PLATINUM (II) COMPLEXES FOR PHOTOCATALYTIC HYDROGEN PRODUCTION/CARBON DIOXIDE REDUCTION
INTRODUCTION

With global energy use set to rise by 51% by 2035[1], renewable sources of energy are the only feasible way to create a secure energy future. One of the biggest opportunities in meeting global energy demand is the successful utilization of solar energy.

Whilst there are many possible ways of harnessing solar energy, perhaps one of the most interesting is mimicking the natural process of photosynthesis, either to the end of reducing carbon dioxide to useful organic molecules, or producing hydrogen from ‘splitting’ water.

Natural photosynthesis is an extremely complex process, involving many multi-electron, multi-species, light dependent and independent reactions. However, the energy to drive the process is derived from the idea of forming a charge separated excited state by the absorption of light. The absorption of light promotes an electron to a higher energy molecular orbital, which leads to an excited state in which an electron is repositioned in spatial and energy coordinates and a positive charge (hole) is left behind[2]. This energy stored in this charge separated state can be used to do work, often by further charge transfer to a subsequent species.

Chemical approaches to artificial photosynthesis are typically designed around the formation of charge separated states. Similar to the natural process, the key steps in this system are charge-transfer excitation (by absorption of light), charge separation, charge accumulation and finally catalysis of the appropriate photochemical half-reactions[3]. Figure 1 below shows a simplified schematic of a charge-transfer photosynthetic scheme for hydrogen production from water[3].

In order to catalyse reactions such as water splitting, complexes of the general type shown above should have the following properties:

- Absorption of visible wavelength radiation
- Long lived charge separated excited state
- Sufficient energy to catalyse the specific reaction in question

The equations below show the half reaction and photochemical potentials for the production of hydrogen and oxygen gas from water[4] (E is the redox potential vs. NHE at pH 7).

\[
\begin{align*}
2\text{H}^+_{(aq)} + 2e^- & \rightarrow \text{H}_2(g) \quad E = -0.41 \text{ V} \\
\text{H}_2\text{O}(l) & \rightarrow 0.5\text{O}_2 + 2e^- + 2\text{H}^+_{(aq)} E = -0.82 \text{ V} \\
\text{H}_2\text{O}(l) & \rightarrow \text{H}_2(g) + 0.5\text{O}_2(2g) \quad E = -1.23 \text{ V} \\
\Delta G & = 4.92 \text{ eV} \\
\end{align*}
\]

It should also be noted that photocatalytic photochemical reduction of CO₂ to a variety of products such as formic acid and methanol is also possible[5-6], the processes involved are considerably more complex and will not be dealt with here.

COMPOUNDS SYNTHESISED

For this project, the synthesis of the compounds shown in figure 3 below was attempted. These type of Platinum (II) dimine acetylides complexes have been shown previously to have long lived charge separated states from absorption of light in the visible region[5-10].
**CHARACTERISATION**

The compound shown above (Pt(bpde)(4-ethynyl-1-pentyloxy benzene)_2) was successfully synthesized. Yield: 0.23g (13%), ^1^H NMR (CDCl_3) δ 10.05 (d, 2H, J = 5.7 Hz), 8.73 (d, 2H), 8.21 (d, 2H, J = 5.7 Hz), 7.43 (d, 4H), 6.87 (d, 2H), 4.50 (qua, 4H), 4.00 (t, 4H, J = 6.5 Hz), 1.80 (qui, 4H, J = 6.5 Hz), 1.38-1.54 (m, 14H), 1.03 (t, 6H). FAB^+ (matrix) m/z: 670. FT-IR (CHCl_3) ν (cm^-1): 1731, 2117. Calculated elemental analysis: C 57.99; H 5.33; N 3.22, Found: C 59.11; H 5.69; N 2.83.

This was further analysed by absorption and emission spectroscopy, and cyclic voltammetry, to see if it showed a long lived charge separated excited state.

**RESULTS**

**ABSORPTION OF LIGHT**

![Absorption Spectrum](image)

<table>
<thead>
<tr>
<th>Wavelength / nm</th>
<th>ε / M^-1 cm^-1</th>
</tr>
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<tbody>
<tr>
<td>449.5</td>
<td>9800 ± 50</td>
</tr>
<tr>
<td>490</td>
<td>9750 ± 50</td>
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Two strong transitions are observed in the visible region (solvent – MeTHF) The measured extinction coefficient values are consistent with those for charge transfer transitions of these type of complex [11].

**EMISSION OF LIGHT AND EXCITED STATE LIFETIME**

![Emission Spectrum](image)

As room temperature emission was very weak, low temperature (77K) emission was carried out.

<table>
<thead>
<tr>
<th>Wavelength / nm</th>
<th>Lifetime / ns</th>
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<tbody>
<tr>
<td>710 (room temp.)</td>
<td>0.7 ± 2</td>
</tr>
<tr>
<td>620 (77K)</td>
<td>2100 ± 20 (t_1, 33%)</td>
</tr>
<tr>
<td></td>
<td>800 ± 10 (t_2, 67%)</td>
</tr>
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Note the graphs have been normalized for comparison. The 77K emission lifetime follows a two-exponential decay, the relative intensities of which are shown in the table below.

**ENERGY OF THE EXCITED STATE: CYCLIC VOLTAMMETRY**

![Cyclic Voltammetry](image)

A plot of current against square root of scan rate for the reduction potentials shows a linear relationship.
relationship, indicating that the process is electrochemically reversible.

The HOMO/LUMO energy gap is estimated from the difference between the oxidation potential and the 1st reduction potential. This gives an estimate of the energy stored in the excited state.

HOMO/LUMO gap = 2.04 eV. This is a similar value to that obtained from emission spectroscopy, and is sufficient energy for water splitting.

**CONCLUSION**

The results detailed above are strongly indicative that this complex has a relatively long lived charge separated excited state, formed by absorption of visible wavelength light. This charge separated state has sufficient energy for catalyzing reactions such as water splitting.

**FURTHER WORK**

In order to fully characterize the excited state of this complex, further spectroscopic tests could be performed, including transient absorption spectroscopy and time-resolved infrared spectroscopy.

In addition, the ester groups could be hydrolysed to provide carboxy groups. These could be used to anchor the complex onto a TiO\textsubscript{2} substrate for incorporation into molecular devices.

**REFERENCES**


