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Preparation of a novel β-CD–dimanganese complex with covalently bound photosensitizer†

Nicole Van Hoof,[a] Tia E. Keyes,*[a] Robert J. Forster,[b] Andrea McNally[a] and Noel R. Russell*[a]

[a] *School of Chemistry, Dublin Institute of Technology, Kevin St., Dublin 8, Ireland. E-mail: tia.keyes@dit.ie*
[b] *School of Chemical Sciences, Dublin City University, Glasnevin, Dublin 9, Ireland*

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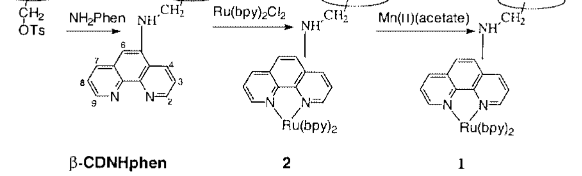
The synthesis and structure of a novel donor–acceptor complex comprised of a photosensitising ruthenium polypyridyl moiety covalently linked to a β-cyclodextrin unit bearing a hydroxy-bridged manganese(III) dimer 1 is described; the dimanganese complex undergoes a photoinduced electron transfer and may represent an attractive model system for elucidating aspects of photosystem II.

The current interest in novel donor–acceptor systems capable of photoinduced charge separation is driven by applications such as biomimetic chemistry, charge storage devices and nanoelectronic components. Recently, a number of elegant systems have been developed,[1] employing flash-quench methods and sacrificial quenchers to mimic part of the photoinitiated processes leading to oxidation of water in photosystem II.[2] We aimed on the other hand to develop a system incorporating a dimanganese site, in which the excited state energy of the sensitiser was sufficient to drive the electron transfer without the need for sacrificial reagents.

In the approach outlined here we have developed a $Ru(bpy)_2$ sensitiser linked *via* a β-cyclodextrin bridge to a hydroxo bridged Mn(III) dimer (Scheme 1). This is the first report in which the donor and acceptor moieties are external to cyclodextrin which acts as the mediating bridge in the D–A system.

By employing the highly rigid CD bridge, the inter-site separation and relative orientation of the reactants is thought to be consistent with those estimated for photosytem II. Moreover, this system mimics an important feature of PSII in that up to 10 water molecules are included in the cyclodextrin. In the photosystem, water oxidation is thought to be thermodynamically promoted by association of water with the Mn sites.

Our synthetic strategy is outlined in Scheme 1. The chelating β-cyclodextrin phenanthroline ligand, was prepared by refluxing 5-amino-1,10-phenanthroline, NH_2phen,[3] with 6^A-deoxy-6^A-*O*-*p*-toluenesulfonyl-β-cyclodextrin[4] in NMP for 5 h, the product was purified *via* recrystallization and purity confirmed by ^1H NMR (ESI†). This ligand was then coordinated to $Ru(bpy)_2$, by reaction with *cis*-$Ru(bpy)_2Cl_2$. The progress of the reaction was monitored by cation exchange HPLC and **2** was purified by column chromatography, on neutral alumina with acetonitrile–methanol (1 : 2 v/v), and isolated as a dichloride salt prior to coordination of the dimanganese centre.



Scheme 1

The ability of β-CD to coordinate metals such as Zn(II), Cu(II), Co(II) and Mn(III) has been known for some time, the metals are proposed to bind as hydroxo bridged dimers to the CD *via* the secondary hydroxyls, O-2 and O-3 of adjacent pyranose rings.[5–7] Mn was shown previously to coordinate effectively to β-CD *via* oxidative addition, on stirring of $Mn(OAc)_2$ and β-CD in an ethanol–DMF mixture containing 0.2 mol dm^{-3} NaOH under an inert atmosphere. Following this procedure, as outlined by Nair and Dismukes,[6] **2** was employed in place of β-CD and the formation of a high yield (*ca.* 60%), of the dimanganese bound complex was observed. The reaction was followed by TLC as **1** was found to be unstable in the aqueous solution employed for HPLC. This complex is soluble but unstable in water decomposing to **2** within minutes. It is stable over weeks in DMF and DMSO. At pH > 9.5 the complex was observed to be stable in water for up to 30 min.

Purity and structural confirmation for ligands and complexes were obtained through cation exchange HPLC, one- and two-dimensional ^1H NMR (ESI†), elemental analysis (ESI†) and magnetic susceptibility studies.

The ^1H NMR spectrum of **2** reveals well-resolved signals between 6 and 10 ppm, integrating for the 23 protons associated with the $Ru(bpy)_2(NH_2phen)$ unit and a complex pattern of signals associated with the β-CD are observed between 3 and 5 ppm. The paramagnetic dimanganese centre causes significant broadening of the ^1H NMR spectrum for **1**. However bands associated with the $Ru(bpy)_2$ unit remained sharp because of their distance from the paramagnetic Mn(III) centres.

Coordination of the bridged Mn(III) sites to the cyclodextrin moiety is accompanied by the appearance or enhancement of prominent features in the FTIR spectrum between 1700 and 1200 cm^{-1} (ESI†). Such bands, ascribed to alterations in included water on coordination of the metal sites, and to the OH bridging groups are analogous to those described previously in the simple Mn_2CD complex and for other OH bridged metallocyclodextrins,[8,9] Their presence is consistent with coordination of the manganese site to the secondary 2- and 3-hydroxy sites on the β-CD.[9–11]

The effective magnetic moment of complex **1** was found to be 3.46 μ_B per Mn at 296 K which is lower than the anticipated value of 4.9 μ_B for the spin-only value for the high-spin d^4 electronic configuration of Mn(III), calculated on the basis that no magnetic interactions are occurring between the metal ions.[12] This value is however, consistent with that reported for Mn_2CD by Nair and Dismukes[6] for a weakly antiferromagnetically coupled OH bridged dimanganese(III) moiety, the (III) oxidation state of which was confirmed to be EPR silent.[13]

Exhaustive experiments were performed on **1** and **2** using positive and negative ion ES and FAB MS techniques. No identifiable molecular ions were observable for either complex, however, the results obtained from ES and FAB positive ion

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† Electronic supplementary information (ESI) available: FTIR, NMR, UV–VIS, elemental analysis and CV data. See http://www.rsc.org/suppdata/cc/b1/b103363h/

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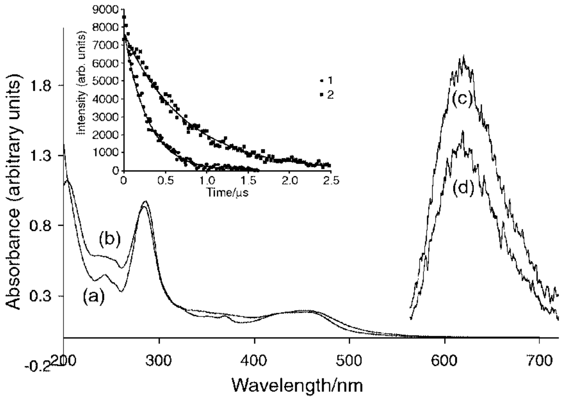

Fig. 1 Absorption of (a) **2** and (b) **1** and normalised emission spectra of (c) **1** and (d) **2** at room temperature in DMF, inset, emission decays of **1** and **2** at room temp. in DMF monitored at 620 nm and excited at 355 nm.

experiments showed the presence of many CD containing ions and also species such as $[Ru(bpy)_2(NHphen\beta\text{-}CD)Cl]^+$ (*m/z* 890) and $[Ru(bpy)_2(NHphen)]^+$ (*m/z* 608) were identified for both **1** and **2**. Although many of the spectra were far too weak to identify ions associated with the $Mn_2(OH)_2$ bridging system in **1** they do support the general structure of the ruthenium coordinated cyclodextrin species. The absorption and emission spectra of **1** and **2** are shown in Fig. 1, the main features in the visible region for both complexes are associated with Ru(II) to bpy charge transfer transitions, 450 nm for **1** (log ε = 4.15) and 453 (log ε = 4.52) for **2**. The strong similarity between the UV–VIS spectra of **1** and **2** is anticipated on the basis that the simple Mn_2CD shows a very weak transition at 480 nm, (log ε = 0.9), which would be expected to have little impact on the strong CT transitions in the visible region. Significantly, no new features are present which would indicate ground state interactions across the molecule or that the manganese oxidation state is altered by comparison with Mn_2CD.

The formal potentials for the $Ru^{2+/3+}$ redox reaction are essentially indistinguishable in **1** and **2** (at 1.06 and 1.09 V *vs.* SCE respectively). Consistent with the spectroscopic data, this conformity suggests that there is little ground state interaction between the Ru and Mn sites. The Mn sites of **1** can be oxidised and reduced within an accessible potential window, with reduction appearing as a single electron step at −1.08 V and oxidation occurring as a single electron step at 1.41 V *vs.* Ag/AgCl. The electrochemical behaviour of Mn is scan rate dependent, under slower scan rate conditions, both $Mn^{2+/3+}$ and $Mn^{3+/4+}$ couples are irreversible. This is thought to be due to decomposition of the complex on formation of Mn(II) and Mn(IV). At faster scan rates (>1000 V s^{-1}) these redox processes become chemically reversible. Thus, while the oxidised state is not indefinitely stable thermodynamically, its lifetime is at least 40 μs.

This observation is important for photoinduced electron transfer and indicates that the Mn(IV) state will be stable if the time constant for back electron transfer is less than a few microseconds.

1 and **2** both emit at cryogenic and room temp. Although emission intensities and lifetimes at 77 K are comparable for **1** and **2**, at room temp. the luminescence of **1** is significantly reduced by binding of the manganese centre, as shown in Fig. 1. This behaviour is reflected by the luminescence quantum yield, where ϕ_{em} of **2**, 0.012, is reduced by 50% to 0.006 for **1** and also in the emission lifetime data (Fig. 1, inset), where the lifetime of **2** is reduced from 820 to 220 ns on coordination of the Mn_2 site. Calculation of the radiative and non-radiative rate constants for **1** and **2** reveals that the primary source of this decrease is a reduction in k_{nr} for **1**.

Assuming electron transfer is the source of quenching in **1,** we have used eqn. (1), where $\tau_{complex}$ is the emission lifetime of

$$k_{et} = (1/\tau_{complex}) - (1/\tau_{model}) \qquad (1)$$

1 and τ_{model} the emission lifetime of a suitable structurally analogous model complex, in this case complex **2**, to estimate the electron transfer rate k_{et}, as 2×10^6 s^{-1}. Consistent with the rather large distance and weak electronic coupling that would be anticipated between the donor and acceptor sites, this electron transfer rate constant is low. This result is entirely consistent with the ground-state spectroscopic and electrochemical data presented earlier. It is important to consider whether a photoinduced electron transfer is likely to involve oxidation or reduction of the Ru^{3+*} centre. An insight into this process can be obtained by combining the ground state spectroscopic and electrochemical data.[14] This analysis reveals that the driving force for manganese oxidation is *ca.* −1.94 eV while the manganese reduction is thermodynamically uphill by *ca.* 0.04 eV. Therefore, it appears that the PET will involve electron transfer from the Mn(III) centre to Ru^{3+*} leading to the formation of Ru^{2+}. We are currently undertaking flash photolysis studies on **1** in order to confirm the photoinduced process is electron transfer and to investigate the issue of subsequent ground state electron transfer reactions.

In conclusion, we present here the synthesis of a novel β-CD bridged D–A complex in which a hydroxy-bridged dinuclear Mn site appears to behave as a donor in an excited state electron transfer. Beyond creating a novel supermolecule with potential biomimetic properties, this work represents a new approach to developing donor–acceptor systems in which interactions can be modulated by simple alterations in the synthetic procedure. For example, a number of alternative metals may be coordinated to the CD in an analogous manner to the manganese described here. Furthermore, the synthetic strategy employed here preserves access to CD cavity by guests such as phenols, quinones and even ferrocene. These guests are likely to allow us direct control over the strength of electronic coupling between donor and acceptor without having to synthetically functionalize the materials.

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12 μ_{eff}, was determined on a Sherwood Scientific, magnetic susceptibility balance, spin only values were calculated according to $\mu_{Mn} = 2[S_{Mn}(S_{Mn}+1)]^{1/2}$.

13 Results to be published.

14 The free energy was estimated from the Rehm–Weller expression; ΔG (eV) = $[E(D^{\cdot+}/D) - E(A/A^{\cdot-})] - E_{0-0}$ where $E(D^{\cdot+}/D)$ and $E(A/A^{\cdot-})$ are the oxidation and reduction potentials of donor and acceptor sites respectively and E_{0-0} is the zero–zero spectroscopic energy calculated from the 77 K emission spectrum.