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.

ChemComm

COMMUNICATION

ChemComm Accepted Manuscript

Photochemical hydrogen production from water catalyzed by CdTe quantum dots/molecular cobalt catalyst hybrid systems†

Kai Han,[a] Mei Wang,*[a] Shuai Zhang,[a] Suli Wu,[a] Yong Yang[a] and Licheng Sun[ab]

A hybrid system with a coordinative interaction between a cobalt complex of a N_2S_2-tetradentate ligand and CdTe quantum dots displayed a high activity (initial TOF 850 h^{-1}) and improved stability (TON 1.44×10^4 based on catalyst over 30 h) for the photochemical H_2 generation from water, with a quantum efficiency of 5.32% at 400 nm.

Direct conversion of solar energy into chemical fuels such as hydrogen by photoinduced water splitting is one of the promising solutions to meet globally ever-increasing energy demands. The key issue for approaching this target is to develop highly efficient, robust, and cheap photocatalytic systems. Many non-noble metal-based homogeneous catalytic systems for photochemical hydrogen generation have been reported over the past decade.[1] In the reported homogeneous photocatalytic systems, molecular catalysts are usually combined with organic dyes and noble metal-containing organometallic photosensitizers, and function in organic solutions or mixtures of organic solvents and water. Only a few systems comprising molecular catalysts and photosensitizers were active for the photochemical H_2 generation in fully aqueous solutions. One of the vital problems of these systems is the low stability for H_2 generation (generally no longer than 15 h) in aqueous solutions, in most cases, due to decomposition of organic and organometallic chromophores.

Compared with molecular chromophores, semiconductor quantum dots (QDs) with good photostability and broad absorption spectral range in the solar spectrum are more promising light harvesting alternatives for building highly efficient and durable photocatalytic systems that are capable of working in water. Photocatalytic hybrid systems built with semiconductor nanoparticles, such as CdX (X = S, Se, Te),[2–6] ZnS,[7,8] and CdSe/ZnS,[9] as light-harvesting materials and with non-noble metal complexes as molecular catalysts were successively reported in recent years.[10] The most active and robust photocatalytic system ever reported is an in situ generated Ni^{2+}-DHLA (DHLA = dihydrolipoic acid)/CdSe hybrid, which achieves 6×10^5 TON of H_2 evolution from water over 110 h of irradiation and the quantum efficiency is over 36%.[4]

Two successful examples for construction of photocatalytic H_2-generation hybrid assemblies by sulphur-coordination of $Fe_2S_2(CO)_6$ to the surface of semiconducting particles, such as InP nanocrystals

and CdSe QDs, were reported in the literatures.[5,11] Very recently, a (bme-dach)Fe(NO) unit has been used as a metallodithiolate ligand in the construction of a proton reduction electrocatalyst.[12] Inspired by the work that adopted [(bme-dach)M(NO)] (M = Fe, Co; H_2bme-dach = N,N'-bis(2-mercaptoethyl)-1,4-diazacycloheptane) complexes as metallodithiolate ligands to various metal centers,[13–15] we envisaged that such complexes bearing a N_2S_2 ligand could be coordinately anchored to the Cd^{2+}-rich surface of CdTe QDs. We chose [(bme-dach)Co(NO)] (**1**, Fig. 1) as catalyst because it has the bidentate sulfur-donor property, good stability and proper reduction potential ($E_{1/2} = -1.08$ V $vs.$ NHE). The CdTe/**1** hybrid assembly with a coordinative interaction between the cobalt complex and QDs was studied for visible light-driven H_2 production in water, which exhibited a TON of 1.44×10^4 mol H_2 per mol catalyst over a period of 30 h and a quantum efficiency of 5.32% at 400 nm. In contrast to the mononuclear catalyst **1**, the analogous dimeric complex [(bme-dach)Co]$_2$ (**2**) that did not show attractive interaction with CdTe QDs displayed the maximum TON of 4990, with a quantum efficiency of 1.49%. The activity and stability of CdTe/**1** hybrid system are among the best results reported to date for the photochemical H_2 evolution from water catalyzed by non-noble metal-based molecular catalysts.
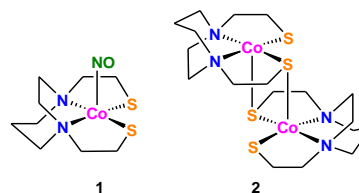

Fig. 1 Structures of molecular cobalt complexes used as catalysts in the present work.

Complexes **1** and **2** were prepared according to the literature procedures.[14,15] The water-soluble thioglycolic acid-stabilized (TGA) CdTe QDs were prepared using a protocol in the literature.[16] The QDs with a desired absorption spectrum were obtained by controlling the reaction time (Fig. S1). On the basis of the equations reported by Peng and coworkers,[17] the diameter (D) and extinction coefficient (ε) of the prepared TGA-CdTe QDs with λ_{max} at 515 nm were calculated to be ~2.7 nm and 8.4×10^5 L mol^{-1} cm^{-1} (see the Supporting Information).
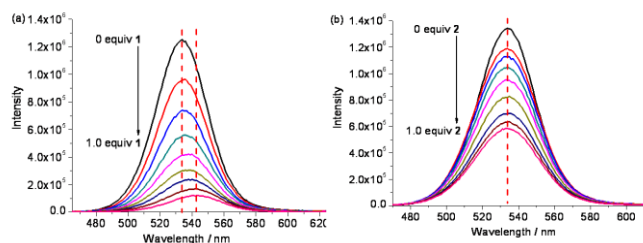
Fig. 2 Fluorescence quenching of the CdTe QDs (5×10^{-5} M) in water at pH 5.5 with titration of (a) **1** and (b) **2** (0–1.0 equiv.).

The interaction of **1** with CdTe QDs was first explored by photoluminescence spectroscopy in aqueous solutions at pH 5.5, which is the medium identical with that used for photocatalytic reactions. The as-prepared CdTe QDs showed an emission band at $\lambda_{max} = 534$ nm with a half band width of 38 nm (Fig. 2). The fluorescence of CdTe QDs was quenched by 91% when 1.0 equiv. (relative to QDs) of **1** was titrated to the aqueous solution of CdTe QDs. Noticeably, the emission band of CdTe QDs was shifted to lower energy by about 10 nm upon titration of **1** (Fig. 2a). In contrast, such a shift of the emission band was not observed upon titration of 1.0 equiv. of **2** to the CdTe solution (Fig. 2b), which only led to the quenching of fluorescence of CdTe QDs by about 56%. These luminescence spectroscopic observations provide evidence for the coordinative anchoring of the mononuclear catalyst **1** to the Cd^{2+}-rich surface of CdTe QDs, while there is no apparent interaction between the dimeric complex **2** and QDs.

The fluorescence spectroscopic data were treated with two models: a Stern-Volmer model with an equation of $I_0/I = 1 + K_{SV}[Q]$, which is suitable for pure dynamic quenching in a homogeneous solution, and a Langmuir adsorption isotherm model with an equation of $\theta = \Delta I/I_0 = ((\Delta I/I_0)_{max} K_L[Q])/(1 + K_L[Q])$ (where θ is the fraction of surface site occupied by the quencher; see the Supporting Information), which is suitable for static quenching caused by single layer adsorption of molecules to the surface of fluorophore particles.[18] As expected, the quenching data obtained from Fig. 2a do not fit the Stern-Volmer equation and the plot of I_0/I versus [**1**] has an apparently upward curvature (Inset in Fig. 3a), while the $I_0/\Delta I$ values show good linear correlation with 1/[**1**] (Fig. 3a). These observations strongly support a static quenching of QDs emission by **1**, at least partially, due to the coordinative anchoring of the complex to the surface of CdTe QDs in the ground state, with the calculated association constant (K_L) of 5.92×10^4 M^{-1}. In contrast, the quenching data obtained from Fig. 2b for the dimeric complex **2** fit well with the Stern-Volmer equation (Fig. 3b), while the plot of $I_0/\Delta I$ versus 1/[**2**] displays a downward curvature (Inset in Fig. 3b), indicating a dominant collisional quenching of QDs emission by **2**, with a dynamic quenching constant (K_{SV}) of 3.24×10^4 M^{-1}.
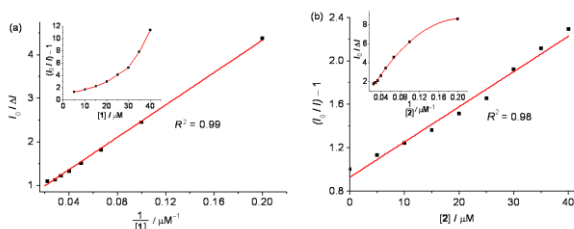

Fig. 3 (a) A Langmuir adsorption isotherm fitting plot with **1** as a quencher (Inset: a Stern-Volmer fitting plot with **1** as a quencher) and (b) a Stern-Volmer fitting plot with **2** as a quencher (Inset: a Langmuir adsorption isotherm fitting plot with **2** as a quencher).

The Förster energy transfer from the excited CdTe QDs to the cobalt catalysts can be ignored because there is no spectroscopic overlap between the absorption of catalyst and the emission of CdTe QDs (Fig. S2). The fluorescence quenching of CdTe by the cobalt complexes is attributed to the electron transfer from QDs to complex. The reduction potentials (E_{red}) of **1** and **2** are −1.08 V and about −0.85 V $vs.$ NHE (Fig. S3),[17] respectively. The excited-state energy (E_{00}) of CdTe QDs calculated from the edge of its absorption at λ_{max} = 515 nm in a pH 5.5 aqueous solution is 2.40 eV and the valence band energy level (E_{vb}) reported for CdTe QDs is 0.09 eV.[19] According to these thermodynamic data, the free-energy changes (ΔG^o) for the electron transfer from the conductive band of CdTe QDs to the cobalt catalyst are estimated to be ca. −1.23 eV for **1** (Fig. 4) and −1.46 eV for **2**, indicating that there is a large driving force for the desired photoinduced electron transfer. Although the thermodynamically estimated driving force for electron transfer from the conductive band of CdTe to **1** is smaller than that calculated for electron transfer to **2**, the addition of **1** resulted in a considerably larger quenching of CdTe emission compared to that caused by **2**, most possibly resulting from the coordinative effect of **1** to the surface of CdTe QDs in aqueous solutions. We assume that when **1** is reduced one of the coordinate amines or thiolates may dissociate as proposed for other 18-e^- non-noble metal molecular catalysts[20] and the further reduction of [**1**]$^-$ could render the cobalt centre basic enough to form a cobalt-hydride species, which catalyzes H_2 generation. Further experimental and computational studies are needed to give a detailed elaboration on the mechanism of the photocatalytic H_2 generation by the CdTe QDs/(bme-dach)Co(NO) hybrid system.
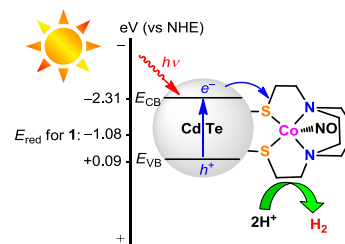

Fig. 4 Schematic electron level diagram for the proposed CdTe/**1** hybrid assembly.

To further confirm the chemically anchoring of **1** on the surface of CdTe QDs, the fine particles were isolated by centrifugation after the aqueous solution of CdTe QDs and **1** was vigorously stirred for 5 h. The inductively coupled plasma-mass spectroscopic (ICP-MS) analysis showed that the amount of **1** grafted on the surface of CdTe QDs was ~0.45% (w/w) in the isolated CdTe/**1** hybrid assembly, whereas only negligible amount of **2** was adsorbed to the CdTe QDs that were isolated from the same procedure as afore-mentioned but with **2** as catalyst. The UV-vis spectrum of CdTe QDs in aqueous solution showed the first exciton (1s) peak at 515 nm (Fig. S4). The CdTe/**1** assembly displayed an essentially identical UV-vis spectrum with CdTe QDs except for a small red-shift of the absorption bands due to the anchoring of the molecules of **1** to the surface of CdTe QDs. More sensitive to coordinative binding of **1** to the surface of QDs is the ν(NO) stretching absorption. The isolated CdTe/**1** assembly displayed a ν(NO) absorption at 1616 cm^{-1} (KBr disk), which is blue shifted by 22 cm^{-1} compared to that of the free cobalt complex **1** (ν(NO) = 1594 cm^{-1}, Fig. S5; ν(NO) = 1600 cm^{-1} in ref. [14]). Similar blue shift (35−48 cm^{-1}) of the ν(NO) band was observed when **1** serves as a bidentate metalloligand via the cis-dithiolato sulfurs to coordinate to the metal centre of W(CO)$_4$ unit.[15]

The catalytic property of **1** for H_2 generation was studied with TGA-CdTe QDs as photosensitizer and ascorbate (HA^-) as sacrificial electron donor in water under illumination ($\lambda > 400$ nm). The amount of H_2 evolved from the catalytic system was determined by GC analysis and the H_2 dissolved in the solution was neglected. Condition experiments showed that the pH value of the aqueous solution has an apparent influence on the performance of the CdTe/**1**/H_2A system for photocatalytic H_2 production, similar to previously reported non-noble metal complex-based photocatalytic systems.[1] As shown in Fig. S6, the maximal rate of H_2 generation was observed at pH 5.5. Increase of pH value to 6.5 or decrease of it to 4.5 caused an apparent drop in the H_2-evolving activity. This pH-dependent effect is related to several factors, particularly the concentrations of proton and electron donor HA^-, the change in the H^+/H_2 reduction potential of catalyst, and the stability of TGA-CdTe QDs. At higher pH, for example, the decrease in the rate of H_2 generation is likely a result of low proton concentration and unfavorable protonation of the catalyst, whereas at a lower pH value, the TGA-protecting group would dissociate from the surface of CdTe QDs, causing aggregation and precipitation of QDs.[21] Additionally, an enhancement of H_2 production was observed when the concentration of H_2A was increased from 0.06 to 0.28 M (Fig. S7).
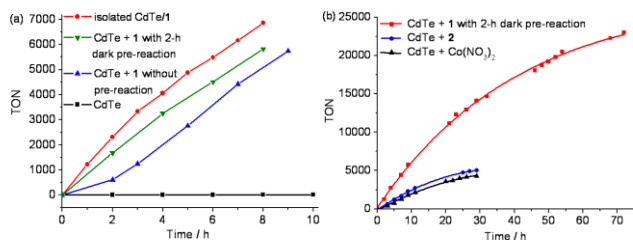

Fig. 5 (a) Photocatalytic H_2 evolution from the isolated CdTe/**1** assembly (CdTe, 2.23×10^{-4} M; **1**, 1.81×10^{-6} M) and from the in situ generated CdTe/**1** hybrid system (CdTe, 2.0×10^{-4} M; **1**, 2.0×10^{-6} M); (b) A comparison of photocatalytic H_2 evolution by the hybrid systems of CdTe (1.0×10^{-4} M) in combination with **1**, **2**, or Co(NO_3)$_2$ (catalyst, 1.0×10^{-6} M); The reactions were carried out in 0.28 M H_2A aqueous solutions at pH 5.5 in illumination using a Xe lamp (300 W) with a cutoff filter ($\lambda > 400$ nm).

As shown in Fig. 5a as well as in Figs. S6a and S7, there existed an apparent inducing period of about 2 h for H_2 evolution when xenon lamp was switched on immediately after CdTe QDs and **1** were separately added to the aqueous solution containing ascorbic acid, while such an inducing period was not observed if irradiation started after the mixture of CdTe QDs and **1** in water was vigorously stirred in the dark for 2 h. The TON (5230 based on the cobalt catalyst) of H_2 evolution from the system in the latter case is higher than the TON (4580) obtained from the one in the former case under otherwise identical conditions over 8 h of illumination. When the isolated CdTe/**1** assembly was used, a TON of 6200 was obtained. The inducing period for H_2 evolution is possibly caused by the time needed for anchoring the cobalt catalyst to the surface of QDs and for reaching the association/dissociation equilibrium. Therefore the following photocatalytic reactions using an in situ generated CdTe/**1** system were all illuminated after 2-h dark pre-reaction of CdTe QDs and **1** in aqueous solution. The considerably higher initial H_2-evolving rate of the isolated CdTe/**1** assembly than the in situ added CdTe and **1** implicates that the coordinative interaction of the molecular cobalt catalyst with QDs could expedite the H_2-generation reaction, although the H_2 generation catalyzed by the free CdTe QDs and **1** cannot be ruled out. Control experiments were run under optimal conditions and showed that no H_2 was detected by GC

analysis if the CdTe/**1**/H_2A system was stirred in the dark and if QDs or H_2A was absent in the catalytic system; only trace of H_2 was evolved if the cobalt catalyst was absent in the catalytic system.

To explore the stability of the hybrid system, photocatalytic reactions were carried out with the in situ generated CdTe/**1** assembly under long-time illumination (Fig. 5b). The CdTe/**1** system exhibited the TON of H_2 evolution up to 1.44×10^4 based on catalyst over 30 h of illumination. The rate of H_2 evolution gradually slowed down, but the system still remained active after 70 h of illumination, giving a TON of 2.3×10^4. In contrast to the mononuclear cobalt complex **1**, much lower H_2-generation activity and shorter durability were observed when the dimeric cobalt complex **2** was used as catalyst under otherwise identical conditions. The H_2 evolution from the CdTe/**2** system levelled off after about 30 h of illumination, giving a total TON of 4990 based on **2**. The quantum efficiency of CdTe/**1** is 5.32% at 400 nm over a 5-h photocatalytic reaction, while the CdTe/**2** system displayed a quantum efficiency of 1.49%. The lower TON and quantum efficiency of the CdTe/**2** system is attributed, at least partly, to the fact that **2** has no coordinative interaction with CdTe as shown by the fluorescence spectra and ICP analysis. In comparison, the recently reported CdSe/[$Fe_2S_2(CO)_6$] hybrid assembly, formed by the coordination of two sulfur atoms of [$Fe_2S_2(CO)_6$] to the surface of CdSe QDs, displayed the TON of H_2 evolution up to 8781 based on catalyst in 0.085 M H_2A aqueous solutions at pH 4.0 in illumination with a LED lamp (410 nm) over 82 h.[5] The TONs of other self-assembled hybrid assemblies, ZnS/[(μ-SPh-4-NH_2)$_2Fe_2(CO)_6$] and CdS/[Co(dmgH)$_2$(Rpy)Cl] (R = H, 2-SH, 4-NMe_2, dmgH = dimethylglyoximate),[3,7] were reported to be 2607 in a H_2A DMF/H_2O (9:1, v/v) solution over 38 h of illumination (Xe lamp without cutoff filter) and 171 in a TEOA CH_3CN/H_2O (9:1, v/v) solution over 17 h of illumination ($\lambda > 420$ nm). The CdSe/ZnS core/shell QDs-cobalt(III) bisglyoxime catalyst hybrid assembly linked by phosphate bonds displayed a TON higher than 150 based on the cobaloxime catalyst in the presence of TEOA and [Et_3NH]Cl in toluene over 10 h of irradiation ($\lambda > 400$ nm).[9] The comparison (Table S1) shows that the activity and stability of CdTe/**1** hybrid assembly is among the best hybrid systems comprising QDs and non-noble metal-based molecular catalysts for photocatalytic H_2 generation.

Fig. 5b shows that the activity of the CdTe/**1** decreases from ~850 mol H_2 per mol catalyst in the first hour to ~190 mol H_2 per mol catalyst in the last hour of illumination for a period of 70 h. To figure out the possible reason for the decrease of the H_2-evolving activity during long-time illumination, the following problems drew our attention: (i) whether the aggregation of CdTe QDs occurred in the system and (ii) if the cobalt complex was decomposed or reduced to cobalt colloids. TEM images (Fig. S8) obtained before and after the photocatalytic reaction show that the size of QDs significantly increased after illumination for 70 h, possibly due to the dissociation of the stabilizing agent TGA. Accordingly, a small red shift (~13 nm) of the absorption band of CdTe QDs is observed after long-time illumination (Fig. S9). The aggregation of QDs could be one of the reasons for the decrease of H_2-generation activity of the CdTe/**1** assembly. In addition, no deposited metallic cobalt particle could be observed in the TEM image of the QDs after used for a 70-h photocatalytic H_2-evolution reaction (Fig. S8b). The direct IR spectroscopic detecting of the QDs isolated from the CdTe/**1** system after the extended photocatalytic reaction did not provide useful information of the adsorbed complex **1** due to the extremely low content of **1** and the overlap of the absorption of the ν(NO) vibration and the H_2O band at 1620−1640 cm^{-1}. We made the catalytic experiments using the isolated CdTe/**1** assembly and analyzed the contents of cobalt anchored on the surface of QDs and dissolved in solution before and after illumination for 30 h using the ICP-MS

analysis, which showed that about ~52% of the grafted-**1** fell off the QDs. In addition, the ligand dissociation of **1** and/or the substitution of dissociated TGA for the bme-dach of the cobalt ion may occur during the long-time photocatalytic reaction. The thereby formed free Co^{2+} ion and/or TGA-Co^{2+} species are less active than **1** for H_2-generation, which is similar with the deactivation of the DHLA (dihydrolipoic acid) stabilized CdSe/cobalt bis(dithiolene) complex hybrid systems reported by Eisenberg and co-workers.[6] The H_2-generation activity of the CdTe/Co^{2+}-DHLA system was significantly inferior to that of the cobalt bis(dithiolene) complex. We found that the rate of H_2 evolution from the CdTe/**1** hybrid was apparently faster than that from the TGA-CdTe/$Co(NO_3)_2$ system (Fig. 5b). The gradual decrease of H_2-evolving rate of the CdTe/**1** system is most possibly due to the aggregation of QDs, the falling off of the grafted complex **1**, and the ligand dissociation and substitution of the cobalt centre in solution.

In conclusion, a new hybrid system was developed via self-assembling of cobalt catalyst [(bme-dach)Co(NO)] (**1**) to the surface of TGA-CdTe QDs and an analogous dimeric cobalt complex [(bme-dach)Co]₂ (**2**) was used as a reference catalyst. The fluorescence and IR spectroscopy revealed that there was an interaction between **1** and CdTe QDs in the ground state. The blue shift of the $v(NO)$ absorption of the isolated CdTe/**1** assembly compared to that of the free complex **1** suggests that the possible way of the interaction between the cobalt catalyst and QDs is the sulphur-coordination of the N_2S_2 ligand (bme-dach) of **1** to the Cd^{2+} ions on the surface of CdTe QDs. Fluorescence spectroscopic studies indicated that the quenching of the CdTe emission by **1** was dominantly via a static quenching model, while the fluorescence quenching by the dimeric cobalt catalyst **2** was through a collisional quenching. The TON of H_2 evolution by the CdTe/**1** hybrid system reached 1.44×10^4 based on **1** over 30 h of illumination, corresponding to a TOF of ca. 700 h^{-1} in the initial 4 h. The H_2-generation activity and durability of the CdTe/**1** are compared favourably to the best results obtained for the previously reported hybrid systems comprising semiconductors and molecular catalysts .

Notes and references

ᵃ State Key Laboratory of Fine Chemicals, DUT-KTH Joint Education and Research Center on Molecular Devices, Dalian University of Technology (DUT), Dalian 116024, China.
E-mail: symbueno@dlut.edu.cn
ᵇ Department of Chemistry, KTH Royal Institute of Technology, Stockholm 10044, Sweden

† Electronic supplementary information (ESI) available. See DOI: 10.1039/c000000x/

1   (a) S. Losse, J. G. Vos and S. Rau, *Coord. Chem. Rev.,* 2010, **254**, 2492; (b) V. Artero, M. Chavarot-Kerlidou and M. Fontecave, *Angew. Chem. Int. Ed.,* 2011, **50**, 7238; (c) F. Wang, W.-G. Wang, H.-Y. Wang, G. Si, C.-H. Tung and L.-Z. Wu, *ACS Catal.,* 2012, **2**, 407; (d) P. Du and R. Eisenberg, *Energy Environ. Sci.,* 2012, **5**, 6012; (e) V. Artero and M. Fontecave, *Chem. Soc. Rev.,* 2013, **42**, 2338.

2   (a) F. Wang, W.-G. Wang, X.-J. Wang, H.-Y. Wang, C.-H. Tung and L.-Z. Wu, *Angew. Chem. Int. Ed.,* 2011, **50**, 3193; (b) J.-X. Jian, Q. Liu, Z.-J. Li, F. Wang, X.-B. Li, C.-B. Li, B. Liu, Q.-Y. Meng, B. Chen, K. Feng, C.-H. Tung and L.-Z. Wu, *Nat. Commun.,* 2013, **4**, 2695; (c) F. Wang, W.-J. Liang, J.-X. Jian, C.-B. Li, B. Chen, C.-H. Tung and L.-Z. Wu, *Angew. Chem. Int. Ed.,* 2013, **52**, 8134.

3   F. Wen, J. Yang, X. Zong, B. Ma, D. Wang and C. Li, *J. Catal.,* 2011, **281**, 318.

4   Z. Han, F. Qiu, R. Eisenberg, P. L. Holland and T. D. Krauss, *Science,* 2012, **338**, 1321.

5   C.-B. Li, Z.-J. Li, S. Yu, G.-X. Wang, F. Wang, Q.-Y. Meng, B. Chen, K. Feng, C.-H. Tung and L.-Z. Wu, *Energy Environ. Sci.,* 2013, **6**, 2597.

6   (a) A. Das, Z. Han, M. G. Haghighi and R. Eisenberg, *Proc. Natl. Acad. Sci. U.S.A.,* 2013, **110**, 16716; (b) Z. Han and R. Eisenberg, *Acc. Chem. Res.,* 2014, **47**, 2537.

7   F. Wen, X. Wang, L. Huang, G. Ma, J. Yang and C. Li, *ChemSusChem,* 2012, **5**, 84.

8   X.-W. Song, H.-M. Wen, C.-B. Ma, M.-Q. Hu, H. Chen, H.-H. Cui and C.-N. Chen, *Appl. Organometal. Chem.,* 2014, **28**, 267.

9   J. Huang, K. L. Mulfort, P. Du and L. Chen, *J. Am. Chem. Soc.,* 2012, **134**, 16472.

10 (a) F. Wen and C. Li, *Acc. Chem. Res.,* 2013, **46**, 2355; (b) L.-Z. Wu, B. Chem, Z.-J. Li and C.-H. Tung, *Acc. Chem. Res.,* 2014, **47**, 2177; (c) M. Wang, K. Han, S. Zhang and L. Sun, *Coord. Chem. Rev.,* 2015, **287**, 1.

11 T. Nann, S. K. Ibrahim, P.-M. Woi, S. Xu, J. Ziegler and C. J. Pickett, *Angew. Chem. Int. Ed.,* 2010, **49**, 1574.

12 C.-H. Hsieh, S. Ding, Ö. F. Erdem, D. J. Crouthers, T. Liu, C. C. L. McCrory, W. Lubitz, C. V. Popescu, J. H. Reibenspies, M. B. Hall and M. Y. Darensbourg, *Nat. Commun.,* 2015, DOI: 10.1038/ncomms4684.

13 M. L. Golden, C. M. Whaley, M. V. Rampersad, J. H. Reibenspies, R. D. Hancock and M. Y. Darensbourg, *Inorg. Chem.,* 2005, **44**, 875.

14 C.-Y. Chiang, J. Lee, C. Dalrymple, M. C. Sarahan, J. H. Reibenspies and M. Y. Darensbourg, *Inorg. Chem.,* 2005, **44**, 9007.

15 J. L. Hess, H. L. Conder, K. N. Green and M. Y. Darensbourg, *Inorg. Chem.,* 2008, **47**, 2056.

16 S. Wu, J. Dou, J. Zhang and S. Zhang, *J. Mater. Chem.,* 2012, **22**, 14573.

17 W. Yu, L. Qu, W. Guo and X. Peng, *Chem. Mater.,* 2003, **15**, 2854.

18 (a) H. W. Tseng, M. B. Wilker, N. H. Damrauer and G. Dukovic, *J. Am. Chem. Soc.,* 2013, **135**, 3383; (b) A. Y. Koposov, P. Szymanski, T. Cardolaccia, T. J. Meyer, V. I. Klimov and M. Sykora, *Adv. Funct. Mater.,* 2011, **21**, 315.

19 T. Rajh, O. I. Mićić and A. J. Nozik, *J. Phys. Chem.,* 1993, **97**, 11999.

20 (a) Z. Han, L. Shen, W. W. Brennessel, P. L. Holland and R. Eisenberg, *J. Am. Chem. Soc.,* 2013, **135**, 14659; (b) P. Zhang, M. Wang, Y. Yang, T. Yao and L. Sun, *Angew. Chem. Int. Ed.,* 2014, **53**, 13803.

21 (a) J. Aldana, N. Lavelle, Y . Wang and X. Peng, *J. Am. Chem. Soc.,* 2005, **127**, 2496; (b) Y. Zhang, L. Mi, P. N. Wang, J. Ma and J. Y. Chen, *J. Lumin.,* 2008, **128**, 1948.

ChemComm Accepted Manuscript