

Electronic Supplementary Information

Title: Biomimetic Photoelectrochemical Device from a Molecular Heterometallic Sodium-Manganese Water Splitting Catalyst

*C. R. Raymond Gan,^{ab} Zhaolin Liu^b, Shi-Qiang Bai,^b Siok Wei Tay^b, Xiaoming Ge^b Ji-En Wu^c and T. S. Andy Hor^{*bc}*

^aNUS Graduate School for Integrative Sciences and Engineering , Center for Life Sciences, #05-01, 28 Medical Drive Singapore 117456, Singapore,

^bInstitute of Materials Research and Engineering, Agency for Science, Technology and Research, 3 Research Link, S117602, Singapore,

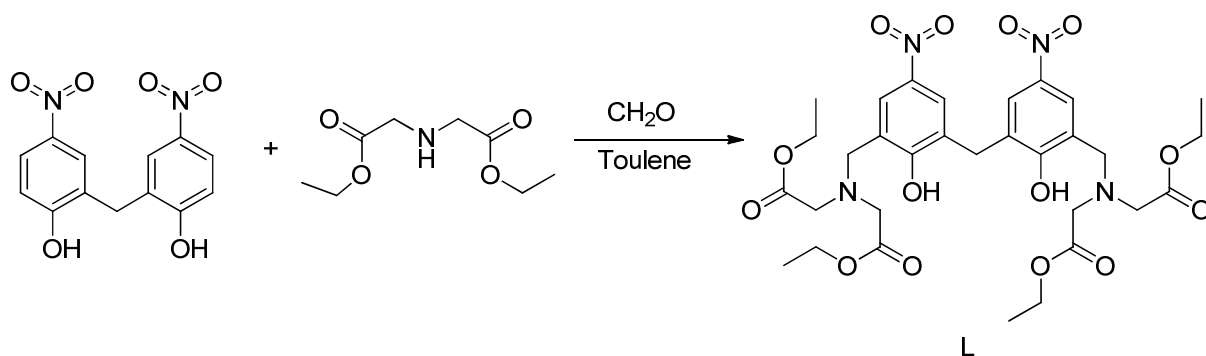
^cDepartment of Chemistry, National University of Singapore, 3 Science Drive 3, S117543, Singapore.

Email: andyhor@nus.edu.sg

Materials and Method

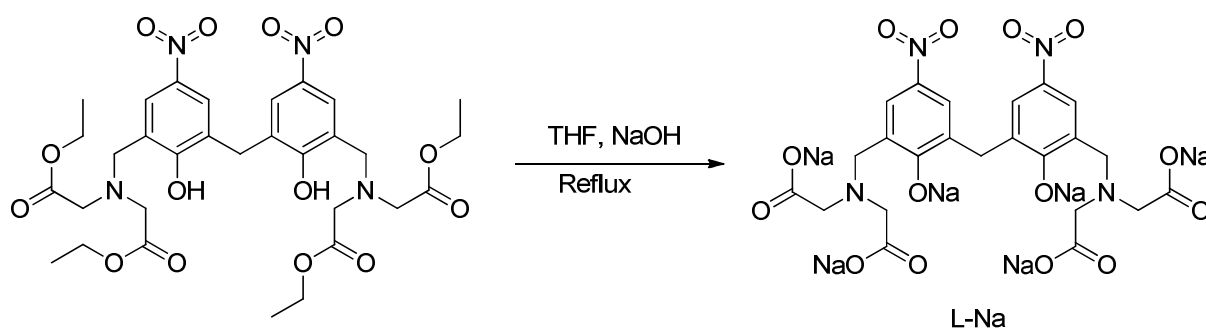
All the reagents were purchased from commercial sources and used as received, unless otherwise noted. Solutions are prepared using high purity water (resistivity > 18MΩ). Indium tin oxide was ultrasonically cleaned with acetone, isopropanol, and water and dried before usage. Ru 535-bis TBA dye was purchased from Solaronix while SOCl_2 , iminodiacetic acid, 4-nitrophenol, paraformaldehyde, Mn salts, 5% Nafion in EtOH/water and Clevios ph1000 were used without further purification.

Synthesis of tetraethyl 2,2',2'',2'''-(3,3'-methylenebis(2-hydroxy-5-nitro-3,1-phenylene))bis(methylene)bis(azanetriyl)tetraacetate (L)



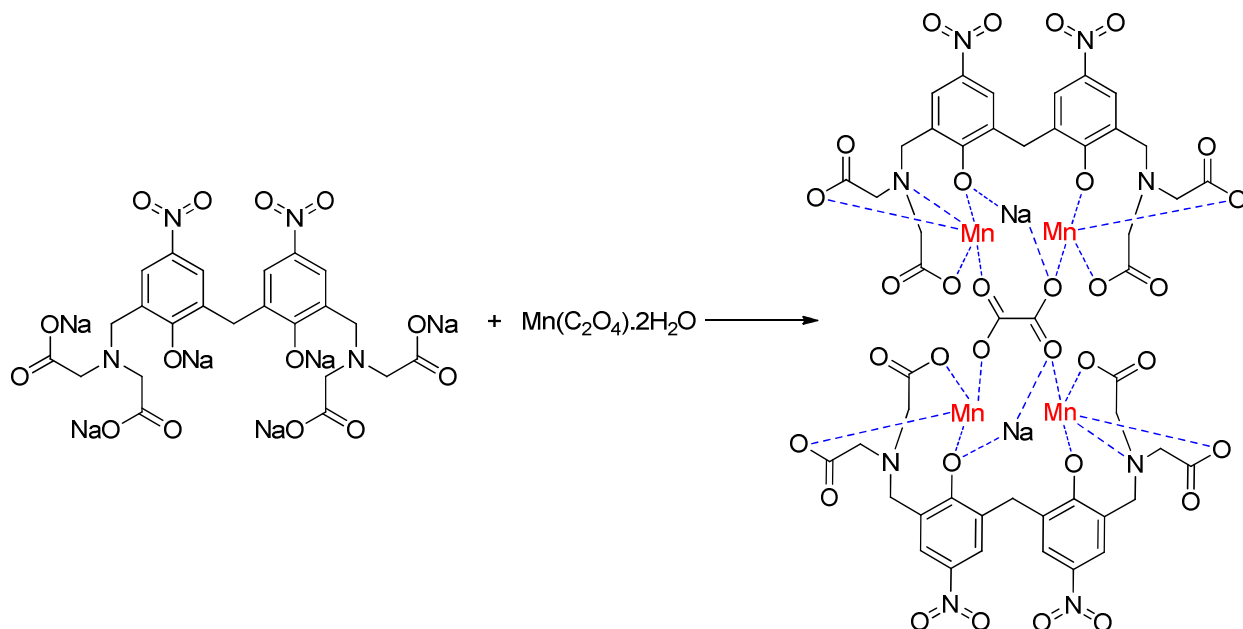
Diethyl 2,2'-azanediyl diacetate¹ (0.65 g, 3.44 mmol), 2,2'-(methylenebis(4-nitrophenol))² (0.5 g, 1.72 mmol), paraformaldehyde (0.10 g, 3.44 mmol) were dissolved in toluene and refluxed for 48 hours under N₂. The excess toluene was vacuumed away and the mixture of products re-dissolved in CH₂Cl₂. The desired product was eluted with CH₂Cl₂ on a silica gel column as yellow viscous oil. Yield: 0.3 g, 26%. ¹H NMR (500MHz, CDCl₃) δ: 7.95 (2H, d, J = 2.5Hz, phenyl), 7.84 (2H, d, J = 2.5Hz, phenyl), 4.22 (8H, q, J = 6.95Hz, CH₂), 4.09 (2H, s, CH₂), 4.05 (4H, s, CH₂), 3.53 (8H, s, CH₂), 1.28 (12H, t, J = 14.5Hz, Me) ¹³C NMR (500MHz, CDCl₃) δ: 170.60, 161.62, 139.98, 127.85, 126.24, 124.10, 121.34, 61.41, 55.60, 53.92, 29.45, 14.12. ESI-MS (*m/z*, %): [L6 + Na]⁺ (715.00, 100). Anal. Calcd. for C₃₁H₄₀N₄O₁₄ (692.67): C, 53.75; H, 5.82; N, 8.09 %. Found: C, 53.59; H, 5.52; N, 7.97 %.

Synthesis of 2,2',2'',2'''-(3,3'-methylenebis(2-hydroxy-5-nitro-3,1-phenylene))bis(methylene)bis(azanetriyl)tetraacetic acid sodium salt (LNa)



Tetraethyl 2,2',2'',2'''-(3,3'-methylenebis(2-hydroxy-5-nitro-3,1-phenylene)) bis(methylene) bis(azanetriyl)tetraacetate (1.052 g, 1.52 mmol) was dissolved in 20 mL of THF before NaOH (0.36 g, 9.00 mmol) in 20 mL of H₂O was added and refluxed for 24 hours. The excess solvent was vacuumed away to yield the desired (very hygroscopic) sodium acetate salt. Yield: 1.08 g, 100%. ¹H NMR (500MHz, D₂O) δ: 8.03 (2H, d, J = 3.15Hz, phenyl), 7.96 (2H, d, J = 3.15Hz, phenyl), 3.59 (2H, s, CH₂), 3.5 (4H, s, CH₂), 3.05 (8H, s, CH₂). ¹³C NMR (500MHz, D₂O) δ: 179.83, 178.02, 131.14, 130.89, 127.76, 127.10, 126.35, 58.81, 54.83, 31.27. ESI-MS (*m/z*, %): [2(L6-acid)+ H]⁺ (580.86, 100). Anal. Calcd. for C₂₃H₁₈N₄Na₆O₁₄·4H₂O (784.41): C, 35.22; H, 3.34; N, 7.14 %. Found: C, 35.71; H, 3.78; N, 7.43 %.

**Synthesis of the [Na₂Mn₄] complex:
[Mn₂Na(H₂O)₃L]₂·C₂O₄·Na₄·11(H₂O)·2(MeOH)·2(EtOH)**



Tetraethyl 2,2',2'',2'''-(3,3'-methylenebis(2-hydroxy-5-nitro-3,1-phenylene)) bis(methylene) bis(azanetriyl)tetraacetic acid sodium salt (0.25g, 0.35mmol) was dissolved in 20ml of DI H₂O before Mn(C₂O₄).2H₂O (0.13g, 0.70mmol) was added and stirred for 1 hour. The resultant orange solution was filtered and layered with 1:1 mixture of MeOH and EtOH over 6 months to yield orange crystals suitable for X-ray crystallography. Yield: 0.1g, 14.2%. ESI-MS (*m/z*, %): [Mn₂NaL]⁻ (706.9, 100), Anal. Calcd. For C₅₃H₄₀Mn₄N₈Na₆O_{58.5}.11(H₂O).2(MeOH).2(EtOH). (2435.98): C, 29.08; H, 3.39; N, 4.60%. Found: C, 28.65; H, 3.71; N, 4.68%. Main IR (cm⁻¹): 3438 (s), 2362 (w), 2341 (w), 1621 (m), 1596 (s), 1493 (w), 1462 (w), 1439 (w), 1406 (w), 1308 (m), 1287 (m), 1143 (s), 1111 (s), 1088 (s), 939 (w), 921 (w), 838 (w), 750 (m), 725 (m), 628 (s).

Table S1: Crystallographic data and refinement parameters for [Na₂Mn₄] complex.

Compound	[Na ₂ Mn ₄]
Empirical formula	C ₅₃ H ₄₀ Mn ₄ N ₈ Na ₆ O _{58.5}
Formula weight	2082.63
Temperature / K	100(2)
Wavelength / Å	0.71073
Crystal system	Monoclinic
Space group	<i>C2/c</i>
<i>a</i> / Å	20.236(2)
<i>b</i> / Å	26.324(4)
<i>c</i> / Å	16.580(2)

$\alpha / ^\circ$	90
$\beta / ^\circ$	110.496(3)
$\gamma / ^\circ$	90
Volume / \AA^3	8272.8(18)
Z	4
Density (calculated) / Mg/m^3	1.672
Absorption coefficient / mm^{-1}	0.748
F(000)	4192
Crystal size / mm^3	$0.60 \times 0.25 \times 0.15$
Theta range for data collection / $^\circ$	2.03–25.00
Reflections collected	23951
Independent reflections	7285 [$R_{\text{(int)}} = 0.0229$]
Data / restraints / parameters	7285 / 133 / 648
GOF	1.041
Largest diff. peak and hole / e.\AA^{-3}	1.745 and -1.369

All measurements were conducted on a Bruker AXS SMART APEX diffractometer, equipped with a CCD area-detector using Mo-K α radiation ($\lambda = 0.71073 \text{ \AA}$). (Table S1) The collecting frames of data, indexing reflection and determination of lattice parameters and polarization effects were performed with the SMART suite programs.³ The integration of intensity of reflections and scaling was carried out by SAINT.⁴ The empirical absorption correction was

performed by SADABS. The space group determination, structure solution and least-squares refinements on $|F|^2$ were carried out with the SHELXS-97 and SHELXL-97.⁵ Anisotropic displacement parameters were refined for the rest of the non-hydrogen atoms. CCDC No.: 949196.

Device fabrication

The TiO₂ paste was prepared accordingly to a known literature procedure⁶ calcinated on ITO/glass respectively at 500 °C for 30 minutes before cooling down to 80 °C and soaking in a 0.3 mM Ru 535-bis TBA dye in room temperature for 24 hours. 100 µl of the appropriate x%PEDOT:PSS/Na₂Mn₄/Nafion solution was immediately pipetted after preparation onto an active area of 0.8 cm x 1.25 cm TiO₂/Ru layer without black tape coverage and subjected to a heat treatment of 40 °C for 24 hours to dry the x%PEDOT:PSS/Na₂Mn₄/Nafion composite membrane.

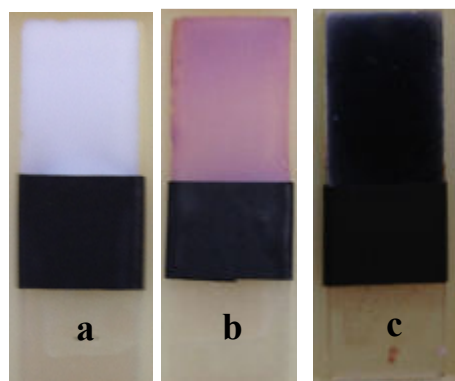


Fig. S1 a) TiO₂ on ITO/glass. b) Ru 535-bis TBA dye adsorbed on ITO/TiO₂. c) ITO/TiO₂/Ru/60%PEDOT:PSS/Na₂Mn₄/Nafion. The devices are translucent when held against light.

PEDOT:PSS/Na₂Mn₄/Nafion solution preparation

12%PEDOT:PSS solution was prepared by mixing 0.23 ml of PEDOT:PSS (Clevios ph1000), 0.78 ml of 5% Nafion in a EtOH/water solution (Aldrich) and 5 μl of the $[\text{Na}_2\text{Mn}_4]$ complex solution (0.08 molL^{-1}) together. The final concentration of the $[\text{Na}_2\text{Mn}_4]$ complex in the final 12%PEDOT:PSS/Nafion solution would be $0.4 \mu\text{molml}^{-1}$ and should be immediately used after homogeneous mixing of the components. 24%, 36%, 48% and 60%PEDOT:PSS/ Na_2Mn_4 /Nafion solution are prepared using the same method described above by varying the PEDOT:PSS to Nafion ratio accordingly.

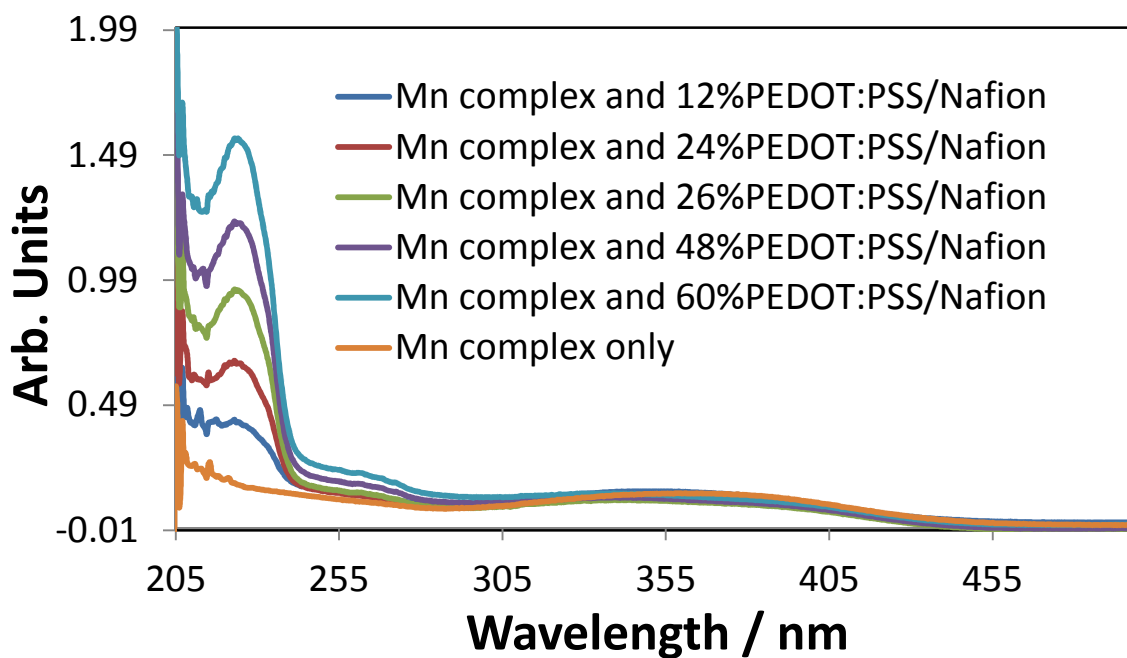


Fig. S2 UV-Vis spectrum of the PEDOT:PSS/Nafion as well as corresponding $[\text{Na}_2\text{Mn}_4]$ complex in solution before drop casting on the Ru/ TiO_2 layer.

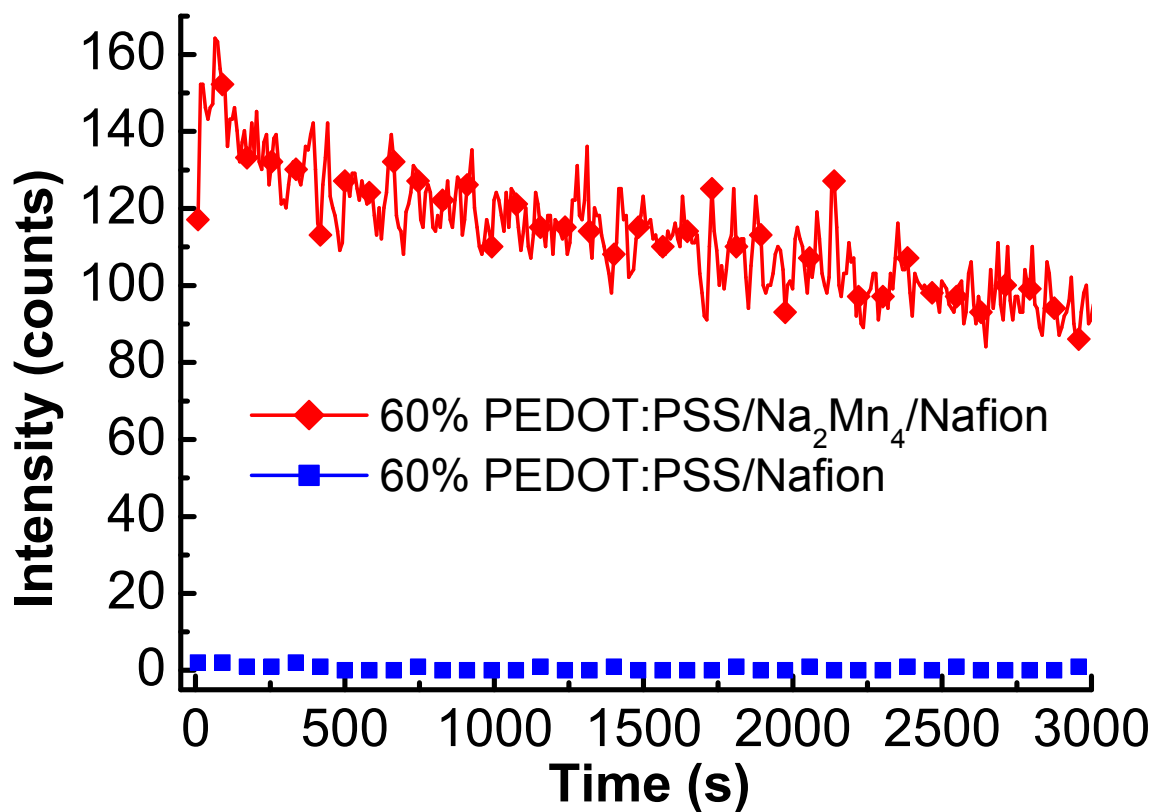


Fig. S3 TOF-SIMS analysis of the Mn signals arising from a $[\text{Na}_2\text{Mn}_4]$ containing compared to a non- $[\text{Na}_2\text{Mn}_4]$ complex containing device as control.

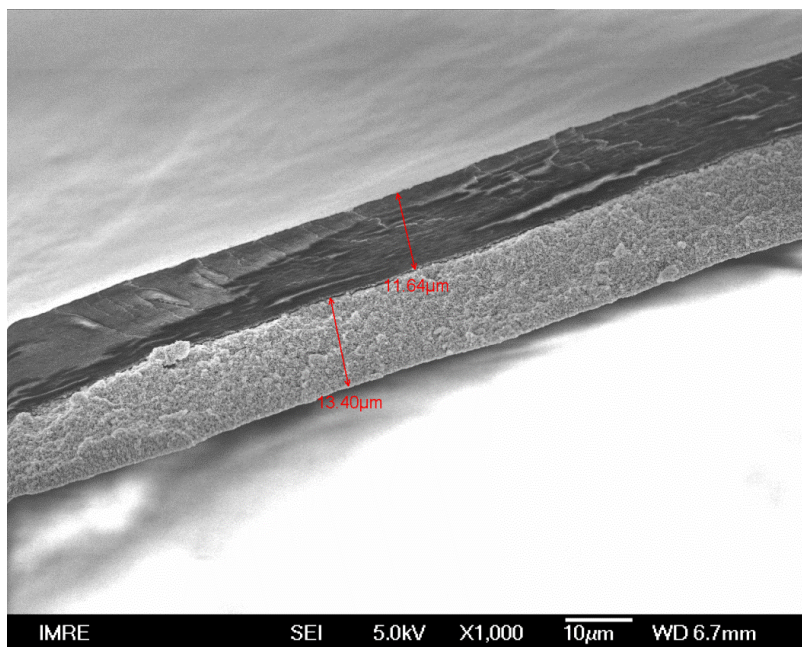


Fig. S4 The cross section area of the TiO_2 and 60%PEDOT:PSS/ Na_2Mn_4 /Nafion composite membrane was obtained by slicing through the TiO_2 /Ru/60%PEDOT:PSS/ Na_2Mn_4 /Nafion composite.

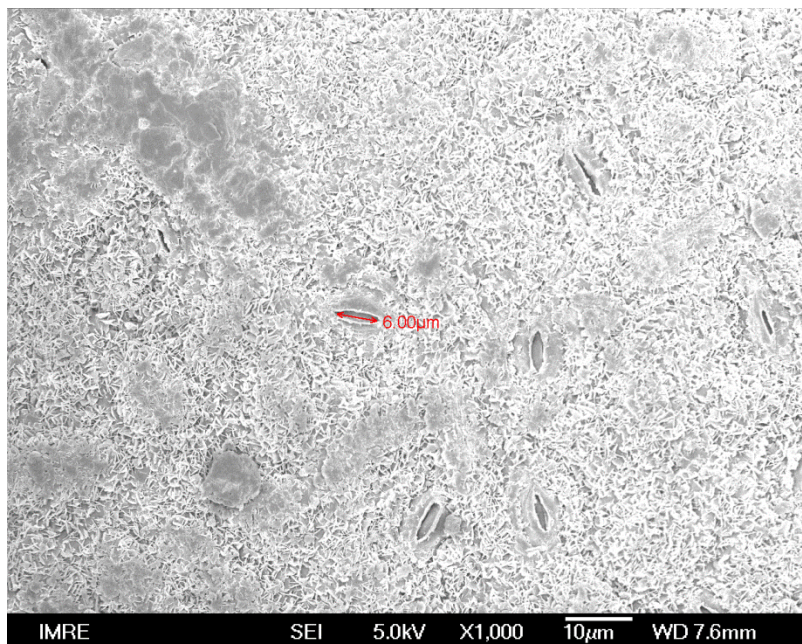


Fig. S5 Surface area of the *rhodomyrtus tomentosa* leaf. Pore size of length 6 µm are scattered throughout the surface.

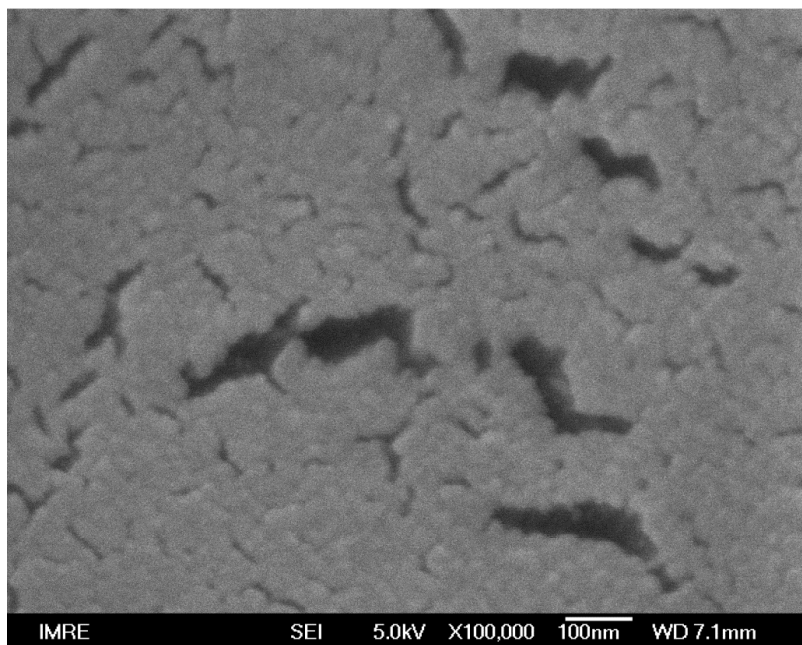


Fig. S6 Close up view on the surface of the membrane confirmed the presence of pores distributed throughout. The size of the pores ranged from tens to several hundred nanometers.

Electron paramagnetic resonance measurements

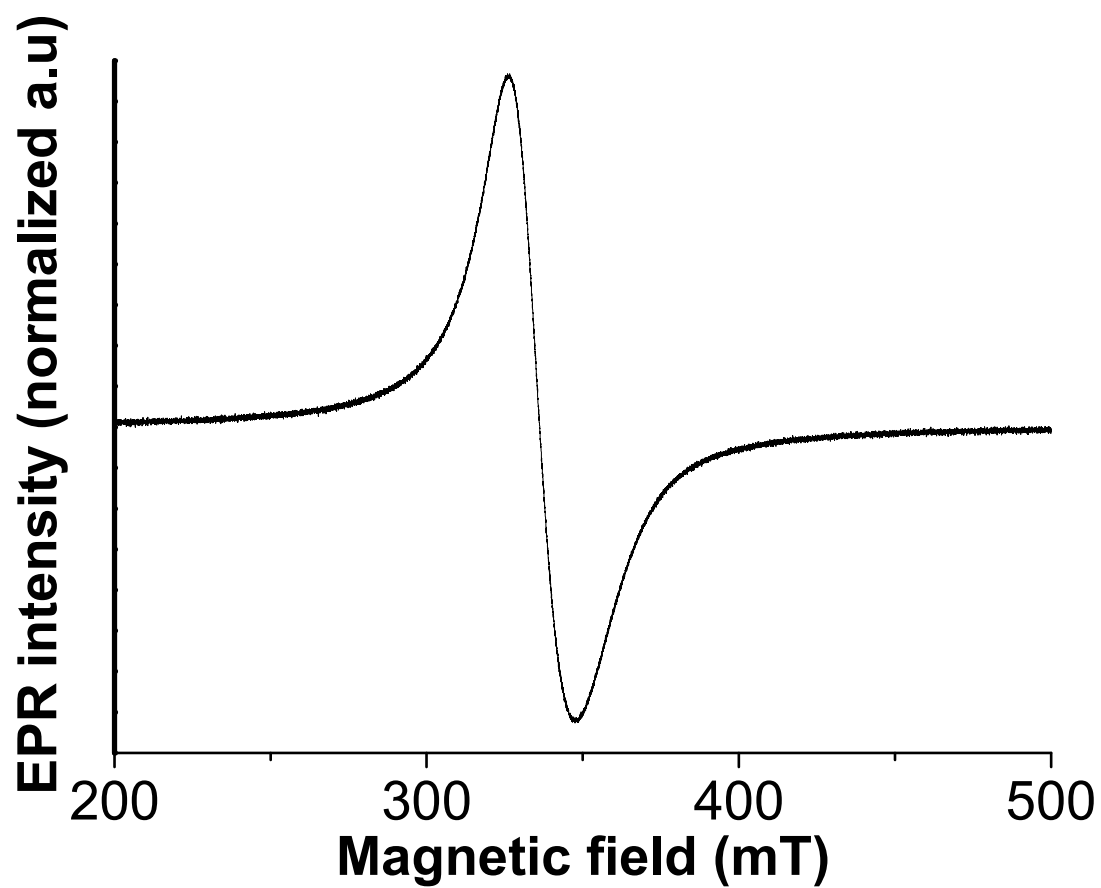


Fig. S7 EPR spectrum of the $[\text{Na}_2\text{Mn}_4]$ complex in DI H_2O .

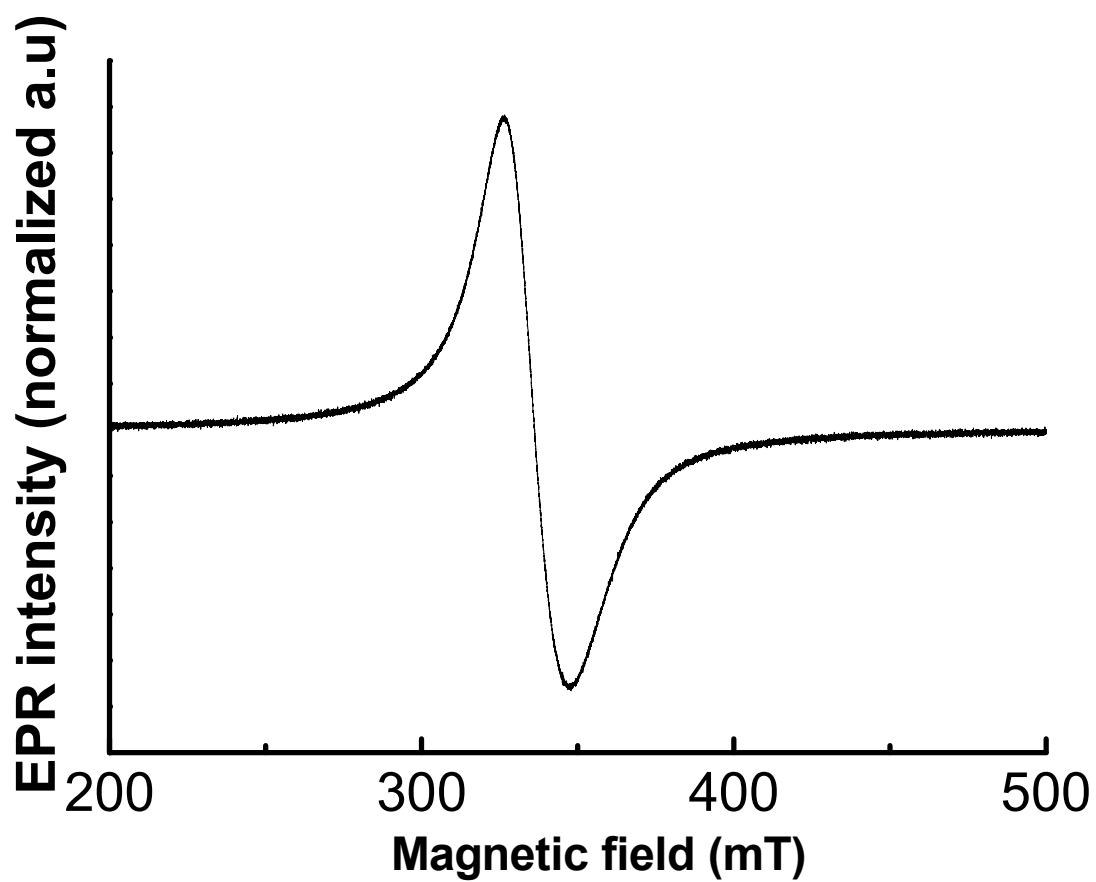


Fig. S8 EPR spectrum of the $[\text{Na}_2\text{Mn}_4]$ complex when deposited within 60%PEDOT:PSS/Nafion composite.

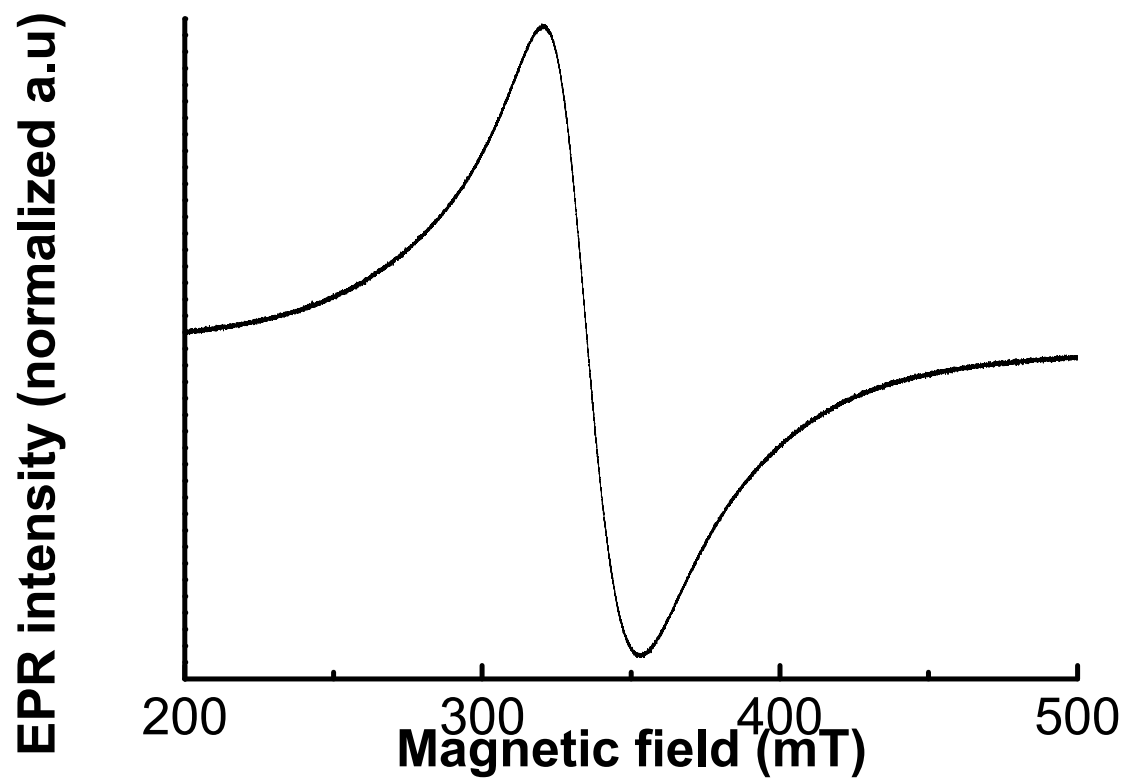


Fig. S9 EPR spectrum of the $[\text{Na}_2\text{Mn}_4]$ complex when deposited within 60%PEDOT:PSS/Nafion composite and subjected to voltage polarization at 1.8 V vs RHE.

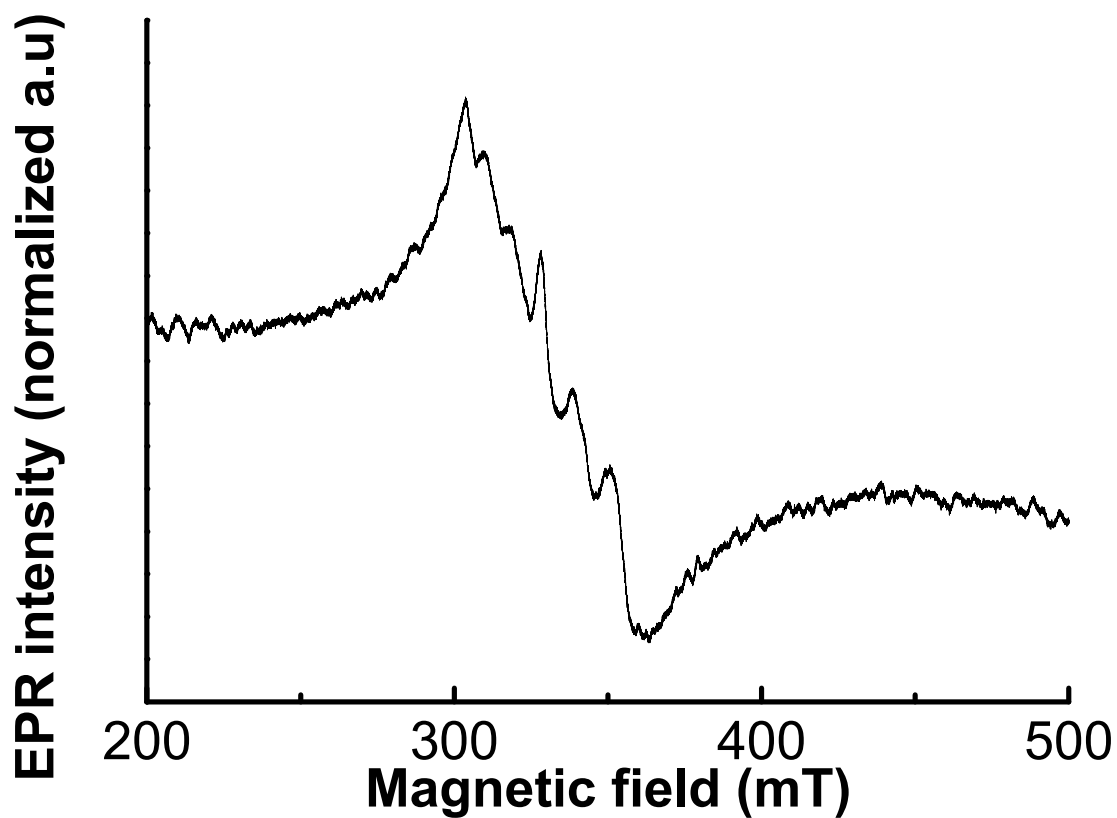


Fig. S10 EPR spectrum of the $[\text{Na}_2\text{Mn}_4]$ complex when deposited within 60%PEDOT:PSS/Nafion composite and subjected to light illumination of 100 mWcm^{-1} under voltage polarization at 1.8 V vs RHE.

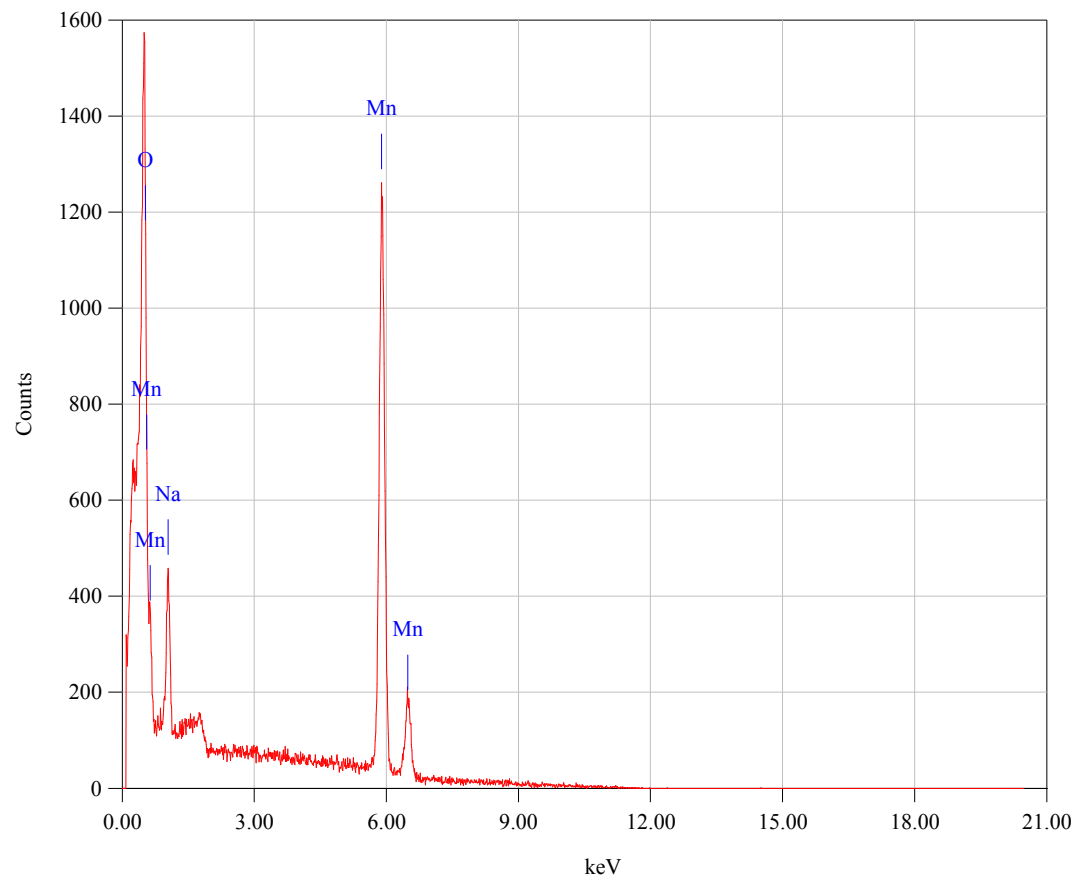


Fig. S11 EDX of the electro-oxidized precipitates isolated from the 60%PEDOT:PSS/Na₂Mn₄/Nafion film after voltage polarization.

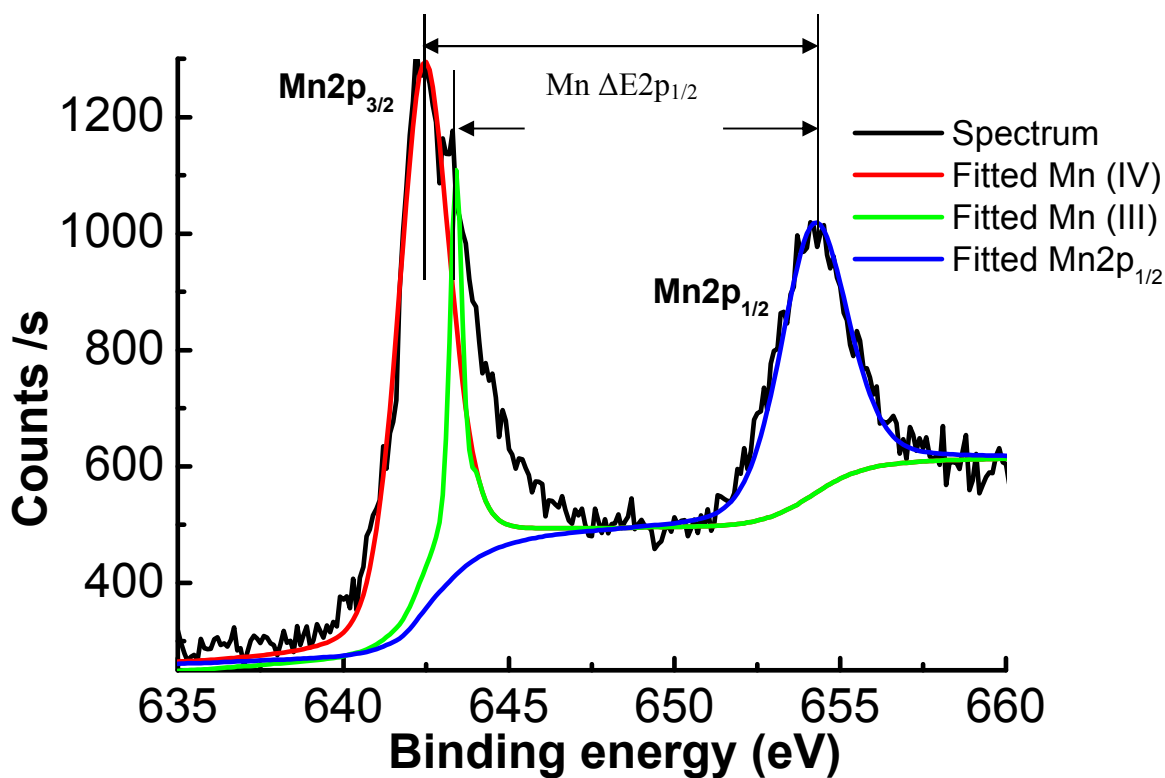


Fig. S12 High resolution XPS spectra of Mn2p from the electro-oxidized precipitates of 60%PEDOT:PSS/Na₂Mn₄/Nafion. The differences in binding energy between the fitted Mn2p_{3/2} and Mn2p_{1/2} peaks are 11.8 eV and 10.6 eV, which corresponds to Mn (IV) and Mn (III) respectively.

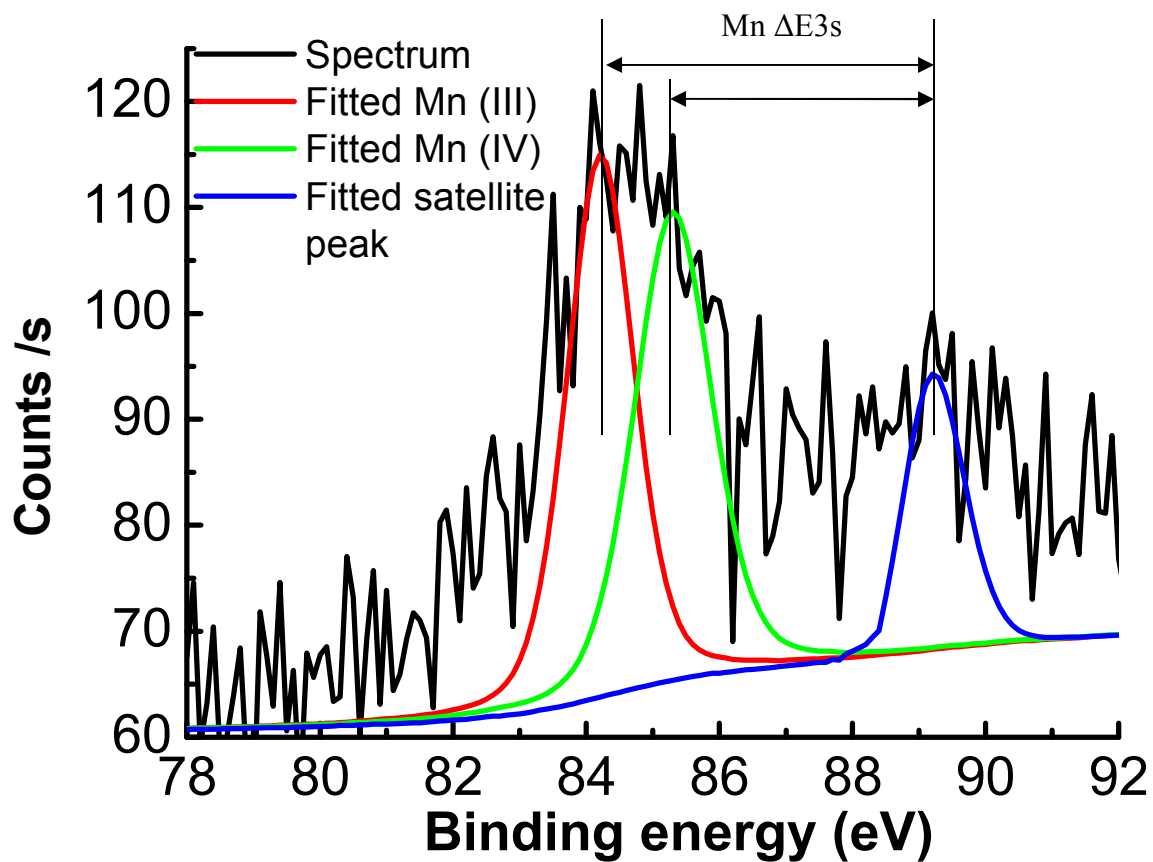


Fig. S13 High resolution XPS spectra of Mn3s from the electro-oxidized precipitates of 60%PEDOT:PSS/Na₂Mn₄/Nafion. The differences between the fitted peaks resulted in binding energy differences of 4.4 and 5.3 eV, which corresponds to Mn (IV) and Mn (III) respectively.

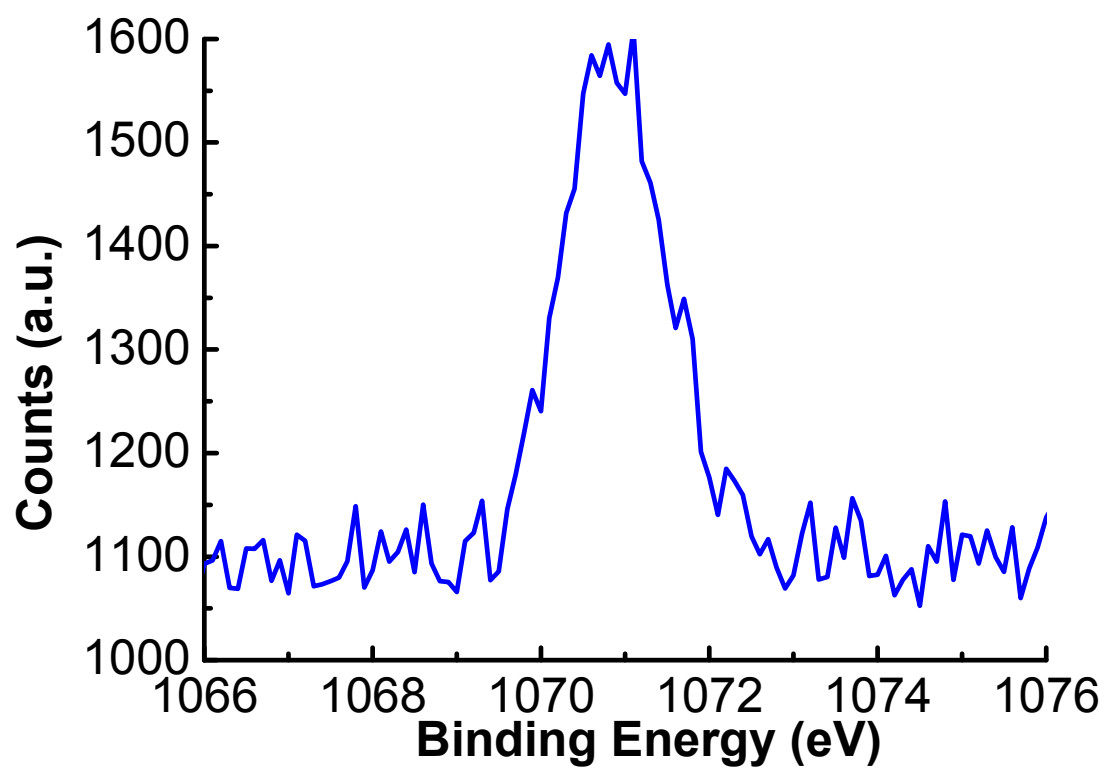


Fig. S14 High resolution XPS spectra of Na 1s from the electro-oxidized precipitates of 60%PEDOT:PSS/Na₂Mn₄/Nafion.. The relative peak position was determined to be 1070.8 eV.

Control experiment

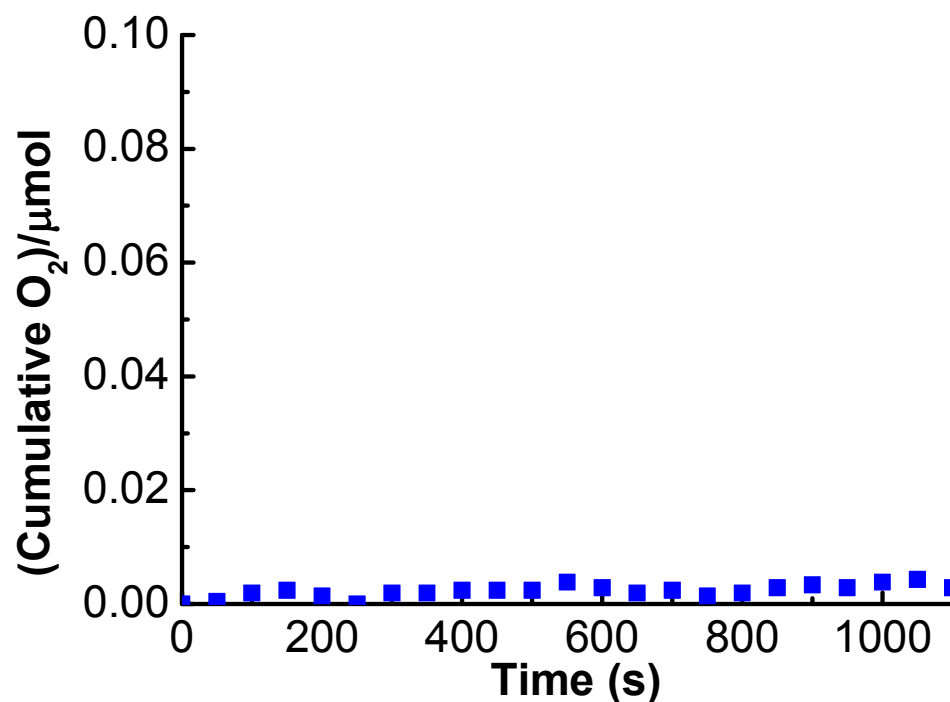


Fig. S15 O₂ evolution of the [Na₂Mn₄] complex (0.1 mM) in the presence of [Ru(bpy)₃]³⁺ (0.3 mM) complex when illuminated with light intensity of 100 mWcm⁻².

References

¹ E. Ashgar, M. Nizam, S. M. Abdel-Latif, *Analytical Lett.*, 2008, **41**, 3074-3087.

² Z. Kilic, N. Gündüz, *Tetrahedron*, 1986, 42, 137-141.

³ SMART, version 5.631, Software Reference Manuals; SAINT, version 6.63, Software Reference Manuals; Bruker AXS GmbH: Karlsruhe, Germany, 2000.

⁴ G. M. Sheldrick, *Software for Empirical Absorption Correction: SADABS*; University of Göttingen, Göttingen, Germany, 2001.

⁵ (a) G. M. Sheldrick, *Program for Crystal Structure Solution: SHELXS-97*, University of Göttingen, Göttingen, Germany, 1997; (b) Sheldrick, G. M. *Program for Crystal Structures Refinement: SHELXL-97*, University of Göttingen, Göttingen, Germany, 1997.

⁶ L. Vesce, R. Riccitelli, *Prog. Photovolt: Res. Appl.* 2012. 20, 960.