

Coumarinic Fluorescent Chemosensors for the Detection of Transition Metal Ions

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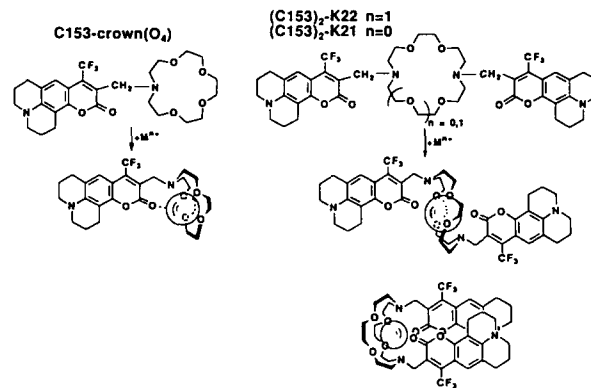
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Fluoroionophores consisting of coumarin-153 linked to mono- and diaza-crown ethers are able to complex transition metal cations (Ni^{2+} , Zn^{2+} , Cd^{2+}) and Pb^{2+} , with concomitant large changes in photophysical properties. The stability constants in acetonitrile are higher than $3 \times 10^6 M^{-1}$ except for Ni^{2+} .

KEY WORDS: Coumarin; transition metal ions; crown ethers; fluoroionophores.

Among the various methods available for detection of ions, those based on fluorescent sensors offer distinct advantages in terms of sensitivity, selectivity, response time, and spatial resolution. Moreover, remote sensing is possible by using optical fibers. Much attention has thus been paid to the design of fluorescent probes for ion recognition (for a review, see Ref. 1). In a previous paper, we reported interesting photophysical effects upon binding of alkali and alkaline-earth metal cations on fluoroionophores consisting of coumarin-153 linked to monoaza- and diaza-crown ethers [2]. The present paper is devoted to the detection of transition metal ions (Ni^{2+} , Zn^{2+} , Cd^{2+}) and a heavy metal ion (Pb^{2+}) by the same kind of fluoroionophores and, in particular, by the newly synthesized compound involving diaza-15-crown-5. The fluoroionophores used in this investigation are shown in Scheme I. The ionophore moieties containing one or two nitrogen atoms are indeed able to complex transition metal ions according to the HSAB principle, which predicts that soft nitrogen centers combine with soft transition metal ions.

The absorption and emission spectra of the ligands and their complexes with perchlorate salts in acetonitrile are exemplified in Figs. 1 and 2. Their photophysical



Scheme I.

properties are reported in Table I. The red shifts upon cation binding have been interpreted previously in terms of direct interaction between the bound cation and the carbonyl group of the coumarin moiety, the electron-withdrawing character of this group being reinforced by the cation [2].

Upon the addition of salt to a $4 \times 10^{-5} M$ solution of the ligand in acetonitrile, the absorbance measured at an appropriate wavelength levels off when one equivalent of salt (or slightly more) is added, which means that the stoichiometry of the complexes is 1:1. However, the isosbestic point expected from the formation of a unique

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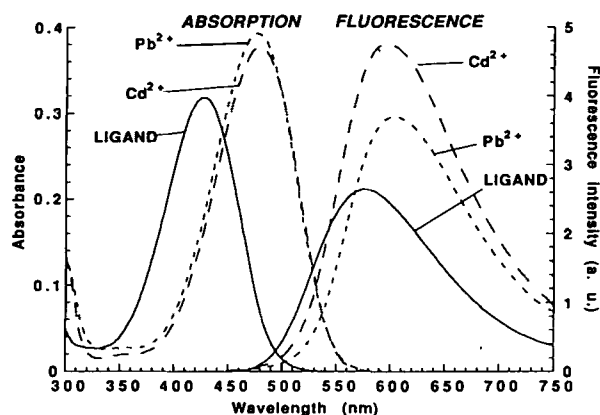


Fig. 1. Absorption and corrected fluorescence spectra of C153-crown(O₄) and its complexes with cadmium and lead perchlorate in acetonitrile at 25°C. The fluorescence is normalized.

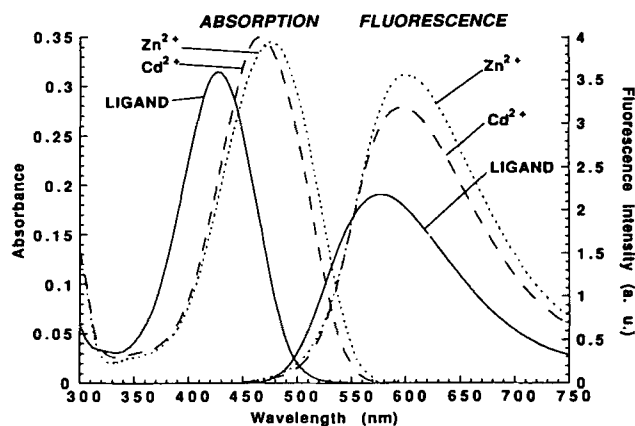


Fig. 2. Absorption and corrected fluorescence spectra of (C153)₂-K22 and its complexes with cadmium and zinc perchlorate in acetonitrile at 25°C.

complex is not well defined in some cases, and formation of complexes other than the ML complex cannot be excluded. Similar observations were reported by Arnaud-Neu *et al.* [3] and Andregg [4] in their study of the complexation of the same aza-crowns alone (i.e., without linked fluorophores) with the same cations. Nevertheless, analysis of our data (variations in absorbance versus cation concentration) leads, in most cases, to a satisfactory fit with a model involving a single complex, 1:1. The stability constants of the complexes that can be

inferred from data analysis are reported in Table I. They are found to be higher than $3 \times 10^6 M^{-1}$ except for Ni²⁺.

Regarding the quantum yield of the ligand and the complexes (Table I), it should be noted first that the addition of an excess of salt by a factor of 100 to a solution of the fluorophore alone (coumarin-153) results in a decrease in quantum yield of 5% at most, even in the case of lead ion, for which a heavy atom effect could have been expected. It is also worth noting that the quantum yields of the ligands are much lower than that of

Table I. Photophysical Characteristics of the Coumarinic Fluorescent Chemosensors and Their Complexes in Acetonitrile at 25°C

	Ligand	Complex				
		H ⁺	Ni ²⁺	Zn ²⁺	Cd ²⁺	Pb ²⁺
C153-crown(O ₄)						
λ _{abs} (nm)	426	460	481	487	481	476
ε × 10 ⁻³ (L·mol ⁻¹ ·cm ⁻¹)	20.3	24.7	21	25	24.6	26.1
logK _s ^a	—	—	5.6	6.8	6.5	7.1
λ _{em} (nm)	578	584	595	598	598	604
Quantum yield	0.12	0.21	0.17	0.18	0.20	0.15
(C153) ₂ -K22						
λ _{abs} (nm)	426	460	450	461	460	456
ε × 10 ⁻³ (L·mol ⁻¹ ·cm ⁻¹)	27.7	35	26.3	35.6	29.3	30.2
logK _s	—	—	—	7.3	7.0	7.9
λ _{em} (nm)	572	583	578	583	580	583
Quantum yield	0.016	0.125	0.020	0.036	0.017	0.017
(C153) ₂ -K21						
λ _{abs} (nm)	426	460	489	486	466	461
ε × 10 ⁻³ (L·mol ⁻¹ ·cm ⁻¹)	27.1	30.3	30.5	31.8	30.2	30.7
logK _s	—	—	5.25	7.3	6.5	7.5
λ _{em} (nm)	577	585	585	600	596	595
Quantum yield	0.055	0.070	0.077	0.085	0.076	0.077

^aThe stability constant is defined as $K_s = [ML]/[M][L]$.

coumarin-153 (0.50 in acetonitrile) and that, in all cases, fluorescence is partially recovered upon cation complexation, the largest effect being observed upon protonation of the nitrogen atom of the crown (Table I). This indicates that quenching by the crown is due partly to photoinduced electron transfer from the nitrogen atom to the coumarin moiety, as observed in anthracene linked to monoaza-15-crown-5 via a methylene group [5]. Upon cation binding, the redox potential of the nitrogen atom is raised, which reduces the probability of electron transfer. Furthermore, in the bis-coumarin fluoroionophores (C153)₂-K22 and (C153)₂-K21, self-quenching is possible because the flexibility of the crowns allows the two coumarin moieties to come into close contact. The quantum yields of the complexes depend on whether their conformation is extended or folded (see Scheme I) [2].

The shift in fluorescence spectra are of interest for practical applications because it allows intensity-ratio measurements at two wavelengths. Here, these shifts are, in some cases, even larger than those observed with alkaline-earth metal cations. C153-crown(O₄) and (C153)₂-K21 both exhibit distinct and large shifts and a marked increase in fluorescence quantum yields. They behave in a similar way but in contradistinction to (C153)₂-K22, which gives only moderate effects, probably for sterical reasons. The linear relationship between the Stokes shift and the charge density of the cation previously established in the case of alkali and alkaline-earth metal cations [2] is no longer valid for the cations considered in this study. Other factors must be taken into account. In fact, following the conclusions drawn by Arnaud-Neu *et al.* [3], one should distinguish between doubly charged cations, with an inner complete 3d

electronic layer (i.e., Cd²⁺ and Pb²⁺, whose behavior is not very different from that of alkaline-earth metal ions), and transition metal cations of the first rank (i.e., Ni²⁺ and Zn²⁺), whose links are imposed by the geometry of their 3d orbitals. The peculiar behavior of Ni²⁺, which induces here only small shifts and forms complexes of weaker stability, can be explained by the rigidity of its geometry, which hinders its insertion into the crown [6].

Further studies in solvents other than acetonitrile or in a mixture of solvents are in progress. A procedure in a mixture of acetonitrile and water was described previously using C153-crown(O₄) for the detection of alkaline-earth metal ions [7] and should be transposable to the cations of this study.

In conclusion, the above-described fluorescent sensors are of potential use for the detection of transition metal ions and lead ion. It should be noted that Zn²⁺ is of biological interest, and Cd²⁺ and Pb²⁺ are implied in pollution problems.

REFERENCES

1. B. Valeur (1994) in J. R. Lakowicz (Ed.), *Probe Design and Chemical Sensing, Topics in Fluorescence Spectroscopy, Vol. 4*, Plenum, New York (in press).
2. J. Bourson, J. Pouget, and B. Valeur (1993) *J. Phys. Chem.* **97**, 4552.
3. F. Arnaud-Neu, B. Spiess, and M. J. Schwing-Weill (1977) *Helv. Chim. Acta* **60**, 2663; (1980) **63**, 2287.
4. G. Anderegg (1975) *Helv. Chim. Acta* **58**, 1218; (1981) **64**, 1790.
5. A. Prasanna de Silva and S. A. de Silva (1986) *J. Chem. Soc. Chem. Commun.* 1709.
6. L. F. Lindoy (1990) in Y. Inoue and G. W. Gokel, (Eds.), *Cation Binding by Macrocycles*, Marcel Dekker, New York, p. 412.
7. J. Bourson, M. N. Borrel, and B. Valeur (1992) *Anal. Chim. Acta* **257**, 189.