

Cite this: DOI: 10.1039/c1cc12390d

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HIGHLIGHT

Photocatalytic hydrogen production

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DOI: 10.1039/c1cc12390d

The efficient storage of solar energy in chemical fuels, such as hydrogen, is essential for the large-scale utilisation of solar energy systems. Recent advances in the photocatalytic production of H₂ are highlighted. Two general approaches for the photocatalytic hydrogen generation by homogeneous catalysts are considered: HX (X = Cl, Br) splitting involving both proton reduction and halide oxidation *via* an inner-sphere mechanism with a single-component catalyst; and sensitized H₂ production, employing sacrificial electron donors to regenerate the active catalyst. Future directions and challenges in photocatalytic H₂ generation are enumerated.

Introduction

The demand for energy continues to monotonically rise to unprecedented levels as the global population increases in number and raises its standard of living.^{1–4} Solar energy emerges as a front-running clean, abundant and secure energy source to meet this demand.^{5–7} However, as with any intermittent source of energy, the large-scale

deployment of solar energy systems requires efficient, cost-effective and energy-dense means to store excess energy for later recovery. Though numerous methods of energy storage exist and will undoubtedly contribute to the technological landscape, perhaps the most attractive means of solar storage is in the chemical bonds of fuels.⁸ And among the many fuel-forming reactions that can be envisioned, the catalytic generation of hydrogen from water and other protic sources remains at the forefront.

Whereas practical, large-scale systems for renewable hydrogen generation may very well be centred on heterogeneous

electrocatalytic or photoelectrocatalytic materials,⁹ homogeneous compounds that promote the hydrogen evolution reaction (HER) are important research targets because they provide mechanistic insights that cannot be achieved with heterogeneous compounds. With homogeneous catalysts, precise details of molecular-scale transformations are often more accessible and greater tunability is possible with modular architectures, thus providing an imperative for the continued study of homogeneous catalysts that promote the HER.

The most recent advances in photocatalytic hydrogen production in

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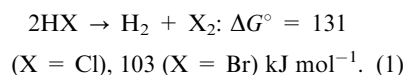
efforts are devoted to bringing personalized, carbon-neutral energy to the poor and those of the non-legacy world.

homogenous systems are discussed. Our group¹⁰ and others^{11–16} have extensively reviewed this topic in recent years, so this Highlight will primarily focus on the last four years of HER photocatalysis. The review comprises two sections. In the first section, we summarize work on single component systems that photocatalytically generate H₂ from HX (X = Cl, Br) solutions; much of the recent progress has been in the optimization of the thermodynamically challenging oxidative half-reaction of X₂ liberation. In the second section, we highlight recent contributions using multi-component, sensitized catalysts with sacrificial electron donors for H₂ generation. In both sections, limitations of current systems and future challenges to be addressed are brought forth.

Single component photocatalytic HX splitting

General principles

Solar energy may be stored by driving the uphill generation H₂ and X₂ from the photocatalytic splitting of HX. The overall reaction and thermodynamics are given by



The large, positive standard free energy values for these reactions, comparable to water splitting on a per-electron basis, demonstrate that considerable amounts of energy storage are possible with HX splitting. Scheme 1 depicts a generalized HX-splitting cycle, demonstrating the

key steps involved in single-component photocatalysis.

The steps in Scheme 1 are colour-coded and numbered for clarity. (i) HX oxidatively adds to the photocatalyst ([Cat]), producing a hydrido-halide intermediate; from here two pathways are possible. (ii) A second HX addition gives a dihydrido-dihalide species, which in (iii) reductively eliminates H₂ in a process that may be photochemical. Alternatively, if the [Cat](H)(X) intermediate formed in (i) possesses a M–H bond that is sufficiently hydridic, direct protonation by HX (iv) produces H₂ and generates the final [Cat](X)₂ intermediate. The sequential HX oxidative addition steps in (i)–(ii) are likely only operative in very reducing bimetallic catalysts, where a +4 change in formal oxidation state is feasible because the oxidative equivalents can be shared between two metals. In monometallic catalysts or complexes with a less reducing resting state, the acid–base pathway in (iv) is most probable. Whatever the mechanism of H₂ production, the final step (v) involves the thermodynamically demanding photoelimination of X₂ to close the cycle. Thus, the challenge in designing single component HX-splitting photocatalysts rests in discovering complexes that are reducing enough to formally reduce protons to hydrogen, while still oxidizing enough to oxidize halides to halogen (X₂). Care must be taken to avoid deleterious photochemistry of hydride-containing intermediates, and the photoreactions must be executed in a manner that allows photogenerated X₂ to be swept from the reaction mixture, either by physical or chemical trapping,

to circumvent back reactions of X₂ with catalytic intermediates. In the case of the latter, the stored energy of X₂ generation is diminished if not lost entirely in the trapping reaction. Thus trapping reactions to produce beneficial products are preferred.

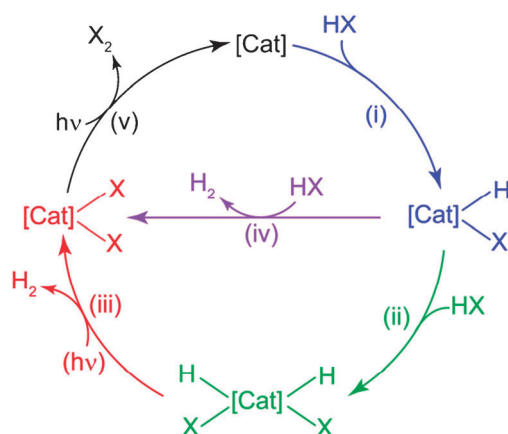
HX Splitting with dirhodium complexes

The generalized steps of Scheme 1 have been brought to fruition with studies from our group over the past decade. In 2001 we disclosed that diphosphazane-bridged dirhodium complexes of the type Rh₂^{0,0}(dfpma)₃L₂ (dfpma = bis(difluorophosphino)methylamine, L = CO, PR₃) are capable of photocatalytically generating H₂ from HX, provided a sufficiently active halogen trap, in this case THF, is present.^{17,18} We later elucidated mechanistic details of the HX-splitting photocycle with a series of model complexes,¹⁹ which demonstrated a four-electron cycle, involving two HX oxidative additions and intermediacy of a dihydrido-dihalide species which photoeliminates H₂.

Photochemical halogen elimination

In our early work with dirhodium complexes, we recognized that the overall H₂-production quantum yield of <1% was solely limited by the quantum yield of halogen photoelimination (step (v) in Scheme 1). In addition, for the dirhodium system an efficient halogen trap was needed for this photoreaction, obviating the energy storage that accompanies authentic X₂ elimination. Thus, much of our work in recent years has focused on optimizing X₂-elimination photochemistry, to gain a better understanding of the design characteristics that beget this challenging photochemical transformation. Fig. 1 collects structures of complexes that are capable of efficient halogen photoelimination and that have progressed our understanding of this process.

Efficient X₂ elimination is achieved in complexes featuring later, more oxidizing metal cores relative to dirhodium complexes. We have studied several classes of metal–metal bonded bimetallic species that have been designed to retain the electronic structure that drives the photoelimination chemistry of the



Scheme 1 General cycle for single-component photocatalytic HX splitting.

original dirhodium complexes. The complex $[\text{Pt}^{\text{III}}\text{Au}^{\text{II}}(\text{dppm})_2(\text{Ph})\text{Cl}_2](\text{PF}_6)$ ($\text{dppm} = \text{bis}(\text{diphenylphosphino})\text{methane}$) (**1**) was prepared, and it was found that, with a high concentration of 2,3-dimethyl-1,3-butadiene (DMBD) as a halogen trap, a quantum yield of 5.7% was achieved for photoelimination of halogen to regenerate the $\text{Pt}^{\text{II}}\text{Au}^{\text{I}}$ precursor.²⁰ This quantum yield represents an almost 10-fold increase over that of isoelectronic d^9-d^7 $\text{Rh}_2^{0,\text{II}}$ complexes.²¹ Even higher solution quantum yields of 38% were obtained with the homobimetallic, bioctahedral d^7-d^7 complex $\text{Pt}_2^{\text{III,III}}(\text{tfepma})_2\text{Cl}_6$ ($\text{tfepma} = \text{MeN}[\text{P}(\text{OCH}_2\text{CF}_3)_2]_2$) (**2**), and with this complex we demonstrated for the first time authentic Cl_2 elimination by photolyzing solid samples and analyzing the volatile photoproducts by in-line mass spectrometry.²² Heterobimetallic complexes $[\text{M}^{\text{II}}\text{Au}^{\text{II}}(\text{dcpm})_2(\text{CO})\text{X}_2](\text{PF}_6)$ ($\text{M} = \text{Ir},^{23} \text{Rh},^{24} \text{X} = \text{Cl}, \text{Br}, \text{dcpm} = \text{bis}(\text{dicyclohexylphosphino})\text{methane}$) (**3**) have also been shown to effectively eliminate halogen in the presence of a DMBD trap, attaining quantum yields of *ca.* 10% for $\text{M} = \text{Ir}, \text{X} = \text{Br}$ and 18% for $\text{M} = \text{Rh}, \text{X} = \text{Br}$; in both cases these values drop considerably as the excitation energy is decreased. In addition to metal–metal bonded homo- and heterobimetallic complexes, we have shown that efficient halogen elimination can be achieved by photolysis of mono- and bimetallic Au^{III} -containing complexes (**4–6**), which lack formal metal–metal interactions.²⁵ These studies establish that a metal–metal bond is not a prerequisite for smooth halogen elimination. With this suite of Au^{III} complexes, quantum yields as high as 25% were obtained, authentic X_2 photoliberation was demonstrated in the solid state, and mechanistic insights into the solution photoreactions were revealed.

Taken together, important criteria for high quantum yield halogen elimination photochemistry emerge from the forgoing results. First, significantly enhanced quantum yields for X_2 photoelimination are engendered with the incorporation of later transition metals into metal–metal bonded phosphine-bridged bimetallic complexes. All of the complexes summarized in Fig. 1 contain metals from group 10 and/or group 11, and they all outperform group 9

homobimetallic complexes in terms of halogen elimination photochemistry. Quantum yields are further augmented by designing complexes that undergo minimal geometric perturbation upon photoreduction. By minimizing structural rearrangements upon photoelimination, X_2 elimination may proceed in the absence of trap, thus defining an authentic energy-storing photoreaction. Diplatinum complex **2** and gold complexes **4–6** are all capable of driving X_2 photoelimination when irradiated in the solid state. In these cases, X_2 may be swept from the reaction vessel to prevent the back reaction of the photoreduced product with X_2 . And finally, in terms of electronic structure, ligand-to-metal charge transfer (LMCT) character in the excited state facilitates the liberation of halogen. Mononuclear Au^{III} halide complexes, which are long known to possess purely LMCT excited states,²⁶ are as effective as their metal–metal bonded counterparts in possessing a halogen elimination photochemistry. Fig. 2 compares electronic absorption spectra of the metal–metal bonded complexes $[\text{Ir}^{\text{II}}\text{Au}^{\text{II}}(\text{dcpm})_2(\text{CO})\text{X}_2](\text{PF}_6)$ with monometallic complexes $\text{Au}^{\text{III}}(\text{PCy}_3)_3\text{X}_3$. The presence of a metal–metal interaction can have a profound effect on the excited state and electronic spectral characteristics. Nevertheless, it is evident from both sets of spectra in Fig. 2 that there is substantial LMCT character in both cases, as verified by the pronounced bathochromic shift upon substitution of Cl^- for Br^- . Our work on these sets of complexes shows that LMCT excited states, in which electron density is shifted from halide-centred to metal-centred orbitals, can weaken $\text{M}-\text{X}$ bonds and promote X_2 elimination.

Challenges and future directions

Our recent efforts have resulted in a much clearer grasp on the criteria for efficient halogen photoelimination, the stage which limited the catalytic efficiency and forbade energy storage in our original single-component HX-splitting dirhodium catalysts. A challenge to moving forward is to design systems where facile H_2 production is married to authentic, high-yielding X_2 elimination. Furthermore, we seek to design

systems where halogen elimination can be promoted with irradiation at wavelengths deeper into the visible spectral region. In addition, we have begun to explore means of designing HX-splitting catalysts based on first-row, earth-abundant metals. Thus far our efforts have shown that Ni–NHC complexes can react with HX and photochemically liberate H_2 ,²⁷ though further studies are needed to render these systems catalytic by coupling X_2 elimination with H_2 production. All of these advances must be made if single-component, photocatalytic HX splitting is ever to become an effective means of storing solar energy *via* HER.

Multi-component photocatalytic H_2 production

General principles

Scheme 2 shows two common, generalized designs for multi-component, sensitized H_2 production from acidic or aqueous protons. In both cases, the net reaction is the photogeneration of a charge-separated state that delivers reducing equivalents to the HER catalyst. In the simpler two-component system, Scheme 2a, the sensitizer (S) absorbs light, and its excited state is reductively quenched by a sacrificial electron donor (D). The reduced sensitizer then transfers an electron to the catalyst (cat) on the way to producing H_2 . In many systems, an additional electron relay (ER) is employed to facilitate charge separation. In this variation, shown in Scheme 2b, the sensitizer is oxidatively quenched by the electron relay (ER), which then transfers an electron from its reduced state (ER^-) to the catalyst. The oxidized sensitizer (S^+) that is generated *via* excited state electron transfer is reduced by the sacrificial electron donor. It should be mentioned that these two schemes represent common, idealized pathways for sensitized H_2 production, but more complicated scenarios often arise. For example, in many cases the catalyst itself can oxidatively quench the sensitizer, and it is also common that the one-electron oxidized sacrificial donor (D^+) is able to deliver a second electron and participates in a further electron transfer event with the catalyst. Competition between different

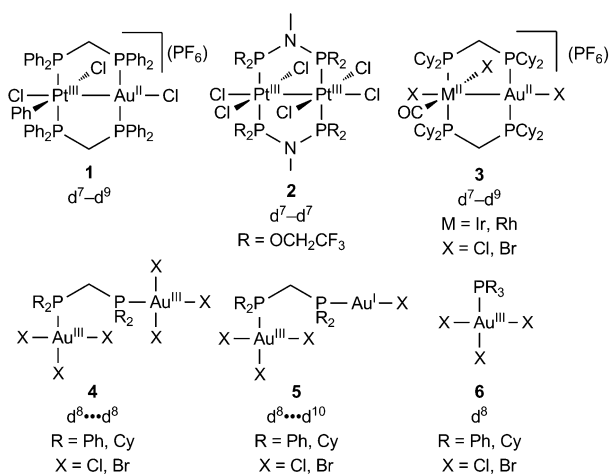


Fig. 1 Structures of complexes which efficiently undergo halogen photoelimination.

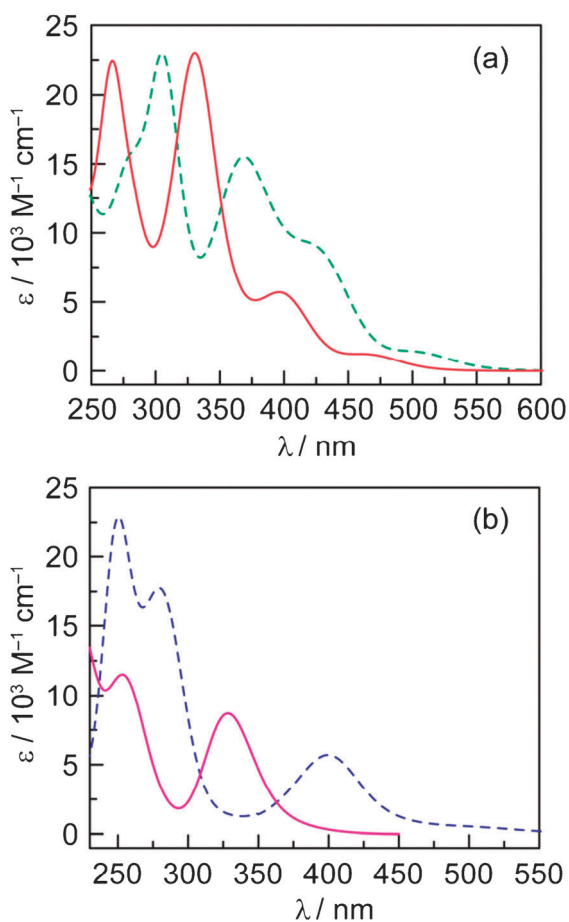
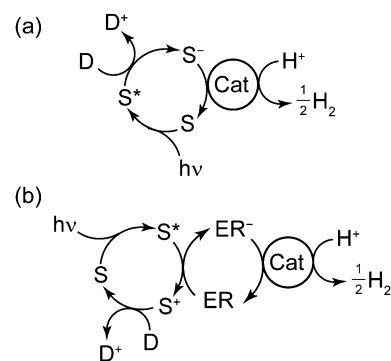


Fig. 2 (a) Electronic absorption spectra of $[\text{Ir}^{\text{II}}\text{Au}^{\text{II}}(\text{dcpm})_2(\text{CO})\text{X}_2](\text{PF}_6)$, $\text{X} = \text{Cl}$ (—), Br (---) (b) Electronic absorption spectra of $\text{Au}^{\text{III}}(\text{PCy}_3)_3\text{X}_3$, $\text{X} = \text{Cl}$ (—), Br (---). All spectra were recorded at 293 K in CH_2Cl_2 .

electron transfer partners can arise, and it is also necessary to account for the possibility of nonproductive charge recombination steps when designing and evaluating multi-component systems. Carefully planned

control experiments and well-executed photophysical quenching studies can help elucidate the preferred electron transfer pathway, but in some scenarios the precise route for H_2 production remains ambiguous.



Scheme 2 General pathways for sensitized H_2 photocatalysis.

Untethered multi-component systems

The first reports of multi-component photocatalytic hydrogen production, using $[\text{Ru}(\text{bpy})_3]^{2+}$ sensitizer, methyl viologen (MV^{2+}) as the electron relay, in concert with a colloidal metal catalyst and sacrificial donor, appeared over 30 years ago.^{28–32} The field has blossomed in recent years, with most of the focus on utilizing different combinations of sensitizer and catalyst to improve catalytic performance. Many new photosensitizers have emerged in recent years, and in general they share features with the popular $[\text{Ru}(\text{bpy})_3]^{2+}$ sensitizer—they are metal-polypyridyl complexes with accessible $^3\text{MLCT}$ states, which are potent reductants and/or oxidants. Many researchers have begun to utilize soluble, molecular species to replace the colloidal metal catalysts, usually platinum, that had dominated the field in previous decades. In particular, glyoxime-ligated cobalt molecular catalysts, which have been demonstrated to be efficient proton-reduction electrocatalysts,^{33,34} have been applied as the HER catalyst in Scheme 2.

Fig. 3 collects structures of some of the new classes of photosensitizers used in photocatalytic H_2 production. Recent efforts by Eisenberg and coworkers have demonstrated the utility of substituted terpyridyl platinum phenylacetylide complexes (**7**) as photosensitizers for sensitized H_2 production from acetonitrile/ water solvent mixtures. Complexes of the type **7** have been used in concert with an MV^{2+} electron relay and colloidal Pt catalyst with triethanolamine (TEOA) sacrificial donor,³⁵ as well as with cobalt glyoxime catalysts

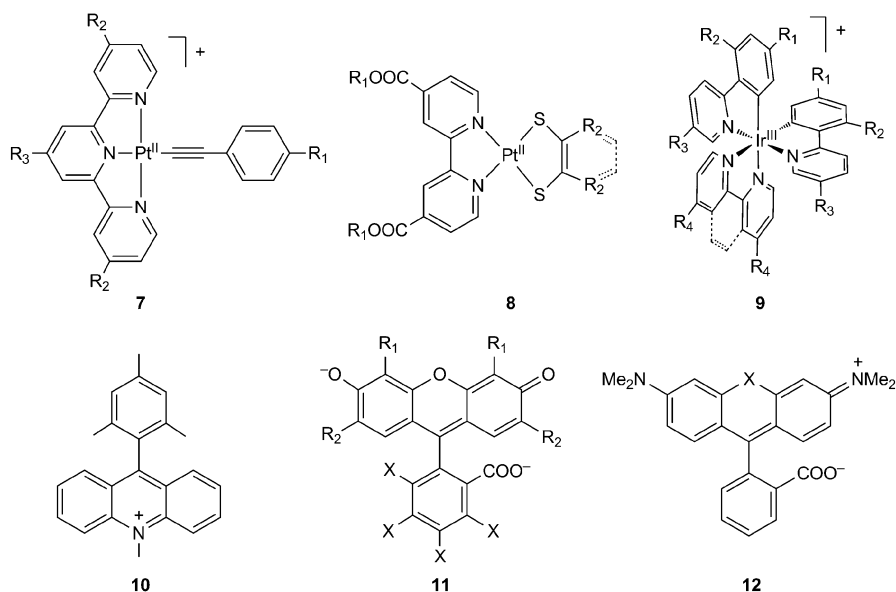


Fig. 3 Examples of photosensitizer constructs.

and TEOA in the absence of an electron relay.³⁶ A more in-depth study of platinum acetylide/cobalt glyoxime combinations followed, where substituent effects, solvent effects, and some mechanistic details were brought forth,³⁷ and Castellano and co-workers have studied the effect of conjugation length in the platinum acetylide chromophore.³⁸ Eisenberg's group has also demonstrated that platinum acetylide (**7**) complexes³⁹ and visible-absorbing platinum dithiolate (**8**) complexes⁴⁰ were effective as sensitizers with a platinised TiO₂ electron relay/catalyst. TiO₂ has also been utilized as an electron relay in combination with phosphonate-substituted [Ru(bpy)₃]²⁺ sensitization and a phosphonated cobalt glyoxime catalyst.⁴¹ A second class of sensitizers that have gained traction in recent years are the heteroleptic, cyclometallated Ir^{III} complexes studied by Bernhard's group, which has used a combinatorial approach to screen numerous complexes of the type **9**, where both the neutral heterocyclic diimine ligand and the anionic cyclometalating phenylpyridine derivative can be systematically altered. These compounds were shown give rise to > 35× higher quantum yields than analogous systems with [Ru(bpy)₃]²⁺ sensitization, with [Co(bpy)₃]²⁺ electron relay/catalyst and TEOA electron donor.⁴² When colloidal platinum generated *in situ* was used as the catalyst, no electron relay was needed and quantum yields as high as 0.26 were

achieved.⁴³ Systematic studies on numerous experimental parameters yielded structure–activity relationships in the sensitizer and yielded some kinetic information about the HER.⁴⁴

In an effort to diversify system design and simultaneously move away from precious-metal sensitizers, a few groups have begun to explore organic dye sensitizers for photocatalytic H₂ production. Fukuzumi and co-workers have demonstrated H₂ production with sensitization provided by a charge-separating acridinium-mesityl construct (**10**), which is combined with platinum nanoparticle catalysts and NADH sacrificial donor in the absence of an electron relay.⁴⁵ Eisenberg's group has also shown that halogenated fluoroscein-based dyes (**11**) sensitize H₂ production catalyzed by a cobalt glyoxime catalyst,⁴⁶ and that heavy-atom rhodamine analogues **12**, where X = S or Se, give rise to even more active and robust photocatalysis.⁴⁷

Tethered sensitizer-catalyst systems

To improve the kinetics of charge injection into the HER catalyst, several groups have begun preparing supra-molecular constructs where the chromophore and catalyst are linked *via* some bridging moiety. Fig. 4 shows examples of some of the constructs that will be considered here. Fontecave and collaborators have tethered photosensitizers to the aforementioned cobalt glyoxime

catalysts such as illustrated by **13**. Complexes like **13**, with Ru^{II} polypyridyl chromophores, achieve *ca.* 100 turnovers with NEt₃ sacrificial donor and HNET₃Cl as the proton source; here it was also revealed that a two-component mixture of sensitizer and catalyst gave marginally smaller turnover numbers compared to the tethered complex.⁴⁸ A related construct featuring a tethered Ir^{III} heteroleptic sensitizer was considerably more robust, and upwards of 300 turnovers could be achieved with otherwise analogous conditions.⁴⁹ Sakai's group has reported extensively on tethered architectures such as **14**, where a ruthenium polypyridyl sensitizer is linked through an amide bond to a Pt^{II} catalyst. The initial report disclosed a *ca.* 1% quantum yield and 5 turnovers when the complex was irradiated in the presence of EDTA.⁵⁰ Subsequent papers have shown that performance can be enhanced by lowering the LUMO energy of the platinum catalyst, which creates a larger electron transfer driving force;⁵¹ a recent report provides some mechanistic insights.⁵² Cautionary tales from Hammarström's⁵³ and Castellano and Eisenberg's⁵⁴ groups show the fragility of these types of group 10 platinum and palladium catalysts, which can be reduced to colloidal metal under certain photocatalytic conditions. Brewer and collaborators have prepared several heteromultimetallic constructs featuring bridging polypyridyl ligands, of which **15**

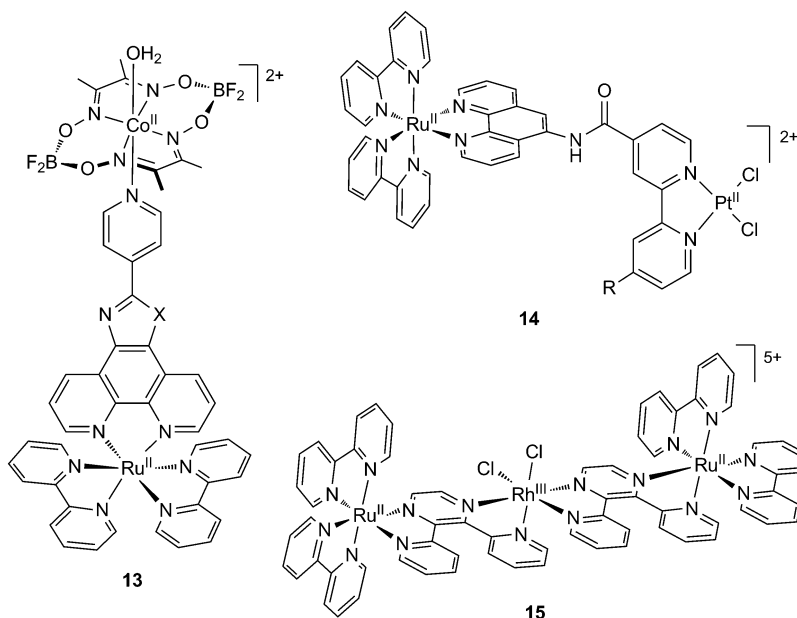


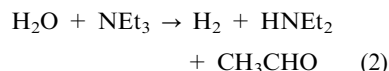
Fig. 4 Examples of tethered photosensitizer/catalyst constructs.

is a representative example. Complex **15**⁵⁵ and its closely related bromide complex^{56,57} show turnover numbers of 30 and 38, respectively, when photolyzed with dimethylaniline as the reductant; other analogues featuring different ligand sets and metal combinations have also been interrogated but with no improvement in activity.⁵⁸ This same group has also studied a Ru^{II}Pt^{II} supramolecular polypyridyl complex, and under similar conditions over 100 turnovers were achieved in a 5 h period.⁵⁹ Other tethered systems have appeared recently including a Ru^{II}Pd^{II} polypyridyl architecture^{60,61} as well as complexes based upon diiron hydrogenase mimics with zinc porphyrin⁶² or rhenium polypyridyl⁶³ sensitization.

Challenges and future directions

In surveying the recent literature on sensitized H₂ photocatalysis, several limitations and challenges become readily apparent. First, the constructs reviewed herein generally have low turnover numbers, with very few examples giving turnover numbers greater than 10³. In many cases both photosensitizer bleaching and catalyst decomposition are cited as reasons for the relative fragility of these multi-component systems. Tethered systems are not systematically more robust, so improvements in all facets of the system design are needed. Finally, and perhaps most

importantly, the thermodynamic limitations of the currently constructed multi-component photocatalytic H₂ systems need to be addressed. The stated goal in developing these systems is solar energy storage. The use of a sacrificial electron donor obviates any energy storage; hence, it must be eliminated for viable energy storage to be achieved. Although the exact thermodynamic parameters of a reaction are often elusive and depend on the chosen electron donor and its exact mode(s) of decomposition, consider the simple example of triethylamine as a sacrificial donor, where a predominant decomposition mechanism is known.¹⁰ Triethylamine is capable of donating two electrons, ultimately forming an iminium cation, which can be hydrolyzed by water. Thus, for aqueous proton reduction with triethylamine as the reductant, the overall reaction is:



Using tabulated thermochemical data,⁶⁴ the ΔH° is calculated to be -120 kJ mol^{-1} . Assuming an entropy term dominated by release of H₂ of *ca.* $+130 \text{ J mol}^{-1} \text{ K}$, the ΔG° for the reaction in eqn (2) is estimated to be -160 kJ mol^{-1} , confirming that the net overall photocatalytic reaction is releasing and not storing energy. The substantial deleterious thermodynamic impact of the electron

donor is analogous to that of the halogen trap that has been employed in the single component HX-splitting schemes described in the first section of this Highlight. In order to advance photocatalytic hydrogen production towards authentic solar energy storage, the reduction of protons must be coupled to a suitable oxidative half-reaction, for example water oxidation to O₂, such that the overall reaction is thermodynamically uphill and reversible. In such a scheme, the holes generated in the initial photoinduced charge-separated state are delivered to a suitable water-oxidation catalyst, and the overall reaction is thus the splitting of water into H₂ and O₂, which is thermodynamically uphill by 1.23 V.⁸ For such a system to be successful, the kinetics of charge separation and injection to the respective catalysts must be able to overcome non-productive charge recombination. Thus advances in both the design of new photosensitizers and catalysts will likely be required for such a scheme to be developed.

Conclusion

Recent advances, mainly covering the last four years of research, in photocatalytic hydrogen production have been the subject of this Highlight. For the single component systems pioneered by our group, much recent effort has been devoted to optimizing and understanding photochemical halogen elimination, the oxidative half reaction in HX splitting photocatalysis. Our work has led to dramatically enhanced solution quantum yields for halogen elimination, authentic “trap-free” X₂ elimination, and a clearer understanding of electronic design criteria for promoting efficient halogen photoelimination. If we are able to integrate these elements into catalysts also capable of generating H₂, an energy-storing photocycle will be realized. In the field of multi-component hydrogen photocatalysis, work of recent years has diversified the combinations of sensitizers and catalysts that can be used for HER. Clear challenges related to system stability must be overcome, and new systems where photogenerated holes are used in a productive half reaction, rather than quenched with a sacrificial donor, must be designed.

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