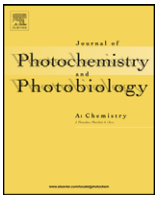
Journal of Photochemistry and Photobiology A: Chemistry 201 (2009) 75–80

Contents lists available at ScienceDirect

Journal of Photochemistry and Photobiology A: Chemistry

journal homepage: www.elsevier.com/locate/jphotochem



A new colorimetric and fluorimetric sensor for metal cations based on poly(propilene amine) dendrimer modified with 1,8-naphthalimide

Ivo Grabchev[a,*], Paula Bosch[b], Mark McKenna[b], D. Staneva[c]

[a] *Institute of Polymers, Bulgarian Academy of Sciences, Akad. G. Bonchev 103 A., 1113 Sofia, Bulgaria*
[b] *Institute of Science and Technology of Polymers, CSIC, Juan de la Cierva 3, 28006 Madrid, Spain*
[c] *Institute of Organic Chemistry with Centre of Phytochemistry Bulgarian Academy of Sciences, 1113 Sofia, Bulgaria*

ARTICLE INFO

Article history:
Received 10 April 2008
Received in revised form
29 September 2008
Accepted 2 October 2008
Available online 19 October 2008

Keywords:
poly(propylene amine)
Dendrimer
Sensors
1,8-Naphthalimide
Fluorescence

ABSTRACT

A new fluorescent first generation poly(propylene amine) dendrimer (PPI), peripherally modified with 4(butylamino-substituted-1,8-naphthalimide), has been synthesized and characterized. Its photophysical characteristics in organic solvents of different polarities were studied, and the influence of sodium hydroxide on its spectral characteristics in *N*,*N*-dimethylformamide is discussed. The complexes formed between the dendrimer and metal cations in solution have been studied with regard to the potential applications of the new dendrimer as a colorimetric and fluorescent sensor for metal ions. The fluorescence intensity of the dendrimer in the presence of metal cations (Zn^{2+}, Co^{2+}, Pb^{2+}, Mn^{2+}, Cu^{2+} and Fe^{3+}) increases substantially revealing its sensor potential.

1. Introduction

Dendrimers are a class of macromolecules that have been attracting a lot of attention and have been extensively studied in recent years [1–3]. They have well-defined three-dimensional structures, having different functional groups that allow the creation of molecules with desired properties. Luminescent dendrimers are a special class of dendrimers, which find use in high technology; especially in optoelectronics, light-harvesting antenna systems for solar energy conversion, sensors for environment pollutants, and in biology and medicine [4–6]. For sensor applications the ability of dendrimers to coordinate metal ions in their interior branches or in their exterior units is exploited in order to enhance the selectivity and sensitivity of the analysis. On the other hand, the presence of more chromophoric moieties in one macromolecule leads to sensing with signal amplification. Our previous studies were focused on the modification of poly(amidoamine) [7] or poly(propylene amine) [8] dendrimers with 1,8-naphthalimide chromophoric groups, and on their eligibility as sensors for transition metal cations and protons based on photoinduced electron transfer.

The present study is focused on the peripherally modification of a first generation poly(propylene amine)amine dendrimer with a 4-butylamino-1,8-naphthalimide chromophore. Its photophysical properties in the presence of transition metal cations and protons have been investigated viewing its use as colorimetric and fluorescent sensors.

2. Experimental

2.1. Materials and methods

Materials

The synthesis of the precursor 4-nitro-1,8-naphthalimide-labelled PPI has been described previously [8b].

Organic solvents (methanol, ethanol, propanol, acetonitrile, *N*,*N*-dimethylformamide (DMF), acetone, dichloromethane, chloroform, tetrahydrofurane 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 $Fe(NO_3)_3{\cdot}9H_2O$ salts were the metal cation sources and used as obtained from Aldrich.

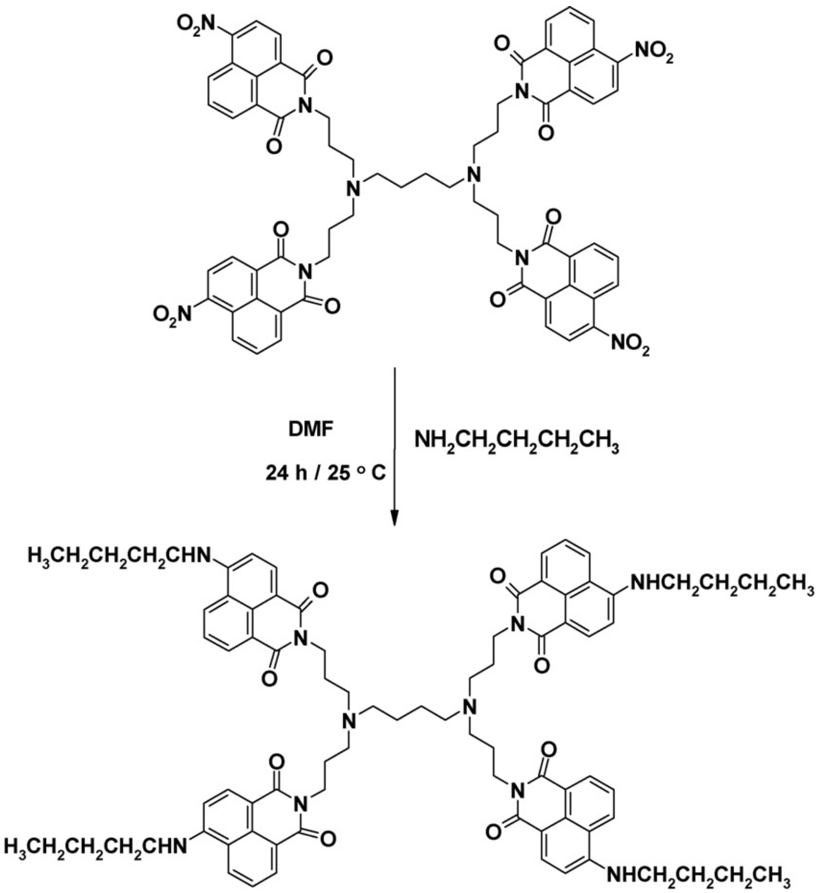
2.2. Synthesis of 4-butylamino-1,8-naphthalimide-labelled dendrimer

0.0005 mol of 4-nitro-1,8-naphthalimide-labelled dendrimer was reacted with 0.002 mol of *n*-butylamine in 50 ml of *N*,*N*-

---

* Corresponding author. Tel.: +359 2 9792293.
E-mail address: grabchev@polymer.bas.bg (I. Grabchev).

1010-6030/$ – see front matter © 2008 Elsevier B.V. All rights reserved.
doi:10.1016/j.jphotochem.2008.10.008



Scheme 1. Synthesis of 4-butylamino-1,8-naphthalimide-labelled poly(propylene amine).

dimethylformamide for 24 h at room temperature. After that 500 ml of water were added to the solution, the precipitate was filtered off, washed with water, and then dried in vacuum at 40 °C. Yield: 85%.

FT-IR (KBr) cm^{-1}: 3367, 2955, 2922, 2867, 1683, 1636, 1528, 1547, 1357, 1245, 774 and 758.

^{1}H NMR ($CDCl_3$, 400 MHz ppm): 8.48 (d, J = 8.4 Hz, 4H, Ar–H), 8.34 (d, J = 8.0 Hz, 4H, Ar–H), 7.90 (d, J = 8.1 Hz, 4H, Ar–H), 7.49 (d, J = 8.3 Hz, 4H, Ar–H), 7.36 (brs, 4H, NH), 6.62 (d, J = 8.8 Hz, 4H, Ar–H), 5.30–5.24 (m, 8H, $\mathrm{C}\mathit{H}_2\mathrm{NH}$–), 4.08–3.94 (m, 8H, $(\mathrm{OC})_2\mathrm{NC}\mathit{H}_2$), 3.33–3.30 (m, 8H, $>\mathrm{NCH_2C}\mathit{H}_2\mathrm{CH_2N}<$, 3.24–3.21 (m, 4H, $>\mathrm{NC}\mathit{H}_2\mathrm{CH_2CH_2C}\mathit{H}_2\mathrm{N}<$, 2.54–2.38 (m, 12H, $\mathrm{C}\mathit{H}_2\mathrm{N}<$), 1.73–1.66 (m, 8H, $\mathrm{CH_2C}\mathit{H}_2\mathrm{CH_3}$), 1.46–1.38 (m, 8H, $\mathrm{C}\mathit{H}_2\mathrm{CH_2CH_3}$) and 0.86–0.92 (m, 12H, $\mathrm{CH_2C}\mathit{H}_3$). ^{13}C NMR ($CDCl_3$) δ (ppm): 164.68, 164.15, 149.53, 134.66, 131.20, 129.80, 125.90, 124.80, 124.63, 124.20, 120.3, 104.50, 43.71, 40.20, 38.80, 31.32, 30.54, 29.98, 20.60 and 14.61.

2.3. Analysis

UV–vis spectrophotometric investigations were performed on a Lambda 35 spectrophotometer at concentrations of 1×10^{-5} mol l^{-1}. The fluorescence spectra were taken on a Perkin Elmer LS55 spectrophotometer at concentrations of 1×10^{-5} mol l^{-1}. The signals of the fluorimeter were corrected for the response of the emission monochromator and detector. The experimental error was estimated to be 2 nm on the absorption and fluorescence maxima and 5% on the molar extinction coefficient [9,10]. Fluorescence quantum yields were determined on the basis of the absorption and fluorescence spectra exiting at the absorption maximum. Fluorescein was used as a reference ($\Phi_F = 0.85$). The error on the quantum yield values is estimated to be 5% according to Refs. [9,10]. The NMR spectra were obtained on an Oxford AS400 operating at 400 MHz and 100 MHz, for ^{1}H and ^{13}C, 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 μl of metal cation stock solution to a known volume of the dendrimer solution (3 ml). The addition was limited to 0.08 ml, so that dilution remains insignificant [11].

3. Results and discussion

3.1. Synthesis of dendrimer

A new 4-butylamino-1,8-naphthalimide-labelled PPI dendrimer was synthesized by nucleophilic substitution of the 4-nitro-1,8-naphthalimide-labelled dendrimer nitro group by butylamine. In this case the electron-accepting carbonyl group of the 1,8-naphthalimide molecule favours the nucleophilic substitution reactions of the nitro group with butylamine [12,13]. The final product was obtained at high yield after precipitation with water and filtration of the solid precipitate (Scheme 1).

3.2. Photophysical properties of the dendrimer in organic solvents

4-Nitro-1,8-naphthalimide-labelled PPI dendrimer absorbs in the near UV region at $\lambda_A = 320$ nm (in DMF) due to the electron-accepting nature of the nitro group. The replacement of the nitro group by an electron-donating butylamino causes a large batochromic shift of the absorption maxima of 99–118 nm, and the

Table 1
Photophysical properties of the dendrimer 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	442	67,760	534	3897	0.75
Ethanol	441	59,300	528	3736	0.73
n-Butanol	442	64,370	526	3613	0.77
Acetonitrile	432	54,660	523	3991	0.80
N,*N*-dimethylformamide	438	58,640	524	3710	0.94
Acetone	430	56,760	515	3838	0.85
Dichloromethane	428	49,680	514	3909	0.97
Chloroform	430	47,700	509	3609	0.98
Tetrahydrofuran	428	57,300	503	3483	0.98
Dimethylsulfoxide	442	57,560	530	3756	0.84
1,4-Dioxane	423	57,500	497	3519	0.96

respective maxima are in the visible region at λ_A = 423–442 nm (Table 1). As seen from the data in Table 1, the solvent polarity influences the position of the absorption maxima, $\Delta\lambda_A$ = 19 nm, as the 1,8-naphthalimide chromophoric system is very sensitive to the solvent polarity. The specific chromophore–solvent interaction, causing a change in the polarization of the 1,8-naphthalimide system also affects the absorption maxima. The molar extinction coefficients (ε) in the long-wavelength band of the absorption spectra are greater than 10,000 mol l^{-1} cm^{-1}, indicating the band has a charge transfer (CT) nature, due to the (π, π^*) character of the $S_0 \rightarrow S_1$ transition. The molar extinction coefficient for the dendrimer is approximately fourfold larger than that of the monomeric 4-butylamino-*N*-allyl-1,8-naphthalimide [14] suggesting no ground state interaction between the 1,8-naphthalimide chromophoric units [15]. Previous studies on some 1,8-naphthalimide-labelled derivatives of first generation have shown similar results [8b].

The dendrimer emits a yellow-green fluorescence with maxima of 497–534 nm, depending on solvent polarity.

Fig. 1 presents the normalized absorption and fluorescence spectra of dendrimer in chloroform solution as an example. In the long-wavelength region the fluorescence spectrum is the mirror image of the absorption one. This is indicative that the planarity of the molecular structure of the 1,8-naphthalimide chromophore is preserved in the exited state. The overlap of the absorption and fluorescence spectra is small, and an aggregation effect has not been observed at the studied concentration ($c = 1 \times 10^{-5}$ mol l^{-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 estimated from the absorption and fluorescence spectra of the dendrimers according to the following equation:

$$\Phi_F = \Phi_{st}\frac{S_u}{S_{st}}\frac{A_{st}}{A_u}\frac{n_{Du}^2}{n_{Dst}^2} \qquad (1)$$

where Φ_F is the emission quantum yield of the sample, Φ_{st} is the emission quantum yield of the standard, A_{st} and A_u represent the absorbance of the standard and sample at the excitation 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} is the solvent refractive index of the standard and sample, u and st refer to the unknown and standard, respectively.

As can be seen from the data in Table 1, the quantum yields of the dendrimer are significantly high (Φ_F = 0.73–0.98) and are solvent polarity dependent. The quantum yields are higher in non-polar media. In polar organic solvents the dendrimer exhibits a weaker emission. An interesting effect on the fluorescence has been observed when alcohols are used as solvents (methanol, ethanol and *n*-butanol). 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 1,8-naphthalimide units and alcohol molecules. The hydrogen bonds between the alcohol hydroxyl groups and the 1,8-naphthalimide system carboxylic oxygen atom (C=O) occur in the hydroxylated alcohol solutions. These H-bonds favour the radiationless transition, causing a decrease of the fluorescence quantum yield of 1,8-naphthalimide fluorophore units [16].

The data obtained are in good agreement with those for the similar monomeric 1,8-naphthalimides [12–14,17,18].

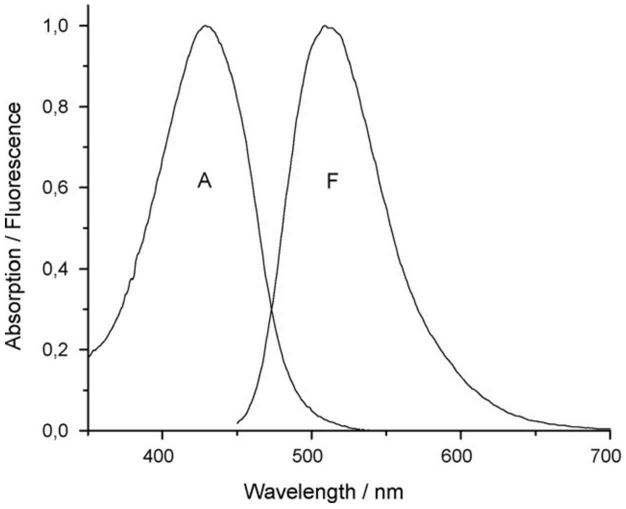


Fig. 1. Normalized absorption and fluorescence spectra of dendrimer in chloroform solution ($c = 1.10^{-5}$ mol l^{-1}).

3.3. *Influence of hydroxyl anions on the absorption and fluorescence intensity of PPI dendrimer*

It is of interest to investigate the influence of hydroxyl anions on the absorption and fluorescence properties of the dendrimer in dry DMF solution. The change in the absorption of dendrimer in the presence of sodium hydroxide is shown in Fig. 2. Upon titration of the dendrimer in DMF solution with different amounts of sodium hydroxide the absorbance at 438 nm is substantially reduced and marked by the formation of two new bands; one the ultraviolet region at 337 nm and another in the visible region with an absorption maximum at 536 nm, with the concomitant formation of a very well pronounced isobestic point in the visible region at 474 nm. The formation of the new bands can be explained by OH^- anions deprotonation of the 1,8-naphthalimide C-4 butylamino substituent. The new peaks appearing at 337 nm and 536 nm are attributed to the negatively charged 1,8-naphthalimide rings (Scheme 2). This increases the electron density at the C-4 nitrogen atoms, hence the respective absorption maximum is bathochromically shifted

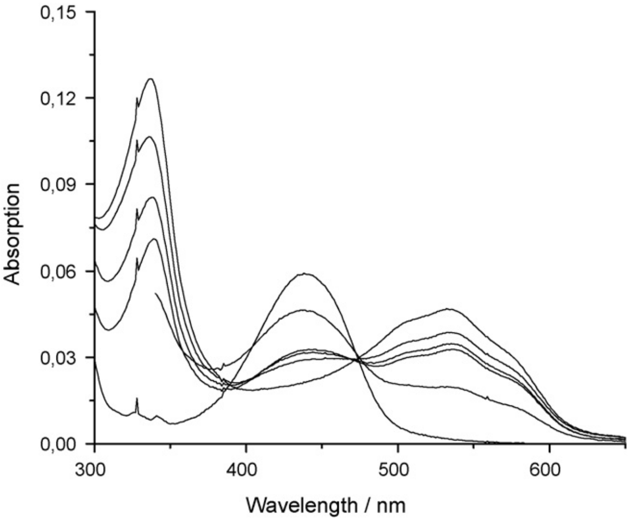


Fig. 2. Absorption spectra of dendrimer in DMF at different concentration of sodium hydroxide. The concentration of dendrimer is 1×10^{-5} mol l^{-1}.

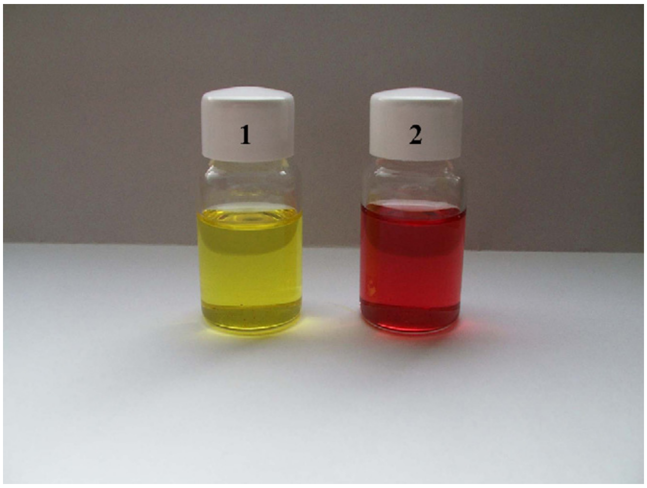


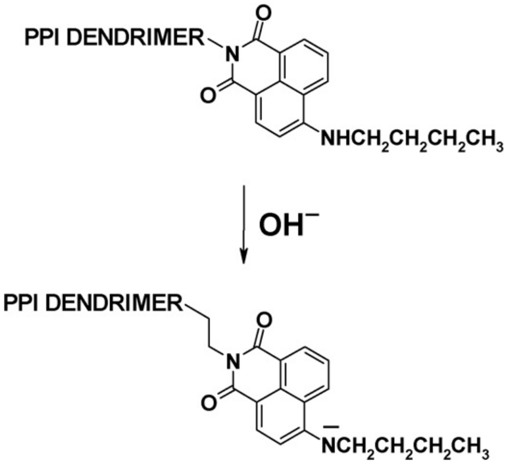
Fig. 3. The colour change of dendrimer in DMF ($c = 1.10^{-5}$ mol l^{-1}) on addition of sodium hydroxide.

98 nm and the solution changes its colour from yellow to red, as seen in Fig. 3. The newly formed band in the visible region assigned to the change transfer is of a vibronic structure having three maxima at 506 nm, 536 nm and 572 nm. No colour response has been observed when DMF contains water. Probably in this case the proton from H_2O reacts with the deprotonated amino anion. Therefore dry solvents should be used for the experiments.

The fluorescence spectrum of the dendrimer solution when excited at 536 nm has a broad and weak red fluorescence band in the 560–750 nm region and a maximum at 603 nm (Fig. 4). The results are in a very good agreement with those reported recently which use bis-1,8-naphthalimide as a fluorophore [19]. This allows the assumption that 1,8-naphthalimide derivatives have great prospects as naked eye sensors for a wide range of hydroxyl ions in DMF solution. Similar results have been reported by Gunnlaugsson et al. [20] and Tian and co-worker [21] using $(C_4H_9)_4NF$ as an agent for the deprotonation of the amino substituent of the 1,8-naphthalimide fluorophore. The sensors these authors developed view detection of fluorine ions. Our investigations aim at producing naked eye sensors for detecting metal cations. The chosen route is based on the fact that the strong bases do not affect the stability of the 1,8-naphthalimide. On the other hand, in the presence of equimolecular amounts of HCl the response is reversible, i.e. the red solution in alkali medium turns yellow again. The newly synthesized fluorophore at pH > 11 exhibits behaviour similar to that of other chromophore systems we have designed [7,22].

3.4. Influence of metal cations on the photophysical properties of dendrimer in DMF solution

The functional properties of the dendrimer in the presence of different metal cations (Zn^{2+}, Ni^{2+}, Pb^{2+}, Co^{2+}, $Cu^{2+}$and Fe^{3+}) have been studied with regard to its application as a colorimetric and fluorescent sensor for these cations. The ability of the dendrimer to detect metal cations has been tested in dry DMF solution by monitoring the changes in the absorption and fluorescent spectra in the presence of these cations. The choice of DMF as a solvent for the spectral measurements was determined by the fact that the dendrimer can change its colour in the presence of hydroxyl cations. In this case, the changes in colour and fluorescence intensity in the presence of the metal cations are of particular importance. Only in pure and dry DMF solution the dendrimer does not change its absorption and fluorescence spectra in the presence of metal cations. Therefore NaOH was added to the solution and upon its



Scheme 2. Deprotanation of butylamino groups from 1,8-naphthalimide units at dendrimer in DMF with sodium hydroxide.

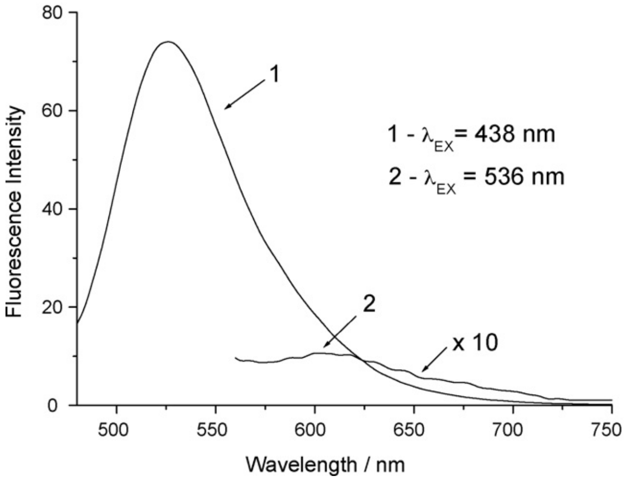


Fig. 4. Fluorescence spectra of dendrimer before (1) and after (2) addition of sodium hydroxide. The concentration of dendrimer is 1×10^{-5} mol l^{-1}.

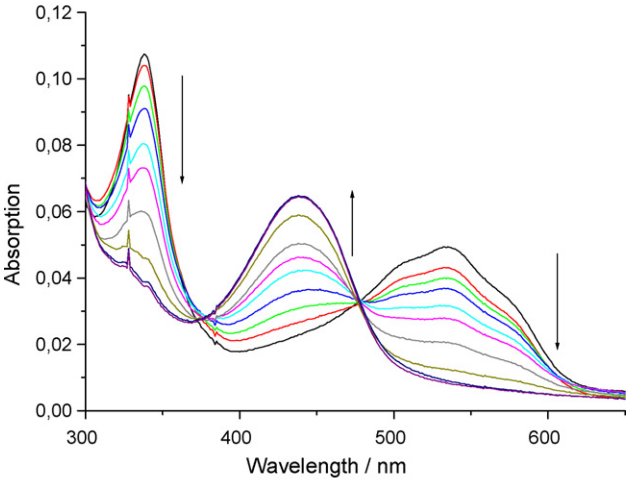


Fig. 5. Changes in the absorption spectra of (PPI dendrimer + NaOH) taken in DMF solution upon addition of Pb^{2+} cations at different concentration from 0 mol l^{-1} to 10^{-4} mol l^{-1}. The concentration of dendrimer is 1×10^{-5} mol l^{-1}.

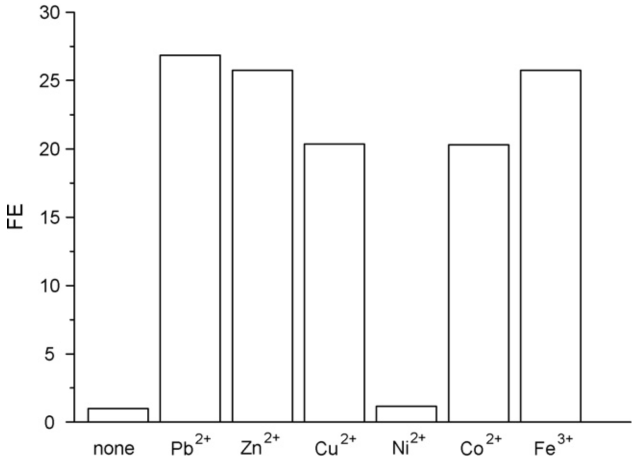


Fig. 7. Fluorescence enhancement factor (*FE*) of PPI dendrimer in the presence of different metal cations ($c = 1 \times 10^{-4}$ mol l^{-1}) in (DMF + NaOH) solution. The dendrimer concentration in solution is $c = 1 \times 10^{-5}$ mol l^{-1}.

change from yellow to red the metal cations were added. Fig. 5 shows the change in the absorption spectra when the aforementioned solution was titrated with different amounts of Pb^{2+}. As can be seen, the absorption of the maxima at 337 nm and 536 nm decrease while the one at 438 nm increases. The addition of Pb^{2+} causes progressive changes in the spectra up to a limiting concentration of 4×10^{-5} mol l^{-1}, after which no more changes have been detected. This is evidence of the fact that four Pb^{2+} interact with the four-deprotonated butylamino nitrogen atoms, thus compensating their electron deficit.

A change in the fluorescence intensity was observed when metal cations were added to the solution. Fig. 6 plots as an example the changes in the fluorescent intensity of the dendrimer as a function of the concentration of Pb^{2+} cations. In this case the excitation is at the isobestic point at 474 nm. The dendrimer free of metal cations has a very weak fluorescence emission in (DMF + NaOH). 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 on addition of Pb^{2+}cations in the 0 to 10^{-4} mol l^{-1} concentration range. The addition of Pb^{2+} at low concentration (up to 4×10^{-5} mol l^{-1}) produces a good enhancement in the fluorescence intensity showing good sensitivity. After reaching a concentration of 4×10^{-5} the increase in the fluorescence is negligible. The insert shows the variation of fluorescence intensity as a function of [Pb^{2+}], where the plateau is reached when the molar ratio [Dendr]:[Pb^{2+}] = 1:4 which corresponds to the number of deprotonated 4-butylamino-1,8-naphthalimide units and the dependence is almost linear. We assume it is due to the graduate complexation process in solution. A small amount of cations of a certain metal forms a complex with only one of the substituents. The figure shows that substituents amount with stoichiometry higher than 1:4 immediately causes the ultimate response. As the metal cations studied are harmful even at small amounts very sensitive naked eye sensors for such cases are worth investigating and producing.

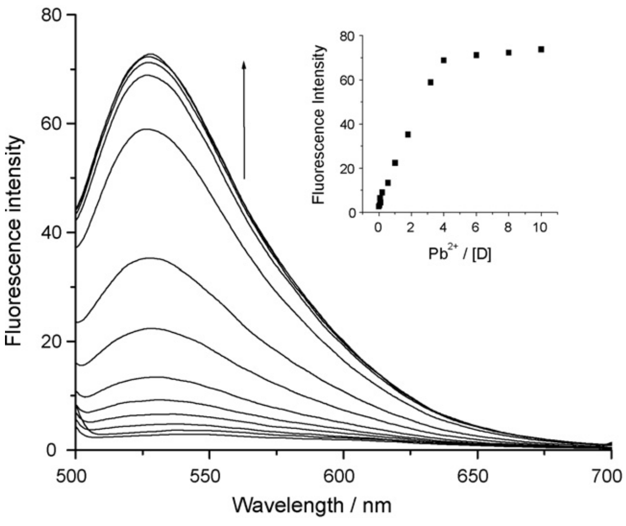


Fig. 6. Fluorescence spectra of (PPI dendrimer + NaOH) in DMF at different concentrations ($\lambda_{EXT} = 474$ nm). The dendrimer concentration is 1×10^{-5} mol l^{-1}. The inset shows the relationship between the fluorescence and Pb^{2+}concentration.

The fluorescence of dendrimer is similarly influenced by the presence of the other metal cations investigated (Fe^{3+}, Zn^{2+}, Co^{2+}, Mn^{2+} Cu^{2+} and Fe^{3+}). Their spectra taken have the same pattern, so have been spared as not giving additional information.

The sensitivity of the functionalized dendrimer towards the guest metal cations is quantitatively measured by the fluorescence enhancement factor (*FE*). The $FE = I/I_0$ is determined from the ratio of the maximum fluorescence intensity (I—after metal ions addition) and the minimum fluorescence intensity (I_0—metal cations free solution). As shown, the nature of the metal cations determines the fluorescence enhancement. The highest enhancement of the fluorescence intensity is observed in the presence of Pb^{2+} cations ($FE = 26.85$). For the other metal cations, a good *FE* has also been observed: 25.74 (Zn^{2+}), 20.30 (Co^{2+}), 25.75 (Fe^{3+}) and 20.35 (Cu^{2+}), respectively. Only in the presence of Ni^{2+} the *FE* is negligible ($FE = 1.26$). The influence of the metal cations under study upon the fluorescence intensity can be ranked as follows (Fig. 7):

$$Pb^{2+} > Zn^{2+} \approx Fe^{3+} > Co^{2+} \approx Cu^{2+} \ggg Ni^{2+}$$

It is worth mentioning that the dendrimer has a colour response addition of Ni^{2+} although its spectral characteristics do not change. Probably Ni^{2+} cannot form a stable complex with the deprotonated butylamino fragments.

Relative experiments were carried out in acetonitrile and THF. In these solvents the dendrimer does not change its spectral characteristics as they cannot furnish the deprotonation of the dendrimeric amino group.

4. Conclusions

A new first generation poly(propylene amine) dendrimer, modified with 4-butylamino-1,8-naphthalimide has been synthesized and its photophysical characteristics have been studied in organic solvents of different polarity. It has been shown that the addition of NaOH changes the colour only of its DMF solution from yellow to red while its fluorescence is quenched. This effect has been utilized to produce a new colorimetric fluorescent sensor based on the dendrimer studied. The addition of metal cations (Zn^{2+}, Co^{2+}, Ni^{2+}, Pb^{2+}, Mn^{2+}, Cu^{2+} and Fe^{3+}) restores the yellow colour of the solution and its fluorescence emission increases. This evidences the lack of selectivity towards the cations studied.

Acknowledgments

This work was supported by the bilateral cooperation between the Bulgarian Academy of Science and Instituto de Ciencia y Tecnología de Polímeros–CSIC, Spain, and M.McK. wishes to thank the MEC for the concession of his contract as part of the I3P programme.

References

[1] M.W.P.L. Baars, E.W. Meijer, Top. Curr. Chem. 210 (2000) 131.
[2] K. Inoue, Prog. Polym. Sci. 25 (2000) 453.
[3] G.R. Newkome, C.D. Shreiner, Polymer 49 (2008) 1.
[4] V. Balzani, P. Ceroni, M. Maestri, V. Vichinelli, Curr. Opin. Chem. Biol. 7 (2003) 657.
[5] (a) V. Balzani, P. Ceroni, M. Maestri, Ch. Saudan, Top. Curr. Chem. 228 (2003) 159;
(b) V. Balzani, F. Vögtle, C.R. Chim. 6 (2003) 867;
(c) V. Balzani, G. Belgamini, P. Ceroni, F. Wogle, Coord. Chem. Rev. 251 (2007) 525.
[6] (a) C. Bargossi, M.C. Fiorni, M. Montalti, L. Prodi, N. Zaccheroni, Coord. Chem. Rev. 208 (2000) 17;
(b) L. Prodi, F. Bolletta, M. Montalti, N. Zaccheroni, Coord. Chem. Rev. 205 (2000) 59.
[7] (a) I. Grabchev, X. Qian, V. Bojinov, Y. Xiao, W. Zhang, Polymer 43 (2002) 5731;
(b) I. Grabchev, V. Bojinov, J.-M. Chovelon, Polymer 44 (2003) 4721;
(c) I. Grabchev, J.-M. Chovelon, V. Bojinov, G. Ivanova, Tetrahedron 59 (2003) 9591;
(d) I. Grabchev, J.-M. Chovelon, X. Qian, N. J. Chem. 27 (2003) 337;
(e) I. Grabchev, J.-P. Soumillion, B. Muls, G. Ivanova, Photochem. Photobiol. Sci. 3 (2004) 1032;
(g) I. Grabchev, R. Betcheva, V. Bojinov, D. Staneva, Eur. Polym. J. 40 (2004) 1249;
(h) S. Sali, I. Grabchev, J.-M. Chovelov, G. Ivanova, Spectrochim. Acta Part A 65 (2006) 591;
(i) I. Grabchev, D. Staneva, R. Betcheva, Polym. Degrad. Stab. 91 (2006) 2257;
(j) I. Grabchev, J.-M. Chovelon, A. Nedelcheva, J. Photochem. Photobiol. A: Chem. 183 (2006) 9.
[8] (a) I. Grabchev, P. Bosch, M. McKenna, A. Nedelcheva, Polymer 48 (2007) 6755;
(b) I. Grabchev, S. Dumas, J.-M. Chovelon, A. Nedelcheva, Tetrahedron 64 (2008) 2113.
[9] H. Turki, S. Abid, R. El Gharbi, S. Fery-Forgues, Comp. Rend. Chim. 9 (2006) 1252.
[10] H. Turki, S. Abid, R. El gharbi, S. Fery-Forgues, R. El Gharbi, Dyes Pigments 73 (2007) 311.
[11] B. Ramachamdram, G. Saroja, N.B. Sankaran, A. Samanta, J. Phys. Chem. B 104 (2000) 11824.
[12] M. Tychopoulous, S. Chorbanian, J. Tyman, R. Brawn, R. Brittain, J. Chem. Soc., Perkin Trans. 2 (1990) 837.
[13] I. Grabchev, I. Moneva, V. Bojinov, S. Guittonneau, J. Mater. Chem. 6 (2000) 1291.
[14] I. Grabchev, V. Bojinov, Ch. Petkov, Dyes Pigments 51 (2001) 1.
[15] T.C. Baros, P. Berci Filho, V.G. Toscano, M.J. Politi, J. Photochem. Photobiol. A: Chem. 89 (1995) 141.
[16] E. Martin, R. Weigand, A. Pardo, J. Lumin. 68 (1996) 157.
[17] I. Grabchev, P. Meallier, T. Konstantinova, M. Popova, Dyes Pigments 28 (1995) 41.
[18] X. Poteau, A. Brown, R. Brown, C. Holmes, D. Mathew, Dyes Pigments 47 (2000) 91.
[19] D. Staneva, I. Grabchev, J.-P. Soumillion, V. Bojinov, J. Photochem. Photobiol. A: Chem. 189 (2007) 192.
[20] T. Gunnlaugsson, P.E. Kruger, P. Jensen, F.M. Pfeffer, G.M. Hussey, Tetrahedron Lett. 44 (2003) 8909.
[21] B. Liu, H. Tian, J. Mater. Chem. 15 (2005) 2681.
[22] I. Grabchev, S. Sali, R. Betcheva, V. Gregoriou, Eur. Polym. J. 43 (2007) 4297.