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First generation poly(propyleneimine) dendrimers functionalised with 1,8-naphthalimide units as fluorescence sensors for metal cations and protons

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Abstract

The synthesis of two new green fluorescent poly(propyleneimine) dendrimers from first generation has been described. The new materials are comprised of a 1,8-naphthalimide fluorophore having a substituent at C-4 position. The substituent in the first case is a *N*,*N*-dimethylaminoethylamino group while in the second one it is *N*-methylpiperazine. The spectroscopic and photophysical characteristics of the new dendrimers determined in organic solvent of different polarity have been presented. Both dendrimers show substantial increases in their fluorescence intensity in the presence of metal cations (Zn^{2+}, Co^{2+}, Ni^{2+}, Pb^{2+}, Mn^{2+}, Cu^{2+}, Fe^{3+} and Ag^{+}) and protons. The influence of the photoinduced electron transfer on their sensing properties has been discussed.

Keywords: Poly(propyleneimine) dendrimer; 1,8-Naphthalimide; Photoinduced electron transfer; Fluorescent sensors; Metal cations; Protons; Fluorescence

1. Introduction

Fluorosensors based on the photoinduced electron transfer (PET) are generally multi-component systems comprising a signalling moiety (fluorophore), a guest binding site (usually termed as receptor) and a spacer unit.[1–3] The components are chosen so that the PET between the receptor and the fluorophore results into 'switching off' the fluorescence. In the presence of a guest, interacting with the electron pair of the receptor, PET between the receptor and fluorophore is hampered. This 'switches on' the fluorescence of the system. Thus, the presence of a guest is signalled by a change in the fluorescence of the system. Notably the structurally simple fluorophore–spacer–receptor system that comprises an electron deficient fluorophore can exhibit fluorescence 'off–on' signalling even in the presence of transition metal cations or protons, well known for their fluorescence quenching abilities.

Dendrimers as monodisperse three-dimensional macromolecular compounds possessing a well defined structure have turned very promising for these purposes. 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.[4]

Our investigations on the synthesis and photophysical properties of some PAMAM derivatives comprising 1,8-naphthalimide units in their periphery have been published.[5] Their fluorescence properties in the presence of different metal cations have showed that these dendrimers could act as effective sensors for metal cations.

In this paper we present the synthesis and functional properties of two new green fluorescent poly(propyleneimine)

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dendrimers (PPI) from first generation having 1,8-naphthalimide units in the periphery. *N*,*N*-Dimethylaminoethylamino and *N*-methylpiperidine as receptors for metal cations and protons have been used as substituents at C-4 position of the 1,8-naphthalimides. The photophysical properties of both dendrimers in the presence of metal cations and protons have been also investigated with regard to their potential application as fluorosensors.

2. Results and discussion

2.1. Synthesis of 1,8-naphthalimide-labelled PPI dendrimers

1,8-Naphthalimide has been chosen as fluorophore for the peripheral functionalization of the PPI dendrimers because its photophysical properties can be modified easily. On the other hand, the 1,8-naphthalimides are a medium sensitive chromophoric class whose fluorescence response based on the energy or photoinduced electron transfer can be used for sensors detecting pollutants of the environment.[6]

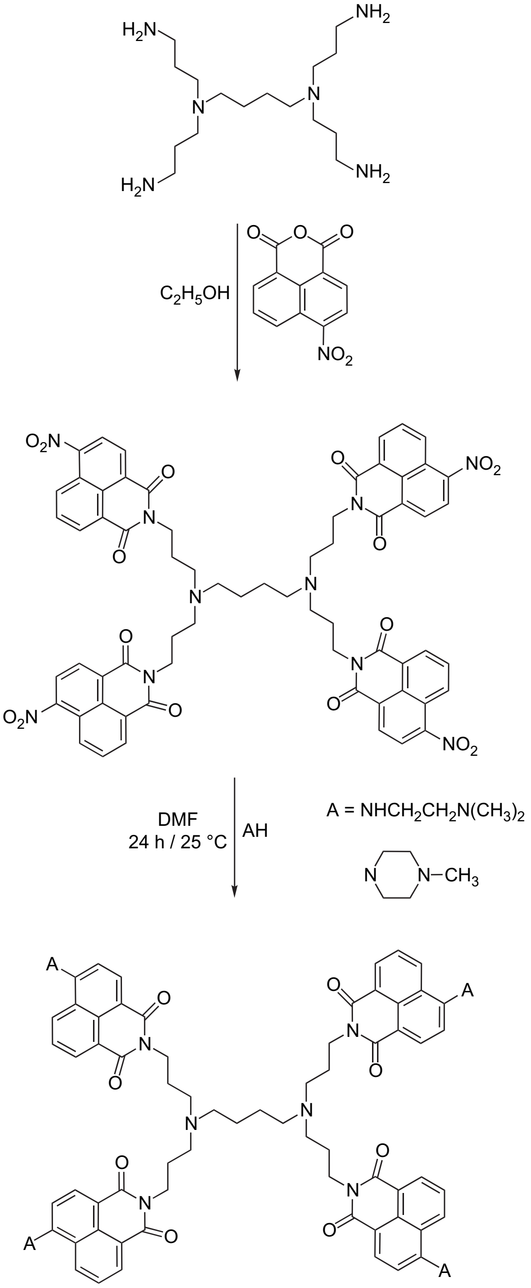
PPI modified dendrimers have been synthesized in a three-step synthetic route, which is depicted in Scheme 1. A commercial PPI of first generation comprising four primary amino groups in its periphery was used as an initial material. The condensation of PPI with 4-nitro-1,8-naphthalanhydride was run in boiling ethanol for 6 h. The course of the reaction was followed on by TLC. After cooling the mixture to room temperature the precipitate was filtered off and dried under vacuum at 40 °C. The nucleophilic substitutions of the nitro group with the investigated *N*,*N*-dimethylaminoethylamine and *N*-methylpiperazine were accomplished in DMF medium at room temperature for 24 h. The nucleophilic substitution is favoured by the electron acceptor carbonyl groups from the naphthalimide structure.[7]

The final products for both PPI dendrimers were obtained after precipitation with water and filtration of the solid residue. FTIR, ^{1}H NMR, ^{13}C NMR spectroscopy studies and elemental analysis confirmed the chemical structure of the products.

2.2. Photophysical properties of PPI1 and PPI2 in organic solvents

The photophysical characteristics of the two dendrimers have been studied in solvents of different polarity with regard to elucidation of the PET processes.

The dendrimer having a nitro group as a substituent in a DMF solution is colourless and has a maximum absorbance at λ_A=336 nm. It does not emit any fluorescence. The lack of colour and fluorescence emission are due to the electron acceptor nature of the nitro group at C-4 position. It fails to get into donor–acceptor interaction with the electron acceptor carbonyl groups in the 1,8-napthalimide fluorophores. Upon substitution of the nitro group with an electron donating amino group the naphthalimide fluorophores are polarized and their solutions are yellow and emit yellow-green fluorescence in all the solvents studied. Tables 1 and 2 summarize the photophysical characteristics of PPI1 and PPI2 dendrimers: the absorption (λ_A) and fluorescence (λ_F) maxima, the molar extinction coefficient (ε), the Stokes shift ($\nu_A-\nu_F$) and fluorescence quantum yield (Φ_F).



Scheme 1. Synthesis of dendrimers PPI1 A=(NHCH$_2$CH$_2$N(CH$_3$)$_2$) and PPI2 A=*N*-methylpiperizine.

Both dendrimers exhibit a positive solvatochromism observed for monomeric 1,8-naphthalimide fluorophores as well as for PAMAM dendrimers comprising 1,8-naphthalimides in their periphery.[5d,5i,5k,8] Comparing the spectra taken in all solvents one can see that the positions of absorption and fluorescent maxima of PPI1 and PPI2 are hypsochromically shifted, which is due to the more pronounced electron donating nature of the secondary amino group positioned on the 1,8-naphthalimide fragment. Hence, the fluorophore is more polarized. On the other hand the conformation changes are

Table 1
Photophysical properties of PPI1 in different organic solvents

Solvent	λ_A (nm)	λ_F (nm)	ε ($l\,mol^{-1}\,cm^{-1}$)	$\nu_A-\nu_F$ (cm^{-1})	Φ_F
Methanol	438	528	44,600	3892	0.022
Ethanol	438	527	44,300	3856	0.031
Propanol	436	526	45,100	3924	0.024
Acetonitrile	434	523	44,800	3921	0.019
DMF	436	526	44,200	3924	0.018
Acetone	432	518	45,600	3843	0.511
Dichloromethane	428	508	45,800	3679	0.601
Chloroform	426	504	45,800	3633	0.861
Tetrahydrofurane	426	505	45,900	3553	0.839

more likely in the case of *N*-methylpiperazine fragment as a cyclic amine. This also affects the photophysical characteristics of PPI2, which is also confirmed by the higher values of the Stokes shift.

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 estimated from the absorption and fluorescence spectra of the dendrimers according to Eq. 1

$$\Phi_F = \Phi_{st}\frac{S_u}{S_{st}}\frac{A_{st}}{A_u}\frac{n^2_{Du}}{n^2_{Dst}} \tag{1}$$

where the Φ_F is the emission quantum yield of the sample, Φ_{st} is the emission quantum yield of the fluorescein, A_{st} and A_u represent, respectively, the absorbance of the standard and sample, while S_{st} and S_u are the integrated emission band areas of the standard and sample, respectively, and n_{st} and n_u are the solvent refractive index of the standard and sample, subscripts u and st refer to the unknown and standard, respectively.

The results obtained about the quantum yield of the dendrimers show that Φ_F depends exclusively on the solvent polarity (Tables 1 and 2). The PET process is accelerated in polar organic solvents thus, leading to lower fluorescence quantum yield.[9] Such behaviour has also been exhibited by similar monomeric 4-*N*,*N*-dimethylaminoethylamino-*N*-alkyl-1,8-naphthalimides and 4-*N*-methylpiperazino-*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.[6d,6i,10,11] The Φ_F values for PPI2, which are relatively lower than those for PPI1 might be on account of the conformational changes in the piperazine ring. They might be caused by the rotation of the piperazine ring around the N–C4 bond and to the changes in the latter's planar position with respect to the naphthalene ring plane.

Table 2
Photophysical properties of PPI2 in different organic solvents

Solvent	λ_A (nm)	λ_F (nm)	ε ($l\,mol^{-1}\,cm^{-1}$)	$\nu_A-\nu_F$ (cm^{-1})	Φ_F
Methanol	418	526	40,500	4912	0.014
Ethanol	416	524	41,000	4954	0.018
Propanol	414	523	40,900	5034	0.013
Acetonitrile	414	520	41,300	4923	0.010
DMF	414	522	40,100	4997	0.011
Acetone	410	516	42,200	5010	0.390
Dichloromethane	408	508	42,600	4825	0.532
Chloroform	404	504	42,500	4911	0.672
Tetrahydrofurane	403	506	42,200	5051	0.644

2.3. *Influence of metal cations on the fluorescence intensity of the dendrimers PPI1 and PPI2*

The ability of the new PPI1 and PPI2 dendrimers to detect metal cations has been tested in acetonitrile solution in the presence of various metal cations (Pb^{2+}, Zn^{2+}, Co^{2+}, Ni^{2+}, Mn^{2+}, Cu^{2+} and Fe^{3+}, Ag^{+}) in view of their potential sensor application. Acetonitrile has been chosen as a solvent for all the spectral measurements in the presence of metal cations since it has a low quantum fluorescent yield and favours the PET fluorescence switch. On the other hand, this solvent guarantees a good solubility of the used PPI1 and PPI2 as ligands, their complexes with metal cations and respective metal salts as source for the metal cations. The influence of the studied metal cations and their concentration upon the fluorescence intensity of new dendrimers has been investigated spectrophotometricaly.

Figure 1 plots an exemplary case of the changes in the fluorescent intensity of PPI1 as a function of the concentration of Pb^{2+} cations. The dendrimers free of metal cations, in acetonitrile have a very weak fluorescence emission. The addition of Pb^{2+} cations to the dendrimer solution leads to a considerable increase in the fluorescence emission. The increase in fluorescence intensity occurs after the addition of Pb^{2+}cations in $0-2\times10^{-5}$ mol l^{-1} concentration range. The addition of Pb^{2+} at concentration 1.66×10^{-6} mol l^{-1} produces 46% enhancement in the fluorescence intensity, which proves good sensitivity. Raising the concentration of the cation ion up to 4×10^{-6} mol l^{-1} also induces an increase in the fluorescence. At a certain moment ($c=4\times10^{-6}$ mol l^{-1}) the solution saturates and the increase in the fluorescence is negligible. The inset shows how a single dendrimer molecule can form a complex with four metal cations

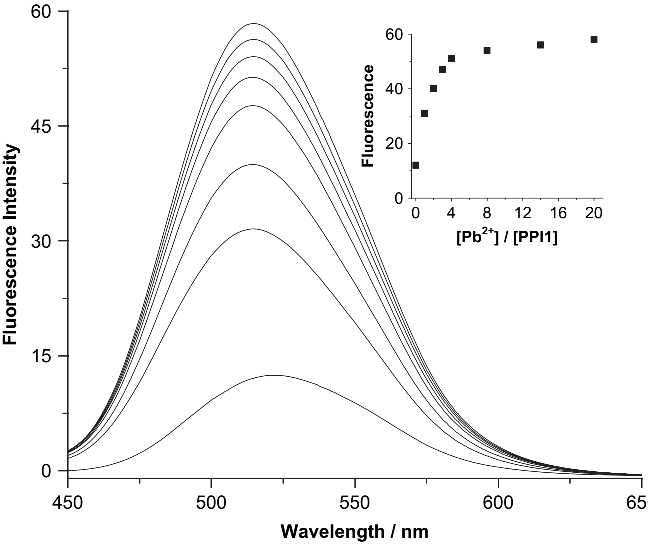
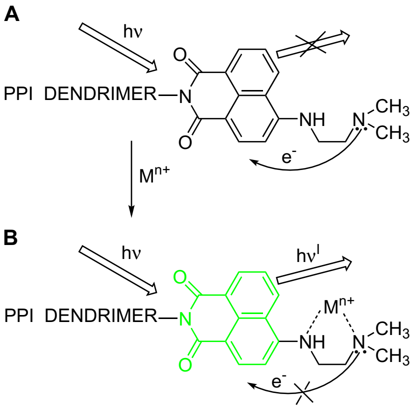


Figure 1. Fluorescence spectra of PPI1 in acetonitrile at various concentrations of Pb^{2+}. The concentrations of Pb^{2+} cations are in order of increasing intensity from 0 to 2×10^{-5} mol l^{-1}. The concentration of dendrimer is 1×10^{-6} mol l^{-1}. The inset displays the relationship between the fluorescence and concentration of Pb^{2+}.

corresponding to the number of its receptor units. It is seen also from Figure 1 that the position of the fluorescence maxima is progressively shifted from 523 to 513 nm with the addition of Pb^{2+} cations, which indicates that the electron donating nitrogen at C-4 position of the 1,8-naphthalimide, in the excited state, participates in PPI1–Pb^{2+} cation complexation. The fluorescence of PPI1 is influenced in the same way by the presence of the other metal cations investigated (Fe^{3+}, Zn^{2+}, Co^{2+}, Ni^{2+}, Mn^{2+}, Cu^{2+} and Ag^{+}).

Scheme 2 illustrates the 'Fluorophore–Spacer–Receptor' supramolecular system when modified with 1,8-naphthalimide PPI dendrimer hosts the guest metal cations. The interaction between the fluorophore (1,8-naphthalimide) and the receptor (*N*,*N*-dimethylamino group) provoking photoinduced electron transfer leads to quenching of the fluorescence emission Scheme 2(A). The presence of the metal cations in the dendrimer solution changes its properties since the system is highly fluorescent in this case (Scheme 2(B)). The substituent at C-4 position of the 1,8-naphthalimide structure is a *N*,*N*-dimethylaminoethylamine residue with which metal cations could coordinate.‘

Thus the presence of metal cations in the dendrimer solution is signalled by an enhancement of the fluorescence intensity (FE). 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).



Scheme 2. Proposed mechanism of fluorescence enhancement of 4-*N*,*N*-dimethylaminoethylamino-1,8-naphthalimide labeled PPI dendrimer.

Figure 2 presents the dependence of fluorescence enhancement on the nature of metal cations. As seen the nature of the metal cations determine the fluorescence enhancement—the slightest increase is in the presence of Co^{2+} cations. Figure 3 shows the FE data of dendrimer PPI2. The presence of metal cations in the dendrimer solution increases significantly the fluorescence intensity. Similarly to the case of PPI1 Co^{2+} cations have the slightest effect. Probably these cations cannot form easily a complex with the receptors of the two dendrimers. Hence, the fluorescence intensity of their complexes is weaker. FE values for PPI2 are higher than those for PPI1. It demonstrates its greater ability to form complexes with the metal cations discussed. This fact is probably due to the chemical nature of the new dendrimer as well as to the geometry of the complexes formed. None of the two dendrimers exhibits selectivity to the metal cations studied.

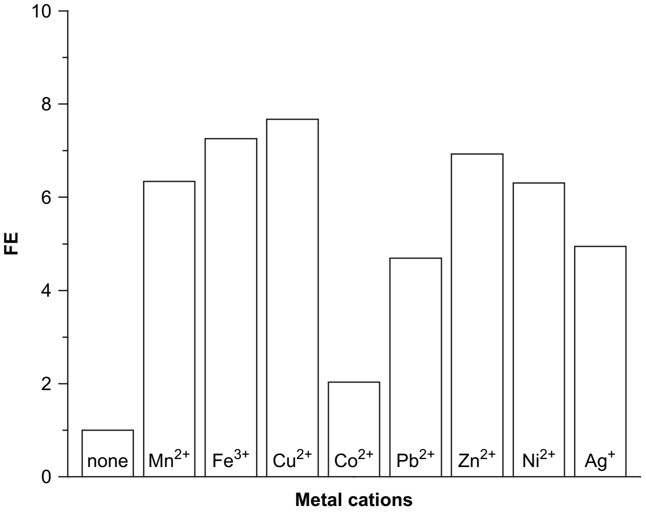


Figure 2. Fluorescence enhancement factor (FE) of dendrimer PPI1 in the presence of different metal cations in acetonitrile solution ($c=4\times10^{-6}$ mol l^{-1}). The dendrimer concentration in the solution is $c=1\times10^{-6}$ mol l^{-1}.

The spectra of a dendrimer–metal cations complex have a Stokes shift smaller than that of the dendrimers alone. That indicates the stabilized planarity of the chromophoric structure after the complexation. In this case the non-radiative emission during the transition from S_1 to the ground state S_0 is smaller and leads to higher fluorescence quantum yields (See Table 3). The highest quantum yield for the PPI1 has been obtained in the presence of Cu^{2+} cations ($\Phi_F=0.231$), while in the case of dendrimer PPI2 Fe^{3+} cations produce the highest quantum yield ($\Phi_F=0.198$).

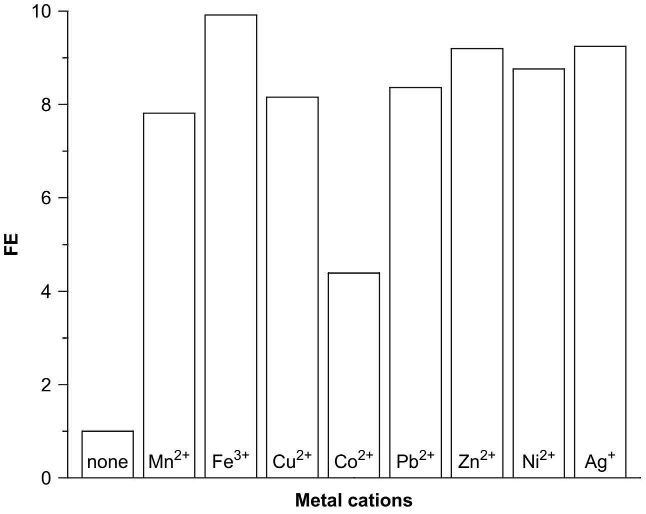


Figure 3. Fluorescence enhancement factor (FE) of dendrimer PP2 in the presence of different metal cations in acetonitrile solution ($c=4\times10^{-6}$ mol l^{-1}). The dendrimer concentration in the solution is $c=1\times10^{-6}$ mol l^{-1}.

Table 3
Quantum yields of dendrimers PPI1 and PPI2 in acetonitrile solution in the presence of metal cations ($c=5\times10^{-6}$ mol l^{-1})

	—	Ag^+	Mn^{2+}	Cu^{2+}	Co^{2+}	Pb^{2+}	Zn^{2+}	Ni^{2+}	Fe^{3+}
PPI1	0.019	0.191	0.204	0.231	0.076	0.163	0.216	0.200	0.218
PPI2	0.010	0.185	0.168	0.161	0.095	0.171	0.184	0.178	0.198

The concentration of the dendrimer is 1×10^{-6} mol l^{-1}.

2.4. Influence of protons on the fluorescence intensity of dendrimers PPI1 and PPI2

As already underlined above, the fluorescence of 1,8-naphthalimide units bonded to the dendrimer periphery, may be affected by a PET weakening, and can be used as a sensor for detecting protons in the medium.

The fluorescence intensity of dendrimers PPI1 and PPI2 versus pH is plotted in Figure 4. The fluorescence intensity was measured in methanol/water (1:4 v/v) and the pH was adjusted by HCl or NaOH addition. The experiments were carried out in the pH range from 3.2 to 11.1. It is clearly shown in Figure 4 that, due to the increasing electrostatic repulsions between protonated sites, the successive neutralizations of the amine sites allows the fluorescence to change over a wider pH scale. Both dendrimers in methanol/water (1:4 v/v) have a fluorescence enhancement: FE=12.5 for PPI1 and FE=10.1 for PPI2, respectively.

The pK_a for the dendrimers under study were calculated using Eq. 2.

$$\mathrm{pH} - \mathrm{p}K_a = \log(I_{\mathrm{Fmax}} - I_{\mathrm{F}})/(I_{\mathrm{F}} - I_{\mathrm{Fmin}}) \qquad (2)$$

The calculated pK_a values for both PPI1 and PPI2 are 7.9 and 6.4, respectively. This significant difference is due to the basic nature of the distal amino groups from the C-4 substituents and their facilities of protonation ability. On the other hand, they correspond to the value already measured for monomeric naphthalimide fluorophore having the same substituents at C-4 position. This shows that the protonation of outer rim remote tertiary amines is responsible for the main part of the fluorescence enhancement.

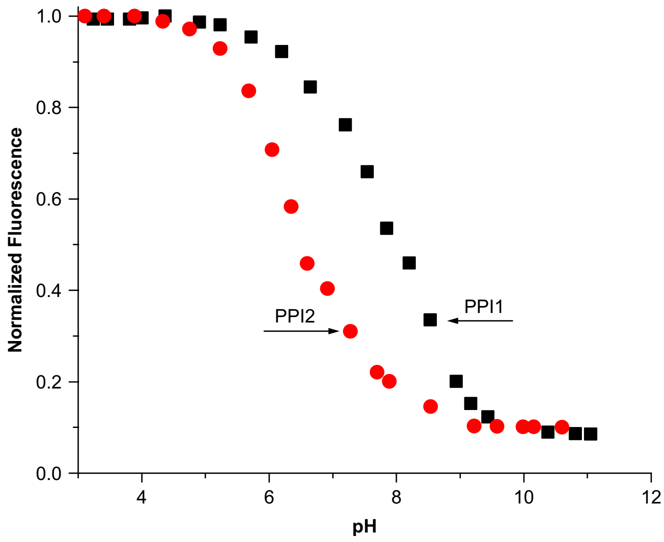


Figure 4. pH dependence of the normalized fluorescence intensity for PPI1 and PPI2 measured at room temperature.

3. Conclusions

Two new green fluorescence poly(propyleneimine) dendrimers with 1,8-naphthalimide units in their periphery have been synthesized by the condensation of poly(propyleneimine) from zero generation and 4-nitro-1,8-naphthalic anhydride. The final products have been obtained by nucleophilic substitution of the nitro groups by the *N*,*N*-dimethylaminoethylamine or *N*-methylpiperizine. The photophysical properties of the dendrimers exhibit a solvatochromic dependence and a good PET in organic solvents. Both derivatives show larger increases in their fluorescence emission in the presence of metal cations like as Zn^{2+}, Co^{2+}, Ni^{2+}, Pb^{2+} Mn^{2+}, Cu^{2+}, Fe^{3+} and Ag^+. In fact, the metal cations interact with the terminal *N*,*N*-dimethylaminoethylamino (PPI1) respective *N*-methylpiperizino (PPI2) groups from the 1,8-naphthalimide chromophoric system. It has also been shown that the fluorescence intensity depends on the nature of these metal cations. The dendrimers show also a considerable increase in their fluorescence intensity at low pH values, suggesting that they could be used as 'on—off' probes in analytical devices for signalling the availability of protons. On the basis of the present investigation it can be assumed that the new dendrimers are suitable materials for the production of fluorescent sensors for detection of metal cations and protons.

4. Experimental part

4.1. Materials and methods

Materials: poly(polypropyleneimine) (PPI) dendrimer from zero generation and 4-nitro-1,8-naphthalic anhydride were used as obtained from Aldrich. All organic solvents (methanol, ethanol, propanol, acetonitrile, *N*,*N*-dimethylformamide, acetone, dichloromethane, chloroform and tetrahydrofuran) used in this study were of spectroscopic grade and used without special treatment. $Cu(NO_3)_2\cdot3H_2O$, $Ni(NO_3)_2\cdot6H_2O$, $Pb(NO_3)_2$, $Mn(NO_3)_2$, $Co(NO_3)_2\cdot6H_2O$, $Fe(NO_3)_3$, $Zn(NO_3)_2\cdot4H_2O$ and $AgNO_3$ were used as sources for metal cations.

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

Poly(propyleneimine) (0.001 mol) and 0.004 mol of 4-nitro-1,8-naphthalic anhydride 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%. FTIR (KBr) cm^{-1}: 3076, 2924, 2852, 1705, 1663, 1582, 1527, 1345, 785, 760. Analysis: $C_{64}H_{52}N_{10}O_{16}$ (1216.2) calcd: C, 63.15; H, 4.27; N, 11.51. Found: C, 63.28; H, 4.22; N, 11.48.

4.1.2. Synthesis of 4-N,N-dimethylaminoethylamino-1,8-naphthalimide-labelled PPI1

4-Nitro-1,8-naphthalimide-labelled dendrimer (0.0005 mol) was reacted with 0.002 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 vacuum at 40 °C. Yield: 73%. FTIR (KBr) cm^{-1}: 3075, 2927, 2856, 1682, 1642, 1580, 1462, 1358, 776, 758. ^1H NMR ($CDCl_3$, 400 MHz, ppm): 8.34 (d, J=8.2 Hz, 4H, Ar–H), 8.18 (d, J=7.1 Hz, 4H, Ar–H), 8.02 (d, J=8.3 Hz, 4H, Ar–H), 7.41 (dd, J=8.2 Hz, J=7.0 Hz, 4H, Ar–H), 7.36 (br s, 4H, NH), 6.48 (d, J=8.4 Hz, 4H, Ar–H), 3.90 (m, 8H, $(OC)_2NC\mathit{H}_2$), 2.51–2.30 (m, 24H, $C\mathit{H}_2N<$+8H, $C\mathit{H}_2N(CH_3)_2$), 2.30–2.11 (m, 8H, $C\mathit{H}_2NH-$), 2.01 (s, 24H, $CH_2N(C\mathit{H}_3)_2$). ^{13}C NMR ($CDCl_3$) δ (ppm): 163.72, 162.84, 150.08, 134.86, 130.62, 129.81, 128.24, 124.55, 121.13, 118.90, 107.71, 103.62, 50.02, 46.15, 40.73, 38.72, 24.35. Analysis: $C_{80}H_{92}N_{10}O_8$ (1330.3) calcd: C, 72.16; H, 6.91; N, 10.52. Found: C, 72.09; H, 6.98; N, 10.46.

4.1.3. Synthesis of 4-N-methylpiperazino-1,8-naphthalimide-labelled PPI2

The synthesis was run according to the same procedure as PPI using *N*-methylpiperazine. Yield: 68%. FTIR (KBr) cm^{-1}: 3074, 2936, 2849, 1693, 1661, 1585, 1485, 1353, 785, 759. ^1H NMR ($CDCl_3$, 400 MHz, ppm): 8.48 (d, J=8.2 Hz, 4H, Ar–H), 8.31 (d, J=8.1 Hz, 4H, Ar–H), 8.14 (d, J=8.4 Hz, 4H, Ar–H), 7.87 (br s, 4H, NH), 7.43 (dd, J=8.1 Hz, J=6.2 Hz, 4H, Ar–H), 6.64 (d, J=8.4 Hz, 4H, Ar–H), 4.12 (m, 8H, $(OC)_2NC\mathit{H}_2$), 2.84–2.60 (m, 24H, $C\mathit{H}_2N<$), 1.84 (m, 32H, $-NC\mathit{H}_2C\mathit{H}_2N-$), 1.14 (m, 12H, $N-C\mathit{H}_3$). ^{13}C NMR ($CDCl_3$) δ (ppm): 164.46, 163.94, 149.34, 134.43, 131.06, 129.59, 125.73, 124.64, 123.22, 120.02, 110.27, 104.32, 51.40, 45.45, 41.67, 25.37, 11.70. Analysis: $C_{84}H_{96}N_{14}O_8$ (1428.4) calcd: C, 70.59; H, 6.72; N, 13.72, Found: C, 70.43; H, 6.68; N, 13.85.

4.2. Analysis

UV–vis spectrophotometric investigations were performed on a Kontron 930 spectrophotometer at 1×10^{-6} mol l^{-1}. The fluorescence spectra were taken on a JASCO FP-6500 spectrofluorimeter at 1×10^{-6} mol l^{-1}. All organic solvents used in this study were of spectroscopic grade. Fluorescence quantum yield was determined on the basis of the absorption and fluorescence spectra. Fluorescein was used as a reference (Φ_F=0.85).

The NMR spectra were obtained on a Bruker DRX-250 spectrometer, operating at 250.13 and 62.90 MHz for ^1H and ^{13}C, respectively, using a dual 5 mm probe head. The measurements were carried out in $CDCl_3$ solution at ambient temperature. The chemical shifts were referenced to tetramethylsilane (TMS). The distortionless enhancement by polarization transfer (DEPT) spectra were recorded under the same conditions as the ^{13}C NMR spectra.

The IR spectra of both 1,8-naphthalimide labelled dendrimers were measured on a Bruker IFS-113v spectrometer at a 2 cm^{-1} resolution using KBr pellets. The effect of the metal cations and protons upon the fluorescence intensity was examined by adding a few μl 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.[12] The pH was adjusted by addition of HCl or NaOH into 100 ml of water/methanol (4:1) solvent. All spectral measurements in this study were performed at room temperature.

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