



Cite this: *Dalton Trans.*, 2015, **44**, 10423

Received 23rd January 2015,  
Accepted 29th April 2015

DOI: 10.1039/c5dt00324e

www.rsc.org/dalton

# Carboxy derivatised Ir(III) complexes: synthesis, electrochemistry, photophysical properties and photocatalytic hydrogen generation†

Avishek Paul, Nivedita Das, Yvonne Halpin, Johannes G. Vos\* and Mary T. Pryce\*

In this contribution the synthesis and characterisation of a series of novel mixed ligand iridium(III) complexes, functionalised with a carboxy ester or phosphonate groups are reported. These groupings are introduced on the 4-position of either the phenyl pyridine or the 2,2'-bipyridyl ligands. A low temperature high yield synthesis for the precursor  $[\text{Ir}(\text{ppy}-\text{COOEt})_2(\mu-\text{Cl})_2]$  was developed. The photophysical and electrochemical properties of these compounds are also described, together with their behaviour as photosensitisers for the generation of hydrogen from water.

## Introduction

Recently there has been considerable interest in the excited state properties of Ir(III) complexes based on cyclometallated ligands of the type  $[\text{Ir}(\text{ppy})_2(\text{L-L})]^n$ , where ppy is 4(2-pyridyl) benzene and L-L a chelating ligand. This interest was instigated by the work of Thompson<sup>1</sup> and others<sup>2</sup> on the application of cyclometallated iridium(III) compounds in the development of OLEDs and more recently have been investigated as dyes in solar cells.<sup>3</sup> While photovoltaic cells generate electricity from sunlight, this energy cannot easily be stored and as a result the development of alternative systems capable of storing solar energy as a fuel or as stock chemicals using molecular photocatalysts is under consideration. Promising options include the development of catalytic systems for the production of hydrogen from water or CO<sub>2</sub> reduction using visible light.<sup>4</sup> Recently, cyclometallated iridium(III) complexes have been studied as photosensitisers for CO<sub>2</sub> reduction, and analogues such as  $[\text{Ir}(\text{ppy})_2(\text{bpy})]^+$ , have shown excellent catalytic efficiency in solar driven hydrogen production in solution.<sup>5</sup> Importantly their photophysical properties can be fine-tuned by ligand modification and as a result a wide range of Ir(III) based complexes have been prepared for various applications.

However, homogeneous photocatalytic systems contain sacrificial agents such as TEA, or TEOA which can damage the catalytic activity of the photocatalyst. Immobilisation of the photocatalysts on NiO surfaces would furthermore increase

their stability, as is shown by Ru-based dyes used in the Grätzel cell.<sup>6</sup> Recently, we reported novel preparation methods for NiO surfaces which would be highly suitable for this propose.<sup>7</sup> The ultimate photocatalytic device is likely to be based on heterogeneous surface bound photocatalytic systems where semiconductor electrodes such as NiO<sub>x</sub> act as an electron donor and this would eliminate the need for sacrificial electron donors. At present carboxy and phosphonate moieties are considered the most suitable linkers and these have been used for the immobilisation of iridium dyes in sensitised solar cells.<sup>8</sup>

In this contribution we report the synthesis and characterisation of a new series of iridium mononuclear complexes functionalised with carboxy ester and phosphonate groups for future immobilisation on p-type semiconductor surfaces such as NiO<sub>x</sub>. (see Fig. 1). The photophysical and electrochemical

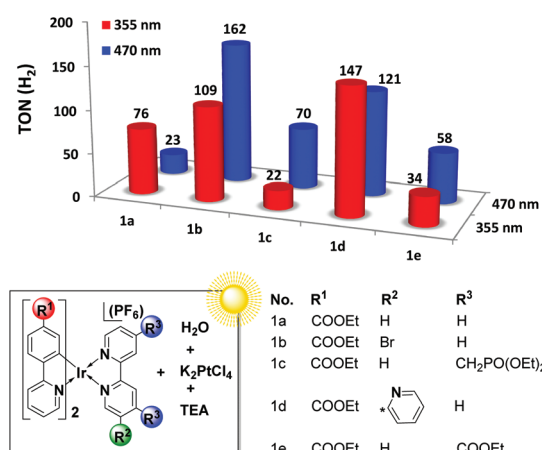


Fig. 1 Molecular structures of the synthesised Ir(III) complexes and photocatalytic hydrogen generation.

School of Chemical Sciences, Dublin City University, Dublin 9, Ireland.

E-mail: mary.pryce@dcu.ie, han.vos@dcu.ie; Fax: (+353) 17005503;

Tel: (+353) 17008005

† Electronic supplementary information (ESI) available. See DOI: 10.1039/c5dt00324e

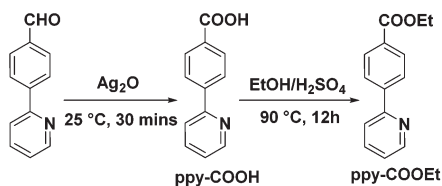
properties of the compounds were investigated and photocatalytic studies on the hydrogen generation capacity of the compounds were carried out. Turnover numbers (TON defined as number of hydrogen molecules formed per molecule of catalyst) of up to 162 for photocatalytic hydrogen generation were obtained. The results obtained indicate that the excited state properties of the cyclometallated Ir(III) complexes are maintained with variation in the R group on the bipyridyl ligand, and in addition the compounds show well defined reversible electrochemistry.

## Results and discussion

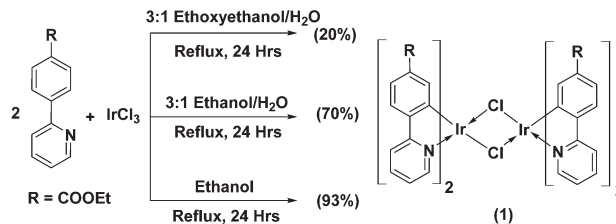
### Synthesis

**Synthetic procedure for ethyl 4-(2-pyridyl)benzoate (ppy-COOEt).** The 4 position of the phenyl ring in phenylpyridine was functionalised with an ethyl carboxy ester group by using 4-(2-pyridyl)benzaldehyde as the starting material. There are many reported procedures for the synthesis of carboxy ester containing phenylpyridines<sup>9,10</sup> such as the Negishi<sup>11,12</sup> and other cross-coupling reactions.<sup>13</sup> In the approach reported in this manuscript, esterification was carried out using a two-step procedure, which is inexpensive and less time consuming than previous reports. The first step involves oxidation of the aldehyde group and the second step is an acid catalysed esterification (see Scheme 1). The oxidation of the aldehyde group can be carried out using various literature procedures.<sup>14</sup> Here the oxidation was carried out using silver oxide and aqueous NaOH solution, providing the products with yields of 90%. The reaction was performed at room temperature and was complete within 30 minutes. 10 cm<sup>3</sup> of THF was added to the reaction mixture to fully dissolve the 4-(2-pyridyl)benzaldehyde. THF was removed from the filtrate by rotary evaporation after filtration of the reaction mixture. The presence of THF in the filtrate can cause the formation of a soluble acidified product which will not precipitate from the aqueous solution and reduce the yield of 4-(2-pyridyl)benzoic acid. 4-(2-Pyridyl)benzoic acid was esterified using a well-studied acid catalysed reaction.<sup>9</sup>

**Synthesis of [Ir(ppy-COOEt)<sub>2</sub>(μ-Cl)]<sub>2</sub>, (1).** Several procedures have been reported to synthesise Ir(III) compounds, containing ppy or functionalised ppy ligands.<sup>15</sup> Many of these synthetic procedures require high boiling point solvents such as ethoxy ethanol, methoxy ethanol and glycerol with 20–50% of water.



**Scheme 1** Reaction scheme for synthesis of ethyl 4-(2-pyridyl)benzoate.



**Scheme 2** Various reaction conditions for the synthesis of [Ir(ppy-COOEt)<sub>2</sub>(μ-Cl)]<sub>2</sub>, (1).

In our case, the ppy ligand was functionalised with thermally unstable carboxy ester or phosphonate groups, thus limiting the possibility of high temperature reactions. When a 3 : 1 ethoxy ethanol/water solvent system was used (see Scheme 2) for the preparation of carboxy ester containing iridium complexes, relatively low yields were obtained (70–6%) and the crude reaction mixture contained a mixture of products.

As a result more benign reaction conditions were considered and the solvent system was altered from ethoxy ethanol/water to ethanol/water. The reaction mixture was heated at reflux temperature for 24 hours in 3 : 1 ethanol/water (Scheme 2). This reaction provided a better yield of about 70% compared to the ethoxyethanol literature procedure which gave a yield of 20%. Surprisingly, the product was soluble in a 3 : 1 ethanol/water mixture but not in water. Therefore, the product was precipitated from the reaction mixture with the addition of excess water. Further optimisation of the yield was obtained by changing from ethanol/water to ethanol. Carrying out the reaction without water provided a 93% yield. The use of an inert (N<sub>2</sub>) atmosphere did not increase the yield. In summary, absolute ethanol was found to be the best solvent for synthesising [Ir(ppy-COOEt)<sub>2</sub>(μ-Cl)]<sub>2</sub>, (1) with excellent yields and without the need for inert conditions.

### NMR spectroscopy

<sup>1</sup>H NMR and 2D NMR spectra of the ligands and the Ir(III) complexes are provided in the ESI (see ESI Fig. S1 to S14†). Interestingly, there are considerable differences in the chemical shifts of the ester groups present in [Ir(ppy-COOEt)<sub>2</sub>(dppb)](PF<sub>6</sub>) (1c) and [Ir(ppy-COOEt)<sub>2</sub>(dceb)](PF<sub>6</sub>) (1e) as shown in Fig. 2. The chemical shifts of the protons in ppy-COOEt ligands do not vary significantly with the addition of a bpy-based ligand. (See also ESI, Fig. S9, S11 and S13†).

NMR data also suggests identical chemical environments for the two-ester groups on the two different ppy-COOEt ligands. Based on this observation, two possible geometries, (I) and (II) (Fig. 3) are possible but crystallographic data are required to identify the correct geometry. NMR data rules out the possibility of geometry (III).

### Electrochemistry

Electrochemical data for all Ir(III) complexes are tabulated in Table 1. A reversible oxidation wave, representing the Ir(III)/Ir(IV) redox couple, is observed in the cyclic voltammogram of

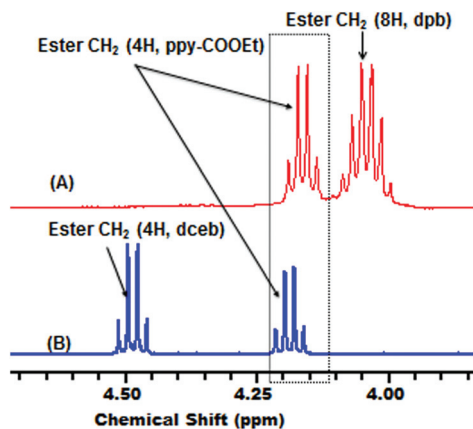


Fig. 2 A comparison of the ester CH<sub>2</sub> groups signals (q) in (A) [Ir(ppy-COOEt)<sub>2</sub>(dpb)](PF<sub>6</sub>), **1c** and (B) [Ir(ppy-COOEt)<sub>2</sub>(dceb)](PF<sub>6</sub>), **1e**.

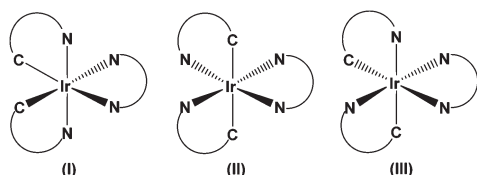


Fig. 3 Three possible geometries of [Ir(C<sup>^N</sup>)<sub>2</sub>(N<sup>^N</sup>)]<sup>+</sup> type complexes.

each complex. This is a one-electron reversible process as indicated by a peak to peak separation ( $\Delta E_p$ ) of between 60 and 100 mV and an anodic to cathodic current ratio close to unity. The oxidation of the dinuclear species, **1** occurs at a potential at least 300 mV less positive than the corresponding process in **1a** through to **1e** as a result of the replacement of the bridging chlorine atoms with bipy type ligands.

Compared to the parent compound [Ir(ppy)<sub>2</sub>Cl]<sub>2</sub>, the oxidation potential of compound **1** is 160 mV more positive, illustrating the electron withdrawing capacity of the ester groups. The bipyridine ligand's strong  $\pi$ -acceptor character is evident when comparing the oxidation potential of **1a** with that of **1** with the latter being 350 mV less positive than the former. The addition of carboxy ester groups on the ppy ligand clearly alters the electrochemical properties of the complexes. Bernhard *et al.* reported an oxidation potential for [Ir(ppy)<sub>2</sub>(bpy)]<sup>+</sup> of 1.25 V vs. SCE<sup>18</sup> at least 220 mV less positive than the corresponding process in compounds **1a** to **1e**. The data show that as expected the carboxy ester substituents act as strong acceptor groups capable of lowering the energy gap between the HOMO and LUMO of the complex by strongly stabilising the LUMO and only slightly stabilising the HOMO.<sup>16</sup>

Several reductive processes are observed in the cyclic voltammograms of each complex. Fig. 4 reveals the cyclic voltammogram of **1a** where multiple quasi-reversible waves are observed. The first (least negative) reduction of both **1** and **1b** is irreversible at slow scan rates (0.01 V s<sup>-1</sup> to <10 V s<sup>-1</sup>). However, at scan rates of 10 V s<sup>-1</sup> and higher the feature

Table 1 Redox properties of compounds (**1a–1e**), vs. SCE,. The electrolyte employed was 0.1 M TBAPF<sub>6</sub> in acetonitrile. Redox data from the literature are included for comparison. \* Not reported

Complex	$E_{1/2, \text{oxidation}}$ (V) [ $\Delta E_p$ (mV)]	$E_{1/2, \text{reduction}}$ [V] [ $\Delta E_p$ (mV)]
<b>1</b>	+1.17 [70]	–1.79 ( $E_{pc}$ ) –1.90 [80] –2.08 [90] –2.23 [50] –2.44 [135]
<b>1a</b>	+1.52 [70]	–1.27 [70] –1.72 [70] –1.93 [75] –2.22 [100] –2.35 [120]
<b>1b</b>	+1.54 [70]	–1.15 ( $E_{pc}$ ) –1.27 [60] –1.70 ( $E_{pc}$ ) –1.75 ( $E_{pc}$ ) –1.95 [75] –2.17 ( $E_{pc}$ )
<b>1c</b>	+1.47 [70]	–1.29 [60] –1.43 [60] –1.80 [90] –2.00 [110]
<b>1d</b>	+1.47 [70]	–1.19 [70] –1.71 [75] –1.89 [70] –2.13 ( $E_{pc}$ )
<b>1e</b>	+1.50 [70]	–0.97 [80] –1.50 [70] –1.90 [80] –2.14 ( $E_{pc}$ )
[Ir(ppy) <sub>2</sub> Cl] <sub>2</sub>	+1.01	Not observed
Ir(ppy) <sub>3</sub> <sup>17</sup>	+0.73 [*]	–2.28 [*] –2.53 [*]
[Ir(ppy) <sub>2</sub> (bpy)] <sup>+</sup> <sup>18</sup>	+1.25 [65]	–1.42 [70]

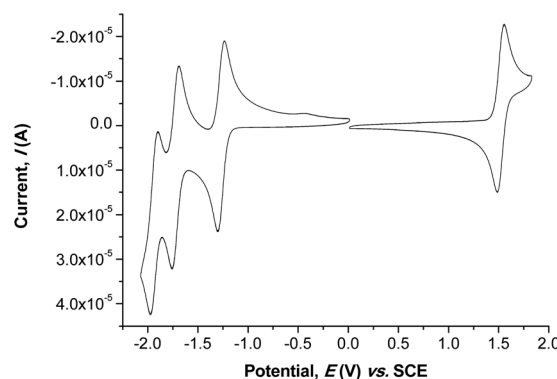


Fig. 4 Cyclic voltammetry of **1a** ([Ir(ppy-COOEt)<sub>2</sub>(bpy)]<sup>+</sup>), using 0.1 M TBAPF<sub>6</sub> in acetonitrile as the supporting electrolyte. Scan rate: 100 mV s<sup>-1</sup>.

becomes quasi-reversible. The first (least negative) reductive process in **1a** to **1e** is observed at considerably more positive potentials when compared to [Ir(ppy)<sub>2</sub>(bpy)]<sup>+</sup> species for which the first reduction is found at –1.42 V vs. SCE (Table 1). This is again associated with electron withdrawing capacity of the ester moiety.

## Photophysical properties

**Absorption spectra.** The absorption data for all the iridium complexes are summarised in Table 2, with spectra for representative complexes displayed in Fig. 5. All spectra obtained in this study are similar to that of other iridium complexes reported in the literature. The absorption bands for the iridium complexes in the UV region ( $\lambda < 300$  nm) are attributed to the ligand-based transition ( $\pi-\pi^*$ ) and the less intense absorption bands in the region greater than 300 nm are assigned to metal  $\rightarrow$  ligand charge transfer ( $^1\text{MLCT}$  and  $^3\text{MLCT}$ ) transitions.<sup>16</sup> In the case of **1e**, the absorption band at the lowest energy ( $\lambda_{\text{max}} = 489$  nm, is more pronounced than any of the other complexes studied. This is at slightly higher energy than of a similar compound,  $[\text{Ir}(\text{ppy})_2(\text{dceb})]^+$  where a  $\lambda_{\text{max}}$  was reported at 530 nm.<sup>19</sup>

**Photophysical data.** The lifetimes and emission quantum yields obtained for complexes **1a–1e** are summarised in Table 2, with the emission spectra displayed in Fig. 6 All complexes have similar emission profiles, with complex **1e**, which contains four carboxy units, substantially red shifted by 80 nm ( $2363\text{ cm}^{-1}$ ) compared to **1a**, which has two carboxy units present. Thus the  $\lambda_{\text{max}}$  can be tuned in these iridium(III) complexes with functionalisation of the ligands. Surprisingly, the dpb ancillary ligand (emission occurs at 554 nm) has the minimum electronic effect on the emission wavelength compared to the bipy ligand (emission occurs at 540 nm). This difference has been attributed to the better mesomeric and inductive ability of the carboxy ester groups compared to the other functional groups. The lifetime data

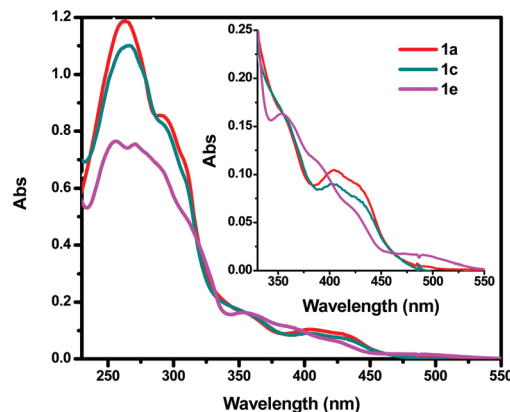


Fig. 5 Absorption spectra of Ir(III) complexes in acetonitrile. (Concentrations of all the complexes are  $\sim 10^{-5}$  M).

obtained for complexes **1a–1e** are all within the range 215–342 ns, and increase to between 320–457 ns when de-aerated. These lifetimes and also the emission quantum yields in this manuscript are somewhat higher to that previously reported in the literature for the parent complex  $[\text{Ir}(\text{ppy})_2(\text{bpy})](\text{PF}_6)$  (338 ns).<sup>21</sup> The excited state lifetimes do not vary significantly with the location or number of carboxy units on the cyclometallated ppy or the bipy based ancillary ligands. The absence of strong vibrational structure in the emission spectra suggests that the emission is mostly  $^3\text{MLCT}$  in character.<sup>22</sup>

Table 2 Photophysical and photocatalytic data for hydrogen production for the Ir(III) complexes<sup>a</sup>

Complex	$\lambda_{\text{abs}}$ (nm)	$\epsilon \times 10^3$ ( $\text{M}^{-1}\text{ cm}^{-1}$ )	$\lambda_{\text{em}}$ (nm)	$\lambda_{\text{em}}$ (nm) 77 K	$\phi_{\text{em}}^a$	$\phi_{\text{em}}^b$	$\tau^a$ (ns)	$\tau^b$ (ns)	$\tau$ (ns) 77 K	TONs ( $\text{H}_2$ )	
										355 nm	470 nm
$[\text{Ir}(\text{ppy})_2(\text{bpy})]^+$	337 477	0.6	583	520	—	0.06	—	338	—		63 <sup>20</sup>
<b>1a</b>	487 427 402 361	0.72 4.29 4.94 7.67	540	570 585	0.035	0.21	256	457	720	76	23
<b>1b</b>	487 422 402 355	0.98 4.38 4.99 9.56	564	565	0.033	0.28	292	424	719	109	162
<b>1c</b>	485 422 402 348	1.13 4.38 4.99 9.07	554	560	0.02	0.19	215	325	724	22	70
<b>1d</b>	495 428 404 356	1.14 3.45 4.57 7.12	566	540 585	0.032	0.20	230	320	740	147	121
<b>1e</b>	489 420 353	1.24 8.02 10.74	619	620	0.03	0.18	342	384	560	34	58

<sup>a</sup> All absorption spectra were obtained at room temperature. Emission spectra were obtained using 355 nm as the excitation wavelength with an absorbance of  $\sim 0.15$ , in nitrogen purged dichloromethane, lifetime measurements were performed at 355 nm in aerated<sup>a</sup> and deaerated<sup>b</sup>  $\text{CH}_2\text{Cl}_2$ , and the emission quantum yields in aerated<sup>a</sup> and deaerated<sup>b</sup>  $\text{CH}_3\text{CN}$ .

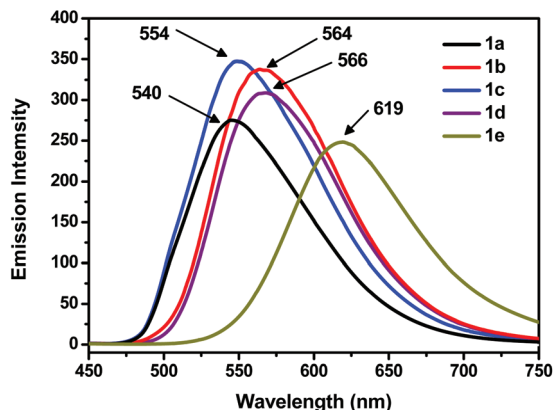


Fig. 6 Emission spectra of the Ir(III) complexes recorded in  $\text{CH}_2\text{Cl}_2$ . All samples had an absorbance of  $\sim 0.15$  at the excitation wavelength (355 nm).

### Photocatalytic hydrogen generation

The iridium complexes, **1a–e** were assessed for their ability to act as a photosensitiser for hydrogen production. The reactions were carried out in mixtures containing acetonitrile/TEA/water (8:1:1) and using  $\text{K}_2[\text{PtCl}_4]$  as the catalyst. Two irradiation wavelengths were employed; 350 and 470 nm, and the TONs obtained are given in Fig. 1 and Table 2, together with plots for hydrogen production over a 24 hour period in Fig. 7. Control vials with no catalyst added produced negligible amounts of hydrogen. For the iridium complexes investigated, TONs at  $\lambda_{\text{exc}} = 355$  nm ranged from 22 to 147, while at  $\lambda_{\text{exc}} = 470$  nm TONs ranged from 23 to 162, where the amount of hydrogen varied with the substituent, and also with the wavelength employed, however no obvious trend was notable. Although these values are not among the highest reported they

do show that the introduction of ester or phosphonate groups do not prevent the compounds from acting as a photosensitiser. In agreement with prior studies reported by Bernhard *et al.*,<sup>20</sup> on similar complexes the water reduction cascade is thought to involve reductive quenching of the excited iridium photosensitiser by TEA, followed by electron transfer to the platinum catalytic centre.

It is difficult to compare TONs reported here to that of the parent compound  $[\text{Ir}(\text{ppy})_2(\text{bpy})]^+$ , as the reaction conditions are very different. However, when our results are compared with the iridium complex  $[\text{Ir}(\text{ppy})_2(\text{bpy})]^+$ , where a TON = 63 was reported, both complexes **1b** and **1d** show improved TONs.<sup>20</sup>

## Conclusions

This study introduces ligands containing the carboxy ester group in heteroleptic monomeric iridium complexes. Modified synthetic procedures for the ligand ppy-COOEt and the associated chloro-bridged iridium precursor complex were developed, with high yields. All the complexes show electrochemical reversibility and they produced hydrogen photocatalytically at the two wavelengths employed. The introduction of the ester or phosphonate groups does not seem to fundamentally change the photophysical behaviour of the compounds. At this stage it is not possible to explain the differences in the efficiencies for photocatalytic hydrogen generation until the nature of the excited states involved are identified. However, it is expected that the nature of the lowest energy triplet excited state may be affected and this is at present under investigation.

## Experimental

### Physical measurements

$^1\text{H}$  NMR (400 MHz) and 2D COSY were recorded in deuterated solvents ( $\text{d}_3$ -acetonitrile,  $\text{CDCl}_3$ ) on a Bruker AC400 NMR and AC600 NMR Spectrometer with TMS or residual solvent peaks as reference. XWIN-NMR processor and ACDLABS 12.0 NMR processor software were employed to process the free induction decay (FID) profiles. The H–H 2-D COSY NMR involved the accumulation of 128 FIDs of 16 scans. Elemental analyses (CHN) were carried out using Exador Analytical CE440 by the Microanalytical Department, University College Dublin, Ireland. UV–Vis absorption spectra were recorded on a Shimadzu 3100 UV-Vis/NIR spectrophotometer with interfaced to an Elonex PC575 desktop computer. Emission spectra were recorded on a Perkin-Elmer LS0B luminescence spectrophotometer, and the excitation wavelength was set at 350 nm. All emission spectra were initially generated by Perkin-Elmer FL Winlab custom built software. The optical densities of all the sample solution for the emission spectra and lifetime studies were approximately 0.1–0.2 A.U. at the excitation wavelength 350 nm.

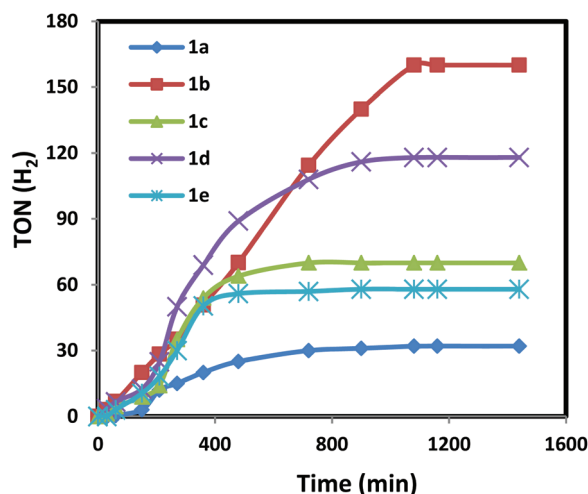


Fig. 7 Amount of hydrogen produced is expressed in TONs at various time intervals from 0 to 24 h using 470 nm as irradiation source.  $[\text{PS}] = [\text{K}_2\text{PtCl}_4] = 1.2 \times 10^{-4}$  M.



Electrochemical experiments were carried out using a CH Instruments Version 8.15 software controlled electrochemical bipotentiostat (CHI750C) with typical analyte concentrations of 1 mM. The working electrode was a glassy carbon (GC) macro electrode (3 mm in diameter) with a Pt wire as the counter electrode. All electrochemical experiments were referenced against a Hg/HgSO<sub>4</sub> reference electrode. All potential values were then calibrated against the saturated calomel electrode (SCE) by adding ferrocene as an internal reference ( $E_{1/2}$  (Fc/Fc<sup>+</sup>) = +0.43 V vs. SCE). The GC electrode was prepared by manually polishing with 0.05 µm alumina slurry (CH Instruments, Inc.) followed by sonicating in Millipore water and finally in acetonitrile. Tetrabutylammonium hexafluorophosphate (TBAPF<sub>6</sub>, Fluka, electrochemical grade ≥99.0%) in acetonitrile (Aldrich anhydrous, 99.8%) was used as electrolyte and solvent respectively. The electrochemical cell was degassed using argon for at least 15 minutes prior to each experiment and a blanket of argon was maintained throughout.

### Photocatalytic hydrogen generation experiments

Photocatalytic hydrogen production experiments were carried out using an air-cooling apparatus for maintaining the solutions at room temperature at 22 °C, during irradiation using LEDs (355 and 470 nm). Acetonitrile used was dried over calcium hydride and the triethylamine dried over sodium before being freshly distilled under nitrogen. The samples were prepared in GC vials (4.9 ml volume, VWR) with a known headspace of 2.9 ml. Photosensitiser (Iridium complexes) and catalyst K<sub>2</sub>[PtCl<sub>4</sub>] were taken in 1 : 1 ratio and dissolved in 4 : 1 Acetonitrile/H<sub>2</sub>O solution containing  $1.2 \times 10^{-4}$  M of PS. 1.9 ml of the Ir/Pt solution and 90 µL of triethylamine were added to the GC vials in 2 ml sample under argon atmosphere. Subsequently, the GC vials were irradiated with 355 ( $22 \times 10^{-3}$  W m<sup>-2</sup>) and 470 nm ( $0.4$  W m<sup>-2</sup>) wavelength LEDs for 18 hours. After irradiation, 100 µL samples were drawn from the headspace and injected into the GC. The experiments were repeated two times.

### Synthesis

All the solvents used for spectroscopy were of spectroscopic grade. IrCl<sub>3</sub>·3H<sub>2</sub>O and 4-(2-pyridyl) benzaldehyde used for the reactions below were obtained from Sigma-Aldrich and used without further purification. All other solvents and reagents used were reagent grade. 4,4'-Dicarboxyethyl-2,2'-bipyridine (dceb) was synthesised according to literature procedure.<sup>23</sup> Synthetic procedure details for 4,4'-bis(diethylmethylphosphonato)-2,2'-bipyridine (dppb),<sup>24</sup> 2,2':5',2''-terpyridine (bpy)<sup>25</sup> and 5-bromo-2,2'-bipyridine (5Brbpy)<sup>26</sup> can be found in ESI.†

**4-(2-Pyridyl)benzoic acid (ppy-COOH).** 4-(2-Pyridyl)benzoic acid (ppy-COOH) was synthesised following a modified literature procedure.<sup>27</sup> 2.94 g (73.5 mmol) of NaOH was dissolved in 50 cm<sup>3</sup> of water and the brown suspension of silver oxide was prepared by adding a solution of 6.32 g (37.22 mmol) of AgNO<sub>3</sub> solution in 50 cm<sup>3</sup> of water. The solution was stirred continuously during the addition of silver nitrate solution to complete the reaction. The brown semisolid mixture was then

cooled in an ice bath. 2 g (10.91 mmol) of 4-(2-pyridyl)benzaldehyde was added to the cooled reaction mixture with stirring. The procedure was modified by adding 10 cm<sup>3</sup> of THF to the reaction mixture for complete dissolution of 4-(2-pyridyl)benzaldehyde. After 30 minutes, no more reactant particle was left to dissolve and a silver mirror appeared on the side of the conical flask. The reaction was completed in 30 minutes as followed by TLC. The black silver suspension was removed by suction filtration. The black residue was further washed with hot water to obtain maximum amount of product. The combined filtrate was acidified with aqueous HCl solution to precipitate out the product from the aqueous solution. The product was then collected by filtration. Yield: 90% (1.95 g, 9.81 mmol). <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>) δ ppm 7.43 (dd, *J* = 7.52, 4.74 Hz, 1 H), 7.94 (dd, *J* = 7.77, 7.77 Hz, 1 H), 8.01–8.10 (m, 3 H), 8.17–8.27 (m, 2 H), 8.72 (dd, *J* = 6.57, 1.01 Hz, 1 H).

**Ethyl 4-(2-pyridyl)benzoate (ppy-COOEt).** Esterification of 4-(2-pyridyl)benzoic acid was performed using a literature procedure.<sup>28</sup> 1 g (5.02 mmol) of 4-(2-pyridyl)benzoic acid was converted to ethyl 4-(2-pyridyl)benzoate. Yield: 93% (1.06 g, 4.66 mmol). <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>) δ ppm 1.35 (t, *J* = 7.07 Hz, 3 H), 4.35 (q, *J* = 7.07 Hz, 2 H), 7.43 (dd, *J* = 7.45, 4.80, 0.88 Hz, 1 H), 7.94 (td, *J* = 7.77, 1.89 Hz, 1 H), 8.04–8.10 (m, 3 H), 8.21–8.28 (m, 2 H), 8.72 (dd, *J* = 4.80, 0.76 Hz, 1 H).

**[Ir(ppy-COOEt)(μ-Cl)]<sub>2</sub>·2H<sub>2</sub>O.** 1.79 mg (2.64 mmol) of IrCl<sub>3</sub>·3H<sub>2</sub>O and 1.2 g (5.28 mmol) of ppy-COOEt were added to 30 cm<sup>3</sup> EtOH and refluxed for 24 hours. The reaction mixture turned from dark brown to orange. The reaction solution was reduced to 2–5 cm<sup>3</sup> by rotary evaporation and 50 cm<sup>3</sup> water was added. A yellow precipitate was collected by filtration. The product was washed with water and diethyl ether, and further recrystallised from DCM/ethanol solution. Yield: 1.67 g (1.24 mmol, 93%). <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>) δ ppm 1.16 (td, *J* = 7.14, 1.64 Hz, 12 H), 4.03–4.15 (m, 8 H), 6.28 (s, 2 H), 6.85 (s, 2 H), 7.42 (dd, *J* = 8.08, 1.77 Hz, 2 H), 7.47 (dd, *J* = 8.08, 1.77 Hz, 2 H), 7.62 (dd, *J* = 7.33, 7.33 Hz, 2 H), 7.72 (t, *J* = 7.20 Hz, 2 H), 7.89 (d, *J* = 8.34 Hz, 2 H), 7.94 (d, *J* = 8.08 Hz, 2 H), 8.13 (t, *J* = 8.46 Hz, 2 H), 8.22 (td, *J* = 7.77, 1.39 Hz, 2 H), 8.33 (d, *J* = 7.83 Hz, 2 H), 8.42 (d, *J* = 8.34 Hz, 2 H), 9.57 (d, *J* = 4.55 Hz, 2 H), 9.87 (d, *J* = 6.06 Hz, 2 H). Elemental analysis of C<sub>56</sub>H<sub>48</sub>Cl<sub>2</sub>Ir<sub>2</sub>N<sub>4</sub>O<sub>8</sub>·2H<sub>2</sub>O; M.W. = 1400.40; Calc: C 48.17, H 3.75, N 4.01. Found: C 48.33, H 3.61 and N 3.78%.

**[Ir(ppy-COOEt)<sub>2</sub>(bpy)](PF<sub>6</sub>), 1a.** [Ir(ppy-COOEt)<sub>2</sub>(bpy)](PF<sub>6</sub>). 100 mg (0.07 mmol) of [Ir(ppy-COOEt)(μ-Cl)]<sub>2</sub> and 25.23 mg (0.16 mmol) of bpy were refluxed in 30 cm<sup>3</sup> 4 : 1 ethanol/dichloromethane mixture for 6 hours in the dark. The solvent was completely removed by rotary evaporation. 30 cm<sup>3</sup> of water was added and sonicated for 10 minutes. The aqueous solution was filtered twice. A saturated aqueous solution of KPF<sub>6</sub> was added to the filtrate and stirred for 30 minutes. The aqueous layer was extracted with DCM. The product was further washed with diethyl ether. The crude product was further purified by recrystallisation from DCM/ethanol solution. Yield: 53% (66.34 mg, 0.07 mmol). <sup>1</sup>H NMR (400 MHz, Acetonitrile-*d*<sub>3</sub>) δ ppm 1.23 (t, *J* = 7.20 Hz, 6 H), 4.18 (q, *J* = 7.07 Hz, 4 H), 6.87 (d, *J* = 1.26 Hz, 2 H), 7.18 (dd, *J* = 7.45, 5.94,

1.52 Hz, 2 H), 7.52 (dd,  $J = 7.71, 5.43, 1.01$  Hz, 2 H), 7.68 (dd,  $J = 8.21, 1.64$  Hz, 2 H), 7.72 (dd,  $J = 5.81, 0.76$  Hz, 2 H), 7.93 (d,  $J = 8.08$  Hz, 2 H), 7.95–8.03 (m, 4 H), 8.13–8.23 (m, 4 H), 8.56 (d,  $J = 8.08$  Hz, 2 H). Elemental analysis for  $C_{38}H_{32}F_6IrN_4O_4P$ , M.W.: 947.88. Calc: C 48.25, H 3.34, N 5.92. Found: C 48.22, H 3.34 and N 5.89%.

**[Ir(ppy-COOEt)<sub>2</sub>(5Br bpy)](PF<sub>6</sub>)·H<sub>2</sub>O, 1b.** [Ir(ppy-COOEt)<sub>2</sub>(5Brbpy)](PF<sub>6</sub>), **1b** was synthesised using synthetic procedure for **1a**. 610.23 mg (0.44 mmol) of [Ir(ppy-COOEt)(μ-Cl)]<sub>2</sub> and 232 mg (0.98 mmol) of 5Brbpy were reacted. Yield: 41% (370 mg, 0.36 mmol). <sup>1</sup>H NMR (400 MHz, Acetonitrile-*d*<sub>3</sub>) δ ppm 1.23 (t,  $J = 7.20$  Hz, 6 H), 4.18 (qd,  $J = 7.07, 4.29$  Hz, 8 H), 6.82 (s, 2 H), 6.88 (s, 2 H), 7.16–7.23 (m, 4 H), 7.54 (ddd,  $J = 7.64, 5.49, 1.26$  Hz, 2 H), 7.64–7.71 (m, 6 H), 7.81 (dd,  $J = 6.57, 1.52$  Hz, 2 H), 7.87–8.02 (m, 12 H), 8.13–8.24 (m, 6 H), 8.34 (dd,  $J = 8.84, 2.27$  Hz, 2 H), 8.47 (d,  $J = 8.34$  Hz, 2 H), 8.54 (d,  $J = 8.08$  Hz, 2 H). Elemental analysis for  $C_{38}H_{31}BrF_6IrN_4O_4P \cdot H_2O$ . M.W.: 1044.79. Calc: C 44.68, H 3.38, N 5.36. Found: C 43.79, H 2.78 and N 5.30%.

**[Ir(ppy-COOEt)<sub>2</sub>(dppb)](PF<sub>6</sub>), 1c.** [Ir(ppy-COOEt)<sub>2</sub>(dppb)](PF<sub>6</sub>) was synthesised using the synthetic procedure for **1a**. 100 mg (0.07 mmol) of [Ir(ppy-COOEt)(μ-Cl)]<sub>2</sub> and 73 mg (0.16 mmol) of dppb were reacted. Yield: 6% (10 mg, 0.008 mmol). <sup>1</sup>H NMR (400 MHz, Acetonitrile-*d*<sub>3</sub>) δ ppm 1.08–1.25 (m, 18 H), 3.42–3.62 (m, 4 H), 3.95–4.12 (m, 8 H), 4.16 (q,  $J = 7.07$  Hz, 4 H), 6.87 (d,  $J = 1.52$  Hz, 2 H), 7.19 (t,  $J = 6.32$  Hz, 2 H), 7.46 (d,  $J = 5.31$  Hz, 2 H), 7.63 (dd,  $J = 8.08, 1.77$  Hz, 2 H), 7.75 (d,  $J = 5.56$  Hz, 2 H), 7.86–7.92 (m, 4 H), 7.96 (t,  $J = 7.33$  Hz, 2 H), 8.19 (d,  $J = 8.08$  Hz, 2 H), 8.76 (br. s., 2 H). Elemental analysis for  $C_{48}H_{56}F_6IrN_4O_{10}P_3 \cdot 2H_2O$ . M.W.: 1284.14. Calc: C 43.68, H 4.71, N 4.36. Found: C 43.84, H 4.36 and N 4.29%.

**[Ir(ppy-COOEt)<sub>2</sub>(bpp)](PF<sub>6</sub>), 1d.** [Ir(ppy-COOEt)<sub>2</sub>(dpp)](PF<sub>6</sub>) was synthesised using the synthetic procedure for **1a**. 200 mg (0.15 mmol) of [Ir(ppy-COOEt)(μ-Cl)]<sub>2</sub> and 75.35 mg (0.32 mmol) 2,5-di(2-pyridyl)pyridine (bpp) were reacted. Yield: 184.5 mg (0.18 mmol, 60%). <sup>1</sup>H NMR (400 MHz, Acetonitrile-*d*<sub>3</sub>) δ ppm 1.23 (td,  $J = 7.14, 1.14$  Hz, 7 H), 4.15–4.22 (m, 4 H), 6.88 (d,  $J = 1.26$  Hz, 1 H), 6.90 (d,  $J = 1.26$  Hz, 1 H), 7.18 (m, 2 H), 7.38 (dd,  $J = 7.58, 4.80$  Hz, 1 H), 7.53 (dd,  $J = 7.64, 5.49$  Hz, 1 H), 7.66 (dt,  $J = 8.08, 1.01$  Hz, 1 H), 7.70 (td,  $J = 8.59, 1.77$  Hz, 2 H), 7.75 (dd,  $J = 6.44, 1.39$  Hz, 1 H), 7.81–7.86 (m, 2 H), 7.90–8.03 (m, 5 H), 8.15–8.23 (m, 3 H), 8.55 (dd,  $J = 5.68, 1.89$  Hz, 1 H), 8.60 (d,  $J = 8.34$  Hz, 1 H), 8.62–8.67 (m, 2 H), 8.70–8.75 (m, 1 H). Elemental analysis for  $C_{34}H_{35}F_6IrN_5O_4P$ ; M.W.: 1024.96; Calc: C 50.49, H 3.45, N 6.85. Found: C 50.37, H 3.33 and N 6.56%.

**[Ir(ppy-COOEt)<sub>2</sub>(dceb)](PF<sub>6</sub>), 1e.** [Ir(ppy-COOEt)<sub>2</sub>(dceb)](PF<sub>6</sub>) was synthesised using the synthetic procedure for **1a**. 100 mg (0.07 mmol) of [Ir(ppy-COOEt)(μ-Cl)]<sub>2</sub> and 48.51 mg (0.16 mmol) of dceb were reacted. Yield: 50% (76.44 mg, 0.07 mmol). <sup>1</sup>H NMR (400 MHz, Acetonitrile-*d*<sub>3</sub>) δ ppm 1.23 (t,  $J = 7.07$  Hz, 6 H), 1.43 (t,  $J = 7.07$  Hz, 6 H), 4.19 (q,  $J = 7.07$  Hz, 4 H), 4.49 (q,  $J = 7.07$  Hz, 4 H), 6.85 (d,  $J = 1.77$  Hz, 2 H), 7.17 (dd,  $J = 7.52, 5.87$  Hz, 2 H), 7.63–7.76 (m, 4 H), 7.94 (d,  $J = 8.08$  Hz, 2 H), 7.95–8.03 (m, 4 H), 8.19 (dd,  $J = 5.56, 0.76$  Hz, 2 H), 8.21 (d,  $J = 7.83$  Hz, 2 H), 9.10 (dd,  $J = 1.64, 0.63$  Hz, 2 H).

Elemental analysis for  $C_{44}H_{40}F_6IrN_4O_8P$ , M.W.: 1092. Calc: C 48.48, H 3.70, N 5.14. Found: C 48.03, H 3.48, and N 4.93%.

## Acknowledgements

The authors thank the Environmental Protection Agency (EPA Grant 2008-ET-MS-3-S2) and SFI/TIDA/E2763, SFI/TIDA/2435 for financial support.

## Notes and references

- (a) S. Lamansky, D. Murphy, F. A. Razzaq, H. E. Lee, C. Adachi, P. E. Burrows, S. R. Forrest and M. E. Thompson, *J. Am. Chem. Soc.*, 2001, **123**, 4304; (b) S. Lamansky, P. Djurovich, D. Murphy, F. A. Razaq, R. Kwong, I. Tsyba, M. Bortz, B. Mui, R. Bau and M. E. Thompson, *Inorg. Chem.*, 2001, **40**, 1704; (c) A. B. Tamayo, S. Garon, T. Sajoto, P. I. Djurovich, I. M. Tsyba, R. Bau and M. E. Thompson, *Inorg. Chem.*, 2005, **44**, 8723.
- (a) S. Culham, P.-H. Lanoë, V. L. Whittle, M. C. Durrant, J. A. G. Williams and V. N. Kozhevnikov, *Inorg. Chem.*, 2013, **52**, 10992; (b) I. M. Dixon, J. P. Collin, J. P. Sauvage, L. Flamigni, S. Encinas and F. Barigelletti, *Chem. Soc. Rev.*, 2000, **29**, 385; (c) E. Orselli, G. S. Kottas, A. E. Konradsson, P. Coppo, R. Fröhlich, L. De Cola, A. van Dijken, M. Büchel and H. Börner, *Inorg. Chem.*, 2007, **46**, 11082; (d) P. H. Lanoë, C. M. Tong, R. W. Harrington, M. R. Probert, W. Clegg, J. A. G. Williams and V. N. Kozhevnikov, *Chem. Commun.*, 2014, **50**, 6831; (e) L. F. Gildea, A. S. Batsanov and J. A. G. Williams, *Dalton Trans.*, 2013, **42**, 10388; (f) K. Beydoun, M. Zaarour, J. A. G. Williams, T. Roisnel, V. Dorcet, A. Planchat, A. Boucekkine, D. Jacquemin, H. Doucet and V. Guerschais, *Inorg. Chem.*, 2013, **52**, 12416; (g) M. Zaarour, A. Singh, C. Latouche, J. A. G. Williams, I. Ledoux-Rak, J. Zyss, A. Boucekkine, H. L. Bozec, V. Guerschais, C. Dragonetti, A. Colombo, D. Roberto and A. Valore, *Inorg. Chem.*, 2013, **52**, 7987.
- E. Baranoff, J.-H. Yum, M. Grätzel and M. K. Nazeeruddin, *J. Organomet. Chem.*, 2009, **694**, 2661.
- (a) For reviews see: E. Fujita, *Coord. Chem. Rev.*, 1999, **185**, 373; (b) A. J. Morris, G. J. Meyer and E. Fujita, *Acc. Chem. Res.*, 2009, **42**, 1983; (c) K. Sakai and H. Ozawa, *Coord. Chem. Rev.*, 2007, **251**, 2753; (d) S. Losse, J. G. Vos and S. Rau, *Coord. Chem. Rev.*, 2010, **254**, 2492; (e) V. Artero, M. Chavarot-Kerlidou and M. Fonecave, *Angew. Chem., Int. Ed.*, 2011, **50**, 7238; (f) A. Inagaki and M. Akita, *Coord. Chem. Rev.*, 2010, **254**, 1220; (g) W. T. Eckenhoff and R. Eisenberg, *Dalton Trans.*, 2012, **41**, 13004; (h) M. Schulz, M. Karnahl, M. Schwalbe and J. G. Vos, *Coord. Chem. Rev.*, 2012, **256**, 1682; (i) P. D. Frischmann, K. Mahata and F. Wurthel, *Chem. Soc. Rev.*, 2013, **42**, 1847.
- (a) B. F. DiSalle and S. Bernhard, *J. Am. Chem. Soc.*, 2011, **133**, 11819; (b) S. Metz and S. Bernhard, *Chem. Commun.*,

- 2010, **46**, 7551; (c) L. L. Tinker and S. Bernhard, *Inorg. Chem.*, 2009, **48**, 10507; (d) P. N. Curtin, L. L. Tinker, C. M. Burgess, E. D. Cline and S. Bernhard, *Inorg. Chem.*, 2009, **48**, 10498; (e) K. P. S. Zanoni, B. K. Kariyazaki, A. Ito, M. K. Brennaman, T. J. Meyer and N. Y. Murakami Iha, *Inorg. Chem.*, 2014, **53**, 4089; (f) F. Gärtner, D. Cozzula, S. Losse, A. Boddien, G. Anilkumar, H. Junge, T. Schulz, N. Marquet, A. Spannenberg, S. Gladiali and M. Beller, *Chem. – Eur. J.*, 2011, **17**, 6998; (g) Y.-J. Yun, Z.-T. Yu, H.-L. Gao, Z.-G. Zou, C. Zheng and W. Huang, *Chem. – Eur. J.*, 2013, **19**, 6340; (h) S. Sato, T. Morikawa, T. Kajino and O. Ishitani, *Angew. Chem., Int. Ed.*, 2013, **52**, 988; (i) D. R. Whang, K. Sakai and S. Y. Park, *Angew. Chem., Int. Ed.*, 2013, **52**, 11612.
- 6 A. Hagfeldt and M. Grätzel, *Acc. Chem. Res.*, 2000, **33**, 269.
- 7 E. A. Gibson, M. Awais, D. Dini, D. P. Dowling, M. T. Pryce, J. G. Vos, G. Boschloo and A. Hagfeldt, *Phys. Chem. Chem. Phys.*, 2013, **15**, 2411.
- 8 (a) Z. Ning, Q. Zhang, W. Wu and H. Tian, *J. Organomet. Chem.*, 2009, **694**, 2705; (b) E. Baranoff, S. Suarez, P. Bugnon, H. J. Bolink, C. Klein, R. Scopelliti, L. Zuppiroli, M. Grätzel and M. K. Nazeeruddin, *ChemSusChem*, 2009, **2**, 305.
- 9 G. Sprintschnik, H. W. Sprintschnik, P. P. Kirsch and D. G. Whitten, *J. Am. Chem. Soc.*, 1977, **99**, 4947.
- 10 C. Gosmini, C. Bassene-Ernst and M. Durandetti, *Tetrahedron*, 2009, **65**, 6141.
- 11 B. M. Coleridge, C. S. Bello, D. H. Ellenberger and A. Leitner, *Tetrahedron Lett.*, 2010, **51**, 357.
- 12 J. L. Bolliger and C. M. Frech, *Chem. – Eur. J.*, 2010, **16**, 11072.
- 13 L. Ackermann, H. K. Potukuchi, A. R. Kapdi and C. Schulzke, *Chem. – Eur. J.*, 2010, **16**, 3300.
- 14 (a) J. J. Kowalczyk, S. K. Agbossou and J. A. Gladysz, *J. Organomet. Chem.*, 1990, **397**, 333; (b) M. Hirano, M. Hirai, Y. Ito, T. Tsurumaki, A. Baba, A. Fukuoka and S. Komiya, *J. Organomet. Chem.*, 1998, **569**, 3; (c) M. E. Padilla-Tosta, J. Manuel Lloris, R. Martínez-Mañez, T. Pardo and J. Soto, *Inorg. Chim. Acta*, 1999, **292**, 28–33; (d) B. R. Travis, M. Sivakumar, G. O. Hollist and B. Borhan, *Org. Lett.*, 2003, **5**, 1031; (e) D. Chatterjee, A. Mitra and R. E. Shepherd, *Inorg. Chim. Acta*, 2004, **357**, 980; (f) K. Kuwabara and A. Itoh, *Synthesis*, 2006, 1949.
- 15 (a) F. Neve, A. Crispini, S. Campagna and S. Serroni, *Inorg. Chem.*, 1999, **38**, 2250; (b) F. J. Coughlin, M. S. Westrol, K. D. Oyler, N. Byrne, C. Kraml, E. Zysman-Colman, M. S. Lowry and S. Bernhard, *Inorg. Chem.*, 2008, **47**, 2039.
- 16 M. S. Lowry and S. Bernhard, *Chem. – Eur. J.*, 2006, **12**, 7970–7977.
- 17 A. Kapturkiewicz and G. Angulo, *Dalton Trans.*, 2003, 3907.
- 18 J. I. Goldsmith, W. R. Hudson, M. S. Lowry, T. H. Anderson and S. Bernhard, *J. Am. Chem. Soc.*, 2005, **127**, 7502.
- 19 D. N. Chirdon, C. E. McCusker, F. N. Castellano and S. Bernhard, *Inorg. Chem.*, 2013, **52**, 8795.
- 20 (a) L. Leonard, N. Tinker, D. McDaniel, P. N. Curtin, C. K. Smith, M. J. Ireland and S. Bernhard, *Chem. – Eur. J.*, 2007, **13**, 8726–8732; (b) Note: The TONs reported in ref. 20a were performed under different conditions to those reported in this manuscript.
- 21 F. O. Garces, K. A. King and R. J. Watts, *Inorg. Chem.*, 1988, **27**, 3464.
- 22 M. S. Lowry, W. R. Hudson, R. A. Pascal Jr. and S. Bernhard, *J. Am. Chem. Soc.*, 2004, **126**, 14129.
- 23 (a) M. K. Nazeeruddin, A. Kay, I. Rodicio, R. Humphry-Baker, E. Mueller, P. Liska, N. Vlachopoulos and M. Graetzel, *J. Am. Chem. Soc.*, 1993, **115**, 6382; (b) K. Wiederholt and L. W. McLaughlin, *Nucleic Acids Res.*, 1999, **27**, 2487.
- 24 I. Gillaizeau-Gauthier, F. Odobel, M. Alebbi, R. Argazzi, E. Costa, C. A. Bignozzi, P. Qu and G. J. Meyer, *Inorg. Chem.*, 2001, **40**, 6073.
- 25 S. Soman, G. Singh Bindra, A. Paul, R. Groarke, J. C. Manton, F. M. Connaughton, M. Schulz, D. Dini, C. Long, M. T. Pryce and J. G. Vos, *Dalton Trans.*, 2012, **41**, 12678.
- 26 (a) Q. Liu, H. Duan, X. Luo, Y. Tang, G. Li, R. Huang and A. Lei, *Adv. Synth. Catal.*, 2008, **350**, 1349–1354; (b) Y.-Q. Fang and G. S. Hanan, *Synlett*, 2003, 0852; (c) A. Lützen and M. Hapke, *Eur. J. Org. Chem.*, 2002, 2292–2297; (d) J. E. Milne and S. L. Buchwald, *J. Am. Chem. Soc.*, 2004, **126**, 13028; (e) U. Kiehne, J. Bunzen, H. Staats and A. Lutzen, *Synthesis*, 2007, 1061.
- 27 E. Campaigne and W. M. LeSuer, *J. Am. Chem. Soc.*, 1948, **70**, 1555.
- 28 G. M. Greenway, A. Greenwood, P. Watts and C. Wiles, *Chem. Commun.*, 2006, 85.