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Synthesis and spectral properties of new green fluorescent poly(propyleneimine) dendrimers modified with 1,8-naphthalimide as sensors for metal cations

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Abstract

Two new fluorescent second generation poly(propyleneimine) dendrimers, peripherally modified with 1,8-naphthalimide, have been synthesized for the first time and characterized. The photophysical characteristics of the new dendrimers have been studied in organic solvents of different polarity. The effect of the chemical nature of the 1,8-naphthalimide C-4 substituent on the photophysical properties of new dendrimers is discussed. The complexes formed between the dendrimers and the metal cations in solution have been studied, with regard to potential applications as fluorescent sensors for metal ion contamination. The results show that the C-4 substituent determines both the response to the presence of metal cations and the selectivity of the sensors.

Keywords: Poly(propyleneimine); Dendrimers; 1,8-Naphthalimide

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1. Introduction

In recent years polymer scientists have developed a considerable number of nonlinear star-shaped structures as an alternative to conventional polymer structures. Star-shaped polymers differ from linear ones in that they are a new type of compound with properties typical of low molecular weight materials.

Dendrimers are a relatively new category of star-shaped polymers [1–3]. They are monodisperse, perfectly branched well defined polymers, possessing a good number of end functional groups. Quite often these functional groups are reactive, thereby allowing modification of the dendrimers. A great deal of attention has been paid to this class of macromolecules owing to their new form of structural organization which combines the properties of low and high molecular weight compounds.

Fluorescent chemosensors are of great importance in chemistry, biology and medicine [4,5]. They allow the immediate detection of different compounds in living organisms and the environment. With their excellent photophysical properties, 1,8-napthalimide derivatives are unsurpassed as a signal fragment in the design of fluorescent chemosensors [6]. The covalent bonding of such sensors to the linear polymer chain preserves their activity and allows the preparation of polymeric sensors [7–10]. In this context, marking dendritic macromolecular architectures with fluorescent fragments is one approach to the development of fluorescent dendrimers possessing tailored properties, with a view to their use in a wide range of applications, including highly efficient fluorescent sensors among others.

The increasing interest in poly(propyleneimine) (PPI) dendrimers is due to the different applications they could find [11]. The possibility of modifying PAMAM dendrimers with

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1,8-napthalimide fluorophores and studies of their photophysical properties have been reported [12].

The synthesis of second generation PPI dendrimers peripherally modified with 1,8-napthalimide has been reported here for the first time. The photophysical characteristics of the newly synthesized compounds are described. It is worth noting here the possibility to use these new fluorescent dendrimers as PET sensors for detecting metal cations.

2. Experimental part

2.1. Materials

The second generation poly(propyleneimine) dendrimer and 4-nitro-1,8-naphthalic anhydride were used as obtained from Aldrich. Organic solvents (methanol, ethanol, propanol, acetonitrile, *N*,*N*-dimethylformamide (DMF), acetone, dichloromethane, chloroform, tetrahydrofuran and dimethylsulfoxide) used in this study were of spectroscopic grade and used as obtained. $Cu(NO_3)_2 \cdot 3H_2O$, $Ni(NO_3)_2 \cdot 6H_2O$, $PbNO_3$, $Co(NO_3)_2 \cdot 6H_2O$, $Zn(NO_3)_2 \cdot 4H_2O$, and $AgNO_3$ salts were the metal cation sources and used as obtained from Aldrich.

2.2. Synthesis of 4-nitro-1,8-naphthalimide-labelled PPI

Poly(propyleneimine) (0.01 mol) and 4-nitro-1,8-naphthalic anhydride (0.08 mol) were dissolved in 50 ml of ethanol. The solution was refluxed and the reaction was monitored by TLC. After 4 h the liquor was poured into 200 ml of water and the resulting precipitate was filtered. Yield: 92%.

2.3. Synthesis of 4-dimethylaminoethylamine-1,8-naphthalimide-labelled PPI (*D1*)

4-Nitro-1,8-naphthalimide-labelled dendrimer of 0.005 mol was stirred with 0.02 mol of *N*,*N*-dimethylethylenediamine in 50 ml of *N*,*N*-dimethylformamide for 24 h at room temperature. After that, 500 ml of water was added to the solution, the precipitate was filtered off, washed with water, and then dried in a vacuum at 40 °C. Yield: 83%. FT-IR (KBr) cm^{-1}: 2943, 2822, 1682, 1638, 1579, 1460, 1356, 1243, 774. ^1H NMR ($CDCl_3$, 400 MHz, ppm): 8.43 (d, $J = 8.4$ Hz, 8H, Ar–H), 8.22 (d, $J = 7.0$ Hz, 8H, Ar–H), 8.06 (d, $J = 8.4$ Hz, 8H, Ar–H), 7.49 (dd, $J = 8.2$, 6.9 Hz, 8H, Ar–H), 7.41 (br s, 8H, NH), 6.58 (d, $J = 8.4$ Hz, 8H, Ar–H), 3.94 (m, 16H, $(OC)_2NCH_2$), 2.60–2.40 (m, 64H + 16H, $CH_2N\langle$ + $CH_2N(CH_3)_2$), 2.20–2.40 (m, 16H, CH_2NH–), 2.18 (s, 48H, $CH_2N(CH_3)_2$). ^{13}C NMR ($CDCl_3$) δ (ppm): 163.60, 162.78, 150.18, 133.96, 130.39, 129.21, 128.06, 124.05, 121.83, 119.90, 107.81, 103.59, 50.88, 45.05, 40.63, 37.70, 24.85.

2.4. Synthesis of 4-propylamino-1,8-naphthalimide-labelled PPI (*D2*)

The synthesis was carried out according to the procedure described for **D1** using *n*-propylamine as the reactant. Yield: 84%. FT-IR (KBr) cm^{-1}: 2957, 2871, 1679, 1638, 1578, 1460, 1354, 1243, 775. ^1H NMR ($CDCl_3$, 400 MHz, ppm): 8.52 (d, $J = 8.4$ Hz, 8H, Ar–H), 8.21 (d, $J = 6.6$ Hz, 8H, Ar–H), 8.04 (d, $J = 8.4$ Hz, 8H, Ar–H), 7.57 (br s, 8H, NH), 7.48 (dd, $J = 8.1$, 6.4 Hz, 8H, Ar–H), 6.54 (d, $J = 8.6$ Hz, 8H, Ar–H), 3.93 (m, 16H, $(OC)_2NCH_2$), 2.60–2.40 (m, 64H, $CH_2N\langle$), 2.20–2.40 (16H, CH_2NH–), 1.65 (m, 16H, CH_2CH_3), 0.92 (t, $J = 7.5$ Hz, 24H, CH_2CH_3). ^{13}C NMR ($CDCl_3$) δ (ppm): 163.32, 162.32, 150.41, 133.936, 130.35, 129.25, 128.26, 123.90, 121.8, 119.93, 107.57, 103.48, 50.84, 44.29, 37.72, 24.79, 20.89, 11.33.

2.5. Analysis

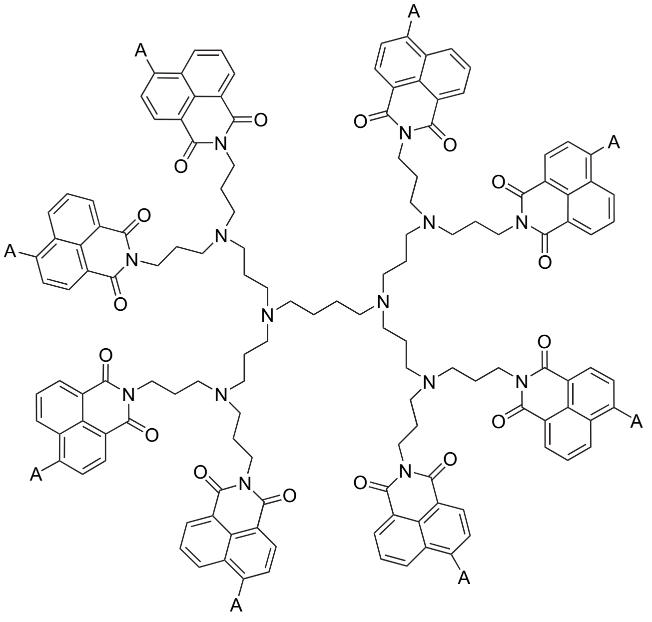
UV–vis spectrophotometric investigations were performed on a Lambda 35 spectrophotometer at concentrations of 1×10^{-6} mol l^{-1}. The fluorescence spectra were taken on a Perkin–Elmer LS55 spectrophotometer at concentrations of 1×10^{-6} mol l^{-1}. Fluorescence quantum yield was determined on the basis of the absorption and fluorescence spectra using fluorescein as a reference ($\Phi_F = 0.85$). The NMR spectra were obtained on an Oxford AS400 operating at 400 and 100 MHz, for ^1H and ^{13}C NMR, respectively. The measurements were carried out in $CDCl_3$ solution at ambient temperature. The chemical shifts were referenced to a tetramethylsilane (TMS) standard. The effect of the metal cations 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 remains insignificant [13].

3. Results and discussion

The chemical structure of 1,8-naphthalimide-labelled PPI dendrimers (**D1** and **D2**) is shown in Scheme 1.

3.1. Synthesis of modified PPI dendrimers *D1* and *D2*

The new 4-amino substituted 1,8-naphthalimide labelled PPI dendrimers were prepared from the second generation poly(propyleneimine), which possesses eight terminal primary amine groups. PPI reacts with 4-nitro-1,8-naphthalic anhydride in ethanol solution, yielding a new compound with eight peripherally 4-nitro-1,8-naphthalimide units. The reaction of the initial 4-nitro-1,8-naphthalic anhydride and the purity of the final products were monitored by TLC. The high molecular weight dendrimer remains at the bottom of the chromatogram. Green fluorescent 4-*N*,*N*-dimethylaminoethylamine-1,8-naphthalimide (**D1**) and 4-propylamino-1,8-naphthalimide (**D2**) PPI dendrimers were obtained by running the reaction at ambient temperature for 24 h during the second step. The nitro group of the 4-nitro-1,8-naphthalimide labelled PPI dendrimer undergoes nucleophilic substitution in *N*,*N*-dimethylformamide solution with the respective amino groups. In this case, the electron-accepting carbonyl group of the naphthalimide moiety favours the nucleophilic substitution reaction of the



A = $NHCH_2CH_2N(CH_3)_2$ (**D1**) $NHCH_2CH_2CH_3$ (**D2**)

Scheme 1. Chemical structure of 1,8-naphthalimide-labelled PPI dendrimers, **D1** and **D2**.

nitro group with the amines [14,15]. The final products were obtained after precipitation with water and filtration of the solid precipitate, which are then subjected to double re-crystallization from ethanol. The **D1** and **D2** dendrimers, obtained in a high yield, are dark yellow solids of a fairly good purity.

3.2. Photophysical properties of dendrimers *D1* and *D2* in organic solvents

The photophysical properties of 1,8-naphthalimides depend mainly on the polarization of the 1,8-naphthalimide molecule. This occurs upon irradiation, resulting in the electron donor–acceptor interaction between the C-4 substituent and the imide carbonyl group of the chromophoric system. In general, the derivatives with alkoxy groups are colourless and have a blue fluorescence emission. The respective amino substituted 1,8-naphtalimide derivatives have a yellow colour and emit a yellow-greenish fluorescence. 1,8-Naphthalimide derivatives are fluorescent compounds that exhibit very interesting photophysical properties. These properties are very often sensitive to the nature of the organic solvents in which they are dissolved. Their photophysical characteristics in organic solvents of different polarity have been investigated: absorption (λ_A) and fluorescence (λ_F) maxima, the extinction coefficient (ε), Stokes shift ($\nu_A - \nu_F$) and fluorescence quantum yield (Φ_F). These measurements will help in the elucidation of the mechanism of the photoinduced electron transfer (PET) proceeding in the dendrimer molecule. The photophysical characteristics of the dendrimers, **D1** and **D2**, in organic solvents of different polarity are presented in Tables 1 and 2, respectively.

Table 1
Photophysical properties of dendrimer **D1** in different organic solvents (see text)

Solvents	λ_A nm	ε $dm^3\,mol^{-1}\,cm^{-1}$	λ_F nm	$\nu_A - \nu_F$ cm^{-1}	Φ_F
Methanol	436	92 800	522	3779	0.016
Ethanol	438	86 000	520	3600	0.018
Propanol	436	84 000	520	3705	0.090
Acetonitrile	431	94 000	519	3934	0.024
N,*N*-Dimethylformamide	439	86 000	521	3585	0.011
Acetone	429	101 600	518	4005	0.075
Dichloromethane	432	103 000	507	3424	0.590
Chloroform	430	98 000	499	3215	0.684
Tetrahydrofuran	426	96 400	502	3553	0.651
Dimethylsulfoxide	442	90 000	523	3504	0.002

The dendrimer with nitro groups at the 1,8-naphthalimide C-4 position (in DMF solution) absorbs in the near UV region at $\lambda_A = 338$, due to the electron-accepting nature of the nitro group, and its solution is colourless. Similar absorption maxima have been observed for monomeric 1,8-naphthalimides comprising nitro groups at C-4 position in their chromophoric system [15]. The replacement of the nitro group by an electron-donating one (*N*,*N*-dimethylaminoethylamino **D1** and propylamino **D2**) leads to a significant bathochromic shift of the absorption maxima of approximately 100 nm. In all organic solvents under study the solutions of both dendrimers exhibit a yellow-green colour.

Fig. 1 shows the absorption and fluorescence spectra of **D1** in chloroform solution as an example. Due to the presence of electron-withdrawing carbonyl groups conjugated with the electron-donating 1,8-naphthalimide C-4 substituent, the long wavelength band in the absorption spectra has a charge transfer character (CT). From the data in Tables 1 and 2 it can be seen that the solvent polarity influences the position of the absorption maxima, $\Delta\lambda_A = 16$ and 14 nm for **D1** and **D2**, respectively, as the polarization of the 1,8-naphthalimide molecules depends strongly on the solvent polarity as well as on the specific chromophore–solvent interactions, causing a change in the polarization of its chromophoric system. On comparing the fluorescent maxima in nonpolar solvents with those in polar solvents, a bathochromic shift is also observed ($\Delta\lambda_F = 24$ and 29 nm). In this case, the greater bathochromic shift can be explained in view of the fact that the dipole moment of the molecule is enhanced upon excitation due to electron

Table 2
Photophysical properties of dendrimer **D2** in different organic solvents (see text)

Solvents	λ_A nm	ε $dm^3\,mol^{-1}\,cm^{-1}$	λ_F nm	$\nu_A - \nu_F$ cm^{-1}	Φ_F
Methanol	443	78 000	523	3453	0.175
Ethanol	442	81 400	521	3430	0.172
Propanol	441	96 000	519	3408	0.223
Acetonitrile	432	80 200	518	3843	0.543
N,*N*-Dimethylformamide	440	52 800	521	3533	0.491
Acetone	431	76 000	513	3709	0.783
Dichloromethane	430	74 000	502	3335	0.960
Chloroform	430	76 000	496	3094	0.970
Tetrahydrofuran	428	85 200	503	3484	0.901
Dimethylsulfoxide	444	98 000	522	3365	0.272

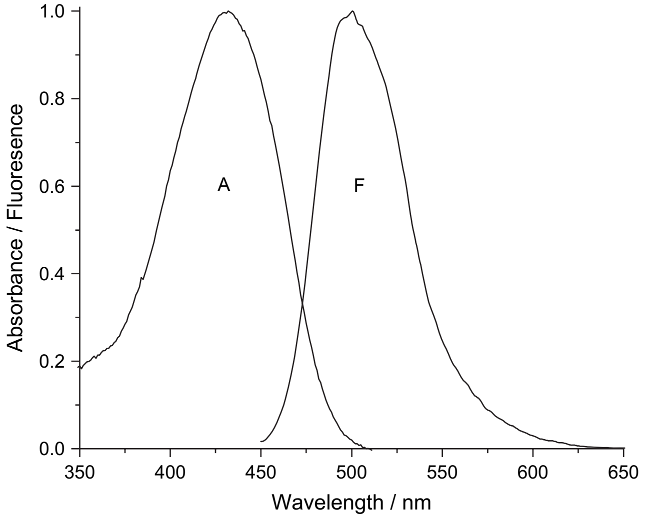


Fig. 1. Normalized absorption (A) and fluorescence (F) spectra of dendrimer **D1** in chloroform solution. The dendrimer concentration is 1×10^{-6} mol l^{-1}.

density redistribution. The excited molecule is better stabilized in polar solvents, because of the stronger interactions with the solvent's dipoles [5]. As seen from the obtained data, the dendrimers **D1** and **D2** under study have a positive solvatochromism.

The molar extinction coefficient ε (at absorption maxima) of both dendrimers **D1** and **D2** is 8-fold higher than that of the monomeric dyes, having a similar substituents at C-4 position [6d,14]. This confirms the full substitution and high purity of the dendrimers we have synthesized and also suggests that no important interaction occurs between the 1,8-naphthalimide chromophoric units in the dendrimer periphery in the ground state [16].

Stokes shift is a parameter that indicates the difference in the properties and structure of the ground state, S_0, and the first excited singlet state, S_1, of the chromophore system. The calculated values for Stokes shift (Eq. (1)) of the dendrimers (Tables 1 and 2) are similar to the values obtained for the PAMAM dendrimers with peripherally 1,8-naphthalimide units [11] and monomeric 1,8-naphthalimides comprising the same substituents [6d,14]. This means that the nature of the main dendrimer matrix in this case does not influence significantly Stokes shift.

$$(\nu_A - \nu_F) = (1/\lambda_A - 1/\lambda_F) \times 10^7 \text{ cm}^{-1} \tag{1}$$

The ability of the dendrimer molecules to emit the absorbed light energy is quantitatively characterized by the fluorescence quantum yield (Φ_F). It has been determined on the basis of the absorption and fluorescence spectra of the dendrimers according to Eq. (2):

$$\Phi_F = \Phi_{st} \frac{S_u}{S_{st}} \frac{A_{st}}{A_u} \frac{n_{Du}^2}{n_{Dst}^2} \tag{2}$$

where Φ_F is the fluorescence quantum yield of the sample, Φ_{st} is the fluorescence 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 indexes of the standard and sample. Subscripts u and s refer to the unknown and standard, respectively.

It has been very interesting to see how the quantum efficiency of dendrimers **D1** and **D2** depends on different environments. As seen from the data in Tables 1 and 2, the quantum yields of both dendrimers are significantly different. The Φ_F values for dendrimer **D1** are between $\Phi_F = 0.002$ (dimethylsulfoxide) and $\Phi_F = 0.684$ (chloroform), whereas for **D2** the respective values are between $\Phi_F = 0.172$ (ethanol) and $\Phi_F = 0.97$ (chloroform). Fig. 2 plots the dependence of the quantum fluorescence yield on the solvent polarity (dielectric constant ε). As can be seen, the quantum yields are considerably higher in nonpolar media for both dendrimers. In polar organic solvents the dendrimers exhibit much weaker emission. This large difference in the quantum yields can be explained by the photoinduced electron transfer (PET) processes, which are accelerated in polar solvents [17]. An interesting effect on the fluorescence has been observed in the case of dendrimer **D2** when alcohols are used as solvents (methanol, ethanol and *n*-propanol). The values of Φ_F are smaller if compared to those obtained in other polar solvents like acetonitrile, DMF or dimethylsulfoxide. The observed effect is due to the interactions between dendrimer 1,8-naphthalimide units and alcohol molecules. The hydrogen bonds between the hydroxyl groups from the alcohols and the carboxylic oxygen atom (C=O) from the 1,8-naphthalimide system occur in the hydroxylated alcohol solutions. These H-bonds favour radiationless transition, causing a decrease of the fluorescence quantum yield of 1,8-naphthalimides [18]. The comparable low values for **D1** obtained in polar solvents are on account of the fact that PET from the distal tertiary nitrogen atom at

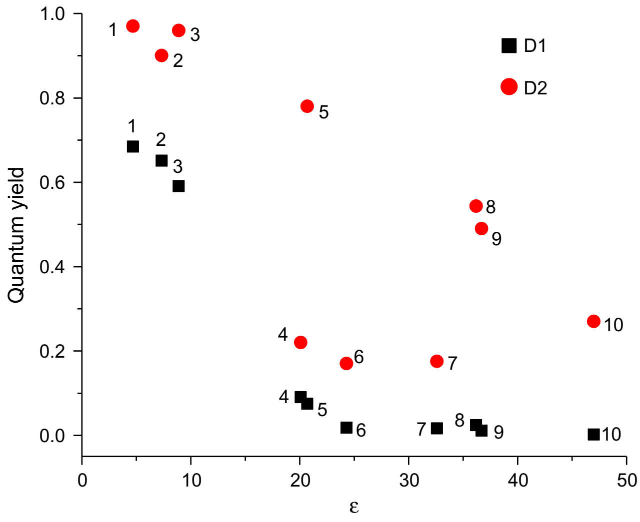


Fig. 2. Dependence of quantum fluorescence yield of dendrimers **D1** and **D2** on the solvent polarity ε: 1 – chloroform, 2 – tetrahydrofuran, 3 – dichloromethane, 4 – propanol, 5 – acetone, 6 – ethanol, 7 – methanol, 8 – acetonitrile, 9 – DMF, 10 – dimethylsulfoxide.

C-4 dominates over the PET occurring from the dendrimer core towards the 1,8-naphthalimide fragment. In the case of **D2**, the latter type of PET dominates.

*3.3. Influence of metal cations on the photophysical properties of dendrimers **D1** and **D2** in acetonitrile solution*

The functional and supramolecular properties of both dendrimers in the presence of different metal cations (Zn^{2+}, Ni^{2+}, Pb^{2+}, Co^{2+}, Cu^{2+} and Ag^{+}) have been studied with regard to their application as PET sensors for these cations. The ability of **D1** and **D2** to detect metal cations has been tested in acetonitrile solution by monitoring the changes in the absorption and fluorescent spectra in the presence of these cations. The choice of acetonitrile as a solvent for the spectral measurements was determined by the fact that both dendrimers are soluble in it and exhibit good photophysical characteristics, with a view to elucidate the mechanism of the PET occurring in the studied dendrimers. In this case, the fluorescence intensity (fluorescence quantum yields) is of particular importance in the absence of the metal cations (see Tables 1 and 2). Acetonitrile solution of the dendrimers is yellow-green in colour, with absorption maxima at $\lambda_A = 431$ and 432 nm. The fluorescence intensity of both dendrimers is different due to their different C-4 substituents. In acetonitrile solution, dendrimer **D1** weakly fluoresces ($\Phi_F = 0.024$), as expected for a good PET fluorescence switch.

Scheme 2 illustrates the ''Fluorophore–Spacer–Receptor'' supramolecular system under study, for metal cations as ''guest'' and modified PPI dendrimer **D1** as ''host''. The interaction between the fluorophore (1,8-naphthalimide) and the receptor (*N*,*N*-dimethylamino group) provokes photoinduced electron transfer and leads to quenching of the fluorescence emission (Scheme 2A). Accordingly, when a metal cation engages the lone electron pair of the receptor nitrogen atom in coordination it reduces the donor potential and consequently leads to a deceleration or a complete ''switching off'' of the electron transfer. The result is a fluorescence emissive complex and the fluorescence of the system is ''switched on'' (Scheme 2B).

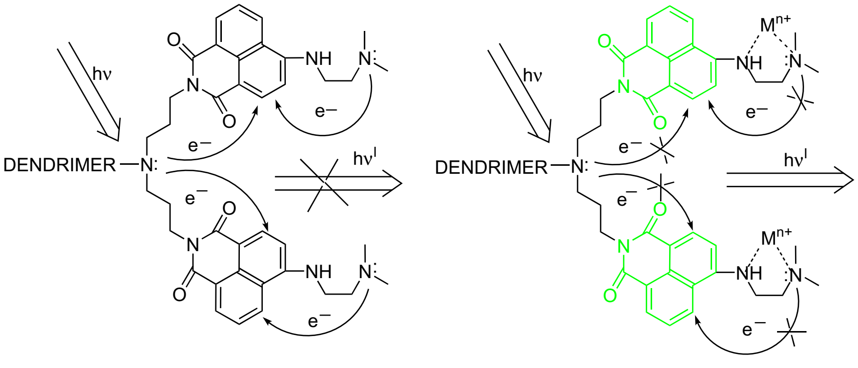
In this case the presence of the guest metal cations in the **D1** solution is signalled quantitatively by fluorescence enhancement factor (FE). $FE = I/I_o$ and is determined from the ratio of the maximum fluorescence intensity (I – after metal ions' addition) and the minimum fluorescence intensity (I_o – metal cations' free). The FE results obtained for the metal cations used in this study are very good, since at least a 5-fold increase in fluorescence intensity is found (Fig. 3). The highest enhancement of the fluorescence intensity is observed in the presence of Pb^{2+} cations (FE = 12.33). For other metal cations, a good FE has also been observed: 10.11 (Zn^{2+}), 8.82 (Co^{2+}), 7.69 (Ag^{+}) 5.32 (Ni^{2+}) and 4.99 (Cu^{2+}). The influence of the metal cations under study upon the fluorescence intensity can be ranked as follows:

$$Pb^{2+} > Zn^{2+} > Co^{2+} > Ag^{+} > Ni^{2+} \approx Cu^{2+}$$

The same effect of fluorescence enhancement has been observed in the case of monomeric 1,8-naphthalimides comprising the same substitutent [6d,8,9]. The investigations have been carried out in the concentration range $10^{-4}/10^{-3}$ mol l^{-1}. The newly synthesized dendrimer is much more sensitive to the presence of metal cations where the maximum effect has been achieved at $c = 10^{-5}$ mol l^{-1}.

As Scheme 2 shows the formation of the complex in the case of **D1** is possible in the amino ''tail'' of the 1,8-naphthalimide units. It is also possible for the metal cations to coordinate in the dendrimer core. The observed total intensity then results from the competitive effects of both complexes formation. The dominating effect in our system is the complex formation in the periphery.

As an example, the fluorescence intensity of **D1** in acetonitrile solution induced by Pb^{2+} is presented in Fig. 4. With the addition of Pb^{2+} to the dendrimer solution up to a concentration of 1×10^{-5} mol l^{-1}, the fluorescence emission increases. In this case the fluorescence enhancement factor is 12.33, but a further increase in the Pb^{2+}concentration causes the fluorescence intensity to decrease. It can also be seen from Fig. 4 that the presence of Pb^{2+} cations induces a hypsochromic shift of the fluorescence maximum ($\Delta\lambda_F = 10$ nm). This blue shift indicates that the switch might bind metal cations via a bidentate



A) OFF - state **B) ON - state**

Scheme 2. Schematic representation of Fluorophore–Spacer–Receptor ON–OFF supramolecular system (**D1**).

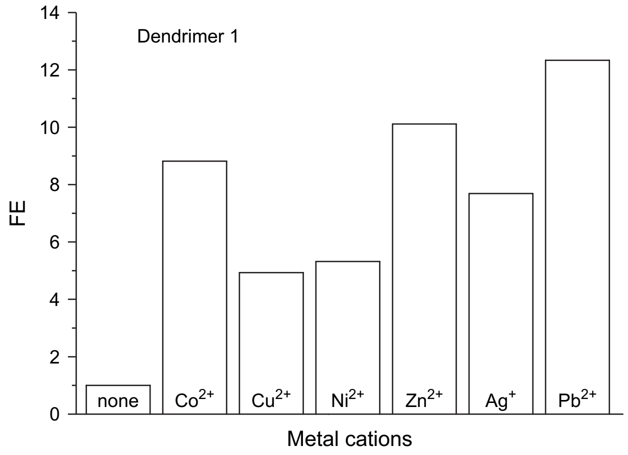


Fig. 3. Fluorescence enhancement factor (FE) of dendrimer **D1** in the presence of different metal cations ($c = 10^{-5}$ mol l^{-1}) in acetonitrile solution. The dendrimer concentration in solution is $c = 1 \times 10^{-6}$ mol l^{-1}.

chelation involving the nitrogen atoms of both the receptor and the 1,8-naphthalimide aromatic amine [12].

The photophysical behaviour of **D2**, which has an *n*-propylamino group as the 1,8-naphthalimide C-4 substituent, is different. This substituent, unlike the *N*,*N*-dimethylaminoethylamino group, is not an electron donor and therefore does not cause a PET process. Hence, the fluorescence quantum yield in acetonitrile is considerably higher ($\Phi_F = 0.583$). No changes in the fluorescence intensity have been observed during the measurements carried out in the presence of the same cations used in the case of **D1** (Zn^{2+}, Ni^{2+}, Pb^{2+}, Co^{2+}, and Ag^{+}). This is an evidence that the cations do not form complexes with the dendrimer molecule. Nevertheless, significant quenching of the fluorescence has been achieved when Cu^{2+} is added to the solution. The quenching is provoked by the formation of a complex between Cu^{2+} ions and the tertiary dendrimer core nitrogen atoms. The result of this complexation is an energy transfer towards the 1,8-naphthalimide units and subsequent quenching of the fluorescence emission.

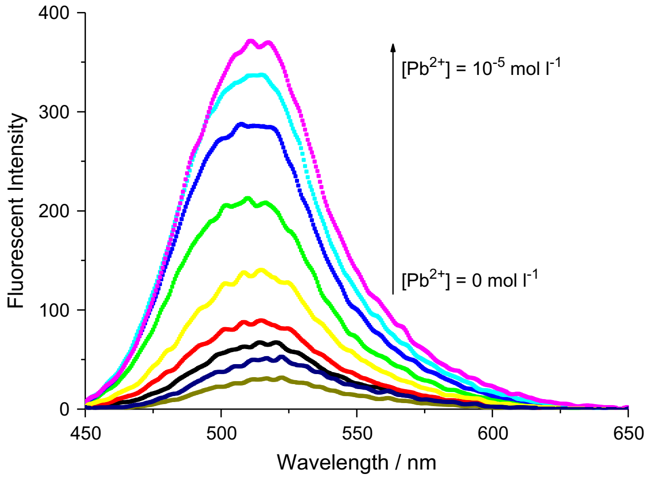


Fig. 4. Fluorescence spectra of **D1** in acetonitrile at different Pb^{2+} concentrations. The concentration of dendrimer is 1×10^{-6} mol l^{-1}.

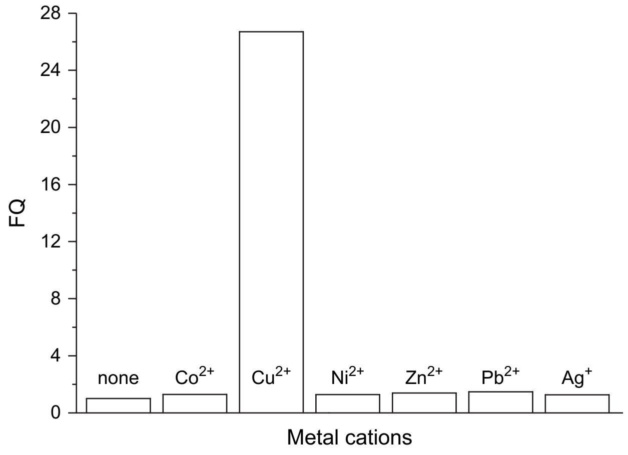


Fig. 5. Fluorescence quenching factor (FQ) of dendrimer **D2** in the presence of different metal cations ($c = 5 \times 10^{-5}$ mol l^{-1}) in acetonitrile solution. The dendrimer concentration in the solution is $c = 1 \times 10^{-6}$ mol l^{-1}.

Fig. 5 shows the dependence of the fluorescence quenching ratio ($FQ = I_o/I$) of dendrimer **D2** in acetonitrile solution on the nature of the metal cation. The FQ is determined from the ratio between the maximum fluorescence intensity (I_o – before the addition of metal cations) and minimum fluorescence intensity (I – after the addition of metal cations). It is seen that the fluorescence quenching depends on the kind of metal cations. The results indicate that this dendrimer can be used as an effective and extremely selective sensor for Cu^{2+} cations.

As shown in Fig. 6, fluorescence quenching of the dendrimer solution is observed upon the addition of Cu^{2+} cations. This dependence has been studied in the 0–1×10^{-5} mol l^{-1} Cu^{2+} cations concentration range. At low Cu^{2+}concentration (1×10^{-6} mol l^{-1}) the quenching effect is 11.5%, which demonstrates good fluorescence sensitivity and a low threshold for sensing this cation. Further addition of Cu^{2+} cations (up to 1×10^{-5} mol l^{-1}) to the dendrimer solution results in

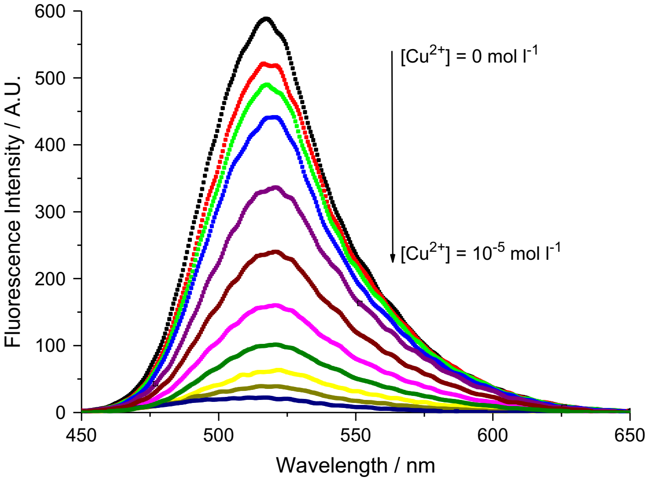


Fig. 6. Fluorescence spectra of dendrimer **D2** in acetonitrile solution at various concentrations of Cu^{2+} cations. The dendrimer concentration in solution is 1×10^{-6} mol l^{-1}.

a decrease of 96% in the fluorescence intensity. Further increase in metal ion concentration has negligible effect. In addition, Fig. 6 shows that the addition of the Cu^{2+} cations does not shift the fluorescence maximum. This agrees with the fact that the complex is formed in the dendrimer core in contrast to the case of **D1** where the complex formation is in the 1,8-naphthalimide tail. The calculated stoichiometry in this case is 1:2.

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

Since some 1,8-naphthalimide derivatives have been used as supramolecular models to design PET based pH sensors [1–3] it was of great interest to investigate the influence of pH on the fluorescence intensity of dendrimers **D1** and **D2**. The fluorescence intensity of both dendrimers was investigated in a pH range of 3.4–10.6 in methanol–water mixed solvent (1:4 v/v). The fluorescence intensity against pH is plotted in Fig. 7. As shown in Fig. 7, only **D1** exhibits high sensitivity to the presence of protons due to the protonation of the distal tertiary nitrogen atoms [$NHCH_2CH_2N(CH_3)_2$] of the C-4 substituents. At pH values up to 6.0 both dendrimers do not change their fluorescence intensity. At $pH > 6$ a drastic decrease in the fluorescence intensity for **D1** has been observed, and finally at $pH = 9.5$ the curve again plateau. The change in the fluorescence intensity of **D1** is negligible. In this case the protonation of the distal tertiary nitrogen atoms of the C-4 substituents stops the PET process and the fluorescence increases. The fluorescence intensity at $pH = 3.4$ is nine times higher than that at $pH = 10.6$. This effect shows that the protonation of the tertiary nitrogen atoms in the dendrimer core has practically no effect on the fluorescence intensity of the new dendrimers. A small reduction of the fluorescence intensity upon protonation has been observed in the case of monomeric 1,8-naphtalimide dye comprising an alkylamino substituent at C-4 position [6e].

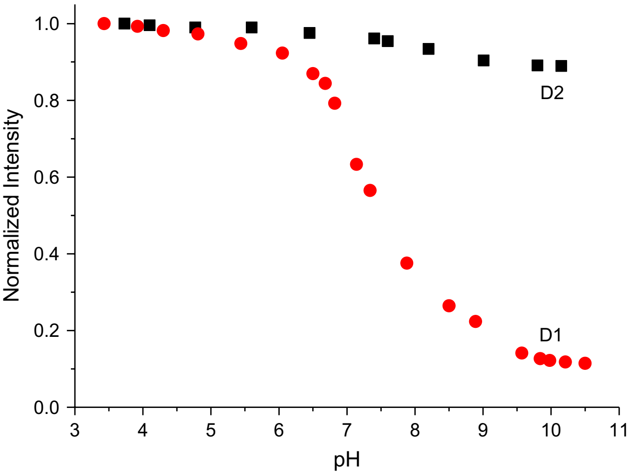


Fig. 7. The influence of pH on the fluorescence intensity at the fluorescence maxima of **D1** and **D2** ($c = 10^{-6}\ mol\,l^{-1}$) investigated in methanol–water (1:4, v/v) solution.

The pH dependence of fluorescence intensity has been analyzed with Eq. (3) and the calculated pK_a value is 7.37. The pK_a value of the PAMAM dendrimer modified with 4-*N*,*N*-dimethylaminoethylamino-1,8-naphthalimide is 8.3 [12e]. These data reveal that nature of the dendrimer core determines its behaviour at different pH.

$$pH - pK_a = \log(I_{F\,max} - I_F)/(I_F - I_{F\,min}) \qquad (3)$$

4. Conclusion

New 1,8-naphthalimide modified second generation poly(propyleneimine) dendrimers have been synthesized for the first time. Their photophysical characteristics have been studied in organic solvents of different polarity. The effect of various metal cations upon the fluorescent intensity has been studied in detail in acetonitrile solution. Particular attention has been paid to the influence of the 1,8-naphthalimide fragment C-4 substituent. The fluorescence intensity of dendrimer **D1**, containing an *N*,*N*-diethylaminoethylenamino group substitutent at C-4 position, increases in the presence of metal ions (Zn^{2+}, Ni^{2+}, Pb^{2+}, Co^{2+}, Cu^{2+} and Ag^{+}), due to the complex formation between the added metal ion and the unshared electron pair from the nitrogen atoms at C-4 position. The newly synthesized dendrimer is a much better sensor than the low molecular weight 1,8-naphthalimide ones. In the case of **D2**, a selective complex formation only with Cu^{2+} occurs. The dendrimer **D1** also shows a considerable increase in the fluorescence intensity at acidic pH values ($pH < 6$), suggesting that it could be used as ON–OFF probes in analytical devices for signalling the presence of protons. On the basis of this present investigation, the new dendrimers show promise for use as PET fluorescent sensors of metal cations and protons present in the environment.

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