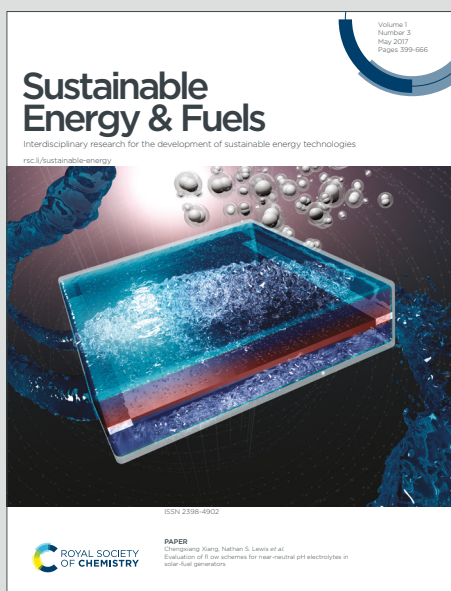


Sustainable Energy & Fuels

Interdisciplinary research for the development of sustainable energy technologies

Accepted Manuscript

This article can be cited before page numbers have been issued, to do this please use: G. Lingamallu, D. N. Narulkar, K. Devulapally, A. K. U, S. N. Dhuri, V. M. Dhavale and A. K. Vardhaman, *Sustainable Energy Fuels*, 2020, DOI: 10.1039/D0SE00232A.



This is an Accepted Manuscript, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this Accepted Manuscript with the edited and formatted Advance Article as soon as it is available.

You can find more information about Accepted Manuscripts in the [Information for Authors](#).

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard [Terms & Conditions](#) and the [Ethical guidelines](#) still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this Accepted Manuscript or any consequences arising from the use of any information it contains.

Journal Name

COMMUNICATION

x/Received 00th January
20xx,

New-fangled Nonheme Manganese (II) Complex for (Electro) Catalytic Oxidation of Water†

 Dattaprasad D. Narulkar,^{†a} Koteswar Devulapally,^{†b, c} Anil Kumar U.,^{†d} Sunder N. Dhuri,^{*a} Vishal M. Dhavale,^{*b, c, d} Anil Kumar Vardhaman,^{*b} Lingamallu Giribabu^{*b, c}

Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

We report a newly designed single-metal-site Mn-complex (**1**) which is synthesized by a simple method, structurally characterized by single-crystal X-ray crystallography and other spectroscopic tools. Electrochemical water oxidation (EcWO) is performed in different physiological pH conditions and found better activity in pH=8 than neutral and acidic pH.

The generation of oxygen through the water oxidation reaction is an energetically uphill reaction; E^0 is 1.23 V. In natural photosystem-II (PS-II), manganese (Mn) based metalloenzymes are considered to be as a good catalyst for oxygen evolution reaction (OER), where Mn_4CaO_5 cluster is an active center for OER and is more efficient in the ambient physiological conditions.¹⁻³ OER in PS-II is solar light-driven process which follows the proton-coupled photo-induced electron transfer pathway. Mimicking the OER of the PS-II is an attractive area of research from the last few decades and also their implementation in electrochemical power sources, catalytic reaction conversions, waste treatments etc.¹⁻⁷ are gaining a lot of attention in the scientific community. Despite many reports on heterogeneous and homogeneous catalysts for an electrochemical OER,⁸⁻¹² the major focus is on homogeneous catalyst system thanks to their easy synthesis with better reproducibility and predictable mechanistic probes; which is very difficult in case of heterogeneous systems. Indubitably, the synthesis of homogeneous catalyst is always depending on the complexity of the structure and need many steps and pre- and post-treatments. Especially in the homogeneous systems

researcher were extensively used d-block metals-based metal-complexes for the OER activity.^{13,14} Among all, the Ru and Ir complexes were showed superior activity, but their low natural abundance restricts their wide-spread usage. In addition, under the potential operating condition, the homogeneous catalyst precipitates and/or forms the metal-oxides which further lead to the confusion of active reaction sites and eventually affect their stability and understanding. Hence, judicious selection of metal with proper ligands to build an effective and robust OER catalyst is a paramount goal of the researchers working in the field of water splitting. In view of this, we have designed a new-fangled, highly water soluble, non-heme, homogeneous penta-dentate ligand based Mn(II) complex catalyst i.e. $[Mn(N3Py2)H_2O](ClO_4)_2$; where, $N3Py2=N,N'$ -dimethyl- N -(2-(methyl(pyridin-2-ylmethyl) amino)-ethyl)- N' -(pyridin-2-ylmethyl) ethane-1,2-diamine (**1**), further the literature reports suggest that the pentadentate ligands when bind to Mn with sixth coordinate (solvent molecule; CH_3CN or H_2O) are much more stable than the tetradentate system, only thing when superoxide or oxo ligand attack on the Mn-center, one nitrogen of pentadentate ligand will un-coordinate to give the six coordinated complex.¹⁵ Towards an application, we have explored the electrochemical OER of complex **1** in phosphate buffer solution of different pH.

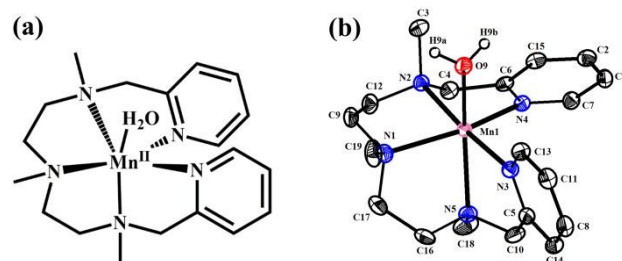


Figure 1. (a) Chemical structure, (b) Single crystal X-ray structure (H atoms and $(ClO_4)_2$ counter ions omitted for the clarity) of the Mn-complex (**1**).

^a School of Chemical Sciences, Goa University, Goa-403206, India.

^b Polymers & Functional Materials Division, CSIR-Indian Institute of Chemical Technology, Uppal Road, Tarnaka, Hyderabad-500 007, India.

^c Academy of Scientific and Innovative Research (AcSIR), Anusandhan Bhawan, 2 Rafi Marg, New Delhi-110001, India.

^d CSIR-Central Electrochemical Research Institute, CSIR Madras Complex, Taramani, Chennai-600 113, India.

E-mail: anil1hnk@gmail.com; vishal.mdhavale@gmail.com; giribabu@iict.res.in; sdhuri@unigoa.ac.in

†These authors contributed equally, Electronic Supplementary Information (ESI) available: [Synthesis procedure, ¹H-NMR, MALDI-TOFs, CCDC 1532120, Electrochemical study parameter details, cyclic voltammetry, etc.]. See DOI: 10.1039/x0xx00000x

Complex **1** was synthesized by modifying earlier reported method.¹⁶ In brevity, $\text{Mn}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ was mixed with N3Py2 ligand in CH_3CN under the stirring and kept for 12 hours under the N_2 atmosphere and subsequent recrystallization afforded pure complex **1** (Scheme S1). Various spectroscopic tools, and single crystal data analysis are performed to confirm the chemical structure of complex **1**, shown in Figure 1. Prior to this, N3Py2 ligand is synthesized and confirmed by $^1\text{H-NMR}$ (Figure S1) and $^{13}\text{C-NMR}$ (Figure S2). The details of NMR-results are discussed in supporting information. Moreover, IR analysis of complex **1** displayed a broad peak at $\nu = 3412 \text{ cm}^{-1}$ which is assigned to the O-H vibration and confirms the presence of water molecule in complex **1** (Figure S3). The UV-Vis spectrum of complex **1** has shown a typical Mn^{II} character; where peaks are observed only in the UV region (Figure S4) due to ligand N3Py2 and no bands are observed in the visible region as $d-d$ transitions are both spin and forbidden in case of high spin Mn^{II} complexes.¹⁷ In Mn^{II} i.e. d^5 case, all the t_{2g} and e_g orbitals are filled with single electron in each i.e. t_{2g}^3 and e_g^2 , as a result, transitions will be spin forbidden and no peak is observed in the visible region (Figure S4).¹⁷ Moreover, the X-band EPR spectrum exhibit an intense six-line hyperfine signal at $g = 2.00$ further revealing the presence of high-spin ($S = 5/2$) Mn^{II} ion in the complex **1** (Figure S5).¹⁸ Furthermore, the ESI-MS of complex **1** in CH_3CN exhibited the two prominent peaks at $m/z = 191.18$ and 481.08 which are assigned to $[\text{Mn}(\text{N3Py2})]^{2+}$ (calc., $m/z = 191.21$) and $[\text{Mn}(\text{N3Py2})(\text{ClO}_4)]^+$ (calc., $m/z = 481.08$) ions, respectively (Figure S6). Complex **1** is reasonably air stable at 25°C which allowed us to isolate pure phase single crystals of **1**. Single-crystal X-ray analysis showed that complex **1** exists in the octahedral geometry with two (ClO_4^-) counter anions; and bond distances of all the Mn-N bonds are found to be very close with average M-N bond distance i.e. 2.28 \AA . The sixth position is occupied by H_2O molecule and Mn-O bond distance is 2.201 \AA (Table S2), which is almost same as Mn-N bond distance. This clearly indicate, the structural and geometrical correctness of complex **1**. The observed bonding characteristics are well matched with the literature report.¹⁸⁻²³ The details of single-crystal analysis are given in Table S1 and S2.

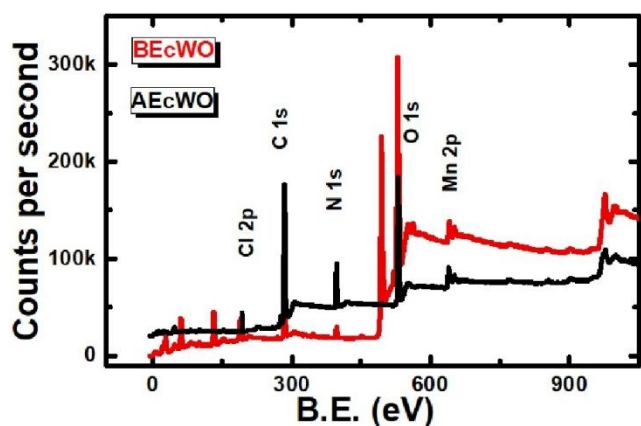


Figure 2. Comparative XPS survey scans of complex **1** recorded BEcWO and AEcWO study.

Furthermore, X-ray photoelectron spectroscopy (XPS) is used to investigate the electronic structure of complex **1**, the survey scans of complex **1** before electrochemical water oxidation (BEcWO) is shown in Figure 2. It is clearly indicating the presence of Mn, Cl, C, O, and N and the respective XPS of the elements are presented in Figure S7a-7e, respectively. Mn 2p spectrum (Figure S7a) displayed the spin-orbit splitting j values as $3/2$ and $1/2$ with specific binding energy difference of 11.6 eV , which support to the oxidation state of Mn present in complex **1** i.e. $+2$. The observed XPS of complex **1** is in well agreement with the predicted single-crystal data. Thus, the formed single-metal-site complex **1** can provide the freedom to understand the behaviour during electrocatalysis.

It is reported, the single-metal-site complexes provide the freedom to establish the mechanistic pathway of the reaction²⁴ hence we tried to explore the prepared complex **1** for EcWO reaction towards the oxygen generation. Complex **1** is a single site moiety which also possesses an open site for the reaction and/or coordinated H_2O molecule can also help for the EcWO. Cyclic voltammetry (CV) experiment is performed for the initial assessment of the complex **1** and later the linear sweep voltammetry (LSV) is recorded to comprehend their OER ability in a phosphate buffer solution. The reason behind investigating the OER activity in a buffer solution is that to realize the mechanism of enzymatic water oxidation reaction at PS-II which also undergoes at physiological pH conditions. Complex **1** formed a homogeneous solution in a phosphate buffer solution, however, it was found that complex **1** is reacting in aq. KOH and precipitating, which could be due to the formation of manganese hydroxide and/or subsequent formation of insoluble metal-oxide. As homogeneous solution becomes a heterogeneous solution on using KOH and lead to confusion in predicting the active site and EcWO mechanism, hence we have selected phosphate buffer in this study.

The CV recorded in a different pH of phosphate buffer solution mainly 5.2, 7, and 8, are shown in Figure S8. The irreversible oxidation peak is observed in the potential range of $1.0\text{-}1.5 \text{ V}$, which corresponds to the oxidation of metal ion to higher oxidation states i.e. $\text{Mn}^{\text{II}}/\text{Mn}^{\text{IV}}$ and the dearth of reversibility could be due to the rapid protonation of higher oxidation state of Mn in an aqueous medium.²⁵ The two irreversible oxidation peaks in the CVs (Figure S8) are slight negatively shifted with increasing pH of the buffer solution. This suggests that proton transfer is coupled with electron transfer in each oxidation process.²⁶ The detailed explanation about the CV is provided in ESI. Furthermore, the OER activity of complex **1** is screened by recording LSV in three different pH buffer solutions, shown in Figure 3a. It can be seen from the LSVs that the complex **1** has slightly better OER activity in a basic phosphate buffer in comparison to the neutral and acidic. The onset potential of complex **1** is found to be **1.8**, **1.68**, and **1.58 V** for the experiment performed in a pH of 5.2, 7 and 8, respectively. The calculated over potentials (η) are in the order of **0.57 V (pH = 5.2) > 0.45 V (pH = 7) > 0.35 V (pH = 8)** for the complex **1**. To make understand clearly, we have constructed the Tafel

graph by plotting $\log(I)$ versus E and Tafel slope is found to be lower in pH of 8 i.e., **330.69 mV/decade**, whereas it is found to be **526.69** and **421.02 mV/decade** in pH of 5.2 and 7, respectively which confirms the complex **1** possesses better OER activity in pH of 8 (**Figure 3b**).

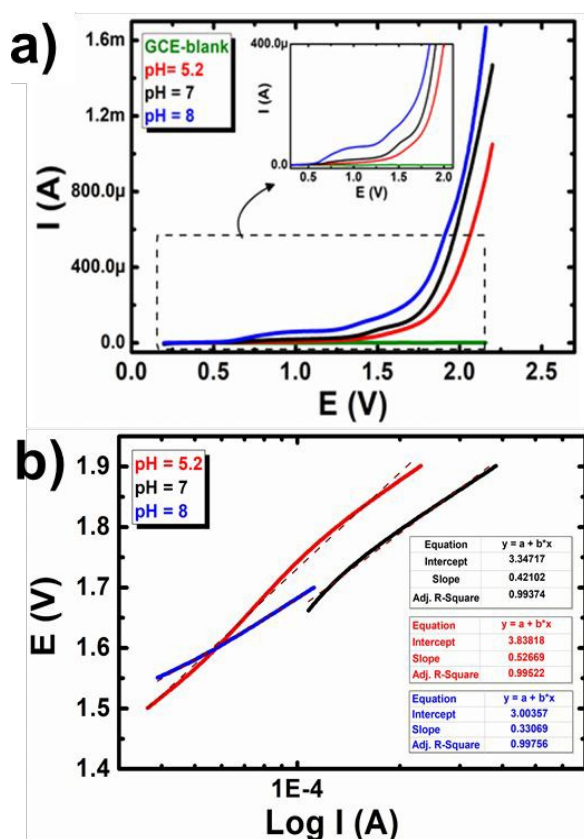


Figure 3. Comparative (a) LSV curves (Condition: Scan rate: 50 mV/s; Rotation: 1600 rpm), and (b) Tafel plots of complex **1** in different pH solution.

The better activity in the basic pH is could be due to the better viability of the catalyst in higher oxidation states and which gives the driving force for the OER activity.^{1,27} The stability of the complex **1** is performed with chronoamperometry test in pH of 5.2, 7, and 8 by applying constant onset potential of 1.8, 1.68, and 1.58 V, respectively for one hour and measured the current output (**Figure S9**). The observed current is 1.0×10^{-6} , 1.88×10^{-6} , and 2.68×10^{-6} A in pH solution of 5.2, 7 and 8, respectively. The observed steady current profile for one hour indicating that the catalyst is stable even under the oxidative etching conditions in the wide range of pH solution. Based on the Faraday law we have quantified the evolved oxygen during the EcWO. The volume of evolved oxygen per hour is found to be in an order of $2.24 \times 10^{-7} \text{ dm}^3$ (pH = 5.2) < $4.21 \times 10^{-7} \text{ dm}^3$ (pH = 7) < $6.0 \times 10^{-7} \text{ dm}^3$ (pH = 8). Moreover, the complex **1** shown better turn-over frequency (TOF) of 0.15 per second in pH of 8 in comparison to in pH 7 (0.083 per second) and 5.2 (0.055 per second) (for more details please see the ESI).

Despite of this, as mentioned above the OER activity is found to be different in different pH electrolyte. It is found to be the

OER LSV-curve of complex **1** recorded after the stability test (i.e. **AECWO**) is matching with LSV recorded before the stability test (i.e. **BECWO**), presented in **Figure S10-S12**. This behavior indicates the robustness of the complex **1** in all the pH buffer solutions. Comparative UV-Vis spectrum of complex **1** recorded **BECWO** and **AECWO** also displayed a similar behavior suggesting the robustness and stability in an all the pH range and applied potential conditions (**Figure S13**). Further, the chemical stability of the complex **1** is also been confirmed by recording the UV-Vis of complex **1** in various pH solution and found that no change in the spectra even after 12 hours (**Figure S14**). The faradaic efficiency (FE) of complex **1** in wide pH range is investigated by using rotating-ring disk electrode (RRDE) study (details are provided in ESI).²⁸ The calculated FE is found to be in order of 83.56 % (pH = 5.2) < 87.21 % (pH = 7) < 92.44 % (pH = 8), at applied disk current of 1 mA/cm^2 , and similar trend is observed for other applied current densities also (**Figure S15**), which certifies the potential of complex **1** as an effective EcWO catalyst.

After the OER experiments, the evolution of O_2 is confirmed by gas chromatography (GC) experiments (**Figure S16a** and **S16b**). The prominent GC-peak at 2.4 minutes corresponds to the blank experiment i.e. **BECWO**. While EcWO, one new GC-peak is observed at ~ 2.3 minutes which is attributed to the evolution of oxygen gas. This is been confirmed with the GC-spectrum recorded with pure oxygen (controlled experiment). Stability of complex **1** is confirmed by thorough analysis. In detail, complex **1** is isolated from the solution **AECWO** and analysed by XPS (**Figure 2** and **S17**) and found that complex **1** is in the same form which suggests that complex **1** is stable even after the EcWO reaction. This observation is also supporting our claim from UV-Vis and electrochemical data.

Based on the experimental data and our understanding we have proposed the mechanism and is emphasized that water oxidation undergoes by stepwise pathways (**Figure S18**). Based on the electrochemical study and previous literature report,^{28,29} the water oxidation may follow the pathway as (**Figure S18**); initial molecule i.e. complex **1**, water as a solvent, the water molecule get coordinate with metal-ion centre and hexa-coordinated complex **1** became the partially hepta-coordinated Mn^{II} complex **2** [$\text{Mn}^{\text{II}}(\text{N3Py2})(\text{H}_2\text{O})$] ($\text{N,N}'$ -dimethyl- N -(2-(methyl(pyridin-2-ylmethyl)amino)ethyl)- N' -(pyridin-2-ylmethyl)ethane-1,2-diamine) (it has five coordination sites from N-atoms) opted as ligand and two water molecules (one water molecule may partially bound) are also bounded with the Mn metal center, this could be concerted, same is already been discussed by Li et. al.²⁹ The complex **2** has total charge of +2. The oxidation of **2** is associated with the release of two protons. After the removal of two H atoms, Mn^{III} complex **3** [$\text{Mn}^{\text{III}}(\text{N3Py2})(\text{OH})_2$]⁺ is generated. In the next step, the complex **4** [$\text{Mn}^{\text{IV}}(\text{N3Py2})\text{O}(\text{OH})$]⁺ was generated and this process also resemble to a proton coupled electron transfer (PCET) which helps to generate the species **4**. Two peaks in the CV data were indirect evidence of formation of both **3** and **4**. Next, short-

lived complex **5** [Mn^V(N3Py2)(O)(O)]⁺ may in-situ generate with the oxidation step and subsequently generate the superoxo moiety i.e. **6**, this step is also seems like a PCET oxidation process. Next, one electron oxidation from the superoxo moiety i.e. **6** generates the intermediate **7**, which subsequently generate **8** by evolution of oxygen and further process may proceed as shown in **Figure S18**.^{29,30} Detailed experimental and theoretical studies are underway in our lab.

In summary, we have designed, synthesized, and characterized penta-dentate based single-metal-site new non-heme Mn(II) complex **1**. Complex **1** is structurally characterized by single crystal X-ray analysis. **EcWO** reaction is investigated for OER and found better activity in a basic phosphate buffer solution in comparison to acidic and neutral. The complete set of electrochemical analysis such as CV, LSV, and stability for **EcWO** has been evaluated in a wide pH range. Based on the results of experimental study, we have suggested water oxidation pathway by complex **1**. Our finding and understanding may be useful to the researcher working in the area of electrochemical water splitting towards the OER and may help to build many more single-metal-site molecular electrocatalyst for future development.

Research support was provided to AKV by Science and Engineering Research Board, India (PDF/2016/001158), and LG DST-SERI. KD, acknowledges Council of Scientific and Industrial Research (CSIR) and Indian Institute of Chemical Technology for Fellowships. VMD acknowledge DST-Inspire Faculty Program (DST/INSPIRE/04/2016/000409) and CSIR-Central Electrochemical Research Institute (CSIR-CECRI) for financial and facility support, respectively. SND thanks CSIR, New Delhi, India for financial assistance (01(2923)/18/EMR-II). We thank Director, CSIR-IICT for his support (IICT/Pubs./2019/435).

References

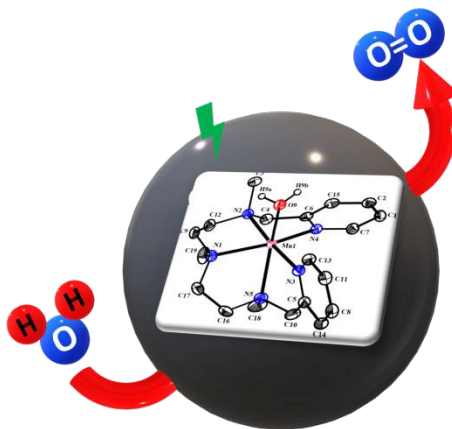
- a) J. Kern et. al., *Nature*, 2018, **563**, 421. b) B. Zhang and L. Sun, *Dalton Trans.*, 2018, **47**, 14381
- a) J. D. Blakemore, R. H. Crabtree, G. W. Brudvig, *Chem. Rev.*, 2015, **115**, 12974. b) A. J. Wu, J. E. Penner-Hahn, V. L. Pecoraro, *Chem. Rev.*, 2004, **104**, 903-938
- J. P. McEvoy, G. W. Brudvig, *Chem. Rev.*, 2006, **106**, 4455-4483; H. Dau, I. Zaharieva, M. Haumann, *Curr. Opin. Chem. Biol.*, 2012, **16**, 3-10.
- Y. Umena, K. Kawakami, J. R. Shen, N. Kamiya, *Nature* 2011, **473**, 55-60.
- K. N. Ferreira, T. M. Iverson, K. Maghlaoui, J. Barber, S. Iwata, *Science* 2004, **303**, 1831-1838.
- B. Loll, J. Kern, W. Saenger, A. Zouni, J. Biesiadka *Nature* 2005, **438**, 1040-1044.
- J. D. Megiatto Jr, A. Antoniuk-Pablant, B. D. Sherman, G. Kodis, M. Gervaldo, T. A. Moore, A. L. Moore, and D. Gust, *Proc. Natl. Acad. Sci. U.S.A.*, 2012, **109**, 15578-15583.
- R. Babu, A. K. Vardhaman, V. M. Dhavale, L. Giribabu, S. P. Singh, *Chem. Commun.*, 2019, **55**, 6779-6782.
- J. V. S. Krishna, N. V. Krishna, S. K. Singh, P. K. Shaw, V. M. Dhavale, A. K. Vardhaman, L. Giribabu, *Euro. J. Inorg. Chem.*, 2018, **14**, 1549-1555.
- S. K. Singh, D. Kumar, V. M. Dhavale, S. Pal, S. Kurungot, *Adv. Mater. Inter.*, 2016, **3**, 1600532.
- S. Mukhopadhyay, J. Debgupta, C. Singh, A. Kar, S. K. Das, *Angew. Chem.*, 2018, **130**, 1936-1941.
- W-T. Lee, S. B. Mucoz, D. A. Dickie, and J. M. Smith, *Angew. Chem.*, 2014, **53**, 9856-9859.
- a) K. J. Young, B. J. Brennan, R. Tagore, G. W. Brudvig, *Acc. Chem. Res.* 2015, **48**, 567-574. b) D. G. H. Hettler, J. N. H. Reek, *Angew. Chem. Int. Ed.* 2012, **51**, 9740 – 9747. c) N. Wang, H. Zheng, W. Zhang, R. Cao, *Chinese J. Catal.*, 2018, **39**, 228-244.
- a) J. P. McEvoy and G. W. Brudvig, *Chem. Rev.*, 2006, **106**, 4455-4483. b) J. D. Blakemore, R. H. Crabtree, and G. W. Brudvig, *Chem. Rev.*, 2015, **115**, 12974-13005.
- D. F. Leto, S. Chattopadhyay, V. W. Day, T. A. Jackson, *Dalton Trans.*, 2013, **42**, 13014-13025.
- D. D. Narulkar, A. K. Srivastava, R. J. Butcher, K. M. Ansy, S. N. Dhuri, *Inorg. Chim. Acta*, 2017, **467**, 405
- S. C. Sawant, X. Wu, J. Cho, K-B. Cho, S. H. Kim, M. S. Seo, Y-M. Lee, M. Kubo, T. Ogura, S. Shaik, W. Nam, *Angew. Chem. Int. Ed.*, 2010, **49**, 8190-8194.
- a) C. Hureau, G. Blondin, M. F. Charlot, C. Philouze, M. Nierlich, M. Cesario, E. Anxolabehere-Mallart, *Inorg. Chem.*, 2005, **44**, 3669. b) B. Hachula, M. Pędras, M. Nowak, J. Kusz, D. Skrzypek, J. Borek & D. Pentak, *J. Coord. Chem.*, 2010, **63**, 67-78
- A. Murphy, G. Dubois, T. D. P. Stack, *J. Am. Chem. Soc.*, 2003, **125**, 5250-5251.
- A. Murphy and T. D. P. Stack, *J. Mol. Catal. A Chem.*, 2006, **251**, 78-88.
- a) J. Chen, Y.-M. Lee, K. M. Davis, X. Wu, M. S. Seo, K.-B. Cho, H. Yoon, Y. J. Park, S. Fukuzumi, Y. N. Pushkar, W. Nam, *J. Am. Chem. Soc.*, 2013, **135**, 6388. b) N. Saravanan, M. Sankaralingam, M. Palaniandavar, *RSC Adv.*, 2014, **4**, 12000-12011.
- N. Saravanan and M. Palaniandavar, *Inorg. Chim. Acta*, 2012, **385**, 100.
- S. Yu, C.-X. Miao, D. Wang, S. Wang, C. Xia and W. Sun, *J. Mol. Catal. A Chem.*, 2012, **353**, 185-191.
- a) J. J. Concepcion, M. -K. Tsai, J. T. Muckerman, T. J. Meyer, *J. Am. Chem. Soc.*, 2010, **132**, 1545-1557. b) M. D. Karkas, Y. -Y. Li, P. E. M. Siegbahn, R. -Z. Liao, B. Akermark, *Inorg. Chem.*, 2018, **57**, 10881-10895. c) D. J. Wasylenko, C. Ganesamoorthy, M. A. Henderson, B. D. Koivisto, H. D. Osthoff, C. P. Berlinguette, *J. Am. Chem. Soc.*, 2010, **132**, 16094-16106.
- I. Garcia-Bosch, A. Company, C. W. Cady, S. Styring, W. R. Browne, X. Ribas, M. Costas, *Angew. Chem. Int. Ed.*, 2011, **50**, 5648-5653.
- a) P. Manna, J. Debgupta, S. Bose, S. K. Das, *Angew. Chem. Int. Ed.*, 2016, **55**, 2425-2430. b) M.-T. Zhang, Z. Chen, P. Kang, T. J. Meyer, *J. Am. Chem. Soc.*, 2013, **135**, 2048-2051.
- B. Lassalle-Kaiser, C. Hureau, D. A. Pantazis, Y. Pushkar, R. Guillot, V. K. Yachandra, J. Yano, F. Neese, E. Anxolabehere-Mallart, *Energy Environ. Sci.*, 2010, **3**, 924-938.
- a) A. T. Swesi, J. Masud, M. Nath, *Energy Environ. Sci.*, 2016, **9**, 1771. b) V. M. Dhavale, S. S. Gaikwad, L. George, R. N. Devi, S. Kurungot, *Nanoscale* 2014, **6**, 13179-13187. c) H. B. Aiyappa, J. Thote, D. B. Shinde, R. Banerjee, S. Kurungot, *Chem. Mater.*, 2016, **28**, 4375-4379.
- Y. -Y. Li, K. Ye, P. E. M. Siegbahn, R. -Z. Liao, *ChemSusChem*, 2017, **10**, 903-911.
- a) P. E. M. Siegbahn, *Inorg. Chem.*, 2000, **39**, 2923-2935. b) T. Privalov, L. Sun, B. Akermark, J. Liu, Y. Gao, M. Wang, *Inorg. Chem.*, 2007, **46**, 7075-7086. c) M. Busch, E. Ahlberg, I. Panas, *Phys. Chem. Chem. Phys.*, 2011, **13**, 15069-15076. d) R. -Z. Liao, M. D. Karkas, B. L. Lee, B. Akermark, P.E.M. Siegbahn, *Inorg. Chem.*, 2015, **54**, 342-351. X. -C. Li, P.E.M. Siegbahn, *Phys. Chem. Chem. Phys.*, 2015, **17**, 12168-12174. e) T. Lee, S. B. Munoz III, D. A. Dickie, J. M. Smith, *Angew. Chem. Int. Ed.*, 2014, **53**, 9856-9859.

Table of contents

Title: New-fangled Nonheme Manganese (II) Complex for (Electro) Catalytic Oxidation of Water

Authors: Dattaprasad N., Koteswar Devulapally, Anilkumar U., S. N. Dhuri,* Vishal M. Dhavale,* Anil Kumar Vardhaman,* Lingamallu Giribabu*

Non-heme single-metal-site Mn-complex catalyst i.e. $[\text{Mn}(\text{N}3\text{Py}2)\text{H}_2\text{O}] (\text{ClO}_4)_2$; where, $\text{N}3\text{Py}2 = \text{N}, \text{N}'\text{-dimethyl-N-(2-(methyl(pyridin-2-ylmethyl) amino)-ethyl)-N}'\text{- (pyridin-2-ylmethyl) ethane-1,2-diamine}$ (**1**) which is displayed good electrochemical water oxidation ability in wide pH range.



Keywords: Oxygen Evolution Reaction, Mn-Complex, Molecular Complex, Water Oxidation, EcWO