

**Supporting Information to**  
**ON THE STABILITY OF MANGANESE *TRIS* ( $\beta$ -DIKETONATE) COMPLEXES AS**  
**REDOX MEDIATORS IN DSSCs.**

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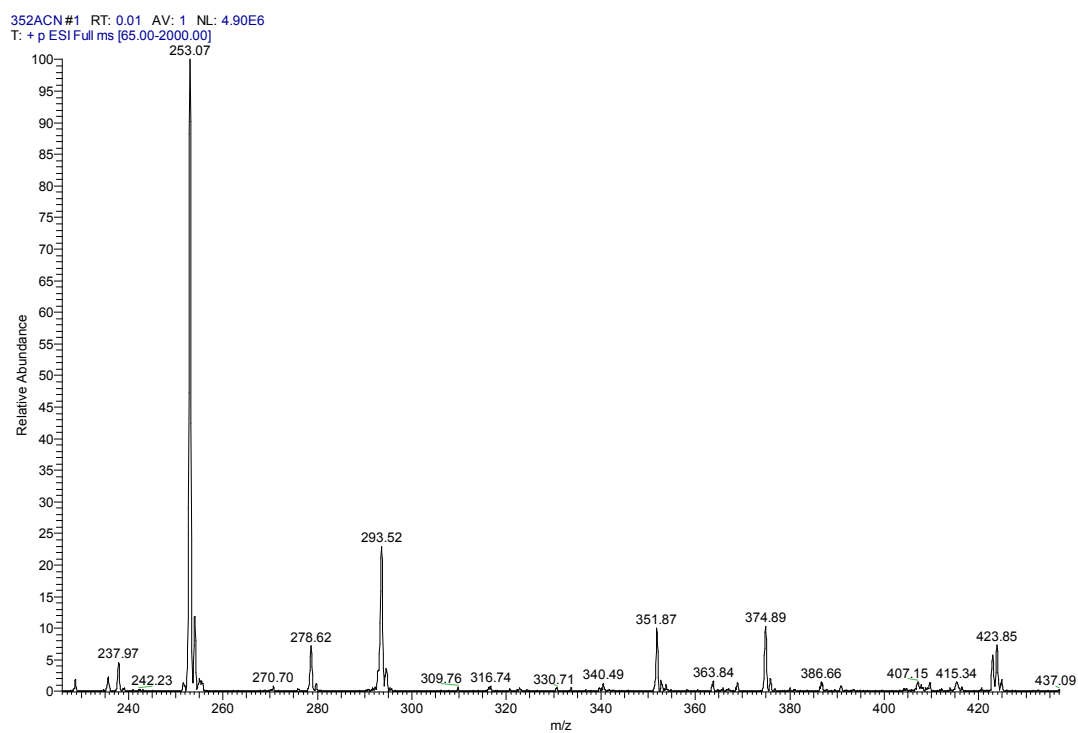
**Table S1a.** Crystallographic Data for *fac*-[Mn(CF<sub>2</sub>)<sub>3</sub>] (complex **2**).

Compound	<i>fac</i> -[Mn(CF <sub>2</sub> ) <sub>3</sub> ] (complex <b>2</b> )
Formula	Mn(III)C <sub>30</sub> H <sub>21</sub> F <sub>6</sub> O <sub>6</sub>
M	646.41
Space group	<i>R</i> -3
Crystal system	Trigonal
a/Å	18.583(1)
b/Å	18.583(1)
c/Å	14.503(1)
α/°	90.00
β/°	90.00
γ/°	120.00
U/Å <sup>3</sup>	4337.3(4)
Z	6
T/K	295
D <sub>c</sub> /g cm <sup>-3</sup>	1.485
F(000)	1968
μ(Mo-Kα)/mm <sup>-1</sup>	0.537
Measured Reflections	3905
Unique Reflections	2071
R <sub>int</sub>	0.0210
Obs. Refl.ns [I≥2σ(I)]	1496
θ <sub>min</sub> -θ <sub>max</sub> /°	4.39 – 27.00
hkl ranges	-23,23;-20,20;-15,18
R(F <sup>2</sup> ) (Obs.Refl.ns)	0.0505
wR(F <sup>2</sup> ) (All Refl.ns)	0.1513
No. Variables/Restraints	130/0
Goodness of fit	1.046
Δρ <sub>max</sub> ; Δρ <sub>min</sub> /e Å <sup>-3</sup>	0.295; -0.327
CCDC Deposition N.	1421029

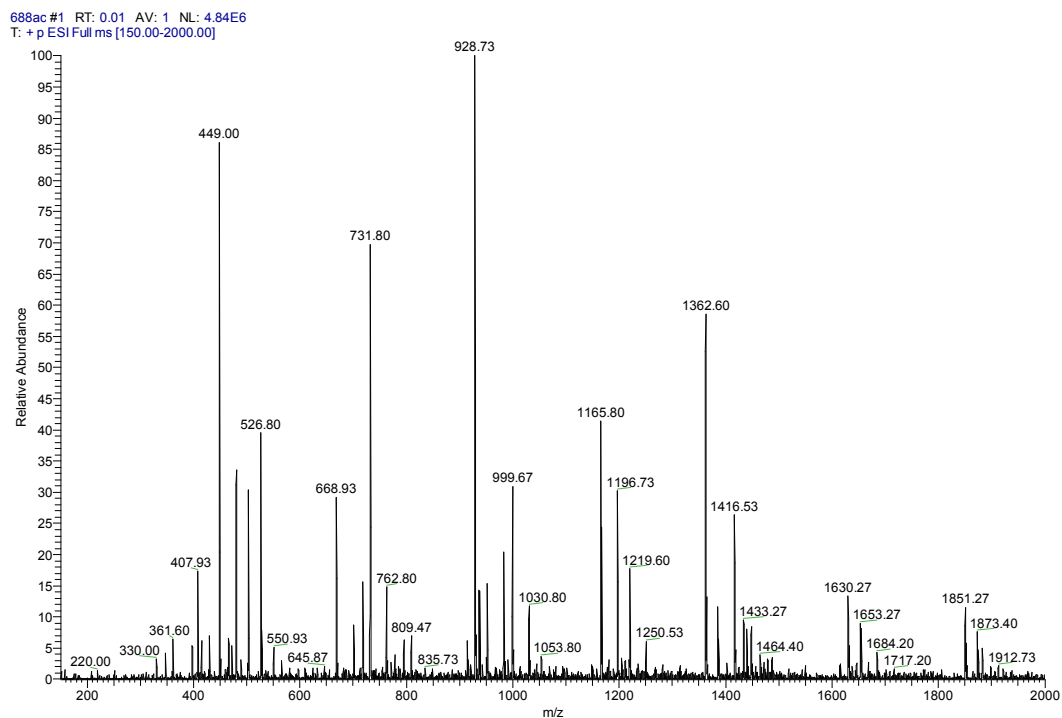
**Table S1b.** Selected bond distances and angles (Å and degrees).

<i>fac</i> -[Mn(CF <sub>2</sub> ) <sub>3</sub> ] (complex <b>2</b> )	
<b>Distances</b>	
Mn1-O1	1.978(2)
Mn1-O2	1.995(2)
<b>Angles</b>	
O1-Mn1-O2	89.17(8)
O1-Mn1-O1'	90.48(8)
O1-Mn1-O2'	91.57(9)
O1-Mn1-O2''	177.92(8)
O2-Mn1-O2'	88.79(8)
O2-Mn1-O2''	91.57(9)

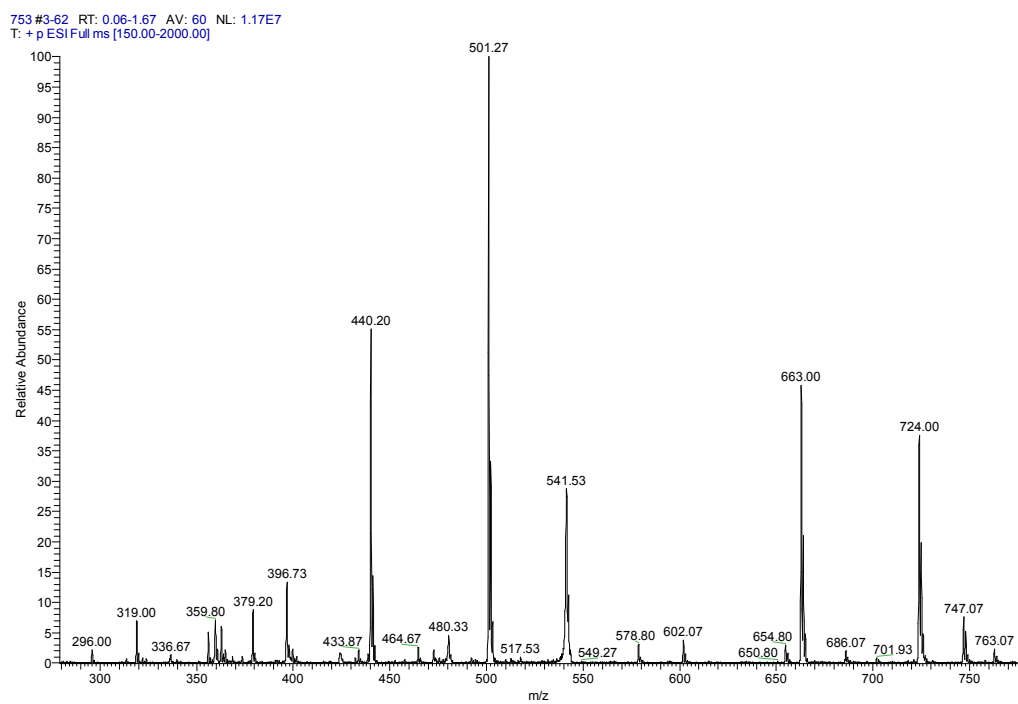
**Figure S1.** ESI mass of  $[\text{Mn}(\text{acac})_3]$  (1)



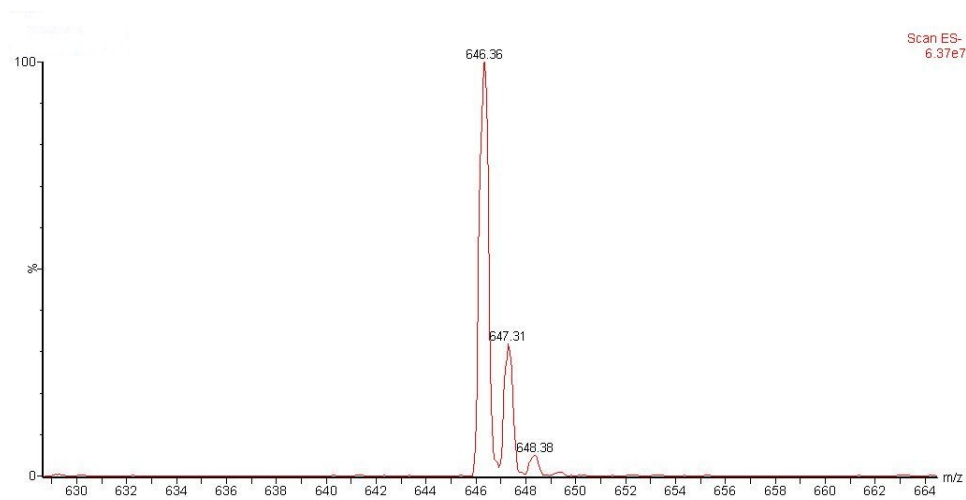
**Figure S2.** ESI mass of  $[\text{Mn}(\text{CF}_2)_3]$  (2).



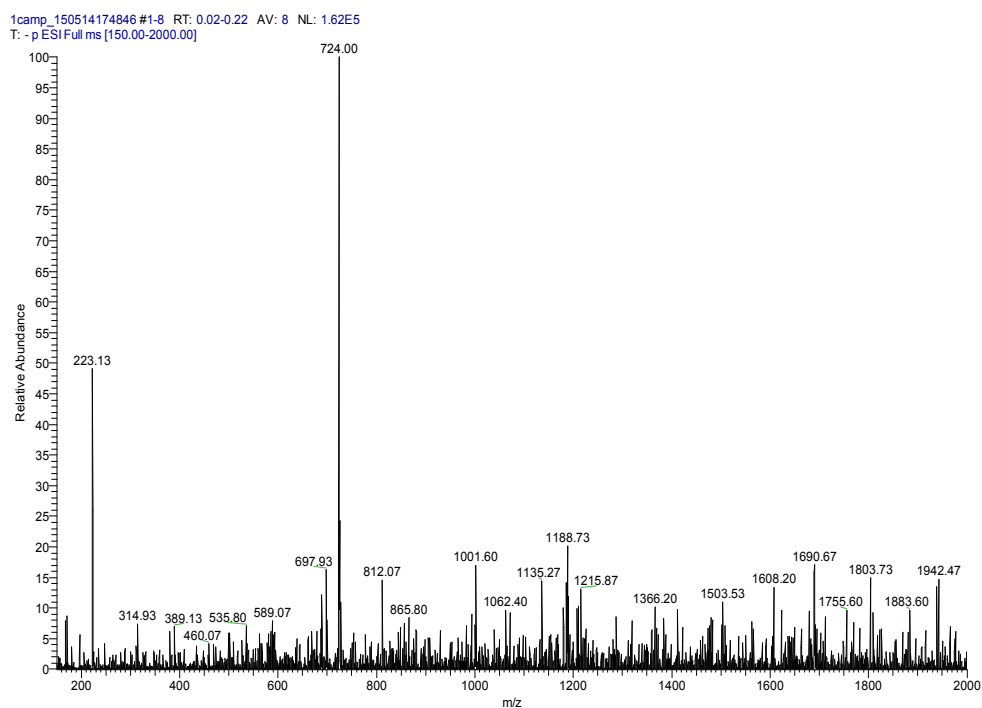
**Figure S3.** ESI mass of  $[\text{Mn}(\text{DBM})_3]$  (**3**).



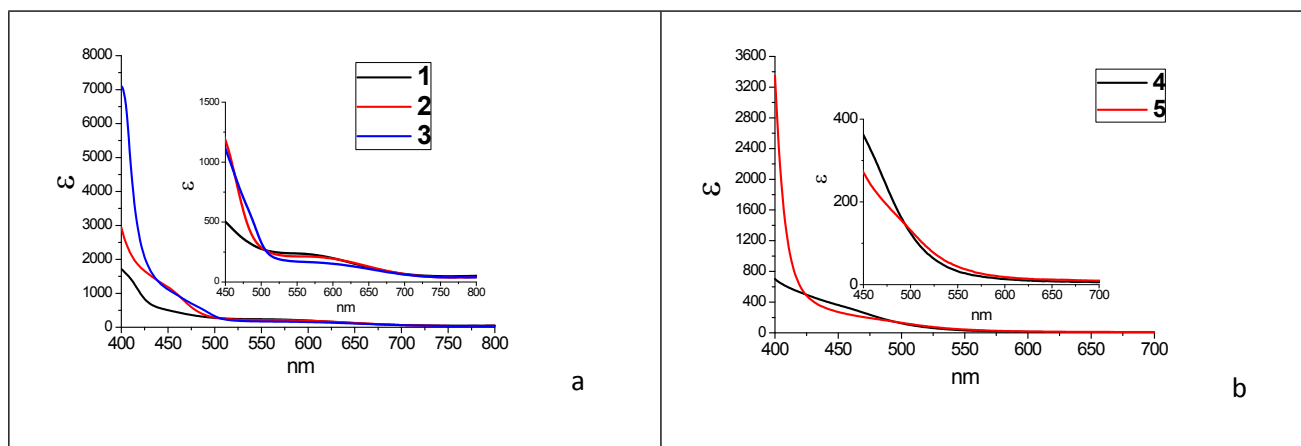
**Figure S4.** ESI of  $[\text{Mn}(\text{CF}_2)_3]\text{TBA}$  (**4**).



**Figure S5.** ESI of  $[\text{Mn}(\text{DBM})_3]\text{TBA}$  (**5**).



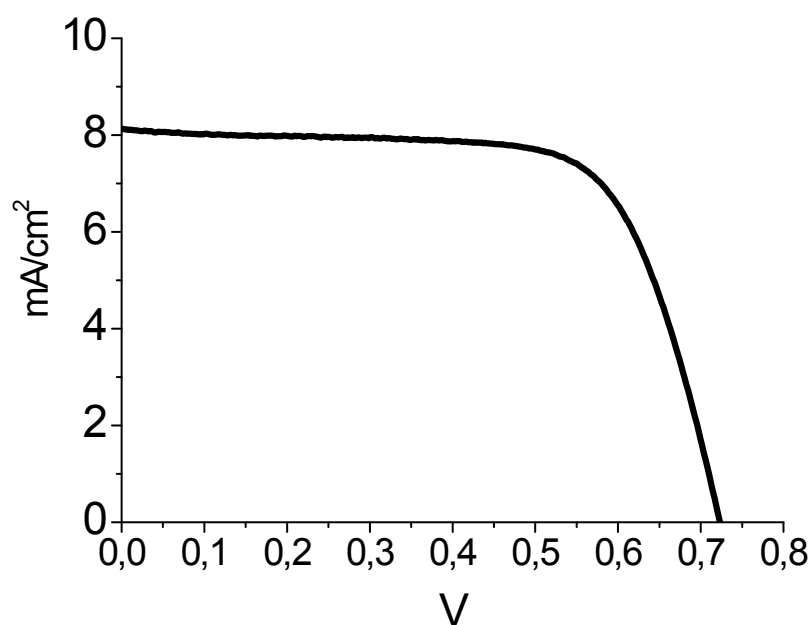
**Figure S6.** Visible spectra of a) **1,2,3** and b) **4,5** complexes.



**Table S2.** Relevant photoelectrochemical data obtained from the JV plots reported in Figure 3. Electrolyte composition: 0.15M **1** or **2**, 0.5M TBP, 0.1M LiCF<sub>3</sub>SO<sub>3</sub>, 0.015M NOBF<sub>4</sub> in A) MPN and B) ACN.

electrolyte	Mn complex	J <sub>sc</sub> mA cm <sup>-2</sup>	V <sub>oc</sub> V	FF	η%
A	[Mn(acac) <sub>3</sub> ] <b>(1)</b>	4.15	0.73	0.64	1.55
	[Mn(CF <sub>2</sub> ) <sub>3</sub> ] <b>(2)</b>	3.69	0.83	0.61	1.89
B	[Mn(acac) <sub>3</sub> ] <b>(1)</b>	5.69	0.73	0.57	2.36
	[Mn(CF <sub>2</sub> ) <sub>3</sub> ] <b>(2)</b>	4.95	0.80	0.69	2.72

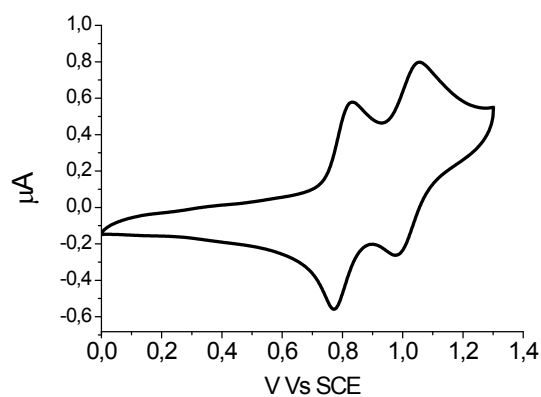
**Figure S7.** JV of MK2 sensitized DSSC based on [Mn(acac)<sub>3</sub>] **(1)**. Electrolyte: 0.50 M **1**, 0.10M NOBF<sub>4</sub>, 1.20 M TBP, 0.05M LiCF<sub>3</sub>SO<sub>3</sub> in ACN.



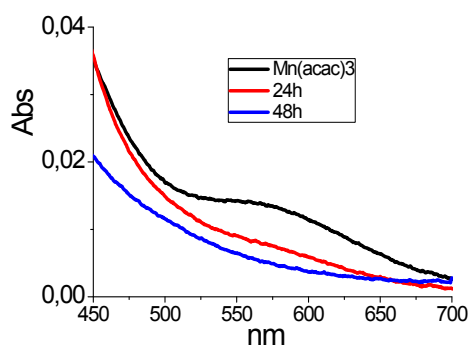
**Table S3.** Relevant parameters obtained from JV analysis of plot reported in Figure S10 and a comparison with reported data.<sup>1</sup>

	<b>Jsc</b> mA cm <sup>-2</sup>	<b>Voc</b> V	<b>FF</b>	<b>PCE</b> %
this paper	8,1	0,73	0,69	4
Ref.1	8,6	0.73	0.69	4.4

**Figure S8:** CV of MK2 in 0.1N LiOCl<sub>4</sub>/ACN solution at scan rate 100 mV sec<sup>-1</sup>, WE glassy carbon, CE Pt wire.

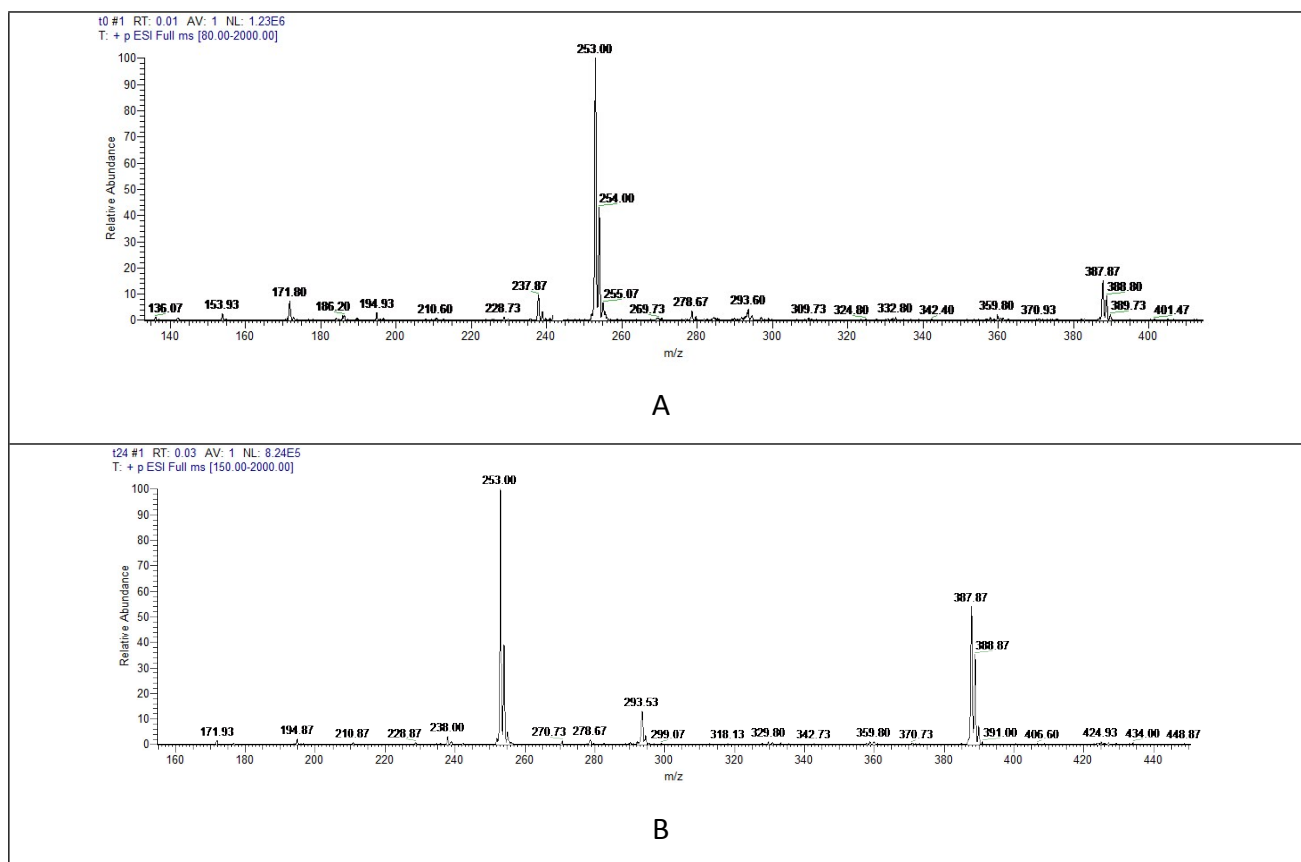


**Figure S9:** Spectral changes of a 0.15M [Mn(acac)<sub>3</sub>] (**1**) solution in 0.1N LiClO<sub>4</sub>/ACN upon 0.5M TBP addition after 24 hr and 48 hr.





**Figure S10.** ESI mass of 0.15M [Mn(acac)<sub>3</sub>] (**1**) based electrolyte after the addition of 0.5M TBP A) immediately B) after 24 hours.



**Table S4a.** Crystallographic Data for *trans*-[Mn<sup>III</sup>(acac)<sub>2</sub>TBP<sub>2</sub>][ClO<sub>4</sub>].

Compound	<i>trans</i> -[Mn <sup>III</sup> (acac) <sub>2</sub> TBP <sub>2</sub> ][ClO <sub>4</sub> ]
Formula	[Mn(III)C <sub>28</sub> H <sub>40</sub> N <sub>2</sub> O <sub>8</sub> ] <sup>+</sup> •[ClO <sub>4</sub> ] <sup>-</sup>
M	623.01
Space group	<i>C2/c</i>
Crystal system	Monoclinic
a/Å	16.325(1)
b/Å	17.663(1)
c/Å	12.491(1)
α/°	90.00
β/°	115.434(10)
γ/°	90.00
U/Å <sup>3</sup>	3252.7(4)
Z	4
T/K	295
D <sub>c</sub> /g cm <sup>-3</sup>	1.272
F(000)	1312
μ(Mo-Kα)/mm <sup>-1</sup>	0.534
Measured Reflections	5347
Unique Reflections	2838
R <sub>int</sub>	0.0785
Obs. Refl.ns [I≥2σ(I)]	1742
θ <sub>min</sub> -θ <sub>max</sub> /°	3.26-25.00
hkl ranges	-19,19;-20,20;-14,14

R(F <sup>2</sup> ) (Obs.Refl.ns)	0.0841
wR(F <sup>2</sup> ) (All Refl.ns)	0.2813
No. Variables/Restraints	220/21
Goodness of fit	1.034
$\Delta\rho_{\max}; \Delta\rho_{\min} / e \text{ \AA}^{-3}$	0.519; -0.513
CCDC Deposition N.	1421030

**Table S4b.** Selected bond distances and angles (Å and degrees).

<i>trans</i> -[Mn <sup>III</sup> (acac) <sub>2</sub> TBP <sub>2</sub> ]ClO <sub>4</sub>	
<b>Distances</b>	
Mn1-O1	1.924(3)
Mn1-O2	1.915(4)
Mn1-N1	2.290(4)
<b>Angles</b>	
O1-Mn1-O2	92.24(16)
O1-Mn1-O1'	180.00
O1-Mn1-O2'	87.76(16)
O2-Mn1-O2'	180.00
O1-Mn1-N1	89.15(16)
O1-Mn1-N1'	90.85(16)
O2-Mn1-N1	90.60(16)
O2-Mn1-N1'	89.40(16)
N1-Mn1-N1'	180.00

**Table S5a.** Crystallographic Data for *trans*-[Mn<sup>II</sup>(CF<sub>2</sub>)<sub>3</sub>TBP<sub>2</sub>]<sup>0</sup>.

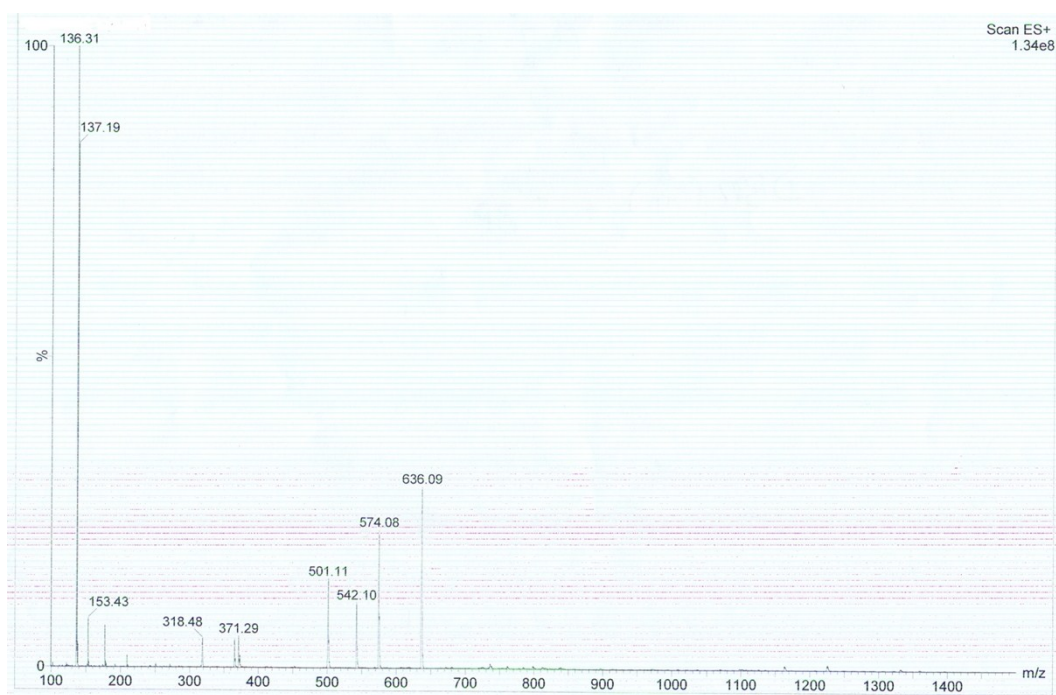
Compound	<i>trans</i> -[Mn <sup>II</sup> (CF <sub>2</sub> ) <sub>3</sub> TBP <sub>2</sub> ] <sup>0</sup>
Formula	Mn(II)C <sub>38</sub> H <sub>40</sub> F <sub>4</sub> N <sub>2</sub> O <sub>4</sub>
M	719.66
Space group	C2/c
Crystal system	Monoclinic
a/Å	18.2229(9)
b/Å	19.0407(10)
c/Å	11.7031(7)
$\alpha/^\circ$	90.00
$\beta/^\circ$	115.785(2)
$\gamma/^\circ$	90.00
U/Å <sup>3</sup>	3656.4(3)
Z	4
T/K	295
D <sub>c</sub> /g cm <sup>-3</sup>	1.307
F(000)	1500
$\mu$ (Mo-K $\alpha$ )/mm <sup>-1</sup>	0.422
Measured Reflections	5464
Unique Reflections	3172
R <sub>int</sub>	0.0265
Obs. Refl.ns [I $\geq$ 2 $\sigma$ (I)]	2230
$\theta_{\min}$ - $\theta_{\max}/^\circ$	3.53– 25.00

hkl ranges	-21,21;-21,22;-13,13
R(F <sup>2</sup> ) (Obs.Refl.ns)	0.0750
wR(F <sup>2</sup> ) (All Refl.ns)	0.2310
No. Variables/Restraints	239/19
Goodness of fit	1.129
$\Delta\rho_{\max}$ ; $\Delta\rho_{\min}$ /e Å <sup>-3</sup>	0.400; -0.384
CCDC Deposition N.	1421031

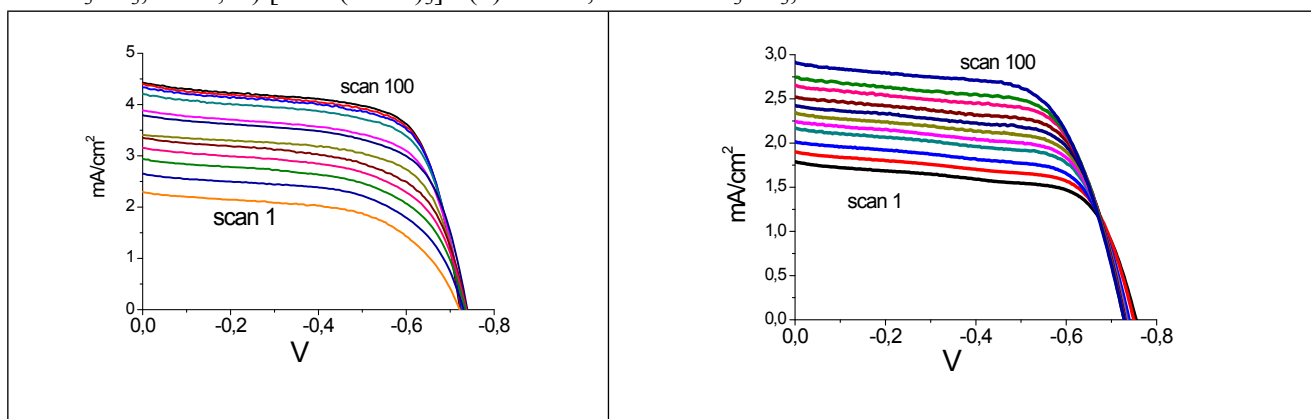
**Table S5b.** Selected bond distances and angles (Å and degrees).

<i>trans</i> -[Mn <sup>II</sup> (CF <sub>2</sub> ) <sub>3</sub> TBP <sub>2</sub> ] <sup>0</sup>	
<b>Distances</b>	
Mn1-O1	2.156(4)
Mn1-O2	2.128(2)
Mn1-N1	2.271(6)
Mn1-N2	2.325(6)
<b>Angles</b>	
O1-Mn1-O2	85.34(11)
O1-Mn1-O1'	177.09(18)
O1-Mn1-O2'	94.69(11)
O2-Mn1-O2'	178.96(16)
O1-Mn1-N1	91.45(9)
O1-Mn1-N2	88.55(9)
O2-Mn1-N1	89.48(8)
O2-Mn1-N2	90.52(8)
N1-Mn1-N2	180.00

**Figure S11.** ESI mass of 0.15M [Mn(DBM)<sub>3</sub>] based electrolyte in DMF after the addition of 0.5M TBP after 24 hours.

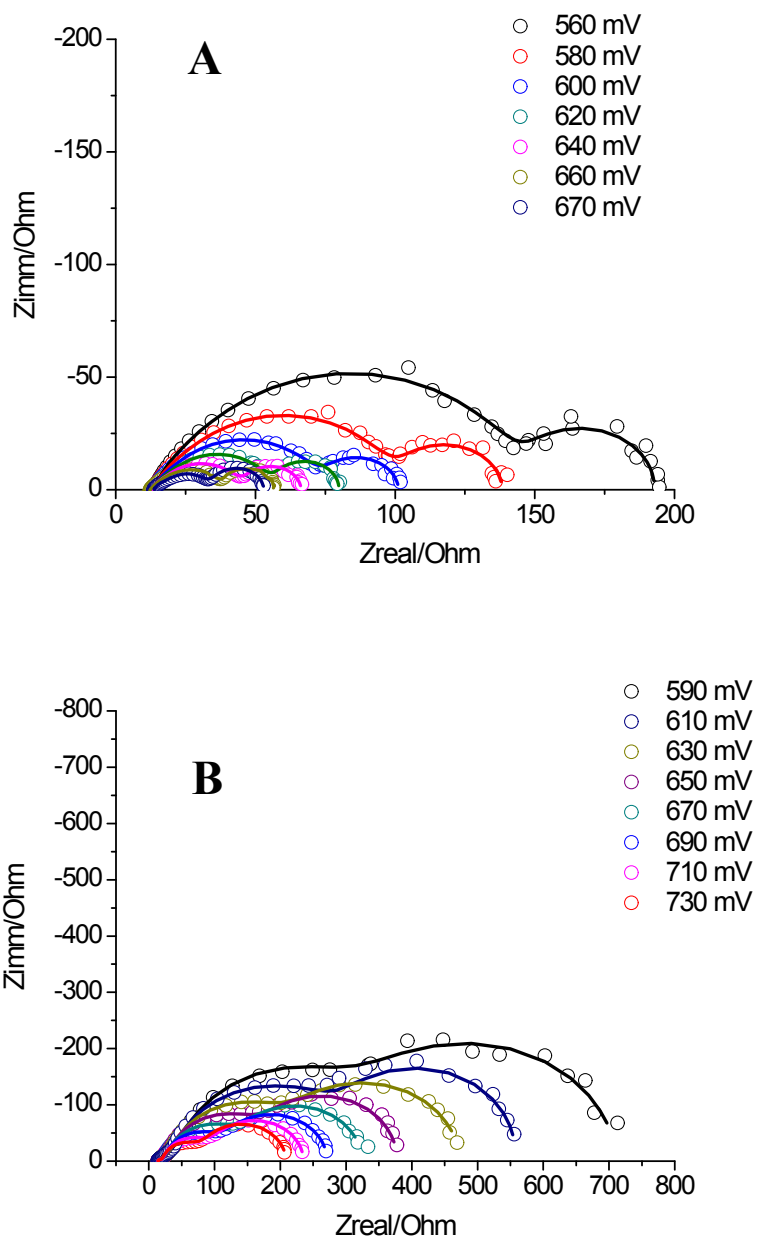


**Figure S12.** Z907/APTS sensitized DSC, electrolyte composition: A)  $[\text{Mn}^{\text{III}}(\text{CF}_2)_3]^0$  (**2**) 0.15M 0.1M  $\text{LiCF}_3\text{SO}_3$ , ACN; B)  $[\text{Mn}^{\text{III}}(\text{DBM})_3]^0$  (**3**) 0.13M, 0.1M  $\text{LiCF}_3\text{SO}_3$ , DMF.



**Figure S13.** Nyquist plots for Z907 sensitized DSC, post treated with APTS and assembled with PEDOT coated counter electrodes based on: A) 0.3/0.03M  $[\text{Mn}^{\text{II/III}}(\text{CF}_2)_3]^{-1/0}$  (**4**) in ACN + 0.1 M  $\text{LiCF}_3\text{SO}_3$ ; B) 0.3/0.03M  $[\text{Mn}^{\text{II/III}}(\text{DBM})_3]^{-1/0}$  (**5**) in ACN/DMF 1/1 + 0.1 M  $\text{LiCF}_3\text{SO}_3$ . AM 1.5G illumination. Circles

indicate experimental data points, continuous lines of the same color are fits to the relevant experimental data.



### References to Supporting Information

(1) Perera, I. R.; Gupta, A.; Xiang, W.; Daeneke, T.; Bach, U.; Evans, R. A.; Ohlin, C. A.; Spiccia, L. *Phys. Chem. Chem. Phys.* **2014**, *16*, 12021.