

Flavonol based ruthenium acetylides as fluorescent chemosensors for lead ions

Jean-Luc Fillaut ^{a,*}, Julien Andriès ^a, Ripu Daman Marwaha ^a, Pierre-Henri Lanoë ^a,
Olivier Lohio ^a, Loic Toupet ^b, J.A. Gareth Williams ^c

^a UMR 6226 CNRS – Université Rennes 1, Sciences Chimiques de Rennes, Avenue du Général Leclerc, 35042 Rennes cedex, France

^b UMR 6626 CNRS – Université Rennes 1, Laboratoire de Physique de la Matière Condensée, Université de Rennes 1, 35042 Rennes cedex, France

^c Department of Chemistry, University of Durham, South Road, Durham DH1 3LE, UK

Received 8 October 2007; received in revised form 25 October 2007; accepted 25 October 2007

Available online 4 November 2007

Abstract

Flavonol based alkynyl ruthenium complexes devoted to the detection of metal traces in solution are described. The sensitivity of both absorption and emission properties of the 3-hydroxyflavone unit as a receptor for the metal cations, and of an alkynyl ruthenium moiety as an extended π -conjugated system, provides an efficient molecular sensor for rapid, sensitive and selective detection of lead(II) cations. © 2007 Elsevier B.V. All rights reserved.

Keywords: Ruthenium acetylides; Luminescent chemosensors; Flavonols; Heavy metal sensors

1. Introduction

Whereas transition metal ions play an important role in many fundamental physiological processes in organisms, heavy metal ions can often have a profoundly detrimental effect upon them. In particular, lead(II) ions can affect almost every organ and system in the human body, causing various symptoms such as anaemia, disorder of the blood, muscle paralysis, memory loss, and mental retardation [1–3]. Development of effective fluorescent chemosensors [4,5] for discriminating lead ions from alkali, alkaline earth metal and transition-metal ions [6–9] is therefore helpful for measuring the amount of lead in contaminated sources [10], including the human body, as well as for clarifying the cellular role of the Pb^{2+} ions in vivo [11].

In a new development of our research on the use of ruthenium alkynyl derivatives as chemosensors [12], we report here on our discovery of a fluorescent sensor based on the association of a flavonol moiety with a transition

metal alkynyl derivative. Our interest in flavonol-containing ruthenium alkynyl derivatives came from the idea that the metal acetylide fragment could allow the absorption and emission properties of the resulting complex to be displaced beyond the limits of that of usual organic compounds, into the useful visible region. Ruthenium alkynyl derivatives have been extensively used, for example, in non-linear optics [13–17] and as molecular wires [18–23]. These properties arise as a result of overlap between the d-orbitals of ruthenium and the conjugated π system and can thus be modified systematically either through variation of the organic π system or by fine-tuning the electron richness of the alkynyl ruthenium moiety itself. We already established that alkynyl ruthenium complexes bearing terminal hydrogen-bond receptors can also act as efficient anion sensors exhibiting large guest-induced colour changes and show high selectivity to fluoride ions [24].

Being sensitive to the perturbations of their environment, 3-hydroxyflavone and its derivatives attract current interest as luminescent probes for analytical chemistry, bio-physics, and cellular biology [25,26]. In particular, 3-hydroxyflavone derivatives coordinate to cations of different charges, radii,

* Corresponding author.

E-mail address: jean-luc.fillaut@univ-rennes1.fr (J.-L. Fillaut).

and electronic properties [27–32]. In this contribution, we discuss the preparation and photophysical properties of a new class of luminescent alkynyl ruthenium complexes, in which the presence of a 3-hydroxyflavone unit provides very attractive properties as a receptor for heavy metal ions and reveals high sensitivity and selectivity towards lead(II) cations.

2. Experimental

Experimental procedures and detailed characterization data for all new compounds are described in the [supplementary material](#) section. In this section, we will describe the most significant synthesis (complexes **5a**, **6a**, **7a**) as illustrative examples.

2.1. *trans*-[RuCl(dppe)₂{C≡CH-*p*-phenyl-(3-hydroxy-4H-chromen-4-one)}]TfO (**5a**)

In a Schlenk tube, [(dppe)₂RuCl]TfO [33,34] (0.22 mmol, 240 mg) was added under argon to the solution of **4a** (58 mg, 0.22 mmol, 1.0 equiv.) in 30 mL of freshly distilled and degassed dichloromethane. The resulting mixture was stirred at room temperature overnight. The dark orange solution formed was pumped to dryness to give a red–orange solid. ¹H NMR (CDCl₃, 200 MHz, δ ppm): 8.23 (dd, 1H, ³J_{H–H} = 7.9 Hz, ³J_{H–H} = 1.4 Hz), 7.80–7.65 (m, 3H), 7.43 (d, 2H, ³J_{H–H} = 8.6 Hz), 7.4–7.0 (m, 40H), 6.7 (br s, 1H, OH), 5.82 (d, 2H, ³J_{H–H} = 8.6 Hz), 4.76 (m, 1H, Ru = C=CH), 2.96 (m, 8H, CH₂ dppe). ³¹P {¹H} NMR (CDCl₃, 75 MHz, δ ppm): 37.09 (s).

2.2. *trans*-[RuCl(dppe)₂{C≡C-*p*-phenyl-(3-hydroxy-4H-chromen-4-one)}] (**6a**)

Triethylamine (0.24 mmol, 34 μL) was then added to the solution of the crude vinylidene **5a** in 50 mL of distilled and degassed dichloromethane and the mixture was stirred at room temperature for 1 h. The resulting orange solution was washed with water (5 × 50 mL) and pumped to dryness (without using any drying agent containing metal cation). The obtained red–orange powder was washed with *n*-pentane to afford the pure compound **6a** (225 mg, 82% calculated from [(dppe)₂RuCl]TfO). Mass spectrum: *m/z* calc. for M+C₆₉H₅₇ClO₃P₄Ru: 1194.19901; Found: 1194.19905; ν_{\max} (KBr/Nujol)/cm⁻¹ 2055 (w) ν (C≡C); ¹H NMR (CDCl₃, 200 MHz, δ ppm): 8.26 (dd, 1H, ³J_{H–H} = 8.0 Hz, ³J_{H–H} = 1.5 Hz), 8.06 (d, 2H, ³J_{H–H} = 8.6 Hz), 7.75–6.95 (m, 44H, aromatics), 6.74 (d, 2H, ³J_{H–H} = 8.6 Hz), 6.0 (br s, 1H, OH), 2.70 (m, 8H, CH₂ dppe) ¹³C {¹H} NMR (CDCl₃, 75 MHz, δ ppm): 172.9 (Cq), 155.3 (Cq), 146.2 (Cq), 137.7 (Cq), 136.2 (qt, ¹J_{P–C} + ³J_{P–C} = 10 Hz, Cq, *Cipso* dppe phenyl), 135.5 (qt, ¹J_{P–C} + ³J_{P–C} = 10 Hz, Cq, *Cipso* dppe phenyl), 134.4 and 134.2 (CH dppe phenyl), 133.9 (m, Cq), 133.2 (CH), 132.6 (Cq), 130.1 (CH), 129.0, 128.9 and 127.3 (CH dppe phenyl), 127.0 (CH dppe phenyl),

125.4 (CH), 124.7 (Cq), 124.3 (CH), 120.8 (Cq), 118.1 (CH), 115.6 (Cq), 30.7 (qt, ¹J_{P–C} + ³J_{P–C} = 23 Hz, CH₂ dppe). ³¹P {¹H} NMR (CDCl₃, 81 MHz, δ ppm): 50.50 (s).

2.3. *trans*-[MeCNRu(dppe)₂{C≡C-*p*-phenyl-(3-hydroxy-4H-chromen-4-one)}]PF₆ (**7a**)

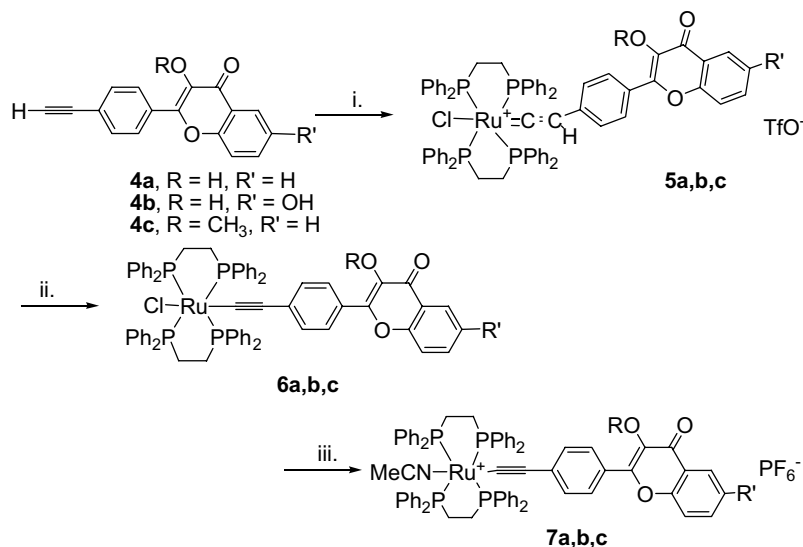
6a (260 mg, 0.20 mmol), 25 mL of dichloromethane and 5 mL of acetonitrile (dry and degassed solvents) was introduced under N₂ atmosphere together with 1 mmol of potassium hexafluorophosphate KPF₆. The resulting mixture was degassed, placed under N₂ atmosphere, and stirred at room temperature for 7 h. The resulting orange solution was washed several times with water and pumped to dryness (without using any drying agent containing metal cation). The obtained dark orange powder was washed with *n*-pentane to afford **7a** as an orange powder (275 mg, 94%). Mass spectrum: *m/z* calc. for C₆₉H₅₇O₃P₄¹⁰²Ru; [M–MeCN]⁺: 1159.2302; Found: 1159.2315. ν_{\max} (KBr/Nujol)/cm⁻¹ 2275 (m) ν (C≡N) and 2070 (w) ν (C≡C); ¹H NMR (CDCl₃, 200 MHz, δ ppm): 8.30 (dd, 1H, ³J_{H–H} = 8.0 Hz, ³J_{H–H} = 1.3 Hz), 8.23 (d, 2H, ³J_{H–H} = 8.4 Hz), 8.1 (m, 8H, aromatics), 7.8–7.1 (m, 29H, aromatics), 6.7 (m, 8H, aromatics), 6.0 (br s, 1H, OH), 2.75 (m, 8H, CH₂ dppe), 1.39 (s, 3H, CH₃CN). ¹³C {¹H} NMR (CDCl₃, 75 MHz, δ ppm): 173.2 (Cq), 155.4 (Cq), 145.3 (Cq), 138.1 (Cq), 134.8 (qt, ¹J_{P–C} + ³J_{P–C} = 11 Hz, Cq, *Cipso* dppe phenyl), 134.4 (CH dppe phenyl), 133.7 (CH), 132.6 (qt, ¹J_{P–C} + ³J_{P–C} = 10 Hz, Cq, *Cipso* dppe phenyl), 132.2 (CH dppe phenyl), 130.7 (Cq), 130.6 and 130.0 (CH dppe phenyl), 129.7 (CH) 128.9 (m, Cq), 128.4 and 128.0 (CH dppe phenyl), 127.7 (CH), 126.9 (Cq, CH₃CN), 125.4 (CH), 124.6 (CH), 124.0 (Cq), 120.7 (Cq), 118.3 (CH), 117.9 (Cq), 30.3 (qt, ¹J_{P–C} + ³J_{P–C} = 24 Hz, CH₂ dppe), 3.5 (CH₃, CH₃CN); ³¹P {¹H} NMR (CDCl₃, 81 MHz, δ ppm): 50.59 (s), –144.12 (sept, ¹J_{P–F} = 712 Hz).

3. Results and discussion

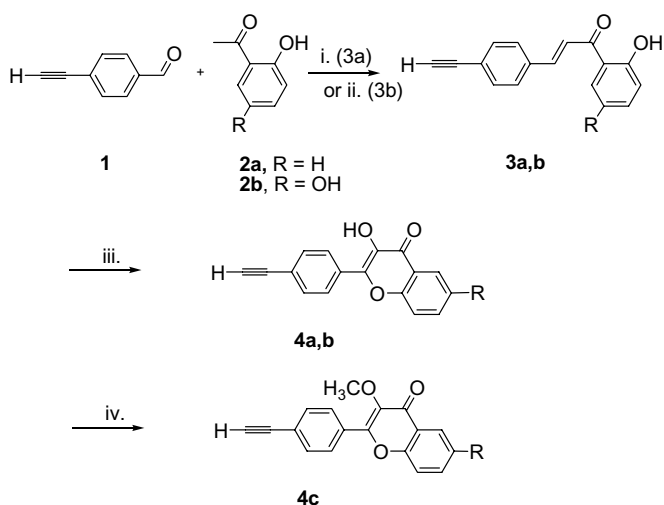
3.1. Synthesis

Scheme 1 shows the synthetic route to the flavonol-containing ruthenium complexes **7a–c**. The alkynes bearing 3-hydroxyflavone **4a** or 3,6-dihydroxyflavone **4b** were obtained via a two step procedure starting from 4-ethynylbenzaldehyde **1** (**Scheme 2**). The first step consisted of a Claisen–Schmidt reaction with 2-acetophenone **2a** or 2,5-dihydroxyacetophenone **2b**, and led to compounds **3a,b**. The second step entailed an Agar–Flynn–Oyamada reaction in basic medium [35–37], and gave rise to the expected terminal alkynes in satisfactory yields (50% overall). **4c** was obtained from **4a** upon addition of methyl iodide in the presence of potassium carbonate.

The flavonol based alkynyl ruthenium compounds **7a–c** were obtained starting from these terminal alkynes *via* a three-step procedure (**Scheme 2**) [38]. The first step consisted of the synthesis of vinylidene species **5**, which were



Scheme 1. The synthesis of flavonol based complexes **5–7**. (i) [(dppe)₂RuCl]TfO; solvent = CH₂Cl₂ for **5a** or THF – CH₂Cl₂ for **5b**; RT, 16 h (dppe: 1,2-bis(diphenylphosphino)ethane, TfO: trifluoromethanesulfonate). (ii) NEt₃, CH₂Cl₂, RT, 1 h. (iii) KPF₆, CH₃CN, CH₂Cl₂, RT, 7 h.



Scheme 2. The synthesis of alkynes bearing 3-hydroxyflavone **4a** or 3,6-hydroxyflavone **4b**. (i) BaOH, 8H₂O, 60 °C, 16 h, 80%. (ii) (a) 3,4-dihydropyran, pyridinium *p*-toluene sulfonate (PPTS), CH₂Cl₂, 99% (b) BaOH, 8H₂O, 60 °C, 16 h. (c) PPTS, THF. (iii) KOH, H₂O₂, DMSO, 0 °C, 16 h, **4a**: 60%; **4b**: 67%. (iv) CH₃I, K₂CO₃, CH₃CN, 40 °C, 16 h, **4c**: 77%.

purified by washing with diethylether in order to remove the excess of the terminal alkyne derivatives **4**. These vinylidene species were characterised by ¹H and ³¹P NMR. The X-ray structure determination of the vinylidene intermediate **5b** indicates that the conjugation in the ligand is almost preserved, even if a lack of coplanarity between the flavonol and the interposed phenyl ring can be observed, and reveals the absence of steric constraints around the terminal organic receptor moiety being located far from the envelope of the dppe ligands (Fig. 1). It is reasonable to assume the same would be observed for the complete series of the flavonol based alkynyl ruthenium complexes **5–7**.

Compounds **6** were obtained upon addition of triethylamine to complexes **5**. These compounds themselves are not viable for testing as sensors for metal salts, as the metal ions react with the chloro ruthenium unit leading to the substitution of the chlorine atom by an acetonitrile solvent molecule. In order to avoid the occurrence of such a competing reaction, the isomerically pure *trans*-[Ru(C≡C–Ar)-(CH₃C≡N)(dppe)₂][PF₆]₂ complexes **7a–c** (*Ar* represents 3-hydroxyflavone or 3,6-hydroxyflavone residues) were deliberately prepared from the chloro complexes **6** in the presence of acetonitrile, KPF₆ and NEt₃ in methylene chloride [39].

3.2. Electronic absorption and emission properties

Compounds **7** are characterised by strong charge transfer absorption bands in the visible region (**7a** λ_{max} = 405 nm in methylene chloride; ε_{max} = 2.9 × 10⁴ dm³ mol⁻¹ cm⁻¹; **7b** λ_{max} = 410 nm; ε_{max} = 3.0 × 10⁴ dm³ mol⁻¹ cm⁻¹), in contrast to the corresponding organic terminal alkynes for which all the transitions are confined to the UV region (**4a** λ_{max} = 350 nm in methylene chloride; ε_{max} = 1.8 × 10⁴ dm³ mol⁻¹ cm⁻¹; **4b** λ_{max} = 360 nm; ε_{max} = 1.9 × 10⁴ dm³ mol⁻¹ cm⁻¹). A broad absorption band is also observed in the visible region for the chloro complexes **6** (e.g. at λ_{max} = 415 nm for **6a**).

Luminescence associated with the flavonol moiety is observed from the complexes upon excitation into these CT bands. For example, **7a** emits at λ_{max} = 560 nm upon excitation at 400 nm, with a quantum yield of emission of 0.016 in acetonitrile at 298 K (Fig. 2). Interestingly, the emission is short-lived, with a lifetime of 2.1 ns (see ESI), that is unchanged upon degassing the solution. This suggests that the emission is *fluorescence*, emanating from a flavonol-based singlet excited state, rather than phosphorescence from a triplet state [40] as commonly observed in many ruthenium(II) coordination compounds when the

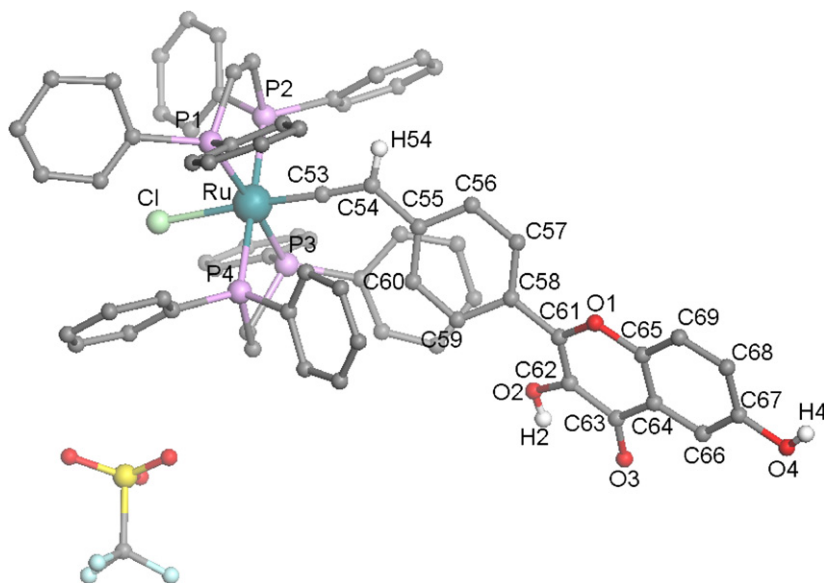


Fig. 1. The X-ray crystal structure of **5b** at 130 K, showing 50% probability ellipsoids (less relevant hydrogen atoms are omitted for clarity). Table 1 gives selected bond lengths [$d/\text{\AA}$] and angles [$\omega/^\circ$] values in **5b**.

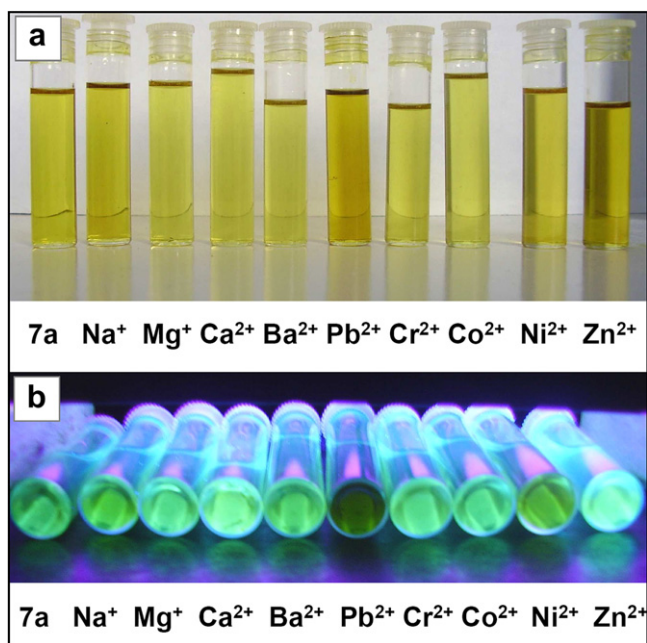


Fig. 2. (a) Colour changes induced by the addition of various metallic salts or Pb^{2+} cations (5 equiv.), to an acetonitrile solution of **7a**. (b) The light emitted by the same solutions upon irradiation at 365 nm. Cations were added in the form of their perchlorate salts. *Caution!* Perchlorate salts of metal complexes are potentially explosive with or without organic ligands and should be handled with care.

frontier orbitals incorporate significant contributions from the metal orbitals. Apparently, in the excited state, the flavonol unit is effectively decoupled from the ruthenium centre.

3.3. Optical sensing of metal ions

To obtain insight into the ability of **1** to selectively sense metal ions, we first investigated colour (absorption) and

fluorescence changes of **7a** upon the addition of various metal ions such as Li^+ , Na^+ , Ba^{2+} , Ca^{2+} , Cd^{2+} , Mg^{2+} , Co^{2+} , Cr^{2+} , Ni^{2+} , Zn^{2+} , and Pb^{2+} in acetonitrile. The qualitative estimation of the affinity of **7a** towards various cations was first performed visually. Fig. 2 shows the appearance of solutions of **7a** in the presence of perchlorate salts in daylight and upon irradiation with a broad-band near-UV lamp (λ_{max} 365 nm). It can be seen that it is not possible to discriminate visually between the cations in daylight (Fig. 2a), *i.e.*, on the basis of absorption, although Pb^{2+} , Ni^{2+} and Zn^{2+} do lead to darker solutions. Conversely, upon irradiation in the near-UV and observation of the fluorescence, there is a dramatic and clear-cut discrimination between Pb^{2+} and the other cations, Mg^{2+} , Cr^{2+} , Co^{2+} , and Ba^{2+} [31,32], and also Ni^{2+} and Zn^{2+} (Fig. 2b).

Quantitative titrations were performed by addition of small amounts of metal perchlorate salts in MeCN (1×10^{-2} mol/L) to **7a** (5×10^{-5} mol/L in MeCN). The test solutions were prepared by placing 5–50 μL of the probe stock solution into a test tube, adding the appropriate aliquot of each metal stock. For the fluorescence measurements, an excitation wavelength of 400 nm was employed, with excitation and emission band passes of 5 nm. Under these conditions, the addition of Na^+ , Ba^{2+} , Ca^{2+} , Co^{2+} , Mg^{2+} or Cr^{2+} did not result in significant changes in either the absorption or emission spectra. In contrast, interaction of **7a** with Pb^{2+} cations resulted in large bathochromic shifts of both absorption and emission spectra (Fig. 3a and b). The presence of small amounts of lead cations results in the disappearance of the initial absorption band at $\lambda_{\text{max}} = 400$ nm and in the appearance of a new long-wavelength absorption band at 465 nm (Fig. 3a). In the fluorescence spectrum, the emission band is shifted by 40 nm to the red (from 565 to 605 nm), with

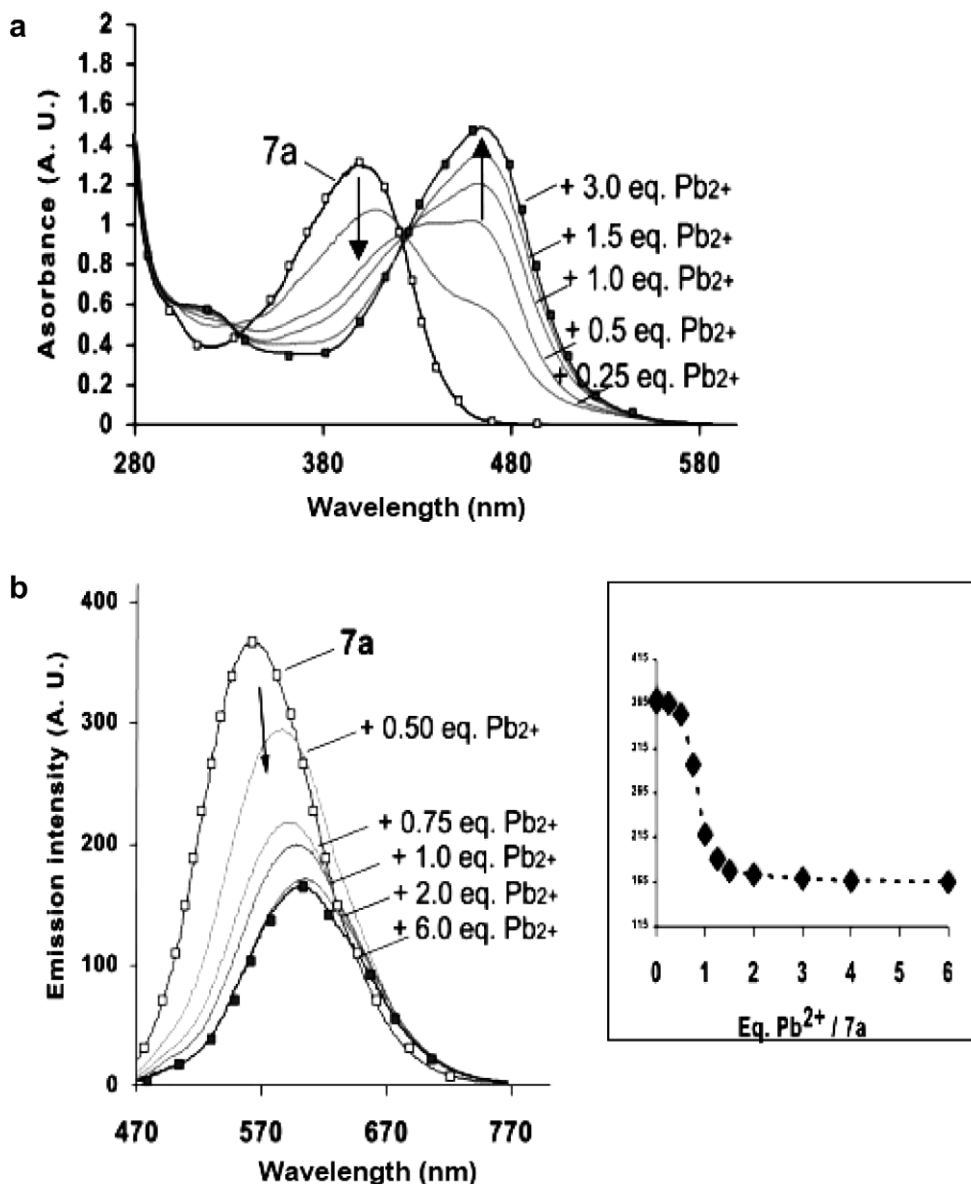


Fig. 3. Changes in the absorption (a) and fluorescence spectra (b) of **7a** (5×10^{-5} mol/L) in air-equilibrated acetonitrile upon addition of Pb^{2+} cations in the form of their perchlorate salt (1×10^{-2} mol/L). Inset: dependence of the emission intensity on Pb^{2+} concentration.

a reduction in the quantum yield to 0.0083. The lifetime of the species formed is too short to measure reliably with our instrumentation (<1 ns). Non-radiative deactivation of the flavonol singlet excited state is probably promoted in the complex by the lower energy of the excited state and also by the heavy atom effect of the Pb^{2+} ion.

The studies of the dependence of absorption and emission spectra on Pb^{2+} concentration allow us to conclude that the flavonol based alkynyl ruthenium sensor **7a** exhibits 1:1 stoichiometry of binding with this cation. An association constant K_a of $8 \pm 0.1 \times 10^6 \text{ mol}^{-1} \text{ dm}^3$ was calculated from absorption spectral data, using iterative non-linear least-squares methods analogous to those previously described [24].

Only two other metal ions have any significant influence on the fluorescence, namely Ni^{2+} and Zn^{2+} . These cations

can compete with lead: association constants of $1.3 \pm 0.2 \times 10^7 \text{ mol}^{-1} \text{ dm}^3$ and $6 \pm 0.1 \times 10^4 \text{ mol}^{-1} \text{ dm}^3$ were calculated from absorption spectral data respectively for the nickel and zinc salts. For Ni^{2+} , the emission is quenched without significant shifting, probably due to an electron-transfer mechanism of deactivation by the high-spin Ni^{2+} ion with its unpaired electrons. The behaviour with Zn^{2+} (Fig. 4) is more complicated: an initial small decline in the intensity, without shifting of λ_{max} , (up to 0.5 equiv. of Zn^{2+} added) is followed at higher concentrations of Zn^{2+} by the appearance of a shoulder to high-energy of the starting band. However, the effect is less pronounced than that induced by lead, and much higher concentrations are required.

Cornard and co-workers reported on spectroscopic investigation of the complex formation of lead(II) with

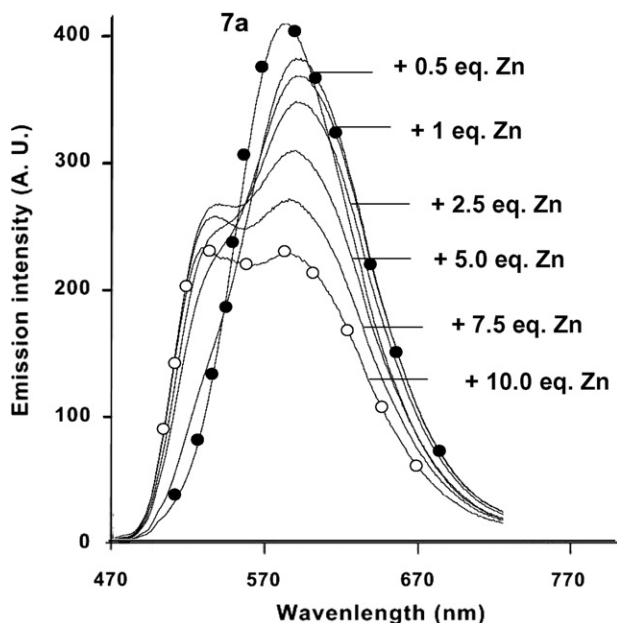


Fig. 4. Changes in the fluorescence spectrum of **7a** (5×10^{-5} mol/L) in air-equilibrated acetonitrile upon addition of Zn^{2+} cations in the form of their perchlorate salt (1×10^{-2} mol/L).

3-hydroxyflavone. These results were similar to ours in main aspects. These authors concluded to the formation of species of stoichiometry (1:1) with a complete deprotonation of the hydroxyl group [41]. Roshall [31,32] previously established, on the basis of the characteristic spectroscopic changes, that flavonol complexes with metal cations can be classified into two groups. In the complexes of the first group, the proton of the flavonol hydroxylic group is not substituted by a metal cation. The metal cation forms a donor–acceptor linkage with the electron lone pair on the oxygen of the C=O group, and does not cause essential changes in the flavonol electronic structure. The properties of these complexes are similar to the properties of flavonols without cations. We can suggest that the complexes that **7a** formed with Na^+ , Ba^{2+} , Ca^{2+} , Co^{2+} , or Mg^{2+} belong to this class, as in these cases the cation binding does not cause essential changes in the flavonol electronic structure, according to our experimental results. In contrast, in the complexes of the second group [27], the flavonol hydroxylic group participates in the formation of the complexes. The interaction of metal cations with flavonols then results in a cyclic arrangement of chelates with metal cations. This stronger interaction results in significant bathochromic shifts of both absorption and emission spectra, as essential changes in the flavonol electronic structure occur. Our result allows us to suggest that the interaction of the Ni^{2+} , Pb^{2+} and Zn^{2+} cations with the flavonol-based alkynyl ruthenium sensor **7a** leads to a chelating complex involving the participation of the hydroxyl group. This is also supported by the observation that **7c**, which lacks the OH group, does not display this behaviour, reflecting the need for the 3-hydroxyl group to deprotonate and allow the metal cations to bind.

3.4. Influence of water on metal ion binding and sensing

Practicable sensors normally need to be able to function in the presence of at least some water. We found that **7a** also exhibits efficient binding of lead in acetonitrile-distilled water (75:25 v/v). Under aqueous conditions, the OH group is partially dissociated under neutral conditions, leading to an anionic form, which inhibits to some extent the complexation of ions from being observed. The optimum pH at which **7a** is mainly in the neutral form and allows the stronger photophysical effects upon lead binding to be observed was found to be 6. Under these conditions, the calculated association constant was lowered ($K_a = 13.5 \pm 0.4 \times 10^3 \text{ mol}^{-1} \text{ dm}^3$) but the selectivity retained. Meanwhile, it is of interest to note that the flavonol-based fluorescence was also maintained in the presence of water.

In conclusion, we have developed a new series of alkynyl ruthenium sensors, destined for the detection of metal traces in solution, in which the receptor units are 3-hydroxyflavone and 3,5-dihydroxyflavone. The sensitivity of both absorption and emission properties of these flavonol based alkynyl ruthenium sensors to the presence of metal cations suggests their use as sensors for metal traces. As a preliminary result, we have shown that the combined use of the 3-hydroxyflavone unit as a receptor for the metal cations, and of an alkynyl ruthenium moiety as an extended π conjugated system, provides an efficient molecular sensor for rapid, sensitive detection of lead(II) cations. Current studies are in progress in our group to improve the selectivity of the complexation of lead using modified receptor units derived from 3-hydroxyflavone.

Acknowledgement

We would like to thank la Région Bretagne for a PhD studentship, and the French Ministry of Research, the French Ministry for Foreign Affairs, the CNRS, and E.U.COST D035-0010-05 for financial support.

Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2007.10.046.

References

- [1] T.A. Florin, T.M.W. Brent, *Pediatrics* 115 (2005) 1767.
- [2] A. Garza, R. Vega, E. Soto, *Med. Sci. Monit.* 12 (2006) RA57.
- [3] J.S. Magyar, T.C. Weng, C.M. Stern, D.F. Dye, B.W. Rous, J.C. Payne, B.M. Bridgewater, A. Mijovilovich, G. Parkin, J.M. Zaleski, J.E. Penner-Hahn, H.A. Godwin, *J. Am. Chem. Soc.* 127 (2005) 9495.
- [4] L. Basabe-Desmonts, D.N. Reinhoudt, M. Crego-Calama, *Chem. Soc. Rev.* 36 (2007) 993.
- [5] B. Valeur, I. Leray, *Inorg. Chim. Acta* 360 (2007) 765.
- [6] P. Jiang, Z. Guo, *Coord. Chem. Rev.* 248 (2004) 205.
- [7] L. Prodi, *New J. Chem.* 29 (2005) 20.
- [8] B. Valeur, I. Leray, *Coord. Chem. Rev.* 205 (2000) 3.

- [9] Y. Mikata, M. Wakamatsu, A. Kawamura, N. Yamanaka, S. Yano, A. Odani, K. Morihira, S. Tamotsu, *Inorg. Chem.* 45 (2006) 9262.
- [10] R. Métivier, I. Leray, B. Valeur, *Chem. Commun.* (2003) 996.
- [11] Q. He, E.W. Miller, A.P. Wong, C.J. Chang, *J. Am. Chem. Soc.* 128 (2006) 9316.
- [12] J.-L. Fillaut, J. Andriès, L. Toupet, J.-P. Desvergne, *Chem. Commun.* 23 (2005) 2924.
- [13] C.E. Powell, M.G. Humphrey, *Coord. Chem. Rev.* 248 (2004) 725.
- [14] S. Di Bella, *Chem. Soc. Rev.* 30 (2001) 355.
- [15] C.E. Powell, M.P. Cifuentes, J.P. Morrall, R. Stranger, M.G. Humphrey, M. Samoc, B. Luther-Davies, G.A. Heath, *J. Am. Chem. Soc.* 125 (2003) 602.
- [16] J.-L. Fillaut, J. Perruchon, P. Blanchard, J. Roncali, S. Golhen, M. Allain, A. Migalska-Zalas, I.V. Kityk, B. Sahraoui, *Organometallics* 24 (2005) 687.
- [17] M.H. Garcia, M.P. Robalo, A.R. Dias, M.T. Duarte, W. Wenseleers, G. Aerts, E. Goovaerts, M.P. Cifuentes, S. Hurst, M.G. Humphrey, M. Samoc, B. Luther-Davies, *Organometallics* 21 (2002) 2107.
- [18] M.I. Bruce, P.J. Low, *Adv. Organomet. Chem.* 50 (2004) 179.
- [19] N.J. Long, C.K. Williams, *Angew. Chem. Int. Ed.* 42 (2003) 2586.
- [20] F. Paul, C. Lapinte, *Coord. Chem. Rev.* 180 (1998) 431.
- [21] S. Rigaut, J. Perruchon, S. Guesmi, C. Fave, D. Touchard, P.H. Dixneuf, *Eur. J. Inorg. Chem.* (2005) 447.
- [22] D. Touchard, P.H. Dixneuf, *Coord. Chem. Rev.* 178–180 (1998) 409.
- [23] B.-S. Kim, J.M. Beebe, C. Olivier, S. Rigaut, D. Touchard, J.G. Kushmerick, X.-Y. Zhu, C.D. Frisbie, *J. Phys. Chem. C.* 111 (2007) 7521.
- [24] J.-L. Fillaut, J. Andriès, J. Perruchon, J.-P. Desvergne, L. Toupet, L. Fadel, B. Zouchoune, J.-Y. Saillard, *Inorg. Chem.* 46 (2007) 5922.
- [25] R.J. Nijveldt, E. van Nood, D.E. van Hoorn, P.G. Boelens, K. van Norren, P.A. van Leeuwen, *Am. J. Clin. Nutr.* 74 (2001) 418.
- [26] R.J. Williams, J.P.E. Spencer, C. Rice-Evans, *Free Rad. Biol. Med.* 36 (2004) 838.
- [27] C. Lapouge, J.P. Cornard, *J. Phys. Chem. A* 109 (2005) 6752.
- [28] Z.P. Wang, L.L. Shi, G.S. Chen, K.L. Cheng, *Talanta* 51 (2000) 315.
- [29] Y. Takahashi, D.A.P. Tanaka, H. Matsunaga, T.M. Suzuki, *J. Chem. Soc., Perkin Trans. 2* (2002) 759.
- [30] X. Poteau, G. Saroja, C. Spies, R.G. Brown, *Sensor. Actuat. A* 113 (2004) 288.
- [31] A.D. Roshal, A.V. Grigorovich, A.O. Doroshenko, V.G. Pivovarenko, A.P. Demchenko, *J. Photochem. Photobiol. A: Chem.* 127 (1999) 89.
- [32] A.D. Roshal, A.V. Grigorovich, A. Doroshenko, V.G. Pivorenko, A.P. Demchenko, *J. Phys. Chem. A* 102 (1998) 5907.
- [33] N. Mantovani, M. Brugnati, L. Gonsalvi, E. Grigiotti, F. Laschi, L. Marvelli, M. Peruzzini, G. Reginato, R. Rossi, P. Zanella, *Organometallics* 24 (2005) 405.
- [34] S. Rigaut, J. Perruchon, L. Le Pichon, D. Touchard, P.H. Dixneuf, *J. Organomet. Chem.* 670 (2003) 37.
- [35] J. Algar, J.P. Flynn, *Proc. Roy. Irish. Acad.* 42B (1934) 1.
- [36] T. Oyamada, *J. Chem. Soc. Jpn.* 55 (1934) 1256.
- [37] M.A. Smith, R.M. Neumann, R.A. Webb, *J. Heterocyclic Chem.* 5 (1968) 425.
- [38] D. Touchard, P. Haquette, S. Guesmi, L. Le Pichon, A. Daridor, L. Toupet, P.H. Dixneuf, *Organometallics* 16 (1997) 3640.
- [39] J.-L. Fillaut, N.N. Dua, F. Geneste, L. Toupet, S. Sinbandhit, *J. Organomet. Chem.* 691 (2006) 5622.
- [40] C.J. Adams, S.J.A. Pope, *Inorg. Chem.* 43 (2004) 3492.
- [41] L. Dangleterre, J.-P. Cornard, *Polyhedron* 24 (2005) 1593.