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Ruthenium and Osmium Podate Cyclodextrins with Dual-function Recognition Sites for Luminescent Sensing

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A multifunctionalised podand cyclodextrin ligand, β-CD-(urebpy)$_7$, with urea–bipyridine binding sites leads to ruthenium and osmium, {Ru[β-CD-(urebpy)$_7$]}[PF$_6$]$_2$ {Os[β-CD-(urebpy)$_7$]}[PF$_6$]$_2$, cyclodextrins. The bipyridine ligands are preorganised by the cyclodextrin cavity encapsulating the ruthenium and osmium core to give photoactive metallocyclodextrins. The podate cyclodextrin complexes show characteristic ruthenium and osmium tri-bipyridine luminescence. It is demonstrated that the ruthenium cyclodextrins participate in sensing schemes through both the cyclodextrin cavity and the urea cage at the bottom of the cyclodextrin rim. Luminescence quenching of the ruthenium emission is observed by addition of anthraquinone guests in the cyclodextrin cavity or addition of dihydrogen phosphate anion.

Keywords: Cyclodextrins; Molecular devices; Supramolecular chemistry; Sensors

The Future of Supramolecular Chemistry

The development of supramolecular systems will be directed towards the design of systems that will either interact with or act as nanoscale devices in a controlled way. For example, the importance of miniature photomolecular devices in nanoscale technology has led to the design of polymetallic supramolecular assemblies. The employment of multi-electron metal centres in a single supramolecular structure provides the basis for the development of molecular energy conversion systems and molecular wires in macromolecular systems, which is a focus of our research.

Zoe Pikramenou obtained her BSc from the University of Athens in Greece. She was then awarded an Academy of Athens scholarship to carry out PhD studies in the USA where she joined the group of Professor Daniel G. Nocera (currently at MIT) at Michigan State University to develop optical supramolecules as sensors for aromatic pollutants. Upon completion of the doctorate, she moved to France to join the group of Professor Jean-Marie Lehn as a Marie Curie fellow and later as a Collège de France research fellow to work on photochromic systems based on photoinduced proton transfer. She then moved to the UK to take up an appointment as a lecturer in the University of Edinburgh before she moved to her current lectureship position in the School of Chemical Sciences at the University of Birmingham. Her research interests involve the design of functional supramolecular systems with emphasis on light-activated functions including lanthanide chemistry and photophysics and cyclodextrin receptor chemistry. In the lanthanide field, the group has developed systems for lanthanides, studied controlled formation of lanthanide complexes with different sensitisers and studied the interaction with DNA. In the cyclodextrin field, energy and electron transfer via non-covalent bonds in aqueous assembled metallocyclodextrin-metalloguest systems has been demonstrated.

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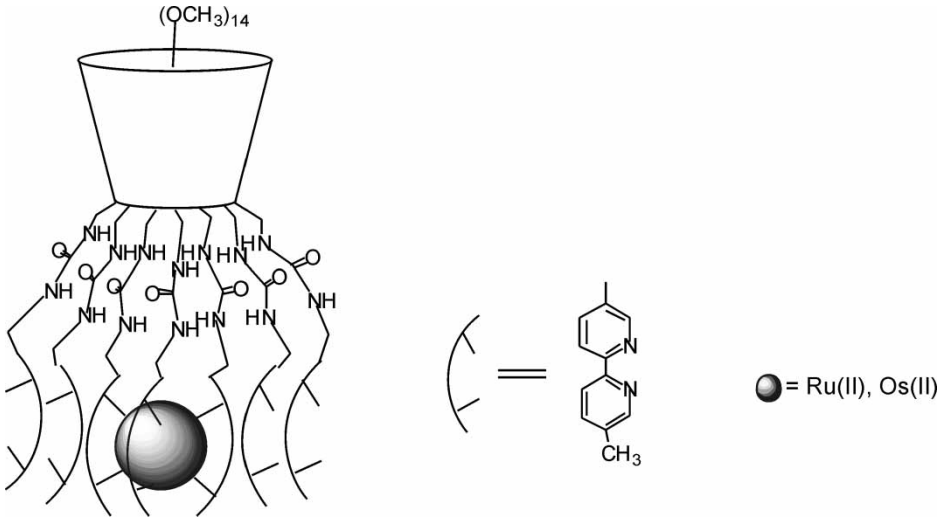
INTRODUCTION

Cyclodextrins are bucket-shaped receptor molecules widely used for a broad range of applications from biotechnology, pharmaceutical and cosmetics to the pesticides industry [1,2]. Their unique feature is the preorganised sugar-based cavity that provides water solubility and a hydrophobic interior for small-molecule binding. The arrangement of the glucose units in cyclodextrins leads to primary hydroxyl groups on the narrow side and secondary hydroxyl groups on the wider site of the cyclodextrin cup. The advantage of such arrangement coupled with the difference in reactivity between primary and secondary hydroxyl groups has led to the development of several functionalisation schemes of the cyclodextrin cup. One of the areas developed is the functionalisation of the rim with ligating groups for metal centres. These "ligating" cyclodextrins have attracted a large amount of interest for catalysis where preorganisation around a metal is important for the function of the active site [3,4]. A recently expanding area is the employment of metallocyclodextrins in the design of sensors of small molecules. The cyclodextrin cavity is a spectroscopically transparent host for small-molecule recognition, and a photoactive metal center is appended on the cyclodextrin rim. The sensing response is based on a "turn-on" or a "turn-off" of metal luminescence signal upon recognition of the guest molecule by the cavity. Lanthanide and ruthenium cyclodextrins [5,6] have been developed for sensing of aromatic hydrocarbons [7–9], quinones [10] and steroids [11]. We have used two approaches for the development of ruthenium cyclodextrins: (1) attachment of a single ruthenium moiety at the functionalised rim of the cyclodextrin and (2) assembly of multiple cyclodextrins around the metal ion [12–14]. A recently developed approach has involved multi-functionalisation of the cyclodextrin cavity with ligating units for attachment of metal centres [15–17]. In this design, the rim of the cyclodextrin is used as a preorganised scaffolding unit for the formation of a second cage at the bottom of the cyclodextrin bucket. Previous approaches for building preorganised structures for metal centre binding have been primarily based on the design of podand and macrocyclic ligand structures [18], with the exception of calixarene receptor chemistry, where introduction of metal binding sites is achieved by functionalisation of the calixarene rims [19,20].

There has been interest in studying encapsulation of ruthenium for the effect of the steric constraints of the complex structure on its photophysical properties. A series of ligands for encapsulating ruthenium metal ions have been designed, based on cage and podand structures [21–26]. We are interested in the design of multiple binding sites on the cyclodextrin rim positioned such that they wrap around the ruthenium and osmium core to yield podand metallocyclodextrins; such cyclodextrin structures are attractive for examining the cage effect in the metal photophysical properties as well as their participation in sensing schemes in comparison with "wheel" cyclodextrins where the metal core is surrounded by three cyclodextrin receptors [27]. In this paper, we report the attachment of ruthenium and osmium photoactive centres at the bottom of a cyclodextrin functionalised with seven bipyridyl ligands (Scheme 1). The ligand provides a multi-binding site based on seven bipyridyl–urea podands for transition metal binding and the cyclodextrin cavity for guest binding. The luminescence properties of the ruthenium and osmium podand cyclodextrin complexes are reported; their dual sensing action is examined by binding of phosphate guests in



SCHEME 1 Schematic representation of the metal podate cyclodextrins.

the urea cage and quinone guests in the cyclodextrin cavity.

RESULTS AND DISCUSSION

Synthesis and Characterisation

The ruthenium complex of the β-CD-(urebpy)$_7$ ligand was prepared using the conventional method for the bipyridine ligands [28,29]. The flexibility of the bipyridine arms allows binding to one ruthenium metal. In previously described tricyclic cages, the ruthenium ion was reacted with the ligands before the capping of the cage structure. The osmium complex was prepared by one-pot reaction of the β-CD-(urebpy)$_7$ ligand with the osmium salt. The reaction was monitored by UV–vis to ensure complete conversion to the tris-bipyridyl species. Previously reported methods for preparation of the osmium complex involved a stepwise addition of the bipyridyl ligands, which was not applicable in our case [30]. The complexes are moderately soluble in organic solvents owing to the presence of the methyl groups on the cyclodextrin and the hexafluorophosphate anion. Previous attempts to prepare a ruthenium compound using a β-CD-(urebpy)$_7$ ligand without the protective methyl groups on the cyclodextrin [31] were unsuccessful, giving a mixture of complexes. The lower solubility of this ligand, together with a possible coordination of ruthenium by the free hydroxyl groups, might account for this result.

NMR, UV–vis spectroscopy and mass spectrometry were employed to identify the complexes. In the ^{1}H NMR spectra, the characteristic cyclodextrin and bipyridine proton pattern are present. The protons of the bipyridine groups bound to the ruthenium or osmium centres show distinct signals with shifts, as expected for the complexation to the metal centre. A signature of the metal binding is the expected upper field shifts ranging from 0.8 to 1.5 ppm of the 6-position of the bipyridyl proton, which is sensitive to the metal presence. The protons 6 of the bipyridines that form the metal coordination appear in the spectrum as three singlets, while for the unbound bipyridines, these protons have a multiplet as the resonance signal. The protons in the positions 3 and 4 are also affected, but these positions are not as sensitive for the metal presence as the position 6. The observed shifts of the bipyridyl protons agree with those observed in the ruthenium complex of the 5,5′-dimethyl-bipyridine ligand. Another interesting feature is that the terminal CH_3 groups of the bipyridine appear as seven singlets owing to the low symmetry of the complex.

We employed several mass spectrometric techniques, and we found that in electrospray conditions, the urea CO–NH bond is sensitive to the cone voltage. The peaks represent fragments of the metal complex unit with podant arms, and, although fragmentation has occurred at the urea CO–NH bond, they have clear isotope patterns for ruthenium and osmium. The breaking of the urea bond has been reported in another case of complexation with transition metal complexes [32].

The UV–vis spectra show the characteristic MLCT bands confirming the coordination of the metal to three of the bipyridyl ligands [33–35]. The ruthenium complex shows the ^{1}MLCT at 450 nm and the osmium the ^{3}MLCT at 652 nm.

Luminescence Studies

Solutions of the {Ru[β-CD-(urebpy)$_7$]}$(PF_6)_2$ complex exhibit room-temperature luminescence upon excitation at the ^{1}MLCT band with a maximum of emission at $\lambda_{em} = 610$ nm (Fig. 1). The band is attributed to the ^{3}MLCT emission of ruthenium tris-bipyridyl complexes. The emission maximum is similar to that obtained from a model ruthenium complex $[Ru(mbpy)_3]^{2+}$ where mbpy = 5,5′-dimethyl-2,2′-bipyridine. The emission quantum yield is found to be 0.01, and the luminescence lifetime is 410 ns in aerated solution and 710 ns in argon-purged solution. The luminescence lifetime is longer than that of the model complex [21,22], which indicates a slower deactivation pathway from reduced vibration deactivation, attributed to induced rigidity in the podand cyclodextrin system. However, the effect is not as prominent as in the closed cage structures or in some of the tri-podand ligands. This can be attributed to the different functional groups in the 5-position of the bipyridine (methylene vs. –CO–) and the different steric

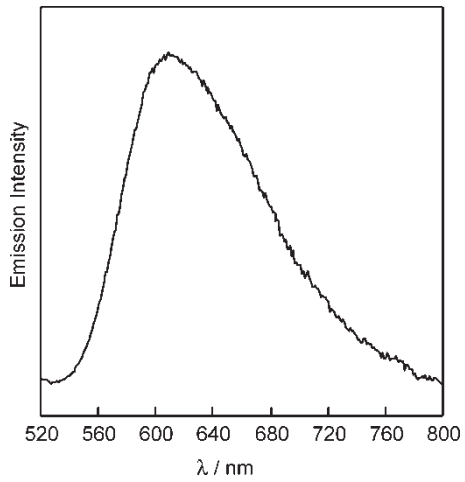


FIGURE 1 Luminescence spectrum of {Ru[β-CD-(urebpy)$_7$]}$[PF_6]_2$ in CH_3CN excitation at $\lambda_{exc} = 460$ nm. The spectrum is corrected for PMT response.

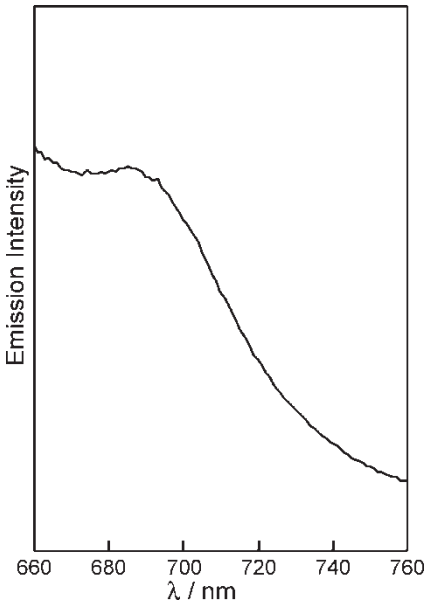


FIGURE 2 Emission spectrum of {[Os[β-CD-(urebpy)$_7$]}[PF$_6$]$_2$ in 25% acetonitrile in butyronitrile at 77 K, $\lambda_{exc} = 480$ nm.

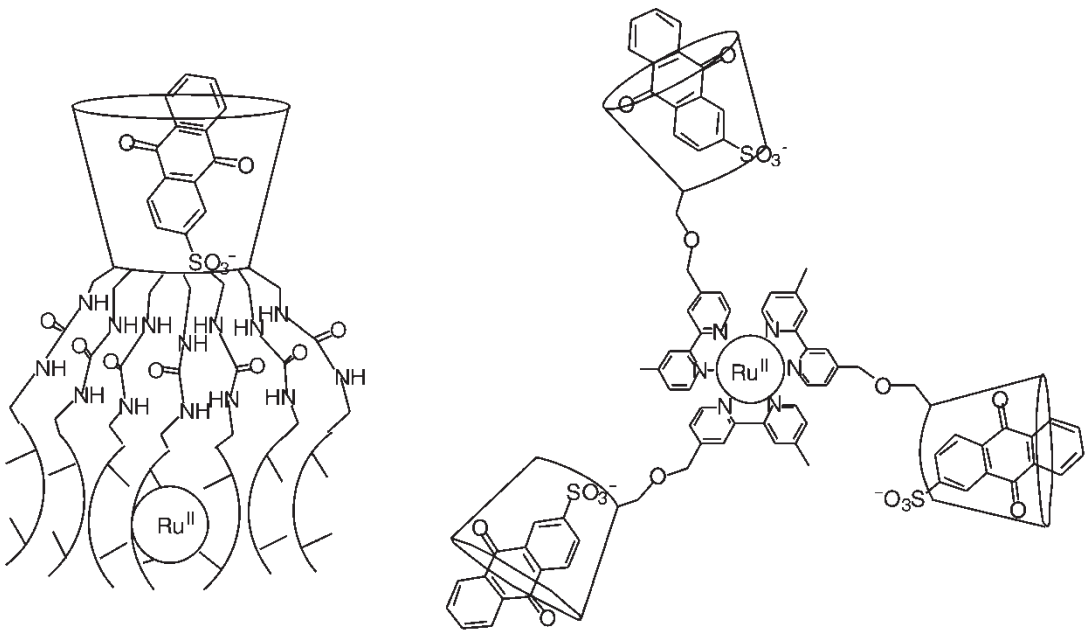
constraints of the cyclodextrin structure that may not allow flexibility of the arms to wrap around the ruthenium to optimise the binding.

The osmium complex shows weak emission at $\lambda_{max} = 690$ nm (Fig. 2); the background signal in the spectrum is due to scattering. The position of the luminescence signal is characteristic of the ^{3}MLCT emission of the osmium tris-bipyridyl complexes [36] and confirms the coordination of three bipyridyl groups around the osmium centre.

Luminescence Sensing of Guests: Recognition in the Cyclodextrin Cavity

We investigated the effect of AQS as a redox active quinone guest on the luminescence properties of the ruthenium cyclodextrin. Quinones are popular electron acceptors for photoinduced reduction processes, involved in many examples in supramolecular assemblies [37–39]. Previous work in our group demonstrated quenching of the ruthenium luminescence in metallocyclodextrins appended with ruthenium–terpyridyl units [10,12]. We have chosen AQS as the quinone guest based on the high binding constant with β-cyclodextrin ($K = 1100 \pm 100\,M^{-1}$) [12] and good solubility properties. We examined the effect of quenching of ruthenium luminescence using the {Ru[β-CD-(urebpy)$_7$]}(PF$_6$)$_2$ and the [Ru(β-CD-mbpy)$_3$][PF$_6$]$_2$ as hosts (Scheme 2). The luminescence spectra of the quenching experiments are shown in Fig. 3.

Upon irradiation at the ruthenium ^{1}MLCT band at 490 nm, the ruthenium emission intensity decreases with increasing concentration of quinone acceptor. The concentrations of the two ruthenium hosts were chosen so that the same number of cyclodextrin cups were present in solution to ensure similar conditions for binding. Addition of 36 equivalents of AQS in microlitre aliquots to solutions of {Ru[β-CD-(urebpy)$_7$]}[PF$_6$]$_2$ and [Ru(β-CD-mbpy)$_3$][PF$_6$]$_2$ leads to 74% and 88% quenching of the ruthenium



{Ru[β-CD-(urebpy)$_7$]}$^{2+}$ with AQS [Ru(β-CD–mbpy)$_3$]$^{2+}$ with AQS

SCHEME 2 The podate (left) and wheel (right) cyclodextrin complexes with AQS guest.

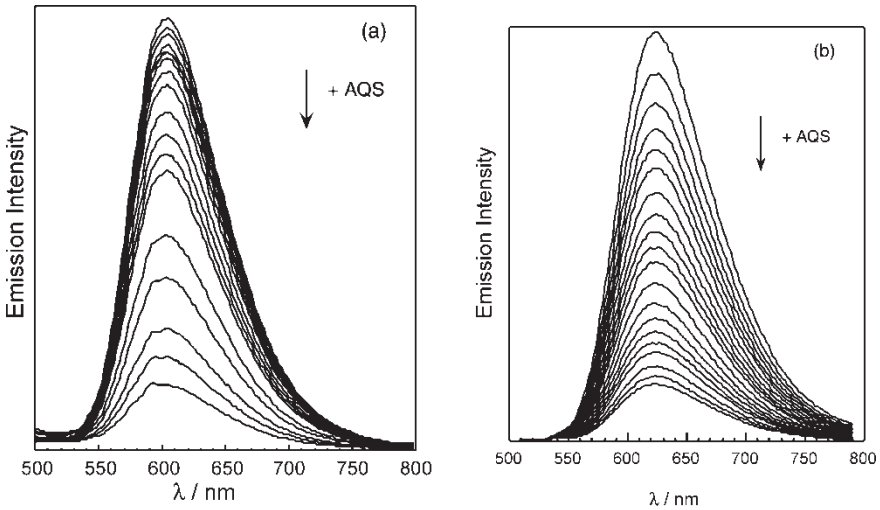


FIGURE 3 Luminescence spectra of (a) $\{Ru[\beta\text{-CD-(urebpy)}_7]\}[PF_6]_2$ (2.6×10^{-5} M) and (b) $[Ru(\beta\text{-CD-mbpy})_3][PF_6]_2$ (7.5×10^{-6} M) with the addition of AQS in buffered solution (pH = 7).

^{3}MLCT emission, respectively. The smaller quenching of the $\{Ru[\beta\text{-CD-(urebpy)}_7]\}[PF_6]_2$ is attributed to the amount of bound AQS. In the concentrations chosen, 70% and 45% of the cyclodextrin cups are occupied with an AQS guest for $[Ru(\beta\text{-CD-mbpy})_3][PF_6]_2$ and $\{Ru[\beta\text{-CD-(urebpy)}_7]\}[PF_6]_2$, respectively. Control experiments, under the same experimental conditions and $[Ru(bpy)_3][PF_6]_2$ as a model complex with no cyclodextrin receptors, have shown that there is a bimolecular component in the quenching in both cases, which contributes to about 50% of the quenching. This is expected in the case of the ruthenium trisbipyridyl core in contrast with ruthenium–terpyridyl units [12] as its excited state is longer-lived, and the bimolecular component is more pronounced. The $[Ru(\beta\text{-CD-mbpy})_3][PF_6]_2$ provides three receptors, but only one anthraquinone can contribute to the quenching process as it is a one-electron transfer process. To demonstrate the binding of AQS where there is no bimolecular contribution to the quenching, we have monitored the ruthenium emission in the presence of excess $\{Ru[\beta\text{-CD-(urebpy)}_7]\}[PF_6]_2$. A steep quenching curve with a local plateau is observed due to the binding of AQS inside the cyclodextrin cup (Fig. 4a); excess AQS leads to a higher quenching effect due to the optmised AQS binding in the cup and some bimolecular quenching contribution (Fig. 4b).

An estimate of the photoinduced electron-transfer rate can be obtained by using emission intensities: $k_{et} = (I_0/I - 1)/\tau_0$. Using the luminescence data,

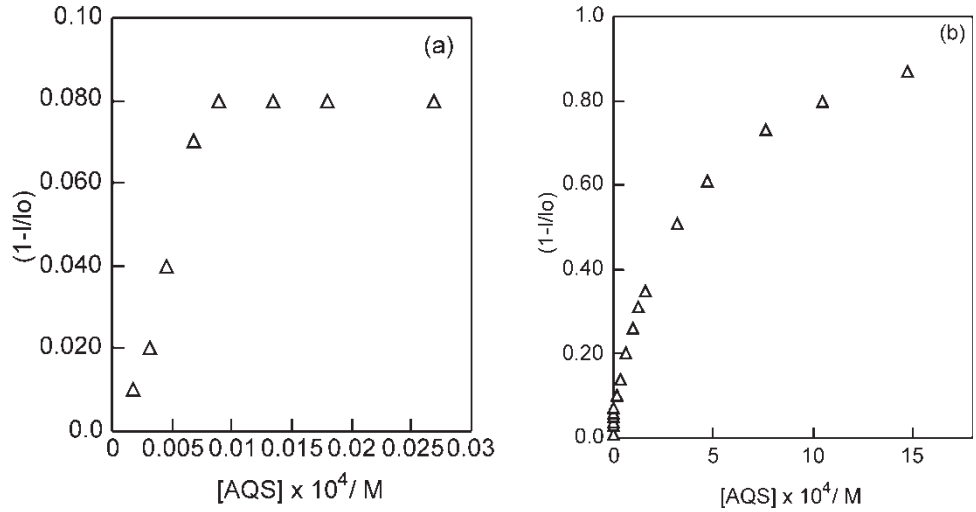


FIGURE 4 Titration plots of the luminescence quenching of $\{Ru[\beta\text{-CD-(urebpy)}_7]\}[PF_6]_2$ (2.6×10^{-5} M) by (a) 0.003–0.1 mol. equiv. of AQS (b) excess of AQS, $\lambda_{exc} = 460$ nm.

corrected for the bimolecular quenching effect, under conditions where most of the ruthenium cyclodextrins cups are occupied by an AQS molecule, we obtained rates of the electron-transfer process of 6.0×10^6 and $6.3 \times 10^5\,s^{-1}$ for {Ru[β-CD-(urebpy)$_7$]}[PF$_6$]$_2$ and [Ru(β-CD-mbpy)$_3$][PF$_6$]$_2$, respectively. The faster rate observed for the {Ru[β-CD-(urebpy)$_7$]}[PF$_6$]$_2$ system may be attributed to the substitution in the 5 position of the bipyridine, which is more efficient for electronic communication.

The electron-transfer rates are much slower than in the case of ruthenium-terpyridyl CDs [8], which may be expected, due to the intrinsic lifetime properties of the photoactive centers. Other reports of non-covalent electron transfer through a cyclodextrin cavity between ruthenium centres and organic acceptors indicate rates around $10^7\,s^{-1}$ [40,41]. The different values of electron-transfer rates may be due to a variety of factors, including driving forces, distance between the metal and the acceptor, and different binding modes of the included guest. An intramolecular electron-transfer rate between a ruthenium bipyridyl core and an anthraquinone via a covalent bridge of $5.3 \times 10^6\,s^{-1}$ was reported [42]; this is in the same order of magnitude as our system, indicating a significant stabilisation of the charge-separated state using non-covalent bonds as a pathway for electron transfer.

We further analysed the photoinduced electron-transfer processes between [Ru(mbpy-β-CD)$_3$]$^{2+}$ and AQS by using time-resolved fluorescence spectroscopy. In principle, the occurrence of photoinduced electron transfer in the supramolecular structure should lead to a shortening of the measured lifetime, τ, relative to the intrinsic lifetime of [Ru(mbpy-β-CD)$_3$]$^{2+}$, τ_0. The electron-transfer rate constant is calculated as $k = (1/\tau) - (1/\tau_0)$. The luminescence decay of the [Ru(mbpy-β-CD)$_3$]$^{2+}$ in the presence of increasing AQS concentrations was investigated. Upon addition of 10 and 60 times excess of AQS to [Ru(mbpy-β-CD)$_3$]$^{2+}$, the lifetime changed from 640 ns to $\tau = 480$ ns and 113 ns, respectively. We expected a growing percentage of a shorter-lived component with a higher AQS concentration. Owing to instrumental limitations, we were not able to observe two separate components, as the charge-separated species is very short-lived and not enough data points could be acquired in that time range. The observed lifetimes give electron-transfer rates of $k = 4.9 \times 10^5\,s^{-1}$ and $k = 7.3 \times 10^6\,s^{-1}$, respectively. The electron-transfer rate at lower AQS concentrations agrees with the value obtained from corrected steady state measurements ($k = 6.3 \times 10^5\,s^{-1}$); the change in the lifetime upon higher AQS concentrations is a strong indication for the presence of an additional, bimolecular quenching process. Control experiments with the model ruthenium tris-bipyridyl complex [Ru(mbpy)$_3$]$^{2+}$ have been carried out at 60 times excess concentrations, and a lifetime shortening of $\tau = 92$ ns has been observed, which gives an electron-transfer rate of $1.1 \times 10^7\,s^{-1}$. An electron-transfer rate of $2.2 \times 10^9\,s^{-1}$ is reported for diffusion-controlled bimolecular process from [Ru(bpy)$_3$]$^{2+}$ to benzoquinone, and our lower rate value indicates that higher AQS concentrations should be used to saturate the ruthenium–bipyridine system with the quencher to obtain a reliable value to compare for bimolecular quenching processes.

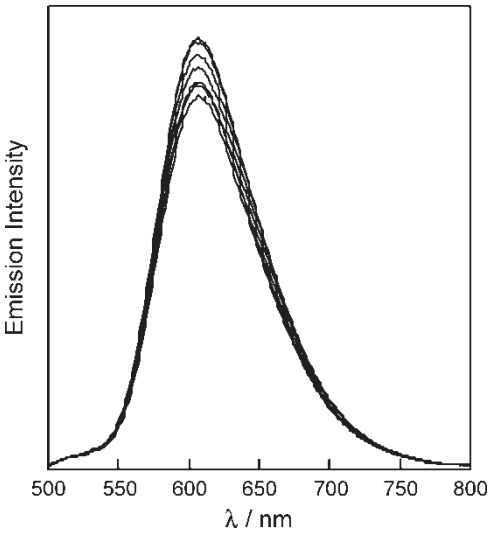


FIGURE 5 Luminescence spectra of {Ru[β-CD-(urebpy)$_7$]}[PF$_6$]$_2$ (2.4×10^{-5} M) upon addition of 0.1–10 equiv. of $H_2PO_4^-$ in dry DMSO.

Luminescent Sensing of Anions: Recognition in the Urea Cage

It has been shown previously that the urea spacers between the cyclodextrin and the bipyridine sites at the bottom of the cyclodextrin act as binding site for *cations* [15]. To examine the function of these spacers in the {Ru[β-CD-(urebpy)$_7$]}[PF$_6$]$_2$ complex as a binding site for *anions*, we tested the binding of dihydrogen phosphate based on previous recognition studies of dihydrogen phosphate by amide spacers between ruthenium bipyridyl sites and calixarene receptors [43]. We monitored the ^{3}MLCT luminescence of ruthenium by addition of 0.1–10 equivalents of $H_2PO_4^-$ (Fig. 5).

The maximum of the band does not shift, but a quenching of the luminescence signal of the ruthenium of around 13% is observed. A correction value of around 3% for the bimolecular contribution to the quenching effect is obtained from control experiments using the model ruthenium complex. The observed quenching is in contrast with the blue shift of the luminescence signal and the enhanced

quantum yield of the ruthenium observed in the calixarene case. However, in our case, the urea cavity is not as easily accessible for binding, and the $H_2PO_4^-$ may be binding to the free urea–bipyridyl arms, which do not affect the rigidity of the ruthenium binding site, therefore not increasing the quantum yield.

CONCLUSIONS

We have shown that cyclodextrins with multiple functionalised binding sites provide podand type structures for encapsulating ruthenium and osmium photoactive metal centres. The photophysical properties of the metal centres resemble the model compounds with some indication of binding-site rigidity around the metal centre, as indicated by the lengthening of the ruthenium luminescence. The ruthenium centre takes part in the photoinduced electron-transfer process to an anthraquinone acceptor guest through the cyclodextrin cavity. The electron transfer through the cavity is faster through the ruthenium podand cyclodextrin rather than through the ruthenium "wheel" cyclodextrin indicating a more efficient pathway. The ruthenium "wheel" cyclodextrin provides better protection of the ruthenium core for bimolecular quenching. The urea cage at the bottom of the cyclodextrin acts as a second recognition site for anions. The sensing effect is smaller than that for the observed ruthenium calixarenes due to the presence of several binding sites and the inaccessibility of the recognition site. Further studies on the design of multifunctional photoactive cyclodextrins are currently under way.

EXPERIMENTAL

Materials

All starting materials were purchased from Aldrich unless otherwise indicated. Ruthenium and osmium starting materials ($RuCl_3{\cdot}3H_2O$ and $OsCl_3{\cdot}3H_2O$) were supplied by Johnson & Matthey. The guests used in the binding studies were commercially available [AQS = anthraquinone-2-sulfonic acid, tetrabutylammonium salt of dihydrogen phosphate anion $Bu_4N(H_2PO_4)$]. Solvents used in synthetic procedures were analytical grade with the exception of HPLC-grade solvents used in the spectroscopic studies. Double deionised water was used where necessary in the spectroscopic studies. All the synthetic procedures were carried out under a nitrogen atmosphere unless otherwise stated. The preparation of heptakis-[2,3-di-*O*-methyl-6-deoxy-6-(5-methyleneureido-5′-methyl-2,2′-bipyridyl)]-cyclomaltoheptaose [β-CD-(urebpy)$_7$] and [Ru(β-CD-mbpy)$_3$][PF_6]$_2$ were previously reported [15,27].

Spectroscopy

NMR spectra were recorded on Bruker AC 300 spectrometer. Electrospray mass spectrometry was performed on a Micromass LC-TOF instrument. Absorption spectra were recorded on a Perkin Elmer Lambda 17 UV–vis spectrometer. Emission spectra were recorded on a Photon Technology International QM-1 steady-state spectrometer described elsewhere and employed with a dual-grating 500/750 nm emission monochromator. Quantum yields were determined using the "optical dilute relative method" [44] using [Ru(2,2′-bipyridyl)$_3$]Cl_2 as a reference with $\Phi = 0.028$ in aerated H_2O [45]. Low-temperature emission spectroscopy was performed in a mixture of butyronitrile/acetonitrile (4:1) degassed by "freeze-pump-thaw" cycles.

Guest Binding Studies

The AQS quenching experiments were performed in buffered solutions (BDH 50 mM phosphate buffer, pH = 7). A stock solution of the quinone was prepared in deionised water. Microlitre quantities of the quinone stock solution were added to a {Ru[β-CD-(urebpy)$_7$]}[PF_6]$_2$ 2.61×10^{-5} M solution. The guest concentration ranged from 1.96×10^{-8} to 1.47×10^{-3} M. The area of the ruthenium emission signal was integrated upon each addition of the guest. In the case of the dihydrogenphosphate anion ($H_2PO_4^-$), experiments were performed under dry conditions in DMSO. Microliter quantities of the anion stock solution were added to a {Ru[β-CD-(urebpy)$_7$]}[PF_6]$_2$ 2.39×10^{-5} M solution. The anion concentration ranged from 2.43×10^{-6} to 2.43×10^{-4} M. The area of the ruthenium emission signal was integrated upon each addition of the guest. Control experiments were performed in buffered solutions under the same conditions using [Ru(2,2′-bipyridyl)$_3$]Cl_2 as a model ruthenium compound without a recognition site in place of the ruthenium-cyclodextrin. The amount of bound guest or occupied cyclodextrin cups is calculated, taking into account a binding constant of AQS to β-cyclodextrin of 1100 M^{-1} [30].

Synthesis

{Heptakis-[2,3-di-O-methyl-6-deoxy-6-(5-methyleneureido-5′-methyl-2,2′-bipyridyl)]-cyclomaltoheptaose} Ruthenium(II) Hexafluorophosphate {Ru[β-CD-(urebpy)$_7$]}(PF_6)$_2$

$RuCl_3{\cdot}3H_2O$ (6.2 mg, 2.76×10^{-5} mmol) was added to ethylene glycol (5 mL) followed by addition of

β-CD-(urebpy)$_7$ (40 mg, 1.38×10^{-5} mmol). The solution was heated to 120°C for 24 h. The solvent was then evaporated, and the residue was washed with ether to remove excess unreacted ligand. The solid was then dissolved in methanol and the counterion exchanged with ammonium hexafluorophosphate. As there was no precipitate, the solvent was evaporated and the salt dissolved in water (3 mL) and extracted with dichloromethane (4 mL) (yield 24.6 mg, 54%).

^{1}H-NMR (300 MHz, CD_3CN): δ in ppm 8.54–8.19 (m, 8H, $H_{6bpy\text{-}unbound}$), 7.83–7.64 (m, 8H, $H_{3bpy\text{-}unbound}$), 7.52–7.37 (m, 20H, $H_{3bpy\text{-}bound}$, $H_{4bpy\text{-}bound}$, $H_{4bpy\text{-}unbound}$), 7.26 (s, 2H, $H_{6bpy\text{-}bound}$), 7.12 (s, 2H, $H_{6bpy\text{-}bound}$), 6.54 (s, 2H, $H_{6bpy\text{-}bound}$), 4.97 (br, 7H, H_{Glu}-1), 3.90–3.58 (m, 28H, CH_2-CD and CH_2-bpy), 3.41–2.89 (m, 70H, H_{Glu}-2 to H_{Glu}-6 and CH_3O-CD), 2.43–2.35 (21H, CH_3-bpy).

UV–Vis in CH_3CN: λ_{max} in nm (ϵ in $M^{-1}\,cm^{-1}$) 450 (6225), 295 (73540), 250 (36190).

{Heptakis-[2,3-di-O-methyl-6-deoxy-6-(5-methyleneureido-5′-methyl-2,2′-bipyridyl)]-cyclomaltoheptaose} Osmium(II) Hexafluorophosphate {[Os[β-CD-(urebpy)$_7$]][PF$_6$]$_2$

To a solution of $OsCl_3{\cdot}3H_2O$ (9.3 mg, 0.026 mmol) in ethylene glycol (6 mL), β-CD-(urebpy)$_7$ (31.4 mg, 0.011 mmol) was added. The mixture was refluxed for 10 days. After cooling to room temperature, the solvent was evaporated. The residue was dissolved in methanol (1.5 mL), and a methanolic solution of ammonium hexafluorophosphate was added. The methanol was evaporated, and the compound was extracted with chloroform. After evaporation, 35.2 mg of the complex were obtained (yield: 95%).

^{1}H-NMR (500 MHz, CD_3CN): δ in ppm 8.33–8.18 (m, 14H, $H_{6bpy\text{-}unbound}$ and $H_{3bpy\text{-}bound}$), 8.09–7.95 (m, 8H, $H_{3bpy\text{-}unbound}$), 7.87–7.79 (m, 8H, $H_{4bpy\text{-}unbound}$), 7.73 (s, 2H, $H_{6bpy\text{-}bound}$), 7.65–7.50 (s, 6H, $H_{4bpy\text{-}bound}$), 7.32 (s, 2H, $H_{6bpy\text{-}bound}$), 6.99 (s, 2H, $H_{6bpy\text{-}bound}$), 4.93 (br, 7H, H_{Glu}-1), 4.68–4.37 (m, 28H, CH_2-CD and CH_2-bpy), 4.12–3.34 (m, 70H, H_{Glu}-2 to H_{Glu}-6 and CH_3O-CD), 2.57, 2.53, 2.52, 2.51, 2.49, 2.47, 2.44 (s, 21H, CH_3-bpy).

UV–Vis in CH_3CN: λ_{max} in nm 652, 463, 387, 366, 339, 330.

The ruthenium and osmium complexes do not combust well, and this is unsurprising, given the presence urea moieties in close proximity to the metal.

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