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

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Abstract

The effect of the rare earth ions (Er^{3+}, Eu^{3+}, Gd^{3+}, Nd^{3+}, Tb^{3+}, Yb^{3+}) upon the fluorescent intensity of a third generation polyamidoamine (PAMAM) dendrimer with a peripheral 1,8-naphthalimide group was investigated. The presence of the rare earth ions were 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 the rare earth ions.

Keywords: Naphthalimide; Fluorescence enhancement; The rare earth ions

1. 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 rare earth ions on the fluorescence intensity of a third generation PAMAM dendrimer with peripheral 1,8-naphthalimide with the capacities of PET sensors for the rare earth ions. 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].

2. Experimental

The polyamidoamine modified dendrimer under study was prepared recently [17]. UV–vis spectrophotometric investigations of the dendrimer were performed on a UV 8500 spectrophotometer (TECHCOMP instruments). The fluorescence spectra were taken on a Cray-E fluorescence spectrophotometer (Varian instruments). The fluorescence quantum yield of

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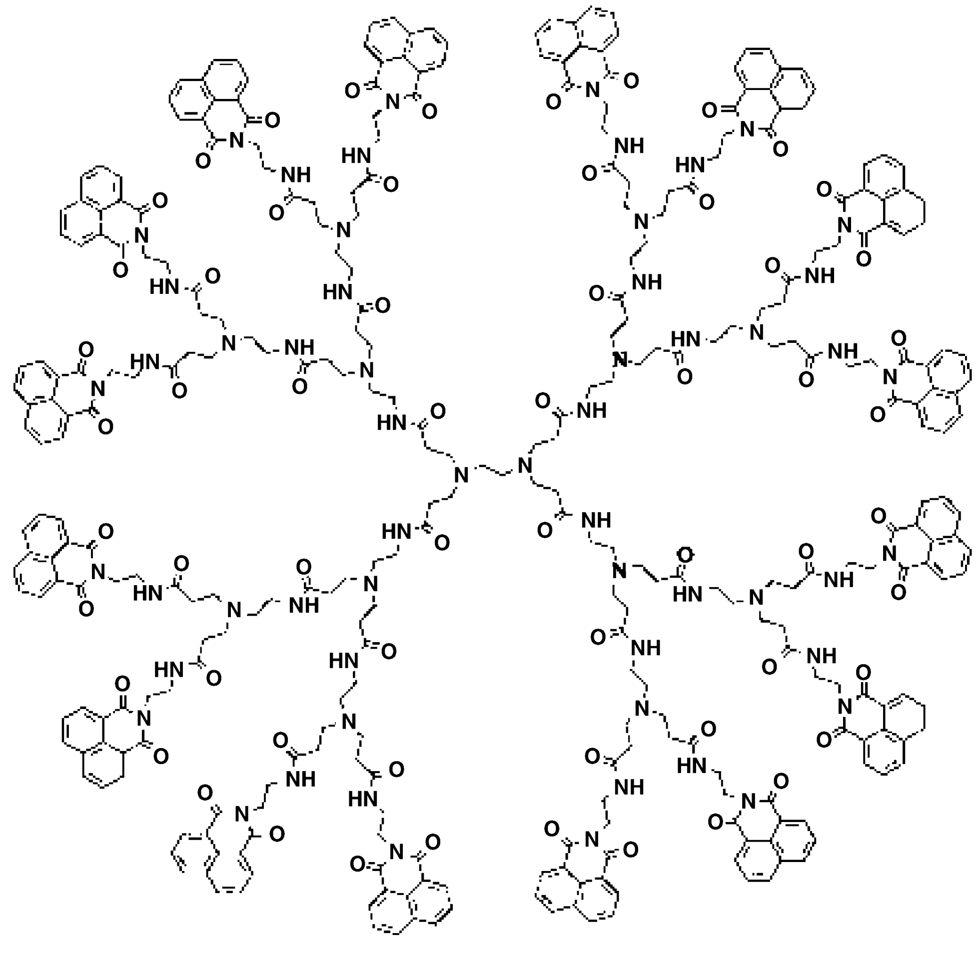


Scheme 1. Dendrimer (D).

the dendrimer was determined on the basis of the absorption and fluorescence spectra of the dendrimer solubilized in chloroform/ethanol (1:1, v/v) and quinine sulfate was used as reference ($\phi_0 = 0.546$ [18]). For both absorption and fluorescence measurements, 10^{-6} M of the dendrimer in chloroform/ethanol (1:1, v/v) was used as both dendrimer and metal salts are well soluble in chloroform/ethanol (1:1, v/v). For all fluorescent measurements, solutions were excited at the excitation maximum of the dendrimer.

3. Results and discussion

The PAMAM dendrimer modified with 1,8-naphthalimide (D) has the following structure (Scheme 1). It is seen that the fluorophore naphthalimide fragment is covalently bonded to the dendrimer molecule. The internal amido groups of PAMAM can become in the reactions with the rare earth ions (receptor). The whole structure gives the possibility of obtaining a coloured and fluorescent dendrimer, having properties including PET and intense fluorescence.

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

In chloroform/ethanol solution the dendrimer in the visible region exhibits a absorption maximum at $\lambda_A = 338$ nm with high extinction coefficient ($\varepsilon = 390544\ \mathrm{mol^{-1}\,l\,cm^{-1}}$), corresponding to a $S_0 \rightarrow S_1$ (π, π^*). Although in the presence of the rare earth ions the peak from the absorption maximum of dendrimer keeps no change, intense of absorption appear apparently decrease, as been shown in Fig. 1. As it can be seen in Fig. 2 the fluorescence excitation spectra of dendrimer dose not reveal significant changes in the excitation maximum (approximately 357 nm) of dendrimer in the presence of the rare earth ions, but the intensity of fluorescence excitation spectra has been found it

Table 1

Photophysical characteristics of dendrimer in chloroform/ethanol (1:1, v/v) in the presence of the rare earth cations (see text)

Metal ion	λ_A (nm)	λ_F (nm)		$\nu_A - \nu_F$ (cm^{-1})	FE	ϕ_F
–	338	384	478	8665	–	0.047
Er^{3+}	338	385	477	8621	2.69	0.099
Eu^{3+}	338	384	479	8709	2.24	0.099
Gd^{3+}	338	384	479	8709	2.47	0.095
Nd^{3+}	338	383	478	8665	1.91	0.063
Tb^{3+}	338	385	478	8665	2.37	0.107
Yb^{3+}	338	386	479	8709	3.09	0.111

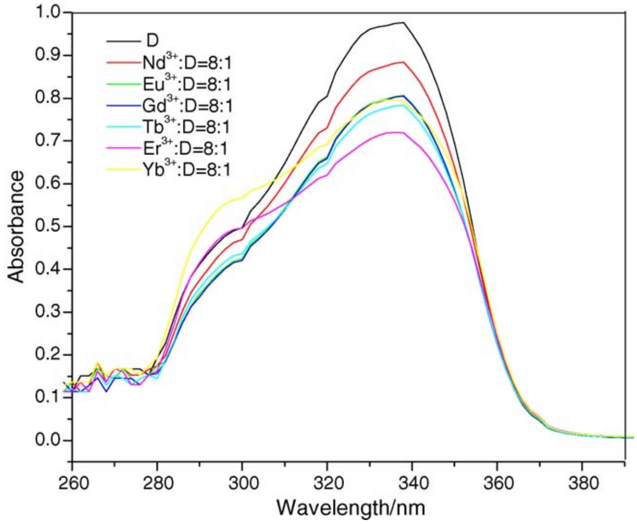


Fig. 1. Changes in the absorption spectra of dendrimer upon titration of a 5.00×10^{-6} M solution of dendrimer in 1:1 chloroform/ethanol solution with the rare earth ions. All the rates of the rare earth ions: dendrimer is 8:1.

obviously increase. The corresponding fluorescence maximum is $\lambda_F = 478$ nm. The ability of the molecule to emit the absorbed light energy is characterized quantitatively by the quantum fluorescence yield ϕ_F. As can be seen from the data in Table 1, the dendrimer has a quantum yield value $\phi_F = 0.047$.

The change of the fluorescence intensity induced by the rare earth metal ions has been investigated and the respective fluorescence responses of the dendrimer chromophore are presented in Figs. 3–9. In the presence of the rare earth ions the peak of the emission maximum of dendrimer has been found no change. As it can be seen in Fig. 9, the addition of the rare earth metal ions leads to an increase of the fluorescence intensity of the dendrimer system different for each the rare earth metal ions in the emission maximum (approximately 478 nm). For example, the dendrimer concentration in chloroform/ethanol solution is 5.00×10^{-6} M, for Er^{3+}, Eu^{3+}, Gd^{3+}, Nd^{3+}, Tb^{3+}, and Yb^{3+}, a plateau is reached for 1.60×10^{-4}, 8.00×10^{-5}, 1.28×10^{-3}, 4.00×10^{-5}, 1.60×10^{-4}, and 6.40×10^{-4} M, respectively. While for Er^{3+} and Gd^{3+}, continuously increases (above 1.60×10^{-4}, 1.28×10^{-3} M, respectively) concentration, fluorescence intensity decreases due to the increasing of quenching from high concentration of the rare earth ions. For Nd^{3+} and Eu^{3+} (above 4.00×10^{-5}, 8.00×10^{-5} M, respectively), continuously increases concentration, fluorescence intensity decreases, but when the concentration go up to 3.2×10^{-4} M, fluorescence intensity keep also a plateau. For Tb^{3+}, when the concentration rise from 1.60×10^{-4} to 9.60×10^{-4} M, fluorescence intensity decreases, while continuously increases Tb^{3+} concentration, flu-

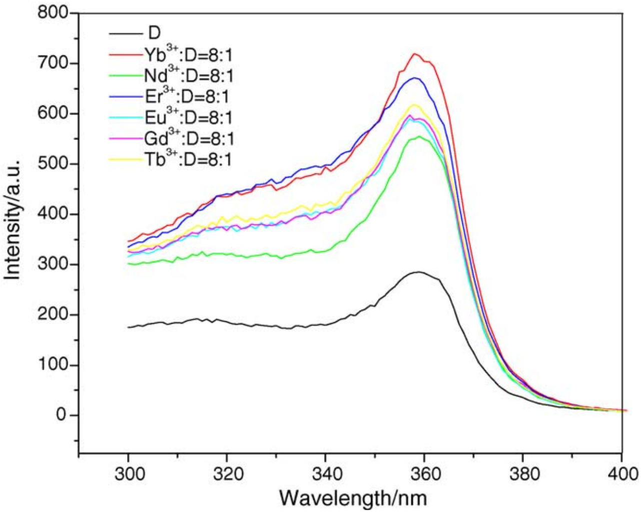


Fig. 2. Changes in the fluorescence excitation spectra of dendrimer upon titration of a 5.00×10^{-6} M solution of dendrimer in 1:1 chloroform/ethanol solution with the rare earth ions. All the rates of the rare earth ions: dendrimer is 8:1. $\lambda_{em} = 478$ nm.

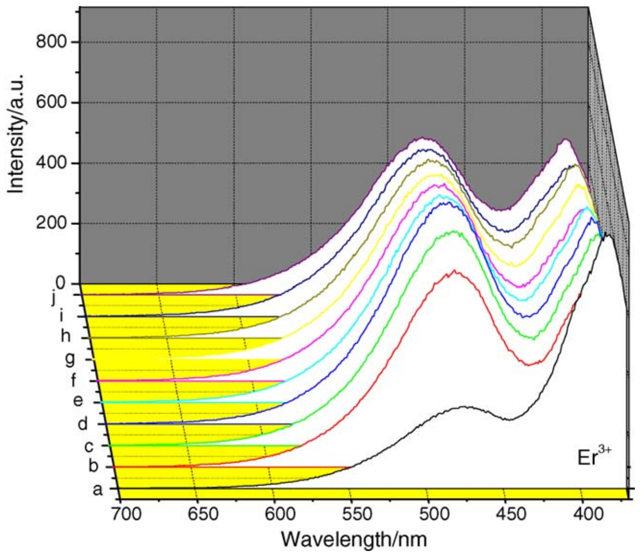


Fig. 3. Changes in the fluorescence emission spectra of dendrimer upon titration of a 5.00×10^{-6} M solution of dendrimer in 1:1 chloroform/ethanol solution with Er^{3+} ions. $\lambda_{ex} = 357$ nm.The rates of concentrations for Er^{3+}: dendrimer are (a) 0:1; (b) 8:1; (c)16:1; (d) 32:1; (e) 64:1; (f) 128:1; (g) 160:1; (h) 192:1; (i) 256:1 and (j) 320:1.

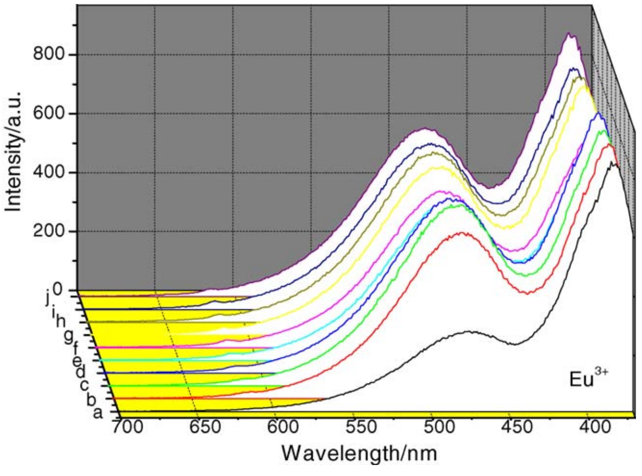


Fig. 4. Changes in the fluorescence emission spectra of dendrimer upon titration of a 5.00×10^{-6} M solution of dendrimer in 1:1 chloroform/ethanol solution with Eu^{3+} ions. $\lambda_{ex} = 357$ nm. The rate of concentrations for Eu^{3+}: dendrimer is (a) 0:1; (b) 8:1; (c) 16:1; (d) 32:1; (e) 64:1; (f) 128:1; (g) 160:1; (h) 192:1; (i) 256:1 and (j) 320:1.

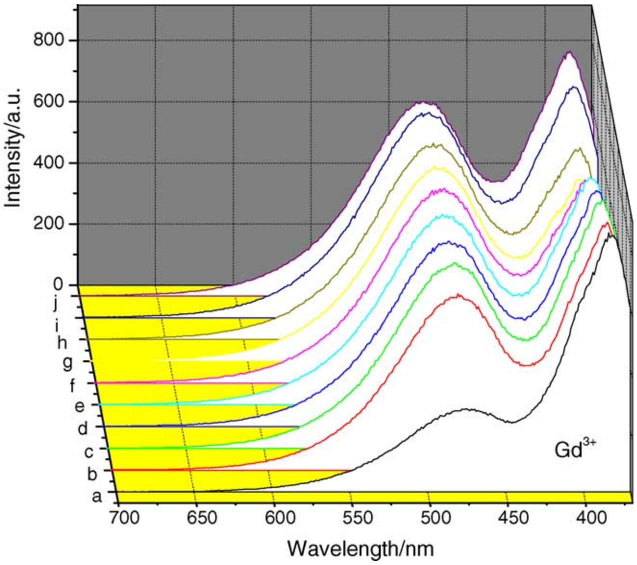


Fig. 5. Changes in the fluorescence emission spectra of dendrimer upon titration of a 5.00×10^{-6} M solution of dendrimer in 1:1 chloroform/ethanol solution with Gd^{3+} ions. $\lambda_{ex} = 357$ nm.The rate of concentrations for Gd^{3+}: dendrimer is (a) 0:1; (b) 8:1; (c)16:1; (d) 32:1; (e) 64:1; (f) 128:1; (g) 160:1; (h) 192:1; (i) 256:1 and (j) 320:1.

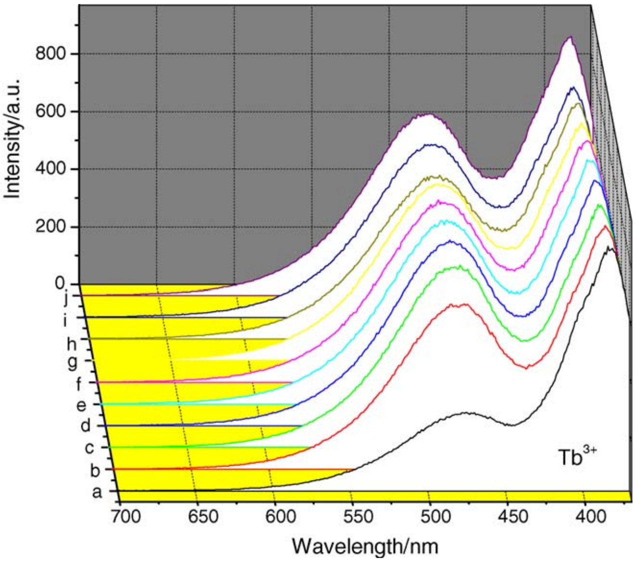


Fig. 7. Changes in the fluorescence emission spectra of dendrimer upon titration of a 5.00×10^{-6} M solution of dendrimer in 1:1 chloroform/ethanol solution with Tb^{3+} ions. $\lambda_{ex} = 357$ nm.The rate of concentrations for Tb^{3+}: dendrimer is (a) 0:1; (b) 8:1; (c) 16:1; (d) 32:1; (e) 64:1; (f) 128:1; (g) 160:1; (h) 192:1; (i) 256:1 and (j) 320:1.

orescence intensity steadily increases. For Yb^{3+}, continuously increases (above 8.00×10^{-4} M) concentration, fluorescence intensity continuously keeps no change.

The 1,8-naphthalimide core is subjected to PET from the atoms comprising the central amino groups of the PAMAM structure. The central dendrimer part [19,20] also becomes involved in the reactions with the metal ions. Obviously, the fluorescence intensity is affected by the formation of a complex between the rare earth metal ions and internal amido groups of PAMAM from dendrimer. Moreover, the formation of this complex causes a change in the polarization of the chromophoric system that evoked by complex formation in the central part of the dendrimer.

Scheme 2 presents an illustrative model of the “Fluorophore – spaced – Receptor” supramolecular system under study for the rare earth metal ions as guest and modified PAMAM dendrimer with 1,8-naphthalimide groups as host. The interaction between the fluorophore (1,8-naphthalimide) and the receptor (internal amido groups of PAMAM) provoking photoinduced electron transfer leads to quenching of the fluorescence emission. The presence of the rare earth metal ions in the dendrimer solution changes its properties since in this case the system fluoresces intensely.

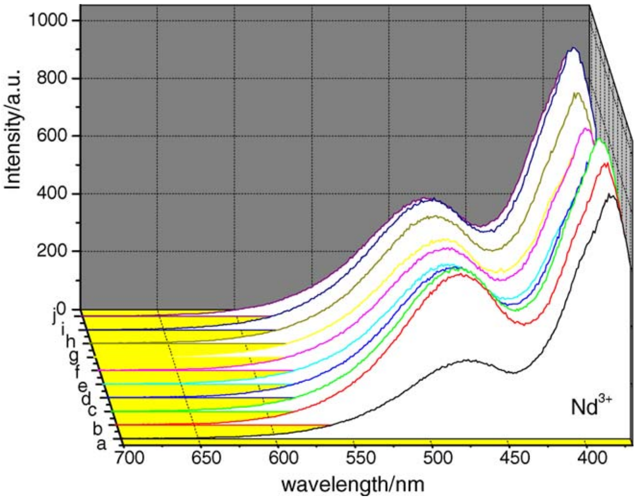


Fig. 6. Changes in the fluorescence emission spectra of dendrimer upon titration of a 5.00×10^{-6} M solution of dendrimer in 1:1 chloroform/ethanol solution with Nd^{3+} ions. $\lambda_{ex} = 357$ nm.The rate of concentrations for Nd^{3+}: dendrimer is (a) 0:1; (b) 8:1; (c)16:1; (d) 32:1; (e) 64:1; (f) 128:1; (g) 160:1; (h) 192:1; (i) 256:1 and (j) 320:1.

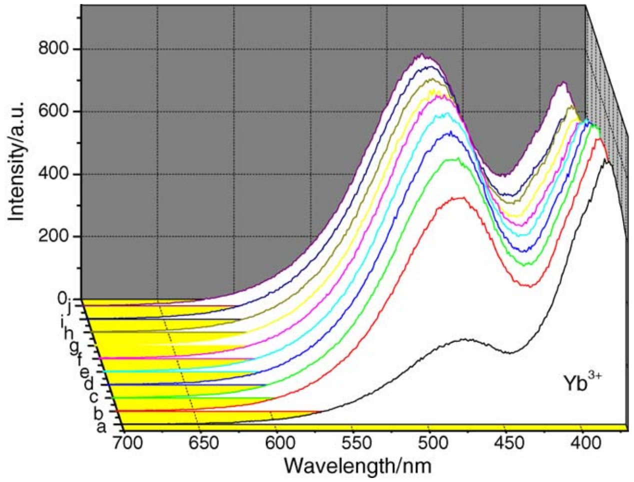


Fig. 8. Changes in the fluorescence emission spectra of dendrimer upon titration of a 5.00×10^{-6} M solution of dendrimer in 1:1 chloroform/ethanol solution with Yb^{3+} ions. $\lambda_{ex} = 357$ nm.The rate of concentrations for Yb^{3+}: dendrimer is (a) 0:1; (b) 8:1; (c) 16:1; (d) 32:1; (e) 64:1; (f) 128:1; (g) 160:1; (h) 192:1; (i) 256:1 and (j) 320:1.

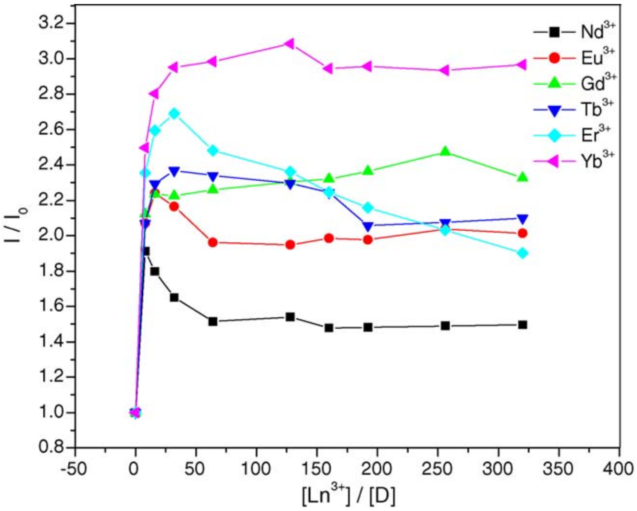
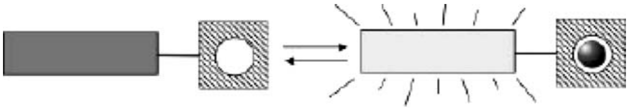


Fig. 9. Changes in the dendrimer fluorescence intensity at 478 nm upon titration of a 5.0×10^{-6} M solution of dendrimer in 1:1 chloroform/ethanol solution with the metal ions. $\lambda_{exc} = 357$ nm.



Scheme 2.

In Fig. 10 is presented the dependence of fluorescence enhancement (FE) on the nature of the rare earth 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 Yb^{3+} ions. In this case only small amounts of Yb^{3+} ions are required to enhance the fluorescence intensity (Fig. 8). Similar behaviour were found for the other ions (Figs. 3–7). The order is $Yb^{3+} > Er^{3+} > Gd^{3+} > Tb^{3+} > Eu^{3+} > Nd^{3+}$. These results are different from 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: $Yb^{3+} > Tb^{3+} > Er^{3+} = Eu^{3+} \approx Gd^{3+} > Nd^{3+}$. The difference from two order result from different the rare earth ions concentration when FE reached maximum fluorescence intensity and absorption and fluorescence spectra, which determined the value of the quantum yield of the dendrimer ϕ_F.

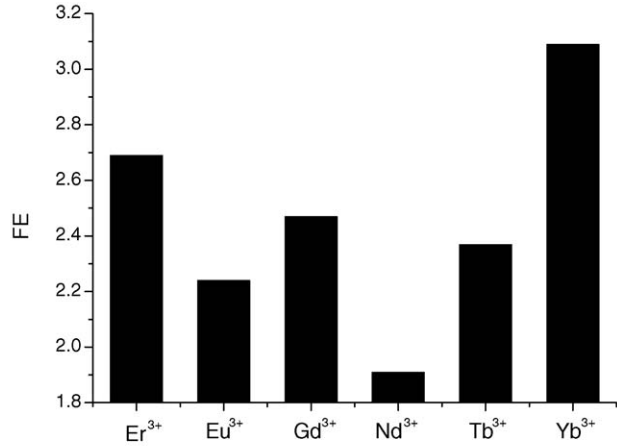


Fig. 10. Fluorescence enhancement (FE) of dendrimer in the presence of different metal ions in chloroform/ethanol (1:1, v/v) solution.

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_1 state. The Stokes shift is given by below equation

$$\nu_A - \nu_F = \left(\frac{l}{\lambda_A} - \frac{l}{\lambda_F}\right) \times 10^7$$

The Stokes shifts of the dendrimer systems with guest metal ions were calculated using the long wavelength maximum and is in the region 8621–8709 cm^{-1} and 8655 cm^{-1} 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.

4. Conclusions

In this paper we have presented the results of a PET photophysical investigation of one polyamidoamine dendrimer with peripheral 1,8-naphthalimide. We have shown that in the presence of metal ions (Er^{3+}, Eu^{3+}, Gd^{3+}, Nd^{3+}, Tb^{3+}, Yb^{3+}) 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.

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