

# E-Futures

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DTC

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



The  
University  
Of  
Sheffield.



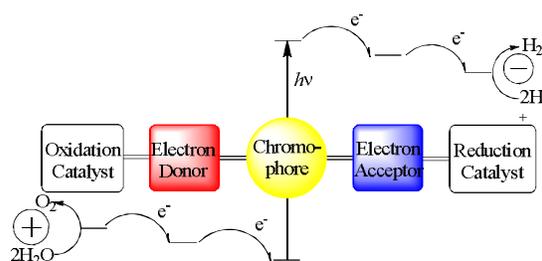
# INTRODUCTION

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 electrochemical half-reactions[3]. Figure 1 below shows a simplified schematic of a charge-transfer photosynthetic scheme for hydrogen production from water[3].

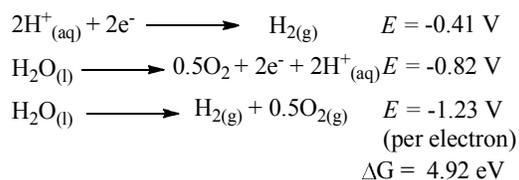


**Figure 1** Simplified photosynthetic scheme showing Donor-Chromophore-Acceptor arrangement within a charge-transfer catalytic system

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

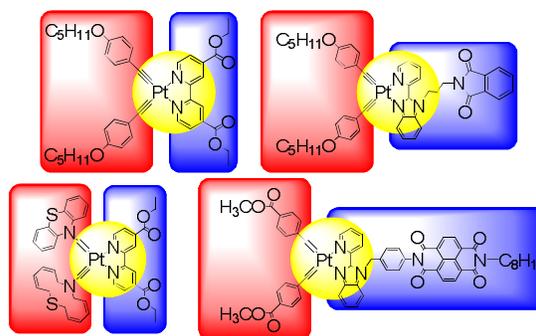
The equations below show the half reaction and electrochemical potentials for the production of hydrogen and oxygen gas from water[4] ( $E$  is the redox potential vs. NHE at pH 7).



It should also be noted that photocatalytic electrochemical reduction of  $\text{CO}_2$  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.

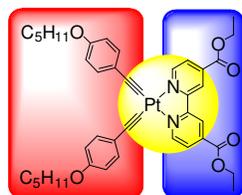
## COMPOUNDS SYNTHESISED

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



**Figure 3** Synthesis Pt(II) complexes. The colour scheme refers to the Donor-Chromophore-Acceptor arrangement seen in Figure 1 above (donor on left, acceptor on right)

## CHARACTERISATION

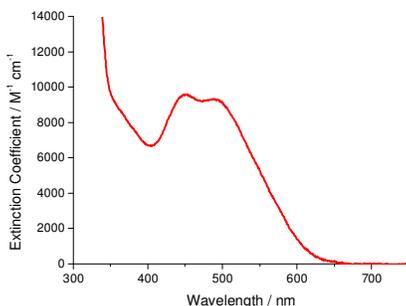


The compound shown above (Pt(bpde)(4-ethynyl-1-pentyloxy benzene)<sub>2</sub>) was successfully synthesized. Yield: 0.23g (13%), <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ: 10.05 (d, 2H, *J* = 5.7 Hz), 8.73 (d, 2H), 8.21 (d, 2H, *J* = 5.7 Hz), 7.43 (d, 4H), 6.87 (d, 4H) 4.50 (qua, 4H), 4.00 (t, 4H, *J* = 6.5 Hz), 1.80 (qui, 4H, *J* = 6.5 Hz), 1.38-1.54 (m, 14H), 1.03 (t, 6H). FAB<sup>+</sup> (matrix) *m/z*: 670. FT-IR (CH<sub>2</sub>Cl<sub>2</sub>) ν (cm<sup>-1</sup>): 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

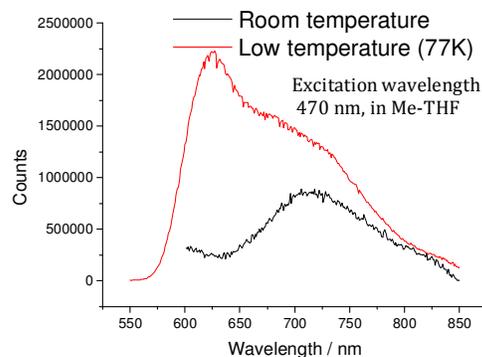


Wavelength / nm	$\epsilon / \text{M}^{-1} \text{cm}^{-1}$
449.5	9800 ± 50
490	9750 ± 50

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

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



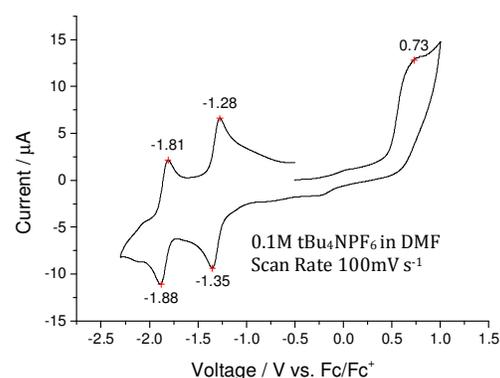
Wavelength / nm	Lifetime / ns
710 (room temp.)	0.7 ± 2
620 (77K)	2100 ± 20 ( <i>t</i> <sub>1</sub> , 33%) 800 ± 10 ( <i>t</i> <sub>2</sub> , 67%)

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 charge separated state (from room temperature emission) 1.74 eV.

The room temperature lifetime of 0.7 ns is quite short, however given the typical charge transfer step to TiO<sub>2</sub> in molecular devices incorporating these type of complexes is typically around 100 fs[8], this is still sufficient.

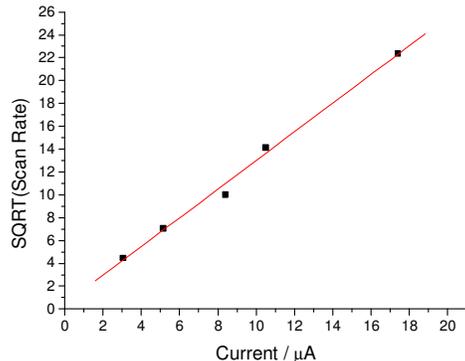
### ENERGY OF THE EXCITED STATE: CYCLIC VOLTAMMETRY



Process	Redox Potential / V
Oxidation	0.73
1 <sup>st</sup> Reduction	-1.31
2 <sup>nd</sup> Reduction	-1.84

A plot of current against square root of scan rate for the reduction potentials shows a linear

relationship, indicating that the process is electrochemically reversible.



The HOMO/LUMO energy gap is estimated from the difference between the oxidation potential and the 1<sup>st</sup> 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<sub>2</sub> substrate for incorporation into molecular devices.

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