

A [Ru^{II}(bipy)₃]-[1,9-diamino-3,7-diazanonane-4,6-dione] two-component system, as an efficient ON–OFF luminescent chemosensor for Ni²⁺ and Cu²⁺ in water, based on an ET (energy transfer) mechanism

Fabrizio Bolletta,^a Ilaria Costa,^b Luigi Fabbrizzi,^{*b} Maurizio Licchelli,^b Marco Montalti,^a Piersandro Pallavicini,^b Luca Prodi^{*a} and Nelsi Zaccheroni^a

^a Dipartimento di Chimica "G. Ciamician", Università degli Studi di Bologna, via Selmi 2, 40126 Bologna, Italy

^b Dipartimento di Chimica Generale, Università di Pavia, v. Taramelli, 12, 27100 Pavia, Italy

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A dioxo-tetramine ligand (1,9-diamino-3,7-diazanonane-4,6-dione ≡ dioxo-2,3,2-tet) has been appended to a Ru^{II}(bipy)₃ unit. This new system, **2**, is water-soluble and capable of sensing Cu²⁺ and Ni²⁺ cations thanks to the strong quenching of the Ru(bipy)₃ fluorescence, which takes place when a metal cation is coordinated by the dioxo-2,3,2-tet binding unit. Coordination requires the energetically expensive deprotonation of the amide nitrogens, so that only Cu²⁺ and Ni²⁺ are able to promote it among the series of divalent first-row transition metal cations. Moreover, the complexation reaction is pH-dependent and one can distinguish between the two metal cations on working at the proper pH. The quenching mechanism has been examined by measuring the lifetime of the excited state of the ruthenium luminophore both on the metal-free and metal-complexed system and by flash photolysis experiments carried out on the complexed systems. The results clearly indicate that an energy transfer mechanism holds both for the Cu²⁺ and Ni²⁺ complex. The characterization of **2** as a water soluble ON–OFF sensor for copper and nickel has also been checked for its lowest detection limit, finding that these two metals can be detected down to a 10^{−7} M concentration. Moreover, also system **3**, containing a dioxo-2,3,2-tet ligand and the Re^I(CO)₃bipy(Cl) luminophore, has been examined as another possible water-soluble ON–OFF fluorescent sensor for the same transition metal cations. Again, only Cu²⁺ and Ni²⁺ are bound with a pH-dependent equilibrium, but incomplete luminescence quenching was observed, which prevented the determination of the quenching mechanism.

Introduction

Luminescence quenching or enhancement is currently receiving a lot of attention as regards its application in sensing cationic, anionic or neutral species in solution.¹ A multi-component approach is commonly employed: a binding unit is covalently connected to a luminophore in a single molecular system. The interaction of a substrate with the binding unit, usually with a 1:1 stoichiometry, induces significant changes in the emitting properties of the luminophore, thus allowing it to signal the presence of the substrate.² Of particular interest is the possibility of building multi-component systems in which a wanted species is selectively bound by the binding unit, and/or, once bound, it causes a selective variation of the luminescence among a series of similar substrates. If the target species is a metal cation, sensors may be synthesized in which the choice of the binding unit can be based on the wide knowledge coming from classical coordination chemistry. We have recently found³ that a well known category of ligands, dioxo-tetraamines (and in particular dioxo-2,3,2-tet ≡ 1,9-diamino-3,7-diazanonane-4,6-dione) can be successfully employed for signalling the presence of Ni²⁺ and Cu²⁺ in aqueous solution, if incorporated in a two-component fluorescent molecule, where the fluorophore is an anthracene fragment (see ligand **1**): in the absence of metal cations the system displays its full fluorescence, but when the transition metal cation is bound by the dioxo-2,3,2-tet unit, according to equilibrium (1), the anthracene emission is quenched through an electron-transfer (eT) mechanism.^{2a} According to this, the system behaves as an ON–OFF sensor.

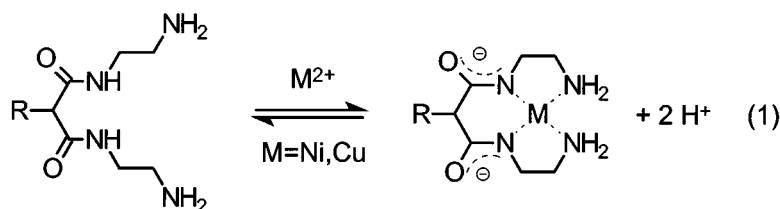
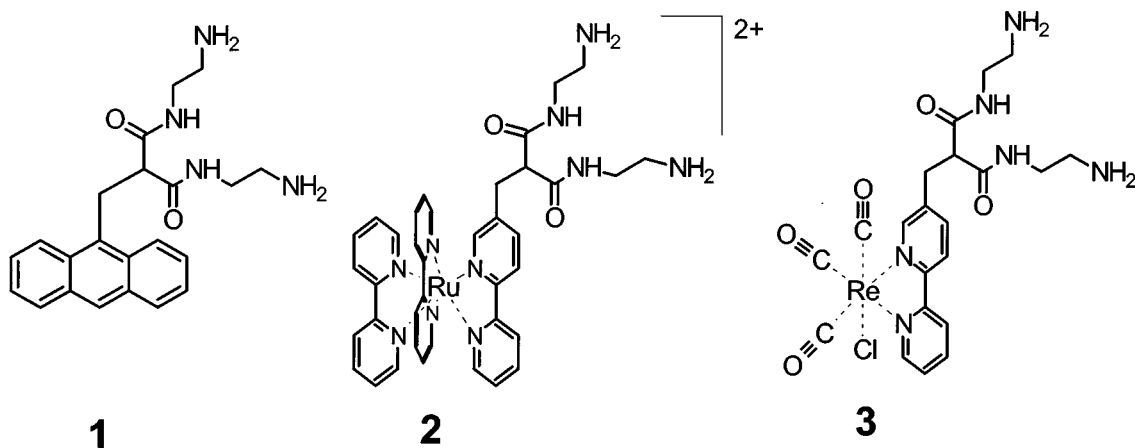
Dioxo-tetramine fragments appear as ligands of choice, as they (i) do not influence significantly the fluorescence of the connected fluorophore;³ (ii) can bind only Ni²⁺ and Cu²⁺ among the series of divalent transition metal cations belonging

to the first transition row; (iii) allow us to select between Ni²⁺ and Cu²⁺, as the complexation process (equilibrium (1)) is pH-dependent and takes place at remarkably different pH values for the two cations. One major drawback of system **1**, however, is the need for organic/aqueous solvent mixtures as the working media due to the pronounced lipophilicity of the anthracene fragment. In view of the possible analytical use of systems of this kind in natural and biologically relevant environments (*i.e.* water as solvent, at a neutral or slightly basic pH) we switched to more hydrophilic luminescent fragments, with the aim of obtaining a water-soluble sensor, selective for Cu²⁺ and Ni²⁺. Thus, the two-component system **2** has been prepared, in which the dioxo-2,3,2-tet binding unit has been appended to the highly fluorescent, water soluble [Ru^{II}(bipy)₃]²⁺ unit (bipy = 2,2'-bipyridine),⁴ a well studied luminophore whose emitting properties have already been found to vary when transition metal cations are bound in an appended tetraaza macrocyclic unit.⁵ In this work, the synthesis, coordinative properties and use of **2** as an ON–OFF sensor for Ni²⁺ and Cu²⁺ in water have been studied and described, with particular attention to the photophysical properties of its metal complexes and to the quenching mechanism. A [Re^I(CO)₃Cl(bipy)] derivative of the dioxo-2,3,2-tet ligand (ligand **3**) has also been prepared with the same aim and an overview of the chemical and photophysical studies on its binding properties towards Ni²⁺ and Cu²⁺ in water is also presented here.

Experimental

Instrumentation

Absorption spectra were recorded with a Perkin-Elmer Lambda 16 spectrophotometer. Uncorrected emission, corrected excit-



ation spectra and phosphorescence lifetimes were obtained with a Perkin-Elmer LS 50 spectrofluorimeter.

The fluorescence lifetimes (uncertainty $\pm 5\%$) were obtained with an Edinburgh single-photon counting apparatus, in which the flash lamp was filled with D_2 . Luminescence quantum yields (uncertainty $\pm 15\%$) were determined using $[\text{Ru}(\text{bpy})_3]^{2+}$ in aqueous solution ($\Phi = 0.028$)⁶ as a reference. In order to allow comparison of emission intensities, corrections for instrumental response, inner filter effects, and phototube sensitivity were performed.⁷ A correction for differences in the refractive index was introduced when necessary. Degassed solutions were obtained with the freeze-thaw-pump method. Emission spectra at 77 K were obtained using quartz tubes immersed in a quartz Dewar filled with liquid nitrogen. Transient absorption experiments were performed as described in reference 8.

Fluorimetric titrations

For the fluorimetric titrations, concentrations of 1×10^{-4} M were used for both **2** and **3**. Metal ions were added as chloride or perchlorate salts. Standard HCl, HClO_4 and NaOH were used for changing the pH conditions for the luminescence vs. pH experiments. Buffers at pH 7.0 and 9.0 were obtained using the lutidine/lutidinium and borate/boric acid couples, respectively.

Syntheses

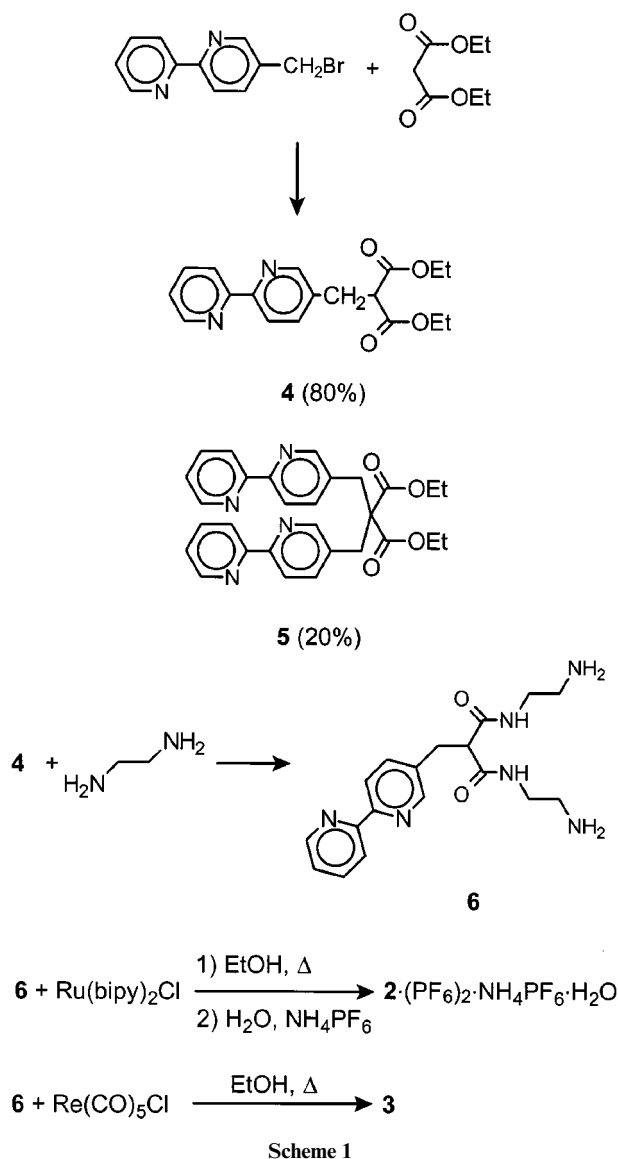
5-(Bromomethyl)-2,2'-bipyridine⁹ was prepared according to literature methods. All the other reagents are commercially available and were used as such, except where indicated in the experimental procedure.

Diethyl (2,2'-bipyridin-5-yl)methylmalonate 4. 1.75 g (7.04 mmol) 5-(bromomethyl)-2,2'-bipyridine were dissolved in 10 ml of dry toluene and added dropwise under a nitrogen atmosphere, over a 20 minute period, to 20 ml of absolute ethanol, in which 1.34 g (8.4 mmol) diethyl malonate and 0.192 g (8.4 mmol) Na had been dissolved. When the addition was complete, the reaction mixture was heated to reflux for 1 hour and then kept well stirred, at room temperature, for 24 hours, after which time the abundant white NaBr precipitate was separated with a paper filter and thoroughly washed with several 2 ml portions of CH_2Cl_2 . The gathered organic solutions were then

evaporated to dryness to give a pale yellow oil, which was a mixture of **4** and of the bis[5-(2,2'-bipyridyl)methyl substituted diethyl malonate derivative **5** (as identified by NMR spectroscopy). The mixture was separated on a basic Al_2O_3 column (using 10:1 v:v *n*-hexane/ethyl acetate as eluent), to give 0.72 g (yield = 35%) of **4** as a colorless oil. NMR (CD_3OD) δ 8.7 (dd, 1H), 8.55 (ds, 1H), 8.35 (m, 2H), 7.8 (dt, 1H), 7.6 (dd, 1H), 7.3 (m, 1H), signals relative to the bipyridine protons; 4.2 (q, 4H, $\text{O}-\text{CH}_2-\text{CH}_3$); 3.65 (t, 1H, $\text{CH}_2-\text{CH}(\text{COOEt})_2$); 3.3 (d, 2H, $\text{CH}_2-\text{CH}(\text{COOEt})_2$); 1.3 (t, 6H, $\text{O}-\text{CH}_2-\text{CH}_3$). IR (NaCl cells, pure sample film) 1732 cm^{-1} (C=O stretch of the ester group).

1,9-Diamino-5-(2,2'-bipyridin-5-ylmethyl)-3,7-diazanonane-4,6-dione 6. 0.35 g (1.2 mmol) of compound **4** were dissolved in 15 ml of dry ethylenediamine (freshly distilled from KOH, under a nitrogen atmosphere), the solution flushed with nitrogen and maintained well stirred at room temperature for 7 days. Excess ethylenediamine was then removed on a rotary evaporator to give a yellowish solid that, on washing with diethyl ether and drying under vacuum, gave a sample of 0.3 g (yield = 70%) of compound **6** as a white, hygroscopic solid. NMR (CD_3OD) δ 8.6 (dd, 1H), 8.5 (ds, 1H), 8.2 (m, 2H), 7.9 (dt, 1H), 7.8 (dd, 1H), 7.4 (m, 1H), signals relative to the bipyridine protons; 3.3 (d, 2H, $\text{CH}_2-\text{CH}-(\text{COONHR})_2$); 3.2 (t, 4H, $\text{NH}-\text{CH}_2-\text{CH}_2$); 2.8 (t, 1H, $\text{CH}_2-\text{CH}-(\text{COONHR})_2$); 2.7 (t, 4H, $\text{CH}_2-\text{CH}_2-\text{NH}_2$).

$[\text{Ru}(\text{bipy})_2(\mathbf{6})](\text{PF}_6)_2 \cdot \text{NH}_4\text{PF}_6$ ($\mathbf{2} \cdot (\text{PF}_6)_2 \cdot \text{NH}_4\text{PF}_6$). 0.122 g (0.342 mmol) of ligand **6** and 0.111 g (0.213 mmol) $\text{Ru}(\text{bipy})_2\text{Cl}_2 \cdot 2\text{H}_2\text{O}$ were added to 12 ml absolute ethanol, under a nitrogen atmosphere. The resulting deep violet mixture was heated to reflux for 3 hours, after which time a bright orange solution was obtained, from which the solvent was then removed on a rotary evaporator. The residue was dissolved in 5 ml H_2O and treated with 0.200 g of solid NH_4PF_6 , obtaining the precipitation of an orange-brown solid. This crude product was then purified on a column of basic Al_2O_3 , using CH_3CN as eluent and then a gradient of mixtures of CH_3CN with 1 M aqueous NH_4PF_6 . From the fractions eluted with 5% aqueous NH_4PF_6 a bright orange solid was obtained after slow evaporation, which was identified as $\mathbf{2} \cdot (\text{PF}_6)_2 \cdot \text{NH}_4\text{PF}_6 \cdot \text{H}_2\text{O}$. Yield: 0.065 g (24%). Anal. calc. for $\text{C}_{38}\text{H}_{46}\text{N}_{11}\text{O}_3\text{P}_3\text{F}_{18}\text{Ru}$: C 33.70, H 3.39, N 11.37%. Found: C 33.40, H 3.51, N 11.12%. Mass spec-



trum (ESI) 915 ($[M + PF_6]^{+}$), 385 ($[M]^{2+}/2$). NMR (CD_3OD): δ 8.6 (m, 6H), 8.2 (m, 5H), 7.9 (m, 2H), 7.7 (m, 4H), 7.6 (m, 2H), 7.4 (m, 4H), signals relative to plain and substituted bipy protons; 2.8–3.4 (m, 11H), signals relative to the $CH_2-CH(CONHCH_2CH_2NH_2)_2$ system.

[Re(CO)₅Cl(6)] 3. 0.190 g (0.53 mmol) of ligand **6** and 0.193 g (0.53 mmol) of $Re(CO)_5Cl$ were dissolved in 20 ml CH_3OH and the colorless solution obtained was heated to reflux under a nitrogen atmosphere for 2.5 hours, after which time it became deep yellow. The volume of the solvent was then reduced to 5 ml on a rotary evaporator and 10 ml of diethyl ether added, to give a yellow oil which precipitated as a thin film on the flask wall. The solvent mixture was mechanically removed and the oil kept under high vacuum for 2 hours, after which time it became a well treatable solid which was collected mechanically. Yield 0.210 g (58%). Anal. calc. for $3 \cdot H_2O$, $C_{21}H_{24}N_6O_5ClRe$: C 37.10, H 3.82, N 12.35%. Found: C 37.01, H 3.90, N 12.11%. Mass spectrum (ESI): 627 ($[M - Cl]^{+}$).

Results and discussion

System **2** as a sensor for Ni^{2+} and Cu^{2+} in water

The two-component system **2** has been prepared with the aim of obtaining a system capable of selectively signalling the presence of nickel and copper cations in water at low concentrations and in biologically relevant conditions (e.g. at pH values close

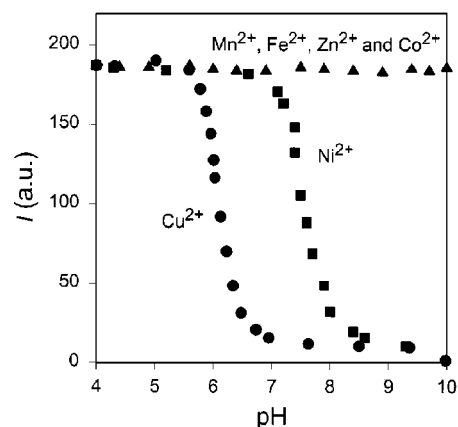


Fig. 1 Luminescence intensity (arbitrary units) vs. pH for solutions containing ligand **2** and a metal cation in 1:1 stoichiometry. The metal species referring to each curve is indicated in the plot.

to the intracellular $H_2PO_4^-/HPO_4^{2-}$ or blood H_2CO_3/HCO_3^- buffers, *i.e.* 7.2 and 7.4, respectively). The solubility in water of the chosen components, $[Ru(bipy)_3]^{2+}$ and the diamine-diamide ligand dioxo-2,3,2-tet, is fair, and the same has been observed for **2**, which can be dissolved in pure water with concentrations ranging up to 10^{-2} M. Moreover, selectivity towards Ni^{2+} and Cu^{2+} should be imparted by the peculiar coordinating properties of the dioxo-2,3,2-tet fragment: it is well established¹⁰ that plain or substituted ligands of this type can bind a metal ion, in a square planar fashion, with the simultaneous release of the two protons of the amide nitrogens, with a pH-dependent complexation equilibrium (see Scheme 1). However, it should be noted that the very endergonic deprotonation of the amide groups can take place only in the presence of metal ions which profit from a large ligand field stabilization, *e.g.* divalent metal cations late in the 3d series. As a matter of fact only Ni^{2+} and Cu^{2+} within the series of M^{2+} cations of the first transition series can promote the deprotonation of the amide nitrogens and form the neutral complex sketched in Scheme 1, with both plain¹¹ and substituted³ dioxo-2,3,2-tet ligands. This makes ligands of this kind selective for these two cations and the different ligand field stabilization (higher in the case of Cu^{2+} with respect to Ni^{2+}) allows the ligand to distinguish between them: complexation with Cu^{2+} takes place at lower pH values than in the case of Ni^{2+} (~2 pH units: *e.g.* with plain dioxo-2,3,2-tet, R = H in Fig. 1, complexation with Ni^{2+} and Cu^{2+} is complete at pH 7 and 9, respectively), and working with solutions buffered at the appropriate pH allows these types of ligands to bind only Cu^{2+} even in the presence of Ni^{2+} .^{3,12}

Complexation properties of **2** towards transition metal cations have been examined by observing the variation of its luminescence intensity (I_f) and lifetime (τ) as a function of pH, in the presence or in the absence of transition metal cations. When no metal cations are added to solutions containing **2**, I_f remains constant over the $2 < pH < 12$ range, as has already been observed for the related system **1** (in acetonitrile/water 4:1 v/v mixtures). In this pH range, the luminescence quantum yield (0.030) and lifetime (440 ns) of **2** in aerated water solutions are very similar to those observed for the $[Ru(bpy)_3]^{2+}$ chromophore under the same conditions,¹³ indicating that the dioxo-2,3,2-tet fragment does not substantially perturb the excited state properties of the Ru core, in agreement with what is generally found for aliphatic amine-functionalized Ru-polypyridine complexes.¹⁴ On the other hand, when Ni^{2+} or Cu^{2+} (as their perchlorate or chloride salts) are added in 1:1 molar ratio with respect to system **2**, the I_f vs. pH plot shows a typical sigmoidal profile (Fig. 1), which indicates that binding of the metal ion by the dioxo-2,3,2-tet fragment, according to equilibrium (1), takes place in the narrow pH range of the steeply descending portion of the figure.³

Thus, from Fig. 1 it can be said that complexation by **2**, under the titration conditions (see the Experimental), begins at pH 5.8 and is complete at pH 6.8 for Cu²⁺, while it begins at pH 7.5 and is complete at pH 8.5 for Ni²⁺. In the descending I_f vs. pH portion can be observed, together with the intensity decrease, the appearance in the excited state decay profile of a second component with a much shorter lifetime (11 and 15 ns for Ni²⁺ and Cu²⁺, respectively), clearly indicating an intramolecular quenching process; this component becomes the only one present at higher pH values. The observed behaviour is not surprising, since transition metal cations are usually capable of quenching fluorescence emission of a series of fluorophores, including [Ru(bipy)₃]²⁺, through electron transfer (eT) or energy transfer (ET) mechanisms, when bound to appended and adjacent ligands.¹⁻³

From eqn. (2), where τ° and τ are the excited state lifetimes of

$$k_q = 1/\tau - 1/\tau^\circ \quad (2)$$

free and complexed **2**, respectively, intramolecular quenching rate constant values, k_q , of $6.4 \times 10^7 \text{ s}^{-1}$ for Cu²⁺ and 8.9×10^7 for Ni²⁺ can be calculated.

In order to better discriminate between eT and ET processes, flash photolysis experiments were carried out on a $5 \times 10^{-5} \text{ M}$ solution of **2** and Cu²⁺ at pH 7 and on a $5 \times 10^{-5} \text{ M}$ solution of **2** and Ni²⁺ at pH 9. In both cases, after the 532 nm excitation pulse, no evidence for the presence of Ru^I species could be detected, while the only transient absorbing species were due to the excited states of the Ru^{II} chromophore. This result indicates that a charge separated species is not formed, or that the back electron transfer reaction is much faster than the forward one, so that the charge separated state cannot accumulate nor, as a consequence, be detected. Furthermore, steady-state quenching experiments performed at 77 K showed that the quenching process was very fast ($1.5 \times 10^7 \text{ s}^{-1}$ and $2.1 \times 10^7 \text{ s}^{-1}$ for Cu²⁺ and Ni²⁺, respectively) also in frozen medium at low temperature, where the charge separated state is strongly destabilized.¹⁵ All these findings suggest that the ET transfer is the more appropriate candidate for explaining the luminescence quenching of **2**.

In this paper, system **2** behaves as an ON-OFF sensor for these two metal cations based on an ET mechanism, as I_f is reduced to less than 5% of its maximum value when complexation processes are complete, and selectivity is proven by the negligible luminescence intensity variation in the I_f vs. pH plots in the presence of other metal centres (1:1 molar ratio), such as Mn²⁺, Fe²⁺, Zn²⁺ and Co²⁺ (see Fig. 1, circles); this suggests that with these metal cations no complexation takes place at the dioxo-2,3,2-tet fragment,¹⁶ in agreement with literature data for both plain and substituted (in the same position as **2**) dioxo-2,3,2-tet ligands.^{3,4,10}

Furthermore, incorporation of Ni²⁺ and Cu²⁺ into the binding part of **2** was checked by titrations of solutions containing **2** and buffered at pH 8.5 and 7.0, respectively: a linear decrease of luminescence is observed, which is completely quenched after the addition of 1 equivalent (*i.e.* ligand/metal molar ratio 1:1) of metal cation.

In addition, working on a solution of **2**, buffered at pH 7.0, no variation in I_f is observed by addition of up to 2 eq. of Ni²⁺ (or other divalent first row transition metal cations), while subsequent addition of Cu²⁺ causes the expected luminescence quenching, demonstrating that selectivity of Cu²⁺ on Ni²⁺ can be obtained by choosing the correct pH value (see Fig. 2). Finally, solutions buffered at pH 7.0 and containing system **2** at concentrations as low as 10^{-7} M revealed an easily detectable variation of I_f on addition of 1 eq. of Cu²⁺, indicating that **2** is a suitable sensor for copper cations under analytically relevant conditions.

Finally, it is worth mentioning that the Re^I derivative, [Re(CO)₃Cl(**6**)], ligand **3**, was synthesized through a straightforward route,^{18,19} in an effort to prepare another easily attain-

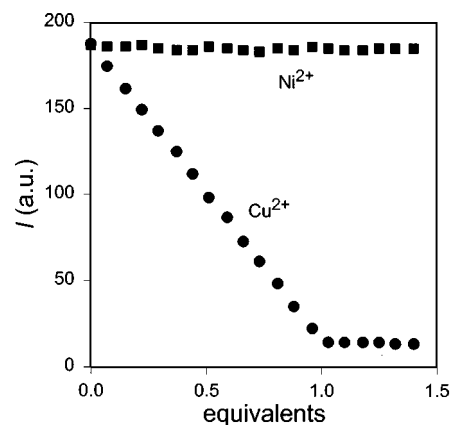


Fig. 2 Luminescence intensity (arbitrary units) vs. equivalents of added Ni²⁺ (■) and Cu²⁺ (●) for ligand **2**, in a solution buffered at pH 7.0.

able, water soluble sensor, selective towards Ni²⁺ and Cu²⁺, similar to **2** and based, in this case, on the well established properties of the Re^I(CO)₃(bipy)Cl luminophore.¹⁸ However, although having the same binding unit as **2**, the behaviour of **3** as a sensor towards Ni²⁺ and Cu²⁺ was less effective. In the presence of 1 eq. of Cu²⁺ and Ni²⁺, in the I_f vs. pH curve a sigmoid curve was observed, which begins and ends, in both cases, at pH values similar to those found for **2**, but I_f is quenched only to 30% and 60% of the full emission value, for Cu²⁺ and Ni²⁺, respectively. Moreover, in buffer solutions containing **3** (pH 7.2 and 8.5, for Cu²⁺ and Ni²⁺, respectively) additions of sub-stoichiometric quantities of aqueous metal perchlorates made I_f decrease, reaching the minimum value (30% and 60% of the starting value for Cu²⁺ and Ni²⁺, respectively) at a metal cation/ligand molar ratio of 0.7 for Cu²⁺ and 0.4 for Ni²⁺, respectively. No changes were observed in the excited state lifetime of the chromophore **3** (51 ns). These data seem to indicate that ligand **3** is not completely available for complexation with metal cations, *i.e.* there is a concurrent equilibrium which involves the dioxo-2,3,2-tet binding unit. However, in water as the working medium, in the absence of any added species and in the examined concentration range (10^{-3} – 10^{-5} M), only the hypothesis of an *intramolecular* interaction can be put forward, possibly due to the folding of the dioxo-2,3,2-tet unit towards the Re centre, *e.g.* due to the dipole-dipole interaction between the amine fragment(s) and the bound Cl⁻ anion. Although quite exotic, this hypothesis could be supported by what has already been found for a related Re(CO)₃(bipyR)Cl system (R = alkyl chains)²⁰ and by the fact that, on changing the medium (*e.g.* in methanol-water mixtures), I_f is quenched to a different extent and, in buffered solutions, it reaches its minimum value at a different cation/ligand molar ratio than in water (this, in particular, excludes the possibility that incomplete quenching and complexation could be due to some luminescent, Re-containing impurity). The observation of the excited state decay of the complexed species is in this case prevented by the quite intense residual luminescence coming from uncomplexed **3**. Thus, although displaying behaviour similar to that found for **2**, the residual fluorescence of system **3**, even in the presence of excess Ni²⁺ and Cu²⁺, makes it less feasible as a sensor for these two cations.

Acknowledgements

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