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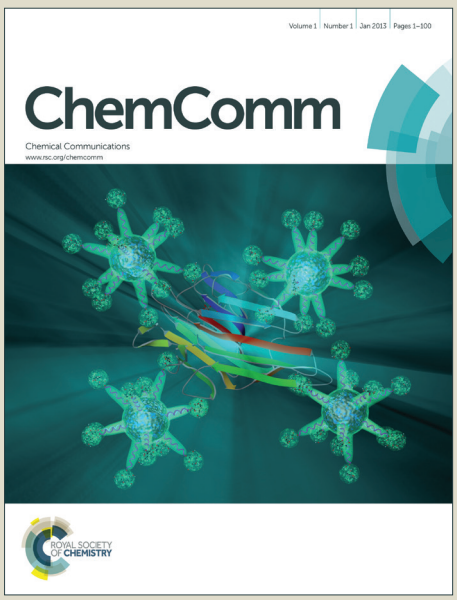

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Pt(II)-Catalyzed Photosynthesis for H_2 Evolution Cycling Between Singly and Triply Reduced Species

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A $PtCl_2$(bpy) derivative tethered to two viologen (MV^{2+}) moieties drives photochemical H_2 evolution via forming a three-electron-reduced species possessing a $bpy^{-\bullet}$–based (or MV^0–based) reducing equivalent. Such species can only form after one electron reduction of both the MV^{2+} sites because of rapid intramolecular electron transfer from $bpy^{-\bullet}$ to MV^{2+}.

Solar-driven water splitting into H_2 and O_2 has been studied intensively to solve the problems arising from global warming and shortage of fossil fuels.[1] In contrast with the great advancement made in the studies of purely inorganic substances,[2] the studies on molecular systems still require substantial advancement in order to meet the criteria required for the practical applications.[3,4] In this context, one of our interests over the past years has been the study of Pt(II)-based molecular H_2-evolving catalysts,[5] including those functionalized with light-harvesting chromophores, which we call 'photo-hydrogen-evolving molecular devices' (**PHEMDs**). The **PHEMDs** can be either photosensitizer-catalyst dyads consisting of a $Ru(bpy)_3^{2+}$-derived chromophore and a Pt(II)-based H_2-evolving catalyst or even simpler mononuclear Pt(II) complexes that possess both of these functionalities.[6] Examples of the latter Pt(II)-only systems include **PV^{2+}** and **$[PtCl_2(5,5'\text{-}MV4)]^{8+}$** depicted in Fig. 1a. These Pt(II)-only single-component photocatalysts evolve H_2 in the presence of a sacrificial electron donor (EDTA; ethylenediaminetetraacetic acid disodium salt) via two consecutive photo-driven electron transfer steps (Z-scheme photosynthesis) leading to the formation of a two-electron-reduced species (**$PHEMD^{2-}$**) which can thermally drive H_2 evolution from water (see Fig. 1b).[7] In these studies, a singly reduced species (**$PHEMD^{-\bullet}$**) is first generated via reductive quenching of the photoexcited state

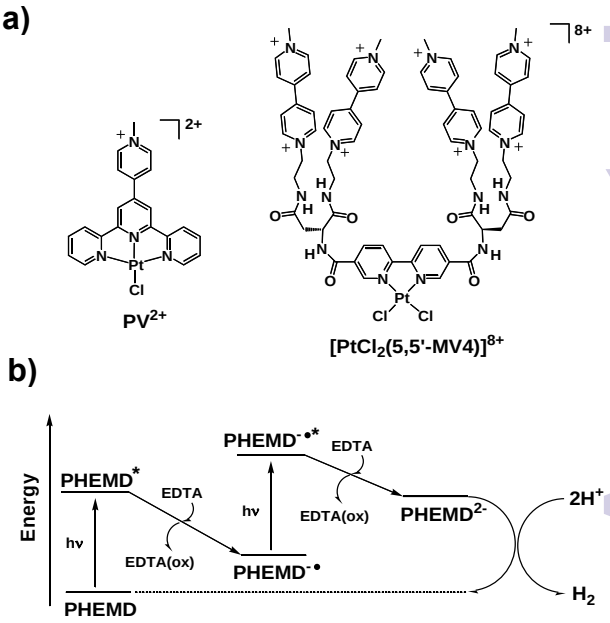

Fig. 1 a) Examples of **PHEMDs.** b) Z-scheme photosynthesis by a **PHEMD**.

(**PHEMD***) by EDTA, followed by photoexcitation of **$PHEMD^{-\bullet}$** leading to a second reduction via the reaction:
$PHEMD^{-\bullet *}$ + EDTA → **$PHEMD^{2-}$** + EDTA(ox), where the asterisked species corresponds to its photoexcited state. An important feature is that the one-electron-reduced species cannot thermally drive H_2 evolution from water.[7a] Thus, H_2 is generated via photochemical activation of the one-electron-reduced species.

Here we report on a new $PtCl_2$(bpy) derivative (bpy = 2,2'-bipyridine) tethered to two pendant viologen units, **$[PtCl_2(bpyMV2)]^{4+}$** in Fig. 2a. This system is found to drive photochemical H_2 evolution only via formation of three-electron-reduced species as illustrated in Figs. 2b,3. Importantly, this molecular system does not consume the initially collected one electron when it photocatalyzes H_2 evolution from water. Thermal paths **HER(1)** and **HER(2)** do not take place, while either path **HER(3)** or **HER(4)** may take place. Thus we will show that a reducing

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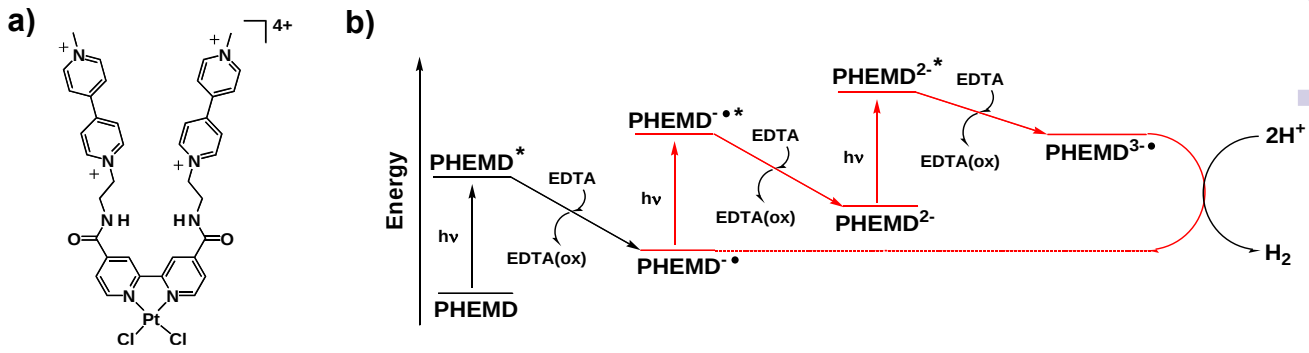

Fig. 2 a) Structure of **[PtCl$_2$(bpyMV2)]$^{4+}$.** b) Photochemical H_2 evolution cycling between singly and triply reduced **[PtCl$_2$(bpyMV2)]$^{4+}$**.

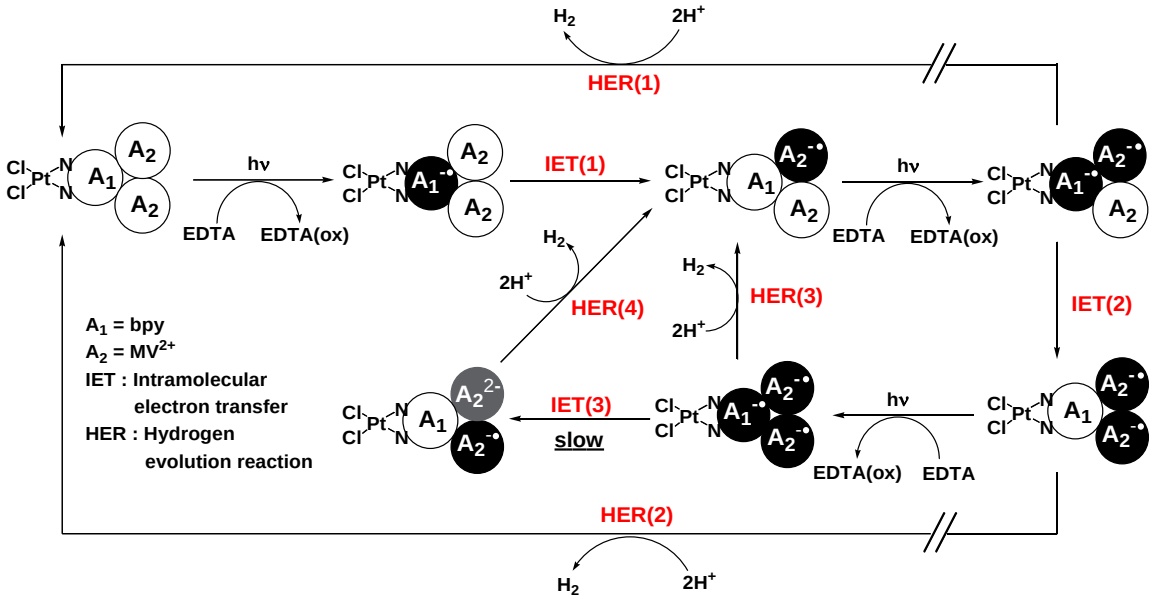

Fig. 3 Reaction model of **[PtCl$_2$(bpyMV2)]$^{4+}$.**

equivalent stored over the bpy ligand is important to drive water reduction to H_2. In other words, the photocatalytic H_2 evolution cycle can be 'switched on' only after filling both the pendant viologen acceptors with a reducing equivalent.

As previously reported for **[PtCl$_2$(5,5'-MV4)]$^{8+}$**,[7b,8] the PtCl$_2$(bpy) chromophore possesses a metal-to-ligand charge transfer (^{1}MLCT) band at 388 nm (Fig. S1), which can be used to generate a triplet excited state (^{3}MLCT state) that can be reductively quenched by a sacrificial electron donor present in solution. **[PtCl$_2$(bpyMV2)]$^{4+}$** does not exhibit emission at room temperature in aqueous solution. However, an emission in the range 500-700 nm is observed for **[PtCl$_2$(bpyMV2)]$^{4+}$** in a methanol/ethanol/N,N-dimethylformamide (MED; 4:4:1) glass at 77 K with the 0-0 and 0-1 vibronic emission peaks respectively centred at 496 and 533 nm with an average lifetime being $\langle\tau\rangle$ = 3.14 μs (see Fig. S3). This long-lived character together with the large Stokes shift (ca. 150 nm) reveals that the emission arises from the triplet.

Electrochemical study reveals that the first and second reductions of **[PtCl$_2$(bpyMV2)]$^{4+}$** occur at -0.80 and -1.20 V vs. Fc/Fc$^+$ (Fig. S4), assignable to the MV^{2+}/MV$^{+\bullet}$ and MV$^{+\bullet}$/MV^0 couples, respectively. These assignments are unambiguous based on the values reported for the series of **PtCl$_2$(bpy)-(MV^{2+})$_n$** (n = 2, 4) dyads.[7b] The third reduction peak is observed at -1.30 V vs. Fc/Fc$^+$ and is assignable to the bpy/bpy$^{-\bullet}$ couple (Fig. S4). These redox properties show that the driving force for the water reduction by a MV$^{+\bullet}$–based reduc[illegible] equivalent is lower than those by the bpy$^{-\bullet}$–and MV^0–based reducing equivalents by 0.5 and 0.4 eV, respectively. This is correlated with our major finding that the bpy$^{-\bullet}$–based (or MV^0–based) reducin[illegible] equivalent must be involved to drive photocatalytic H_2 formatio[illegible] with this system.

Next, we focus on the photo-driven electron storage behaviour of **[PtCl$_2$(bpyMV2)]$^{4+}$** in the presence of EDTA. As previously observe[illegible] for the series of **PtCl$_2$(bpy)-(MV^{2+})$_n$** dyads,[7b] photoirradiation [illegible] **[PtCl$_2$(bpyMV2)]$^{4+}$** results in growth of bands in the visible to nea[illegible] infrared region (Fig. 4a). The broad absorption features appearin[illegible] above 800 nm are characteristic of those derived from the (MV$^+$)$_2$ [illegible] dimer species (i.e., **[PtCl$_2$(bpy)-(MV$^+$)$_2$]$^{2+}$**).[9] The geometrical and electronic structures of **[PtCl$_2$(bpy)-(MV$^+$)$_2$]$^{2+}$** were computed for both closed-shell and open-shell singlet states, in which a clos[illegible] shell singlet state turned out to be a unique solution for this two electron-reduced system. The optimized geometry of **[PtCl$_2$(bpy)-(MV$^+$)$_2$]$^{2+}$** (singlet) has a structure in which two singly reduce[illegible] viologen planes are stacked intramolecularly in a staggered fashion (Fig. S5). Absorption features simulated using the TD-DFT results (Fi[illegible] S10) are somewhat consistent with the observed spectral features. Formation of this (MV$^+$)$_2$ π-dimer species saturates after around 10 min irradiation. The molar absorptivity of the two-electron-reduce[illegible]

species at 353 nm (ε_{353} = 24000 $M^{-1}cm^{-1}$) was independently determined by adding a large excess of $Na_2S_2O_4$ (see Fig. S6). This absorptivity value was used to calibrate the number of electrons stored per molecule, which corresponds to the vertical axis in Fig. 4b. The results reveal that approximately two electrons are stored per molecule under steady-state conditions. Moreover, the two-electron-reduced species generated in the above experiments shows only a minor decay over 1 h and does not exhibit a considerable decay over 15 h when it is left at 20 °C in the dark under Ar (see Fig. S7), indicating that thermal reduction of water by this species ($[PtCl_2(bpy)\text{-}(MV^{+})_2]^{2+}$ + $2H^+$ → $[PtCl_2(bpy)\text{-}(MV^{2+})_2]^{4+}$ + H_2) is not a major path to H_2 evolution. As previously reported,[5c] electrochemically generated non-tethering free $MV^{+\bullet}$ does bleach in the presence of $PtCl_2$(dcbpy) (dcbpy = 4,4'-dicarboxy-2,2'-bipyridine) due to the occurrence of thermal H_2 evolution reaction catalysed by $PtCl_2$(dcbpy) (see Fig. S13). This is correlated with the fact that the redox potential of $(MV^{+})_2$ π-dimer is 0.15 V positive-shifted compared to that of the free $MV^{+\bullet}$ species, as reported ($E_{1/2}((MV^{+})_2/(MV^{2+})_2)$= -0.55 V vs. SCE; $E_{1/2}(MV^{+\bullet}/MV^{2+})$= -0.70 V vs. SCE).[10]

Photochemical H_2 evolution by **$[PtCl_2(bpyMV2)]^{4+}$** in the presence of EDTA is shown in Fig. 5a. The turnover number (TON) reaches 18 after 24-h irradiation. Importantly, the H_2 evolution ra… remains nearly constant within 24 h, showing that this molecula… photocatalyst is relatively stable. Note that viologen tethers ar… essential to enhance the H_2-evolving activity of such $PtCl_2$(bpy)… derivatives, since photoirradiation of $PtCl_2$(dcbpy) and EDTA does not lead to H_2 evolution.[7b] In situ dynamic light scattering (DL… measurements were also carried out to check for colloidal platinur… formation. The light scattering intensity during the photocatalys… using **$[PtCl_2(bpyMV2)]^{4+}$** at first increases due to dispersion of unidentified particles (Fig. S8 red). However, upon exposure of th… resultant solution to air, the light scattering intensity abruptly decreases and the initial blank level of scattering intensity can be recovered (see Fig. S8 blue). Therefore, the observed dispersio… during the photolysis must be caused by partial precipitation of som… reduced forms of **$[PtCl_2(bpyMV2)]^{4+}$** that have lower solubility i… aqueous media. Precipitation of such reduced species has often been observed in our previous studies.[6i] These observations clearly ru… out colloidal platinum formation under our photolysis conditions.

Importantly, we observe quite clear ON-OFF behaviour fo… H_2 generation upon turning ON and OFF the light irradiation (see Fig. 5b). As discussed above for Fig. 4, the major chemical species in solu…

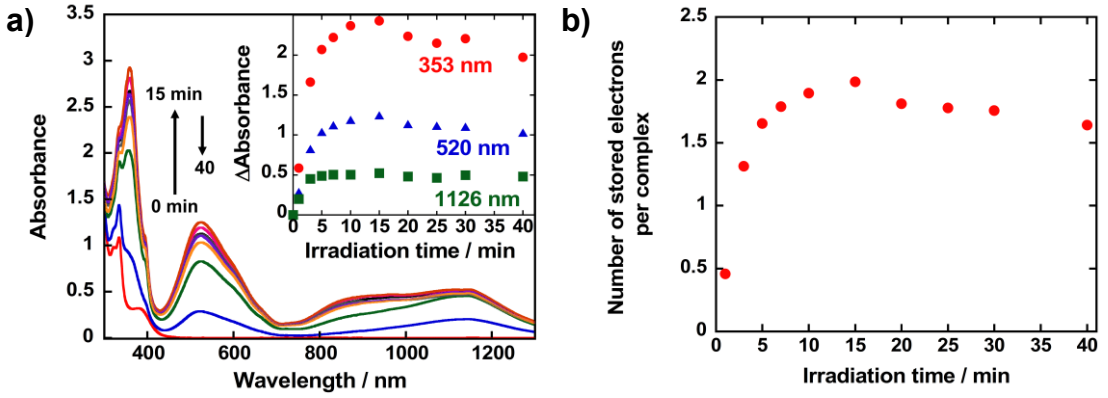

Fig. 4 a) Spectral changes during the photolysis of an aqueous acetate buffer solution (pH 5.0; at 20 °C under Ar) containing 0.1 mM **$[PtCl_2(bpyMV2)]^{4+}$**, 0.1 M NaCl, and 30 mM EDTA. Inset: Absorbance changes at 353 nm (red), 520 nm (blue), and 1126 nm (green) during photolysis. b) Changes in the total number of electrons stored over **$[PtCl_2(bpyMV2)]^{4+}$** during photolysis shown in Fig. 4a.

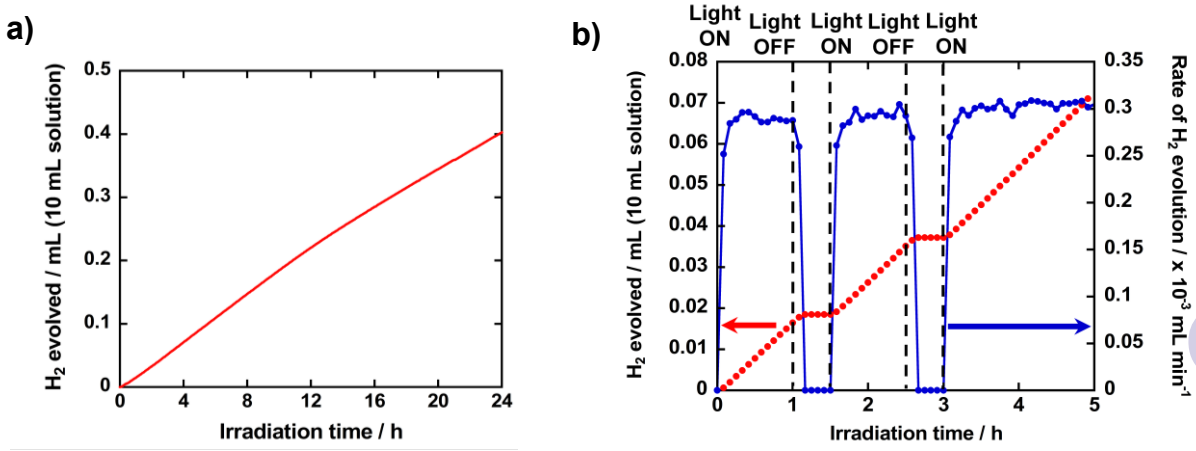

Fig. 5 a) Photochemical H_2 production from an aqueous acetate buffer solution (pH 5.0, 10 mL; at 20 °C under Ar) containing 0.1 mM **$[PtCl_2(bpyMV2)]^{4+}$**, 0.1 M NaCl, and 30 mM EDTA. b) Photoresponse of H_2 production. Red and blue dots correspond to the amount of H_2 evolved and the rate of H_2 evolution, respectively, where experimental conditions are the same as those in Fig. 5a.

is a two-electron-reduced species at each light-off time shown in Fig. 5b, which re-confirms that thermal reduction of water by **$[PtCl_2(bpy)\text{-}(MV^{+})_2]^{2+}$** does not proceed under these conditions. As a result, we can conclude that the observed H_2 evolution results from the photoexcitation of the two-electron-reduced species. This has a similarity to the H_2 evolution via two consecutive photo-driven electron transfer steps discovered for **PV^{2+}** in which photoexcitation of **$PV^{+\bullet}$** is essential to generate the doubly reduced species (**PV^{0}**) which thermally reduces water to H_2.[7a] With **$[PtCl_2(bpyMV2)]^{4+}$**, photoexcitation of the two-electron-reduced species obviously plays a major role in generating species that drives thermal H_2 evolution from water. We now assume that **HER(3)** predominates **HER(4)** because of the slower nature of **IET(3)** (lower driving force for this IET; ΔG_{IET} = -0.1 eV; see Fig. S4) as well as the lower driving force for the H_2 evolution via **HER(4)**. The initial minor decay of reduced species seen in Fig. S7b might correspond to the occurrence of **HER(4)**. Nevertheless, the more detailed studies are needed to further clarify this observation.

Our above results indicate that **$[PtCl_2(bpyMV2)]^{4+}$** is a unique system which can only drive H_2 evolution via formation of three-electron-reduced species which include a $bpy^{-\bullet}$–based (or MV^{0}–based) reducing equivalent, as illustrated with path **HER(3)** (or **HER(4)**). Possibly, this is due to the close location of MV^{2+} with regard to the bpy moiety, which enables rapid intramolecular electron transfer from $bpy^{-\bullet}$ to one of the adjacent MV^{2+} units, if there is any un-reduced MV^{2+} site. In other words, the **IET(2)** step in Fig. 3 is much faster than the competing H_2 evolution path **HER(1)**. On the contrary, we assume that the **$[PtCl_2(5,5'\text{-}MV4)]^{8+}$** family can adopt the thermal path **HER(1)** since they can photocatalyze H_2 evolution while a portion of the multiple MV^{2+} sites remain un-reduced, presumably due to the slower nature of both the **IET(1)** and **IET(2)** steps.[7b] As a result, we conclude that all the MV^{2+} sites in **$[PtCl_2(bpyMV2)]^{4+}$** must be reduced in order to generate a $bpy^{-\bullet}$ (or MV^{0}) site required to drive the H_2 evolution process.

Finally we note that the quantum yield of H_2 formation is relatively low for the present system ($\Phi(0.5H_2)$ = 0.02%; Figs. S11,12). This is likely due to quenching of the $PtCl_2$(bpy)-based ^{3}MLCT state by the $(MV^{+})_2$ π-dimer moiety in close proximity, as demonstrated by the complete quenching of emission from **$[PtCl_2(bpy)\text{-}(MV^{+})_2]^{2+}$** in a frozen media at 77 K (Fig. S14). Extended studies are still ongoing in our laboratory.

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Notes and references

1. A. J. Esswein and D. G. Nocera, *Chem. Rev.*, 2007, **107**, 4022.
2. (a) A. Kudo and Y. Miseki, *Chem. Soc. Rev.*, 2009, **38**, 253; (b) K. Sayama, K. Mukasa, R. Abe, Y. Abe and H. Arakawa, *Chem. Commun.*, 2001, 2416; (c) K. Maeda, K. Teramura, D. Lu, T. Takata, N. Saito, Y. Inoue and K. Domen, *Nature*, 2006, **440**, 295.
3. (a) M. Wang, L. Chen and L. Sun, *Energy Environ. Sci.*, 2012, **5**, 6763; (b) Z. Han, W. R. McNamara, M.-S. Eum, P. L. Holland and R. Eisenberg, *Angew. Chem. Int. Ed.*, 2012, **51**, 1667; (c) B. Mat J. Fize, J. Moussa, H. Amouri, A. Pereira, V. Artero, G. Izzet and A. Proust, *Energy Environ. Sci.*, 2013, **6**, 1504; (d) S. Losse, J. G. Vos and S. Rau, *Coord. Chem. Rev.*, 2010, **254**, 2492; (e) H. L W. Guo, K. Wu, Z. Chen, J. Bacsa, D. G. Musaev, Y. V. Geletii, S M. Lauinger, T. Lian and C. L. Hill, *J. Am. Chem. Soc.*, 2014, **13** 14015; (f) T. Stoll, M. Gennari, J. Fortage, C. E. Castillo, M Rebarz, M. Sliwa, O. Poizat, F. Odobel, A. Deronzier and M.-N Collomb, *Angew. Chem. Int. Ed.*, 2014, **53**, 1654.
4. (a) L. Duan, F. Bozoglian, S. Mandal, B. Stewart, T. Privalov, A. Llobet and L. Sun, *Nat. Chem.*, 2012, **4**, 418; (b) D. J. Wasylenko R. D. Palmer and C. P. Berlinguette, *Chem. Commun.*, 2013, **4** 218; (c) J. J. Concepcion, D. K. Zhong, D. J. Szalda, J. T Muckerman and E. Fujita, *Chem. Commun.*, 2015, **51**, 4105; (d) J. J. Concepcion, M.-K. Tsai, J. T. Muckerman and T. J. Meyer, *J. Am. Chem. Soc.*, 2010, **132**, 1545; (e) L. Kohler, N. Kaveevivitchai, R. Zong and R. P. Thummel, *Inorg. Chem.*, 2 **53**, 912; (f) L. Wang, M. Mirmohades, A. Brown, L. Duan, F Li, O Daniel, R. Lomoth, L. Sun and L. Hammarström, *Inorg. Che*, 2015, **54**, 2742.
5. (a) H. Ozawa, Y. Yokoyama, M. Haga and K. Sakai, *Dalton Tra* 2007, 1197; (b) K. Sakai and H. Ozawa, *Coord. Chem. Rev.*, 200 **251**, 2753. (c) K. Yamauchi, S. Masaoka and K. Sakai, *J. Am. Chem. Soc.*, 2009, **131**, 8404.
6. (a) H. Ozawa, M. Haga and K. Sakai, *J. Am. Chem. Soc.*, 2006, **128**, 4926; (b) S. Masaoka, Y. Mukawa and K. Sakai, *Dal Trans.*, 2010, **39**, 5868; (c) H. Ozawa, M. Kobayashi, B. Balan, S Masaoka and K. Sakai, *Chem. Asian J.*, 2010, **5**, 1860; (d) M Hirahara, S. Masaoka and K. Sakai, *Dalton Trans.*, 2011, **40**, 3967; (e) H. Ozawa and K. Sakai, *Chem. Commun.*, 2011, **4** 2227; (f) G. Ajayakumar, M. Kobayashi, B. Balan, S. Masaoka and K. Sakai, *Dalton Trans.*, 2011, **40**, 3955; (g) C. V. Sunees B. Balan, H. Ozawa, Y. Nakamura, T. Katayama, M. Muramatsu Y. Nagasawa, H. Miyasaka and K. Sakai, *Phys. Chem. Chem Phys.*, 2014, **16**, 1607; (h) R. Okazaki, S. Masaoka and K. Saka *Dalton Trans.*, 2009, 6127; (i) K. Yamauchi and K. Sakai, *Dalton Trans.*, 2015, **44**, 8685.
7. (a) M. Kobayashi, S. Masaoka and K. Sakai, *Angew. Chem. Int. Ed.*, 2012, **51**, 7431; (b) K. Kitamoto and K. Sakai, *Angew. Chem. Int. Ed.*, 2014, **53**, 4618.
8. M. Ogawa, G. Ajayakumar, S. Masaoka, H.-B. Kraatz and K Sakai, *Chem. Eur. J.*, 2011, **17**, 1148.
9. C. Lee, Y. M. Lee, M. S. Moon, S. H. Park, J. W. Park, K. G. Kim and S.-J. Jeon, *J. Electroanal. Chem.*, 1996, **416**, 139.
10. W. S. Jeon, H.-J. Kim, C. Lee and K. Kim, *Chem. Commun.*, 200 1828.