A polyamidoamine dendrimer with peripheral 1,8-naphthalimide groups capable of acting as a PET fluorescent sensor for metal cations

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Received (in Montpellier, France) 15th May 2002, Accepted 18th October 2002
First published as an Advance Article on the web 8th January 2003

The effect of some metal ions (Fe^{2+}, Ni^{2+}, Zn^{2+}, Pb^{2+}) upon the fluorescent intensity of a first generation polyamidoamine dendrimer with a peripheral 4-dimethylaminoethylamine-1,8-naphthalimide group was investigated. The presence of metal ions was found to evoke a photoinduced electron transfer leading to an enhancement in the fluorescence. The results obtained reveal the capacities of these systems to act as sensitive detectors of environment pollution by metal ions. The metal ions inhibit the photodegradation of the dendrimer molecule which exhibits PET properties.

Introduction

Dendrimers are monodisperse, hyperbranched and well defined, three-dimensional polymers possessing a very high concentration of surface functional groups. At present the interest in dendrimer chemistry has been increasing intensively. The study of these branched molecules extends to all areas including synthesis, characterization and potential applications.[1–4] Bonding a dye into the dendrimer structure gives it new properties and new areas of applications.[5] Dendrimers with electroactive groups have found applications as components in different sensors and electroluminescent devices. On the other hand the introduction of different types of chromophores in dendrimer macromolecules makes these macromolecules photoactive with potential applications in photochemical molecular devices.[6–10] Some of these compounds have also been investigated for use as biosensors.[11,12]

It is well known that polyamidoamines (PAMAMs) form a novel class of industrial dendrimers which possess a definite molecular composition with different terminal functional groups.[1–4] The design and modification of the PAMAM dendrimers with fluorescent units could give new and interesting properties.

Photoinduced electron transfer (PET) fluorescent sensors are of great interest and promise because of their various applications.[13] The designs of multi-component PET fluorescence sensors are chosen so that the electron transfer between the fluorophore as signaling unit and the receptor results in "switching off" of the fluorescence intensity. The presence in the system of guests (metal ions or proton) capable of binding with the lone pair electrons of the receptor, causes the PET interaction to be cut off and the fluorescence of the system is "switched on".

In this paper we investigated the influence of different transition metal ions on the fluorescence intensity of a first generation PAMAM dendrimer with peripheral 4-dimethylaminoethylamine-1,8-naphthalimide with the capacities of PET sensors for transition metal ions. 4-Dimethylaminoethylamine-1,8-naphthalimide was chosen as the fluorophore component in the dendrimer molecules in view of earlier investigations into its possible use in monomeric PET sensors for protons and transition metal ions.[14–16]

Experimental

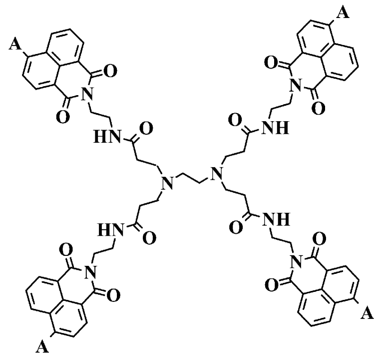
The polyamidoamine (PAMAM) modified dendrimer under study was prepared recently.[17] UV-Vis spectrophotometric investigations of the dendrimer were performed on a UVIKON 930 spectrophotometer (KONTRON instruments). The fluorescence spectra were taken on a SFM 25 spectrophotometer (KONTRON instruments). The fluorescence quantum yield of the dendrimer was determined on the basis of the absorption and fluorescence spectra of the dendrimer solubilized in *N*,*N*-dimethylformamide (DMF) and Rhodamine 6G was used as reference ($\Phi o = 0.88^{18}$). For both absorption and fluorescence measurements, 10^{-6} M of the dendrimer in DMF was used as both dendrimer and metal salts are well soluble in DMF. For all fluorescent measurements, solutions were excited at the absorption maximum of the dendrimer.

A solar simulator (Suntest CPS+, HERAEUS), equipped with a 1.5 kW xenon arc lamp, protected with an adequate filter to simulate the solar spectrum between 290 nm and 800 nm, was used and the experiments were carried out in ordinary atmosphere at 20 °C.

Results and discussion

The PAMAM dendrimer modified with 4-dimethylaminoethylamine-1,8-naphthalimide has the following structure (Scheme 1).

It is seen that the fluorophore naphthalimide fragment is covalently bonded to the dendrimer molecule. The substituent **A** in position C-4 of the 1,8-naphthalimide structure is a



where **A** represent $NHCH_2CH_2N(CH_3)_2$

Scheme 1

dimethylaminoethylamine residue ($–NHCH_2CH_2N(CH_3)_2$) with which metal ions can react (receptor). The whole structure gives the possibility of obtaining a coloured and fluorescent dendrimer, having properties including PET, intense yellow-green fluorescence and photostability.

The functional properties of the dendrimer have been investigated with regard to its application as a PET sensor for metal cations. Table 1 presents the basic photophysical characteristics obtained in DMF solution: absorption (λ_A) and fluorescence (λ_F) maxima, Stokes shift ($\nu_A - \nu_F$), and quantum yield of fluorescence (Φ_F).

In DMF solution the dendrimer exhibits a yellow-green colour with the absorption maximum at $\lambda_A = 428$ nm. The corresponding fluorescence maximum is $\lambda_F = 522$ nm. The ability of the molecule to emit the absorbed light energy is characterized quantitatively by the quantum fluorescence yield Φ_F. The quantum yield of the dendrimer Φ_F is determined on the basis of its absorption and fluorescence spectra. As can be seen from the data in Table 1, the dendrimer has a quantum yield value $\Phi_F = 0.11$.

The change of the fluorescence intensity induced by metal ions has been investigated and the respective fluorescence responses of the dendrimer chromophore are presented in Figs. 1–4. As it can be seen the addition of metal ions leads to an increase of the fluorescence intensity of the dendrimer system different for each metal ions. For example for Fe^{2+} and Ni^{2+}, a plateau is reach for 1.10^{-4} M and 2.10^{-4} M, while for two others (Zn^{2+} and Pb^{2+}) a steady increase occurs. On the other hand then no change of the absorption maxima in comparison with the dendrimer free from the metal ions has been observed. The fluorescence emission increases after the addition of metal ions into the dendrimer solution up to one concentration different for the different metal sales. Above this concentration the fluorescence intensity decreases due to the increasing of quenching from high concentration of transition metal ion.

The 1,8-naphthalimide core is subjected to PET from the atoms comprising the central amino groups of the PAMAM structure and to another PET from the terminal amino groups of the dialkylamino moieties. In this case the latter PET is a major factor.[17] In fact the metal cations interact with the dimethylamino groups from the 1,8-naphthalimide chromophoric system.[19] The central dendrimer part[20,21] also becomes involved in the reactions with the metal ions. Obviously, the fluorescence intensity is much more affected by the formation of a complex between the metal ions and the dialkylamino moieties from the 1,8-naphthalimide structure. Moreover, the formation of this complex causes a change in the polarization

Table 1 Photophysical characteristics of dendrimer in DMF in the presence of metal ions (see text)

Metal ion	λ_A/ nm	λ_F/ nm	$\nu_A - \nu_F$/ cm^{-1}	$\Delta\lambda_F$/ nm	FE	Φ_F	E_F
Zn^{2+}	428	496, 519	4096	3	4.51	0.58	0.48
Ni^{2+}	428	496, 517	4022	5	5.51	0.64	0.53
Fe^{2+}	428	496, 518	4059	5	10.81	0.69	0.57
Pb^{2+}	428	496, 516	3984	6	3.42	0.49	0.41
—	428	522	4207	—	—	0.11	0.09

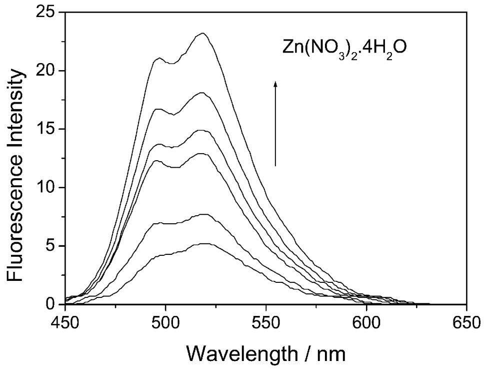


Fig. 1 Fluorescence spectra of dendrimer in *N*,*N*-dimethylformamide at various concentrations of Zn^{2+} ions. The concentrations of Zn^{2+} ions are, in order of increasing intensity, from 0 to 8×10^{-3} M. The concentration of dendrimer is 1×10^{-6} M.

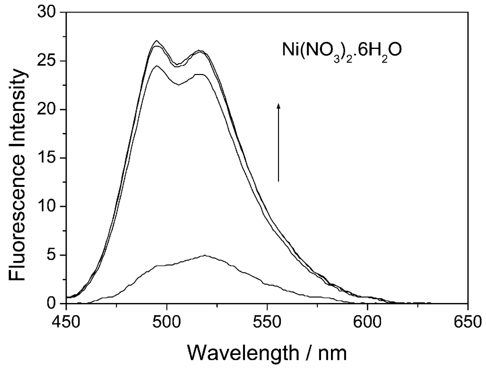


Fig. 2 Fluorescence spectra of dendrimer in *N*,*N*-dimethylformamide at various concentrations of Ni^{2+} ions. The concentrations of Ni^{2+} ions are, in order of increasing intensity, from 0 to 2×10^{-4} M. The concentration of dendrimer is 1×10^{-6} M.

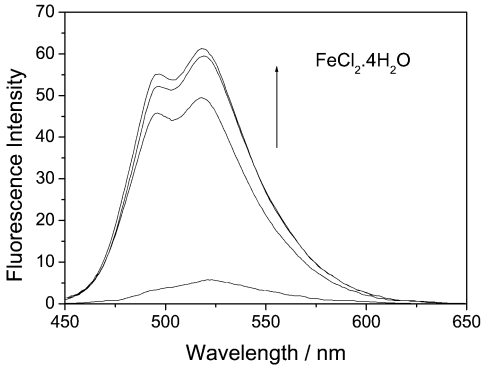


Fig. 3 Fluorescence spectra of dendrimer in *N*,*N*-dimethylformamide at various concentrations of Fe^{2+} ions. The concentrations of Fe^{2+} ions are, in order of increasing intensity, from 0 to 1×10^{-4} M. The concentration of dendrimer is 1×10^{-6} M.

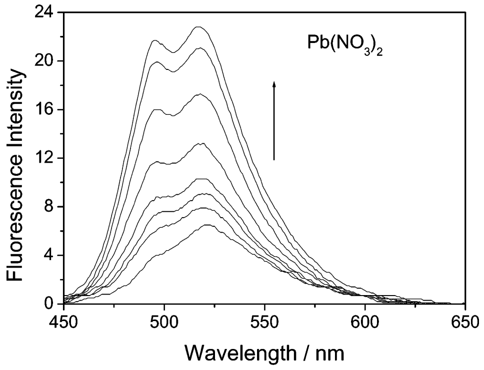


Fig. 4 Fluorescence spectra of dendrimer in *N*,*N*-dimethylformamide at various concentrations of Pb^{2+} ions. The concentrations of Pb^{2+} ions are, in order of increasing intensity, from 0 to 5×10^{-3} M. The concentration of dendrimer is 1×10^{-6} M.

of the chromophoric system greater than that evoked by complex formation in the central part of the dendrimer.

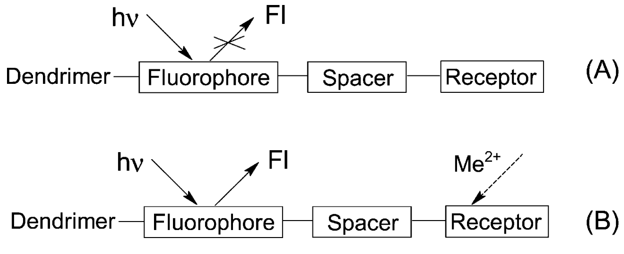
Scheme 2 presents an illustrative model of the "Fluorophore–Spacer–Receptor" supramolecular system under study for metal ions as guest and modified PAMAM dendrimer with 1,8-naphthalimide as host.

The interaction between the fluorophore (1,8-naphthalimide) and the receptor (dimethylamino group) provoking photoinduced electron transfer leads to quenching of the fluorescence emission, Scheme 2 (A). The presence of the transition metal ions in the dendrimer solution changes its properties since in this case the system fluoresces intensely, Scheme 2 (B).

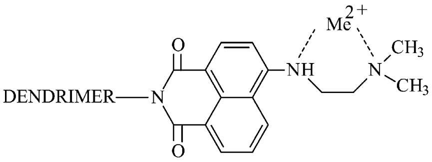
The presence of the guest metal ions is signalled by fluorescence enhancement (FE). The metal ions induce a hypsochromic shift of the fluorescence maximum ($\Delta\lambda_F = 3$–6 nm). On the other hand all metal ions under study induce a second maximum which is hypsochromically shifted ($\Delta\lambda_F = 26$ nm), indicative also of the interaction between the dendrimer and metal ions in the excited state. The hypsochromic shift and the second fluorescent maximum in this case can be explained by the formation of a coordination interaction between the nitrogen atom at the C-4 position of the naphthalene ring, the nitrogen atom and the metal ions from the dimethylamino group, as can be seen in Scheme 3.

In Fig. 5 is presented the dependence of FE on the nature of the metal ions. The FE was determined from the ratio of maximum fluorescence intensity (after metal ion addition) and minimum fluorescence intensity (in the absence of metal ions). The highest FE value was observed in the presence of Fe^{2+} ions. In this case only small amounts of Fe^{2+} ions are required to enhance the fluorescence intensity (Fig. 3). Similar behaviour was found for Ni^{2+} ions (Fig. 2). In contrast to this in the other two cases the fluorescence intensity increase regularly with the increases of the concentration of the Zn^{2+} and Pb^{2+} ions (Figs. 1 and 4). These results are similar to those found for the fluorescence quantum yields. As can be seen from Table 1 the fluorescence quantum yields are considerably higher in the presence of the metal ions, in the order:

$$Fe^{2+} > Ni^{2+} > Zn^{2+} > Pb^{2+}$$



Scheme 2



Scheme 3

Besides Φ_F, the energy yield of fluorescence, E_F, can also be used:[22]

$$E_F = \Phi_F \lambda_A / \lambda_F \qquad (1)$$

The respective results from E_F were 0.41–0.57 for the systems containing the dendrimer with metal ions and 0.09 for the dendrimer alone.

The Stokes shift is a parameter which indicates the difference in the properties and structure of the fluorescent compounds between the ground S_0 state and the first exited S_1state. The Stokes shift is given by eqn. 2.

$$\nu_A - \nu_F = (1/\lambda_A - 1/\lambda_F) \times 10^7 \qquad (2)$$

The Stokes shifts of the dendrimer systems with guest metal ions were calculated using the long wavelength maximum and is in the region 3984–4096 cm^{-1}, lower than those obtained for the dendrimer alone. This means that in the presence of the metal ions the conformation change of the dendrimer systems is less pronounced.

With regard for the practical application of the fluorescent PET system it is worth studying its photostability. Fig. 6 shows the kinetics of photodegradation of the dendrimer in *N*,*N*-dimethylformamide solution. It has been found that the photodegradation of the dendrimer follows a pseudo-first order reaction. In Table 2 are listed the calculated rate constants K_p of the dendrimer photodegradation. As can be seen, the degradation is higher when the dendrimer is used alone. It should be noted that all of the metal ions studied have a photostabilizing effect. Fe^{2+} and Ni^{2+} ions provide the best photostability. That observed in the presence of Pb^{2+} ions is much lower than those in the other cases. The photostabilizing effect is due probably to the increase of the fluorescence intensity in the presence of metal ions and re-emission of the absorbed UV light as long wavelength visible light. As a result the degrading effect of high energy UV light upon the dendrimer molecule is reduced. On the other hand, the reduced photodegradation

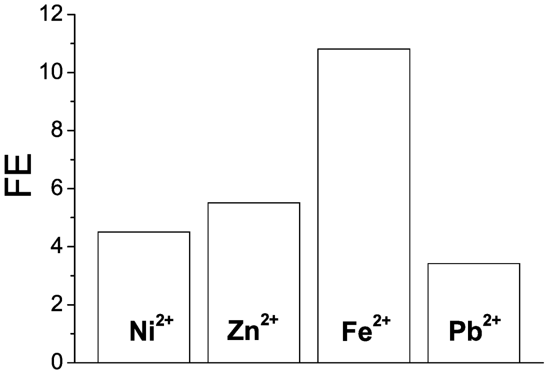


Fig. 5 Fluorescence enhancement (FE) of dendrimer in the presence of different metal ions in *N*,*N*-dimethylformamide solution.

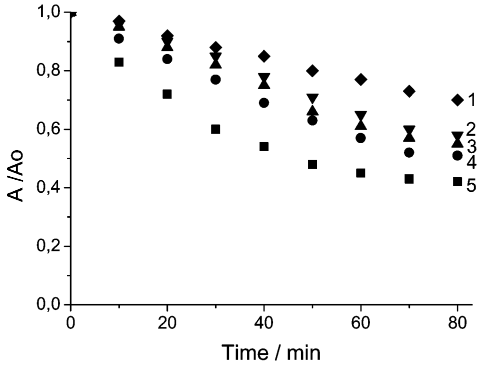


Fig. 6 Photodegradation of PAMAM dendrimer in the presence of: (1) Fe^{2+} ($c = 1 \times 10^{-4}$ M), (2) Ni^{2+} ($c = 2 \times 10^{-4}$ M), (3) Zn^{2+} ($c = 8 \times 10^{-3}$ M), (4) Pb^{2+} ($c = 5 \times 10^{-3}$ M), and (5) with no metal ions. The concentration of dendrimer is 1×10^{-6} M.

Table 2 Rate constants K_p of photodestruction of dendrimer and dendrimer/metal ion systems in *N*,*N*-dimethylformamide solution

System	K_p/s^{-1}
Dendrimer + Zn^{2+}	1.03×10^{-4}
Dendrimer + Ni^{2+}	0.38×10^{-4}
Dendrimer + Fe^{2+}	0.36×10^{-4}
Dendrimer + Pb^{2+}	1.83×10^{-4}
Dendrimer	5.26×10^{-4}

might be due to the fact that the presence of metal ions eliminates the possibility for photoinduced electron transfer which leads to amine oxidation.

Conclusions

In this paper we have presented the results of a PET photophysical investigation of one polyamidoamine dendrimer with peripheral 4-dimethylaminoethylamine-1,8-naphthalimide. We have shown that in the presence of metal ions (Fe^{2+}, Ni^{2+}, Zn^{2+}, Pb^{2+}) the fluorescence intensity of the dendrimer molecule is higher. After these metal ions bind strongly with the receptor, the fluorophore can give rise to good fluorescence enhancement in the dendrimer system. It was shown that the fluorescence intensity depends on the nature of the metal ions. The metal ions have a photostabilizing effect on the dendrimer molecule. On the basis of the present investigation it can be assumed that the new dendrimer investigated is suitable for use as a fluorescent sensor of metal ions.

Acknowledgements

Dr. Ivo Grabchev acknowledges the grant from the NATO science program for the fellowship research stay at the Claude Bernard University - Lyon 1, France.

References

1 M. Fischer and F. Vögtle, *Angew. Chem., Int. Ed.*, 1999, **38**, 884.
2 K. Unoue, *Prog. Polym. Sci.*, 2000, **25**, 453.
3 F. Vögtle, S. Gesterman, R. Hasse, H. Schwierz and B. Windisch, *Prog. Polym. Sci.*, 2000, **25**, 987.
4 A. W. Bosman, H. M. Janssen and E. W. Meijer, *Chem. Rev.*, 1999, **99**, 1665.
5 P. Froehling, *Dyes Pigments*, 2001, **48**, 187.
6 T. Weil, U. M. Wiesler, A. Herrmann, R. Bauer, J. Hofkens, F. C. De Schryver and K. Müllen, *J. Am. Chem. Soc.*, 2001, **123**, 8101.
7 (*a*) S. Gilat, A. Adronov and J. Fréchet, *J. Org. Chem.*, 1999, **64**, 7474; (*b*) S. Gilat, A. Adronov and J. Fréchet, *Angew. Chem., Int. Ed.*, 1999, **38**, 1422; (*c*) A. Adronov and J. Fréchet, *Chem. Commun.*, 2000, 1701.
8 D. M. Jingle and D. V. McGrath, *J. Am. Chem. Soc.*, 1999, **121**, 4912.
9 S. Fomie, E. Rivera, L. Fomina, A. Ortiz and T. Ogawa, *Polymer*, 1998, **39**, 3551.
10 (*a*) F. Vögtle, M. Gorka, R. Hesse, P. Ceroni, M. Maestri and V. Balzani, *Photochem. Photobiol. Sci.*, 2002, **1**, 76; (*b*) V. Balzani, P. Ceroni, S. Gestermann,Gorka and F. Vögtle, *Chem. Commun.*, 2000, 853; (*c*) V. Balzani, P. Ceroni, S. Gestermann, M. Gorka and F. Vögtle, *J. Chem. Soc., Dalton Trans.*, 2000, 765.
11 J. Wang and M. Jiang, *J. Am. Chem. Soc.*, 1998, **120**, 8281.
12 A.-C. Chang, J. Gillespie and M. Tabacco, *Anal. Chem.*, 2001, **73**, 467.
13 (*a*) A. P. de Silva, H. Q. N. Gunatatne, T. Gunnlauggson, A. J. M. Huxley, C. P. McCoy, J. T. Radmancher and T. E. Rice, *Chem. Rev.*, 1997, **97**, 1515; (*b*) K. Rurack, *Spectrochim. Acta, Part A*, 2001, **57**, 2161; (*c*) K. Rurack and U. Resch-Gender, *Chem. Soc. Rev.*, 2002, **31**, 116.
14 A. P. de Silva, H. Q. N. Gunaratne, J.-L. Habib-Jiwan, C. P. McCoy, T. E. Rice and J.-P. Soumillion, *Angew. Chem.*, 1995, **34**, 1728.
15 K. Mitchel, R. Brown, D. Yuan, S.-C. Chang, R. Utecht and D. Lewis, *J. Photochem. Photobiol. A: Chem.*, 1998, **115**, 157.
16 L. Daffy, A. de Silva, H. Q. Nimal Gunaratne, Ch. Hunder, P. L. Mark Lunch, T. Werner and O. Wolfbeis, *Chem. Eur. J.*, 1998, **4**, 1810.
17 I. Grabchev, X. Qian, V. Bojinov, Y. Xiao and W. Zhang, *Polymer*, 2002, **43**, 5731.
18 I. Olmstedt, *J. Phys. Chem.*, 1979, **83**, 2581.
19 I. Grabchev, X. Qian, Y. Xiao and R. Zhang, *New J. Chem.*, 2002, **26**, 920.
20 M. Diallo, L. Balogh, A. Shafgati, J. Jonson, W. Goddard and D. Tomalia, *Environ. Sci. Technol.*, 1999, **33**, 820.
21 R. Crooks, M. Zhao, L. Sun, V. Chechik and L. Yeung, *Acc. Chem. Res.*, 2001, **34**, 181.
22 A. Terenin, *Photonics of Dyes and Related Organic Compounds*, Science, Leningrad, Russia, 1967.