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Sensors for detecting metal ions and protons based on new green fluorescent poly(amidoamine) dendrimers peripherally modified with 1,8-naphthalimides

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Abstract

Two recently synthesized poly(amidoamine) dendrimers from zero and second generation whose periphery comprises fluorescent 4-piperidino-1,8-naphthalimide units have been investigated as potential sensors of metal cations and protons. The photophysical characteristics of the dendrimers have been determined by fluorescence and absorption spectroscopy. Experiments have been performed in the presence of Zn^{2+}, Ni^{2+}, Ce^{3+}, Cu^{2+}, Co^{2+} and Ag^{+} cations. The increase in the fluorescence intensity of the dendrimers in the presence of protons indicates their sensitivity to the protons. The response of the dendrimers ligands depends on the nature of the added metal cations. The best performance is accomplished for detecting Cu^{2+} and Co^{2+} cations. The results obtained reveal the capacities of these systems to act as reliable detectors of environment pollution by metal cations and protons.

Keywords: Dendrimers; PAMAM; 1,8-Naphthalimides; Sensors; Environmental

1. Introduction

Environment pollution has been a major concern of the present industrial societies. The protection from pollution, especially by chemical industries, has put the challenge to chemists and photophysicists in many countries. Many scientific teams have been advancing first of all in the inventing of novel detectors of versatile pollutants. The determination of heavy and transition metal cations in the environment has been of great interest. Sensors for pollution by metal ions have been of particular actuality [1,2].

Dedrimers are three-dimensional macromolecular compounds possessing a well-defined structure. The design of luminescent dendrimers with regard to their exploitation, especially for environment protection has been among the vanguard topics in the field of dendrimer studies. Introducing fluorophores of various nature and fluorescence emission into the core or periphery of the dendrimers allows altering the desired properties of the new materials [3].

Tomalia et al. [4] were the first to report on the preparation of poly(amidoamine) (PAMAM) dendrimer structures. The specifics of these polymers are their interiors containing both secondary (amide) and tertiary amines, while their peripheries are functionalized with various groups able to furnish desired properties. Recent investigations have demonstrated the potential of PAMAM dendrimer molecules to coordinate metal cations [5].

1,8-Naphthalimides and their 4-substituted derivatives constitute a very versatile class of compounds characterised by intensive fluorescence and a very good photostability [6] which find applications in a large variety of areas.

The results from our investigations on the synthesis and photophysical properties of some new luminescent PAMAM dendrimers comprising 1,8-naphthalmide units in their periphery have been already published [7]. The papers

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report on the fluorescence properties of the dendrimers exhibited in the presence of different bivalent metal cations. Enhancement or quenching of the fluorescence intensity depending on the generation of PAMAM has been observed. We have found that these dendrimers causing photoinduced electron transfer or energy transfer can act as chemosensors for metal cations.

The present work describes the functional properties of zero and second generation PAMAM dendrimers comprising 4-piperidino-1,8-naphthalimide fluorescent units in their periphery. The photophysical and photochemical characteristics of both PAMAM dendrimers have been investigated in the presence of different metal cations and protons viewing their potential implementation as indicators of environment pollutants.

2. Experimental part

2.1. Materials and methods

The modified PAMAM dendrimers with 1,8-napthalimide derivatives under study have the structures presented in Schemes 1 (D1) and 2 (D2). Their syntheses have been described recently [7a,7b].

4-Nitro-1,8-naphthalimide-labelled PAMAM [7a,7b] was used as an initial product to prepare the 4-piperodino-1,8-naphthalimide fluorescent dendrimer from zero (D1) or second (D2) generation. The reactions proceed in *N*,*N*-dimethylformamide solution by nucleophilic substitution of the nitro group of 4-nitro-1,8-naphthalimide-labelled PAMAMs with piperidino groups at ambient temperature for 24 h. In this case the electron accepting carbonyl group of the naphthalimide molecule favors the nucleophilic substitution reactions.

UV–vis spectrophotometric investigations were performed on a diode array spectrophotometer (HP 8453) at 10^{-6} mol/l. The fluorescence spectra were taken on a Perkin-Elmer (LS 5) spectrophotometer at 10^{-6} mol/l. Both measurements were carried out in *N*,*N*-dimethylformamide solution (DMF) from Merck). Fluorescence quantum yield was determined on the basis of the absorption and fluorescence spectra. Fluorescein (Aldrich) was used as reference ($\Phi_{st} = 0.87$ [8]).

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 [7e]. $CuSO_4{\cdot}5H_2O$, $CoSO_4{\cdot}7H_2O$, $Ce(NO_3)_3{\cdot}6H_2O$, $AgNO_2$ (Fluka) and $ZnSO_4{\cdot}7H_2O$, $Ni(NO_3)_2{\cdot}6H_2O$ (Aldrich) were investigated as sources for metal cations.

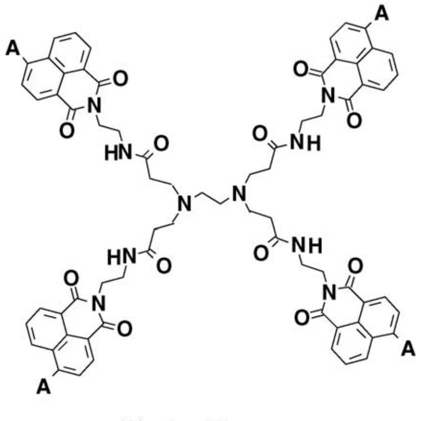
3. Results and discussion

3.1. Spectral characteristics of dendrimer D1 and D2

It is well known that the photophysical properties of the 1,8-naphthalimides depend basically on the polarisation of naphthalimide molecule due to the electron donor–acceptor interaction occurring between the substituents at C-4 and the carbonyl groups from the imide structure of the chromophoric system.

Table 1 presents the photophysical characteristics of the dendrimers under study in DMF solution: the absorption (λ_A) and fluorescence (λ_F) maxima wavelength, the extinction coefficient (ε), Stokes shift ($\nu_A - \nu_F$), oscillator strength (*f*) and the quantum yield of fluorescence (Φ_F). 4-Piperidino-*N*-allyl-1,8-naphthalimide has been used as a monomeric naphthalimide unit [6b].

Both dendrimers D1 and D2 in DMF solution are highly colored in yellow-green with absorption maxima at $\lambda_A = 409$ and 410 nm, respectively, and emit intense fluorescence between 450 and 700 nm with maxima at $\lambda_F = 532$ and 536 nm, respectively. Fig. 1 presents the normalised absorp-



(A) piperidine

Scheme 1. Chemical structure of the zero generation PAMAM dendrimer D1 peripherally modified with four 4-piperidino-1,8-naphthalimide units.

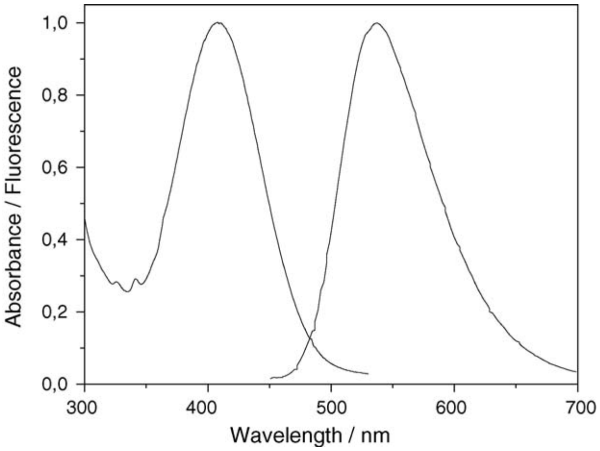
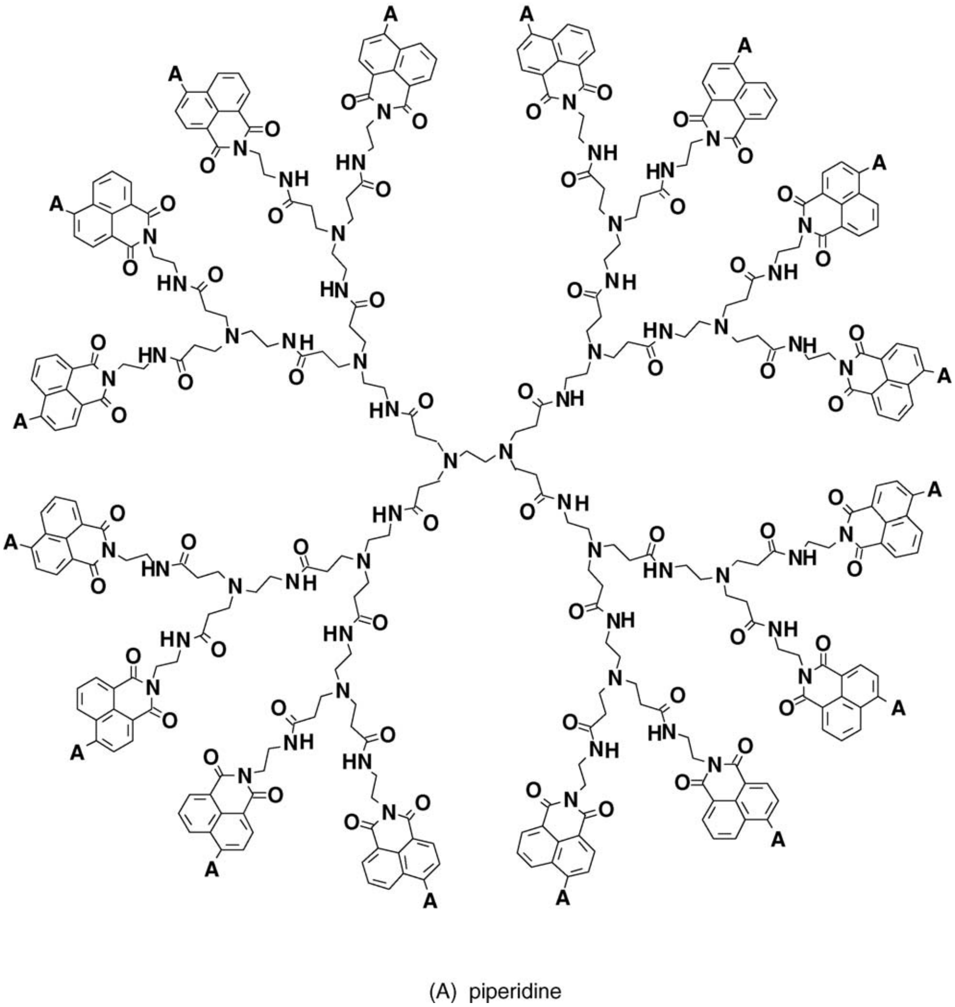


Fig. 1. The normalised absorption and fluorescence spectra of D2 in DMF solution.



Scheme 2. Chemical structure of the second generation PAMAM dendrimer D2 peripherally modified with sixteen 4-piperidino-1,8-naphthalimide units.

tion and fluorescence spectra of D2 as an example. The fluorescence curve is approximately a mirror image of the absorption maximum in the long-wavelength region, which indicates that the molecular structure of the 1,8-naphthalimide fluorophores is maintained in the excited state and that the fluorescence emission prevails. The overlap between the absorption and fluorescence spectra is low and the re-absorption and aggregation are negligible at the concentration 10^{-6} mol/l.

The molar extinction coefficients ε (at 410 nm) of D1 and D2 are 43 800 and 193 300 l/mol cm, respectively, while that of the analogous monomeric 1,8-naphthalimide having the same substituent at C-4 is $\varepsilon = 11\,200$ l/mol cm. As seen the values of the dendrimers achieved are 4- or 16-fold higher than that of the monomer, which suggests that no important ground state interaction occurs between the 1,8-naphthalimide chromophoric units in the dendrimer periphery [9]. This also confirms the high purity of the dendrimers we have synthesized.

The fact that the molar extinction coefficients are higher than 10^4 l/mol cm indicate that the long-wavelength band of the absorption spectra is a band of charge transfer /CT/ which occurs as a result from a $\pi \rightarrow \pi^*$ electron transfer during the $S_0 \rightarrow S_1$ transition.

The Stokes shift indicates the difference in the properties and structure of the fluorophores in the ground state S_0 and

Table 1
Photophysical characteristics of dendrimers 1 and 2 in DMF solution

	λ_A (nm)	ε (l/mol cm)	λ_F (nm)	$\nu_A - \nu_F$ (cm^{-1})	δ_A (nm)	δ_F (nm)	f	Φ_F
D1	409	43800	532	5653	80	85	0.92	0.09
D2	410	193300	536	5734	84	87	3.54	0.26
1,8-Naphthalimide	408	11200	530	5641	79	84	0.22	0.05

in the first exited state S_1. The Stokes shift is given by Eq. (1)

$$\nu_A - \nu_F\,(\mathrm{cm}^{-1}) = \left(\frac{1}{\lambda_A} - \frac{1}{\lambda_F}\right) \times 10^7 \qquad (1)$$

The Stokes shift values for D1 and D2 are 5653 and 5734 cm^{-1}, respectively. In the case of monomeric 1,8-naphthalimide dyes the Stokes shift is 5641 cm^{-1}.

An important parameter of the fluorescent compounds is the oscillator strength (*f*). It reveals the effective number of electrons taking part in the transition from the ground S_0 to the excited S_1 state, and is proportional to the area of the absorption spectrum. The values of oscillator strength can be calculated using the following equation:

$$f = 4.32 \times 10^{-9}\,\Delta\nu_{1/2}\varepsilon_{\max} \qquad (2)$$

where $\Delta\nu_{1/2}$ is the width of the absorption band (in cm^{-1}) at $1/2\varepsilon_{\max}$. The calculated values of *f* in DMF solution are 0.92 and 3.54, which are respectively 4- and 16-fold larger than those of the analogous monomeric 1,8-naphthalimide (f = 0.22).

The fluorescence efficiency of D1 and D2 is estimated by measuring their fluorescent quantum yield Φ_F using Eq. (3) on the basis of the absorption and fluorescence spectra taken in DMF. Fluorecein has been used as a standard.

$$\Phi_F = \Phi_{st}\frac{S_u}{S_{st}}\frac{A_{st}}{A_u}\frac{n_{Du}^2}{n_{Dst}^2} \qquad (3)$$

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} the solvent refractive index of the standard and sample, *u* and *s* refer the unknown and standard, respectively.

As seen from the data in Table 1, D1 and D2 have low quantum yield of fluorescence $\Phi_F = 0.09$ (D1) and 0.26 (D2) which can be explain by a possible conformation changes in the fluorophore chromophoric system. The value for D2 is higher compared to that for D1, because the former has four-folds more 1,8-naphthalimide fluorescent units in its molecule.

Both dendrimers D1 and D2 have a broad absorption band (δ_A = 79–84 nm) in the visible region. This suggests a high sensitivity to the energy gap evoked by the intermolecular interaction between the ground and intramolecular excited state of the dendrimers. The half-bandwidths in the absorption spectra of D1 and D2 $\delta_A < \delta_F$ are narrower than those of their fluorescence spectra.

3.2. The influence of metal cations on the dendrimer fluorescence

In organic solvents some transition metal cations can quench or enhance fluorescence intensity of the PAMAM dendrimers modified with 1,8-naphthalimide units. It has been shown that absorption and fluorescence parameters of the dendrimers depend on the nature of the substituent at C-4 position in their 1,8-naphthalimide chromophorous systems [7]. The fluorescent characteristics of D1 and D2 have been studied in different media viewing their practical application as effective fluorescent sensors able to detect metal ions in the environment.

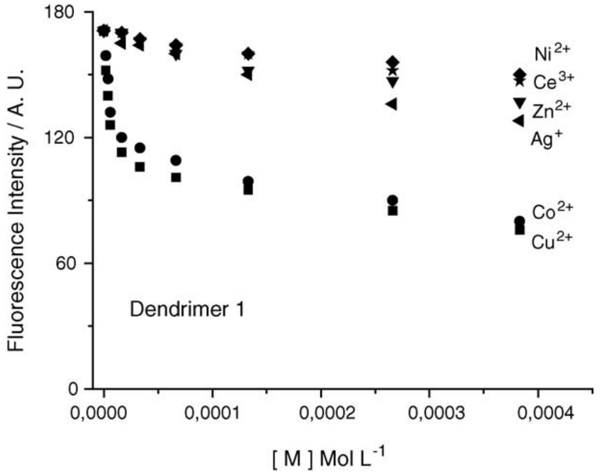


Fig. 2. The fluorescence intensity response of D1 (1×10^{-6} mol/l) in *N*,*N*-dimethylformamide solution to the different metal cations. The metal cation concentration is 10^{-6} to 10^{-4} mol/l.

The ability of D1 and D2 to detect metal cations has been tested in DMF solution by monitoring the changes in their absorption and fluorescent spectra in the presence of various cations.

Figs. 2 and 3 plot the change in the fluorescence intensity of D1 and D2 in the presence of different metal cations (D1: λ_{ex} = 409 nm and λ_{em} = 532 nm; D2: λ_{ex} = 410 and λ_{em} = 536 nm). The data about both dendrimers show that the quenching of the florescence emission depends on the nature

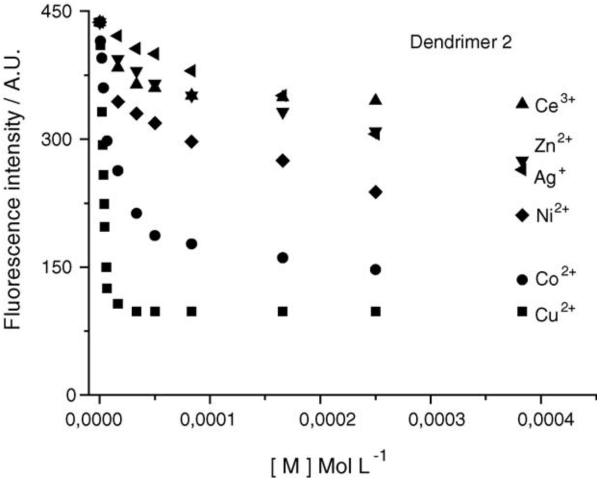


Fig. 3. The fluorescence intensity response of D2 (1×10^{-6} mol/l) in *N*,*N*-dimethylformamide solution to the different metal cations. The metal cation concentration is 10^{-6} to 10^{-4} mol/l.

Table 2
Relative fluorescence intensity (%) of dendrimers D1 and D2 in the presence of different metal cations

	Free of ions	Ce^{3+}	Cu^{2+}	Co^{2+}	Ni^{2+}	Zn^{2+}	Ag^{+}
D1 (%)	100	86.0	44.4	46.8	80.1	87.7	74.8
D2 (%)	100	80.1	22.3	28.6	65.1	63.9	63.0

of the metal cations. As shown in Figs. 2 and 3, at low metal concentration ($[M^{P+}] > 10^{-5}$ mol/l and $[D2] = 10^{-6}$ mol/l), the fluorescence intensity decreases linearly with the increase in the metal ion concentration. For most of the metal ions studied, the dendrimers (D1 or D2) and the quenching metal cations form a non-fluorescent complex containing more than one metal cation per ligand:

$$\text{D1 (or D2)} + n\text{M}^{P+} \rightleftarrows [\text{D1 (or D2)M}_n]^{nP+}_{\text{NON-FLUORESCENT}}$$

Figs. 2 and 3 also present the difference in the curve pattern when using different metal cations. The fact can be explained by the different coordination potencies of the cation used. In the case of D1 and D2 the highest quenching effect is observed in the presence of Cu^{2+} and Co^{2+} cations. In the case of Ni^{2+}, Zn^{2+}, Ce^{3+} and Ag^{+} cations the decrease of the fluorescence intensity is lower (Table 2). The data in Table 2 indicate that, at high metal concentrations ($M^{P+} \gg$ D1 or D2) at which the equilibrium of the direct reaction is maximum shifted, most metal cation exhibit considerable quenching of the fluorescence of D1 and D2. It is also seen that the quenching of the fluorescence intensity of D2 a someway stronger.

The fluorescence spectra of D2 taken in a DMF solution (at 10^{-6} mol/l concentration) in the presence of Cu^{2+} cations as "guest" at various concentrations are presented in Fig. 4 as a typical example. The decrease of the fluorescent intensity has been observed with increasing the concentration of Cu^{2+} cations. This dependence has been studied in the $0–10^{-4}$ mol/l concentration range of Cu^{2+} cations. At 6.66×10^{-6} mol/l Cu^{2+} concentration the quenching effect is 6% of the initial value. The addition of 2.66×10^{-5} mol/l of Cu^{2+} cations reduces the fluorescence intensity to 33%. But this effect is valid only in the 10^{-6} to 6.66×10^{-5} mol/l concentration range of Cu^{2+} cations. At concentrations higher than 6.66×10^{-5} mol/l the fluorescence does not change.

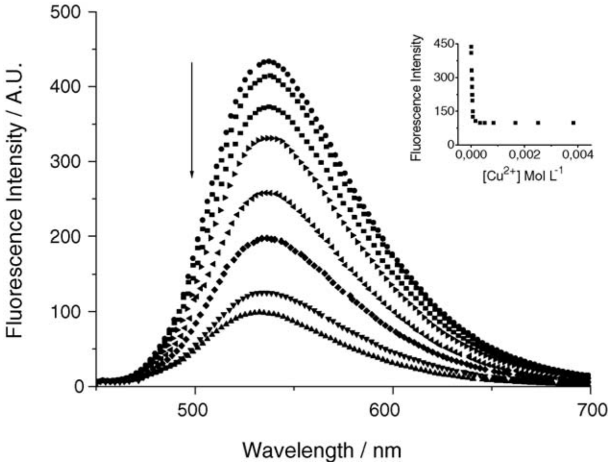


Fig. 4. Fluorescence spectra of D2 (1×10^{-6} mol/l) in *N*,*N*-dimethylformamide solution in the presence of different concentration of Cu^{2+} cations. The insert shows the dependence of the fluorescence intensity on the metal ions concentration.

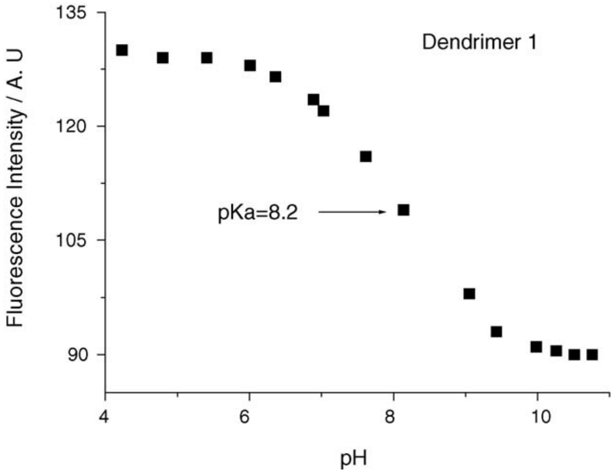


Fig. 5. The influence of pH on the fluorescence intensity of D1 (1×10^{-6} mol/l) in a solution of ethanol and water (1:4, v/v).

The absorption and fluorescence maxima of the D1 and D2 in the presence of metal cations appear at the same position as those in the spectra of the cations free dendrimers. This fact indicates that the solution sites responsible for the metal cations coordination have to be bonded to the tertiary aliphatic amines from the interior part of the dendrimer molecule. The fluorescence quenching in this case is caused by an electron or energy transfer reaction between the metal complex formed by the dendrimer core and 1,8-naphthalimide fluorophore units in the dendrimer periphery.

The results from the spectral characterisation of dendrimers D1 and D2 performed in the presence of metal ions reveal that the newly synthesized materials are highly sensitive to Cu^{2+} and Co^{2+} present in the systems studied. This makes them reliable detectors of Cu^{2+} and Co^{2+} ion pollution in the environment especially at industrial sites. The data obtained show that D2 possesses higher sensor capacities.

3.3. *Influence of protons on the fluorescence intensity of the dendrimers D1 and D2*

The pH intensity of D1 and D2 has been investigated in the 4–11 pH value range in a ethanol–water mixed solvent (1:4, v/v). As shown in Figs. 5 and 6 dendrimers D1 and D2 exhibit high sensitivity to the presence of protons. But their response to pH changes is different. As seen the increase in pH up to 6.0–6.5 does not change the fluorescence intensity. Higher pH values cause a drastic decrease in it and finally pH 10.0 the curve reaches again a plateau. The pH dependence

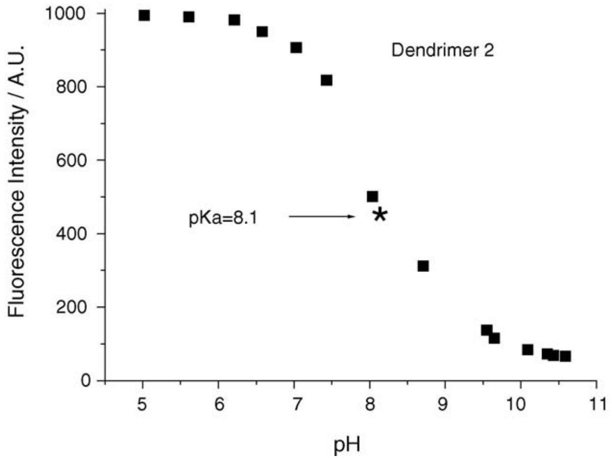


Fig. 6. The influence of pH on the fluorescence intensity of D2 (1×10^{-6} mol/l) in a solution of ethanol and water (1:4, v/v).

of fluorescence intensity has been analyzed with the Eq. (4).

$$\mathrm{pH} - \mathrm{p}K_\mathrm{a} = \log \frac{I_{\mathrm{F}_\mathrm{max}} - I_\mathrm{F}}{I_\mathrm{F} - I_{\mathrm{F}_\mathrm{min}}} \qquad (4)$$

The calculated $\mathrm{p}K_\mathrm{a}$ values are 8.2 for D1 and 8.1 for D2. These value corresponds to the one already measured for poly(amidoanine) dendrimers of second generation ($\mathrm{p}K_\mathrm{a} = 8.1$) [7e].

For both dendrimers the fluorescence emitted by the protonated form is higher than the emitted by the molecular form. The pH dependence of the florescence intensity observed is more pronounced in case of D2. In this case the increase is 20-fold higher for D2 protonated form while for D1 protonated form it is only 1.5-fold. These results point at the fact these dendrimers can be used as pH sensors, hence as detectors of pollution in aqueous media. A maximum of sensitivity has been observed at pH just below neutrality ($\mathrm{pH} < 6$).

4. Conclusion

The potential of two poly(amidoamine) dendrimers of zero and second generation as polychelatogenes, to bind metal cations and protons has been investigated by absorption and fluorescence spectroscopy. The dendrimers periphery comprises 4-piperydino-1,8-naphthalimide units as fluorophores. The studies aimed at evaluating the capacity of these dendrimers to sense metal ion and proton pollutants in different media. The fluorescence intensity of both dendrimers from zero and second generation is quenched by the metal cations. The quenching of the fluorescence intensity depends on the nature and concentration of the metal cations. In the presence of protons the fluorescence intensity of the dendrimers increases. The better fluorescence quenching has been observed in the case of the dendrimer of second generation. The results from the investigations presented allow the suggestion that the newly synthesized dendrimers are suitable fluorescence sensors of environment pollution by metal cations and protons.

Acknowledgments

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