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Energetic Requirements for Iridium(III) Complex Based Photosensitisers in Photocatalytic Hydrogen Generation

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A new family of Ir(III) complexes were synthesised and employed as light-induced hydrogen-production photosensitisers in aqueous systems, where hydrogen evolution was only observed when the PS* was reduced by the sacrificial agent, NEt₃, signifying a minimum potential difference of >0.2 V between E(PS*/PS) and E(NEt₃/NEt₄) is required for efficient hydrogen production [i.e., E(PS*/PS) > 1.19 V versus NHE]. The analytical method developed here is demonstrated useful for screening new photosensitisers for light-driven hydrogen generation.

More importantly, the energy requirements for hydrogen generation, which involves charge transfer processes, have not yet been fully established with many studies relying on PL quenching studies. The problem with this approach is that it is difficult to analyse those photosensitisers with weak emission. In order to build our understanding of the effect of PS energy levels on photon-driven catalytic hydrogen production activity and establish the minimum energetic requirements for PS, we report the synthesis and characterisation of a new family of [Ir(C^N)₂(N^N)]⁺ complexes (PS2–PS6, Fig. 1) bearing a range of π-conjugated C^N ligands (L2–L6). We evaluate the relative hydrogen-generation performance of the new PS by comparing with the prototypical Ir(III) complex, PS1. From Stern-Volmer measurements and kinetics studies, we confirm that the reduction of the excited state of PS, PS*, by the sacrificial agent is the rate-determining step for the overall hydrogen generation process. We have found that for a PS to be effective in photocatalytic hydrogen generation, there has to be a sufficiently high driving force for PS* to be reduced to PS⁺ by the sacrificial agent, to enable the subsequent electron transfer from PS* to the catalyst.

Figure 1. Chemical structures of Ir(III) complexes PS1–PS6 and the respective C^N ligands L1–L6.

Results and discussion

Synthesis and characterisation. The new family of [Ir(C^N)₂(N^N)]⁺ complexes, PS2–PS6, was synthesised in four
steps as outlined in Scheme 1, involving ligand synthesis, complexation to form a chloro-bridged iridium(III) dimer, fication with the N^N co-ligand (i.e., 4,4′-dimethyl-2,2′-bipyridine, dmebpy), and finally counteranion exchange with potassium hexafluoride (KPF6). While benzo[h]quinoline ligand L2 is commercially available, L3–L6 were first prepared from 2-chloro-4-methylquinoline with the corresponding arylboronic acids under Suzuki-Miyaura cross-coupling reaction conditions (Scheme 1). Under these conditions, L3–L6 were obtained in excellent yields of 80% – 99%. The first step in the complexes formation involved heating iridium(III) trichloride trihydrate (IrCl3·3H2O) with the corresponding C^N ligands in 2-ethoxyethanol and water under standard cyclometallation conditions to give the respective chloro-bridged Ir(III) dimers in ≈47% – 80% yields. Subsequent co-ligation with the N^N ancillary ligand to form PS2–PS4 was achieved by treating the corresponding Ir(III) dimers with dmebpy in a mixture of dichloromethane and methanol heated at reflux (Method A). We found higher reaction temperatures (Method B) were necessary in the synthesis of more bulky PS5 and PS6 due to the more sterically hindered ligands, L5 and L6. Finally, the desired Ir(III) complexes PS2–PS6 bearing a PF6 counteranion were obtained by an anion exchange process with KPF6 from the corresponding [Ir(C^N)L(N^N)]Cl complexes in water. Importantly, for complete anion exchange, it was found large excess of KPF6 was required for PS5 and PS6. The overall yields for the last two steps were around 51% – 86% for PS2–PS6. The obtained mass and NMR spectra of PS2–PS6 were consistent with their structures shown in Scheme 1. Single crystals of PS3 were grown and showed that the Ir-N bonds of the C^N ligands were trans to one another (see Supporting Information). The 1H NMR spectra of PS3 showed one set of the C^N ligand signals and single signal for the methyl protons attached to the bipyridyl, which was consistent with the trans arrangement of Ir-N bonds and observed for all the complexes.

Scheme 1. Synthesis of the Ir(III) complex photosensitisers. Reagents and conditions: (i) 2-chloro-4-methylquinoline, Pd(PPh3)4, 2 M Na2CO3aq, toluene, ethanol, 100 °C, Ar; (ii) IrCl3·3H2O, 2-EtOEtOH, water, 120 °C, Ar; (iii) Method A (for PS2–PS4): 4,4′-dimethyl-2,2′-bipyridyl, dichloromethane, methanol, 55 °C, Ar; or Method B (for PS5 and PS6): 4,4′-dimethyl-2,2′-bipyridyl, ethylene glycol, 150 °C, Ar; (iv) KPF6, water, r.t.

Photophysical properties. The solution UV-visible absorption spectra of the Ir(III) complexes were recorded in dichloromethane at room temperature (Fig. 2), and are compared with that of PS1. As can be seen in Fig. 2, the absorption spectra of the new photosensitisers are comprised of three main absorption regions. The intense absorption bands with high molar extinction coefficients (ε) of ≈20,000 – 94,000 dm3 mol−1 cm−1 at higher energy (<300 nm for PS1–PS4, and <440 nm for PS6, and <500 nm for PS5) consist of the spin-allowed ligand-centred transitions (1LC, i.e., π → π∗ transitions of the C^N ligands and N^N ligands). The ligand centred transitions are slightly red-shifted relative to the corresponding free ligands. The weaker absorptions at longer wavelengths (<380 – 440 nm for PS2, >380 – 470 nm for PS3, >420 – 520 nm for PS4, >480 – 540 nm for PS5, and >440 – 500 nm for PS6) correspond to the singlet inter-ligand charge-transfer (1MLCT) and singlet “metal-to-ligand charge-transfer” transitions (1MLCT) containing 1MLCTCN and 1MLCTN^N character. Finally, the weak absorptions at longer wavelengths (inset of Fig. 2) can be ascribed to triplet excitations including 1LC, 1LLCT, 1MLCTCN and 1MLCTN^N transitions.

As shown in Fig. 2, the absorption characteristics of the Ir(III) complexes are strongly dependent on the C^N ligands. PS1 and PS2 have similar onsets to absorption with that of PS3 being at a slightly longer wavelength, which is due to the extended π-conjugated of the phenylquinoline ligand. By replacing the ligand phenyl ring in PS3 with a naphthalene or pyrene to give PS4 and PS5, respectively, there is a significant red shift in the onset of absorption, up to ≈600 nm (inset of Fig. 2) for PS4 and PS5. Although PS6 has carbazole-based ligands, there is only a small red shift in absorption with respect to its parent complex, PS3 (inset of Fig. 2). Interestingly, the molar extinction coefficient of PS6 is nearly doubled between 250 and 550 nm (Fig. 2), compared to PS3.

Next, the solution photoluminescence (PL) spectra of PS1–PS6 were measured in deoxygenated dichloromethane at room temperature and are plotted in Fig. 3 with the PL data summarised in Table 1. Upon photoexcitation at 410 nm, all the Ir(III) complexes were luminescent in the visible region with PL peaks in the range of 550 – 624 nm apart from PS3, which had a PL peak at 704 nm, and is consistent with the trends observed in the absorption spectra (Fig. 2). Interestingly, the profiles of the PL spectra fall into two different families (Fig. 3). PS1, PS2 and PS6 have broad featureless profiles while PS3–PS5 have more structured PL spectra with a clear shoulder at longer wavelengths. A broad emission spectrum has been ascribed to transitions with strong 1MLCT character, [i.e., C^N π-orbital and Ir(III) d-orbital to the N^N π*-orbital], which is mainly due to the presence of the low-lying π*-orbitals of the dinecene ligands, while the more structured PL has been attributed to transitions that have a higher proportion of 1LC character (i.e., π → π∗ transitions) in the excited states.

Given the similarity in the onset to the absorption, it is not surprising that PS1 and PS2 have similar PL peaks (PS1 (<580 nm, Fig. 3). What is perhaps surprising is that the PL spectrum of PS3 is blue shifted relative to PS1, although this difference may well arise from the fact that PS3 has more 1LC character in its emission. As expected in extending the conjugation length of the ligand in moving from PS3 to PS4 and PS5 the emission becomes more red-shifted. In the case of PS6, the low energy emission (with a PL peak at 624 nm)
is similar to that reported for other Ir(III) complexes bearing aryl carbazolyl C=N ligands.\textsuperscript{25}

The solution photoluminescence quantum yields (PLQYs) of the Ir(III) complexes were measured in degassed tetrahydrofuran (THF) using a relative method with coumarin 30 as the reference.\textsuperscript{25} We measured PS1 to have a PLQY of 28\%, which is comparable to that (31\%) reported in dichloromethane.\textsuperscript{19b} PS2 was found to have a similar moderate PLQY (24\%) (Table 1), whereas PS3 and PS4 with the phenyl and napthylquinoline ligands were found to have higher PLQYs of 80\% and 41\%, respectively. In contrast, the pyrene and carbazole containing complexes had low PLQYs of 1.4\% and 6\% for PS5 and PS6, respectively.

Table 1. Photophysical characterisations.

<table>
<thead>
<tr>
<th>Ir(III) complex</th>
<th>PL peaks* /nm</th>
<th>$E_g$(opt)$^b$ /eV</th>
<th>PLQY$^c$ /%</th>
<th>$\tau$ /µs</th>
<th>$k_{rd}^d /10^5$/s$^{-1}$</th>
<th>$k_{nr}^d /10^5$/s$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>PS1</td>
<td>580</td>
<td>2.45</td>
<td>28 ± 4</td>
<td>0.53</td>
<td>5.3</td>
<td>13.6</td>
</tr>
<tr>
<td>PS2</td>
<td>583</td>
<td>2.43</td>
<td>24 ± 3</td>
<td>0.62</td>
<td>3.9</td>
<td>12.3</td>
</tr>
<tr>
<td>PS3</td>
<td>550, 578sh</td>
<td>2.34</td>
<td>80 ± 5</td>
<td>2.37</td>
<td>3.4</td>
<td>0.8</td>
</tr>
<tr>
<td>PS4</td>
<td>616, 654sh</td>
<td>2.08</td>
<td>41 ± 4</td>
<td>3.34</td>
<td>1.2</td>
<td>1.8</td>
</tr>
<tr>
<td>PS5</td>
<td>704, 771sh</td>
<td>1.93</td>
<td>1.4 ± 0.1</td>
<td>3.11</td>
<td>0.045</td>
<td>3.2</td>
</tr>
<tr>
<td>PS6</td>
<td>624</td>
<td>2.27</td>
<td>6 ± 2</td>
<td>0.13</td>
<td>4.6</td>
<td>72.3</td>
</tr>
</tbody>
</table>

* Measured in dichloromethane. \( ^b \) Measured in degassed THF with excitation at 410 nm. \( ^c \) Derived from PLQY = $k_r/(k_r + k_{nr})$ and $\tau = 1/(k_r + k_{nr})$.\textsuperscript{24}

The excited-state lifetimes of the Ir(III) complexes were measured in degassed THF with the values summarised in Table 1. The excited state lifetimes were found to be of order a microsecond, reflecting the phosphorescent nature of the emission of the Ir(III) complexes, and are comparable to those of reported for other Ir(III) complexes with 2,2'-bipyridyl N\(^\circ\)N co-ligands. The excited state lifetimes of the complexes can be divided into two families, namely, those with the longer excited-state lifetimes of 2.4 – 3.3 µs (PS3–PS5), and those with much shorter PL lifetimes of 0.13 – 0.62 µs (for PS1, PS2 and PS6). The longer excited state lifetimes for PS3–PS5 can be attributed to their more significant \(^1\)LC character in the emissive state,\textsuperscript{25} and are consistent the more structured PL spectra as discussed earlier.

The radiative ($k_r$) and non-radiative ($k_{nr}$) rate constants of the complexes were calculated from the PLQY values and excited state lifetimes.\textsuperscript{24} While most of the Ir(III) complexes had a typical $k_r$ in the order of $10^6$ s$^{-1}$,\textsuperscript{19,27} PS5 had a relatively low $k_r$ ($10^5$ s$^{-1}$) due to the higher proportion of \(^1\)LC emission arising from the pyrenylquinoline ligands and PS6 had a slightly larger $k_{nr}$ ($7.2 \times 10^5$ s$^{-1}$).\textsuperscript{28}

**Electrochemical properties.** Cyclic voltammetry (CV) was used to investigate the electrochemical behaviour and determine the redox potentials of the complexes. The cyclic voltammetry was carried out on solutions of the complexes in THF using 0.1 M of tetra-n-butylammonium hexafluorophosphate (TBAH) as a supporting electrolyte under an argon atmosphere. The cyclic voltammograms are shown in the Supporting Information (Figures S2–S7) and the $E_{1/2}$ values are listed in Table 2 against NHE.\textsuperscript{28}

We found that PS1 had a chemically quasi-reversible oxidation in THF with an $E_{1/2}(ox)$ at +1.58 V versus the NHE, which is similar to that reported for Ir(ppy)$_2$(bpy)PF$_6$ in acetonitrile (+1.52 V versus NHE).\textsuperscript{3} PS3 and PS4 also exhibited a chemically quasi-reversible oxidation in THF with the $E_{1/2}(ox)$s at +1.57 V and +1.53 V versus NHE, respectively. The oxidation $E_{1/2}$ of PS2, PS5 and PS6 could not be determined in THF but in dichloromethane, a quasi-reversible process for PS2 and reversible processes for PS5 and PS6 were observed with $E_{1/2}(ox)$s of +1.51 V, +1.08 V and +1.24 V versus NHE for PS2, PS5 and PS6, respectively. The less positive oxidation potentials for PS5 and PS6 can be attributed to the C=N ligands consisting of the pyrene moiety and carbazolyl units making the complexes easier to oxidise.\textsuperscript{29}

In contrast to oxidation, the Ir(III) complexes all showed several reversible reductions in deoxygenated THF at ambient temperature. The first reduction potentials of all the compounds, PS1–PS6, were essentially the same at around -1.1 V versus the NHE, and are comparable to those of similar Ir(III) complexes bearing with 2,2'-bipyridyl N\(^\circ\)N co-ligands. It can, therefore, be deduced that the first reduction corresponds to the reduction of the bipyridyl ligand due to its low-lying $\pi$-orbitals.\textsuperscript{19b,30} Two or more chemically quasi-reversible reductions were also observed at more negative potentials for the Ir(III) complexes (see Table 2 and Supporting Information), which can be attributed to the reductions of the two C=N ligands.

**Hydrogen generation.** Hydrogen-generation efficiencies of the new PS were evaluated using a similar method reported,\textsuperscript{2b,11} where the reaction mechanisms (see below) and the role of sacrificial NET$_3$ and hydrogen source had been previously studied.\textsuperscript{16,2b,4} Typically, the test reaction mixtures contained 1.00 µmol of PS, 0.48 µmol of K$_2$PtCl$_6$, 2.0 mL of NET$_3$,\textsuperscript{14} 2.0 mL of H$_2$O, and 10 mL of THF unless otherwise stated, and a 150 W Xenon lamp was used as the light source. In this work, the evolved hydrogen was collected in a gas burette, which was further analysed by GC to confirm H$_2$ formation. The volume
generated was measured and converted to moles using the ideal gas equation. Turnover numbers (TONs) were calculated by dividing the moles of hydrogen atoms (H) obtained by the moles of PS used \([i.e., n(H)/n(PS)]\).  

Table 2. Electrochemical properties of the Ir(III) complex PS.  

<table>
<thead>
<tr>
<th>Ir(III) Complex</th>
<th>(E_{1/2}^{(ox)}) vs NHE</th>
<th>(E_{1/2}^{(red)}) vs NHE</th>
<th>(E(PS^*/PS)^d) vs NHE</th>
</tr>
</thead>
<tbody>
<tr>
<td>PS1</td>
<td>1.58a</td>
<td>-1.13, -2.05, -2.31</td>
<td>+1.31</td>
</tr>
<tr>
<td>PS2</td>
<td>1.51b</td>
<td>-1.07, -1.75, -2.04</td>
<td>+1.36</td>
</tr>
<tr>
<td>PS3</td>
<td>1.57a</td>
<td>-1.15, -1.59, -1.89</td>
<td>+1.19</td>
</tr>
<tr>
<td>PS4</td>
<td>1.53a</td>
<td>-1.13, -1.56, -1.83</td>
<td>+0.95</td>
</tr>
<tr>
<td>PS5</td>
<td>1.08b</td>
<td>-1.07, -1.26, -1.66, -1.92, -2.11</td>
<td>+0.86</td>
</tr>
<tr>
<td>PS6</td>
<td>1.24b</td>
<td>-1.15, -1.75, -1.90</td>
<td>+1.12</td>
</tr>
</tbody>
</table>

\(E_{1/2}^{(ox)}\) versus NHE, measured in THF.  
\(E_{1/2}^{(red)}\) versus NHE, measured in dichloromethane.  
\(E(PS^*/PS)^d\) was determined by \(E_{1/2}^{(red)} + E_{\text{opt}}\).  

Representative kinetic traces of hydrogen evolution are shown in Fig. 4 and the overall TONs of the photosensitisers are summarised in Table 3. While PS1–PS3 were found to produce hydrogen, PS4–PS6 did not show detectable activities despite their relatively high absorption extinction coefficients (Fig. 2) and long excited-state lifetimes (Table 1). The TON of PS2 was determined to be \(\approx1,340\), which is slightly higher than that of PS1 under the same conditions. Compared to PS1 and PS2, we found PS3 displayed a relatively low TON of \(\approx400\). The turnover frequency (TOF) was calculated from the initial 5 minutes of hydrogen formation when the process was in a linear range. PS1 and PS2 were found to have similar TOF of 33 and 35 min\(^{-1}\), respectively, while PS3 was lower (21 min\(^{-1}\)).  

![Figure 4](https://example.com/image)  

**Figure 4.** Representative kinetic traces of hydrogen evolution photo-reactions with different photosensitisers. Photo-reactions contained 1.00 \(\mu\)mol of PS, 0.48 \(\mu\)mol of \(K_2PtCl_6\), 2.0 mL of NEt\(_3\), 2 mL of \(H_2O\), and 10 mL of THF at 20 °C.

<table>
<thead>
<tr>
<th>Complex</th>
<th>(\tau_0^a)</th>
<th>(K_{SV}(NEt)_3^b)</th>
<th>(K_C((NEt)_3))</th>
<th>(k_d(NEt)_3)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PS1</td>
<td>3.3</td>
<td>4.5 ± 0.2</td>
<td>4.1 ± 0.5</td>
<td>12.4 ± 0.4</td>
</tr>
<tr>
<td>PS2</td>
<td>0.31</td>
<td>4.2 ± 0.4</td>
<td>3.5 ± 0.4</td>
<td>11.3 ± 0.2</td>
</tr>
<tr>
<td>PS3</td>
<td>1.22</td>
<td>0.4 ± 0.2</td>
<td>0.3 ± 0.1</td>
<td>0.3 ± 0.1</td>
</tr>
<tr>
<td>PS4–PS6</td>
<td>no PL quenching observed</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\(\tau_0\) is the phosphorescence lifetime of the PS in the absence of NEt\(_3\).  
\(K_{SV}\) was obtained from fitting the steady-state Stern-Volmer equation, where \(PL_{0}/PL = 1 + K_{SV}(NEt)_3\), where \(PL_{0}\) is the initial solution phosphorescence of the PS and \(PL\) is the solution phosphorescence of the PS with \(NEt\(_3\).  
\(K_C\) was obtained from fitting the time-resolved Stern-Volmer equation, where \(PL_{0}/PL = 1 + K_{SV}(NEt)_3\), where \(PL_{0}\) is the initial phosphorescence lifetime of the PS and \(PL\) is the phosphorescence lifetime of the PS after addition of \(NEt\(_3\).  
\(k_d\) was calculated by \(k_d = k_{SV}/\tau_0\).

As can be seen in Table 4, PS2 showed similar \(K_{SV}\) and \(K_C\) values to PS1, which is likely due to their similar C-N ligand structure. However, PS3 displayed an order of magnitude smaller \(K_{SV}\) and \(K_C\) values than those of PS1 and PS2, indicating that there was much less PL quenching, and hence a much lower \(k_d\) value of \(0.3 \times 10^6 \text{ M}^{-1}\text{s}^{-1}\) for PS3 than PS2 (11.3 \(\times 10^6 \text{ M}^{-1}\text{s}^{-1}\)). The PL of PS4–PS6 was not quenched by NEt\(_3\). Importantly, the quenching process of PS1–PS3 is predominantly collision in nature.

While the trends in collisional quenching rate are consistent with the hydrogen-generation results (Table 3), the fact that PS3 has a significantly longer excited-state lifetime than PS1 and PS2 but exhibits much smaller collisional \(K_C\) values would suggest insufficient driving force for electron transfer from \(NEt_3\) to PS*. Hence the performance of PS3 is limited by the second step in the mechanism proposed by Berhard et al.:  

\[(1)\] \(\text{PS} \xrightarrow{hv} \text{PS}^*\)  
\[(2)\] \(\text{PS}^* + \text{NEt}_3 \rightarrow \text{PS}^* + \text{NEt}_3^*\)  
\[(3)\] \(\text{PS}^* + \text{H}_2 \xrightarrow{Pt} \text{PS} + 1.2\text{H}_2\)  

where \(E_2\) and \(E_1\) are the potential difference of step (2) and (3), respectively; \(E(PS^*/PS)\) is the reduction potential of PS in its excited state (i.e., PS*); \(E(\text{NEt}_3^*/\text{NEt}_3)\) is the oxidation potential of \(\text{NEt}_3\); \(E(\text{H}_2/\text{H}_2^+)\) is the hydrogen reduction potential and \(E(\text{PS}^*/\text{PS})\) is the reduction potential of PS. For electron transfer...
to occur in steps 2 and 3, $E_2$ and $E_3$ must be greater than zero, meaning that the values of $E(PS*/PS)$ must be larger than $E(\text{NEt}_3/\text{NEt}_3)$ and $E(PS*/PS)$ must be more negative than $E(H^+/H_2)$. While $E(PS*/PS)$ corresponds to the first reduction potential of the PS, $E(PS*/PS)$ cannot be directly measured. Andreidas et al. estimated $E(PS*/PS)$ from $E(PS/PS) + E_g(\text{opt})$, where $E_g(\text{opt})$ is the optical bandgap (Table 1), although it should be noted that the mirror image rule needs to be met for the analysis to be considered valid.

Following the method of Andreidas et al., we estimated the $E(PS*/PS)$ with the data listed in Table 2. Fig. 5 illustrates the energy levels of the photosensitisers against $E(\text{NEt}_3/\text{NEt}_3)$ and $E(H^+/H_2)$.

**Figure 5.** Summary of $E(PS/PS)$ of the Ir(III) complex PS1–PS6 versus NHE and the calculated $E(PS*/PS)$ by $E(PS/PS) + E_g(\text{opt})$.

From Fig. 5, it can be seen that all the PS have more negative $E(PS/**PS)$ potentials than $E(H^+/H_2)$, indicating that if PS were formed for PS1–PS6, there would be sufficient driving force to accomplish the electron transfer in step 3 of the mechanism. In fact, for the hydrogen-generating complexes, it was found that the performance of the PS was independent of the platinum catalyst concentrations (see Supporting Information, Figure S8), which agrees with the catalyst not being involved in the rate-determining step. In contrast, the new Ir(III) PS have a large variation in the value of $E(PS*/PS)$. The less positive values of $E(PS*/PS)$ for PS4 and PS5 are close to that of $E(\text{NEt}_3/\text{NEt}_3)$, and hence step 2 should not occur, which is what was observed in spite of the strong absorption and long excited-state lifetimes (Table 1). For PS1–PS3, $E(PS*/PS)$ are all more positive than $E(\text{NEt}_3/\text{NEt}_3)$ with the difference ranging from 0.26 – 0.43 V, which again is consistent with Stern-Volmer measurements and these complexes generate hydrogen. In fact, the trend observed in the Stern-Volmer measurements follows the energetics of the system, with the results of the larger Stern-Volmer constant values of PS1 and PS2 consistent with the higher driving force for PS* reduction to give PS in step 2. In spite of PS6 having an ($E_2$) of $0.19$ V, no hydrogen generation was observed and no PL quenching was measured in the Stern-Volmer measurements. This indicates that an energy difference of $0.2$ V is insufficient for triethylamine to generate PS from PS* although the role of the short excited state lifetime [it is the shortest of all the complexes in this study (Table 1)] cannot be discounted.

**Summary**

A new family of Ir(III) complex photosensitisers ligated with π-conjugated cyclometallated ligands and bipyridyl N=N co-ligand were synthesised in excellent yields. High hydrogen-generation TONs of $\approx 400 – 1,400$ were achieved for PS1–PS3 using NEt3 sacrificial reagent and Pt catalyst. We showed that the rate-determining step in the hydrogen generation is the reduction of the excited photosensitiser. With the current family of materials, it was found that the difference in energy between $E(PS*/PS)$ and $E(\text{NEt}_3/\text{NEt}_3)$ had to be greater than $0.2$ V, which is likely to be a general phenomenon for complexes of this type. However, while energetics play a key role in hydrogen generation in some cases the lifetime of the excited state appears to be a second order effect, for example in the case of PS6. Thus this work provides a framework for designing and screening efficient photosensitisers for light induced hydrogen generation from aqueous system.

**Acknowledgements**

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**Experimental**

**Materials and general methods.** Anhydrous tetrahydrofuran was dried over sodium using benzophenone as an indicator, and distilled immediately prior to use. Thin layer chromatography was performed on Aldrich aluminum plates coated with silica gel 60 P254 and visualised with long (365 nm) and short (254 nm) wavelengths UV irradiation. Column chromatography was performed with Merck silica gel (0.063 – 0.200 mm). All solvents used for chromatography were distilled before use. When solvent mixtures are used as eluent, the ratios were given by volume. Kugelrohr distillations were performed using a Büchi B-585 Kugelrohr. 1H and 13C NMR spectra were recorded on Bruker AV300, AV400 and AV500 spectrometers. Chemical shifts are referenced in parts per million (ppm) and referenced to the residual solvent peak, i.e., 7.26 ppm for CDCl3 and 2.50 ppm for DMSO-d6 for the 1H NMR, and 77.0 ppm for CDCl3 and 39.50 ppm for DMSO-d6 in 13C NMR. Coupling constants, $J$, are reported in hertz (Hz). Peak multiplicities are labeled in the following manner: singlet (s), doublet (d), triplet (t), broad (br), multiplet (m), doublets of doublets (dd), doublets of triplets (dt). ESI mass spectra were recorded on a Bruker HCT 3D Ion Trap using methanol as the solvent and EI mass spectra were recorded on a Finnigan MAT 900 XL. High resolution electrospray ionisation (HRESIMS) accurate mass measurements were carried out on a Bruker MicrOTOF-Q (quadrupole - Time of Flight) instrument with a Bruker ESI source. MALDI-TOF mass spectra were recorded on an Applied Biosystems Voyager MALDI-TOF mass spectrometer using dithranol as the matrix. Elemental microanalyses were carried out using a Carlo Erba NCHS Analyser Model NA 1500 microanalyser at School of Chemistry and Molecular Biosciences, the University of Queensland.

Absorption spectra were recorded on a Varian Cary 5000 UV-Vis-NIR spectrophotometer in spectroscopic grade dichloromethane in 10 × 10 mm quartz cuvettes and λmax values were quoted in nm and shoulders denoted as “sh”. Fluorescence spectra were measured using a Jobin-Yvon Horiba Fluorolog in steady-state mode using a xenon lamp as the excitation source. Photoluminescence quantum yields (PLQY’s) were determined by using the relative method with coumarin 30 in ethanol (PLQY = 81%), cross-calibrated with quinine sulfate in 0.5 M
H$_2$SO$_4$ (PLQY = 55%), as the reference.\textsuperscript{2a} All solutions were prepared in spectroscopic grade tetrahydrofuran in a concentration with an optical intensity of approximately 0.1. Five freeze-pump-thaw cycles were typically employed to degas the solutions. An excitation wavelength of 410 nm was used for the PL measurements. Stern-Volmer measurements were performed by measuring the PL intensity of a degassed PS solution before and after 5 additions of 25 μL of known concentrations of NE$_3$. To ensure the concentration of the PS in the cuvette remained constant with each addition the NE$_3$ was dissolved in a PS solution with the same concentration as the solution in the cuvette. Furthermore, after each addition of the NE$_3$ the mixture was degassed to prevent oxygen quenching. Lifetime measurements were carried out using a Fluorolog 3 with TCSPC capability. The excitation source was an LED emitting at 441 nm and pulsed at 100 KHz with a pulse width of 1.2 ns. The PL was detected at the emission peak of the material and the lifetimes obtained by fitting to the PL decays with single exponentials convolved with the instrument response function.

Cyclic voltammetry (CV) was performed in a standard three-electrode system at room temperature using a solution comprising 1 mM Ir(III) complex and 0.1 M tetra-n-butylammonium hexafluorophosphate (TBAB, Fluka, electrochemical grade) as electrolyte in distilled THF or dichloromethane, a glassy carbon working electrode, a Pt wire counter electrode and a Ag/AgNO$_3$ solution as the reference electrode at a scan rate of 100 mV/s. The solutions were purged with argon and measured under an argon atmosphere. Sublimed ferrocene (Fc) was used as a standard and measured under the same conditions as the samples. $E_{1/2}$(ox) and $E_{1/2}$(red) versus NHE were calculated using the standard potentials of Fc$^+$/$\text{Fc}$.

Hydrogen generation experiments. The hydrogen generation reactions were performed in a triethylamine/photosensitiser/Pt triple-component system.\textsuperscript{7} Typically, 1.00 mL of a 1.0 mM photosensitiser stock solution in dichloromethane was added to a 30 mL Schlenk tube and the solvent removed under reduced pressure. Then 10 mL of THF was added to dissolve the photosensitiser and a Ag/AgNO$_3$ solution as the reference electrode at a scan rate of 100 mV/s. The solutions were purged with argon and measured under an argon atmosphere. Sublimed ferrocene (Fc) was used as a standard and measured under the same conditions as the samples. $E_{1/2}$(ox) and $E_{1/2}$(red) versus NHE were calculated using the standard potentials of Fc$^+$/$\text{Fc}$.

PS$_3$. A mixture of L$_3^{3a}$ (1.00 g, 4.56 mmol), iridium trichloride trihydrate (670 mg, 1.90 mmol), 2-ethoxethanol (30 mL) and water (10 mL) was heated in an oil bath held at 130 °C under argon for 16 h. The reaction was allowed to cool to room temperature. Water (100 mL) was added to the mixture. The resulting precipitate was collected by filtration, washed with water (250 mL), methanol (100 mL) and diethyl ether (250 mL), and dried to give the iridium dimer as a red powder (1.01 g, 80%), which was used without further purification in the next step. The mixture of the iridium dimer (117 mg, 0.10 mmol), 4,4′-dimethyl-2,2′-bipyridyl (38 mg, 0.21 mmol), dichloromethane (10 mL) and methanol (6 mL) was heated in an oil bath held at 55 °C under argon for 16 h. The mixture was allowed to cool to room temperature and solvents were removed under reduced pressure. A solution of KPF$_6$ (239 mg, 1.30 mmol) in 7 mL of water was added to the mixture, which was manually shaken for 1 minute at room temperature. The formed orange precipitates were then filtered and washed subsequently with distilled water (250 mL) and diethyl ether (250 mL). The precipitate was recrystallised by vapour diffusion of diethyl ether to dichloromethane solution to give PS$_2$ as an orange solid (90 mg, ~51%); mp >300 °C (decomp.). $\lambda_{\text{max}}$(dichloromethane)/nm: 255 (logε/dm$^3$/mol cm$^{-1}$ 4.84), 308 (4.43), 324 (4.36), 421 (3.82), 477 (2.91). $\lambda$ NMR (300 MHz, CDCl$_3$): $\delta$=2.29 (s, 6H), 6.32 (d, J=6.4, 2H), 7.06 (d, J=5.3, 2H), 7.15 (t, J=7.4, 2H), 7.42–7.49 (m, 4H), 7.66 (d, J=8.8, 2H), 7.70 (d, J=5.6, 2H), 7.85 (d, J=8.8, 2H), 7.92 (d, J=4.1, 2H), 8.24 (d, J=8.1, 2H), 8.53 (s, 2H). $\delta$ NMR (100 MHz, DMSO-d$_6$): $\delta$=2.80, 120.09, 122.74, 124.11, 125.47, 126.65, 128.37, 129.14, 129.45, 129.63, 133.68, 137.47, 140.16, 147.48, 148.44, 149.49, 151.43, 155.38, 156.34. m/z [MALDI-TOF]: Anal. Cal. for C$_{38}$H$_{34}$Ir$_2$N$_4$: 731.19 (56%), 732.19 (25%), 733.19 (100%), 734.20 (42%), 735.20 (9%), 736.20 (1%). Found: 731.35 (69%), 732.36 (38%), 733.34 (100%), 734.35 (52%), 735.34 (14%), 736.35 (2%). HRMS (ESI): m/z for [C$_{38}$H$_{34}$Ir$_2$N$_4$]: 733.1943; found: 733.1933.
PS4. A mixture of L4′2b (606 mg, 2.25 mmol), iridium trichloride trihydrate (330 mg, 0.94 mmol), 2-ethoxyethanol (20 mL) and water (6.5 mL) was heated in an oil bath held at 130 °C under argon for 16 h. The mixture was allowed to cool to room temperature. Water (100 mL) was added to the reaction mixture to give precipitates. The precipitates were collected and recrystallized by vapor diffusion of diethyl ether to dichloromethane solution to give PS5 as a red solid (133 mg, ≈55%); mp >300 °C (decomp.). λmax(dichloromethane)/nm: 279 (logε/dm−1 mol−1 cm1) 4.94, 295sh (4.87), 345 (4.48), 385sh (4.45), 429sh (4.72), 449 (4.83), 503sh (3.90). 1H NMR (500 MHz, DMSO-d6): δ=2.34 (s, 6H), 2.89 (s, 6H), 7.05 (dt, J=7.0 & 1.1, 2H), 7.28 (d, J=5.6, 2H), 7.45–7.52 (m, 4H), 7.55 (d, J=8.8, 2H), 7.66 (s, 2H), 7.78 (dd, J=9.1, 2H), 7.92 (d, J=5.7, 2H), 7.95 (t, J=7.6, 2H), 8.05 (dd, J=8.4 & 1.0, 2H), 8.13 (t, J=7.6, 2H), 8.15 (s, 2H), 8.28 (d, J=7.6, 2H), 8.34 (d, J=9.5, 2H), 8.76 (s, 2H), 9.07 (d, J=9.5, 2H). 13C NMR (100 MHz, DMSO-d6): δ=18.82, 20.57, 121.70, 122.61, 123.25, 124.27, 124.43, 125.12, 125.26, 125.28, 125.95, 126.34, 126.63, 126.75, 128.33, 129.05, 129.14, 129.60, 129.68, 130.11, 130.62, 131.91, 133.39, 146.92, 147.55, 148.19, 149.22, 151.21, 154.47, 170.11. m/z [MALDI-TOF]: Anal. Cal. for C83H84IrN43: 1059.32 (51%), 1060.32 (38%), 1061.32 (100%), 1062.32 (66%), 1063.33 (23%), 1064.33 (6%). Found: 1059.49 (43%), 1060.50 (40%), 1061.49 (100%), 1062.49 (63%), 1063.51 (27%), 1064.49 (15%). HRMS (ESI): m/z for [C83H84IrN43]+: 1061.3190; found: 1061.3196.

PS6. A mixture of L6 (850 mg, 2.50 mmol), iridium trichloride trihydrate (250 mg, 0.71 mmol), 2-ethoxyethanol (20 mL) and water (6.5 mL) was heated in an oil bath held at 130 °C under argon for 20 h. The mixture was allowed to cool to room temperature. Water (40 mL) was added to the reaction mixture to give red precipitates. The precipitates were filtered, washed thoroughly with water (100 mL), methanol (100 mL) and diethyl ether (250 mL) and dried to give the chloro-bridged iridium dimer as a red solid (400 mg, ≈63%), which was used without further purification in the next step. A mixture of the chloro-bridged iridium dimer (174 mg, 0.10 mmol), 4,4′-dimethyl-2,2′-bipyridyl (37 mg, 0.21 mmol), and ethylene glycol (6 mL) was heated under argon in an oil bath held at 150 °C for 20 h. The mixture was allowed to cool to room temperature. Water (50 mL) was added to the reaction mixture. The mixture was extracted with diethyl ether (3 x 30 mL). The ether extracts were combined and the solvent was removed under reduced pressure. A solution of KPF6 (1.00 g, 5.43 mmol) in 15 mL of water was added to the mixture, which was manually shaken for 1 minute at room temperature. The precipitates formed were filtered and washed subsequently with water (250 mL), a mixture of water/methanol (5:1, 50 mL) and diethyl ether (100 mL). The precipitate was collected and recrystallized by vapor diffusion of diethyl ether to dichloromethane solution to give PS6 as a red solid (170 mg, ≈73%); mp >300 °C (decomp.). λmax(dichloromethane)/nm: 306 (logε/dm−1 mol−1 cm1) 4.97, 341 (4.74), 356sh (4.63), 405 (4.64), 453sh (4.09), 516sh (3.06). 1H NMR (500 MHz, DMSO-d6): δ=2.39 (s, 6H), 2.91 (s, 6H), 3.17 (s, 6H), 6.46 (s, 2H), 7.00 (dt, J=7.0 & 1.1, 2H), 7.21 (d, J=6.4 & 1.8, 2H), 7.30–7.43 (m, 8H), 7.46 (d, J=5.1, 2H), 7.98 (t, J=8.5, 4H), 8.21 (d, J=7.7, 2H), 8.31 (s, 2H), 8.66 (s, 2H), 9.19 (s, 2H). 13C NMR (100 MHz, DMSO-d6): δ=18.55, 20.65, 28.34, 109.20, 112.59, 118.52, 118.60, 119.23, 119.53, 120.54, 123.08, 124.47, 124.67, 125.17, 125.39, 125.76, 126.78, 128.73, 129.88, 137.45, 140.33, 142.50, 145.66, 146.99, 147.81, 149.33, 151.16, 154.80, 169.48. m/z [MALDI-TOF]: Anal. Cal.
for Cs$_3$H$_4$Ir$_6$N$_6$: 1017.34 (53%), 1018.34 (35%), 1019.34 (100%), 1020.34 (62%), 1021.35 (20%), 1022.35 (4%). Found: 1017.65 (65%), 1018.67 (34%), 1019.66 (100%), 1020.65 (59%), 1021.67 (24%), 1022.64 (5%). HRMS (ESI): m/z for [Cs$_3$H$_4$Ir$_6$N$_6$]$^+$: 1019.3408; found: 1019.3415.

Notes and references

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†Electronic Supplementary Information (ESI) available: synthesis and characterisation details of L5 and L6; crystallographic data of PS3 (CCDC988597); redox CV of PS1–PS6; and hydrogen generation kinetics of PS2. See DOI: 10.1039/b000000x/


15 CCDC988597 (PS3) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.
