED}(\mu A)$	I_{OX}/I_{RED}	$E_{OX}(V)$	$E_{RED}(V)$	$E_{1/2}(V)$	$E_{OX} - E_{RED}(V)$	$D(\text{cm}^2 \cdot \text{s}^{-1})$
Me ₁₀ Fc	9	10	0.96	0.17	0.01	0.09	0.17	6.8E-07
Et ₂ Fc	10	10	0.99	0.57	0.43	0.50	0.15	6.2E-07
EtFc	13	13	1.00	0.64	0.48	0.56	0.16	1.3E-06
Fc	16	16	1.00	0.71	0.53	0.62	0.18	1.3E-06
BrFc	13	13	1.02	0.87	0.70	0.79	0.17	9.0E-07
Br ₂ Fc	12	11	1.09	1.01	0.86	0.94	0.15	8.8E-07

CV measurements were made on 3 mM solution of the analyte in benzonitrile containing 0.1 M Bu₄NPF at a scan rate of 20 mVs⁻¹. The diffusion coefficient was calculated from CVs recorded at scan rates of 10, 20, 50, 100, and 150 mVs⁻¹. All potentials were measured vs. Ag / AgNO₃ and converted to the NHE scale using $E_{1/2} \text{Fc} = 0.62 \text{ V vs. NHE}$

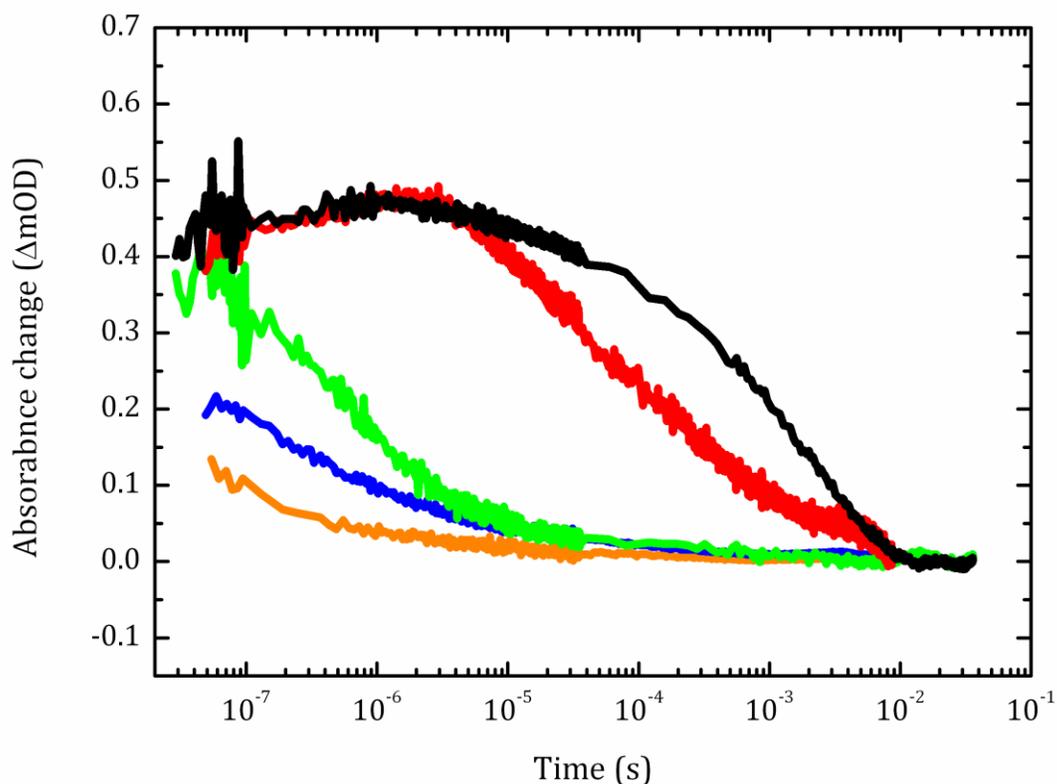
SI-T4 Tabulated J-V data ^{a)}

	$E_{1/2}$ (dye) - $E_{1/2}(R_{10}Fc)$		10 mW*cm⁻²				100 mW*cm⁻²				IPCEmax (%)
	$E_{1/2}$ (V) ^{d)}	$E_{1/2}$ (V) ^{d)}	V_{oc} (mV)	J_{sc} (mA * cm ⁻²)	FF (%)	η (%)	V_{oc} (mV)	J_{sc} (mA * cm ⁻²)	FF (%)	η (%)	
Me ₁₀ Fc ^{b)}	0.09	0.90	351±14	1.36±0.06	0.48±0.01	2.2±0.2	437±22	6.6±0.3	0.40±0.01	1.1±0.1	79
Et ₂ Fc ^{c)}	0.51	0.48	483±23	1.34±0.09	0.64±0.02	4.0±0.4	641±35	13.3±1.4	0.50±0.05	4.2±0.6	77
EtFc ^{c)}	0.57	0.42	540±20	1.34±0.06	0.69±0.01	4.9±0.5	669±20	12.8±1.3	0.56±0.04	4.8±0.2	79
Fc ^{c)}	0.63	0.36	608±3	1.31±0.06	0.70±0.02	5.4±0.4	737±22	12.5±1.2	0.57±0.03	5.2±0.2	76
BrFc ^{c)}	0.80	0.19	584±32	0.64±0.06	0.61±0.01	2.2±0.4	671±8	9.3±0.9	0.48±0.05	3.0±0.3	40
Br ₂ Fc ^{c)}	0.94	0.05	519±15	0.52±0.03	0.58±0.01	1.5±0.08	599±13	4.4±0.3	0.46±0.02	1.2±0.1	30

a) Electrolytes contained 100 mM reduced mediator, 12.5 mM oxidized mediator and 10 mM chenodeoxycholic acid, results are averaged from 3 devices; b) CV, J-V and IPCE recorded in benzonitrile electrolyte; c) CV, J-V and IPCE recorded in acetonitrile electrolyte; d) $E_{1/2}$ values measured vs. Ag/AgNO₃ and converted to the NHE scale using $E_{1/2} Fc = 0.63$ V vs. NHE (ACN) and 0.62 V vs. NHE (BZN)

Transient Absorption

Figure SI-F2 shows the transient absorption traces of devices filled with different concentrations of ferrocene dissolved in acetonitrile containing 10 mM chenodeoxycholic acid. While a concentration of 100 and 10 mM led to too fast regeneration of dye⁺, a concentration of 1 mM led to insufficient regeneration. Thus, 5 mM was chosen as a concentration for the transient absorption study using different ferrocene derivatives.



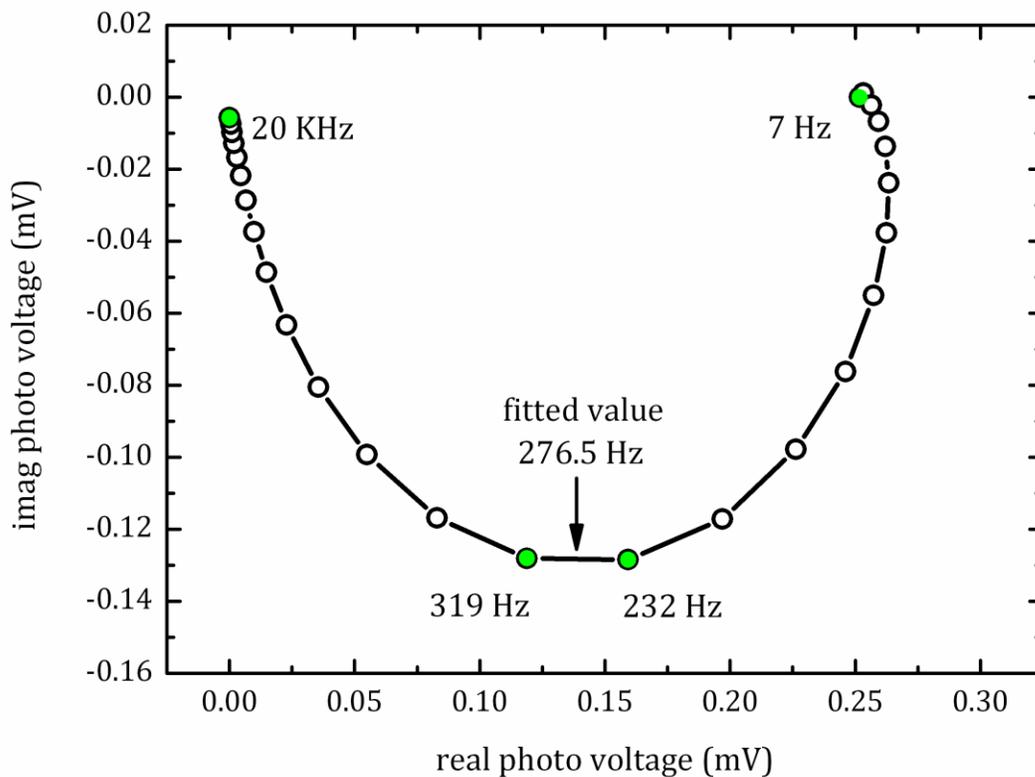
SI-F1: Transient absorption spectra, recorded at 900 nm, excitation at 532nm with electrolytes containing 0 mM Fc (black), 1 mM Fc (red), 5 mM Fc (green), 10 mM (blue) and 100 mM Fc (orange). All measurements were made in acetonitrile containing 10 mM chenodeoxycholic acid.

SI-T5: Tabulated fitted parameters from the analysis of TAS data

Sample	$\Delta OD_{(t=0)}$ (mOD)	$\tau_{(ww)}$ (s)	rel. error (%)	β	rel. error (%)	Γ	rel. error (%)	τ_{obs} (s)	rel. error (%)	k_{obs} (s ⁻¹)	rel. error (%)	k_{reg} (s ⁻¹ *mol ⁻¹)	rel. error (%)	R ²
Acetonitrile														
Dye only	4.50E-04	1.46E-03	1.5	0.646	0.8	0.89	0.1	3.11E-03	3.2	3.21E+02	3.2	--	--	0.99
Br ₂ Fc	4.00E-04	2.52E-04	2.2	0.482	0.8	1.03	0.9	1.12E-03	4.7	8.89E+02	4.8	-- ^{a)}	-- ^{a)}	0.98
Br ₂ Fc 100 mM	5.00E-04	1.71E-04	0.7	0.408	0.3	1.28	0.8	1.31E-03	2.2	7.61E+02	2.2	--	--	0.99
BrF _c	4.00E-04	5.33E-05	8.2	0.379	2.8	1.47	5.4	5.46E-04	21.8	1.83E+03	21.7	-- ^{a)}	-- ^{a)}	0.91
BrF _c 100 mM	4.50E-04	7.64E-08	3.7	0.149	0.8	422.04	8.7	1.45E-03	14.5	6.89E+02	14.5	3.68E+03	27.1	0.97
Fc	4.50E-04	9.62E-07	4.1	0.562	3.5	0.93	1.9	2.82E-06	13.9	3.55E+05	13.4	7.10E+07	13.4	0.94
EtFc	4.50E-04	4.49E-07	5.3	0.455	4.2	1.10	5.6	2.38E-06	21.2	4.19E+05	20.0	8.38E+07	20.1	0.89
Et ₂ Fc	4.50E-04	4.21E-07	5.5	0.441	4.5	1.15	6.7	2.49E-06	23.5	4.02E+05	22.3	8.04E+07	22.3	0.88
Benzonitrile														
Dye only	5.00E-04	2.04E-04	1.8	0.503	0.7	1.00	0.6	8.02E-04	3.9	1.25E+03	3.9	--	--	0.996
Br ₂ Fc	6.00E-04	9.61E-05	1.3	0.490	0.7	1.02	0.6	4.07E-04	3.4	2.46E+03	3.4	-- ^{a)}	-- ^{a)}	0.997
BrF _c	5.50E-04	2.57E-04	1.5	0.458	0.0	1.09	0.7	1.34E-03	3.4	7.45E+02	3.3	-- ^{a)}	-- ^{a)}	0.997
Fc	4.50E-04	8.98E-06	1.9	0.790	2.1	0.90	0.6	1.30E-05	5.9	7.70E+04	5.8	1.52E+07	5.9	0.96
EtFc	4.50E-04	5.68E-06	0.9	0.681	1.2	0.89	0.0	1.08E-05	3.3	9.22E+04	3.2	1.82E+07	3.3	0.98
Et ₂ Fc	4.50E-04	5.08E-06	0.8	0.730	1.1	0.89	0.1	8.46E-06	2.9	1.18E+05	2.9	2.34E+07	3.0	0.99
Me ₁₀ Fc	4.50E-04	2.93E-06	1.3	0.597	1.4	0.90	0.4	7.45E-06	4.6	1.34E+05	4.6	2.66E+07	4.7	0.98

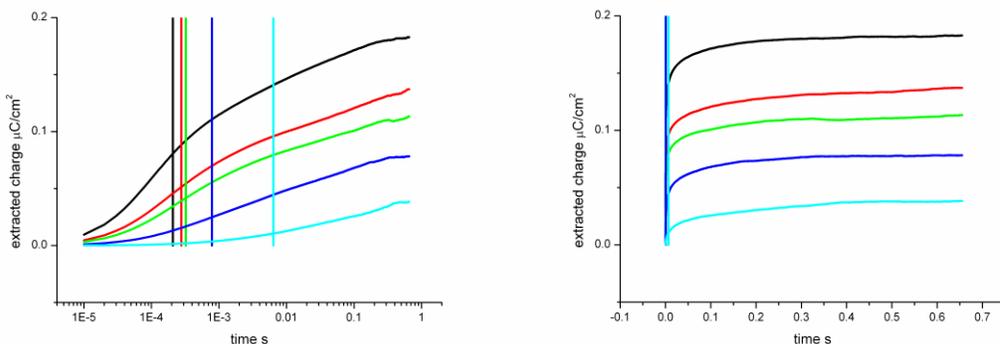
All TAS measurements were made using 900 nm probe light. Laser excitation occurred at 532 nm, 6 ns pulses, typical pulse intensity was 3 μJ cm⁻² pulse⁻¹, 10 Hz repetition rate. Kinetic traces were averaged from 1536 laser pulses. Fitting of the data was done using the Origin program. The initial signal magnitude $\Delta OD_{(t=0)}$ was estimated and fixed during the fitting routine to achieve a representing fit a) Insufficient dye regeneration - no regeneration rate was calculated.

IMVS

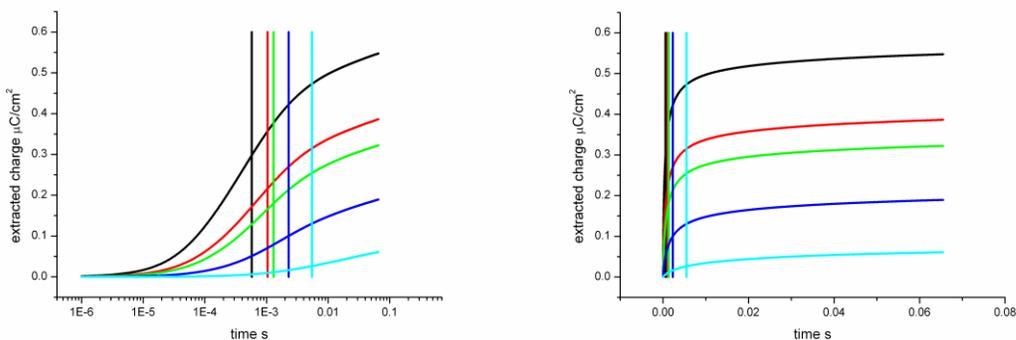


SI-F2: IMVS- plot measured on a ferrocene mediated device containing 100 mM Fc, 12.5 mM FcTFSI, 10 mM chenodeoxycholic acid in acetonitrile. Frequency range 7 Hz to 20 KHz. Green circles indicate start and end point of the measurement as well as the closest points to f_{\min} . Arrow indicates f_{\min} determined by a custom written fitting software according to Peter *et al.*¹

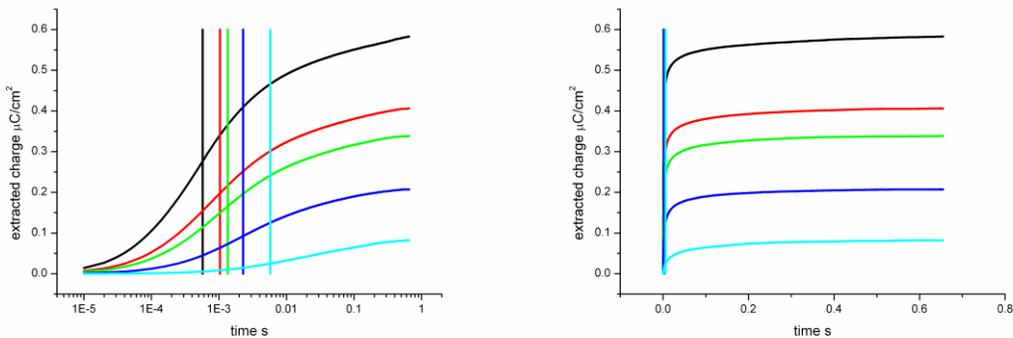
Charge Extraction



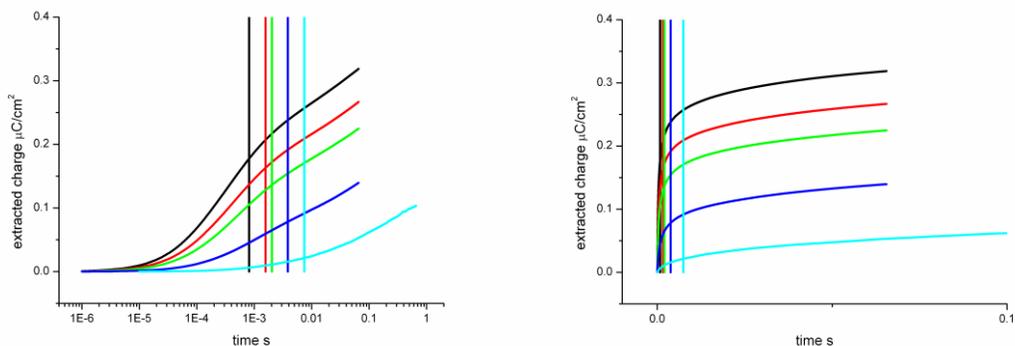
SI-F3: Extracted charge vs. time plot of a DSC with a BrFc mediator measured at different light intensities represented by black - 1 sun, red - 0.25 sun, green - 0.1 sun, blue - 0.05 sun, cyan - 0.01 sun. The straight lines indicate one electron life time determined by IMVS. Left logarithmic time scale, right linear time scale.



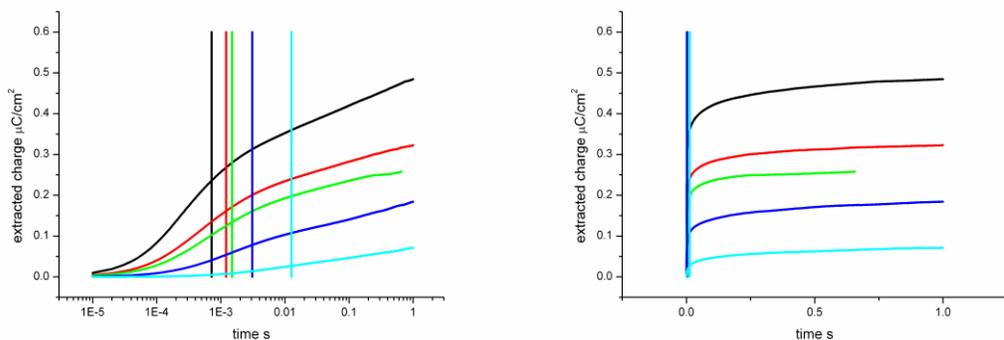
SI-F4: Extracted charge vs. time plot of a DSC with a Fc mediator measured at different light intensities represented by black - 1 sun, red - 0.25 sun, green - 0.1 sun, blue - 0.05 sun, cyan - 0.01 sun. The straight lines indicate one electron life time determined by IMVS. Left logarithmic time scale, right linear time scale.



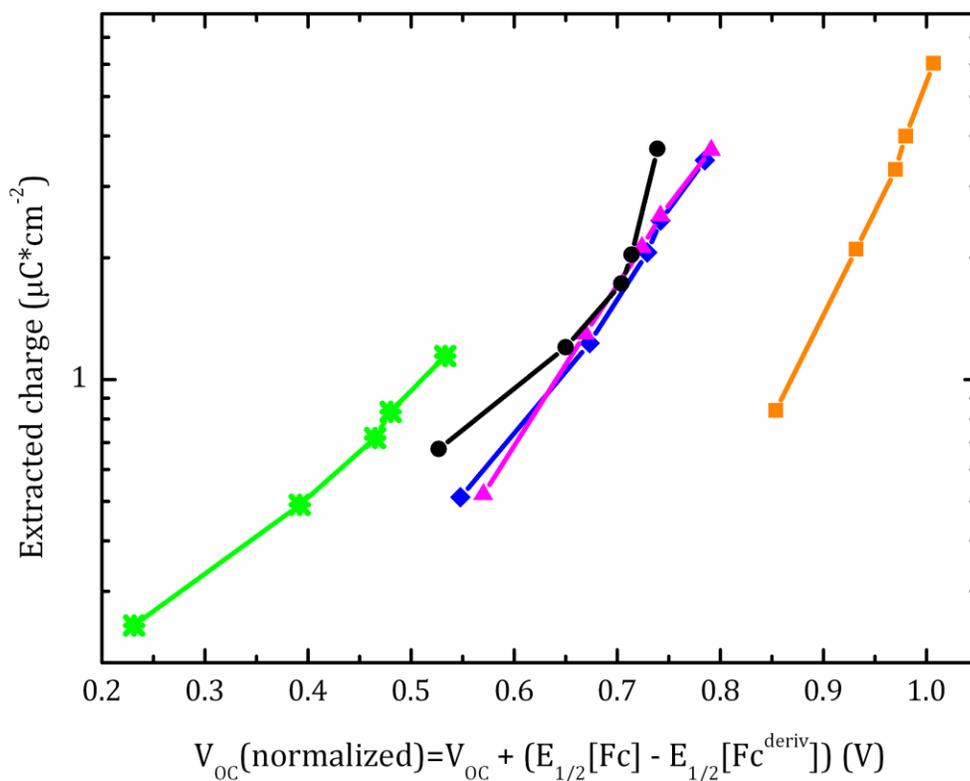
SI-F5: Extracted charge vs. time plot of a DSC with an EtFc mediator measured at different light intensities represented by black - 1 sun, red - 0.25 sun, green - 0.1 sun, blue - 0.05 sun, cyan - 0.01 sun. The straight lines indicate one electron life time determined by IMVS. Left logarithmic time scale, right linear time scale.



SI-F6: Extracted charge vs. time plot of a DSC with a Et_2Fc mediator measured at different light intensities represented by Black - 1 sun, red - 0.25 sun, green - 0.1 sun, blue - 0.05 sun, cyan - 0.01 sun. The straight lines indicate one electron life time determined by IMVS. Left logarithmic time scale, right linear time scale.



SI-F7: Extracted charge vs. time plot of a DSC with a Me_{10}Fc mediator measured at different light intensities represented by black - 1 sun, red - 0.25 sun, green - 0.1 sun, blue - 0.05 sun, cyan - 0.01 sun. The straight lines indicate one electron life time determined by IMVS. Left logarithmic time scale, right linear time scale.



SI-F8: Extracted charge vs. normalized V_{OC} , measured on devices containing 100 mM of the reduced species, 12.5 mM of the oxidized species and 10 mM cheno in acetonitrile for BrFc (green snowflakes), Fc (blue diamonds), EtFc (pink triangles), Et₂Fc (black circles) and benzonitrile Me₁₀Fc (orange squares). Film thickness 2.3 μm transparent 18 nm particle layer, 6.0 μm 400 nm particle scattering layer.

References

- (1) Peter, L. M.; Wijayantha, K. G. U. *Electrochem. Commun.* **1999**, *1*, 576-580.