DOI: 10.1002/ejic.200501122

A Prospective Study of the Use of the $[Os(tpy)_2]^{2+}$ (tpy = 2,2′;6′:2′′-Terpyridine) Core as Signalling Scaffolding for the Development of Chemical Sensors

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Keywords: Chemosensors / Osmium terpyridines / Macrocyclic ligands / Fluorescent probes / Thin films

The heteroleptic osmium(II) complex $[Os(L^1)(Me\text{-}phtpy)][PF_6]_2$ (L^1 = 1-[4′-*p*-tolyl-(2,2′:6′,2′′-terpyridyl)]-1,4,8,11-tetraazacyclotetradecane, Me-phtpy = 4′-*p*-tolyl-2,2′:6′,2′′-terpyridine) has been prepared, characterized and its potential use for chemical sensing purposes studied. The complex contains a polyazacycloalkane as "binding site" and a $Os(tpy)_2^{2+}$ core that acts as a "signalling subunit". The emission intensity of the osmium complex was quenched in acetonitrile/water (1:1 v/v) by Cu^{2+} and Ni^{2+}. Potentiometric titrations of $[Os(L^1)(Me\text{-}phtpy)]^{2+}$ in the presence of Cu^{2+} were carried out in order to determine thermodynamic binding constants in acetonitrile/water (70:30 v/v, 0.1 mol·dm^{-3} tetrabutylammonium perchlorate). With Cu^{2+} the receptor $[Os(L^1)(Me\text{-}phtpy)]^{2+}$ forms the complex $\{Cu[Os(L^1)(Me\text{-}phtpy)]\}^{4+}$ at neutral pH. Moreover it undergoes two stepwise protonation processes at acid pH related to the partial protonation of the cyclam core and forms two hydroxo complexes at basic pH. The Ni^{2+} complexes of the osmium receptor $[Os(L^1)(Me\text{-}phtpy)]^{2+}$ are able to act as an anion fluorogenic chemosensor in acetonitrile/water mixtures. A displacement of the quenching effect to more acidic pH in the Ni^{2+}–$[Os(L^1)(Me\text{-}phtpy)]^{2+}$ system was observed for anions in the order ATP > AMP > chloride. A prospective study of the use of the $[Os(L^1)(Me\text{-}phtpy)]^{2+}$ complex as a fluorogenic sensor for oxygen was also carried out by incorporation of the complex in sol-gel silica films made with TEOS and MTEOS. Significant quenching of the osmium fluorescence by oxygen was observed. The oxygen response of the films showed good stability and repeatability. The study suggested that the $Os(tpy)_2^{2+}$ core might act as suitable signalling scaffolding in chemical sensing systems of cations, anions and gases.

Introduction

The development of new chemosensors for the selective sensing of cations and anions based on the covalent or non-covalent coupling of binding sites and signalling subunits is an area of interest. These programmed molecular systems, when appropriately designed, are capable of transducing guest binding processes into suitable signalling events such as changes in colour, fluorescence or redox properties of the formed molecular ensemble. Among different output signals, those based on changes in emission properties are especially attractive and a number of different fluorogenic chemosensors have been described for anion[1] and cation[2] sensing. Both all-organic and metal-based fluorogenic subunits have been widely used. Among metal-based luminescent systems, the complexes of ruthenium and rhenium are well known and have been used as signalling subunits in a considerable number of reported chemosensors.[3] In fact, the polypyridyl complexes of d^6 metal cations, with their strong metal-to-ligand charge transfer absorptions and emitting excited states, are good candidates as signalling reporters. In this sense, the most widely used metal-based signalling framework has been the $Ru(bpy)_3^{2+}$ core.[4] In contrast, the analogous $Ru(tpy)_2^{2+}$ scaffolding has been used as a signalling unit in very few cases.[5–10] $Ru(tpy)_2^{2+}$ might show certain advantages versus $Ru(bpy)_3^{2+}$, that is, it is relatively easy to functionalise the terpyridine core. The most serious drawback in using the $Ru(tpy)_2^{2+}$ scaffolding is its usually very low quantum yield when compared with that found for the $Ru(bpy)_3^{2+}$ systems. In order to maintain the use of the terpyridine framework but in an attempt to enhance the emission properties of the signalling unit at room temperature, we have moved in this paper from ruthenium to osmium as an alternative metal centre. Thus, for instance, the quantum yield at room temperature of the $Ru(tolyl\text{-}tpy)_2^{2+}$ complex (tolyl-tpy = bis[4′-(*p*-tolyl)-2,2′:6′,2′′-terpyridine]) is 3.2×10^{-5}, whereas that observed with osmium as the metal centre, $Os(tolyl\text{-}tpy)_2^{2+}$, is more than 500 times larger (φ = 0.021).[11] Although the osmium–terpyridine complexes have received less consideration than other metal–terpyridine systems, their photophysical properties

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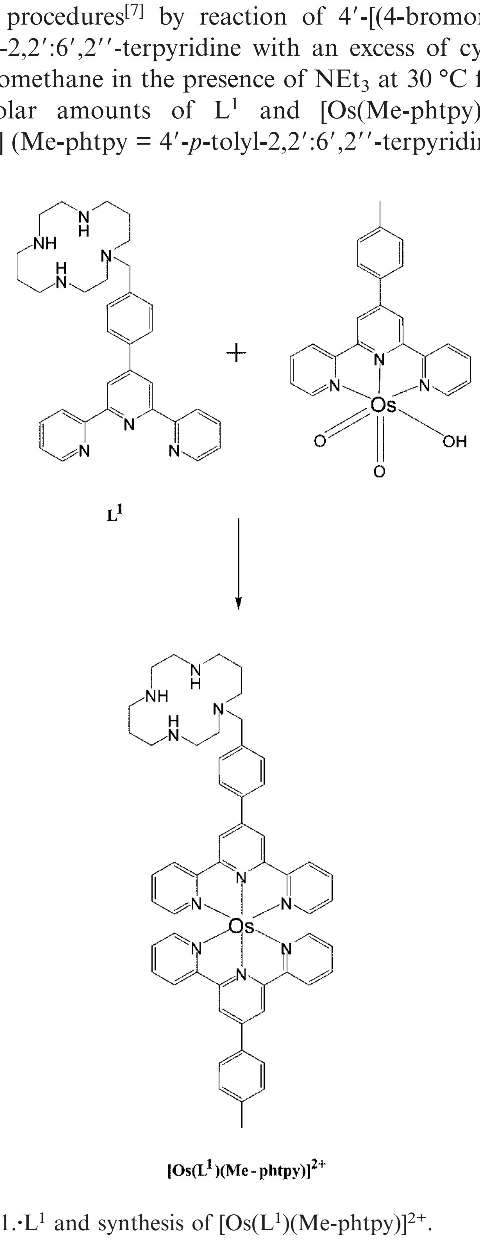
are well known because of comparative studies with the ruthenium analogues.[12]

Some of us have previously reported ruthenium bis-terpyridine functionalised systems as chemosensors for metal cations and anions.[6–10] However, and as far as we know, there are very few examples of the use of the $Os(tpy)_2^{2+}$ core as a signalling subunit for chemosensing purposes. As part of our interest in the development of chemical sensors for cations,[13] anions[14] and neutral guests,[15] we report here a prospective use of the osmium–terpyridine scaffolding as signalling reporter for the fluorogenic sensing of metal cations, anions and gases.

Results and Discussion

Synthesis and Characterisation

The ligand L^1 was synthesised following previously reported procedures[7] by reaction of 4′-[(4-bromomethyl)-phenyl]-2,2′:6′,2′′-terpyridine with an excess of cyclam in dichloromethane in the presence of NEt_3 at 30 °C for 24 h. Equimolar amounts of L^1 and $[Os(Me\text{-}phtpy)O_2OH\cdot(NO_3)_2]$ (Me-phtpy = 4′-*p*-tolyl-2,2′:6′,2′′-terpyridine) were reacted in a THF/water (1:1 v/v) mixture in the presence of hydrazine hydrate as reductant to yield a complex mixture containing several Os–tpy derivatives. The desired heteroleptic derivative $[Os(L^1)(Me\text{-}phtpy)][PF_6]_2$ was isolated from the reaction mixture by column chromatography in silica using a mixture of acetonitrile/water/saturated aqueous solution of KNO_3 (85:10:5 v/v/v) as eluent and further precipitation with ammonium hexafluorophosphate (see Scheme 1). The high-resolution FAB mass spectrum of the $[Os(L^1)(Me\text{-}phtpy)][PF_6]_2$ complex showed peaks at *m*/*z* 1325, 1180 and 1033 corresponding to $[Os(L^1)(Me\text{-}phtpy)][PF_6]_2$, $[Os(L^1)(Me\text{-}phtpy)][PF_6]$ and $[Os(L^1)(Me\text{-}phtpy)]$ fragments, respectively. The high-resolution FAB mass spectra also showed the expected isotopic distribution of peaks corresponding to the Os(192), Os(190) and Os(189) isotopes. The ^1H NMR spectra of the osmium complex were also in agreement with the proposed formulation.



Scheme 1. L^1 and synthesis of $[Os(L^1)(Me\text{-}phtpy)]^{2+}$.

Fluorogenic Sensing of Metal Cations

The synthesised osmium(II) complex $[Os(L^1)(Me\text{-}phtpy)]^{2+}$ contains a polyazacycloalkane as “binding site” and an $Os(tpy)_2^{2+}$ core able to act as a “signalling subunit”. In the first step, the studies shown below were carried out to identify the effect that the coordination of metal cations on the cyclam fragment has on the emission properties of the signalling osmium–terpyridine reporter. The electronic spectrum of the $[Os(L^1)(Me\text{-}phtpy)]^{2+}$ complex is as expected for an $Os(tpy)_2^{2+}$ chromophore[11] with two bands in the visible region because of the spin-allowed d→π metal-to-ligand charge transfer (MLCT) transition (λ_{max} = 470 nm) and the spin-forbidden MLCT band (λ_{max} = 670 nm).

The studies below were performed in acetonitrile–water mixtures because of the insolubility in pure water of the $[Os(L^1)(Me\text{-}phtpy)][PF_6]_2$ complex in a wide pH range. Excitation at 670 nm resulted in the emission at 740 nm. This emission of the $[Os(L^1)(Me\text{-}phtpy)]^{2+}$ complex remains unaltered within 5% in the 2–12 pH interval (see Figure 1). This behaviour is similar to that found for some ruthenium–terpyridine–polyamine analogues.[8] This indicates that in these systems there are no pH-dependent PET processes from the lone pair of the cyclam nitrogens to the photoexcited fluorophore as is usually found in polyazaalkanes bearing polycyclic aromatic hydrocarbons as signalling units.[2]

Steady-state fluorescence experiments as a function of the pH in the presence of equimolar amounts of metal cations M^{2+} ($M^{2+} = Cu^{2+}$, Zn^{2+}, Cd^{2+}, Hg^{2+}, Pb^{2+} and Ni^{2+}) resulted in noticeable changes only in the presence of Cu^{2+} and Ni^{2+}, whereas the emission intensity versus pH profile stayed unaltered in the presence of the remaining cations. The metal cation Cu^{2+} induced an important quenching of the $Os(tpy)_2^{2+}$ emission in the 3–12 pH range, whereas Ni^{2+} gave a similar quenching at basic pH (see Figure 1). This behaviour is significantly different to that found for the

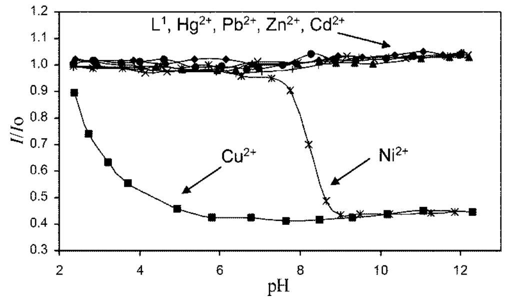


Figure 1. Emission intensity of the system $[Os(L^1)(Me\text{-}phtpy)]^{2+}$–$M^{2+}$–$H^+$ as a function of the pH in acetonitrile/water (70:30 v/v) mixture, $[\{Os(L^1)(Me\text{-}phtpy)\}^{2+}] = 10^{-4}$ mol·dm^{-3}, in the presence of 1 equiv. of metal cation (λ_{ex} = 670 nm, λ_{em} = 740 nm).

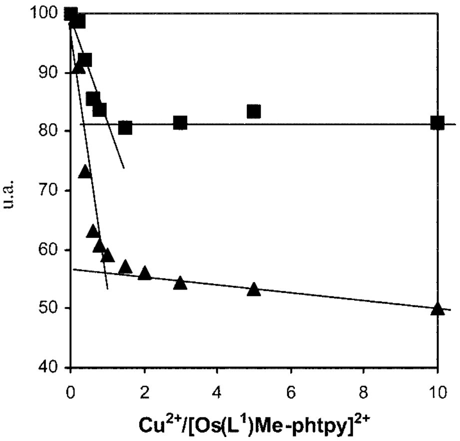


Figure 2. Steady-state fluorescence intensity (▲) and contribution of the lifetime of the free $[Os(L^1)(Me\text{-}phtpy)]^{2+}$ to the global decay (■) as a function of the Cu^{2+} equivalents in acetonitrile/water (70:30 v/v) mixture.

analogous $[Ru(L^1)(Me\text{-}tpy)]^{2+}$ compound (Me-tpy = 4′-methyl-2,2′:6′,2′′-terpyridine),[9] for which quenching was observed in a narrower pH window (5–9 pH range). In recent years a certain number of fluorogenic molecular probes for copper and nickel have been reported.[16–18] When compared with them, the complex $[Os(L^1)(Me\text{-}phtpy)]^{2+}$ shows some advantages; it displays fluorogenic sensing properties in mixed aqueous solutions and shows emission properties in the far end of the visible window where usually few fluorescence interferences are found.

Additional time-resolved emission studies of the ligand $[Os(L^1)(Me\text{-}phtpy)]^{2+}$ in the presence of Cu^{2+} were carried out in acetonitrile and in acetonitrile/water (70:30 v/v) solutions at neutral pH. In both cases the concentration of the osmium complex was 3×10^{-5} M. The ligand $[Os(L^1)(Me\text{-}phtpy)]^{2+}$ shows a monoexponential decay in both acetonitrile and acetonitrile/water mixtures with lifetime values of 107 ns and 112 ns, respectively. In the presence of certain amounts of Cu^{2+}, a biexponential decay was observed. One of the species has the same lifetime as $[Os(L^1)(Me\text{-}phtpy)]^{2+}$, whereas the other showed significantly shorter lifetime values of 22 and 28 ns respectively for acetonitrile and acetonitrile/aqueous solutions. This second lifetime was assigned to the formation of Cu^{2+}–$[Os(L^1)(Me\text{-}phtpy)]^{2+}$ complexes. In fact, when we compare the intensity of steady-state fluorescence and the contribution of the 107 ns component to the global decay, we observe that they follow the same tendency (see Figure 2), which is in agreement with the assignment of the 25 ns species to the copper complex that induced the quenching of the fluorescence of the $Os(tpy)_2{}^{2+}$ core. Upon increasing amounts of Cu^{2+}, in water, the lifetime at 112 ns does not undergo significant changes. On the contrary, when only acetonitrile is employed as solvent, the lifetime at 108 ns decreases to a value lower than 95 ns in the presence of an excess of Cu^{2+}. This suggests that in acetonitrile the free Cu^{2+} displays some kind of additional interaction with the fluorogenic group that is avoided in the presence of water, probably because of a stronger solvation of the metal. The curves in Figure 2 also reach an asymptotic behaviour between 1 and 2 equiv., suggesting the formation of $[Os(L^1)(Me\text{-}phtpy)]^{2+}$:$Cu^{2+}$ 1:1 complexes.

In order to obtain more information about the nature of the cation–ligand interaction, we have performed additional coordination studies for the Cu^{2+}–$[Os(L^1)(Me\text{-}phtpy)]^{2+}$ system by the use of potentiometric titrations.

Potentiometric Studies

The protonation and coordination behaviour of the $[Os(L^1)(Me\text{-}phtpy)]^{2+}$ complex was studied by potentiometric titrations with KOH of previously acidified acetonitrile/aqueous solutions (70:30 v/v, 0.1 mol·dm^{-3} tetrabutylammonium perchlorate) of $[Os(L^1)(Me\text{-}phtpy)][PF_6]_2$. The resulting protonation constants are shown in Table 1. For comparison purposes, the protonation constants of the ligand L^1[9] are also included in Table 1. Os^{II}–terpyridine complexes are very stable and kinetically inert, therefore titration experiments could be carried out without observing demetallation on the $Os(tpy)_2{}^{2+}$ framework. L^1 gives rise to five protonation constants in acetonitrile/aqueous solutions. The first two correspond to protonation of the cyclam fragment whereas the remaining three are more difficult to assign and might correspond to either protonation of the terpyridine or the cyclam units. The existence of a large number of protonation sites in L^1 makes the last two protonations too acidic and those constant values could not be determined. For the $[Os(L^1)(Me\text{-}phtpy)]^{2+}$ complex only three protonations were observed. This is in agreement with the results found for cyclam in acetonitrile/water (70:30 v/v) mixtures, in which only three protonation processes ($\log K$ = 11.6, 9.49 and 2.01, respectively) were found.[9] The protonation constants for the $[Os(L^1)(Me\text{-}phtpy)]^{2+}$ complex are very close to those reported for the analogous Ru-containing complex $[Ru(L^1)(Me\text{-}tpy)]^{2+}$.[9] This was an expected behaviour that indicated that the simple modification of the metal centre in the M–terpyridine core does not significantly affect the protonation of the anchored cyclam unit.

Table 1. Logarithms of the protonation constants of L^1 and $[Os(L^1)(Me\text{-}phtpy)]^{2+}$ in acetonitrile/water (70:30 v/v) (298 K, 0.1 mol·dm^{-3} tetrabutylammonium perchlorate).

Reaction	log β
$[Os(L^1)(Me\text{-}phtpy)]^{2+} + H^+ \leftrightarrows [Os(L^1)(Me\text{-}phtpy)H]^{3+}$	10.42(3)
$[Os(L^1)(Me\text{-}phtpy)H]^{3+} + H^+ \leftrightarrows [Os(L^1)(Me\text{-}phtpy)H_2]^{4+}$	18.90(4)
$[Os(L^1)(Me\text{-}phtpy)H_2]^{3+} + H^+ \leftrightarrows [Os(L^1)(Me\text{-}phtpy)H_3]^{5+}$	23.81(5)
$[L^1H]^+ + H^+ \leftrightarrows [L^1H_2]^{2+}$	19.34(4)
$[L^1H_2]^{2+} + H^+ \leftrightarrows [L^1H_3]^{3+}$	23.95(3)
$[L^1H_3]^{3+} + H^+ \leftrightarrows [L^1H_4]^{4+}$	26.89(3)
$[L^1H_4]^{4+} + H^+ \leftrightarrows [L^1H_5]^{5+}$	29.51(2)

Table 2 shows the stability constants obtained for the formation of Cu^{2+} complexes with $[Os(L^1)(Me\text{-}phtpy)]^{2+}$ in acetonitrile/water (70:30 v/v) mixtures from potentiometric titrations with KOH of previously acidified solutions of 1:1 mixtures of Cu^{2+} and $[Os(L^1)(Me\text{-}phtpy)][PF_6]_2$. The distribution diagram of $[Os(L^1)(Me\text{-}phtpy)]^{2+}$–$H^+$–$Cu^{2+}$ is shown in Figure 3. The receptor $[Os(L^1)(Me\text{-}phtpy)]^{2+}$ forms the complex $\{Cu[Os(L^1)(Me\text{-}phtpy)]\}^{4+}$ that exists at neutral pH (see Figure 3). This complex undergoes two stepwise protonation processes at acid pH and forms two hydroxo complexes at basic pH. The hydroxo complexes are formed by OH^- coordination to the Cu^{2+} centre to give most likely an octahedral configuration, whereas protonation processes at acidic pH involve the partial protonation of the cyclam subunit. The logarithm of the stability constant for the formation of the $\{Cu[Os(L^1)(Me\text{-}phtpy)]\}^{4+}$ complex is 14.2. This value is very close to that found for the formation of the analogous ruthenium complex $\{Cu[Ru(L^1)(Me\text{-}tpy)]\}^{4+}$ ($\log K = 13.30$), in agreement with the almost identical nature of the receptor.[9] The constant for the formation of the $\{Cu[Os(L^1)(Me\text{-}phtpy)]\}^{4+}$ complex can be compared with that found, under similar conditions (acetonitrile/water, 70:30), for the formation of the complex $[Cu(tmfcyclam)]^{2+}$ ($\log K = 19.06$), where tmfcyclam is a cyclam-substituted derivative [tmfcyclam = 1,4,8,11-tetrakis(ferrocenylmethyl)-tetraazacyclotetradecane].[9] Despite the somewhat different nature of both coordination sites in these complexes, the lower stability constants found for the former with Cu^{2+} are in agreement with the electrostatic repulsions imposed by the $Os(tpy)_2^{2+}$ core on the Cu^{2+}–cyclam coordination process.

Table 2. Logarithms of the stability constants of the system $[Os(L^1)(Me\text{-}phtpy)]^{2+}$–$H^+$–$Cu^{2+}$ in acetonitrile/water (70:30 v/v) (298 K, 0.1 mol·dm^{-3} tetrabutylammonium perchlorate).

Reaction	log β
$[Os(L^1)(Me\text{-}phtpy)]^{2+} + Cu^{2+} + 2H^+ \leftrightarrows [Os(L^1)(Me\text{-}phtpy)CuH_2]^{6+}$	24.38(9)
$[Os(L^1)(Me\text{-}phtpy)]^{2+} + Cu^{2+} + H^+ \leftrightarrows [Os(L^1)(Me\text{-}phtpy)CuH]^{5+}$	20.64(8)
$[Os(L^1)(Me\text{-}phtpy)]^{2+} + Cu^{2+} \leftrightarrows [Os(L^1)(Me\text{-}phtpy)Cu]^{4+}$	14.20(8)
$[Os(L^1)(Me\text{-}phtpy)]^{2+} + Cu^{2+} + H_2O \leftrightarrows [Os(L^1)(Me\text{-}phtpy)Cu(OH)]^{3+} + H^+$	5.01(5)
$[Os(L^1)(Me\text{-}phtpy)]^{2+} + Cu^{2+} + 2H_2O \leftrightarrows [Os(L^1)(Me\text{-}phtpy)Cu(OH)_2]^{2+} + 2H^+$	–5.45(7)

From the stability constants obtained from potentiometric methods and emission studies shown in Figure 1 it is possible to determine which species are responsible for the quenching observed in the interaction of Cu^{2+} with the $Os(tpy)_2^{2+}$ signalling unit. This can be seen in Figure 3, which shows both the distribution diagram and the emission intensity versus pH profile for the $[Os(L^1)(Me\text{-}phtpy)]^{2+}$–$H^+$–$Cu^{2+}$ system. It can be observed that the quenching of the emission of the $Os(tpy)_2^{2+}$ core is related to the formation of Cu^{2+}–$[Os(L^1)(Me\text{-}phtpy)]^{2+}$ complexes independently of the nature of the species formed. Neither the partial coordination of the cyclam macrocycle by the protons to form $\{Cu[Os(HL^1)(Me\text{-}phtpy)]\}^{5+}$ and $\{Cu[Os(H_2L^1)(Me\text{-}phtpy)]\}^{6+}$ nor the coordination of OH^- to the Cu^{2+} cation to form $\{Cu(OH)[Os(L^1)(Me\text{-}phtpy)]\}^{3+}$ and $\{Cu(OH)_2[Os(L^1)(Me\text{-}phtpy)]\}^{2+}$ produce significant changes in the emission intensity of the $Os(tpy)_2^{2+}$ core. The enhancement at acid pH is due to demetallation of the Cu^{2+} to recover the emissive $[Os(L^1)(Me\text{-}phtpy)]^{2+}$ species.

This behaviour contrasts significantly with that observed for the Cu^{2+}–$[Ru(L^1)(Me\text{-}tpy)]^{2+}$ system, for which the quenching of the emission intensity of the $Ru(tpy)_2^{2+}$ core was only found at neutral pH and attributed to the existence of the $\{Cu[Ru(L^1)(Me\text{-}tpy)]\}^{4+}$ complex in the solution.[9] In that case, the partial protonation of the macrocycle or Cu^{II} coordination with OH^- induced the recuperation of the emission intensity. In our system the different complexes formed have no effect on the emission of the $Os(tpy)_2^{2+}$ core in the $[Os(L^1)(Me\text{-}phtpy)]^{2+}$–$H^+$–$Cu^{2+}$ system, suggesting that the deactivation path should be different to that of $Ru(tpy)_2^{2+}$ in the analogous $[Ru(L^1)(Me\text{-}tpy)]^{2+}$–$H^+$–$Cu^{2+}$ ensemble. For the latter, a deactivation by energy transfer (ET) mechanisms was suggested, bearing in mind that photoelectron transfer (PET) processes were unlikely because of the large difference between the reduction of the $Cu(cyclam)^{2+}$ fragment and the oxidation of the Ru^{II} core.

From a simple thermodynamic cycle the free energy associated to a photoelectron transfer from the excited state of the Os or Ru complex to the Cu–cyclam core can be calculated from the redox potentials of the metal–terpyridine and copper–cyclam cores and the λ_{em} from the excited state of the metal–terpyridine group by using the equation: $\Delta G = -F[E_{Cu^{II}/Cu^{I}} - E_{M^{III}/M^{II}}] - hcN_A/\lambda_{em}$ where M = Os or Ru. The oxidation of the Ru^{II} core in $[Ru(Me\text{-}tpy)_2]^{2+}$ is +1.3 V versus SCE, whereas the oxidation of the Os^{II} metal centre in $[Os(L^1)(Me\text{-}phtpy)]^{2+}$ is found at +0.84 V versus SCE. Additionally, the λ_{em} for the Os and Ru complexes is 740 and 670 nm, respectively. Unfortunately, the Os system did not show any defined reduction peak for the Cu^{II}–cyclam core. Nevertheless, it might be possible to get some conclusion from the comparison between the oxidation potentials and λ_{em} from the Ru and Os complexes. Thus, from the above equation it can be observed that a reduction in the oxidation potential of the $M(tpy)_2^{2+}$ core would favour the occurrence of photoelectron transfer processes, whereas a reduction of the energy of the excited state (longer λ_{em}) would disfavour this. When we move from Ru to Os there

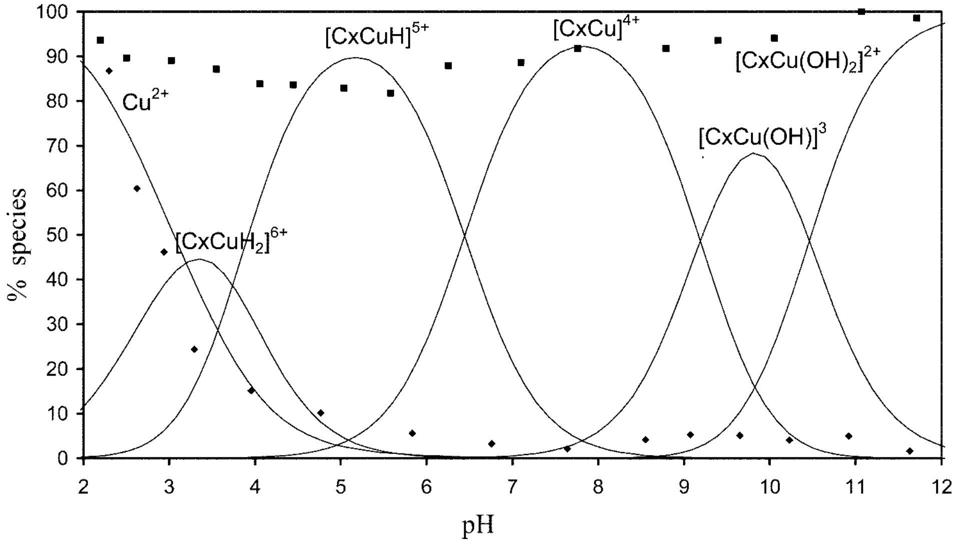


Figure 3. Species distribution diagram of the system $[Os(L^1)(Me\text{-}phtpy)]^{2+}$–$H^+$–$Cu^{2+}$ in acetonitrile/water (70:30 v/v) from the data of Table 2. The experimental values of intensity of fluorescence of $[Os(L^1)(Me\text{-}phtpy)]^{2+}$ (■) and $[Os(L^1)(Me\text{-}phtpy)]^{2+}$–$Cu^{2+}$ (♦) [Cx = $Os(L^1)(Me\text{-}phtpy)$] are also included.

is a fall in the oxidation potential of almost 500 mV that is not compensated by the difference in λ_{em} from the excited states of Os and Ru (λ_{em} at 740 and 670 nm), which correspond to an energy of only 180 mV. This indicates that a PET process from the excited state of the $M(tpy)_2^{2+}$ core to the Cu^{II}–cyclam moiety is thermodynamically more favourable to occur for Cu^{2+}–$[Os(L^1)(Me\text{-}phtpy)]^{2+}$ than for the analogous ruthenium Cu^{2+}–$[Ru(L^1)(Me\text{-}phtpy)]^{2+}$ complex.

Attempts to determine stability constants from potentiometric titrations for the Ni^{2+}–$[Os(L^1)(Me\text{-}phtpy)]^{2+}$ system were unsuccessful, most likely because of the presence of kinetically slow coordination processes. Nevertheless, the Ni^{2+} cation would be expected to form similar complexes to those found for Cu^{2+}, that is, the formation of the $\{Ni[Os(L^1)(Me\text{-}phtpy)]\}^{4+}$ complex at near neutral pH and the formation of hydroxo complexes and protonation of the cyclam macrocycle at basic and acidic pH, respectively. Assuming this general behaviour it might tentatively be suggested that the quenching in the case of the Ni^{2+} cations occurs in the pH range where the square-planar 1:1 $\{Ni[Os(L^1)(Me\text{-}phtpy)]\}^{4+}$ complex and the corresponding hydroxo complexes exist in solution.

Anion Sensing

As we have found above, the complex $[Os(L^1)(Me\text{-}phtpy)]^{2+}$ can protonate in acetonitrile/water media to give highly positively charged species. We believed that some of these formed species in mixed aqueous environments might be used as chemosensors for the fluorogenic sensing of anions. In order to check this possibility, certain anions were added to acidified solutions of $[Os(L^1)(Me\text{-}phtpy)]^{2+}$ and the emission of the $Os(tpy)_2^{2+}$ core monitored at different pH values. Unfortunately, the emission versus pH profile of the $[Os(L^1)(Me\text{-}phtpy)]^{2+}$ complex remained unaltered in the presence of the anions studied (Br^-, Cl^-, phosphate, sulfate, ATP, ADP and GMP). As an alternative, we also carried out similar studies with the Cu^{2+}–$[Os(L^1)(Me\text{-}phtpy)]^{2+}$ systems. However, unfortunately no change in the emission intensity of the $Os(tpy)_2^{2+}$ core was observed at any pH in the presence of the above-mentioned anions. This might be because, as we have found above, to observe a recovery of emission intensity in the Cu^{2+}–$[Os(L^1)(Me\text{-}phtpy)]^{2+}$ system it appears necessary to remove the copper from the macrocycle, whereas none of the anions is able to produce an interaction strong enough to take out the Cu^{2+} from the cyclam.

The research in this section has been completed by studying the effect that the presence of anions has on the emission behaviour of the Ni^{2+}–$[Os(L^1)(Me\text{-}phtpy)]^{2+}$ system (see Figure 4). As can be seen, the anions ATP, ADP and chloride show a remarkable behaviour and are able to significantly change the emission intensity versus pH profile of the Ni^{2+}–$[Os(L^1)(Me\text{-}phtpy)]^{2+}$ ensemble. Other anions (Br^-, phosphate, sulfate and GMP) are not shown but they did not induce significant emission changes. In all cases the Ni^{2+} quenching effect is shifted to the acidic range, suggesting these anions stabilise the formation of the nickel complex. In fact, the interaction of the Ni^{2+}–$[Os(L^1)(Me\text{-}phtpy)]^{2+}$ complex with anions would reduce the neat charge of complex. This would decrease the repulsion with the protonated cyclam core at acidic pH, resulting in a stabilization of the Ni^{2+}–$[Os(L^1)(Me\text{-}phtpy)]^{2+}$ system in a wider pH range with the concomitant fluorescence quenching due to the presence of the Ni^{2+} cation in the cyclam core. On the contrary, it seems that the anions are not able to produce an extra stabilisation of Cu^{2+} in the macrocycle because the quenching effect of Cu^{2+} is not shifted in the presence of anions (see above). The pH value at which the

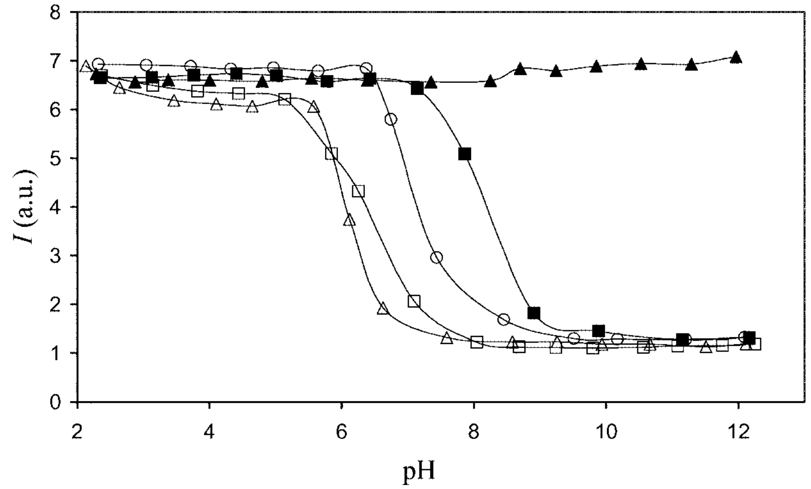


Figure 4. Emission intensity of the system $[Os(L^1)(Me\text{-}phtpy)]^{2+}$–$Ni^{2+}$–$H^+$–$A^{n-}$ as a function of the pH in acetonitrile/water (70:30 v/v) mixture, $[\{Os(L^1)(Me\text{-}phtpy)\}^{2+}] = 10^{-4}\,mol\cdot dm^{-3}$, in the presence of 1 equiv. of anion unless otherwise noted ($\lambda_{ex} = 670\,nm$, $\lambda_{em} = 740\,nm$). $[Os(L^1)(Me\text{-}phtpy)]^{2+}$ (▲), Ni^{2+} (■), chloride (○), ADP, (□) and ATP (△).

demetallation is produced (about 4 units lower than in the case of Ni^{2+}) is probably too low and the compensation of charge with anions is too weak to produce a significant effect in the fluorescence emission.

Selectivity can, for example, be achieved by changing the pH. For instance, addition of anions to the Ni^{2+}–$[Os(L^1)(Me\text{-}phtpy)]^{2+}$ system at pH 6.5 would result in a significant quenching only in the presence of ATP and ADP anions. A displacement of the quenching effect to more acidic pH is observed for anions in the order ATP > AMP > chloride. A similar sequence would also be expected (ATP > ADP > chloride) in relation with the strength of the interaction of these anions with the $\{Ni[Os(L^1)(Me\text{-}phtpy)]\}^{4+}$ complex. This is a somewhat attractive behaviour that indicated that the Ni^{2+} complex of the $[Os(L^1)(Me\text{-}phtpy)]^{2+}$ system acts as an anion fluorogenic chemosensor in mixed aqueous environments.

Oxygen Sensing

Finally, we have also tested the oxygen-sensing properties of the osmium complex $[Os(L^1)(Me\text{-}phtpy)]^{2+}$. There are a certain number of examples in the literature of the use of ruthenium–polypyridyl complexes for the detection of oxygen both in air[19] and as dissolved oxygen in water.[20] These studies are usually carried out either by immobilising the complex in polymer films or in sol-gel-derived films. In these systems the oxygen concentration is proportional to the degree of quenching of the ruthenium complex emission in the presence of oxygen. In most of the cases the complexes used for the preparation of oxygen sensors are $Ru(bipy)_3^{2+}$. On the contrary, there are very few examples of oxygen sensors using osmium complexes.[21]

Thus, we have performed studies directed to test the use of the $[Os(L^1)(Me\text{-}phtpy)]^{2+}$ complex as a gas-phase oxygen

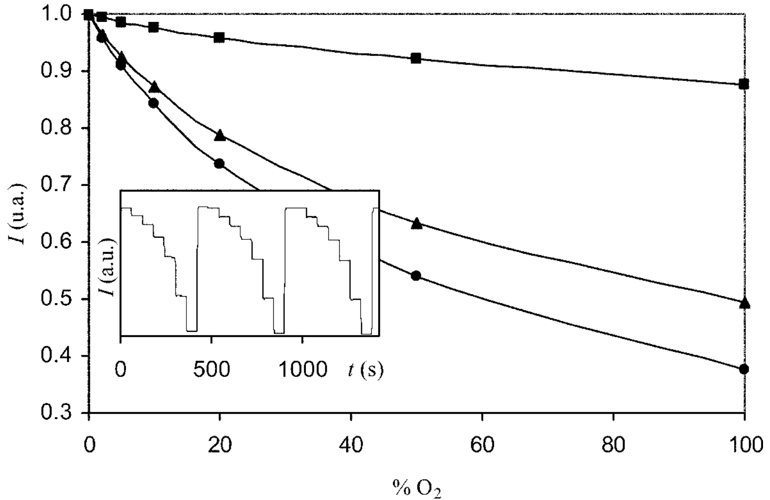


Figure 5. Emission intensity in different N_2:O_2 mixtures. MTEOS (■), MTEOS/TEOS, 1:1 (▲), TEOS (●).

sensor. The studies have been carried out using sol-gel silica films in which the osmium complex has been immobilised. Additionally, in order to study the influence of the sol-gel matrix we have used two different silica precursors, tetraethoxysilane (TEOS) and methyl tryethoxysilane (MTEOS). These precursors have a different number of hydrolysable positions and different speed of hydrolysis. Furthermore, the MTEOS precursor has a methyl group that increases the hydrophobicity of the final matrix. The emission intensity of the $[Os(L^1)(Me\text{-}phtpy)]^{2+}$ complex in the presence of different O_2/N_2 mixtures (λ_{ex} = 470 nm, λ_{em} = 740 nm) was measured and it was observed that oxygen produced a significant quenching of the osmium fluorescence. Figure 5 plots the emission intensity of the osmium core as a function of the concentration of oxygen for three different films made with TEOS, MTEOS and TEOS/MTEOS in 1:1 molar ratio. Table 3 shows the characteristics of the films prepared. As can be seen in Figure 5 and Table 3, the choice of precursor has a significant effect on the sensor response. Thus, films made with TEOS display a larger quenching (63% of the original emission intensity) in the presence of oxygen than that found for films with MTEOS (13% of the original osmium emission). As can also be seen in Table 3, the response time (time for the intensity to drop to 90% of the original value for a certain concentration of O_2) for films fabricated with TEOS was approximately 10 times larger than for the films made with MTEOS. This is most likely due to the presence of silanol groups in the former films that are able to retain some water in the structure hence slowing the sensor response time. The presence of the hydrophobic CH_3 groups in the matrix made with MTEOS avoids this effect and enhances the accessibility of the gas in the films, resulting in shorter response times. The films prepared showed a good stability and repeatability, indicating a very reversible process (see inset of Figure 5).

Table 3. Response parameters of the films.

Film	Quenching O_2 [%]	Response time 90% [s]
MTEOS	13	6.7
MTEOS/TEOS, 1:1	52	4.4
TEOS	63	44.1

Conclusions

A new osmium bis-terpyridine derivative attached to a cyclam receptor unit has been prepared and its ability to act as a fluorogenic chemosensor has been studied. The osmium complex $[Os(L^1)(Me\text{-}phtpy)]^{2+}$ is able to act as a fluorogenic sensor of copper and nickel in mixed aqueous environments, whereas the emission of the osmium–terpyridine core remains unaltered in the presence of other metal cations. Additionally, changes in the emission of the nickel complex have shown to be capable of sensing anions such as ATP, ADP and chloride in mixed aqueous solutions. Finally we have demonstrated good gas-phase oxygen sensitivity of sol-gel-based thin films in which the complex has been immobilised. All these studies indicate that osmium–terpyridine systems might behave as suitable and versatile signalling subunits for different sensing purposes.

Experimental Section

General Remarks: $[Os(Me\text{-}phterpy)O_2OH\cdot(NO_3)_2]$, 4′-[4-methylphenyl]-2,2′:6′,2′′-terpyridine and 1-[4′-*p*-tolyl-(2,2′:6′,2′′-terpyridyl)]-1,4,8,11-tetraazacyclotetradecane (L^1) were prepared according to published methods. All other reagents were obtained from commercial sources and were used as received.

Synthesis of $[Os(L^1)(Me\text{-}phtpy)][PF_6]_2$: The synthesis of the osmium complex $[Os(L^1)(Me\text{-}phtpy)]^{2+}$ was carried out following a general procedure described previously.[22] A mixture of L^1 (195.06 mg, 0.35 mmol), $[Os(Me\text{-}phterpy)O_2OH\cdot(NO_3)_2]$ (238.6 mg, 0.35 mmol) and hydrazine hydrate (0.65 mL) as a reducing agent in water/THF (1:1 v/v) were heated to 50 °C for 10 min. Ammonium hexafluorophosphate was added to the resulting deep red solution and the THF was eliminated under reduced pressure until the appearance of a precipitate that was filtered. This precipitate was purified by column chromatography over silica using acetonitrile/aqueous/saturated KNO_3 aqueous solution 85:10:5 as eluent. The product was finally isolated as its PF_6^- salt (19 mg, 4.1% yield). The osmium complexes are toxic and they should be handled carefully. ^1H NMR (300 MHz, CD_3CN, 25 °C) δ = 2.5–3.5 (m), 4.1 (s, 2 H), 7.13–7.20 (m, 4 H), 7.368 (t, 4 H), 7.61–7.70 (m, 4 H), 7.864 (t, 4 H), 8.137 (d, 2 H), 8.282 (d, 2 H), 8.699 (t, 4 H), 9.082 (s, 2 H), 9.109 (s, 2 H). FAB^+: 1325 $[Os(L^1)(Me\text{-}phtpy)]^{2+}\cdot 2PF_6^-$, 1180 $[Os(L^1)(Me\text{-}phtpy)]^{2+}\cdot PF_6^-$, 1033 $[Os(L^1)(Me\text{-}phtpy)]^{2+}$. High resolution FAB^+ $C_{54}H_{57}F_{12}N_{10}OsP_2$ (192) calcd. 1327.36662, found 1327.36961. $C_{54}H_{57}F_{12}N_{10}OsP_2$ (190) calcd. 1325.36358, found 1325.35995. $C_{54}H_{57}F_{12}N_{10}OsP_2$ (189) calcd. 1324.36328, found 1324.38587.

Preparation of the Films for Oxygen Sensing: Aqueous HCl (0.1 M) and the corresponding Si precursor were added to $[Os(L^1)(Me\text{-}phtpy)][PF_6]_2$ (20 mg, 15 μM) solved in acetonitrile (see Table 4). The solution was stirred for 30 min at room temperature and aged in the oven at 70 °C for several hours. Glass slides were coated by dip coating (3 mm·s^{-1}), and the films aged in the oven at 70 °C for 24 h.

Table 4. Details for the preparation of the oxygen-sensing films.

TEOS [%]	ACN [mL]	HCl [mL]	MTEOS [mL]	TEOS [mL]	Oven [h]
0	3.280	0.630	1.800	–	1
50	2.995	0.536	0.847	0.946	4
100	2.840	0.563	–	1.800	5

Physical Measurements and Instrumentation: Photochemical data were obtained with a FS900CDT steady-state T-Geometry Fluorometer from Edinburgh Analytical Instruments. ^1H NMR spectra were recorded with a Varian Gemini spectrometer. Potentiometric titrations were carried out in acetonitrile/water (70:30, v/v, 0.1 mol·dm^{-3} tetrabutylammonium perchlorate) under nitrogen using a vessel water-thermostatted at 25.0 ± 0.1 °C. The tritant was added by means of a Crison microburette 2031. Further details of the potentiometric experiments have been published previously.[23] The concentrations of the metal ions were determined using standard methods. The computer program SUPERQUAD[24] was used to calculate the protonation and stability constants. The titration curves for each system (about 250 experimental points, corresponding to at least three titration curves; pH range investigated 2.5–10.2; ligand and metal ions concentration about 1.0×10^{-3} mol·dm^{-3}) could be treated either as a single set or as separate entities without significant variation in the values of the stability constants. Finally, the sets of data were merged together and treated simultaneously to give the quoted stability constants.

Oxygen sensitivity was measured employing a Nichia blue LED (470 nm) as an excitation source and S1223 photodiode from Hamamatsu as detector placed at 90° to the LED. Appropriate optical filters were used to isolate the excitation from the emission light. Oxygen/nitrogen mixtures were delivered using computer-controlled mass-flow controllers from Kinetic Systems, Dublin, Ireland.

Acknowledgments

We thank the Ministerio de Ciencia y Tecnología (projects REN2002-04237-C02-01 and MAT2003-08568-C03-02) and UPV (project PPI-06-03) for support. J. V. R.-L. thanks the Ministerio de Educación y Ciencia for a Doctoral Fellowship.

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Received: December 19, 2005