ChemComm

New fluoroionophores from aniline dimer derivatives: a variation of cation signalling mechanism with the number of amino groups

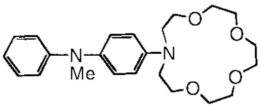
Pascale Crochet, Jean-Pierre Malval and René Lapouyade*

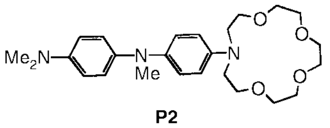
Laboratoire d'Analyse Chimique par Reconnaissance Moléculaire (LACReM), Ecole Nationale Supérieure de Chimie et de Physique de Bordeaux (ENSCPB), Talence, France. E-mail: lapouyad@enscpb.u-bordeaux.fr

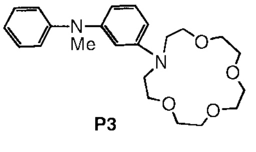
Received (in Liverpool, UK) 18th October 1999, Accepted 10th January 2000

New fluoroionophores, *N*-peralkylated dimers of aniline, are described.

The direct connection of an ionophore to a luminophore provides an optical ion sensor if these two components are in electronic interaction in the ground state or in the excited state.[1] Sensing is based on the modification of the two components interaction when the ion is recognized by the ionophore. According to the nature of the ionophore–fluorophore interaction, the fluorescence signal is modified in intensity or/and in energy. Fluoroionophores which undergo spectral shift on cation binding allow the measurement of the cation concentration from the ratio of the fluorescence intensity at two different wavelengths. To obtain this wavelength dependence of the fluorescence intensity, fluoroionophores with two emitting states, monomer–excimer (exciplex)[2] or ICT–TICT states,[3] the populations of which are ion-dependent, have been designed.[4] In particular, when the ionophore has a heteroatom which is a ligand of the ion and which also takes part in the first electronic transition of the fluorophore, the recognition of an ion stabilizes the heteroatom electronic pair and the fluorophore has the electronic configuration of the unsubstituted compound. The fluorescence spectrum of the ion-probe complex will be that of the probe or of the unsubstituted fluorophore (or a mixture of the two) depending on the relative rate constants of radiative emission and of the decoordination of the cation from the probe.[5] We have prepared and characterized the optical properties of *N*-peralkylated *meta*- and *para*-dimers of aniline with the monoaza-15-crown-5 ionophore replacing the dialkylamino group at one end of the molecules (**P1** and **P3**) and the *para*-dimethylamino derivative of **P1** with the amino group in the *para* position (**P2**). The comparison of **P1** and **P3** should provide an additional example of the '*meta* effect'.[6] The addition of the Me_2N group in **P2** should, upon cation binding, restore the photoinduced charge transfer encountered for **P1**, as we have recently observed with similar electronically symmetrical stilbenes.[7] We report here that the calcium complexes of the azacrown derivative of the peralkylated aniline dimer and its *p*-dimethylamino derivative (**P1** and **P2**) do not decoordinate in the excited state and consequently lead to new emission bands, upon cation recognition, blue-shifted for **P1** because of cation-inhibition of the CT process, and red-shifted for **P2** as a result of a cation-induced electron acceptor group which leads to a charge transfer band.


P1


P2


P3

The three compounds[8] were synthesized from an Ullmann coupling of the aniline derivatives with iodonitrobenzene, followed by methylation of the secondary amine,[9] reduction of the nitro group and transformation of the resulting primary amine into the aza-15-crown-5.[10]

The absorption spectra of **P1**–**P3** extend to 340 nm and do not show significant shift with increasing solvent polarity, whereas the fluorescence, always unstructured, is red-shifted in polar solvents (Table 1). This behaviour could be attributed to rapid relaxation of the initially formed Franck–Condon excited state to a charge-transfer (CT) state. Let us assume that there is only one emitting state, whatever the polarity of the solvent; by applying the Lippert–Mataga equation[11] we can estimate dipole moments of 20.6, 8.8 and 12.2 D for **P1**, **P2** and **P3** respectively (Table 1). The monoexponential decay of **P1** implies one emitting state or several in fast equilibrium. Nevertheless the charge transfer (CT) character of the fluorescing state is large for the *p*-aniline dimer (**P1**) where we can calculate, from the Rhem–Weller equation[12] ($\Delta G = E_{ox} - E_{red} - E_{ex}$), neglecting the Coulomb part of the stabilization energy, an exergonic stabilisation energy $\Delta G = -0.36$ eV for charge separation from the *p*-phenylenediamine group in the excited state ($E_{ox} - E_{ex} = -3.78$ eV for *N,N,N′,N′*-tetramethyl-*p*-phenylenediamine) to the benzene substituent ($E_{red} = -3.42$ eV).[13] The excited state dipole moments of the *meta* isomer (**P3**) and of the symmetrical derivative (**P2**) are lower, relative to **P1**, because the electron donor group in **P3** has a higher oxidation potential and the potential electron acceptor substituent (dimethylaniline) in **P2** has a more negative reduction potential.

Addition of calcium perchlorate to solution of the probes in MeCN leads to the absorption spectra of the corresponding compounds without the azacrown substituent; for example, the absorption spectrum of the calcium–**P2** complex superposes with the absorption of **P1**. In fact the absorption spectra are not markedly shifted but the absorption intensity is altered enough to allow the measurement of the complexation constant K_s by a nonlinear least-squares analysis of the absorption intensity *versus* the concentration of the cation using the relation derived by Valeur[14] for probes with a sufficiently high K_s that the

Table 1 Fluorescence emission data for **P1**–**P3** and their calcium complexes

	λ_{max}/nm			ϕ_F[b]		τ_F/ns (preexp)
	Hexane	MeCN	μ_e/D[a]	Hexane	MeCN	MeCN
P1	391	489	20.6	0.05	0.03	4.20
P2	404	427	8.8			
P3	377	374	12.2			
P1–Ca		417				1.60 (66) 4.84 (34)
P2–Ca		536				

[a] Calculated according to $\nu_{flu} = -2\mu_e(\mu_c - \mu_g)/hca^3\{(\varepsilon - 1)/(2\varepsilon + 1)\text{-}(n^2 - 1)(4n^2 + 1)\}$ + constant, with $a = 4.55$ Å and $\mu_g = 1.67$ D from AM1 calculation for **P1**, $a = 4.81$ Å and $\mu_g = 0$ for **P2** and $a = 4.55$ Å and $\mu_g = 0$ for **P3**. [b] Diphenylanthracene ($\phi_F = 0.9$ in cyclohexane) as the actinometer for all compounds excited at 330 nm.

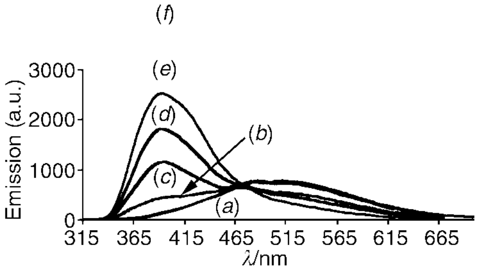


Fig. 1 Influence of Ca^{2+} on the fluorescence of a 1.86×10^{-5} M solution of **P1** in acetonitrile: $[Ca^{2+}] = 0$ M (*a*); 3.15×10^{-6} M (*b*); 6.3×10^{-6} M (*c*); 1.26×10^{-5} (*d*); 1.89×10^{-5} M (*e*); 5.67×10^{-4} M (*f*).

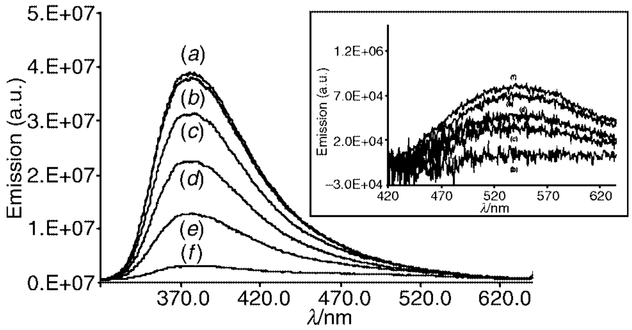


Fig. 2 Fluorescence spectra of **P2** (8.50×10^{-4} M) in acetonitrile with increasing amount of $Ca(ClO_4)_2$: $[Ca^{+2}] = 0$ M (*a*); 2.88×10^{-6} M (*b*); 8.64×10^{-6} M (*c*) 1.15×10^{-5} M (*d*); 1.73×10^{-5} M (*e*); 2.88×10^{-5} M (*f*).

concentration of the uncomplexed cation cannot be approximated to the concentration of the salt added. We obtained log $K_s = 5.3$ and 5.6 for **P1** and **P2**, respectively.[15] These values are higher than those found with fluoroionophores of the stilbene series built with the same ionophore but with the electron-accepting substituent in the *para* position (log $K_s \cong 4$) or even with a *p*-dimethylamino group (log $K_s \cong 4.9$).[7] The value of the complexation constants increases with the electron density on the nitrogen atom of the ionophore.

The effect of calcium on the fluorescence spectra of **P1** and **P2** is marked, while being peculiar for each compound (Fig. 1 and Fig. 2): the fluorescence of the probes is quenched, and a new emission appears of similar intensity and on the high energy side for **P1**, and with very low quantum yield ($< 10^{-4}$) and at longer wavelength for **P2**.

The complexation constants obtained from the fluorescence spectra have the same value as those from the absorption spectra. The fluorescence of the complex **P1**–Ca is in the same wavelength region as the fluorescence of Ph_2NMe and that of the complex **P2**–Ca corresponds to that of **P1**.

These characteristics indicate that there is no decoordination of the cation during the excited state lifetime of the probes. With **P1** the cation lowers the energy of the electron pair on the nitrogen atom of the azacrown, which accordingly is decoupled from the π aromatic system. In a first approximation we can estimate that the **P1**–Ca complex has the same electronic configuration as Ph_2NMe. With the same reasoning, we could consider that **P2**–Ca is identical to **P1**, but if the spectral position and the solvatochromism of the emission are comparable, the quantum yield of fluorescence of the **P2**–Ca complex is very low. The Ca–nitrogen atom interaction, which should be reinforced in the excited state, could open a new channel for non-radiative deactivation. In conclusion these *N*-peralkylated dimers of aniline provide interesting fluoroionophores with high complexation constants and distinct fluorescence shifts upon cation complexation. In conjugation with the phenyl-azacrown ionophore, the PhMeN substituent is an electron donor in the ground state of the probe, while the benzene group can be an electron acceptor with the probe in the excited state. As cation recognition by the azacrown should have the same electronic effect as protonation, the results reported here should be pertinent to the fluorescence modification of polyaniline when the protonic level of doping is increased. Longer and conformationaly constrained oligoanilines are under study to achieve oligomeric fluorescent cation probes[16a,b] and to better understand the electronic properties of polyaniline.

We thank Colette Belin and Jean-Pierre Desvergne for help with the fluorescence experiments and the Ecole Nationale Supérieure de Chimie et de Physique de Bordeaux for financial support.

Notes and references

1 *Chemosensors of Ion and Molecule Recognition*, ed. J.-P. Desvergne and A. W. Czarnik, Kluwer, Boston, 1997; W. Rettig and R. Lapouyade, *Topics in Fluorescence Spectroscopy*, ed. J. R. Lakowicz, Plenum, New York, 1994, vol. 4, pp. 109–149; B. Valeur and E. Bardez, *Chem. Br.*, 1995, **31**, 216.

2 H. Bouas-Laurent, A. Castellan, M. Daney, J.-P. Desvergne, G. Guinand, P. Marsau and M. Riffaud, *J. Am. Chem. Soc.*, 1986, **108**, 315.

3 J.-F. Letard, S. Delmond, R. Lapouyade, D. Braun, W. Rettig and M. Kreissler, *Recl. Trav. Chim. Pays-Bas*, 1995, **114**, 517.

4 For a review see: A. Prasanna de Silva, H. Q. Nimal Gunaratne, T. Gunnlaugsson, A. J. Huxley, C. P. McCoy, J. T. Rademacher and T. E. Rice, *Chem. Rev.*, 1997, **97**, 1515.

5 R. Mathevet, G. Jonusauskas, C. Rulliere, J.-F. Letard and R. Lapouyade, *J. Phys. Chem.*, 1995, **99**, 15 709.

6 F. D. Lewis and J.-S. Yang, *J. Am. Chem. Soc.*, 1997, **119**, 3834.

7 S. Delmond, J.-F. Letard, R. Lapouyade, R. Mathevet, G. Jonusauskas and C. Rulliere, *New. J. Chem.*, 1996, **20**, 861.

8 The structure of the compounds was confirmed by ^1H, ^{13}C NMR and MS.

9 A. Barco, S. Benetti, G. P. Pollini and P. G. Baraldi, *Synthesis*, 1976, 124.

10 H. Maeda, S. Furuyoshi, Y. Nakatsuji and M. Okahara, *Bull. Chem. Soc. Jpn.*, 1983, **56**, 212.

11 E. Z. Lippert, *Z. Naturforsch., Teil. A*, 1955, **10**, 541; N. Mataga, Y. Kaifu and M. Koizumi, *Bull. Chem. Soc. Jpn.*, 1956, **29**, 465.

12 D. Rehm and A. Weller, *Ber. Bunsenges. Phys. Chem.*, 1969, **73**, 834.

13 J. Mortensen and J. Heinze, *Angew. Chem., Int. Ed. Engl.*, 1984, **23**, 84.

14 J. Bourson, J. Pouget and B. Valeur, *J. Phys. Chem.*, 1993, **97**, 4552.

15 (*a*) When complexed with calcium the very efficient photoconversion of the *meta* isomer **P3** to carbazole derivatives precludes an accurate measurement of K_s. This photoreaction parallels the well-studied photocyclization of Ph_2NMe to *N*-methylcarbazole [ref. 15(*b*)]; (*b*) K. H. Grellmann, W. Kühnle, H. Weller and T. Wolff, *J. Am. Chem. Soc.*, 1981, **103**, 6889.

16 (*a*) B. Waug and M. R. Wasielewski, *J. Am. Chem. Soc.*, 1997, **119**, 12; (*b*) Q. Zhai and T. M. Swager, *J. Am. Chem. Soc.*, 1995, **117**, 12 593.

Communication a908393f