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Photophysical investigations on the sensor potential of novel, poly(propylenamine) dendrimers modified with 1,8-naphthalimide units

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ABSTRACT

Novel poly(propylenamine) first and second generation dendrimers in which the periphery was modified with 1,8-naphthalimide units were synthesized. Acetonitrile solutions of the materials were subjected to photophysical investigation to evaluate their capability to detect metal cations, by monitoring changes in their absorption and fluorescence spectra in the presence of Ag^+, Cu^{2+}, Co^{2+}, Ni^{2+}, Fe^{3+} and Zn^{2+}. The potential of the dendrimers to detect metal ion pollutants was estimated.

1. Introduction

In recent years, fluorescent compounds comprising different chemical structures have been investigated as chemosensors [1]. The utilization of 1,8-naphthalimide derivatives as fluorescent sensors is based upon the fact that in protonated solution or in the presence of metal cations these compounds display high photoinduced electron transfer (PET) resulting in the “off-on switching” of fluorescence [2]. Luminescent dendrimers based on 1,8-naphthalimide, which are a combination of conventional dendrimers and low M_r fluorescence compounds, meet the requirements of optoelectronics, light-harvesting antenna systems for solar energy conversion, sensors for environment pollutants, as well as those of biology and medicine [3–9]. The well-defined, three-dimensional macromolecular structures of such dendrimers have reactive functional groups at both their core and periphery, thereby allowing relatively easy tailoring of desired properties. Hence, an increase in the number of chromophoric moieties within a single dendrimer macromolecule leads to an amplification of sensing signal. In contrast, the selectivity and sensitivity of analysis can be enhanced so as to exploit their ability to coordinate metal ions within either the interior branches or exterior units [9].

The present authors have recently studied the modification of dendrimers with 1,8-naphthalimides and their 4-substituted derivatives in response to the needs of vanguard sensors for preventing environmental pollution and waste waters recovery [10–19]. Current attention focused on poly(propylenamine) (PPA) dendrimers, one of a new commercial class of dendrimers that offer interesting properties [20,21]. These dendrimers comprise only tertiary amino groups at their core and primary amino groups in the periphery; their luminescent characteristics can be customized by modifying their periphery using versatile fluorophores.

This paper concerns the modification of poly(propylenamine) dendrimers from first and second generation with a 1,8-naphthalimide chromophore. The photophysical properties of the novel dendrimers in the presence of transition metal cations and protons have been investigated and discussed with regard to their practical utilization.

2. Experimental

2.1. Materials and methods

First and second generation poly(propylenamine) dendrimers and 1,8-naphthalic anhydride were used as obtained from Aldrich. $Cu(NO_3)_2 \cdot 3H_2O$, $Ni(NO_3)_2 \cdot 6H_2O$, $AgNO_3$, $Co(NO_3)_2 \cdot 6H_2O$, $Fe(NO_3)_3$ and $Zn(NO_3)_2 \cdot 4H_2O$, were used as source for metal cations.

UV–visible spectrophotometry was performed using a Kontron 630 spectrophotometer at concentrations of 10^{-6} mol l^{-1}. Steady-state

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emission spectra were recorded on a JASCO FP-6500 spectrofluorimeter at concentrations of 10^{-6} mol l^{-1}; fluorescence quantum yield ϕ_L were determined, according to equation (1),

$$\phi_L^S = \frac{I_L^S}{I_L^{Ref}} \frac{\left(1-10^{-OD^{Ref}}\right)}{\left(1-10^{-OD^S}\right)} \frac{n_S^2}{n_{Ref}^2} \phi_L^{Ref} \tag{1}$$

where I_L, the emission intensity, was calculated from the spectrum area $\int I(\lambda)d\lambda$, OD represents the optical density at the excitation wavelength and n the optical density of each solvent. The superscripts "S" and "Ref" refer to the sample and to the standard, respectively. Fluorescence quantum yield was determined on the basis of the absorption and fluorescence spectra. Anthracene was used as a reference ($\Phi_0 = 0.26$).

NMR spectra were obtained using an Oxford AS operating at 300 MHz for ^{1}H; measurements were carried out in $CDCl_3$ solution at ambient temperature and chemical shifts were referenced to tetramethylsilane (TMS) standard. 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 [22]. The pH was adjusted by addition of HCl and NaOH into the 100 ml of water–acetonitrile (4:1) solvent, and was measured on a Meterlab pHM240 pH meter from Radiometer Copenhagen. All spectral measurements in this study were performed at room temperature.

*2.2. Synthesis of 1,8-naphthalimide-labelled poly(propylenamine) from first generation (**D1**)*

First generation 0.001 M of poly(propylenamine) and 0.004 M of 1,8-naphthalic anhydride were dissolved in 50 ml ethanol. The solution was refluxed and the reaction was monitored using TLC. After 6 h 200 ml water was added and the resulting precipitate was filtered and dried in vacuum. Yield: 54%.

FT-IR (KBr) cm^{-1}: 3066, 2956, 2792, 1698, 1658, 1589, 1441, 1383, 1347, 1234, 778; ^{1}H-NMR ($CDCl_3$, 300 MHz ppm): 8.48 (d, $J = 8.3$ Hz, 8H, Ar–H), 8.08 (d, $J = 8.0$ Hz, 8H, Ar–H), 7.65 (t, 8H, Ar–H), 4.19 (t, 8H, $(OC)_2NCH_2$), 2.62 (t, 8H, $CH_2N<$), −2.48 (br. s, 4H, $>NCH_2CH_2CH_2CH_2N<$), 1,88 (Kv, 8H, $>NCH_2CH_2CH_2N<$), 1.47 (br. s, 4H, $>NCH_2CH_2CH_2CH_2N<$).

Analysis: $C_{64}H_{56}O_6N_8$ (1036.4): Calcd. C 74.11, H 5.44, N 8.01; Found C 73.88, H 5.38, N 8.10.

*2.3. Synthesis of 1,8-naphthalimide-labelled poly(propylenamine) from second generation (**D2**)*

The synthesis was carried out according to that for **D1** using poly(propylenamine) second generation dendrimer. Yield: 65%.

FT-IR (KBr) cm^{-1}: 3068, 2939, 1700, 1658, 1538, 1365, 1345, 1234, 781; ^{1}H-NMR ($CDCl_3$, 300 MHz ppm): 8.36 (d, $J = 8.8$ Hz, 16H, Ar–H), 8.08 (d, $J = 8.0$ Hz, 16H, Ar–H), 7.65 (t, 16H, Ar–H), 4.10 (t, 16H, $(OC)_2NCH_2$), 2.74–2.35 (m, 32H, $CH_2N< + 4H, >NCH_2CH_2CH_2CH_2N<$), 2.08–1,34 (m, 24H, $>NCH_2CH_2CH_2N< + 4H, >NCH_2CH_2CH_2CH_2N<$).

Analysis: $C_{136}H_{128}N_{14}O_{16}$ (2212.9): Calcd. C 73.76, H 5.83, N 8.85; Found C 73.49, H 5.79, N 8.80.

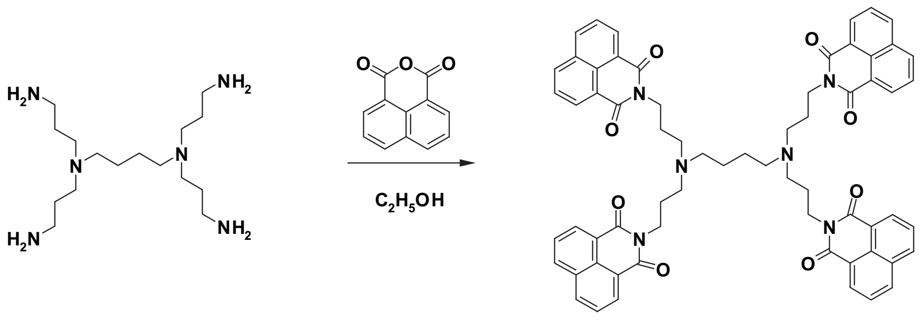
3. Results and discussion

Novel, 1,8-naphthalimide-labelled poly(propylenamine) dendrimers **D1** and **D2** were prepared using commercial poly(propylenamine) dendrimers from first and second generation which possess four and eight primary amine groups in their periphery, respectively. 1,8-naphthalic anhydride reacts with the primary amine groups in ethanol solution by the condensation reaction shown in Scheme 1 thus providing the novel compound comprising 1,8-naphthalimide units in its structure (**D1**). The same procedure was used to obtain dendrimer (**D2**) having eight 1,8-naphtalimide units in its periphery (Scheme 2). Both **D1** and **D2** were obtained as solids by filtration. FT-IR and ^{1}H spectra obtained for **D1** and **D2** in chloroform solutions are presented in the Experimental section above.

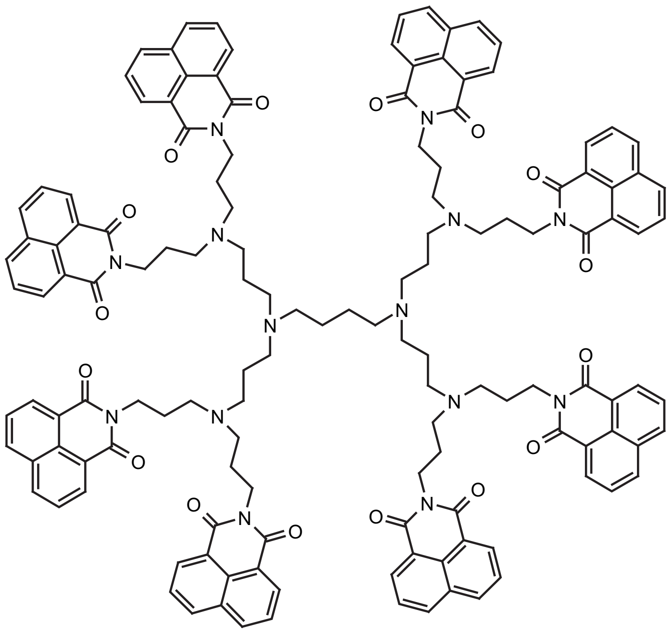
The UV–Vis spectra of the poly(propylenamine) dendrimers **D1** and **D2** have been investigated in acetonitrile solution at concentration 10^{-6} mol l^{-1}. The basic photophysical characteristics of the dendrimers depend on the polarization of 1,8-naphthalimide units. It is well known that the polarization of 1,8-naphthalimide chromophoric system depends on the electron donor-acceptor interaction between the C-4 substituent and the carbonyl groups. In the case when the substituent is a hydrogen atom which does not posses electron donor ability, the respective 1,8-naphthalimide absorbs in the UV region and emits very weak fluorescence [23].

Table 1 summarizes the basic spectral characteristics of dendrimers **D1** and **D2**: absorption (λ_{abs}) and fluorescence (λ_{fl}) maxima, molar extinction coefficient (ε), Stokes shift ($\nu_A - \nu_F$) and quantum fluorescence yield (Φ_F).

The absorption spectra of both dendrimers are approximately identical and have a maximum at 326 nm. The molar extinction coefficients (ε) of the absorption maxima are higher than 10,000 mol l^{-1} cm^{-1}, indicating that this is a charge transfer (CT) band, due to the $S_0 \rightarrow S_1$ transition. On the other hand the molar extinction coefficient for both dendrimers is approximately four- (**D1**) and eight-fold (**D2**) larger than that of the monomeric 1,8-naphthalimide derivatives having a hydrogen atom as a substituents at C-4 position [23a], suggesting no ground state interaction between the 1,8-naphthalimide chromophoric units [24]. The studies on 1,8-naphthalimide-labelled PAMAM derivatives of zero and second generation gave similar results [10,11]. The Stokes' shift which is a parameter indicating the difference in the properties and structure of the fluorophores in the ground (S_0) and first excited singlet state (S_1) is 4010 cm^{-1} for both dendrimers.



Scheme 1. Synthesis of poly(propylenamine) dendrimer **D1**.



Scheme 2. Chemical structure of the second generation poly(propylenamine) dendrimer **D2**.

The small values of the calculated quantum fluorescence yield ($\Phi_F = 0.003$ and $\Phi_F = 0.007$) for both dendrimers is also due to the absence of electron donating substituents at C-4 position of the 1,8-naphthalimide units. The values obtained are in good agreement with those for similar monomeric 1,8-naphtalimides [23] or PAMAM dendrimers modified by 1,8-naphthalimide units in the periphery [10,11].

3.1. *Influence of metal cations on the fluorescence intensity of the dendrimers* ***D1*** *and* ***D2***

The ability of both dendrimers to detect metal cations has been tested in acetonitrile solution by monitoring the changes in their absorption and fluorescence spectra in the absence and in the presence of various metal cations. Experiments have been performed in the presence of different metal cations: Ag^+, Cu^{2+}, Co^{2+}, Ni^{2+}, Fe^{3+} and Zn^{2+}. In the presence of those cations in the dendrimer solution the dendrimer acts as a ligand during the interaction between the components which is signalled by the changes in the fluorescence intensity. These changes depend on the electronic configuration of the metal cation used and on the molecular structure of the ligand. When the ligand is **D1** some of the metal cations (Ag^+, Ni^{2+}, Fe^{3+} and Zn^{2+}) induce a negligible enhancement of the fluorescence intensity. On the other hand, Cu^{2+} and Co^{2+} cations give non-fluorescent complexes and as a result a quenching of the fluorescence has been observed. It is better pronounced in the case of Cu^{2+}. The enhancement (FE) and the quenching (FQ) of the fluorescence emission have been used as a qualitative parameter. The FE = I/Io is determined as the ratio between the maximum fluorescence intensity (I – after metal ion addition) and the minimum fluorescence intensity (Io – free of metal cations solution). The FQ = Io/I has been determined from the ratio between the maximum fluorescence intensity (Io – solution free of metal cations) and the fluorescence intensity in the presence of metal cations (I). Fig. 1 presents the calculated FQ and FE results for **D1**.

Table 1
Photophysical characteristics of dendrimers **D1** and **D2** in acetonitrile (see text).

Dendrimer	λ_A (nm)	ε (l mol^{-1} cm^{-1})	λ_F (nm)	$\nu_A - \nu_F$ (cm^{-1})	Φ_F
D1	326	42000	375	4010	0.003
D2	326	82200	375	4010	0.007

The influence of Co^{2+} cations on the fluorescence intensity of the **D1** at different amounts of Co^{2+} cations is presented in Fig. 2. As seen higher Co^{2+} concentration causes a decrease of the fluorescence emission $\lambda_F = 375$ nm. Meanwhile a second fluorescence maximum appears at $\lambda_F = 468$ nm which isosbestic point is at 420 nm. The fluorescence band with maximum at $\lambda_F = 375$ nm is assigned to the typical monomeric fluorescence emission of 1,8-naphthalimide fluorophores available in the dendrimer molecule. The occurrence of the second maximum is due to excimer fluorescence emission. The latter is a result from the energy transfer between two identical chromophores – one of them is in the ground state, the other – in the excited state. **D1** has four naphthalimide units and they are quite mobile that allows to get close enough during the complexation with the metal ions and to propagate both monomeric and excimeric fluorescence, depending on the orientation of 1,8-naphthalimide units. Excimeric fluorescence is produced by Ag^+, Co^{2+}, Ni^{2+}, Fe^{3+} and Zn^{2+}. The best effect is achieved in the presence of Zn^{2+}, when the increase in the excimer fluorescence is a 65fold one. In most cases the metal ions cause an increase in the excimer fluorescence which is more significant than the fluorescence increase of the monomer. Hence the enhanced excimer fluorescence could signal the availability of metal ions in the medium studied. Such a phenomenon has not been observed during the investigations on PAMAM dendrimers whose periphery has been modified with 1,8-naphthalimides. The fact might be explained with the existence of amide groups in the dendrimers interiors that can form hydrogen bonds thus stabilizing the entire structure [10,11].

The stoichiometry of the **D1**-metal cations complex was estimated to be 1:1 by the fluorescence titration results as shown in Fig. 3 in the case when Co^{2+} cations were used. In the case the complex is formed at the tertiary nitrogen atoms located in the inner parts of the dendrimer molecule.

Fig. 4 shows the fluorescence quenching of **D2** upon the addition of cations. As seen the strongest effect is observed for Co^{2+} and Cu^{2+}. The complexation with metal cations in the dendrimer core leads to 'switching on' of the PET-effect resulting in fluorescence quenching. While Ni^{2+}, Ag^+ and Zn^{2+} cations do not affect the fluorescence intensity of the dendrimer. Probably with those cations the dendrimer does not form a stable complex.

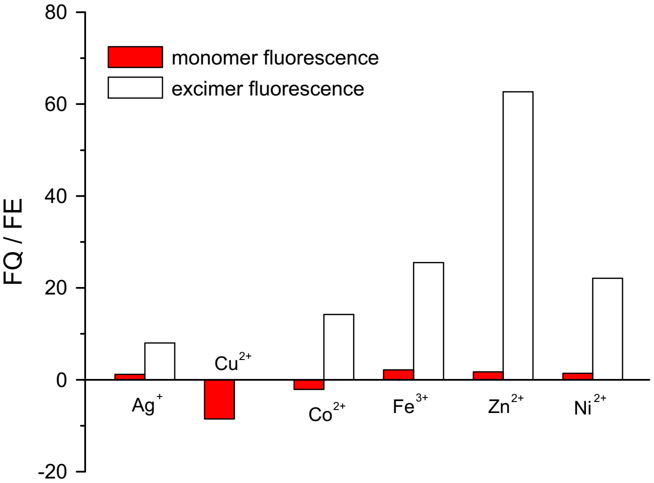


Fig. 1. Effect of the metal cations at concentration $c = 10^{-5}$ mol l^{-1} on the fluorescence of **D1** in acetonitrile solution. The concentration of dendrimer is 10^{-6} mol l^{-1}.

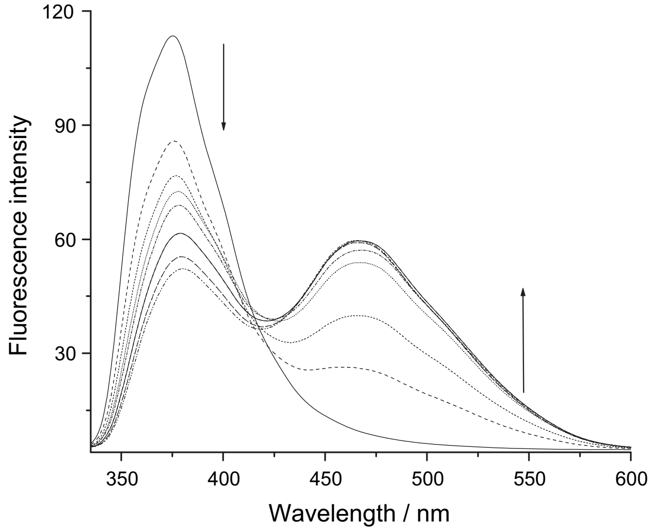


Fig. 2. Influence of Co^{2+} cations on the fluorescence spectra of the **D1**. The concentration of dendrimer in acetonitrile is 10^{-6} mol l^{-1}.

The fluorescence spectra of **D2** taken in an acetonitrile solution (at 10^{-6} mol l^{-1} concentration) in the presence of Co^{2+} cations at various concentrations is presented as a typical example in Fig. 5. The decrease of the fluorescence intensity has been observed with increasing the concentration of Co^{2+} cations. This dependence has been studied in the $0 \div 2 \times 10^{-5}$ mol l^{-1} concentration range of Co^{2+} cations. It is obvious that the initial addition of the Co^{2+} cations (2×10^{-6} mol l^{-1}) to the dendrimer solution leads to a decrease of the fluorescent intensity. The respective quenching effect is 32% which indicates very good sensor sensitivity. Upon further addition of Co^{2+} into the dendrimer solution, the intensity of fluorescence also decreases up to 2×10^{-6} mol l^{-1} as Fig. 5 shows. After this concentration the change in fluorescence intensity is negligible. The estimated stoichiometry of the complex (**D2**–$2Co^{2+}$) is 1:2 as can be seen from the insert of Fig. 5. We suppose the complex with the metal ions is formed most probably with tertiary nitrogen atoms from the core of the dendrimer molecule as is the case with D. Excimer fluorescence has not been observed in the spectra of the **D2** unlike in those of **D1**. It absence could be assigned to the conformation changes occurring in molecule of **D2**.

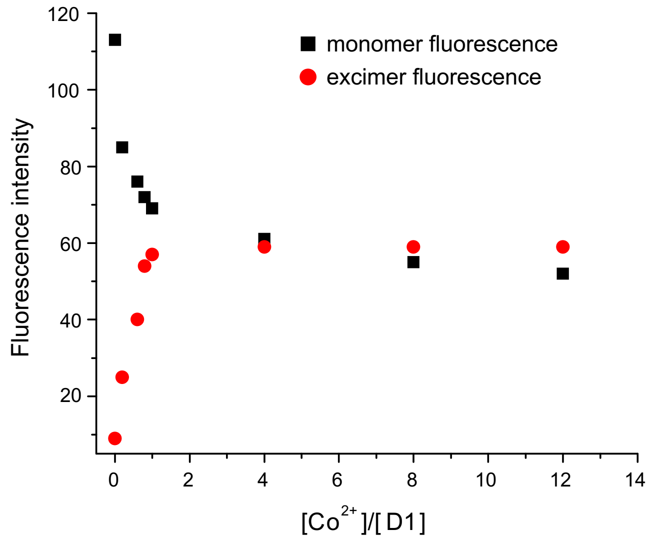


Fig. 3. Dependence of the monomer and excimer fluorescence of **D1** on the concentration of the Co^{2+} cations.

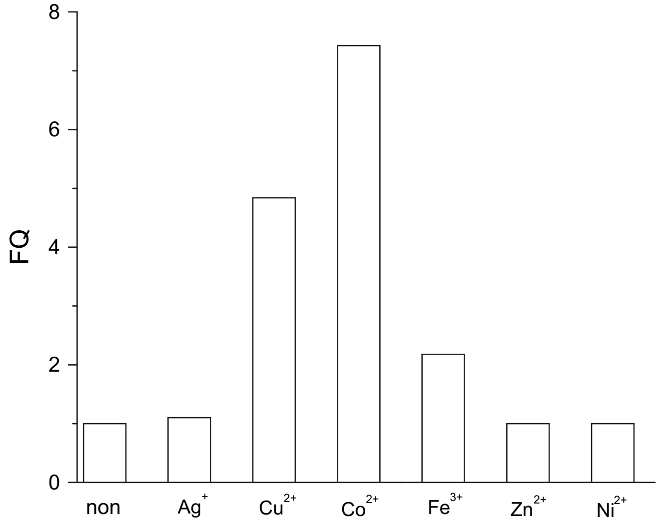


Fig. 4. Fluorescence quenching factor (FQ) of dendrimer **D1** in the presence of different metal cations ($c = 2 \times 10^{-5}$ mol l^{-1}) in acetonitrile solution. The dendrimer concentration in solution is $c = 1 \times 10^{-6}$ mol l^{-1}.

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

The pH values of organic compounds are very important for understanding their participations in different chemical and biological processes that depend on proton transfer.

The influence of protons on the photophysical parameters of the poly(propylenamine) amine derivatives from first and second generation have been investigated in acetonitrile–water mixed solvents (1:4 v/v) and the data is presented in Fig. 6.

The experiments have been carried out in the pH range from 2.6 to 11.3. As seen from the results the new dendrimers are sensitive to kthe presence of protons. For both dendrimers the increase in the proton concentration results into an enhancement of their fluorescence. The phenomenon is due to the fact that at acidic pH values the tertiary nitrogen atoms are protonated which quenches

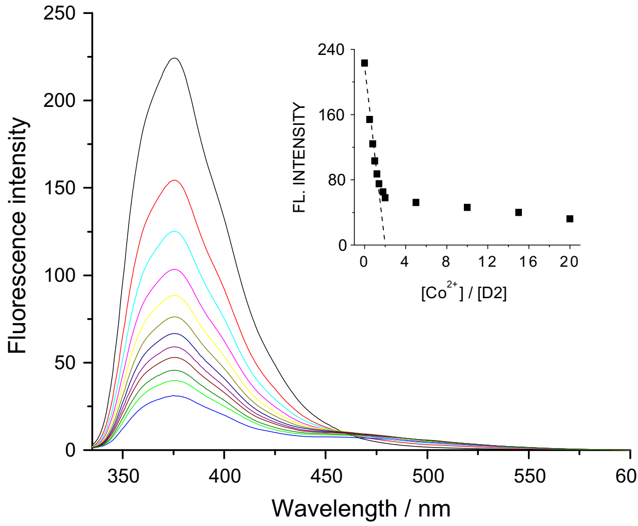


Fig. 5. Fluorescence spectra of **D2** (1×10^{-6} mol/l) in acetonitrile solution in the presence of different concentration of Co^{2+} cations. The insert shows the dependence of the fluorescence intensity on the concentration of Co^{2+} cations.

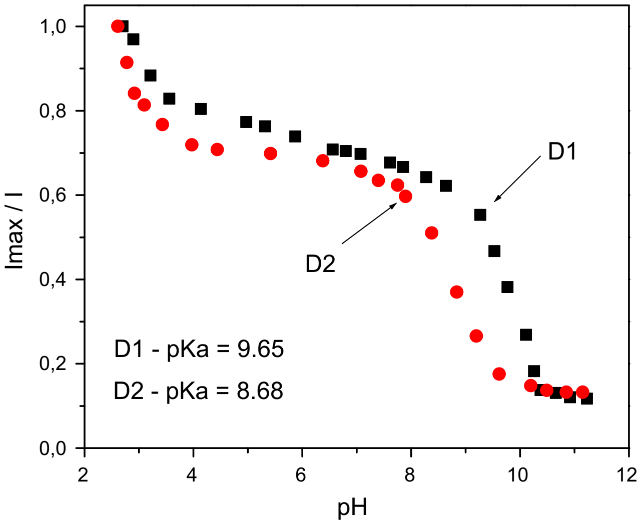


Fig. 6. The influence of pH on the fluorescence intensity at the fluorescence maxima of **D1** and **D2** ($c = 10^{-6}$ mol l^{-1}) investigated in methanol–water (1:4, v/v) solution.

the photoinduced electron or energy transfer upon excitation, thus 'switching on' the fluorescence.

The pH dependence of fluorescence intensity has been analyzed with Equation (2).

$$pH - pKa = \log(I_{Fmax} - I_F)/(I_F - I_{Fmin}) \quad (2)$$

The calculated pKa values for **D1** and **D2** dendrimers are 9.65 and 8.68, respectively. The pKa value of the PPA dendrimer modified with 4-*N*,*N*-dimethylaminoethylamino-1,8-naphthalimide is 7.37 [20]. The difference in pKa values in the case of **D2** are owing to the protonation that occurs not only at the tertiary nitrogen atoms but in the receptor fragments of the peripheral 1,8-naphthalimide units.

4. Conclusion

The effect of different metal cations (Ag^+, Cu^{2+}, Co^{2+}, Ni^{2+}, Fe^{3+} and Zn^{2+}) on fluorescence intensity were investigated in acetonitrile solution. The metal cations form complexes with the dendrimer ligands of stoichiometry 1:1 for **D1** and 1:2 for **D2**, respectively. Only in the case of **D1** was excimer fluorescence emission registered in the presence of metal cations that was not observed when investigating PAMAM dendrimers. It can be assumed that the dendrimers can detect metal cations and protons at concentrations up to 2×10^{-5} mol l^{-1}. Unfortunately **D1** does not exhibit sensor selectivity; in the case of **D2**, fluorescence quenching was observed only upon the addition of Cu^{2+} и Co^{2+}, the remaining ions producing a negligible effect. The results contribute to the understanding of the dendrimer's sensing mechanism and map a route to the tailored synthesis of better performing chemosensors.

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