

pH-Controlled Fluorescent Emission in the Nickel(II) Complex of a Bifunctional Tetramine Macrocycle

Luigi Fabbrizzi,* Francesco Foti, Maurizio Licchelli, and Antonio Poggi

Università di Pavia, Dipartimento di Chimica Generale, via Taramelli 12, I-27100 Pavia, Italy

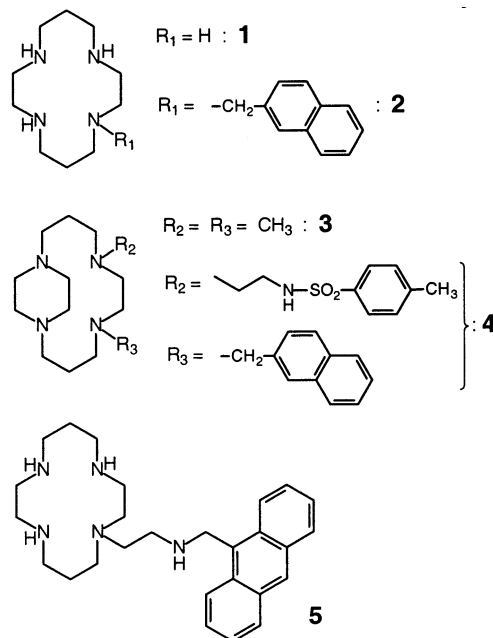
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In the Ni^{II} complex of a reinforced tetramine macrocycle, equipped with both a sulfonamide pendant arm and a naphthalene fragment, light emission of the fluorophore is pH-controlled, as a result of a change of the geometry of the complex.

Tuning the light emission of a fluorogenic molecular fragment, following a given input, represents one of the most effective ways to process a signal at the molecular level.¹ Of special interest are those systems in which both the light-emitting moiety and the subunit sensitive to the external stimulus are components of the same molecule. In this case, signal transduction takes place intramolecularly and can be controlled by designing an appropriate architecture of the multicomponent system.²

We recently observed that in the Ni^{II} complex of the functionalized macrocycle **2**, in which the 14-membered ring of cyclam (**1**) is linked through a –CH₂– spacer to a light-emitting naphthalene fragment, the emission intensity of the fluorophore is affected by the spin state of the metal center.³ For instance, the high-spin [Ni^{II}(**2**)Cl₂] complex, in a CH₂Cl₂ solution, exhibits a rather low quantum yield: $\Phi = 0.007$. On the other hand, for the low-spin complex [Ni^{II}(**2**)(ClO₄)₂], Φ is distinctly higher (0.019). Quenching of naphthalene fluorescence takes place through an electronic energy transfer (ET) mechanism involving the Ni^{II} ion encircled by the macrocycle and the nearby excited fluorophore. It appears that the double electron exchange responsible for the ET process is remarkably more efficient in the presence of the high-spin metal ion (two unpaired electrons) than with the low-spin center, which is diamagnetic and is characterized by a more compact electronic configuration.

On these bases, we wished to design a dynamic molecular system based on a Ni^{II} macrocyclic complex, in which the metal spin state, and hopefully the emission of an appended fluorophore, could be controlled through a chemical input, e.g., a change of pH. In this perspective, we chose the



tetramine ligand **3**, in which the cyclam ring has been reinforced by linking two amine nitrogen atoms by a further ethylenic chain. The rigidified framework of **3** guarantees the formation of the sole low-spin complex⁴ and prevents the occurrence of the high–low spin interconversion.⁵ Then, we equipped the reinforced macrocycle with two distinct functionalizations: (i) a 1-naphthylmethyl group (the fluorescent fragment) and (ii) a pendant arm containing a sulfonamide group, to give **4**. The sulfonamide group itself does not show coordinating tendencies, but it can deprotonate at relatively low pH values, to bind a transition metal. Deprotonation of the sulfonamide group belonging to a pendant arm, on coordination to a metal center, has been observed in macrocyclic complexes of Zn^{II}.⁶ Tetraaza macrocycles armed with a coordinating side chain have been named *scorpionands* (due to the presence of an aggressive tail which bites from the top the chelated metal), and their Ni^{II} complexes display pH-dependent spin interconversion.⁷

* Corresponding author. E-mail: luigi.fabbrizzi@unipv.it.

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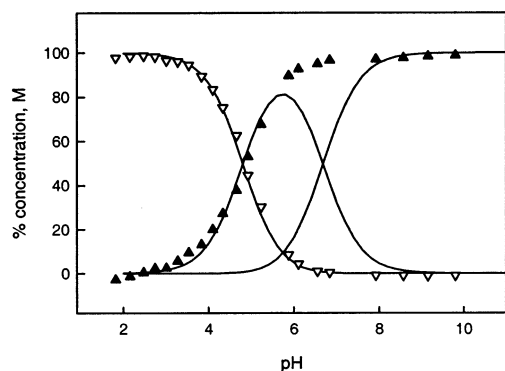


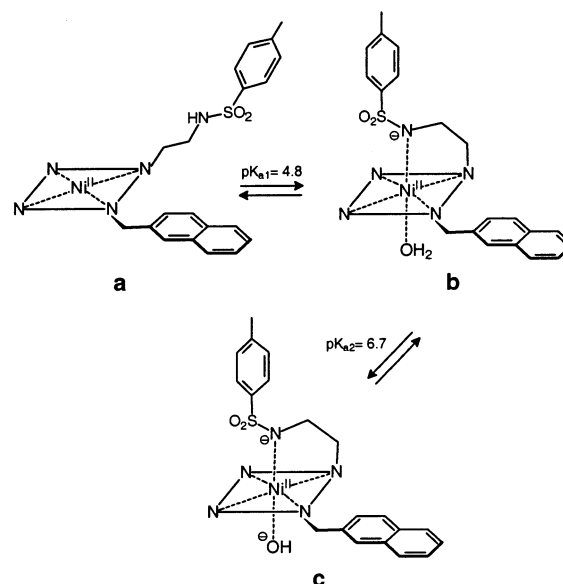
Figure 1. Solid lines represent the % concentration profiles of the complexes $[\text{Ni}^{\text{II}}(\text{LH})]^{2+}$, $[\text{Ni}^{\text{II}}(\text{L})]^{+}$, $[\text{Ni}(\text{L})(\text{OH})]$, in order of increasing pH ($\text{LH} = \mathbf{4}$). Symbols indicate the molar absorbance of the bands centered at $\lambda_{\text{max}} = 490$ nm (low-spin complex, ∇) and at $\lambda_{\text{max}} = 390$ nm (high-spin complex, \blacktriangle).

In particular, at low pH values, the pendant arm is in the protonated form and cannot coordinate the metal, which exhibits a square-planar geometry and is in the low-spin state. At higher pH values, the pendant arm deprotonates and goes to bind the metal, thus stabilizing the high-spin state.

We had therefore to verify (i) if the pH-controlled attack-detachment of the pendant arm takes place in the Ni^{II} complex of the difunctional macrocycle **4** and (ii) if this process produces any effect on the emission properties of the proximate naphthalene fragment. Thus, we investigated the acidic behavior of the $[\text{Ni}^{\text{II}}(\mathbf{4})](\text{ClO}_4)_2$ complex salt, by carrying out potentiometric titrations on an EtOH/ H_2O solution (4:1, v/v), made 0.1 M in NaClO_4 , at 25 °C. We observed that the complex behaves as a diprotic acid, with $\text{p}K_{\text{A}1} = 4.40 \pm 0.02$ and $\text{p}K_{\text{A}2} = 6.68 \pm 0.04$. Thus, three species are present at the equilibrium: an undeprotonated ligand complex, a deprotonated species, and a doubly deprotonated species. Their concentration profiles at varying pH are shown in Figure 1.

The first dissociation step is ascribed to the deprotonation of the sulfonamide group, which occurs with the simultaneous binding of the pendant arm to the metal. From a geometrical point of view, this should involve the change from a square-planar arrangement, complex of formula $[\text{Ni}^{\text{II}}(\text{LH})]^{2+}$, to a five- or six-coordinate complex, of formula $[\text{Ni}^{\text{II}}(\text{L})]^{+}$. In the case of six-coordination, the coordination polyhedron (a distorted octahedron) should be completed by a water molecule. The occurrence of a drastic geometrical change is substantiated by spectrophotometric investigations. In particular, an acidic solution of the complex (pH = 2–3) is orange and shows a d–d absorption band centered at 490 nm (molar absorbance $\epsilon = 475 \text{ M}^{-1} \text{ cm}^{-1}$): such spectral features are those expected for a square-planar low-spin complex.⁵ On increasing pH, the color of the solution changes from yellow to pale blue, while the intensity of the band at 490 nm decreases and new weak bands develop at 390 and 645 nm. These latter bands are those expected for a high-spin Ni^{II} complex.⁵ Thus, binding of the pendant arm stabilizes the triplet state of the Ni^{II} center. The assignment

Scheme 1



of the electronic features is corroborated by the fact that the pH profiles of molar absorbances of the bands at 490 nm (low-spin, open triangles in Figure 1) and at 390 nm (high-spin, full triangles) superimpose well on the concentration curves of $[\text{Ni}^{\text{II}}(\text{LH})]^{2+}$ and $[\text{Ni}^{\text{II}}(\text{L})]^{+}$, respectively. The hypothesized geometrical change occurring when one moves from $[\text{Ni}^{\text{II}}(\text{LH})]^{2+}$ to $[\text{Ni}^{\text{II}}(\text{L})]^{+}$ is sketched in Scheme 1, **a** to **b** process.

The second step should involve the deprotonation of a water molecule to give an OH^- ion, which coordinates the metal, giving rise to the $[\text{Ni}^{\text{II}}(\text{L})(\text{OH})]$ complex (**c**). In the case that the **b** complex, $[\text{Ni}^{\text{II}}(\text{L})]^{+}$, is six-coordinated, the hydroxide ion originates from the deprotonation of a metal-bound water molecule.

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On increasing pH, the color of the solution changes from yellow to pale blue, while the intensity of the band at 490 nm decreases and new weak bands develop at 390 and 645 nm (see spectra at varying pH in Figure 2).

These latter bands are those expected for a high-spin Ni^{II} complex. Thus, binding of the pendant arm stabilizes the triplet state of the Ni^{II} center. The assignment of the electronic features is corroborated by the fact that the pH profiles of molar absorbances of the bands at 490 nm (low-spin, open triangles in Figure 1) and at 390 nm (high-spin, full triangles) superimpose well on the concentration curves of $[\text{Ni}^{\text{II}}(\text{LH})]^{2+}$ and $[\text{Ni}^{\text{II}}(\text{L})]^{+}$, respectively. The hypothesized geometrical change occurring when one moves from $[\text{Ni}^{\text{II}}(\text{LH})]^{2+}$ to $[\text{Ni}^{\text{II}}(\text{L})]^{+}$ is sketched in Scheme 1, **a** to **b** process.

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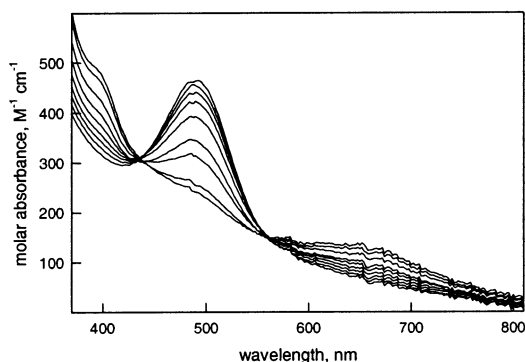


Figure 2. Spectra at varying pH of an aqueous-ethanolic solution of $[\text{Ni}^{\text{II}}(\mathbf{4})]^{2+}$. On increasing pH, the band at 490 nm decreases, while the bands at 390 and 645 nm increase.

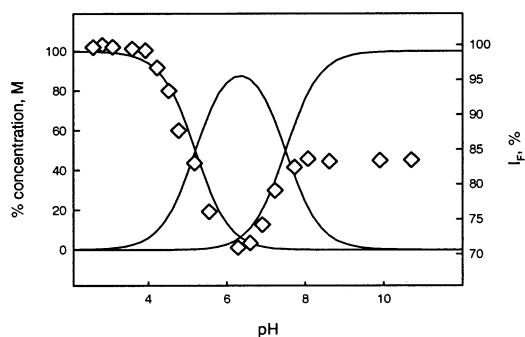


Figure 3. Fluorescence emission, I_F , at $\lambda_{\text{max}} = 337$ nm of the naphthalene fragment of the $[\text{Ni}^{\text{II}}(\mathbf{4})]^{2+}$ complex at varying pH. I_F values (\diamond) have been overlaid on the concentration profiles of the three complex species present at the equilibrium.

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Then, we measured the emission spectra of a solution of the $[\text{Ni}^{\text{II}}(\mathbf{4})](\text{ClO}_4)_2$ complex salt at varying pH. The spectra were those expected for the naphthalene fluorogenic fragment, and their intensity was observed to be significantly pH-dependent. Values of fluorescence intensity, I_F , measured at $\lambda_{\text{max}} = 337$ nm, over the 2–12 pH range (open diamonds), have been overlaid on the distribution diagram in Figure 3. It is seen that I_F keeps the highest value over the 2–4 pH interval, then decreases, to reach a minimum at pH = 6.5. In particular, the I_F profile superimposes well on the concentration curve of the complex $[\text{Ni}^{\text{II}}(\text{LH})]^{2+}$. On the other hand, minimum emission corresponds to the highest concentration of the $[\text{Ni}^{\text{II}}(\text{L})]^+$ complex (95%). Finally, I_F increases again, superimposing well on the ascending arm of the concentration profile of the $[\text{Ni}^{\text{II}}(\text{L})\text{OH}]$ complex, and reaches a plateau in correspondence of the formation of 100% of it.

The partial fluorescence quenching, which takes place at $\text{pH} \geq 4$, is therefore associated with the $\mathbf{a} \rightarrow \mathbf{b}$ process of Scheme 1 and may be, at least in part, associated with the change of the spin state of the metal center, from low-spin to high-spin. In particular, the high-spin form is expected to promote a more efficient ET mechanism. Actually, the ET nature of the quenching process in $[\text{Ni}^{\text{II}}(\text{L})]^+$ has been demonstrated by measuring the emission spectrum of an EtOH solution of the complex, frozen at 77 K. In fact, on glassifying the solution, no revival of fluorescence is observed, a behavior expected when a genuine ET mecha-

nism is operating. Thus, the pH-induced binding of the pendant arm to the metal is signaled by quenching of fluorescence, and we suggest that the signal transduction mechanism is related to the concurrent low-spin to high-spin conversion. However, other factors can contribute to the pH-dependent quenching of fluorescence: they should include, for instance, the orientation of the naphthalene fragment, which can be influenced by pH (and which, in Scheme 1, has been drawn in the plane of the macrocycle only conventionally). On the other hand, a moderate addition of standard acid, to change back pH from 6.5 to 4, induces the prompt detachment of the pendant arm, with simultaneous high-to-low spin conversion, events which are signaled by fluorescence revival.

The second step, $\mathbf{b} \rightarrow \mathbf{c}$, is associated with the coordination of the hydroxide ion. Formation of the $[\text{Ni}^{\text{II}}(\text{L})\text{OH}]$ complex induces a moderate recovery of fluorescence (to 50% of the original value). Spectrofluorimetric investigations at 77 K showed that an ET mechanism is responsible for the partial quenching occurring in the $[\text{Ni}^{\text{II}}(\text{L})\text{OH}]$ complex. Accounting for the rather different quenching activity observed in the $[\text{Ni}^{\text{II}}(\text{L})]^+$ and $[\text{Ni}^{\text{II}}(\text{L})\text{OH}]$ complexes is not straightforward. OH^- binding should induce a geometrical change and a subtle modification of the electronic structure of the high-spin metal center. It is possible that these geometrical and electronic changes are reflected in a different interaction with the nearby excited naphthalene fragment, which results in a different extent of the ET efficiency. No more detailed hypotheses can be brought forward in the absence of defined structural information.

System $\text{Ni}^{\text{II}}\mathbf{4}$ is a multicomponent luminescent device, whose emission can be tuned by varying pH, in a three-stage mode. It is reminiscent of the previously reported system, $\text{Ni}^{\text{II}}\mathbf{5}$, in which the fluorophore (an anthracene fragment) was appended to the dangling side chain, and whose emission depended upon its position with respect to the metal: high when far away (detached pendant arm) and low when close (coordinated pendant arm).⁸ In the present system, the fluorophore is fixed on the macrocyclic framework, to witness and signal events related to the metal center. In particular, the pH-controlled motion of the sulfonamide pendant arm is signaled by quenching-revival of naphthalene emission. The reported system represents a further example of luminescent molecular device, whose emission can be mechanically controlled.⁹

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Supporting Information Available: Synthesis of **4**, elemental analysis, NMR, and ESI mass spectrometric data for **4** and precursors. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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