

Photo-excitable Ruthenium(II) Chromophore Quencher Complexes for Charge Separation

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I. INTRODUCTION

Most organisms on the planet are dependant in some way upon plants and other photosynthetic species, such as bacteria and algae. Photosynthesis is one of the most important reactions in the world; it changed our atmosphere, and has been providing a source of food and energy for almost all life. This reaction harvests energy from sunlight and stores it as chemical energy, essentially converting carbon dioxide and water into sugars and oxygen. Photosynthesis has been successful in powering life for about 3.5 billion years [2] and we are now trying to mimic it, as we have mimicked many of nature's other designs. So why do we want to do this? Photosynthesis captures about 100T_w of solar radiation [4], this is 6 times the power used by the human population, but still only a minute fraction of the total incident radiation. If we could harness any of this considerable resource we could use it as a power source either for electricity generation or to drive small-molecule reactions such as reducing carbon dioxide or splitting water. If we could store solar energy in fuel cells by splitting water to hydrogen and oxygen, these could be later recombined to release energy in a controlled way we can exploit. The aim of this mini-project was to synthesise a ruthenium complex for potential use in artificial photosynthesis.

Photosynthesis

Photosynthesising plant tissues contain small membrane bound organelles called chloroplasts. Chloroplasts are evolutionarily derived from cyanobacteria, they contain all the photosynthetic apparatus of the cell. There are 2 main compartments within a chloroplast that are involved in photosynthesis: thylakoid membranes and the stroma. The thylakoids are stacks of folded, interconnecting membranes where light-dependant reactions of splitting water, photolysis, and oxygen production occur. The stroma is an enzyme-rich fluid region where the 'dark reactions' of photosynthesis occur. Namely the Calvin cycle, fixing carbon dioxide and reducing it to manufacture simple sugars.

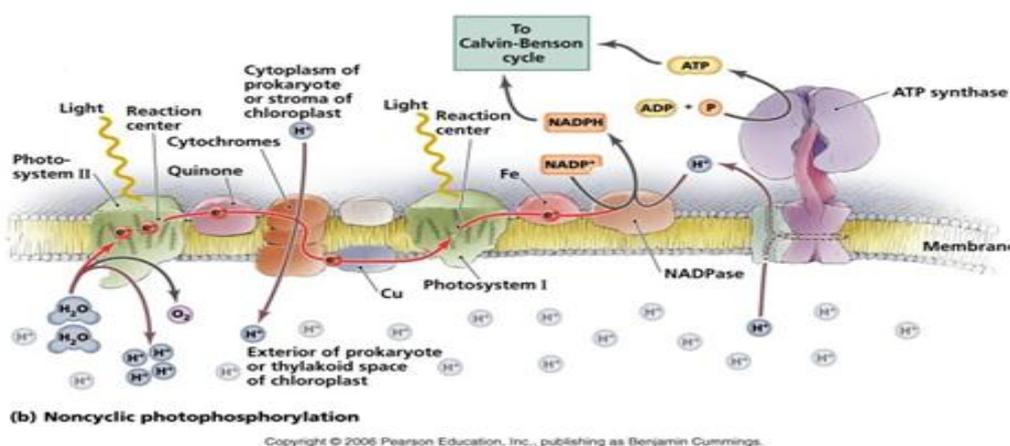


Figure 1: [5] Electron transport chain across thylakoid membrane of chloroplast: Electron donor and acceptor molecules initiate a cascade of electrons and holes in opposite directions, outwards from the chromophore, stabilising the charge separation.

Charge separation in photosynthesis

The first stage of photosynthesis is light harvesting by pigments arranged in what is called an antenna complex. The colour of the light absorbing compound is complimentary to the absorbed light, so, this means that green light is worst for photosynthesis. There are 2 main reaction centres in chloroplasts, PSII and I, these have absorption maxima in the red region of the visible light spectrum at 680 and 700nm. The wavelengths that the antenna complex absorbs are tuned, depending on the environment a plant is in.

When a photon encounters a pigment molecule, or chromophore, an electron in this molecule gains energy and is excited to a higher energy level, creating an electron-hole pair. This charge separation is vital for photosynthesis. In free chlorophyll, this excited state as an electron/hole pair, only has a lifetime of about 10^{-9} seconds. However, in the chloroplast, a series of electron donors and acceptors initiate a cascade of electrons and holes in opposite directions, outwards from the chromophore. This is known as the electron transport chain (Figure 1). This separation of charges extends the lifetime of the excited state.

The potential energy from charge separation across the membrane is used to pump protons across the membrane in an attempt to recombine the electron/hole pair. However, pumping hydrogen ions then leaves and osmotic and charge imbalance across the thylakoid. The protons flow back, driving ATP synthesis and the reduction of NADP. These molecules are carried into the Calvin cycle for sugar production.

Artificial Photosynthesis

In order to mimic photosynthesis, any synthetic system needs to include the following vital elements (Figure 2):

- 1) A chromophore to absorb visible light
- 2) Charge separation using electron donors/acceptors
- 3) Organisational principle to control chemical reactions.

It is possible to synthesise artificial antennae complexes and reaction centres. There are currently 2 ways to produce the chromophore. This mini-project uses metal to ligand charge transfer, the other method uses porphyrins and metalloporphyrins. In photosynthesis, charge separation is long-lived due to a large distance between the excited and final electron acceptors, so there is only weak coupling and slow charge recombination. The process is efficient due to short, fast electron transfers. These 2 facets are what artificial photosynthesis needs to emulate to stabilise charge separation so that different parts of the complex have opposite charges and can be coupled to oxidation and reduction reactions. This project attempts to synthesise an artificial chromophore with a Ru centre.

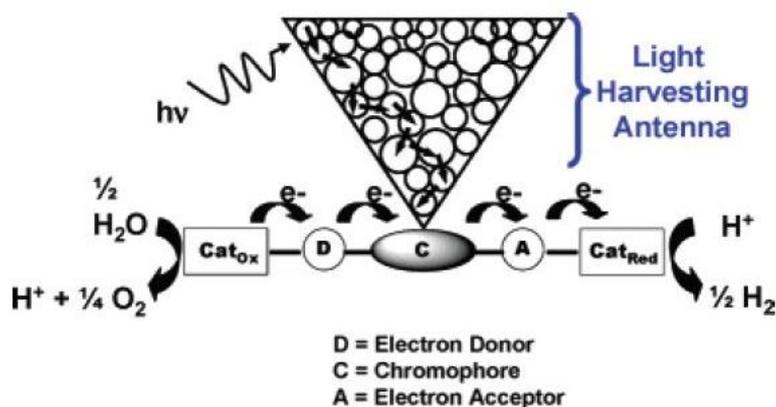


Figure 2: Essential elements for artificial photosynthesis. Photons are harvested by antennae complex and energy is passed to the chromophore to excite electrons. Electron donors and acceptors separate charge allowing redox reactions to occur in different parts of the system. Photolysis, photochemical splitting of water is illustrated here [1].

II. SYNTHESIS OF RUTHENIUM CHROMOPHORE

See appendix for protocols.

Synthetic pathway

- 1) Making and adding tris(1-pyrazole) methane (tpm). This tridentate ligand caps the ruthenium atom, removing chirality and preventing a mix of stereoisomers being synthesised (Figure 4A).
- 2) Synthesising (Figure 3) and attaching an acceptor ligand (qdppn) to withdraw electron density (Figure 4B).
- 3) Adding a donor ligand, initially 4-aminopyridine (Figure 4C), to feed electron density towards Ru and move the hole away.

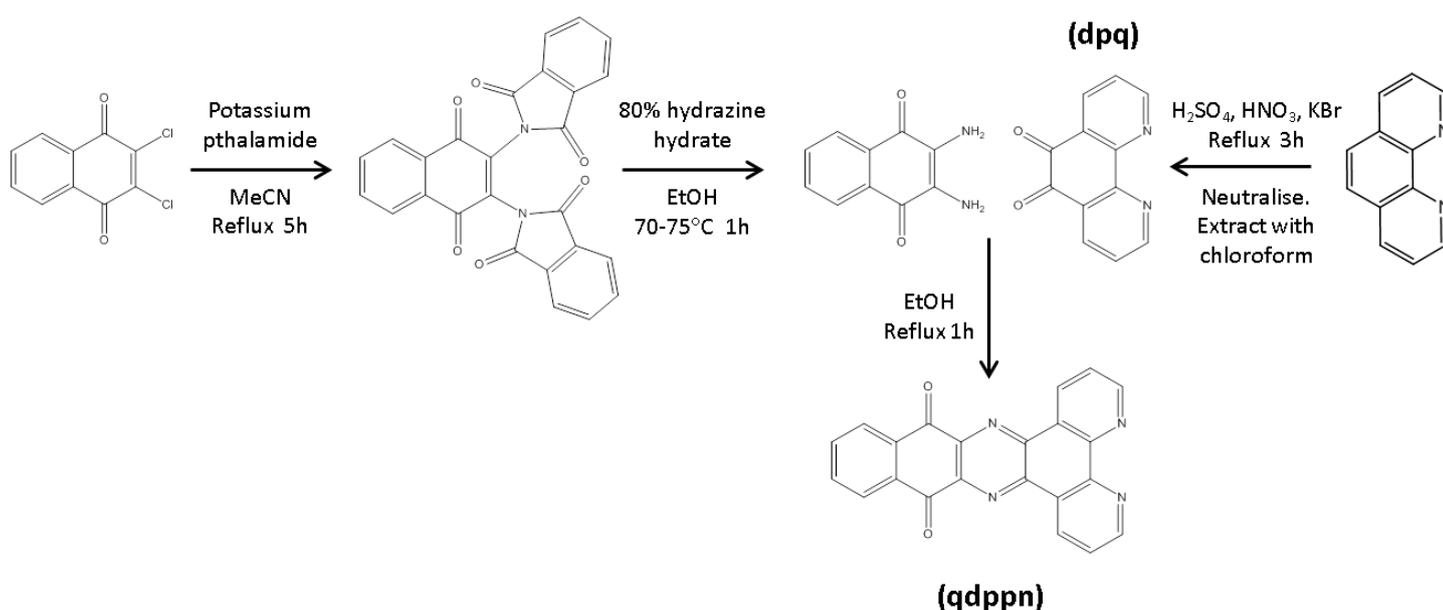


Figure 3: Ligand synthesis. qdppn ligand produced in 2 modules: 2,3-diamino-1,4-dinaphthoquinone via 2,3-diphthalamide-1,4-naphthoquinone [6], and 1,10-phenanthroline-5,6-dione (dpq), and then combined.

III. FUTURE WORK

Later attempts to synthesise qdppn from dpq and 2,3-diamino-1,4-dinaphthoquinone were not successful and a new protocol for this reaction needs to be developed. When (tpm)Ru(qdppn)(4-aminopyridine) is synthesised, spectroscopic studies can be used to determine the charge separation properties of the complex and the lifetime of its excited state. These studies would be useful in determining its suitability for development as a component of an artificial photosynthesis system.

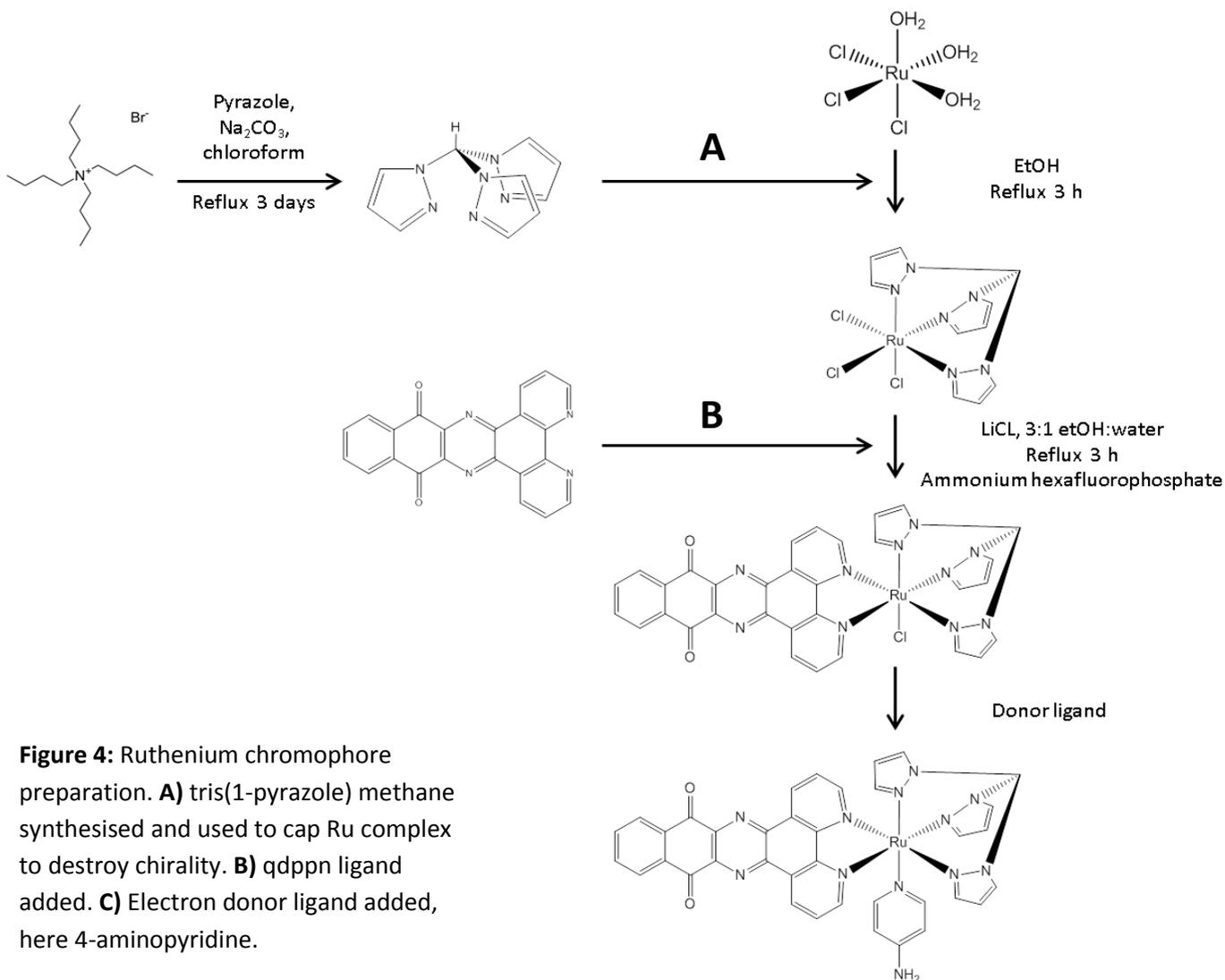


Figure 4: Ruthenium chromophore preparation. **A)** tris(1-pyrazole) methane synthesised and used to cap Ru complex to destroy chirality. **B)** qdppn ligand added. **C)** Electron donor ligand added, here 4-aminopyridine.

IV. ACKNOWLEDGEMENTS

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V. REFERENCES

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