

FRONTIER



Cite this: *Dalton Trans.*, 2022, **51**, 14022

Received 13th June 2022,
Accepted 8th August 2022

DOI: 10.1039/d2dt01870e

rsc.li/dalton

Photo-generation of H₂ by heterometallic complexes

Franco Scalambra,[†] Ismael Francisco Díaz-Ortega[†] and Antonio Romerosa^{†*}

Multiple and different metals in a complex can accomplish single and sequential multi-step reactions, providing valuable procedures to obtain chemicals in one-pot synthetic routes. Biology has shown how cooperative catalysis is a powerful method for the synthesis of complicated molecules. One of the most attractive targets for current chemists is the synthesis of H₂ by a simple and economical procedure, mainly if it is produced from water using visible light as the energy source. This review aims to show how heterometallic complexes have been recently used to catalyze the photochemical production of H₂.

Introduction

Natural metalloenzymes containing more than one metallic moiety occupy a large portion of metal-containing proteins and cofactors¹ and are a paradigmatic example of efficient catalysts, mostly due to their multi-metallic composition that provides a cooperative single-molecule platform for multi-step catalytic reactions. Their efficiency, expressed in terms of atom-² and step-economy,³ and stereoselectivity are known to be outstanding compared to any artificial system. Thus, it is not a surprise that, so far, these species have inspired the design of a wide variety of synthetic strategies to help in the synthesis of fine chemicals and energy vectors.^{4–11} In principle, this nature-inspired approach should be more economical and eco-friendly than any other anthropic solution. However, the design and synthesis of catalytically useful heterometallic complexes are laborious,¹² being one of the most important challenges of enzyme-inspired synthesis. Natural multi-metallic catalysts transform chemical substrates *via* the cumulative and cooperative influences of the metal centers thanks to well-defined electronic cascades and nucleophilic/electrophilic reactions. Nevertheless, the reaction can occur only when the substrate is positioned in the right orientation and the metallic sites adopt the appropriate geometry.¹³ These spatial requirements are usually fulfilled by both covalent and non-covalent bonding,¹⁴ and sometimes by external factors such as light.¹⁵ Moreover, another significant feature of multi-metallic catalysis is the improvement of the reaction rate by increasing the concentration of substrates in a confined

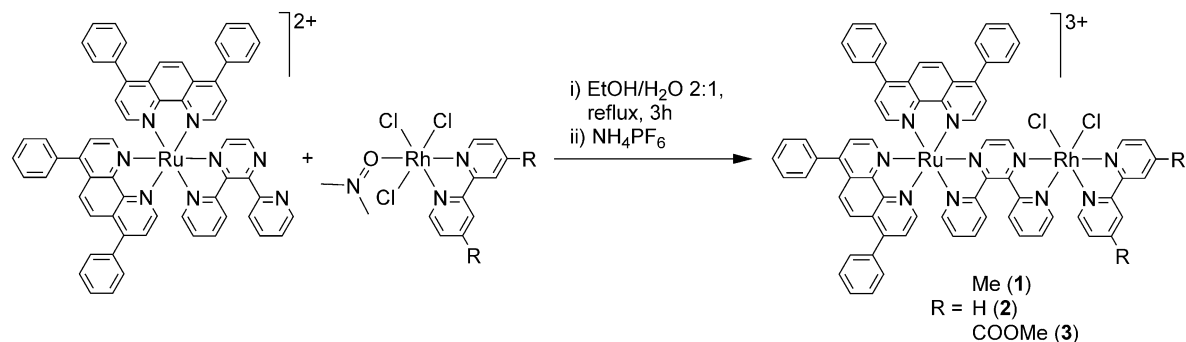
space.^{16–23} All these very finely tuned mechanisms are not easy to emulate using small molecules.

Molecular hydrogen is one of the most promising energetic vectors as it can be obtained from water and its combustion with O₂ gives water again releasing a large amount of energy. Despite this attractive energetic virtuous circle, producing H₂ from water is energetically demanding and the efficiency and costs of the currently employed processes still display a large margin of improbability.^{24–26} One of the most attractive procedures to overcome this energy issue may be the use of visible radiation, ideally solar radiation, to drive the splitting of the water molecules and the formation of H₂. In this field, during the last five years, a few but significant heterometallic complexes have been studied as photocatalysts for this reaction, most of them being constituted by a photosensitizer and catalytic metal centres connected by an adequate bridging ligand.^{27–41} This strategy provides electrons to the catalytic centres avoiding dispersive diffusion and collision events in the reaction media among the catalytic centre and photosensitizer molecules, increasing the efficiency and durability. Herein, we describe the most recent heterometallic systems developed to photo-produce H₂ using heterometallic complexes and to show how they display significant advantages in comparison with monometallic complexes.

Experimental and theoretical studies

Not long ago, in 2017, three Ru(II)–Rh(III) dimetallic complexes were presented: [Ru(Ph₂phen)₂(dpp)RhCl₂(4,4'-R-bpy)](PF₆)₃ (R = Me (1), H (2), COOMe (3)); Ph₂phen = 4,7-diphenyl-1,1'-phenanthroline; dpp = 2,3-bis(2-pyridyl)pyrazine; bpy = 2,2'-bipyridine (Scheme 1).⁴² The evaluation of their properties as photocatalysts for hydrogen production showed that their

Área de Química Inorgánica-CIESOL, Universidad de Almería, Almería, Spain.
E-mail: romerosa@ual.es, scalambra@ual.es, ifdior@ual.es; Fax: +34950015008;
Tel: +34638140119



Scheme 1 Synthesis of 1–3.

activity is correlated with the bipyridine- σ -donating ability and the rate of Rh–Cl dissociation upon electrochemical reduction. Despite their similarity, complex 3, containing the weaker σ -donating dmeb (dmeb = 4,4'-dimethyl ester-2,2'-bipyridine) ligand and showing the highest rate constant for chloride dissociation, generated the largest amount of H₂ from water in the presence of *N,N*-dimethylaniline as the electron donor, its maximum quantum yield ($\Phi_{\text{H}_2, \text{max}}$) being 0.004 after 4 h under photolysis (Table 1).

The resulting amount of H₂ was not significant for practical use but motivating conclusions were obtained from the performed studies. The photocatalytic reduction of H₂O was

determined to occur *via* electron collection at the Rh centre, which is photoinitiated at the Ru chromophore by extraction of 1 electron from the sacrificial donor. To allow the overall process, it is important that light absorption occurs by the lowest energy transition Ru(d π) \rightarrow dpp(π^*), with a ¹MLCT character, which induces the population of a weakly-emissive short-lived Ru(d π) \rightarrow μ -dpp(π^*) ³MLCT excited state, which undergoes intramolecular electron transfer to populate a non-emissive, photochemically-active Ru(d π) \rightarrow Rh(d σ^*) ³MMCT excited state.

The same year, an interesting theoretical DFT and TDDFT study was published, which compared the excited states that

Table 1 Reaction conditions for hydrogen generation using the catalysts described herein

λ_{exc}	[Cat]	Solvent	[Cat]	SED ^a	H ⁺ source ^a	TON	TOF (h ⁻¹)	Amount of H ₂ (μmol)	Ref.	
470 nm	1	DMF	1.3×10^{-4} M	DMA 1.5 M	H ₂ O 0.62 M (DMAH ⁺) (CF ₃ SO ₃ ⁻) 1.1×10^{-4} M	30 (20 h)	1.50	18	42	
	2					35 (20 h)	1.75	21		
	3					63 (20 h)	3.15	37		
	5					130 (18 h)	7.22	16		
452 nm	8	CH ₃ CN	1×10^{-1} M	TEOA 5×10^{-1} M	HBF ₄ 5×10^{-2} M	180 (2.3 h)	78.2	9×10^4	45	
						525 nm	251 (3.8 h)	83.6		12.5×10^4
595 nm	11-Cl ₂ 11-I ₂ 12-Cl ₂ 12-I ₂ 12-I ₂	CH ₃ CN/TEA/H ₂ O 6 : 3 : 1	5.2×10^{-5} M	TEA 2.8 M	M	70 (18 h)	3.88	9	43	
630 nm						130 (18 h)	7.22	16		
470 nm						180 (18 h)	10	9×10^4		
470 nm						78 (110 h)	0.71	3.9×10^4		
480 nm	13 + [Ru] ^b (1 : 1)	CH ₃ CN/H ₂ O 1 : 1	1×10^{-4} M	TEA 3.8×10^{-1} M	M	25 (48 h)	0.52	—	60	
	13 + [Ru] ^b (1 : 3)					2 (48 h)	0.04	—		
	13 + [Ru] ^b (1 : 10)					7 (48 h)	0.14	—		
	14					256 (48 h)	5.33	—		
	15 + 16					465 (48 h)	9.68	—		
Simulated solar light ^d	15 + 16	CH ₃ CN/H ₂ O (1 : 1)	2.5×10^{-4} M	TEOA 2.6×10^{-1} M	M	49 (24 h)	2.04	—	62	
	16 + [Ir] ^c					3 (3 h)	1	16 (0.75 h)		
	17					16 (3 h)	5.33	78		
	18					5 (3 h)	1.66	25		
480 nm	20	DMA/TEOA (4 : 1)	5×10^{-5} M	BIH 1×10^{-1} M	3,5-F ₂ -PhOH 1×10^{-1} M	92 (3 h)	30.66	18.6	64	
						[BI-(OH)H] 1×10^{-1} M	85 (3 h)	28.33		16.6
						See text	157.5 (3 h)	52.5		30.9

DMA = *N,N*-dimethylaniline; TEA = triethylamine; TEOA = triethanolamine; BIH = 1,3-dimethyl-2-phenyl-2,3-dihydro-1*H*-benzo[*d*]imidazole; 3,5-F₂-PhOH = 3,5-difluorophenol; [BI-(OH)H] = 2-(1,3-dimethyl-2,3-dihydro-1*H*-benzo[*d*]imidazol-2-yl)phenol. ^a Solvent, if not explicitly specified. ^b [Ru] = [Ru(bpy)₃]²⁺. ^c [Ir] = [Ir(ppy)₂(bpy)]PF₆. ^d Using a Xe lamp with an AM1.5 global filter.

induce the H_2 production catalyzed by $[\text{Ru}(\text{bpy})_2(2,5\text{-tpy})]^{2+}$ (4), $[\text{Ru}(\text{bpy})_2(2,5\text{-tpy})\text{Pd}(\text{CH}_3\text{CN})\text{Cl}]^{2+}$ (5), $[\text{Ru}(\text{bpy})_2(2,6\text{-tpy})]^{2+}$ (6), and $[\text{Ru}(\text{bpy})_2(2,6\text{-tpy})\text{Pd}(\text{CH}_3\text{CN})\text{Cl}]^{2+}$ (7), (Fig. 1).⁴³

The obtained results supported that for complexes containing the linear bridging ligand 2,5-tpy (4 and 5), the lowest-lying triplet excited state has $^3\text{MLCT}$ character. For 5, the lifetime of the $^3\text{MLCT} \rightarrow ^3\text{MC}_{\text{Ru}}$ decay is slow enough to allow efficient and long-lived photocatalysis. In contrast, for the complexes featuring the non-linear bridging ligand (6 and 7), the lowest excited state was found to have $^3\text{MC}_{\text{Ru}}$ character, resulting in a fast decay behaviour that lowers the catalytic efficiency and justified the inactivity of 7. Thus, through an appropriate choice of ligands and geometry, the performance of the catalyst can be tuned, acting on the character and the lifetime of the excited state. This result supports the finding published by J. G. Vos *et al.*⁴⁴ which showed how heterodimetallic complexes are better than monometallic complexes to photocatalytically produce H_2 , in contrast to the combination of the complexes 5 and 7.

Also in 2017, three Ir-based complexes were presented and studied as catalysts for H_2 generation. One of them is the dimetallic complex 8 (Fig. 2) ($\text{Hpiq} = 1\text{-phenylisoquinoline}$; $\text{L} = 2,2';5',4''\text{-terpyridine}$),⁴⁵ which is a dyad with vectorial electron transfer. The activity of 8 (0.1 M) to produce H_2 from HBF_4 in CH_3CN (0.05 M) in the presence of triethanolamine (0.5 M) under irradiation centred at 452 nm, 525 nm, 595 nm and 630 nm was compared with those of the combination of the

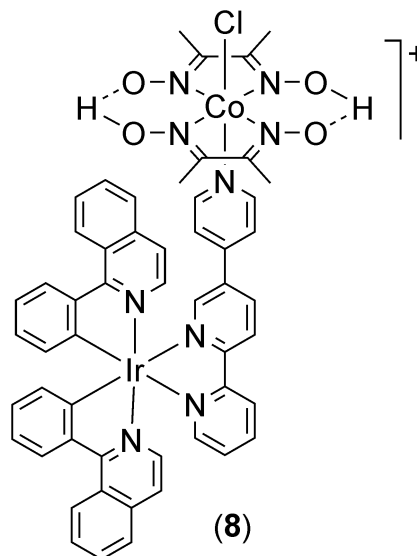


Fig. 2 Structure of complex 8.

corresponding monometallic Ir and Co complexes (Table 1) under the same reaction conditions.

The authors attributed the better performance of the dimetallic complex 8 to the covalent connections between Ir and Co moieties, which enhance electronic transfer and stabilize the molecule, such as in previously published

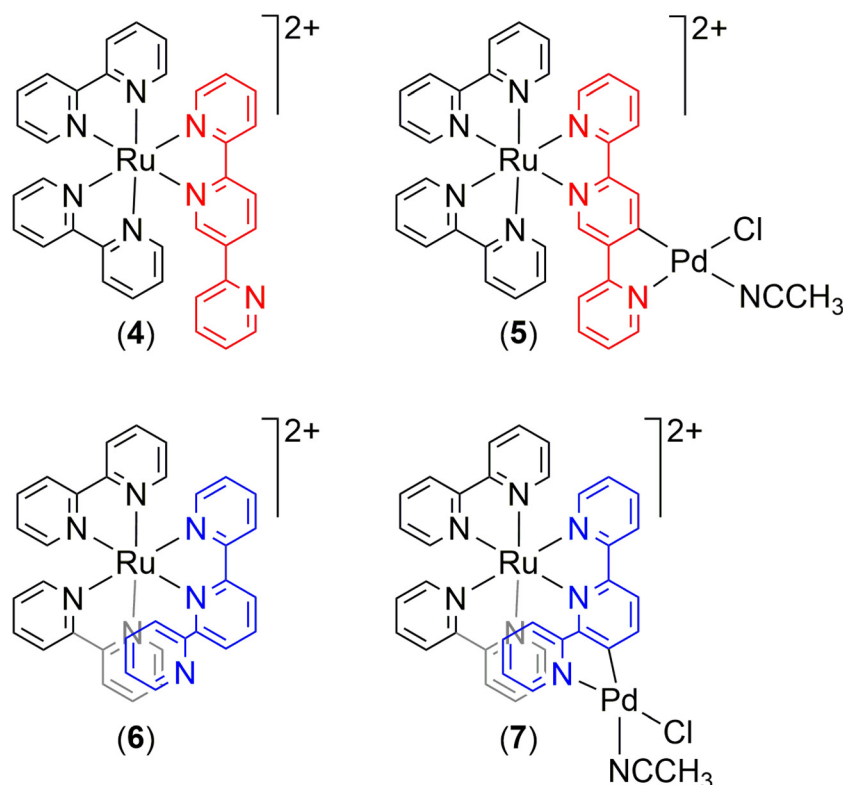


Fig. 1 Structures of 4–7.

results for similar systems.^{46–48} The covalent bridge among metal units should indeed promote the electron transfer from the reduced photosensitizer to the catalyst centre while lowering the probability of decomposition.⁴⁹ This suspicion was confirmed when the stability of the dinuclear compound **8** was found to be similar to that of the previously reported Ir–Co complexes used as a dyad.^{46,50} It is also important to point out that complex **8** promotes the photocatalytic proton reduction upon absorption in the yellow- and red-light regions, giving however a lower TON than that under green light.

An additional consideration that should be made for the design of photocatalysts for H₂ is that metals such as Ru, Pt or Ir are very useful but scarce in the Earth's crust, and for this reason they are very expensive. An ideal catalyst should be cheap, easy to be obtained and recyclable. Only under these conditions can it be generally and practically used. Therefore, when possible, scarce and expensive metals should be substituted with abundant and cheap ones. Nevertheless, also easily recyclable complexes should be synthesized in order to make the H₂ generation process sustainable. Among these metals, Fe, Ni and Co stand out as good candidates to be employed, instead of their expensive “neighbours” noble metals. Examples of heterodinuclear complexes were published looking to satisfy this need by replacing the Ru-based photosensitizer with a cheaper moiety. This strategy led to the porphyrin Pt/M complexes **9–11** (M = Cu (**9**), Co (**10**), Zn (**11**)), in which a porphyrin-phenanthroline hybrid ligand is coordinated to the non-Pt metal and serves as a photosensitizer. This ligand is also covalently bonded to a Pt halide through the exposed nitrogen atoms of the phenanthroline scaffold, which is in charge of proton reduction (Fig. 3).⁵¹ The choice of the porphyrin ligand was based on its cheap and easy

synthesis,^{52–58} while Pt was preferred over Pd due to its lower tendency to form nanoparticles.⁵⁹

Complexes **9–11** were evaluated as photocatalysts for H₂ generation in acetonitrile/water (6 : 1) mixtures under 470 nm light, using triethylamine (30%) as a sacrificial electron donor.

It was shown that the activity of these complexes strongly depends on the nature of the metal centre accommodated in the porphyrin moiety, as well as on the halogen ions bonded to platinum(II). The activities of the compounds to photocatalyze the generation of H₂ from water were compared in acetonitrile under monochromatic light at 470 nm and an inert atmosphere, using water (10%) as a proton source and triethylamine (30%) as the sacrificial electron donor.³⁷ Their activities were compared also with the known Ru catalysts [RutpphzPtX₂] (**12**) (tpphz = tetrapyrrodo[3,2-*a*:2',3'-*c*:3'',2''-*h*:2''',3'''-*j*]phenazine; X = Cl (**12-Cl₂**), I (**12-I₂**))⁶⁰ under the same conditions. Complexes containing Pt–Cu (**9**) and Pt–Co (**10**) were not active, while the Pt–Zn complex (**11**) showed a different activity depending on the halide bonded to Pt. The complex **11-I₂**, in which the Pt is bonded to two iodides, displayed lower activity than the Ru–Pt complex **12-I₂** (2 vs. 256 for TON_{48h}), while **11-Cl₂** was *ca.* 4 times more active than **12-Cl₂** (25 vs. 7 for TON_{48h}). Experimental studies supported that initially a doubly reduced (and protonated) species forms, which further evolves to give rise to H₂. More recently, it was also showed that the generation of H₂ by **12-I₂** can be improved after 48 h upon reactivation of the inactive complex that is formed under irradiation by the reduction of the tpphz bridge. The restoration of the reduced species was achieved by oxidation with singlet oxygen photochemically generated *in situ*. This reparation process was cyclically used up to eight times, allowing the extension of the total reaction time to 444 h and obtaining a total TON > 3000.⁶¹

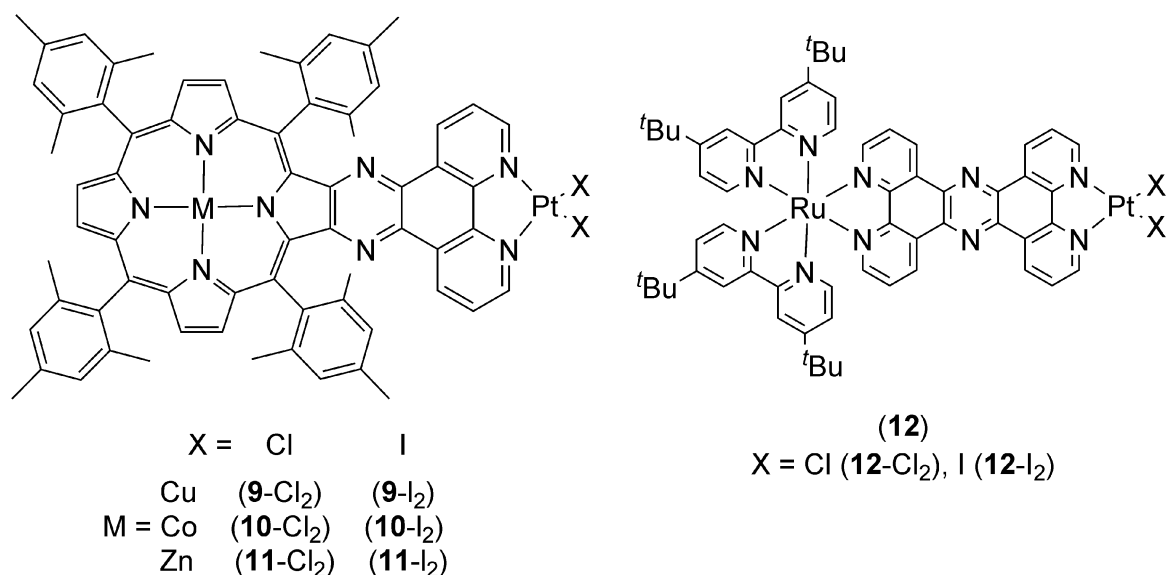


Fig. 3 Structures of complexes **9–12**.

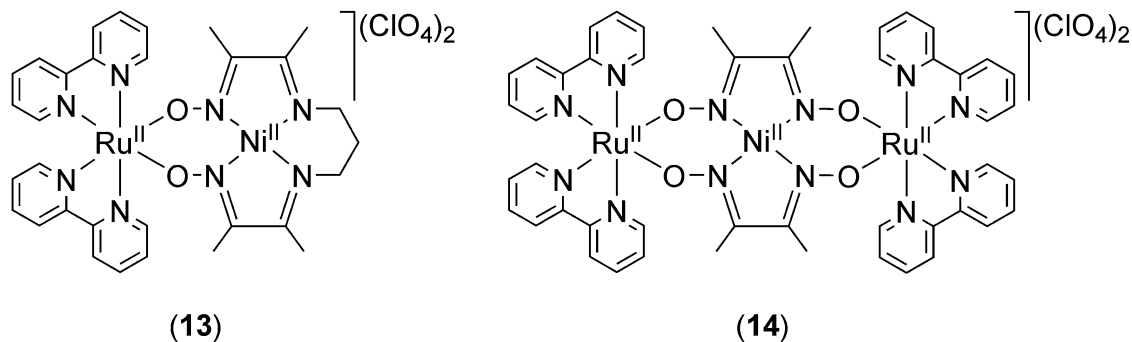


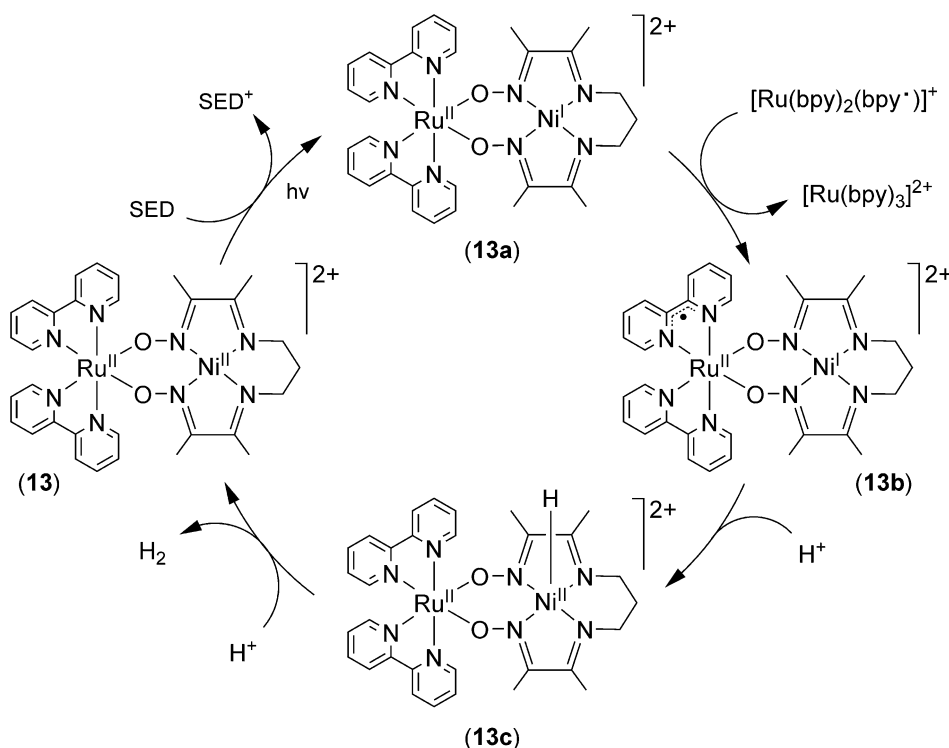
Fig. 4 Structures of complexes **13** and **14**.

In 2021 one of the most interesting systems for the photogeneration of hydrogen from water using the heterometallic Ru–Ni complexes **13** and **14** (Fig. 4) as catalysts was published.⁶² These complexes were evaluated for the generation of H₂ in a mixture of acetonitrile/water (1 : 1) at pH 11, with triethylamine (5% v/v) as the sacrificial electron donor and employing a blue light source at 480 nm.

The catalytic studies showed the different activities both catalysts have, despite being parent compounds. Dimetallic complex **13** requires the presence of the photosensitizer [Ru(bpy)₃]²⁺ (Table 1), which is necessary to promote the reduction of 2H⁺. In fact, during the catalytic cycle, after the formation of **13a** upon excitation and one-electron reductive quenching through SED → SED⁺, the Ni centre needs a second

electron to accomplish the proton reduction. The required electron is supplied to **13a** by the photosensitizer, giving the triplet complex **13b**. Then, the protonation of **13b** affords the [Ru^{II}Ni^{II}] hydride **13c**, which reacts with an additional proton to generate H₂ and restore **13** (Scheme 2).

Interestingly, the trimetallic complex **14** photocatalyzed the generation of H₂ (TON_{24h} = 49) better than **13** but without an additional photosensitizer. It is proposed that complex **14** undergoes intramolecular multielectron transfer from Ru to Ni, while at the Ni centre the generation of dihydrogen occurs. The experimental and DFT studies suggested that during the catalytic cycle the molecular complex is the unique catalytic compound, and species containing Ni(0) do not form during the reaction. Complex **14** evolves into **14a** [Ru^{II}Ni^IRu^{II}(bpy)⁰]



Scheme 2 The proposed mechanism for the generation of H₂ when **13** is used as the catalyst.

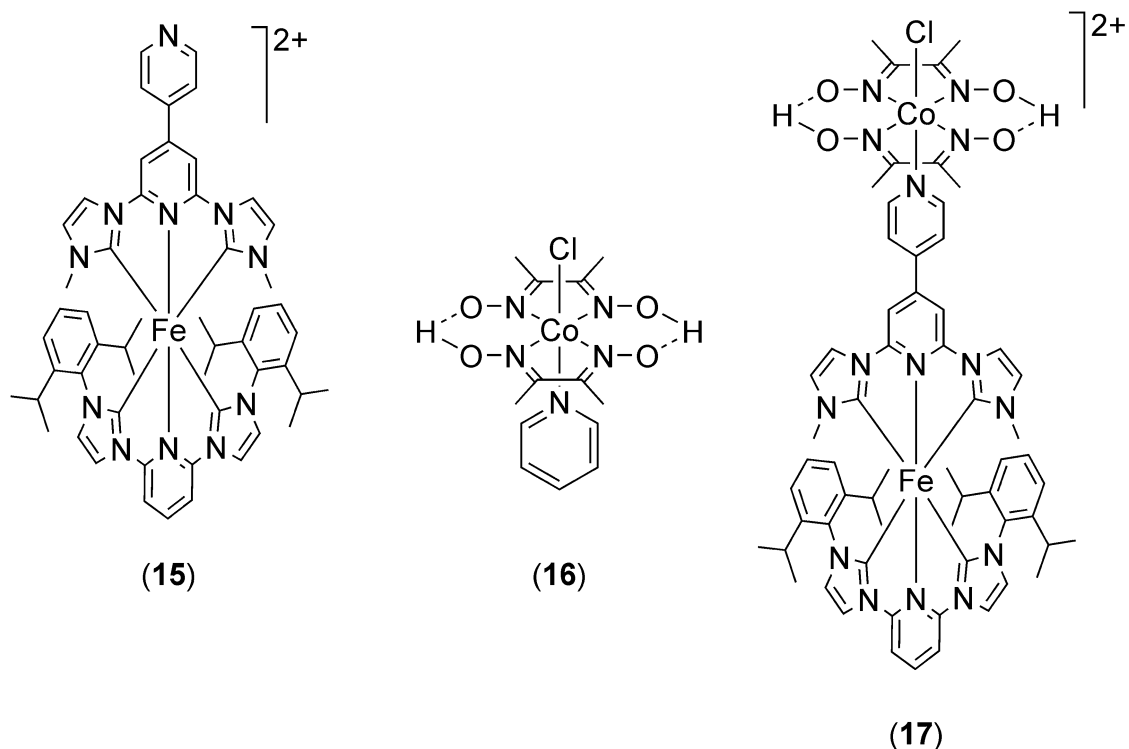


Fig. 5 Structures of complexes 15–17.

convenient alternative should be the use of abundant and easily recyclable metals, complexes containing noble metals are still the best option to develop useful catalysts to photogenerate H_2 . In this line, a series of complexes containing Ru and Rh (**18–20**) were prepared (Fig. 6) and evaluated.⁶⁴

A trace amount of H_2 was photo-generated catalytically by **20** in an Ar-saturated mixture of dimethylacetamide/triethanolamine (4 : 1, v/v) under irradiation at $\lambda = 480$ nm, using as the

reductant 1,3-dimethyl-2-phenyl-2,3-dihydro-1*H*-benzo-[*d*]imidazole (BIH). Nevertheless, the generation of H_2 was significantly improved when the BIH was substituted for a proton source such as 3,5-difluorophenol (3,5- F_2 -PhOH) or 2-(1,3-dimethyl-2,3-dihydro-1*H*-benzo[*d*]imidazol-2-yl) phenol (BI(OH)H). The H_2 generation quantum yields (Φ_{H_2}) after 3 h of irradiation were respectively 11.0% (3,5- F_2 -PhOH) and 9.9% (BI(OH)H). A similar reaction under CO_2 led to different and interesting results, as without the addition of a proton donor, H_2 was produced as the main product with a very high Φ_{H_2} (16.4%), and only small amounts of HCOOH and CO were detected. This particular behaviour was justified by the evidence that TEOA reacts with CO_2 -generating protons as showed by Fujita *et al.*⁶⁵ which gives rise to an acidic zwitterionic alkyl carbonate.

In all the performed studies the dimetallic **20** showed the highest activity for the H_2 production, probably due to the faster electron transfer from the Ru photosensitizer unit to the Rh catalyst centre.⁶⁶ It was also shown that the photocatalytic ability of the $\text{Ru}^{\text{II}}\text{-Rh}^{\text{III}}$ photocatalysts largely depends on the diimine ligand of the Rh centre, which can give rise to HCOOH instead of H_2 as the main product, under the same reaction conditions. Additionally, the introduction of electron-donating methoxy substituents at the 6,6'-positions of the bipyridine unit of the bridging ligand induces the formation of H_2 with high selectivity, producing only a small amount of HCOOH, similarly to that observed for Ru-mononuclear systems containing bpy.⁶⁷ The analogue complex without sub-

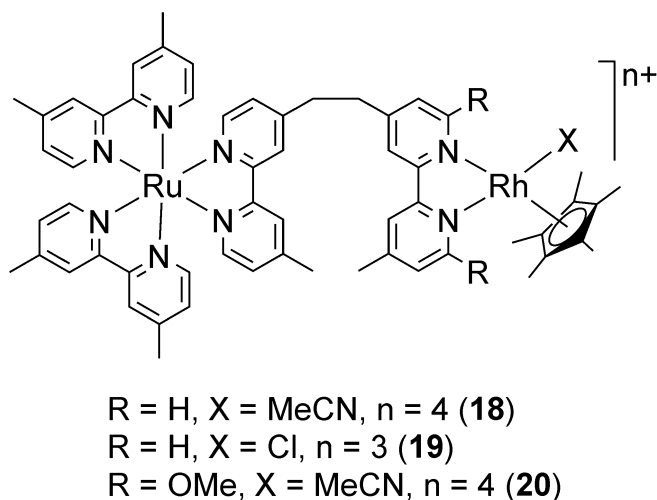


Fig. 6 Structures of complexes 18–20.

stitution on the bipyridine unit of the bridging ligand (**18**) does not significantly produce H₂ photocatalytically due to the fact that Ru^{II}–Rh^{III}(H) and/or Ru^{II}–Rh(Cp*H) do not react with protons, even under a CO₂ atmosphere. In fact, after excitation, the reactivity of complex **18** goes towards the reduction of CO₂ to HCOOH rather than the generation of H₂ (after 3 h of irradiation: TON_{HCOOH} = 82, Φ_{HCOOH} = 15.5%; TON_{H₂} = 34, Φ_{H_2} = 3.2%). It seems that electron-donating substituents at the 6,6' positions of the bpy ligand in **20** introduce the electron density close to the Rh, helping the formation of Ru^{II}–Rh^{III}(H)–OMe and/or Ru^{II}–Rh(Cp*H)–OMe species. These intermediates could assist mutual interactions between the proton source and hydride species, leading to a faster H₂ evolution.⁶⁸

Remarks

The reaction conditions employed for the photogeneration of H₂ using the active catalysts described before, as well as their TOFs, TONs and the amount of produced H₂ are summarized in Table 1. Based on the reported data, the most robust catalyst is the Ru/Pt complex **12-I₂**, showing a TON of 465 at a concentration of 5.2×10^{-5} M after 48 h. Also, the Ir/Co complex **8** showed a TON as high as 251, but after 3.8 h. Nevertheless, **8** is the catalyst that displayed the highest TOF (83.6 h⁻¹), being able to produce 12.5×10^4 μmol of hydrogen in 3.8 h at 0.1 M concentration. For what concerns the reactions involved in direct H₂O reduction, without an additional source of protons, among the complexes reviewed in this work, **12-I₂** is again the best catalyst. So far, maybe due to solubility reasons, there is still a lack of heterometallic catalysts that can work in pure H₂O and, therefore, designing and synthesizing heterometallic water-soluble photocatalysts for the generation of H₂ from water should be an utmost projection for future developments. Finally, it would be beneficial to substitute the commonly used organic sacrificial electron donors for more eco-friendly electron sources. In this sense, the most virtuous approach should be the use of water as an electron source, which could be achieved by coupling the heterometallic catalysts with electrode systems or molecular devices active for water oxidation, for example.

Conclusions

Despite the interesting results obtained to date stronger efforts need to be carried out to develop a more efficient catalyst for the photo-generation of H₂. Some important considerations for the design of these compounds should be taken into account. Firstly, the appropriate choice of the ligands is of extreme importance, which determines the energy of the excited states that need to be finely tuned to avoid fast and non-productive decay pathways. Also, anchoring the photosensitizer to the catalytic centre *via* covalent bonds generally improves the efficiency of the catalyst but this point should

also be supported by the ³MLCT state lifetime at the photosensitizer, which must be long enough to allow inter-metallic electron transfer. The metal centres support the photo-collection and proton reduction, therefore appropriate metals should be chosen, with an eye on their price, abundance in the Earth's crust and recyclability. Noble-metal-based moieties are still the most efficient, but investigations conducted on first-row metals have shown that good catalysts can be obtained also with metals such as Ni or Co. So far, the results obtained are very promising and show that the heterometallic systems are very good photocatalysts for hydrogen generation from water under solar irradiation, which would be the best procedure to generate industrially this important energy vector.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

The authors thank Junta de Andalucía (Secretaría General de Investigación y Transformación Económica, Industria, Conocimiento y Universidades. Dirección General de Investigación y Transferencia del Conocimiento. Consejería de Transformación Económica, Industria, Conocimiento y Universidades) for funding the group PAI FQM-317 and the project PY20_00791, and the Universidad de Almería for the project UAL2020-RNM-B2084 (both projects co-funded by the European Commission FEDER program).

Notes and references

- 1 S. M. Jung, J. Lee and W. J. Song, *J. Inorg. Biochem.*, 2021, **223**, 111552.
- 2 B. M. Trost, *Science*, 1991, **254**, 1471–1477.
- 3 P. A. Wender and B. L. Miller, *Nature*, 2009, **460**, 197–201.
- 4 M. Sawamura and Y. Ito, *Chem. Rev.*, 1992, **92**, 857–871.
- 5 J.-A. Ma and D. Cahard, *Angew. Chem., Int. Ed.*, 2004, **43**, 4566–4583.
- 6 H. Yamamoto and K. Futatsugi, *Angew. Chem., Int. Ed.*, 2005, **44**, 1924–1942.
- 7 M. Kanai, N. Kato, E. Ichikawa and M. Shibasaki, *Synlett*, 2005, 1491–1508.
- 8 E. N. Jacobsen and M. S. Taylor, *Angew. Chem., Int. Ed.*, 2006, **45**, 1520–1543.
- 9 S. Mukherjee, J. W. Yang, S. Hoffmann and B. List, *Chem. Rev.*, 2007, **107**, 5471–5569.
- 10 M. Shibasaki, M. Kanai, S. Matsunaga and N. Kumagai, *Acc. Chem. Res.*, 2009, **42**, 1117–1127.
- 11 J. Park and S. Hong, *Chem. Soc. Rev.*, 2012, **41**, 6931–6943.
- 12 P. Gale, T. Gunnlaugsson and P. Ballester, *Chem. Soc. Rev.*, 2010, **39**, 3810–3830.
- 13 A. C. Ghosh, C. Duboc and M. Gennari, *Coord. Chem. Rev.*, 2021, **428**, 213606.

- 14 I. D. Young, M. Ibrahim, R. Chatterjee, S. Gul, F. D. Fuller, S. Koroidov, A. S. Brewster, R. Tran, R. Alonso-Mori, T. Kroll, T. Michels-Clark, H. Laksmono, R. G. Sierra, C. A. Stan, R. Hussein, M. Zhang, L. Douthit, M. Kubin, C. de Lichtenberg, L. Vo Pham, H. Nilsson, M. H. Cheah, D. Shevela, C. Saracini, M. A. Bean, I. Seuffert, D. Sokaras, T. C. Weng, E. Pastor, C. Weninger, T. Fransson, L. Lassalle, P. Bräuer, P. Aller, P. T. Docker, B. Andi, A. M. Orville, J. M. Glowina, S. Nelson, M. Sikorski, D. Zhu, M. S. Hunter, T. J. Lane, A. Aquila, J. E. Koglin, J. Robinson, M. Liang, S. Boutet, A. Y. Lyubimov, M. Uervirojnangkoorn, N. W. Moriarty, D. Liebschner, P. v. Afonine, D. G. Waterman, G. Evans, P. Wernet, H. Dobbek, W. I. Weis, A. T. Brunger, P. H. Zwart, P. D. Adams, A. Zouni, J. Messinger, U. Bergmann, N. K. Sauter, J. Kern, V. K. Yachandra and J. Yano, *Nature*, 2016, **540**, 453–457.
- 15 M. Suga, F. Akita, M. Sugahara, M. Kubo, Y. Nakajima, T. Nakane, K. Yamashita, Y. Umena, M. Nakabayashi, T. Yamane, T. Nakano, M. Suzuki, T. Masuda, S. Inoue, T. Kimura, T. Nomura, S. Yonekura, L. J. Yu, T. Sakamoto, T. Motomura, J. H. Chen, Y. Kato, T. Noguchi, K. Tono, Y. Joti, T. Kameshima, T. Hatsui, E. Nango, R. Tanaka, H. Naitow, Y. Matsuura, A. Yamashita, M. Yamamoto, O. Nureki, M. Yabashi, T. Ishikawa, S. Iwata and J. R. Shen, *Nature*, 2017, **543**, 131–135.
- 16 M. D. Ward, C. A. Hunter and N. H. Williams, *Acc. Chem. Res.*, 2018, **51**, 2073–2082.
- 17 L. J. Jongkind, X. Caumes, A. P. T. Hartendorp and J. N. H. Reek, *Acc. Chem. Res.*, 2018, **51**, 2115–2128.
- 18 C. J. Brown, F. D. Toste, R. G. Bergman and K. N. Raymond, *Chem. Rev.*, 2015, **115**, 3012–3035.
- 19 N. C. Gianneschi, M. S. Masar and C. A. Mirkin, *Acc. Chem. Res.*, 2005, **38**, 825–837.
- 20 M. Yoshizawa, J. K. Klosterman and M. Fujita, *Angew. Chem., Int. Ed.*, 2009, **48**, 3418–3438.
- 21 M. Otte, *ACS Catal.*, 2016, **6**, 6491–6510.
- 22 M. D. Pluth, R. G. Bergman and K. N. Raymond, *Acc. Chem. Res.*, 2009, **42**, 1650–1659.
- 23 M. Raynal, P. Ballester, A. Vidal-Ferran and P. W. N. M. van Leeuwen, *Chem. Soc. Rev.*, 2014, **43**, 1660–1733.
- 24 Fuel-Cell Breakthroughs For Hydrogen Aviation https://www.fch.europa.eu/sites/default/files/FCH%20Docs/EG0321335ENN_002%20%28ID%2012364809%29.pdf (accessed August 2022).
- 25 B. A. Pinaud, J. D. Benck, L. C. Seitz, A. J. Forman, Z. Chen, T. G. Deutsch, B. D. James, K. N. Baum, G. N. Baum, S. Ardo, H. Wang, E. Miller and T. F. Jaramillo, *Energy Environ. Sci.*, 2013, **6**, 1983–2002.
- 26 Fuel Cells and Hydrogen Joint Undertaking, Programme Review Report 2020–2021, <https://www.fch.europa.eu/publications/programme-review-report-2020-2021>, (accessed August 2022).
- 27 D. M. Cropek, A. Metz, A. M. Müller, H. B. Gray, T. Horne, D. C. Horton, O. Poluektov, D. M. Tiede, R. T. Weber, W. L. Jarrett, J. D. Phillips and A. A. Holder, *Dalton Trans.*, 2012, **41**, 13060–13073.
- 28 M. Elvington, J. Brown, S. M. Arachchige and K. J. Brewer, *J. Am. Chem. Soc.*, 2007, **129**, 10644–10645.
- 29 S. M. Arachchige, J. Brown and K. J. Brewer, *J. Photochem. Photobiol., A*, 2008, **197**, 13–17.
- 30 T. A. White, S. L. H. Higgins, S. M. Arachchige and K. J. Brewer, *Angew. Chem., Int. Ed.*, 2011, **50**, 12209–12213.
- 31 R. Zhou, B. Sedai, G. F. Manbeck and K. J. Brewer, *Inorg. Chem.*, 2013, **52**, 13314–13324.
- 32 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**, 1654–1658.
- 33 G. F. Manbeck, T. Canterbury, R. Zhou, S. King, G. Nam and K. J. Brewer, *Inorg. Chem.*, 2015, **54**, 8148–8157.
- 34 R. Zhou, G. F. Manbeck, D. G. Wimer and K. J. Brewer, *Chem. Commun.*, 2015, **51**, 12966–12969.
- 35 G. F. Manbeck, E. Fujita and K. J. Brewer, *J. Am. Chem. Soc.*, 2017, **139**, 7843–7854.
- 36 D. Ghosh, H. Takeda, D. C. Fabry, Y. Tamaki and O. Ishitani, *ACS Sustainable Chem. Eng.*, 2019, **7**, 2648–2657.
- 37 S. Rau, B. Schäfer, D. Gleich, E. Anders, M. Rudolph, M. Friedrich, H. Görls, W. Henry and J. G. Vos, *Angew. Chem., Int. Ed.*, 2006, **45**, 6215–6218.
- 38 M. Karnahl, C. Kuhnt, F. W. Heinemann, M. Schmitt, S. Rau, J. Popp and B. Dietzek, *Chem. Phys.*, 2012, **393**, 65–73.
- 39 K. Sakai and H. Ozawa, *Coord. Chem. Rev.*, 2007, **251**, 2753–2766.
- 40 J. K. White and K. J. Brewer, *Chem. Commun.*, 2015, **51**, 16123–16126.
- 41 J. Liu and W. Jiang, *Dalton Trans.*, 2012, **41**, 9700–9707.
- 42 H. J. Sayre, T. A. White and K. J. Brewer, *Inorg. Chim. Acta*, 2017, **454**, 89–96.
- 43 J. Cao and Y. Zhou, *Phys. Chem. Chem. Phys.*, 2017, **19**, 11529–11539.
- 44 G. Singh Bindra, M. Schulz, A. Paul, R. Groarke, S. Soman, J. L. Inglis, W. R. Browne, M. G. Pfeffer, S. Rau, B. J. MacLean, M. T. Pryce and J. G. Vos, *Dalton Trans.*, 2012, **41**, 13050–13059.
- 45 C. Lentz, O. Schott, T. Auvray, G. Hanan and B. Elias, *Inorg. Chem.*, 2017, **56**, 10875–10881.
- 46 A. Jacques, O. Schott, K. Robeyns, G. S. Hanan and B. Elias, *Eur. J. Inorg. Chem.*, 2016, **12**, 1779–1783.
- 47 E. Rousset, D. Chartrand, I. Ciofini, V. Marvaud and G. S. Hanan, *Chem. Commun.*, 2015, **51**, 9261–9264.
- 48 M. Schulz, M. Karnahl, M. Schwalbe and J. G. Vos, *Coord. Chem. Rev.*, 2012, **256**, 1682–1705.
- 49 E. Deponti and M. Natali, *Dalton Trans.*, 2016, **45**, 9136–9147.
- 50 A. Fihri, V. Artero, A. Pereira and M. Fontecave, *Dalton Trans.*, 2008, **41**, 5567–5569.
- 51 P. Lang, J. Habermehl, S. I. Troyanov, S. Rau and M. Schwalbe, *Chem. – Eur. J.*, 2018, **24**, 3225–3233.
- 52 C. Y. Lin, C. F. Lo, L. Luo, H. P. Lu, C. S. Hung and E. W. G. Diau, *J. Phys. Chem. C*, 2009, **113**, 755–764.

- 53 J. K. Park, J. Chen, H. R. Lee, S. W. Park, H. Shinokubo, A. Osuka and D. Kim, *J. Phys. Chem. C*, 2009, **113**, 21956–21963.
- 54 M. V. Martínez-Díaz, G. de La Torre and T. Torres, *Chem. Commun.*, 2010, **46**, 7090–7108.
- 55 L. L. Li and E. W. G. Diau, *Chem. Soc. Rev.*, 2012, **42**, 291–304.
- 56 M. Urbani, M. Grätzel, M. K. Nazeeruddin and T. Torres, *Chem. Rev.*, 2014, **114**, 12330–12396.
- 57 Y. Wang, X. Li, B. Liu, W. Wu, W. Zhu and Y. Xie, *RSC Adv.*, 2013, **3**, 14780–14790.
- 58 B. Liu, W. Zhu, Y. Wang, W. Wu, X. Li, B. Chen, Y. T. Long and Y. Xie, *J. Mater. Chem.*, 2012, **22**, 7434–7444.
- 59 M. G. Pfeffer, B. Schäfer, G. Smolentsev, J. Uhlig, E. Nazarenko, J. Guthmuller, C. Kuhnt, M. Wächtler, B. Dietzek, V. Sundström and S. Rau, *Angew. Chem., Int. Ed.*, 2015, **54**, 5044–5048.
- 60 M. G. Pfeffer, T. Kowacs, M. Wächtler, J. Guthmuller, B. Dietzek, J. G. Vos and S. Rau, *Angew. Chem., Int. Ed.*, 2015, **54**, 6627–6631.
- 61 M. G. Pfeffer, C. Müller, E. T. E. Kastl, A. K. Mengele, B. Bagemihl, S. S. Fauth, J. Habermehl, L. Petermann, M. Wächtler, M. Schulz, D. Chartrand, F. Laverdière, P. Seeber, S. Kupfer, S. Gräfe, G. S. Hanan, J. G. Vos, B. Dietzek-Ivanšić and S. Rau, *Nat. Chem.*, 2022, **14**, 500–506.
- 62 N. el Harakeh, A. C. P. de Morais, N. Rani, J. A. G. Gomez, A. Cousino, M. Lanznaster, S. Mazumder, C. N. Verani, N. el Harakeh, A. Cousino, C. N. Verani, A. C. P. de Morais, J. A. G. Gomez, M. Lanznaster, N. Rani and S. Mazumder, *Angew. Chem., Int. Ed.*, 2021, **60**, 5723–5728.
- 63 M. Huber-Gedert, M. Nowakowski, A. Kertmen, L. Burkhardt, N. Lindner, R. Schoch, R. Herbst-Irmer, A. Neuba, L. Schmitz, T. K. Choi, J. Kubicki, W. Gawelda and M. Bauer, *Chem. – Eur. J.*, 2021, **27**, 9905–9918.
- 64 D. Ghosh, D. C. Fabry, D. Saito and O. Ishitani, *Energy Fuels*, 2021, **35**, 19069–19080.
- 65 R. N. Sampaio, D. C. Grills, D. E. Polyansky, D. J. Szalda and E. Fujita, *J. Am. Chem. Soc.*, 2020, **142**, 2413–2428.
- 66 Y. Yamazaki, K. Ohkubo, D. Saito, T. Yatsu, Y. Tamaki, S. Tanaka, K. Koike, K. Onda and O. Ishitani, *Inorg. Chem.*, 2019, **58**, 11480–11492.
- 67 T. K. Todorova, T. N. Huan, X. Wang, H. Agarwala and M. Fontecave, *Inorg. Chem.*, 2019, **58**, 6893–6903.
- 68 W. H. Wang, J. F. Hull, J. T. Muckerman, E. Fujita and Y. Himeda, *Energy Environ. Sci.*, 2012, **5**, 7923–7926.