Supramolecular Metal Ion Sensing using Luminophoric Labels based on Ruthenium(II) Bis-terpyridine and Tris-bipyridine Scaffoldings

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Abstract. Two unique systems are described where modification of the photophysical properties is observed in the presence of an adventitious cation. In the first system an enhancement of the emission properties of linear ruthenium(II) bis-terpyridine bearing a central chelating centre is found. In the second system restoration of the emissive properties of the chromophore is observed due to a conformation control of intramolecular electron transfer in a calix[4]quinone bearing an appended ruthenium(II) tris-bipyridine chromophore.

Key words: ruthenium-complexes, calix[4]quinone, acetylene function, molecular electronics, luminescence, photochemistry, electron transfer, sensors, switches

1. Introduction

Considerable attention in the last decade in molecular sensors was propelled by potential applications in biology, medicine, analytical chemistry, environmental and material science, information technology and data storage. Many attempts at the design and construction of chemosensors employing optical absorption and luminescence changes as output signals have been reported and some comprehensive reviews have recently appeared in the literature [1–4]. Amongst these molecular systems, sensitive and selective chemosensors based on conjugated polymers bearing recognition sites have also been studied [5, 6].

Detailed information has been gathered on signal recognition events from fluorescent sensors and switches made up from a plethora of molecular compounds ranging from purely organic molecules to late transition metal complexes. There is, however, still a lack of readily available sytems based on more subtle chemical processes such as conformational changes, the relative orientation of the donor and acceptor units, electrostatic control of the detection process and enhancement of electronic conjugation in wires .... . These systems deserve particular interest, because their well-defined architectures are reminiscent of natural biological regulatory processes and helps to mimic systems where electron or energy transfer

between remote sites could be triggered by injection of a low concentration of a specific mediator cation into the system.

A chemosensor is a molecular device consisting of several independent components which have to be properly connected on a superstructure and possess a specific function. Such systems are constructed by assembling at least three main subunits:

- a photo- or electroactive fragment displaying a physical property which could be easily tuned,
- a molecular receptor or pocket which is sensitive to external stimulation and affect the property of the photo- or electroactivce unit,
- a spacer connecting the different components in order to maintain a structural integrity and to allow proper communication between them.

We will describe here two unique systems. The first is based on a linear molecule (a so-called photoactive molecular-scale wire) in which the detection of an adventitious guest resulted in a marked increase in the luminescence of the chromophoric unit. This situation is illustrated in Figure 1a. In the second example sketched in Figure 1b, the luminescence is restored by inhibition of intramolecular electron transfer due to a cation driven conformational change.

Our aims are (i) to investigate the potential of molecular wires as novel chemosensors (ii) to discover novel stable donor/acceptor systems built on calix[4]-diquinone and (iii) to demonstrate that subtle chemical processes such as conformational changes and electrostatic control of intramolecular electron transfer processes could be used to detect guest compounds in solution.

2. Luminescence Enhancement of Ruthenium(II) Bis-terpyridine in the Presence of Adventitious Cations

Much attention has recently been focused on the search for new multicomponent molecular systems comprising discrete redox and/or photoactive subunits separated by well-defined spacer groups and fruitful advances in the understanding of intramolecular information transfer have been achieved [7]. Recent investigations from our laboratory have described compelling experimental evidence to the effect that polyacetylenes operate as extremely effective molecular-scale wires for conducting electronic charge between redox-active terminals. Unsaturated bridges offer the best possibility for connecting photoactive subunits in a pre-determined arrangement that provides for [modest-to-strong] electronic coupling along the molecular axis [8].

We found that attaching an acetylenic function at the $4'$-position of terpyridine chelators caused a spectacular prolongation of the triplet lifetime ($\tau \approx 720$ ns) [9], especially in those cases where the acetylene group was the bridge for a ditopic ligand capped with the "Ru(terpy)" metallo-fragments. This upgrade of the photophysical properties provides new opportunities to construct elaborate molecular
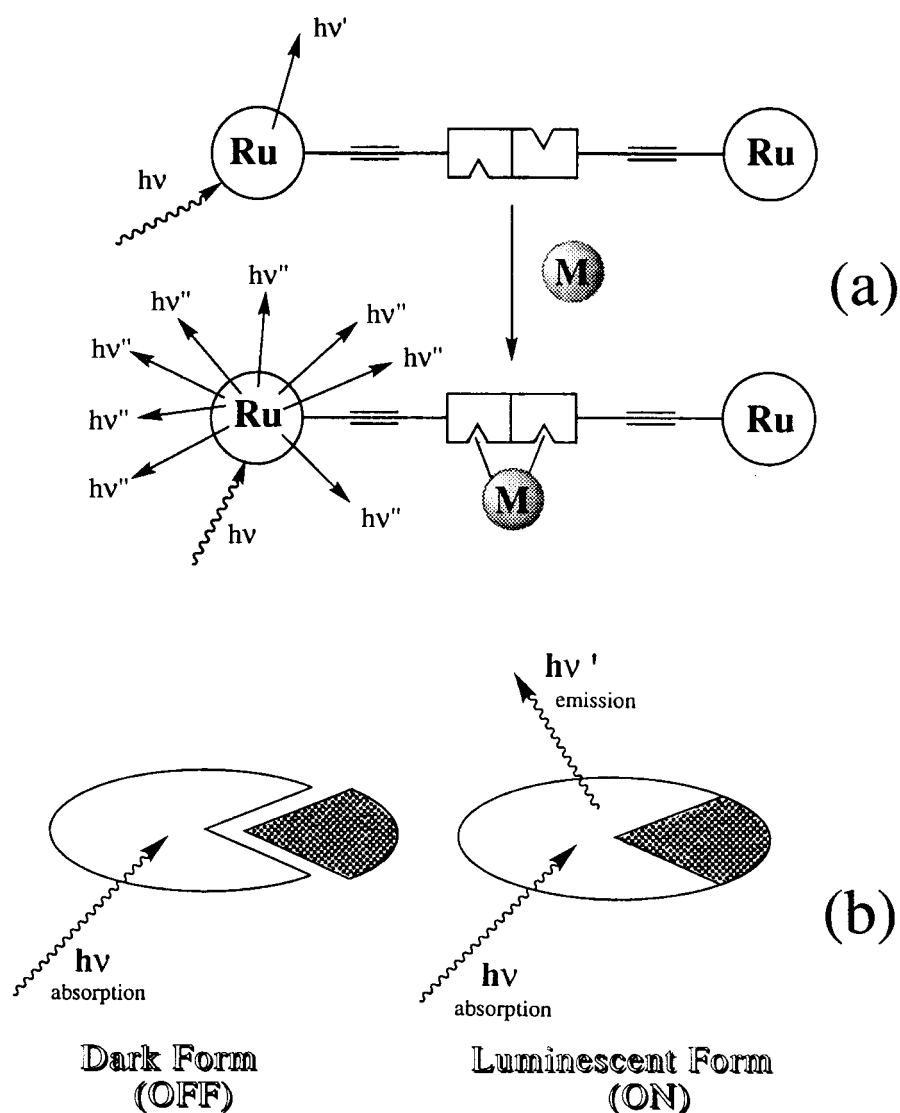
Figure 1. Schematic representation of the concept of photochemical detection of adventitious cations: (a) with photoactive wires and (b) with calix[4]diquinone bearing an appended chromophore.

assemblies around the photoactive "Ru(terpy)" unit. An alternative strategy for extending the length of the acetylenic bridge and to use the brigde as anchoring unit for additional guests is to use a central chelating aromatic core connected to the luminophoric centres via triple bonds such as in compound **1** (Insert 1).

Complex **1** is the prototype of a new class of rigid binuclear complexes possessing an accessible coordination site in the bridging ligand. Binding of adventitious cations to the central 2,2′-bipyridine provides a simple means by which to tune
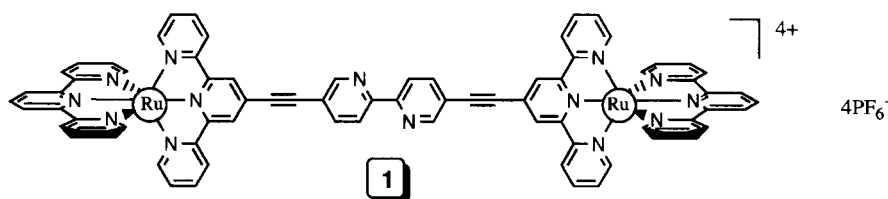
Insert 1. Molecular formula for dinuclear ruthenium (II) complex **1**.

further the electronic properties of the bridge and to detect the presence of guest cations. Protonation of the interspersed bipyridyl function causes a slight increase in emission yield (Figure 2) and the triplet lifetime increases to 115 ns. There is a 5 nm red-shift of the luminescence maximum that suggests protonation lowers the energy of the bridge. Even so, electrostatic repulsion between adjacent protonated pyridine rings prevents the bipyridyl unit adopting a favorable geometry for effective electronic coupling. Complexation of the vacant bipyridyl function with Zn^{II} cations causes more significant modification of the photophysical properties (Figure 2). In this case, the emission yield doubles, the triplet lifetime increases to 210 ns, and there is a further 17 nm red shift to the emission maximum. These changes are considered to reflect the increased level of electronic coupling across the bipyridyl unit due to the adoption of a coplanar geometry upon complexation. The process can be followed more conveniently in aqueous solution where we find a pK of 3.9 ± 0.1. This value is somewhat lower than that of 2,2′-bipyridine ($pK = 4.5 \pm 0.2$) due to the π-character of the acetylene functions and/or the neighboring ruthenium(II) cations.

Binding constants (K) were measured for several cations in neutral aqueous solution by monitoring the luminescence intensity of the terminal Ru(terpy) metallo-fragments as a function of cation concentration (Figure 3). Both the magnitude of K and the photophysical properties of the resultant 1 : 1 complexes depend on the nature of the added cation. Three sets of cations have been tested which could be classified depending on the effect observed on the photophysical properties:

- The first group of cations bind weakly to the vacant 2,2′-bipyridine subunit (log K = 1.6, 0.8, 1.7 respectively for Li^+, K^+, and Mn^{2+}) and barely perturb the photophysical properties of **1** in deoxygenated solution.
- The second group of cations bind moderately strongly to the bpy (log K = 4.4, 3.6, 3.0, respectively for Ba^{2+}, Cd^{2+}, and Zn^{2+}) and cause a substantial increase in luminescence intensity and lifetime without apparent change to the absorption spectral profile. In these latter cases, coordination of the cation causes a pronounced red shift to the emission maximum (ca. 22 nm for Cd^{2+}).
- The third group of cations are strong binders (log K = 3.2, 4.2 respectively for Ag^+ and Hg^{2+}) but cause a marked decrease in luminescence from the terminal Ru(terpy)-based chromophore. Since both Ag^+ and Hg^{2+} cations are easily reduced it seems reasonable to attribute luminescence quenching to electron
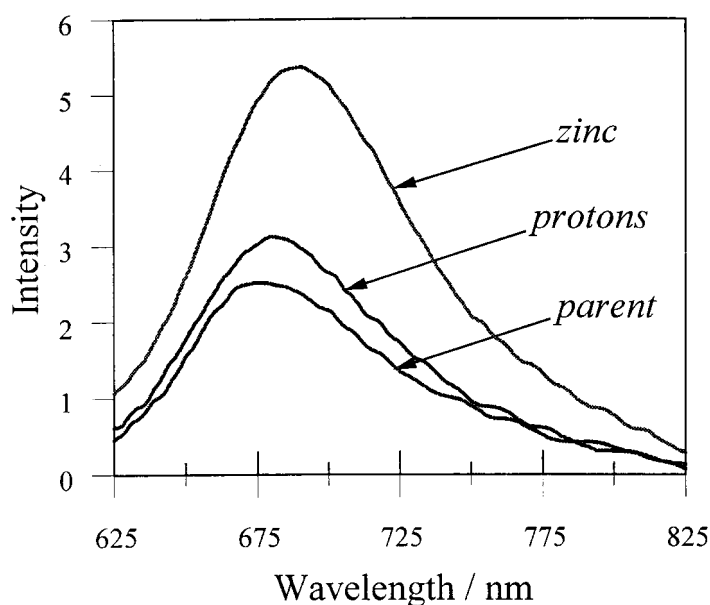
Figure 2. Luminescence spectra recorded in deoxygenated acetonitrile for the bipyridine bridged binuclear ruthenium complex **1** (parent). Protonation of the interspersed bipyridyl unit causes a small red shift and enhancement in luminescence, while complexation with zinc(II) cations (zinc) gives rise to a more substantial red shift and enhancement.

transfer from the triplet state of a Ru(terpy)-based chromophore to a bound cation.

In summary the cations that amplify luminescence from the terminal chromophores are the most interesting since amplification is a measure of electron delocalization over the entire ditopic ligand and an elegant way to detect the presence of an adventitious cation. The studies of these *embryonic* chemical sensors highlight the crucial role played by the chemical linker between the analyte binding site and the luminophoric centre. The future of this family of compounds resides in the construction of functionalised binding sites which will favour selective recognition of cations.

3. Restoration of Luminescence by Inhibition of Electron Transfer in Ru(II) Tris-bipyridine Calix[4]quinone Complexes in the Presence of Guest Cations

Electron transfer, one of the few processes that can compete with deactivation of a short-lived excited state, opens the possibility to construct simple devices for use as chemosensors [2]. Numerous studies have shown that the rate of electron transfer increases with decreasing separation between the donor and acceptor sites, reaching a maximum when the reactants are in orbital contact [11]. Thus, when the
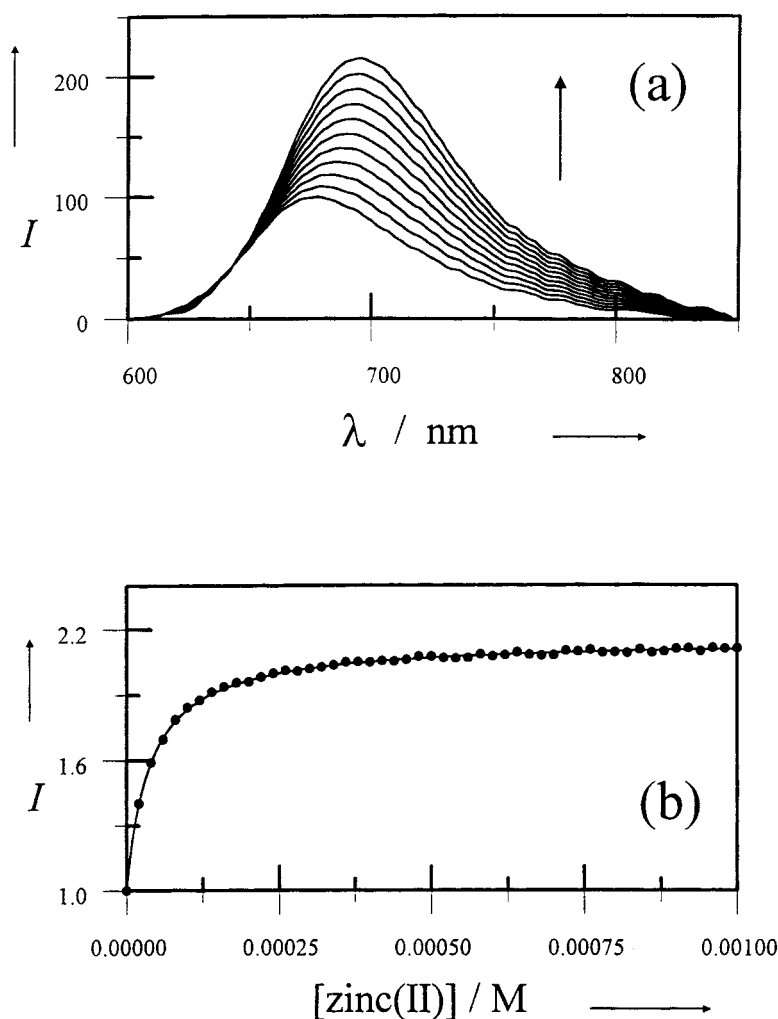
Figure 3. Luminescence titration following complexation between **1** and Zn^{2+} cations in acetonitrile. (a) overlay of luminescence spectra recorded during the titration showing the progressive increase in intensity and red-shift noted for the emission peak on coordination of the cation to the vacant bipyridine site. (b) correlation between emission quantum yield and concentration of added Zn^{2+} cations, with the solid line representing a nonlinear, least-squares fit to formation of a 1 : 1 complex having log K = 4.42 and ϕ/ϕ_{LUM} = 2.15.

redox partners comprise the terminals of a flexible hydrocarbon chain the rate of light-induced electron transfer depends on the conformation of the donor/acceptor scaffold; being fast for close conformers and slow for extended distances. This provides a facile means by which to construct a reversible optoelectronic switch if the molecular conformation can be modulated by external stimulation [12]. We have designed a simple example of such artificial *tropism* in which cation binding
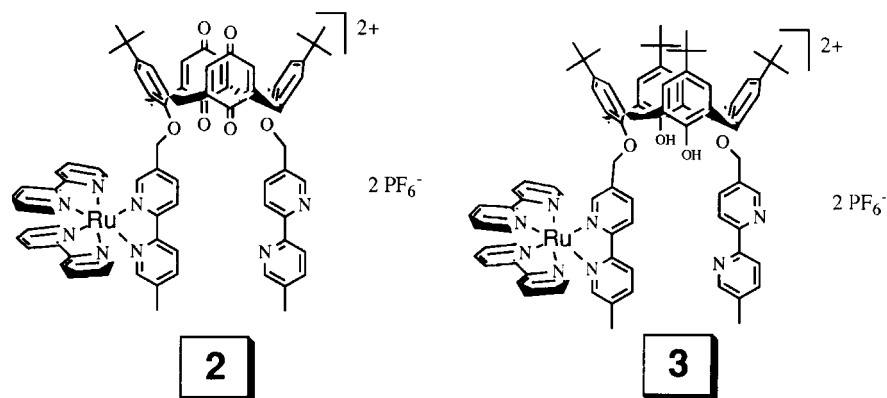
Insert 2. Molecular formulae for mononuclear Ru(II) complexes: in the quinone form **2** and the hydroquinone form **3**.

elongates a flexible molecule and, since electron transfer occurs preferentially in the closed conformation, restores luminescence from the appended chromophore.

Construction of a suitable system requires the cooperation of three discrete components; namely, an electron-rich chromophore, an electron acceptor, and a chelator, joined together by a flexible superstructure in such a way as to maintain the chelator between the redox-active units. Compound **2** being a calix[4]diquinone functionalized with a pendant 2,2'-bipyridine unit and a ruthenium(II) tris(2,2'-bipyridyl) moiety, meet the essential requirements (Insert 2).

Illumination of the metal centre in compound **3** gave rise to relatively intense phosphorescence, while emission from the calix[4]diquinone-derived species **2** was barely detectable. Luminescence quenching in **2** is attributed to light-induced electron transfer from the triplet state of the metal complex to a nearby quinone. The thermodynamic driving force for this reaction, estimated from cyclic voltammetry and luminescence spectroscopy, is modest ($\Delta G° = -0.26$ eV) but both forward and reverse electron-transfer steps are favored by diffusional contact between the partners. NMR studies and molecular dynamics simulations (MDS) of **2** at ambient temperature confirm that the calix[4]diquinone platform exists in a state of fluctional motion in solution. MDS clearly indicates that the coordinated bpy ligands come into contact with those of the quinoids of the macrocyclic receptor, in the 1,3-alternated conformation (Figure 4a).

Addition of an inorganic salt to the phenolic compound **3** had no observable effect on the photophysical properties of the pendant metal subunit. For the calix[4]-diquinone-derived Ru(II) complex **2**, addition of a cation caused a progressive increase in phosphorescence (Figure 5). Complexation of a cation causes amplification of luminescence from the appended ruthenium(II) tris(2,2′-bipyridine) complex. With barium perchlorate as the salt it was demonstrated that addition of excess 18-crown-6, this being a more avid complexer, extinguished luminescence from $2 \subset Ba^{2+}$ due to extraction of the cation [13].
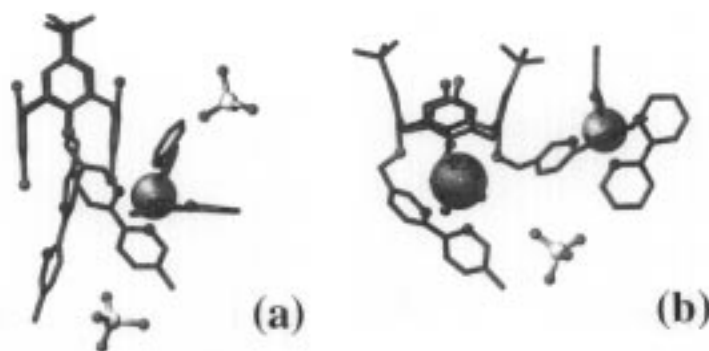
Figure 4. Energy-minimized conformations derived from molecular dynamics simulations for (a) **2** and (b) **2** $\subset$ Ba^{2+} in a matrix of acetonitrile molecules. Many different conformers are predicted to exist in dynamic equilibrium in the absence of added cation and the structure shown in (a) corresponds to the conformation most favorable for rapid electron transfer.

The inorganic *monocations* are characterized by their relatively high binding constants (K = 420, 400 and 185 M^{-1} respectively for Li$^+$, Na$^+$ and K$^+$) and by their triplet lifetimes of ca. 150 ns whereas the *dications* form less stable complexes possessing triplet lifetimes around 700 ns (K = 22, 16, 12, 30 and 2650 M^{-1} respectively for Ca^{2+}, Ba^{2+}, Sr^{2+}, Cd^{2+} and Zn^{2+}). The stability constant is controlled, to a large extent, by electrostatic repulsion associated with the appended ruthenium(II) tris(2,2′-bipyridyl) complex. Protons bind avidly (K = 15850 M^{-1}) to the vacant bpy residue present in **2** but have little effect on the photophysical properties.

Detailed (^{1}H and ^{13}C) NMR studies and MDS made with the barium perchlorate complex indicate that the cation binds to the lower rim of the calix[4]diquinone receptor [14] where it is held in place by coordination to the four oxygen atoms and two nitrogen atoms provided by the free bpy. The bound cation forces the macrocycle to adopt a cone conformation and repels the dangling Ru(II) tris(2,2′-bipyridine) moiety (Figure 4b). This has the effect of minimizing orbital contact between the chromophore and the quinone to such an extent that electron transfer is markedly inhibited.

In summary, the dramatic drop in k$_{ET}$ that accompanies cation binding to **2** can be attributed to an electrostatically-driven conformational change that serves to separate the reactants. This is a powerful effect that occurs in addition to restriction of fluctuational motions of the quinoid walls known to take place upon cation complexation. Amplification of emission depends only on the electronic charge of the cation, with k$_{ET}$ remaining *ca.* 10-fold higher for a monocation than for a dication, although protons give an anomolously weak effect [15].
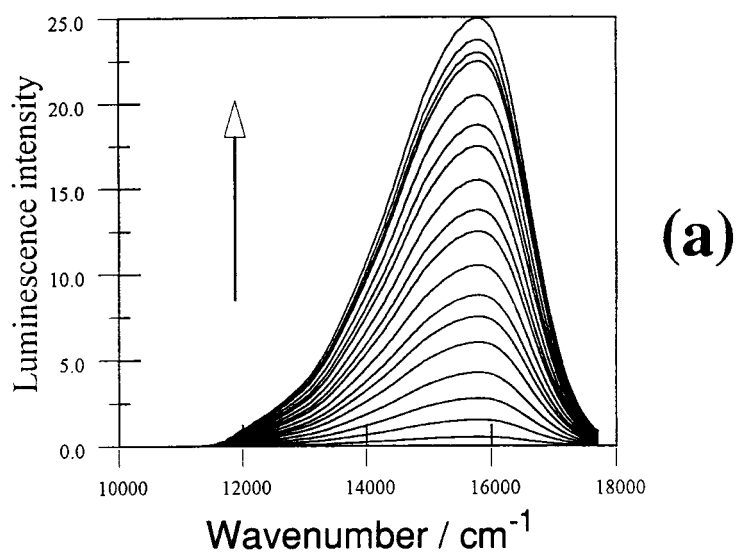
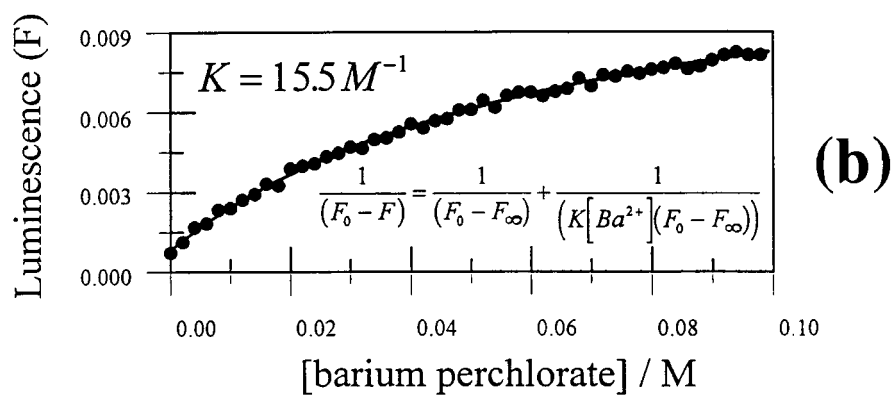*Figure 5.* (a) Effect of increasing concentration of Ba(ClO$_4$)$_2$ on the emission yield of compound **2** in deoxygenated acetonitrile solution. (b) correlation between emission quantum yield and concentration of added Ba^{2+} cations, with the solid line representing a nonlinear, least-squares fit to formation of a 1 : 1 complex having K = 15.5 M^{-1}.

4. Conclusion

We have designed, charaterized and studied the photochemistry of two reversible molecular systems in which transduction of a stoichiometric cation complexation resulting in a phosphorescence signal is occuring. In the first system luminescence is enhanced due to a decrease of the LUMO energy of the spacer by complexation of adventitious cations. In the second system, luminescence is restored as a consequence of intramolecular electron transfer inhibition due to unfavorable orbital orientation and overlapping. Before practical applications can be proposed for such molecular-scale switches it will be necessary to increase the association constant by providing a more idealized binding pocket. Work is in progress in order to gain specificity and sensibility and to immobilize such sensors arrays on optical transparent surfaces. More elaborated scaffolds attached to macroscopic supports should supply the necessary selectivity to form reliable sensors. Increasing the association constant of a molecular recognition event will certainly increase the sensitivity of the sensor but will also affect the reversibility of the resulting system. This is also very important for the practical use of metal-sensing.

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