Photoactive ruthenium(II) cyclodextrins responsive to guest binding

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A terpyridine functionalised cyclodextrin has been synthesised and ruthenium photoactive centres appended to give luminescent metallo-cyclodextrins which respond to guest binding.

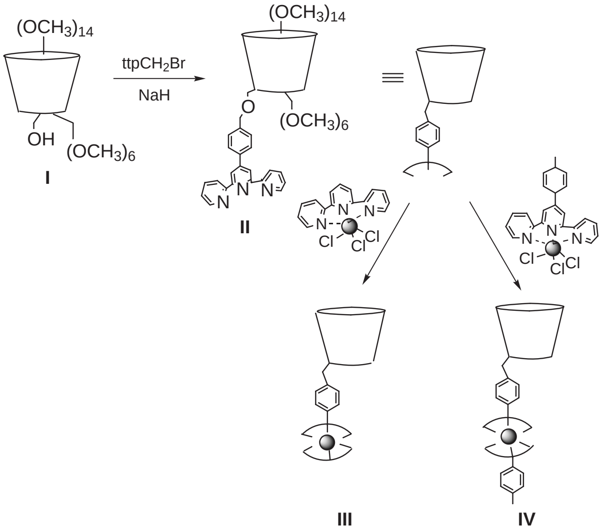
Biology provides many examples of light-sensitive macro- or supra-molecular intelligent systems that are capable of inducing directional motion of electrons and excitation energy. The design of supramolecular systems[1] that perform similar functions is of great interest particularly for their application towards the development of photomolecular devices.[2] Photoactive transition metal systems are very attractive candidates as units for the construction of molecular devices due to their photosensitisation and electrochemical properties.

Research in this area has mainly concentrated on building covalently linked metal complexes.[2] Photophysical studies have shown that the spatial organisation of the photoactive units is important for both energy and electron transfer processes and consequently this has led to the development of rigid polymetallic arrays using appropriate spacer units to covalently link metal centres.[3] High molecular complexity is inevitable in this approach since several features are accumulated in a single molecular component and synthetic challenges limit the choice of photoactive units. In this paper we introduce an alternative approach based on non-covalent links between components. It involves the design of photoactive metal-appended receptors that can act as sensor units upon introduction of a guest molecule in their cavity. When the guest is a metal complex the communication between the appended metal centre and the metallo-guest, brought together in space *via* non-covalent interactions, may then be established. Few examples of the previously reported metallo-receptors[4] have demonstrated their sensor properties.[5] Our design involves a terpyridine functionalised cyclodextrin which can form complexes with photoactive metals. The hydrophobic microenvironment of the cyclodextrin cavity allows the binding of appropriate guest molecules that trigger a change in the luminescence of the appended metal centre. We have synthesised a β-cyclodextrin functionalised with a tolyl-terpyridine unit (β-CD–ttp, **II**) and studied the formation of its luminescent complexes with ruthenium (Scheme 1). When an electron-accepting guest is added to the ruthenium functionalised CD, quenching of the ruthenium emission is observed.

An important precursor for the synthesis is the mono-6-hydroxy permethylated β-CD **I** which allows selective monofunctionalisation of the primary cyclodextrin side and solubility in organic solvents. A recently developed synthetic route for this derivative[6] proposed a convenient method to easily access compound **I** in good yield. Coupling of the cyclodextrin to the terpyridyl fragment was achieved through the reaction of **I** with 4′-[*p*-(bromomethyl)phenyl]-2,2′ : 6′,2″-terpyridine, ttpCH$_2$Br, under Williamson ether conditions using an excess of NaH in THF. The reaction was followed by TLC (Al$_2$O$_3$; ethyl acetate–methanol 30 : 1; R_f: β-CD–ttp = 0.7 and β-CDOH = 0.22) and after three days the terpyridine functionalised CD **II** was isolated in 50% yield after extraction by CH$_2$Cl$_2$ and size exclusion chromatography.

The 600 MHz ^{1}H NMR spectrum of **II** in CDCl$_3$ shows the fourteen aromatic protons in the range 7.2–8.8 ppm, the seven anomeric protons of the cyclodextrin at 5.0–5.2 and the rest of the cyclodextrin protons in the range 3.0–4.1 ppm. The methylene protons of the tolyl-terpyridine unit are diastereotopic due to the chirality of the CD and appear as two doublets at 4.62 and 4.68 ppm. The connectivities were elucidated by ^{1}H–^{1}H TOCSY spectroscopy. The formula of the compound was also confirmed by FAB-MS and elemental analysis.

Reaction of equimolar quantities of **II** with Ru(tpy)Cl$_3$ or Ru(ttp)Cl$_3$ in methanol with addition of *N*-ethyl morpholine afforded [(β-CD–ttp)Ru(tpy)][PF$_6$]$_2$ **III** and [(β-CD–ttp)Ru(ttp)][PF$_6$]$_2$ **IV** respectively after precipitation with ammonium hexafluorophosphate and size-exclusion chromatography (BioBeads SX2, DMF–THF 1 : 1) (tpy = 2,2′ : 6′,2″-terpyridine, ttp = 4′-(*p*-tolyl)-2,2′ : 6′,2″-terpyridine). The FAB mass spectra of **III** and **IV** show peaks at m/z = 2216 and 2306 corresponding to $\{M - [PF_6]\}^+$ and at m/z = 2071 and 2161 corresponding to $\{M - 2[PF_6]\}^{2+}$, respectively. The 600 MHz ^{1}H NMR spectra of **III** and **IV** show the characteristic aromatic proton patterns of terpyridine and tolyl-terpyridine in the region 7.0–9.2 ppm similar to the ones observed for [Ru(ttp)(tpy)]$^{2+}$ and [Ru(ttp)$_2$]$^{2+}$.[7] Complex **III** exhibits an MLCT absorption at 484 nm but it does not emit at room temperature upon excitation at the MLCT band. It is known that [Ru(tpy)$_2$]$^{2+}$ emits only at low temperature at $\lambda_{\max}$ = 598 nm and that [Ru(ttp)$_2$]$^{2+}$ emits at 640 nm at room temperature.[8] Interestingly, [(β-CD–ttp)Ru(tpy)][PF$_6$]$_2$ **III** emits at 77 K with an emission maximum at 622 nm (Fig. 1) which lies in between the values of the [Ru(tpy)$_2$]$^{2+}$ and [Ru(ttp)$_2$]$^{2+}$ emissions, as expected due to the electronic effects of the ligands. We have independently synthesised [Ru(tpy)(ttp)]$^{2+}$ and it shows the same emission behaviour as **III**.[9] The MLCT absorption of [(β-CD–ttp)Ru(ttp)][PF$_6$]$_2$ **IV** is centred at 490 nm and leads to room temperature emission with $\lambda_{\max}$ at 635 nm consistent with the expected MLCT emission. The UV-transparent cyclodextrin cavity does not perturb the luminescence properties of the complexes.



Scheme 1

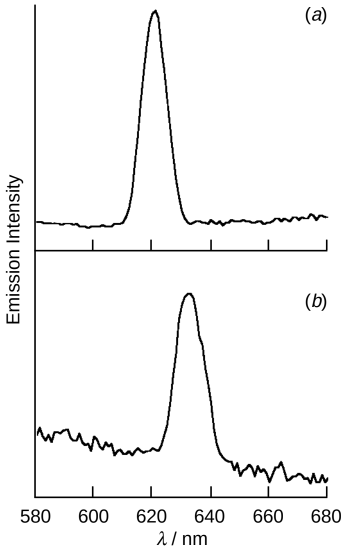


Fig. 1 Emission spectra of (*a*) [(β-CD–ttp)Ru(tpy)][PF_6]$_2$ in acetonitrile at 77 K, λ_{exc} = 480 nm, and (*b*) [(β-CD–ttp)Ru(ttp)][PF_6]$_2$ in acetonitrile at room temperature, λ_{exc} = 490 nm

In order to study the potential of metallo-CDs to participate in energy and electron transfer processes between the appended metal and a guest we initially selected an organic redox active guest, anthraquinone-2-carboxylic acid. The effect on the MLCT emission of the ruthenium centre of complex **IV** upon introduction of an equimolar amount of the guest was examined. Addition of microliter quantities of a 9.8 × 10^{-4} M solution of the guest in acetonitrile induced partial quenching, up to 20%, of the MLCT emission of complex **IV** (Fig. 2). We attribute this quenching effect to electron transfer between the appended metal and the guest, consistent with previous cases when quinones covalently attached to ligands of ruthenium complexes quench the MLCT emission.[10] In the absence of the cyclodextrin receptor the quenching of the MLCT emission is not observed upon addition of anthraquinone-2-carboxylic acid to a solution of [Ru(ttp)$_2$]$^{2+}$ under similar conditions. Further photophysical studies of the electron transfer process, and examination of the relation of the guest with the binding constant and the distance of the ruthenium centre, are in progress.

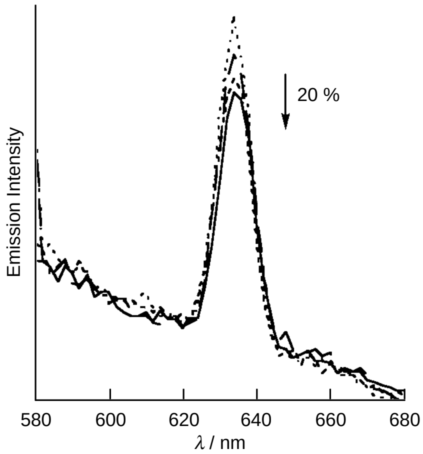


Fig. 2 Emission spectra of 1.9 × 10^{-5} M [(β-CD–ttp)Ru(ttp)][PF_6]$_2$ in 10% acetonitrile in water upon addition of 0.25, 0.5, 1 molar equivalents of anthraquinone-2-carboxylic acid, λ_{exc} = 490 nm

We have established the formation of photoactive metallocyclodextrins based on a new terpyridine functionalised cyclodextrin and confirmed the communication between guest molecules in the cavity and a ruthenium centre appended to the cyclodextrin cavity. We are currently extending our approach to the inclusion of metallo-guests in the ruthenium cyclodextrins and studying their involvement in energy and electron transfer processes between the appended metal and the metallo-guest.

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Notes and References

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