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Green fluorescence poly(amidoamine) dendrimer functionalized with 1,8-naphthalimide units as potential sensor for metal cations

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Abstract

The photophysical characteristics of a fluorescent PAMAM dendrimer from second generation with sixteen 4-*N*,*N*-dimethylaminoethylamino-1,8-naphthalimide units have been studied in organic solvents of different polarity. A positive solvatochromisme and dependence of the fluorescence quantum yield have been observed. The functional characteristics of PAMAM dendrimer in acetonitrile solution in the presence of some metal cations (Zn^{2+}, Ni^{2+}, Pb^{2+}, Mg^{2+}, $Mn^{2+}$and Ag^{+}) have been investigated. An enhancement in the fluorescence intensity has been observed when Zn^{2+}, Ni^{2+}, Pb^{2+} and Mg^{2+} cations are used.

Keywords: Dendrimers; 1,8-Naphthalimides; Sensors; Fluorescence; Photoinduced electron transfer

1. Introduction

The poly(amidoamine) dendrimers (PAMAM) are a novel class of commercial dendrimers which were synthesized and investigated for the first time by Tomalia et al. [1]. PAMAM dendrimers consist of an ethylenediamine core from which polyamidoamine repeating units extend in all directions. The terminal amine groups in their periphery can be substituted with different functional groups. The modification of the PAMAM dendrimers with fluorescent units could give new interesting properties and open prospect for new applications [2–5].

Our investigations on the synthesis and functional properties of some new PAMAM derivatives from zero and second generations decorated with 1,8-naphthalmide units in their periphery have been published recently [6–13]. The fluorescence properties of the novel compounds in the presence of different metal cations show that these dendrimers could act as fluorescent sensors for metal cations and protons [6–11]. The sensoring properties of this fluorescing dendrimer are based on the complexing ability of the PAMAM core. When the dendrimer comprises 1,8-naphthalimide in the periphery having as substituent group like ($-NHCH_2CH_2N(CH_3)_2$) capable of forming a complex with metal cations both effects act in opposite directions. The fluorescence is enhanced when the outer rim receptors host protons or metal cations and this is understood as the inhibition of the photoinduced electron transfer (PET) originating from this part of the molecule [9]. Enhancement or quenching of the fluorescence intensity depending on the PAMAM generation has been observed [9,11].

In this work the study is focused on the photophysical investigation of one fluorescent PAMAM dendrimer of second generation having sixteen 4-*N*,*N*-dimethylaminoethylamino-1,8-napthalimide units in its periphery. The functional properties of the dendrimer have been investigated in organic solvents of different polarity. Its photophysical and supramolecular properties have been also studied in the presence of some metal cations.

2. Experimental part

2.1. Materials and methods

The modified PAMAM dendrimer with 4-*N*,*N*-dimethylaminoethylamino-1,8-napthalimide derivative under study has

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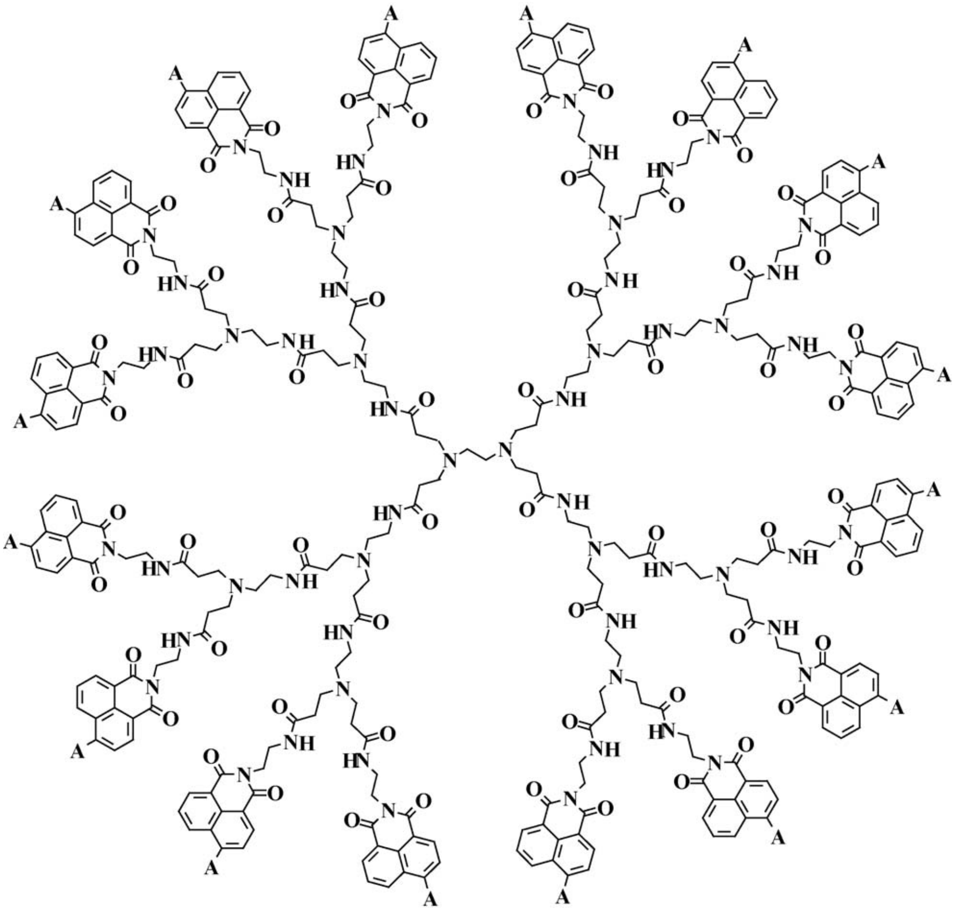


A: $NHCH_2CH_2N(CH_3)_2$

Scheme 1. Chemical structure of the second generation PAMAM dendrimer peripherally modified with sixteen 4-*N*,*N*-dimethylaminoethylamino-1,8-naphthalimide units.

the structure presented in Scheme 1. The synthesis of the dendrimer has been described recently [9].

Organic solvents (methanol, ethanol, butanol, acetonitrile, dichloromethane, chloroform and tetrahydrofuran) used in this study were of spectroscopic grade. The absorption measurements were performed using a UV–vis Double Beam Spectrophotometer Uvikon 930 at concentration 10^{-6} mol l^{-1}. The fluorescence spectra were taken on an FP-6500 Jasco spectrofluorometer at concentration 10^{-6} mol l^{-1}. Fluorescence quantum yield was determined on the basis of the absorption and fluorescence spectra. Fluorescein (Aldrich) was used as a reference ($\Phi_F = 0.86$ [14]).

The effect of the metal cations and protons upon the fluorescence intensity was examined by adding a few microliters of stock solution of the metal cations to a known volume of the dendrimer solution (3 ml). The addition was limited to 0.08 ml, so that dilution remained insignificant [15]. $Zn(NO_3)_2 \cdot 4H_2O$, $Ni(NO_3)_2 \cdot 6H_2O$, $Pb(NO_3)_2$, $Mn(NO_3)_2 \cdot H_2O$, $Mg(NO_3)_2 \cdot 6H_2O$ and $AgNO_3$ were used as sources for metal cations.

3. Results and discussion

3.1. Photophysical characteristics in organic solvents of different polarity

4-Aminosubstituted-1,8-naphthalimide derivatives can be treated as a combination of two sub-systems: viz. a naphthalene ring and a dicarboximide (–CO–NR–CO–) group in a six-membered ring. The polarization of the 1,8-naphthalimide molecule occurs upon irradiation as a result from the electron donor–acceptor interaction between the respective substituents at naphthalene rings and the carbonyl groups from the imide structure of the chromophoric system. On the other hand, the photophysical properties of 1,8-naphthalimides may also depend on the interaction between the carbonyl groups and the substituent at the imide nitrogen atom. Thus the bonding of 1,8-naphthalimides units to the commercial PAMAM dendrimers gives the latter some new interesting photophysical properties.

Table 1 presents the spectral characteristics of the PAMAM dendrimer labeled with 1,8-naphthalimide (Scheme 1) in organic

Table 1
Photophysical characteristics of the dendrimer in different organic solvents

Solvent	λ_A (nm)	λ_F (nm)	ε ($dm^3\,mol^{-1}\,cm^{-1}$)	$\nu_A - \nu_F$ (cm^{-1})	Φ_F	λ_{S_1} (nm)	E_{S_1} ($kJ\,mol^{-1}$)
Methanol	436	544	192000	4553	0.023	486	246.3
Ethanol	435	542	194000	4538	0.030	489	244.8
Butanol	435	541	189000	4504	0.034	490	244.3
Acetonitrile	435	544	198000	4606	0.018	491	243.8
Dichloromethane	434	538	198000	4454	0.640	485	246.8
Chloroform	433	534	197000	4368	0.801	483	247.8
Tetrahydrofuran	431	532	198000	4404	0.820	483	247.8

solvents of different polarity: the absorption (λ_A) and fluorescence (λ_F) maxima, the extinction coefficient ($\log \varepsilon$), Stokes shift ($\nu_A - \nu_F$), quantum yield of fluorescence (Φ_F) and the energy of the first exited state (E_{S_1}).

The empirical parameter of solvent polarity ($E_T(30)$ kcal mol^{-1}) was used to characterized the polarity of the medium [16]. The results summarized in Table 1 show that in all organic solvents the dendrimer absorbs in the visible region at $\lambda_A = 431$–436 nm. In the visible region at λ_A maximum the molar extinction coefficients of the dendrimer are high ($\varepsilon = 189\,000$–$198\,000\ dm^3\,mol^{-1}\,cm^{-1}$), indicating that the long wavelength band in the absorption spectra (in the visible region) is a band of charge transfer, due to $n \rightarrow \pi^*$ electron transfer at $S_0 \rightarrow S_1$ transition. In all organic solvents under study the dendrimer emits fluorescence between 450 and 650 nm with λ_F maxima in the 532–544 nm region. Fig. 1 plots the absorption and fluorescence maxima of the dendrimer. As seen the polarity of the organic solvents has a negligible effect upon the position of the absorption ($\Delta\lambda_A = 5$ nm) and fluorescence ($\Delta\lambda_F = 12$ nm) maxima. Moreover, the 4-*N*,*N*-dimethylaminoethylamino-1,8-naphthalimide labeled PAMAM dendrimer has a positive solvatochromisme.

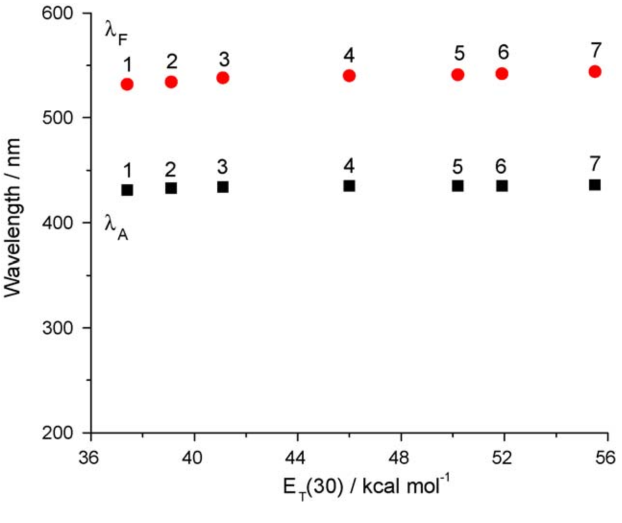


Fig. 1. Dependence of absorption (A) and fluorescence (F) maxima of 4-*N*,*N*-dimethylaminoethylamino-1,8-naphthalimide labeled PAMAM dendrimer on the empirical parameter of solvent polarity $E_T(30)$: 1, tetrahydrofuran; 2, chloroform; 3, dichloromethane; 4, acetonitrile; 5, butanol; 6, ethanol; 7, methanol.

The Stokes shift values range obtained in this work is $\nu_A - \nu_F = 4368$–$4606\ cm^{-1}$. They depend on the polarity of the organic solvents used. It is seen that in the non-polar media the values of Stokes shift are lower, if compared to those obtained in polar media (Table 1).

Fig. 2 shows as an example the normalized absorption and fluorescence spectra of the dendrimer in acetonitrile solution. The overlap of the absorption and fluorescence spectra is small and aggregation effect has not been observed at the studied concentration ($c = 1 \times 10^{-6}\ mol\,l^{-1}$) of the dendrimer.

Absorbing light the investigated dendrimer passes from the basic singlet S_0 to the first excited state S_1. The energies of the first excited state (E_{S_1}) and the corresponding λ_{S_1} have been determined (Table 1). The energies of the lowest exited singlet state, $E_{S_1} = 243.8$–$247.8\ kJ\,mol^{-1}$ are obtained from the locations of intersections of the normalized absorption and fluorescence spectra of the dendrimer taken in different organic solvents. Emitting fluorescence light the fluorophore molecule is deactivated via fluorescence light emission, and passes from the S_1 to the basic S_0 state.

The polarity of the organic solvents is of great importance for the photophysical properties of the dendrimer under study and especially for the quantum fluorescence yield. The fluorescence efficiency of the dendrimer is estimated by measuring the fluorescent quantum yield Φ_F using Eq. (1) on the basis of the

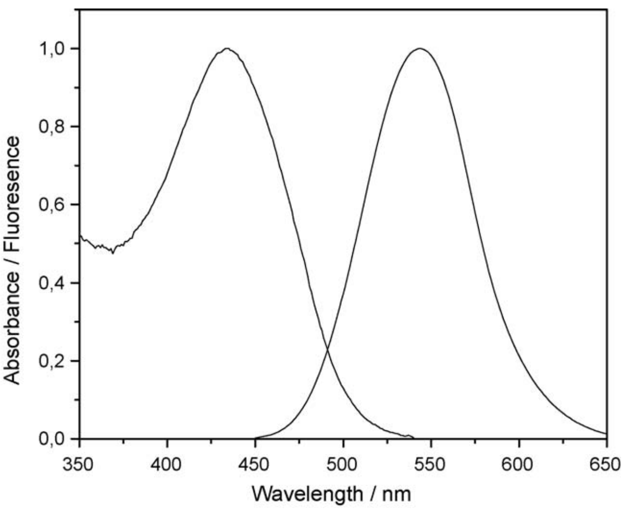


Fig. 2. Normalized absorption and fluorescence spectra of 4-*N*,*N*-dimethylaminoethylamino-1,8-naphthalimide labeled PAMAM dendrimer in acetonitrile solution ($c = 1 \times 10^{-6}\ mol\,l^{-1}$).

absorption and fluorescence spectra.

$$\Phi_{\mathrm{F}} = \Phi_{\mathrm{st}}\frac{S_{\mathrm{u}}}{S_{\mathrm{st}}}\frac{A_{\mathrm{st}}}{A_{\mathrm{u}}}\frac{n_{\mathrm{Du}}^2}{n_{\mathrm{Dst}}^2} \qquad (1)$$

where the Φ_F is the emission quantum yield of the sample, Φ_{st} the emission quantum yield of the standard, A_{st} and A_u represent the absorbance of the standard and sample at the excited wavelength, respectively, while S_{st} and S_u are the integrated emission band areas of the standard and sample, respectively, and n_{Dst} and n_{Du} are the solvent refractive index of the standard and sample, ‘u’ and ‘st’ refer the unknown and standard, respectively.

Fig. 3 shows the dependence of quantum fluorescence yields on the nature of the solvents. As seen from Fig. 3 and Table 1 the values of the quantum fluorescence yield depend strongly on the polarity of the environment. The lower Φ_F has been observed in acetonitrile ($\Phi_F = 0.018$) and its value increases more than 40 times in tetrahydrofuran solution ($\Phi_F = 0.82$). This great difference in the quantum yields is due to the PET that is quenched in non-polar media. The quenching leads to restored fluorescence emission. Such behavior has also been exhibited by similar monomeric 4-*N*,*N*-dimethylaminoethylamino-*N*-alkyl-1,8-naphthalimides. They have a small Φ_F in polar organic solvents and very well pronounced PET properties in the presence of protons or transition metal ions [17,18].

3.2. *Influence of metal cations on the photophysical properties*

It is well known that the environment sensitive fluorophores are a specific chromophoric class whose fluorescence response based on the energy or photoinduced electron transfer can be used for sensors detecting environment pollutants [19–21].

Of particular interest has been to investigate the photophysical properties of the dendrimer in the presence of different metal cations (Zn^{2+}, Ni^{2+}, Pb^{2+}, Mg^{2+}, $Mn^{2+}$and Ag^+). Its functional and supramolecular properties have been investigated with regard to its application as a PET sensor for these cations. In acetonitrile solution the dendrimer is colored in yellow-green with absorption maximum at $\lambda_A = 435$ nm and fluoresce feebly ($\Phi_F = 0.018$), with maximum at $\lambda_F = 544$ nm as expected for a good PET fluorescence switch.

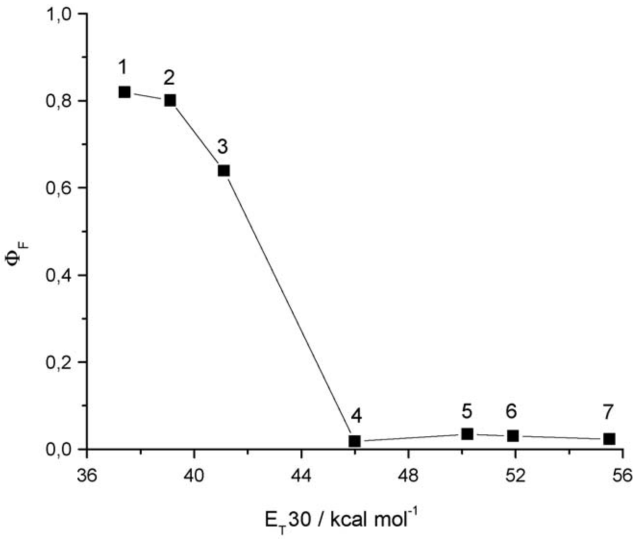


Fig. 3. Dependence of quantum fluorescence yields (Φ_F) of 4-*N*,*N*-dimethylaminoethylamino-1,8-naphthalimide labeled PAMAM dendrimer on the empirical parameter of solvent polarity $E_T(30)$: 1, tetrahydrofuran; 2, chloroform; 3, dichloromethane; 4, acetonitrile; 5, butanol; 6, ethanol; 7, methanol.

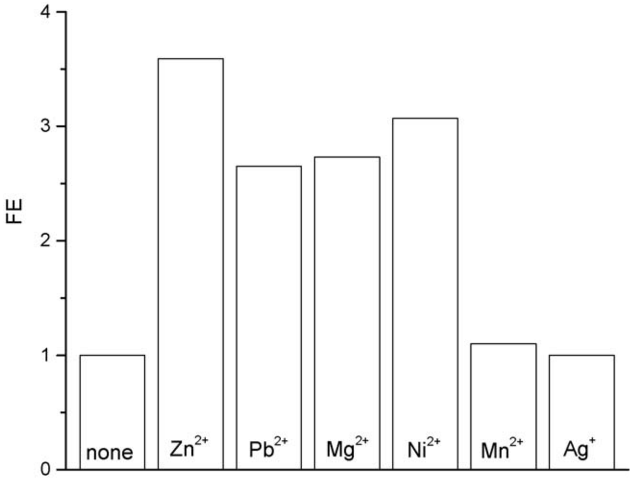


Fig. 4. Fluorescence enhancement factor (FE) of 4-*N*,*N*-dimethylaminoethylamino-1,8-naphthalimide labeled PAMAM dendrimer in the presence of different metal cations ($c = 1 \times 10^{-4}$ M) in acetonitrile solution. The dendrimer concentration in the solution is $c = 1 \times 10^{-6}$ mol l^{-1}.

The substituent A at C-4 position in the 1,8-naphthalimide structure is a *N*,*N*-dimethylaminoethylamine residue ($-NHCH_2CH_2N(CH_3)_2$) with which metal cations could coordinate. The whole structure gives the possibility to obtain a fluorescent dendrimer having PET properties or energy transfer of the 1,8-naphthalimide (Scheme 1).

The presence of metal cations as guest in the dendrimer solution is signaled by an enhancement of the fluorescence intensity (FE). Fig. 4 and Table 2 show the dependence of the nature of metal cations on the fluorescence enhancement. The FE = *I*/*I*$_0$ has been determined from the ratio of maximum fluorescence intensity *I* (upon the addition of metal cations) and minimum fluorescence intensity I_0 (before the addition of metal cations). It is seen that the fluorescence enhancement depends on the nature of the metal cations and on the different ability to coordinate with the dendrimer ligand. The highest effect has been observed in the presence of Zn^{2+} cations. The rank of the response can be

Table 2
Photophysical characteristics of 4-*N*,*N*-dimethylaminoethylamino-1,8-naphthalimide labeled PAMAM dendrimer in acetonitrile solution in the presence of metal ions

Cations	λ_A (nm)	λ_F (nm)	$\Delta\lambda_F$ (nm)	$\nu_A - \nu_F$ (cm^{-1})	Φ_F
Free of ions	435	544	–	4606	0.018
Zn^{2+}	435	527	17	4013	0.464
Pb^{2+}	435	527	17	4013	0.412
Mg^{2+}	435	528	16	4049	0.373
Ni^{2+}	435	530	14	4120	0.426
Mn^{2+}	435	542	2	4538	0.020
Ag^+	435	544	0	4606	0.018

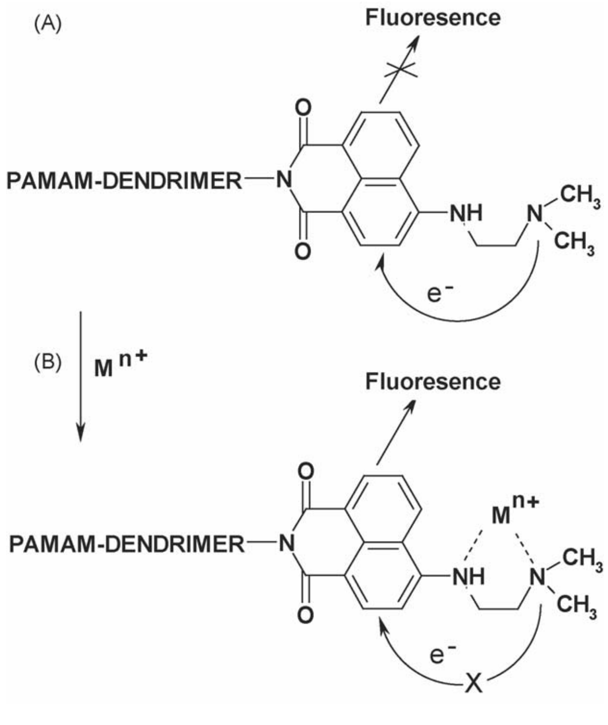
presented as follows:

$$Zn^{2+} > Ni^{2+} > Pb^{2+} \approx Mg^{2+} > Mn^{2+} \approx Ag^{+}$$

In this case the 1,8-naphthalimide units are subjected to a PET proceeding from the tertial nitrogen atoms comprised in the central amino groups of the dendrimer. Simultaneously occurs another PET from the terminal amino groups of *N*,*N*-dialkylamino moieties to the 1,8-naphthalimide. The interaction between the 1,8-naphthalimide as a fluorophore and the *N*,*N*-dimethylamino group as a receptor provoking PET leads to a quenching of the fluorescence emission (Scheme 2A). The presence of the transition metal cations in the dendrimer solution changes its properties since in this case the system fluoresces intensively (Scheme 2B). The enhancement of fluorescence intensity and the hypsochromic shift of the fluorescence maximum (Table 2) confirm the formation of a coordination interaction between the metal cations and nitrogen atom (–NH) at C-4 position of the naphthalene ring and the *N*,*N*-dimethylamino group [9,11].

Table 2 collects the absorption (λ_A) and fluorescence (λ_F) maxima, shift in the fluorescence maxima ($\Delta\lambda_F$), Stokes shift ($\nu_A - \nu_F$), and quantum yield of fluorescence (Φ_F) in the presence of different metal cations.

The typical change in the fluorescence intensity of the dendrimer in acetonitrile solution induced by metal cations is presented in Fig. 5 when using Zn^{2+} cations as an example. The limit of detection was found to be 1×10^{-6} mol l^{-1}. With the addition of Zn^{2+} cations into the dendrimer solution at concentration up to 1×10^{-5} mol l^{-1} the fluorescence emission increases. At further increases in the concentration up to 1×10^{-4} mol l^{-1} the fluorescence change is negligible. In this case the fluorescence enhancement factor is FE = 3.6 ($c = 1 \times 10^{-4}$ mol l^{-1}) but at a higher concentration the fluorescence intensity decreases as the high concentration of Zn^{2+} cations quenches the fluorescence. As Fig. 5 shows the presence of Zn^{2+} cations induces a hypsochromic shift of the fluorescence maximum ($\Delta\lambda_F = 17$ nm), due to the complexation with the *N*,*N*-dimetylamino groups from the 1,8-naphthalimides chromophoric system [17,18,22]. The figure insert plots the fluorescence intensity versus the concentration of metal ions. The plot suggests that the stoichiometry of the complex between the ligand and Zn^{2+} is 1:19. That means the nitrogen atoms comprised in the substitutent at C-4 of the 1,8-naphthalimide are predominantly subjected to the coordination with metal cations. Besides, the tertial nitrogen atoms from the core are also involved in this coordination.



Scheme 2. Schematic presentation of fluorescence enhancement mechanism of 4-*N*,*N*-dimethylaminoethylamino-1,8-naphthalimide labeled PAMAM dendrimer.

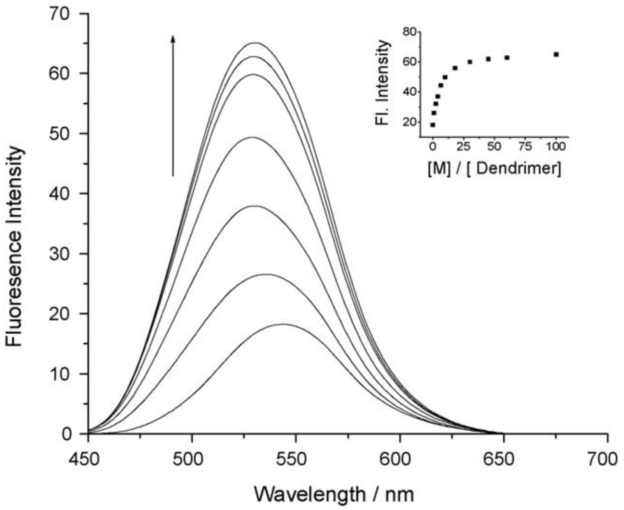


Fig. 5. Fluorescence spectra of 4-*N*,*N*-dimethylaminoethylamino-1,8-naphthalimide labeled PAMAM dendrimer in acetonitrile at various concentrations of Zn^{2+} ions. The concentrations of Zn^{2+} cations are in order of increasing intensity from (0 to 1) × 10^{-4} mol l^{-1}. The concentration of dendrimer is 1×10^{-6} mol l^{-1}. The insert shows the dependence of the fluorescence intensity on the metal ions concentration.

The metal cations like Zn^{2+}, Ni^{2+}, Pb^{2+} and Mg^{2+} increase the quantum yield of fluorescence of the dendrimer ($\Phi_F = 0.373$–0.464), if compared to those of the solution free of cations ($\Phi_F = 0.018$). The highest effect has been also observed in the presence of Zn^{2+} cations ($\Phi_F = 0.464$). In the case of Mg^{2+} and Ag^{+} the quantum yields are similar to those of the dendrimer alone. That means that either the cations of these two metals do not coordinate with the dendrimer at nitrogen atoms comprised in the substituent at C-4 in the 1,8-naphtalimide units or the fluorescence enhancement is neutralized by the transfer of energy from the dendrimer core to the 1,8-naphthalimide fluorophore.

The dendrimer complex with metal cations has a Stokes shift smaller than that of the dendrimer, indicating the stabilization of the planarity of the chromophoric structure. In this case the nonradiative emission during the transition from S_1 to the ground state S_0 is smaller thus increasing the quantum yields of fluorescence.

4. Conclusion

The results from the photophysical investigations of 4-*N*,*N*-dimethylaminoethylamino-1,8-naphthalimide labeled PAMAM dendrimer from second generation in organic solvents of different polarity have shown a positive solvatochromisme with high quantum fluorescence yield in non-polar media. In acetonitrile solution the presence of some metal cations (Zn^{2+}, Ni^{2+}, Pb^{2+}, Mg^{2+}) enhances the fluorescence intensity of the dendrimer. It has been shown that the fluorescence intensity depends on the nature of those metal cations. The peripheral 1,8-naphthalimide units are subjected to a PET from the nitrogen atoms comprised in the central amino groups of PAMAM structure as well as to another one from the terminal *N*,*N*-dialkylamino groups at the substituent at C-4 position. In fact the metal cations interact with the terminal *N*,*N*-dimetylamino groups from the 1,8-naphthalimide chromophoric system, as well as with the central part of the dendrimer. The results from the investigations presented allow the suggestion that the dendrimer has the potential of fluorescence sensor of environment pollution by metal cations as Zn^{2+}, Ni^{2+}, Pb^{2+}, Mg^{2+}.

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