

**Supporting Information for:**

**Introducing Manganese Complexes as Redox Mediators for Dye Sensitized  
Solar Cells.**

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## Synthesis of K4

The synthetic strategy for the dye **K4** is shown in Scheme 1.

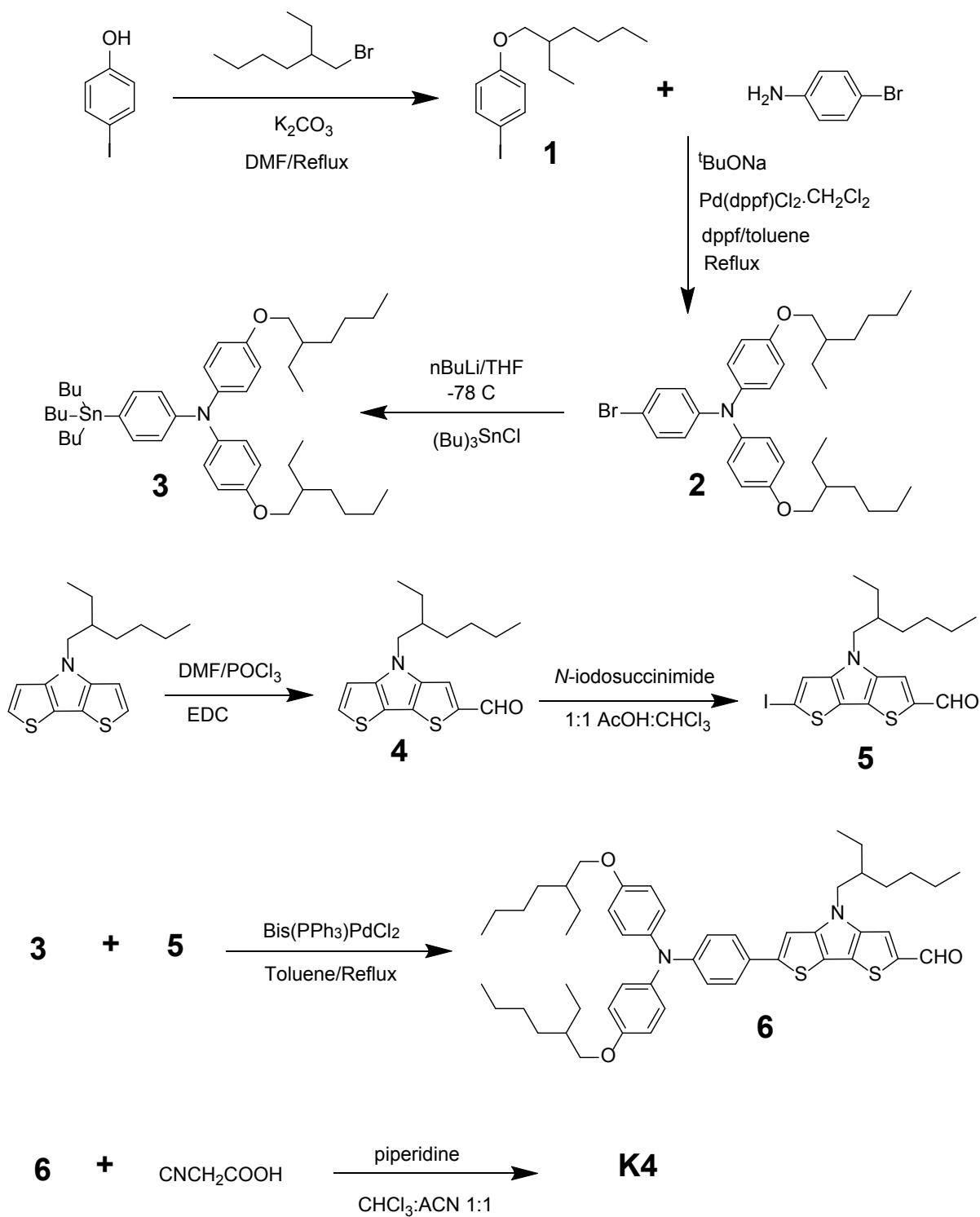


Figure S1: Synthetic scheme for **K4**

### Synthesis of 1-((2-ethylhexyl)oxy)-4-iodobenzene (**1**)

4-Iodophenol (14.0 g, 63.6 mmol) and 2-ethylhexyl bromide (14.7 g, 76.4 mmol) were dissolved in dimethylformamide (DMF) (150 mL) in a 500 ml round bottom flask and potassium carbonate (13.2 g, 95.4 mmol) was added at room temperature. The resulting reaction solution was refluxed for 3 hrs and the solution was removed under vacuum. The resulting suspension was worked up with water and dichloromethane. The organic layer was separated, washed with water and brine (saturated sodium chloride solution), dried over anhydrous  $\text{Na}_2\text{SO}_4$  and recovered to obtain crude oil which was subjected to column chromatography on silica (silica gel 60; 0.063–0.200 mm) (eluent: 100% hexane) to yield 13.0 g (62 %) of **1** as colourless.  $^1\text{H}$  NMR (400MHz,  $\text{CD}_2\text{Cl}_2$ )  $\delta$  7.58–7.54 (m, 2H), 6.73–6.69 (m, 2H), 3.86–3.79 (m, 2H), 1.75–1.67 (m, 1H), 1.53–1.29 (m, 8H), 0.95–0.90 (m, 6H)

### Synthesis of 4-bromo-N,N-bis(4-((2-ethylhexyl)oxy)phenyl)aniline (**2**)

4-Bromoaniline (500 mg, 2.90 mmol) was added to toluene (40.0 ml) in a 250 ml round bottom flask followed by sodium *t*-butoxide (835 mg, 8.70 mmol) at room temperature. [1,1'-Bis(diphenylphosphino)ferrocene]dichloropalladium(II) mixed with dichloromethane (82.0 mg, 0.10 mmol) was added to this mixture followed by [1,1'-bis(diphenylphosphino)ferrocene] (221 mg, 0.40 mmol) and the resulting suspension was stirred for 15 minutes at room temperature. Compound **1** (2.9 g, 8.7 mmol) was added at once and the resulting reaction mixture was heated to reflux overnight. The solvent was evaporated under reduced pressure at room temperature to obtain crude dark brown oil which was subjected to column chromatography on silica (silica gel 60; 0.063–0.200 mm) (hexane : ethyl acetate 9:1) to yield 870 mg (52 %) of **2** as light brown oil.  $^1\text{H}$  NMR (400MHz,  $\text{CDCl}_3$ ) :  $\delta$  7.22–7.18 (m, 2H), 7.01–6.97 (m, 4H), 6.81–6.74 (m, 6H), 3.81–3.76 (m, 4H), 1.73–1.64 (m, 2H), 1.50–1.26 (m, 16H), 0.94–0.86 (m, 12H)

### Synthesis of 4-((2-ethylhexyl)oxy)-N-(4-((2-ethylhexyl)oxy)phenyl)-N-(4(tributylstannyl)phenyl)aniline (**3**)

A solution of *n*-BuLi (0.80 ml, 1.30 mmol, 1.60 M in hexane) was added drop-wise to a solution of compound **2** (500 mg, 0.86 mmol) in THF (20.0 ml) at –78 °C. After stirring for 30 min at –78 °C, tributylchlorostannane (0.30 mL, 1.10 mmol) was added in one portion. The dry ice bath was removed and the reaction mixture was allowed to warm slowly to room temperature, followed by stirring overnight. Water (50.0 ml) was slowly added, and the solution was extracted with

dichloromethane. The organic layer was washed with brine, dried over anhydrous MgSO<sub>4</sub>, filtered and concentrated under reduced pressure to afford a light brown oil (900 mg), which was used without further purification for the next step.

#### Synthesis of 4-(2-ethylhexyl)-4*H*-dithieno[3,2-*b*:2',3'-*d*]pyrrole-2-carbaldehyde (**4**)

4-(2-ethylhexyl)-4*H*-dithieno[3,2-*b*:2',3'-*d*]pyrrole (540 mg, 1.80 mmol) was dissolved in ethylene dichloride (25.0 ml) in a 100 ml round bottom flask and dimethylformamide (149 mg, 2.10 mmol) was added at room temperature. The resulting solution was cooled to 0 °C and POCl<sub>3</sub> (0.50 ml, 5.60 mmol) was added drop wise. The reaction mixture was allowed to warm to room temperature and was then refluxed overnight. It was then cooled down to room temperature and worked up with saturated sodium acetate solution and the product was extracted in chloroform. The organic layer was washed with water, brine, dried over Na<sub>2</sub>SO<sub>4</sub> and recovered to get a crude yellow oil which was subjected to column chromatography on silica (silica gel 60; 0.063–0.200 mm) (hexane : dichloromethane 9 : 1) to yield 540 mg (76 %) of **4** as a dark yellow oil. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 200 MHz): δ 9.88 (s, 1H), 7.63 (s, 1H), 7.36 (m, 1H), 6.98 (m, 1H), 4.11–4.08 (m, 2H), 2.04–1.88 (m, 1H), 1.41–1.21 (m, 8H), 0.95–0.81 (m, 6H)

#### Synthesis of 4-(2-ethylhexyl)-6-iodo-4*H*-dithieno[3,2-*b*:2',3'-*d*]pyrrole-2-carbaldehyde(**5**)

Compound **4** (450 mg, 1.40 mmol) was added in a 1:1 solvent mixture (25.0 ml) of acetic acid and chloroform in a 100 ml round bottom flask and *N*-iodosuccinimide (412 mg, 1.80 mmol) was added at room temperature. The resulting solution was stirred overnight at room temperature in the absence of light. The reaction mixture was worked up with water and the product was extracted in to chloroform. The organic layer was washed with 20% sodium thiosulphate followed by water, dried over Na<sub>2</sub>SO<sub>4</sub> and recovered to yeild **5** as a crude dark brown oil (400 mg, 64 %), which was used without further purification for the next step. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 200 MHz): δ 9.88 (s, 1H), 7.60 (s, 1H), 7.19 (s, 1H), 4.08–4.02 (m, 2H), 1.99–1.84 (m, 1H), 1.40–1.17 (m, 8H), 0.95–0.84 (m, 6H)

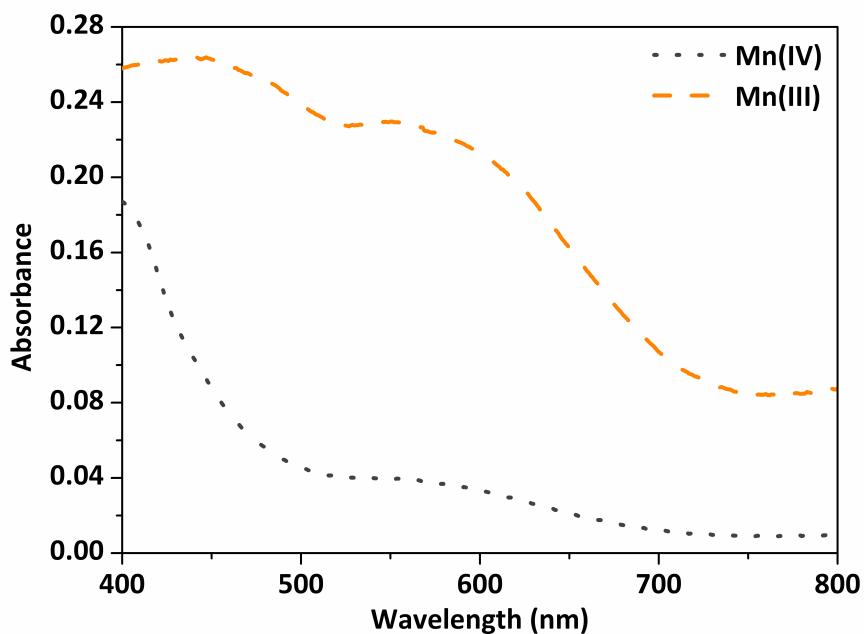
#### Synthesis of 6-(4-(bis(4-((2-ethylhexyl)oxy)phenyl)amino)phenyl)-4-(2-ethylhexyl))-4*H*-dithieno[3,2-*b*:2',3'-*d*]pyrrole-2-carbaldehyde (**6**)

Compound **3** (900 mg, 1.10 mmol) was dissolved in toluene (25.0 ml) in a 100 mL round bottom flask and compound **5** (355 mg, 0.80 mmol) was added at room temperature. The resulting solution was degassed with N<sub>2</sub> for 30 minutes and bis(triphenylphosphine)palladium(II) dichloride (140 mg,

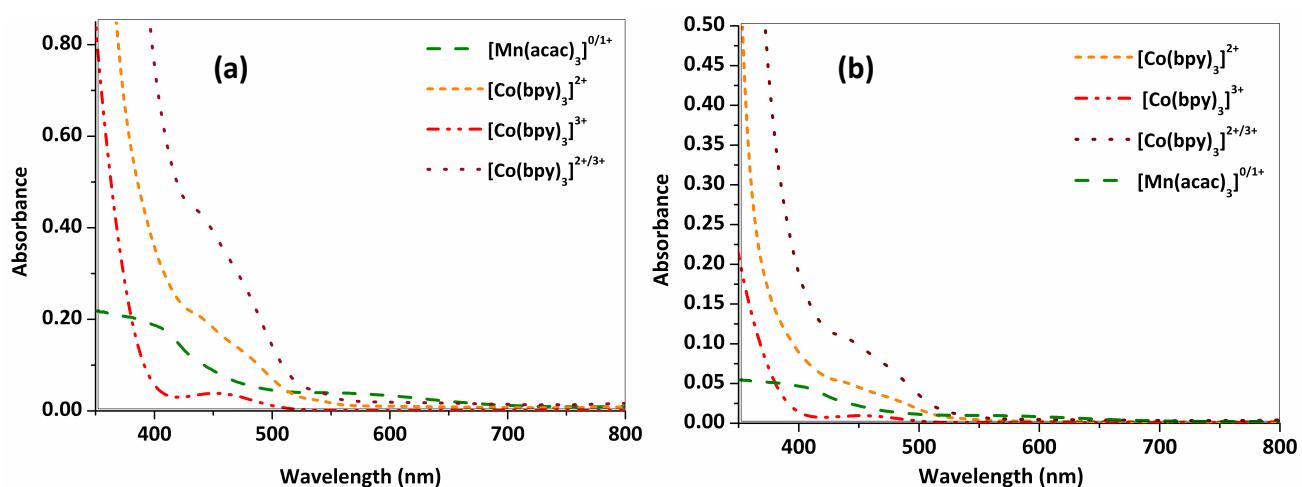
0.20 mmol) was added at room temperature. The yellow reaction mixture was refluxed overnight. The solvent was evaporated under reduced pressure and the residue was purified by silica gel (silica gel 60; 0.063–0.200 mm) chromatography (hexane: ethyl acetate 8: 2) to yield 320 mg (35 %) of **6** as an orange oil. <sup>1</sup>H NMR (400MHz, CDCl<sub>3</sub>): δ 9.87 (s, 1H), 7.60 (s, 1H), 7.47 (m, 2H), 7.12–7.08 (m, 4H), 7.06 (s, 1H), 6.97–6.93 (m, 2H), 6.89–6.85 (m, 4H), 4.12–4.07 (m, 2H), 3.87–3.82 (m, 4H), 2.03–1.95 (m, 1H), 1.77–1.70 (m, 2H), 1.54–1.31 (m, 24H), 0.98–0.90 (m, 18H)

#### Synthesis of 3-6-(4-(bis(4-((2-ethylhexyl)oxy)phenyl)amino)phenyl)-4-(2-ethylhexyl))-4*H*-dithieno[3,2-*b*:2',3'-*d*]pyrrol-2-yl)-2-cyanoacrylic acid (**K4**)

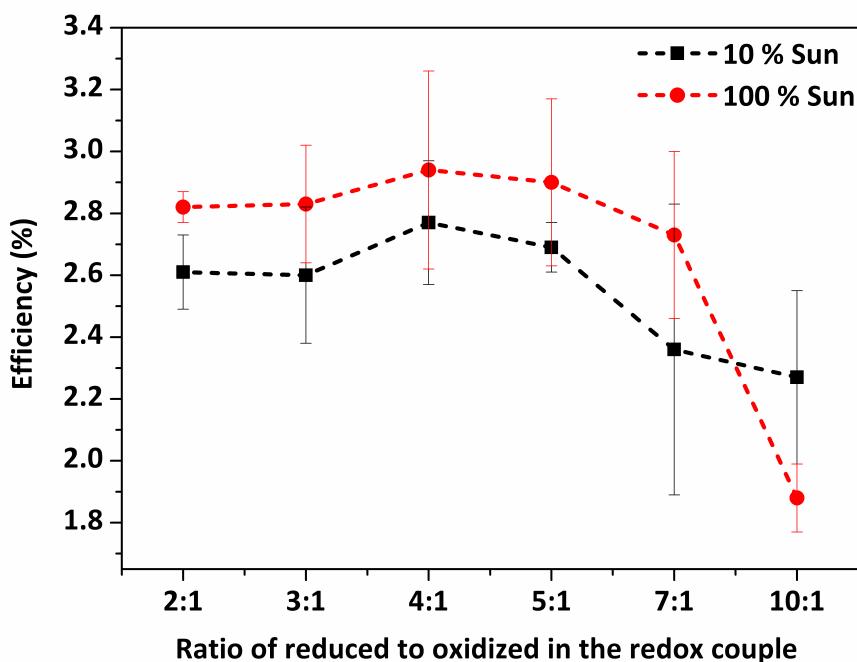
Compound **6** (200 mg, 0.20 mmol) was dissolved in a 1:1 solvent mixture (20.0 mL) of chloroform and acetonitrile in a 100 mL RB flask at room temperature. Cyanoacetic acid (83.3 mg, 0.90 mmol) was added in one portion followed by the addition of piperidine (0.10 mL) at room temperature. The resulting red solution was refluxed overnight. The solvent was removed and the residue was dissolved in chloroform, washed with 2N hydrochloric acid followed by water and brine. The organic layer was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and recovered to get crude oil which was subjected to column chromatography on silica gel (silica gel 60; 0.063–0.200 mm) (chloroform: methanol 8:2) to yeild 100 mg (48 %) of **K4** as deep cherry solid. M. Pt.: 152–158 °C; IR (neat, cm<sup>-1</sup>) 3440 (bd), 2957, 2928, 2871 (m, Ar –C=C-H str), 2208 (w, -CN str), 1690 (m, -COOH), 1575, 1506, 1463 (s, Ar –C=C str), 136 (m), 1319 (m), 1239 (s), 825 (m); <sup>1</sup>H NMR (400MHz, DMSO) : δ 8.22 (s, 1H), 7.93 (s, 1H), 7.58 (m, 1H), 7.55 (m, 2H), 7.08–7.02 (m, 4H), 6.96–6.91 (m, 4H), 6.84–6.78 (m, 2H), 4.18 (m, 2H), 3.85 (m, 4H), 2.01–1.92 (m, 1H), 1.73–1.62 (m, 2H), 1.50–1.20 (m, 24H), 0.92–0.79 (m, 18H); HRMS/EI(high-resolution mass spectrometry/electron impact): calculated for C<sub>54</sub>H<sub>67</sub>N<sub>3</sub>O<sub>4</sub><sup>32</sup>S<sub>2</sub> (m/z) 885.4568; found = 885.4581.



**Figure S2:** Comparison of the absorption spectra of 1.0 mM solution of  $[\text{Mn}(\text{acac})_3]$  and 1.0 mM solution of  $[\text{Mn}(\text{acac})_3]^{1+}$  in acetonitrile.



**Figure S3:** Comparison of the absorption spectra of the  $[\text{Mn}(\text{acac})_3]^{0/1+}$  based electrolyte, 0.01 M  $[\text{Co}(\text{bpy})_3]^{3+}$ , 0.40 M  $[\text{Co}(\text{bpy})_3]^{2+}$  and  $[\text{Co}(\text{bpy})_3]^{2+/3+}$  based electrolyte: (a) in the solution; (b) absorbance calculated based on an estimate of the thickness of a typical device (25  $\mu\text{m}$ ). The  $[\text{Mn}(\text{acac})_3]^{0/1+}$  based electrolyte consisted of 0.50 M  $[\text{Mn}(\text{acac})_3]$ , 0.10 M  $\text{NOBF}_4$ , 1.20 M tBP and 0.050 M  $\text{LiBF}_4$  in acetonitrile. The  $[\text{Co}(\text{bpy})_3]^{2+/3+}$  based electrolyte consisted of 0.10 M  $[\text{Co}(\text{bpy})_3]^{3+}$ , 0.40 M  $[\text{Co}(\text{bpy})_3]^{2+}$ , 1.20 M tBP and 0.050 M  $\text{LiTFSI}$  in acetonitrile.



**Figure S4:** Dependence of the efficiency of the DSC measured at simulated one sun ( $1000 \text{ W m}^{-2}$ ) and 0.1 sun light intensity on the  $[\text{Mn}(\text{acac})_3] / [\text{Mn}(\text{acac})_3]^+$  ratio in the electrolyte. The concentration of  $[\text{Mn}(\text{acac})_3]^+$  was kept constant at 0.10 M by adding 0.10 M  $\text{NOBF}_4$  and the concentration of  $[\text{Mn}(\text{acac})_3]$  was varied as 0.20, 0.30, 0.40, 0.50, 0.70 and 1.0 M. The acetonitrile electrolyte also contained 0.50 M tBP and 0.10 M  $\text{LiBF}_4$ .

**Table S1:** Detailed photovoltaic parameters obtained on devices used for the optimization of the ratio of the redox couple.

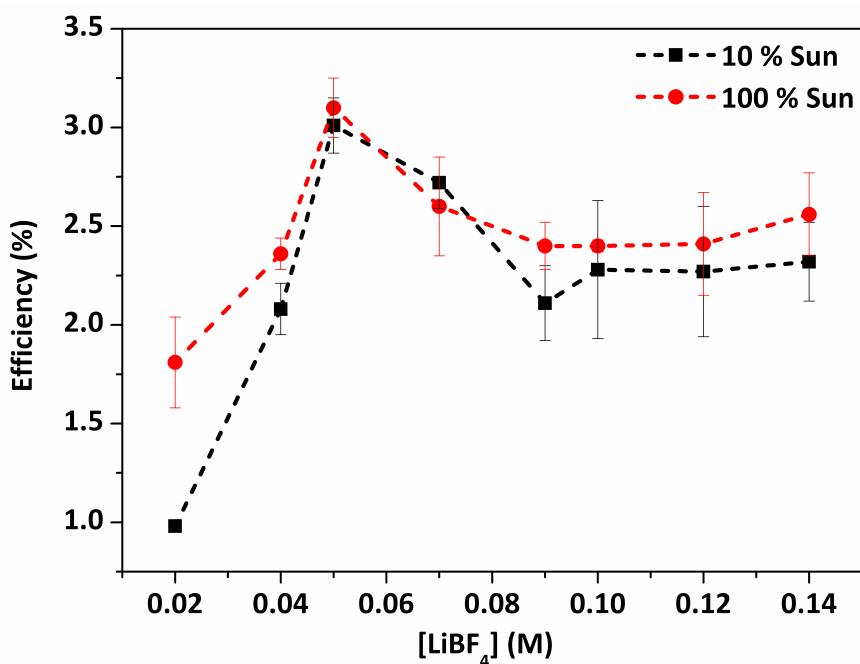
**S1 A:** 0.1 Sun illumination.

<b>Redox couple ratio (reduced: oxidized)</b>	$V_{OC}$ (mV)	$J_{SC}$ (mA cm <sup>-2</sup> )	Fill Factor	Efficiency (%)
2:1	619 ± 9	0.6 ± 0.1	0.77 ± 0.01	2.6 ± 0.1
3:1	606 ± 20	0.6 ± 0.1	0.77 ± 0.01	2.6 ± 0.2
4:1	613 ± 4	0.6 ± 0.1	0.76 ± 0.01	2.8 ± 0.2
5:1	625 ± 12	0.6 ± 0.1	0.76 ± 0.01	2.7 ± 0.1
7:1	631 ± 15	0.7 ± 0.1	0.69 ± 0.06	2.4 ± 0.4
10:1	643 ± 19	0.5 ± 0.4	0.76 ± 0.01	2.3 ± 0.3

**S1 B:** One Sun illumination.

<b>Redox couple ratio (reduced: oxidized)</b>	$V_{OC}$ (mV)	$J_{SC}$ (mA cm <sup>-2</sup> )	Fill Factor	Efficiency (%)
2:1	697 ± 9	5.4 ± 0.1	0.75 ± 0.02	2.8 ± 0.1
3:1	687 ± 16	5.6 ± 0.1	0.75 ± 0.03	2.8 ± 0.2
4:1	712 ± 2	5.6 ± 0.1	0.74 ± 0.01	2.9 ± 0.1
5:1	706 ± 11	5.6 ± 0.2	0.74 ± 0.01	2.9 ± 0.3
7:1	656 ± 20	5.8 ± 0.1	0.71 ± 0.03	2.7 ± 0.3
10:1	718 ± 19	3.1 ± 0.4	0.77 ± 0.03	1.9 ± 0.1

The electrolyte used to optimise the K4 based cells contained variable amounts of [Mn(acac)<sub>3</sub>] and fixed concentrations of NOBF<sub>4</sub> (0.10 M), tBP (0.50 M) and LiBF<sub>4</sub> (0.10M) in acetonitrile. The working electrode consists of a 4 µm transparent layer and a 6 µm scattering layer. PEDOT was used as the counter electrode. For each concentration ratio six cells were constructed to obtain the average value.



**Figure S5: Dependence of the efficiency of the DSCs measured at simulated one Sun ( $1000 \text{ W m}^{-2}$ ) and 0.1 Sun on LiBF<sub>4</sub> concentration.** The LiBF<sub>4</sub> concentration in the electrolyte varied from 0.020 M to 0.140 M. The electrolyte consisted 0.50 M [Mn(acac)<sub>3</sub>], 0.10 M NOBF<sub>4</sub> and 0.50 M tBP in acetonitrile.

**Table S2:** Detailed photovoltaic parameters obtained for the devices used for the optimization of concentration of LiBF<sub>4</sub>.

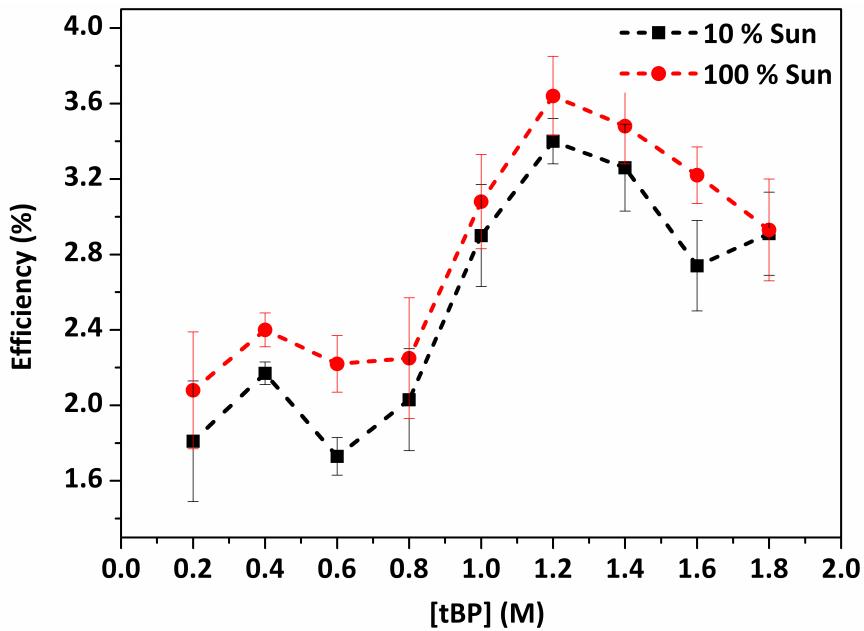
**S2 A:** 0.1 Sun illumination.

[LiBF <sub>4</sub> ] (M)	V <sub>oc</sub> (mV)	J <sub>sc</sub> (mA cm <sup>-2</sup> )	Fill Factor	Efficiency (%)
0.020	650 ± 2	0.4 ± 0.1	0.64 ± 0.04	1.0 ± 0.2
0.040	669 ± 18	0.4 ± 0.1	0.74 ± 0.01	2.1 ± 0.1
0.050	641 ± 18	0.6 ± 0.1	0.75 ± 0.01	3.0 ± 0.1
0.070	663 ± 1	0.6 ± 0.1	0.74 ± 0.01	2.7 ± 0.1
0.090	653 ± 2	0.5 ± 0.1	0.71 ± 0.04	2.1 ± 0.2
0.100	643 ± 5	0.5 ± 0.1	0.74 ± 0.02	2.3 ± 0.3
0.120	653 ± 1	0.5 ± 0.1	0.75 ± 0.01	2.3 ± 0.3
0.140	649 ± 6	0.5 ± 0.1	0.76 ± 0.01	2.3 ± 0.4

**S2 B:** One Sun illumination.

[LiBF <sub>4</sub> ] (M)	V <sub>oc</sub> (mV)	J <sub>sc</sub> (mA cm <sup>-2</sup> )	Fill Factor	Efficiency (%)
0.020	728 ± 9	4.2 ± 0.5	0.59 ± 0.04	1.8 ± 0.2
0.040	747 ± 21	4.2 ± 0.3	0.76 ± 0.01	2.4 ± 0.1
0.050	723 ± 18	5.8 ± 0.4	0.74 ± 0.01	3.1 ± 0.1
0.070	743 ± 3	4.5 ± 0.9	0.79 ± 0.01	2.6 ± 0.3
0.090	731 ± 2	4.5 ± 0.2	0.72 ± 0.02	2.4 ± 0.1
0.100	716 ± 5	4.6 ± 0.7	0.74 ± 0.01	2.4 ± 0.1
0.120	728 ± 1	4.5 ± 0.5	0.73 ± 0.01	2.4 ± 0.3
0.140	727 ± 7	4.6 ± 0.9	0.76 ± 0.01	2.6 ± 0.2

Cells were made with K4 dye and [Mn(acac)<sub>3</sub>]<sup>0/+1+</sup> electrolyte consisted 0.50 M [Mn(acac)<sub>3</sub>], 0.10 M NOBF<sub>4</sub> and 0.50 M tBP in acetonitrile. The working electrode consists of 4 μm transparent layer and 6 μm scattering layer. PEDOT was used as the counter electrode. For each concentration six cells were constructed to obtain the average value.



**Figure S6: Dependence of the DSC efficiency at simulated one Sun ( $1000 \text{ W m}^{-2}$ ) and 0.1 Sun on tBP concentration.** The tBP concentration was varied from 0.20 M to 1.80 M for an acetonitrile electrolyte also containing 0.50 M  $[\text{Mn}(\text{acac})_3]$ , 0.10 M  $\text{NOBF}_4$  and 0.050 M  $\text{LiBF}_4$ .

**Table S3:** Detailed photovoltaic parameters obtained for the devices used for the optimization of concentration of 4-tertiary-butylpyridine (tBP).

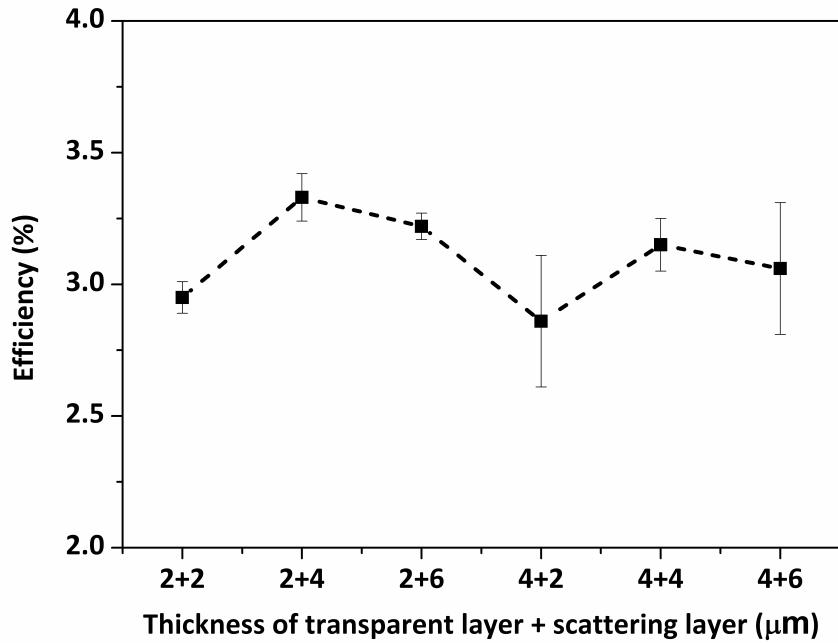
**S3 A:** 0.1 Sun illumination.

[tBP] (M)	V <sub>OC</sub> (mV)	J <sub>SC</sub> (mA cm <sup>-2</sup> )	Fill Factor	Efficiency (%)
0.60	631 ± 11	0.4 ± 0.1	0.78 ± 0.01	1.8 ± 0.3
0.80	607 ± 3	0.4 ± 0.1	0.68 ± 0.01	1.7 ± 0.4
1.00	691 ± 12	0.5 ± 0.1	0.78 ± 0.01	2.9 ± 0.3
1.20	640 ± 13	0.7 ± 0.1	0.76 ± 0.02	3.4 ± 0.1
1.40	643 ± 15	0.7 ± 0.1	0.77 ± 0.01	3.3 ± 0.2
1.60	622 ± 4	0.6 ± 0.1	0.73 ± 0.01	2.9 ± 0.2
1.80	649 ± 19	0.6 ± 0.1	0.71 ± 0.02	2.9 ± 0.2

**S3 A:** One Sun illumination.

[tBP] (M)	V <sub>OC</sub> (mV)	J <sub>SC</sub> (mA cm <sup>-2</sup> )	Fill Factor	Efficiency (%)
0.60	703 ± 11	3.9 ± 0.4	0.77 ± 0.07	2.1 ± 0.3
0.80	686 ± 14	4.3 ± 0.2	0.74 ± 0.02	2.2 ± 0.1
1.00	772 ± 15	5.2 ± 0.2	0.76 ± 0.01	3.1 ± 0.2
1.20	726 ± 16	6.9 ± 0.1	0.73 ± 0.02	3.6 ± 0.2
1.40	731 ± 12	6.5 ± 0.2	0.73 ± 0.01	3.5 ± 0.2
1.60	709 ± 8	6.2 ± 0.3	0.74 ± 0.01	3.3 ± 0.2
1.80	739 ± 9	5.6 ± 0.2	0.70 ± 0.01	2.9 ± 0.3

Cells were made with K4 dye and  $[\text{Mn}(\text{acac})_3]^{0/1+}$  electrolyte consists of 0.50 M  $[\text{Mn}(\text{acac})_3]$ , 0.10 M  $\text{NOBF}_4$  and 0.05 M  $\text{LiBF}_4$  in acetonitrile. The working electrode consists of 4  $\mu\text{m}$  transparent layer and 6  $\mu\text{m}$  scattering layer. PEDOT was used as the counter electrode. For each concentration 6 cells were constructed to obtain the average value.

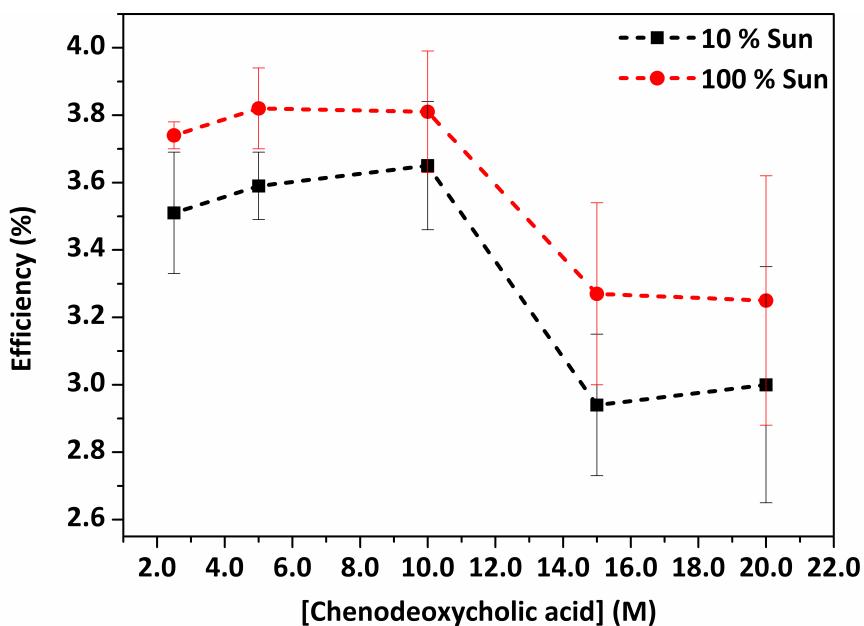


**Figure S7: Dependence of the DSC efficiency at simulated one Sun ( $1000 \text{ W m}^{-2}$ ) irradiation on  $\text{TiO}_2$  layer thickness.** The electrolyte consisted of 0.50 M  $[\text{Mn}(\text{acac})_3]$ , 0.10 M  $\text{NOBF}_4$ , 1.20 M tBP and 0.050 M  $\text{LiBF}_4$  in acetonitrile.

**Table S4:** Detailed photovoltaic parameters obtained under one Sun illumination for the devices used for the optimization of layer thickness of the  $\text{TiO}_2$  layer

$\text{TiO}_2$ layer thickness (transparent : scattering) / $\mu\text{m}$	$V_{OC}$ (mV)	$J_{SC}$ ( $\text{mA cm}^{-2}$ )	Fill Factor	Efficiency (%)
2+2	$713 \pm 12$	$5.6 \pm 0.1$	$0.74 \pm 0.02$	$3.0 \pm 0.1$
2+4	$728 \pm 6$	$6.1 \pm 0.1$	$0.76 \pm 0.01$	$3.3 \pm 0.1$
2+6	$750 \pm 13$	$6.1 \pm 0.1$	$0.69 \pm 0.01$	$3.2 \pm 0.1$
4+2	$755 \pm 6$	$5.4 \pm 0.1$	$0.70 \pm 0.04$	$2.9 \pm 0.2$
4+4	$725 \pm 18$	$6.0 \pm 0.1$	$0.72 \pm 0.01$	$3.1 \pm 0.1$
4+6	$731 \pm 6$	$6.0 \pm 0.1$	$0.70 \pm 0.01$	$3.1 \pm 0.2$

Cells were made with K4 dye and  $[\text{Mn}(\text{acac})_3]^{0/1+}$  electrolyte consists of 0.50 M  $[\text{Mn}(\text{acac})_3]$ , 0.10 M  $\text{NOBF}_4$ , 1.20 M tBP and 0.05 M  $\text{LiBF}_4$  in acetonitrile. PEDOT was used as the counter electrode. For each layer thickness six cells were constructed to obtain the average value. The  $\text{TiO}_2$  layer thickness is denoted as the thickness of the transparent  $\text{TiO}_2$  layer + the thickness of the scattering  $\text{TiO}_2$  layer.



**Figure S8: Dependence of the efficiency of DSCs at simulated 1 Sun and 0.1 Sun irradiation on chenodeoxycholic acid (cheno) concentration.** The concentration of cheno was varied from 2.50 mM to 20.0 mM in the electrolyte containing 0.50 M  $[\text{Mn}(\text{acac})_3]$ , 0.10 M  $\text{NOBF}_4$ , 0.050 M  $\text{LiBF}_4$  and 1.20 M tBP in acetonitrile.

**Table S5:** Detailed photovoltaic parameters obtained for the devices used for the optimization of concentrations of chenodeoxycholic acid.

**S5 A:** 0.1 Sun illumination.

[Chenodeoxycholic acid] (mM)	$V_{OC}$ (mV)	$J_{SC}$ (mA cm $^{-2}$ )	Fill Factor	Efficiency (%)
2.50	$613 \pm 4$	$0.8 \pm 0.1$	$0.74 \pm 0.04$	$3.5 \pm 0.2$
5.00	$617 \pm 2$	$0.8 \pm 0.2$	$0.76 \pm 0.01$	$3.6 \pm 0.1$
10.00	$678 \pm 9$	$0.7 \pm 0.1$	$0.74 \pm 0.02$	$3.7 \pm 0.2$
15.00	$626 \pm 7$	$0.7 \pm 0.1$	$0.75 \pm 0.02$	$2.9 \pm 0.4$
20.00	$615 \pm 12$	$0.7 \pm 0.1$	$0.74 \pm 0.01$	$3.0 \pm 0.5$

**S5 B:** One Sun illumination.

[Chenodeoxycholic acid] (mM)	$V_{OC}$ (mV)	$J_{SC}$ (mA cm $^{-2}$ )	Fill Factor	Efficiency (%)
2.50	$719 \pm 4$	$7.0 \pm 0.3$	$0.67 \pm 0.03$	$3.7 \pm 0.1$
5.00	$722 \pm 2$	$7.5 \pm 0.2$	$0.70 \pm 0.01$	$3.8 \pm 0.1$
10.00	$765 \pm 8$	$7.8 \pm 0.2$	$0.72 \pm 0.01$	$3.9 \pm 0.2$
15.00	$728 \pm 4$	$6.3 \pm 0.1$	$0.72 \pm 0.01$	$3.3 \pm 0.3$
20.00	$718 \pm 4$	$6.7 \pm 0.1$	$0.67 \pm 0.04$	$3.2 \pm 0.4$

Cells were made with K4 dye and  $[\text{Mn}(\text{acac})_3]^{0/1+}$  electrolyte consists of 0.50 M  $[\text{Mn}(\text{acac})_3]$ , 0.10 M  $\text{NOBF}_4$ , 1.20 M tBP and 0.05 M  $\text{LiBF}_4$  in acetonitrile. The working electrode consists of 4  $\mu\text{m}$  transparent layer and 6  $\mu\text{m}$  scattering layer. PEDOT was used as the counter electrode. For each concentration six cells were constructed to obtain the average value.

**Table S6:** Detailed photovoltaic parameters of the devices made with K4 and  $[\text{Mn}(\text{acac})_3]^{0/1+}$  electrolyte with different counter electrodes at one Sun ( $1000 \text{ W m}^{-2}$ ) irradiation.

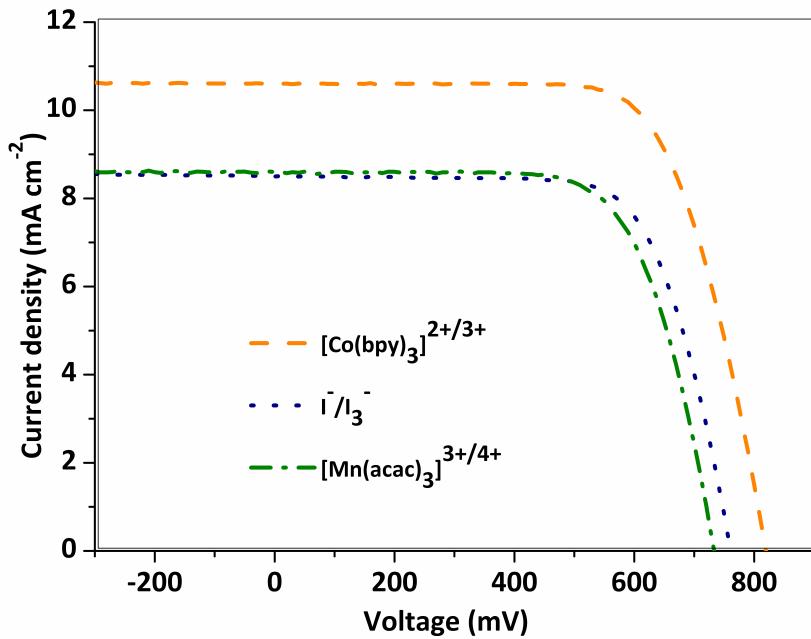
Counter electrode	$V_{oc}$ (mV)	$J_{sc}$ (mA cm $^{-2}$ )	Fill factor	Efficiency (%)
Au SC/FTO	$776 \pm 9$	$4.6 \pm 0.2$	$0.74 \pm 0.01$	$2.6 \pm 0.2$
Pt SC/FTO	$788 \pm 4$	$4.4 \pm 0.1$	$0.66 \pm 0.01$	$2.3 \pm 0.1$
Pt TD/FTO	$759 \pm 2$	$6.2 \pm 0.1$	$0.59 \pm 0.01$	$2.8 \pm 0.2$
PEDOT/FTO	$725 \pm 9$	$6.6 \pm 0.1$	$0.75 \pm 0.01$	$3.2 \pm 0.1$

Cells were made with K4 dye and  $[\text{Mn}(\text{acac})_3]^{0/1+}$  electrolyte consists of 0.20 M  $[\text{Mn}(\text{acac})_3]$ , 0.10 M  $\text{NOBF}_4$ , 0.50 M tBP and 0.10 M  $\text{LiBF}_4$  in acetonitrile. The working electrode consists of 4  $\mu\text{m}$  transparent layer and 6  $\mu\text{m}$  scattering layer. Different counter electrodes (Gold sputter coated (Au SC), Pt sputter coated (Pt SC), Pt thermally decomposed (Pt TD) and PEDOT) were used to construct the cells. For each concentration six cells were constructed to obtain the average value.

**Table S7:** Parameters fitted using  $Z_{\text{view}}$  (version 2.3) from EIS measurements under dark conditions.

Electrolyte	$R_{ct}$ ( $\Omega$ )
Au SC/FTO	$237.4 \pm 0.9$
Pt SC/FTO	$168.5 \pm 0.4$
Pt TD/FTO	$101.4 \pm 0.2$
PEDOT/FTO	$4.2 \pm 0.7$

$R_{ct}$  , Charge transport resistance at counter electrode/electrolyte interface. Cells were made with  $[\text{Mn}(\text{acac})_3]^{0/1+}$  electrolyte consisted of 0.20 M  $[\text{Mn}(\text{acac})_3]$ , 0.10 M  $\text{NOBF}_4$ , 0.50 M tBP and 0.10 M  $\text{LiBF}_4$  in acetonitrile. Different counter electrodes (Gold sputter coated (Au SC), Pt sputter coated (Pt SC), Pt thermally decomposed (Pt TD) and PEDOT) were used to construct the cells. For each concentration six cells were constructed to obtain the average value.

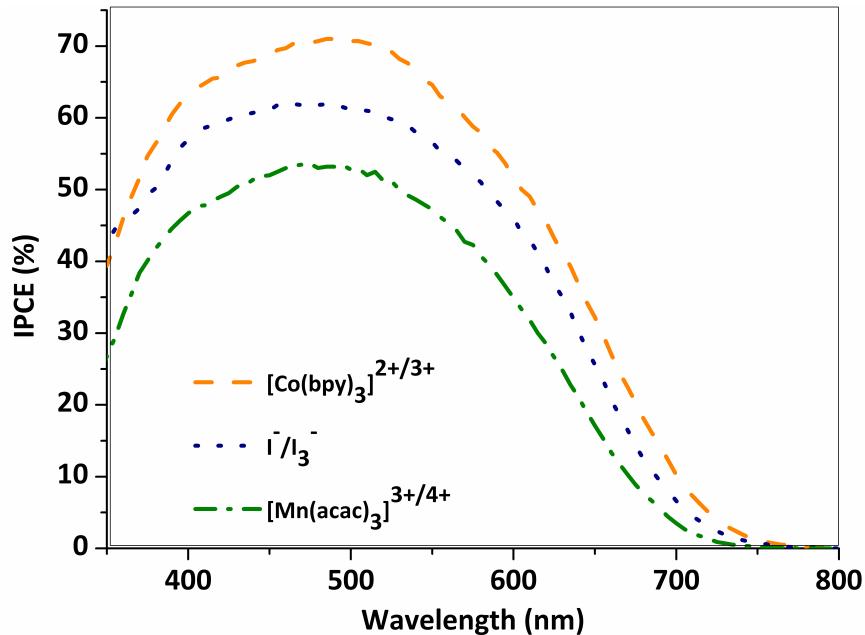


**Figure S9: Comparison of the IV curves for DSC based on  $\text{I}/\text{I}_3^-$ ,  $[\text{Co}(\text{bpy})_3]^{2+/3+}$  and  $[\text{Mn}(\text{acac})_3]^{0/1+}$  electrolytes sensitized with MK2.** Electrolyte composition: (I)  $\text{I}/\text{I}_3^-$  electrolyte: 0.03 M  $\text{I}_2$ , 0.50 M tBP, 0.6 M 1-butyl-3-methylimidazolium iodide (BMII) and 0.10 M GuSCN in acetonitrile/ valeronitrile (85:15 vol%); (II)  $[\text{Co}(\text{bpy})_3]^{2+/3+}$  electrolyte: 0.165 M  $[\text{Co}(\text{bpy})_3](\text{B}(\text{CN})_4)_2$ , 0.045M  $[\text{Co}(\text{bpy})_3](\text{B}(\text{CN})_4)_3$ , 0.80 M tBP, and 0.10 M  $\text{LiClO}_4$  in acetonitrile; (III)  $[\text{Mn}(\text{acac})_3]^{0/1+}$  electrolyte: 0.50 M  $[\text{Mn}(\text{acac})_3]$ , 0.10 M  $\text{NOBF}_4$ , 1.20 M tBP and 0.05 M  $\text{LiBF}_4$  in acetonitrile. The working electrode consists of 4  $\mu\text{m}$  transparent layer and 6  $\mu\text{m}$  scattering layer. PEDOT was used as the counter electrode for  $[\text{Mn}(\text{acac})_3]^{0/1+}$  based devices and Pt for  $\text{I}/\text{I}_3^-$  and  $[\text{Co}(\text{bpy})_3]^{2+/3+}$  based devices.

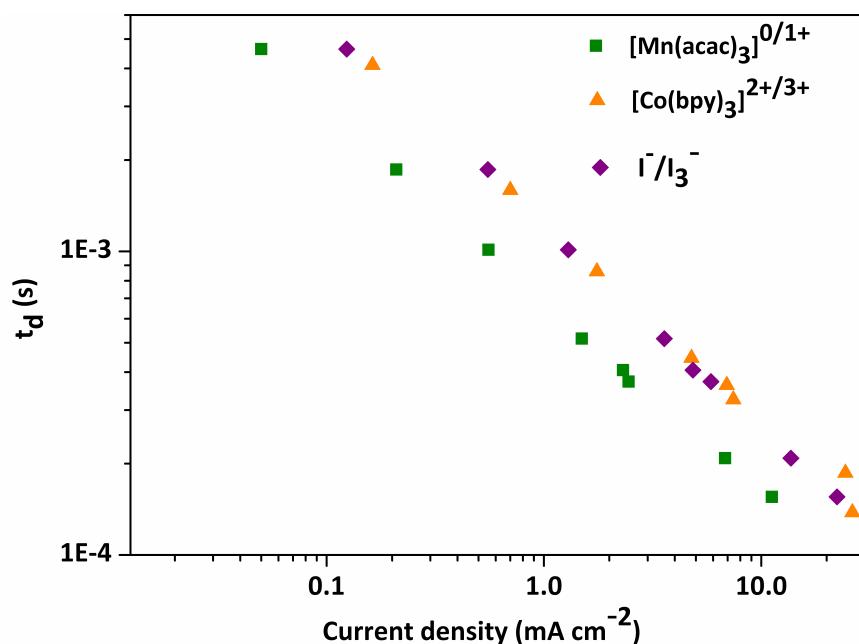
**Table S8:** Detailed photovoltaic parameters of the devices made with MK2 and  $\text{I}/\text{I}_3^-$ ,  $[\text{Co}(\text{bpy})_3]^{2+/3+}$  and  $[\text{Mn}(\text{acac})_3]^{0/1+}$  electrolytes at one Sun (1000 W m<sup>-2</sup>) irradiation.

Electrolyte	$V_{oc}$ (mV)	$J_{sc}$ (mA cm <sup>-2</sup> )	Fill factor	Efficiency (%)
$[\text{Co}(\text{bpy})_3]^{2+/3+}$	$820 \pm 10$	$10.6 \pm 0.1$	$0.70 \pm 0.01$	$6.1 \pm 0.2$
$\text{I}/\text{I}_3^-$	$761 \pm 7$	$8.5 \pm 0.4$	$0.71 \pm 0.02$	$4.6 \pm 0.2$
$[\text{Mn}(\text{acac})_3]^{0/1+}$	$733 \pm 9$	$8.6 \pm 0.3$	$0.69 \pm 0.01$	$4.4 \pm 0.1$

Cells were made with MK2 dye and  $I/I_3^-$ ,  $[Co(bpy)_3]^{2+/3+}$  and  $[Mn(acac)_3]^{0/1+}$  electrolytes mentioned in Figure S9. The working electrode consists of 4  $\mu m$  transparent layer and 6  $\mu m$  scattering layer. PEDOT was used as the counter electrode for  $[Mn(acac)_3]^{0/1+}$  based devices and Pt for  $I/I_3^-$  and  $[Co(bpy)_3]^{2+/3+}$  based devices. For each concentration six cells were constructed to obtain the average value.



**Figure S10:** Comparison of the IPCE curves for DSC based on  $I/I_3^-$ ,  $[Co(bpy)_3]^{2+/3+}$  and  $[Mn(acac)_3]^{0/1+}$  electrolytes sensitized with MK2. IPCE spectra were recorded at low light conditions (< 2% Sun).



**Figure S11: Mean charge transport time ( $\tau_a$ ) vs short circuit current density, measured by IMPS.**  $I/I_3^-$  based electrolyte (diamonds),  $[Co(bpy)_3]^{2+/3+}$  based electrolyte (triangles) and  $[Mn(acac)_3]^{0/1+}$  based electrolyte (squares)

**Table S9:** Comparison of the photovoltaic parameters obtained under one Sun illumination for devices constructed with the N719 sensitizer and with various thicknesses of the transparent  $TiO_2$  layer.

<b><math>TiO_2</math> layer thickness (transparent : scattering) / <math>\mu m</math></b>	<b><math>V_{oc}</math> (mV)</b>	<b><math>J_{sc}</math> (mA cm<math>^{-2}</math>)</b>	<b>Fill Factor</b>	<b>Efficiency (%)</b>
1+4	$799 \pm 30$	$5.2 \pm 0.2$	$0.78 \pm 0.01$	$3.2 \pm 0.3$
2+4	$771 \pm 8$	$7.9 \pm 0.3$	$0.73 \pm 0.01$	$4.4 \pm 0.2$
3+4	$762 \pm 7$	$6.8 \pm 0.3$	$0.73 \pm 0.04$	$3.8 \pm 0.2$

Cells were made with K4 dye and  $[Mn(acac)_3]^{0/1+}$  electrolyte consists of 0.50 M  $[Mn(acac)_3]$ , 0.10 M  $NOBF_4$ , 1.20 M tBP and 0.05 M  $LiBF_4$  in acetonitrile. PEDOT was used as the counter electrode. For each layer thickness six cells were constructed to obtain the average value. The  $TiO_2$  layer thickness is denoted as the thickness of the transparent  $TiO_2$  layer + the thickness of the scattering  $TiO_2$  layer.