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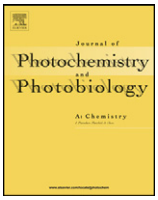

A new detector for metal cations based on the combined effect of photoinduced electron transfer and a light harvesting system

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ABSTRACT

A new tripod comprising three 1,8-naphthalimide units having different substituents at C-4 of the naphthalimide structure has been synthesized. The new dendron has two 4-ethoxy-1,8-naphthalimide units as an energy donor and a 4-*N*,*N*-dimethialaminoethilenidamino-1,8-naphthalimide acceptor to facilitate the donor–acceptor energy transfer. The main photophysical characteristics of the dendron have been studied in organic solvents of different polarity. The established energy transfer efficiency of is about 99% revealing the excellent antenna capacities of the dendron. The fluorescence intensity of the dendron has been studied in an acetonitrile solution in the presence of metal ions of various nature (Cu^{2+}, Co^{2+}, Zn^{2+}, Ni^{2+}, and Pb^{2+}) using two different excitation wavelengths of 365 nm and 435 nm. The detection limit of metal cations has been determined.

1. Introduction

The fluorosensors are molecular devices able to detect diferent analites via the changes in their spectral characteristics [1–3]. Presently the fluorosensors developed and utilized are of two types: low molecular weight compounds and polymers (both linear and star-shaped). Being molecular devices powered by light and possessing extremely high sensitivity to various external signals polymeric fluorosensors have gained particular interest [4].

The artificial light harvesting systems which absorb light and transfer energy to reaction center have a very important role in the scientific researches. These artificial light-harvesting molecules are especially designed, so that the light emitted by a certain part of the molecule to be absorbed by another of its fragment [5–10]. The ideal light harvesting system absorbs light efficiently in a relatively broad region covering most of the sunlight spectrum. The efficient energy transfer within the system could be achieved by the combined effect of different chromophores. The development of highly efficient light-harvesting systems remains a challenging task. The choice of the chromophores depends on the complete overlap of their spectra. They should meet the requirements for suitable energy levels, types of bonding, connection sites, synthesis strategy, etc.

This paper reports on the synthesis and characterization of a novel fluorescent sensor based on a new dendron comprising derivatives of 4-substituted-1,8-naphthalimide. The photosensitive 1,8-naphthalimide groups are designed to act as donor–acceptor moieties thus obtaining molecules whose signal will be enhanced by an energy transfer. The effectiveness of the dendron as a metal ion detector is evaluated by the photoinduced electron transfer occurring in the presence of metal ions and protons in the medium.

2. Experimental

2.1. Materials

Organic solvents (methanol, ethanol, acetonitrile, *N*,*N*-dimethylformamide (DMF), acetone, dichloromethane, chloroform and tetrahydrofurane) used in this study were of spectroscopic grade, and used as obtained. $Cu(NO_3)_2{\cdot}3H_2O$, $Ni(NO_3)_2{\cdot}6H_2O$, $PbNO_3$, $Co(NO_3)_2{\cdot}6H_2O$ and $Zn(NO_3)_2{\cdot}4H_2O$, salts were the metal cation sources and used as obtained from Aldrich. The synthesis of the precursor D1 has been described previously [11].

2.2. Synthesis of dendron D2 (Scheme 1)

Compound D1 (0.01 mol) was placed into a round bottom flask with 20 ml of 2-methoxyethanol. The mixture was stirred, *N*,*N*-dimetialmoethilenidamine (0.05 mol) was added and the reaction mixture was heated to 80 °C. The complexion of

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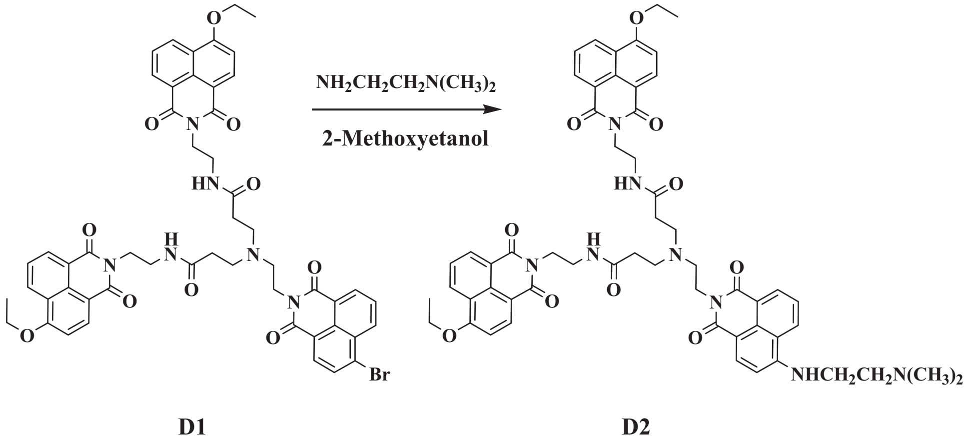


Scheme 1. Synthesis of dendron D2.

reaction was followed by TLC (dichloromethane:methanol, 25:1). After that the solvent was removed under reduced pressure, the crude product was purified via column chromatography: dichloromethane:methanol (25:1) thus obtaining a dendron D2 with high yield and purity. Yield = 94%.

^{1}H NMR ($CDCl_3$, 600.13 MHz, ppm): δ 8.59 (d, J = 8.4 Hz, 1H), 8.33 (d, J = 7.3 Hz, 2H), 8.29 (d, J = 7.2 Hz, 2H), 8.25 (d, J = 8.4 Hz, 1H), 8.23 (d, J = 8.2 Hz, 2H), 8.11 (d, J = 8.4 Hz, 1H), 7.97 (t, J = 5.9 Hz, 2H), 7.65–7.55 (m, 4H), 6.98 (d, J = 8.4 Hz, 2H), 6.7 (d, J = 8.6 Hz, 1H), 4.14(q, J = 6.7 Hz, 4H), 4.05 (d, J = 5.3 Hz, 4H) 3.85 (t, J = 7.0 Hz, 2H), 3.46–3.39 (m, 4H), 2.62 (t, J = 6.0 Hz, 4H), 2.57 (t, J = 6.6 Hz, 2H), 2.47 (t, J = 7.5 Hz, 2H), 2.23 (s, 6H), 2.15–2.05 (m, 6H), 1.43 (t, J = 6.8, 6H).

^{13}C NMR ($CDCl_3$, 150.92 MHz, ppm): δ, 171.3, 163.7, 163.4, 163.1, 162.6, 159.2, 150.4, 134.2, 134.1, 130.7, 130.8, 129.3, 128.5, 128.4, 127.9, 127.8, 124.2, 122.5, 121.9, 119.9, 114.0, 107.4, 106.4, 106.3, 103.7, 64.5, 56.9, 49.7, 49.3, 45.4, 44.3, 40.9, 40.0, 36.53, 33.0, 14.3

API-ES-MS (positive) m/z calcd: 1002.2; found: 1003.2 ([M+H]$^+$), 1004.2 ([M+2H]$^+$), 1025.2 ([M+Na]$^+$).

Analysis: $C_{56}H_{58}O_{10}N_8$ (1002.2): Calcd. C 67.06, H 5.78, N 11.18; Found C 67.58, H 5.83, N 11.29.

2.3. Methods and 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 PerkinElmer 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 for the absorption and fluorescence maxima and 5% for the molar extinction coefficient [12,13]. Fluorescence quantum yields were determined on the basis of the absorption and fluorescence spectra taken at wavelength excitation at the absorption maximum. Fluorescein was used as a reference ($\Phi_F = 0.85$). ^{1}H (600.13 MHz) and ^{13}C (150.92 MHz) spectra were acquired on an AVANCE AV600 II + NMR spectrometer. Unambiguous assignment of the signals was made on the basis of the gradient enhanced versions of COSY, HSQC, HMBC, NOESY, 1D selective NOE and DOSY experiments. The measurements were carried out in $CDCl_3$ solution at ambient temperature. The chemical shifts were referenced to a tetramethylsilane (TMS) standard. Electrospray mass spectroscopic measurements were carried out using a Hewlett–Packard Series 1100 MSD. 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 remained insignificant [14].

3. Results and discussion

3.1. Photophysical characteristics of dendron D2 in organic solvents

1,8-Naphthalimide derivatives have a unique chemical structure combining two subsystems: a naphthalene core and a dicarboxyimide group (–OC–NR–CO) bonded in a six-membered ring. The polarization of 1,8-naphthalimide molecule results from the donor–acceptor interaction of the electron–acceptor carbonyl groups in the imide structure with the C-4 substituent in the naphthalene core. This polarization leads to fluorescence emission of blue, yellow and green shades. Thus alternating the donor–acceptor ability of the substituent at C-4 position one can tailor the colour properties and the fluorescence intensity of 1,8-naphthalimide compounds.

It is well known that 1,8-naphthalimide derivatives having alkoxy groups at C-4 position are colorless with blue fluorescence while the amino substituted 1,8-naphthalimides have a yellow colour and emit green fluorescence [15].

The new molecule thus synthesized is a light harvesting system whose design ensures the occurrence of an energy transfer from 4-ethoxy-1,8-naphthalimide fragment to the 4-*N*,*N*-dimethylaminoethylenediamino-1,8-naphthalimide moiety. On the other hand, the introduced receptor fragment (4-*N*,*N*-dimethylaminoethylenediamine) enables the formation of complexes with metal ions. Due to the combination of the above effects D2 is capable of sensitive detection of metal ions.

The functional properties of D2 have been investigated in eight organic solvents of different polarity. Table 1 summarizes the basic photophysical characteristics of D2: absorption (λ_A) and fluorescence (λ_F) maxima, Stokes shift ($\nu_A - \nu_F$) and quantum yield of fluorescence (Φ_F).

As seen from Table 1 D2 has two well pronounced absorption maxima. The first maximum is in the UV region at λ_A = 361–366 nm and is characteristic of the alkoxy 1,8-naphthalimide derivatives. The second one is in the visible region at λ_A = 420–437 nm and is typical of the *N*,*N*-dimethilaminoethilendiamino-1,8-naphthalimide fragment in D2 structure. The ratio of the molar extinction coefficients (ε) is about 2:1 and its higher values correspond to the ethoxy fragments. The extinction coefficients obtained (ε) are about twice higher, if compared to those of the monomeric 4-ethoxy-1,8-naphthalimide derivatives [16]

Table 1
Photophysical properties of the dendron in different organic solvents (see text).

Solvents [E_T (30)/kcal mol^{-1}]	λ_A (nm)	ε (dm^3 mol^{-1} cm^{-1})	λ_F^{a} (nm)	$\nu_A - \nu_F$ (cm^{-1})	Φ_F
Ethanol	366	25,500			
[51.9]	437	14,100	528	3943	0.011
Acetonitrile	365	23,800			
46.0	435	11,050	520	3518	0.019
N,*N*-Dimethylformamide	365	24,800			
43.8	437	11,300	519	3615	0.021
Acetone	364	27,100			
42.2	434	14,600	509	3395	0.116
Dichloromethane	364	24,200			
41.1	420	15,700	494	3566	0.598
Chloroform	369	22,170			
39.1	433	11,000	499	3054	0.719
Tetrahydrofuran	363	23,200			
37.4	432	11,800	501	3188	0.736
Dioxan	361	26,300			
36.0	427	14,900	501	3455	0.723

[a] Fluorescence maxima ($\lambda_{EXT} = 435$ nm).

while (ε) is measurable with those of the monomeric 4-*N*,*N*-dimethylaminoethylenediamine derivatives of 1,8-naphthalimide [17,18].

Fig. 1 presents as an example the normalized absorption and fluorescence spectra of D2. As seen the absorption spectrum has two characteristic maxima at $\lambda = 365$ nm and $\lambda = 435$ nm. The fluorescence spectra are recoded at an excitation at $\lambda_{EXT} = 365$ nm (Spectrum 2) and at $\lambda_{EXT} = 435$ (Spectrum 3). Upon excitation two fluorescence maxima also occur in the region wherein 4-ethoxy derivatives of 1,8-napthalimide derivatives absorb ($\lambda_{EXT} = 365$ nm). The more intense maximum is at 435 nm while the weaker one is at 500 nm. Fig. 1 demonstrates clearly that the fluorescence maximum at 436 nm overlaps with the absorption maximum characteristic of 4-*N*,*N*-dimethilaminoethilenidamino-1,8-naphthalimide from D2. Upon excitation at $\lambda_{EXT} = 435$ nm (Spectrum 3) the spectrum has a single fluorescence maximum at 520 nm. That reveals the realization of a complete energy transfer from the ethoxy fragments to 4-*N*,*N*-dimetialmoethilenidamino 1,8-naphthalimide unit (Scheme 2). Fig. 1 shows how the fluorescence colour has changed from blue to green upon the addition of 4-*N*,*N*-dimethilaminoethilenidamino-1,8-naphthalimide to the D2. That shows that fluorescence is emitted solely by the 4-*N*,*N*-dimetialmoethilenidamino-1,8-naphthalimide moiety.

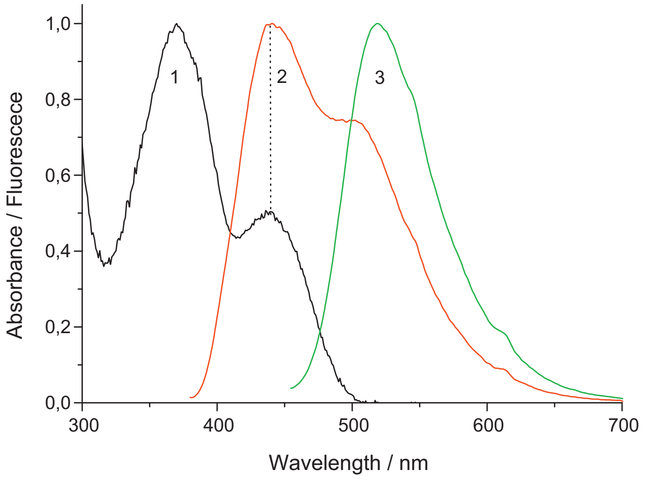
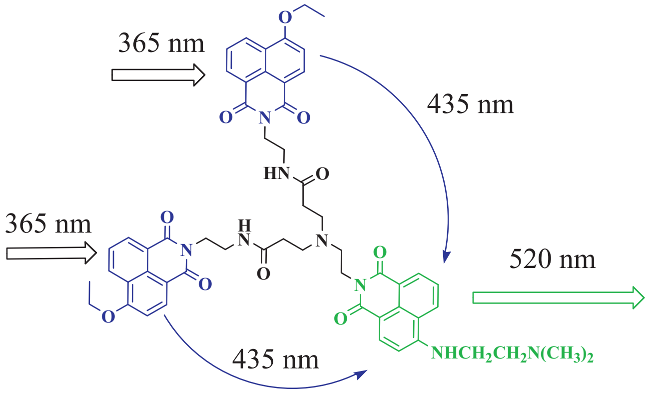


Fig. 1. Absorption and fluorescence spectra of D2 in acetonitrile solution ($c = 10^{-6}$ mol l^{-1}): (1) absorption spectrum, (2) fluorescence spectrum ($\lambda_{EXT} = 365$ nm), fluorescence spectrum ($\lambda_{EXT} = 435$ nm).



Scheme 2. Proposed mechanism of energy transfer of dendron D2.

Comparing the unquenched donor emission of compound D1 and the quenched emission of antenna dendron D2 it has been found that the energy-transfer efficiency is 99% [19]. This result has been also confirmed by the comparison of the normalized absorption and excitation spectra of D2 (Fig. 2) [20], although it is known that both methods of determining the energy-transfer efficiency are less accurate when the quantitative values are close [21].

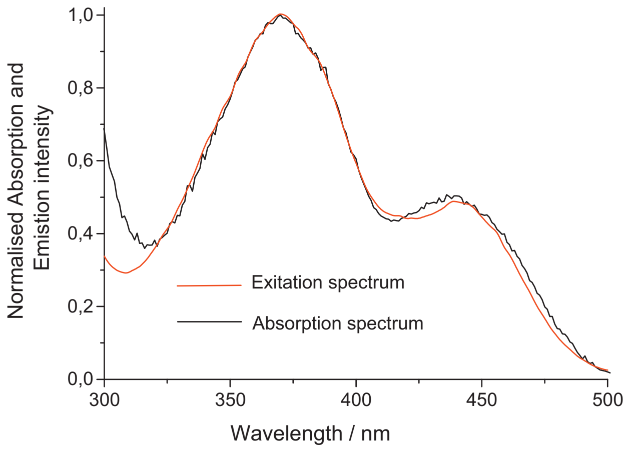


Fig. 2. Normalized absorption and excitation spectra of antenna dendron D2 ($c = 10^{-6}$ mol l^{-1}).

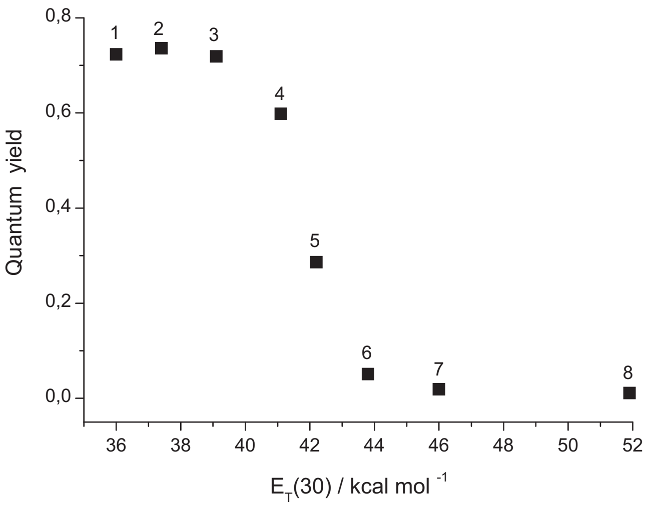


Fig. 3. Dependence of quantum fluorescence yield of dendron D2 on the empirical solvent polarity parameter (E_T 30/kcal mol^{-1}): (1) dioxane, (2) tetrahydrofurane, (3) chloroforme, (4) dichloromethane, (5) acetone, (6) DMF, (7) acetonitrile, and (8) ethanol.

The quantum fluorescence yield of D2 in all organic solvents has been calculated on the basis of the results obtained from the absorption and fluorescence spectra using 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 Φ_{st} is the quantum yield of the reference, A_{st} and Au represent the absorbance of the reference and the sample, respectively, S_{st} and S_u are the integrals of the emission of the reference and the sample respectively, and n_{Dst} and n_{Du} are the refractive index of the reference and the sample, respectively.

It has been worth investigating how the quantum efficiency of dendron D2 depends on environment polarity. As seen from the data in Table 1 the quantum yields of D2 are significantly different and its values are between $\Phi_F = 0.011$ (ethanol) and $\Phi_F = 0.736$ (tetrahydrofuran). Fig. 3 plots the dependence of the quantum fluorescence yield on the empirical parameter of solvent polarity (E_T 30/kcal mol^{-1}). As seen the quantum yields are considerably higher in non-polar media while in polar organic solvents the emission of D2 is much weaker. This large difference in the quantum yields can be explained by the photo-induced electron transfer (PET) processes, which are accelerated in polar solvents [22]. This dependence is also similar for the cases when 4-*N*,*N*-dimetialmoethilenidamino 1,8-naphthalimide fluorophore is bonded to the periphery of PAMAM and PPA dendrimers and when being a monomeric unit, respectively [23–27].

Stokes shift ($\nu_A - \nu_F$) is an important parameter of the fluorescent compounds. It indicates the difference in the properties and structure of the fluorophores between the ground S_0 and the first excited state S_1. The calculated values of Stokes shift at $\lambda_{EXT} = 435$ are in the 3054–3943 cm^{-1} region.

3.2. *Influence of metal cations on the fluorescence intensity of D2*

The presence of metal cations in the dendron solution is signaled 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). Fig. 4 shows *FE* values for dendron D2 in the presence of different metal cations. As seen the presence of metal cations (Zn^{2+}, Pb^{2+} and Cu^{2+}) in the dendron solution increases significantly the fluorescence intensity while Co^{2+} and Ni^{2+} cations have a smaller effect. Probably the cations of these two metals cannot form a stable complex with the receptor.

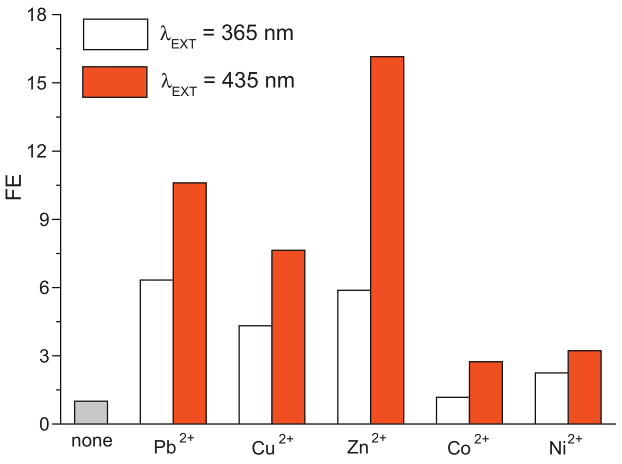


Fig. 4. Fluorescence enhancement factor (FE) of denron D2 in the presence of metal cations in acetonitrile solutions ($c = 10^{-6}$ mol l^{-1}) at two different excitation wavelength ($\lambda_{EXT} = 365$ nm) and ($\lambda_{EXT} = 435$ nm). The dendron concentration is ($c = 10^{-6}$ mol l^{-1}).

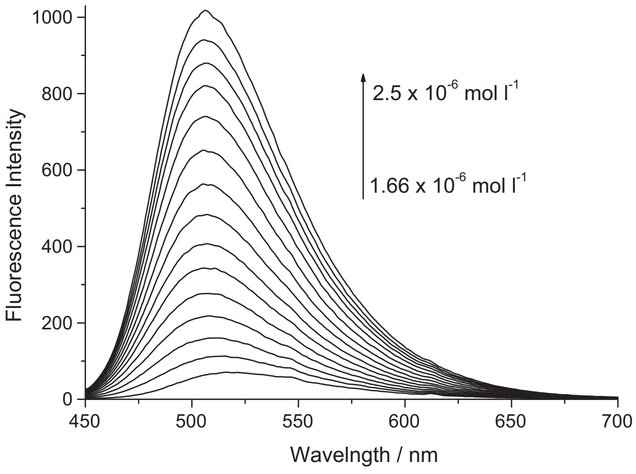


Fig. 5. Fluorescence spectra of D2 in acetonitrile solution ($c = 1 \times 10^{-6}$ mol l^{-1}, $\lambda_{EXT} = 435$ nm) in the presence of Zn^{2+} at concentration 1.66×10^{-6}–2.5×10^{-6} mol l^{-1}.

The changes in the fluorescence intensity of dendron D2 at $\lambda_{EXT} = 435$ nm in the presence of Zn^{2+} at various concentrations are shown in Fig. 5. As seen the fluorescence intensity increases progressively with the increasing Zn^{2+} concentration. Simultaneously with the increase the fluorescence maximum shifts from 520 nm to 500 nm. The fact reveals that the complex is formed at *N*,*N*-dimetilaminoethilenidamino fragment of D2. The hypsochromic shift is due to the weakened electron-donor ability of the nitrogen atom at C-4 whose electron couple is engaged in the complex formation with Zn^{2+} ions. It has been found that with the increase in fluorescent intensity of 6.5% the detection limit for Zn^{2+} ions reaches 1.66×10^{-6} mol l^{-1}.

Fig. 6 shows the changes in the fluorescence intensity at $\lambda_{EXT} = 365$ nm in the presence of Zn^{2+} at various concentrations (1.0×10^{-7}–1.4×10^{-6} mol l^{-1}). The fluorescence spectrum has two maxima at 435 nm and at 490 nm. With the increasing concentration of metal ions the emission of yellow–green fluorescence increases ($\lambda = 490$ nm) and a well structured maximum appears at about 500 nm. The intensity of the blue fluorescence emission having a maximum at 435 nm remains almost unchanged. That

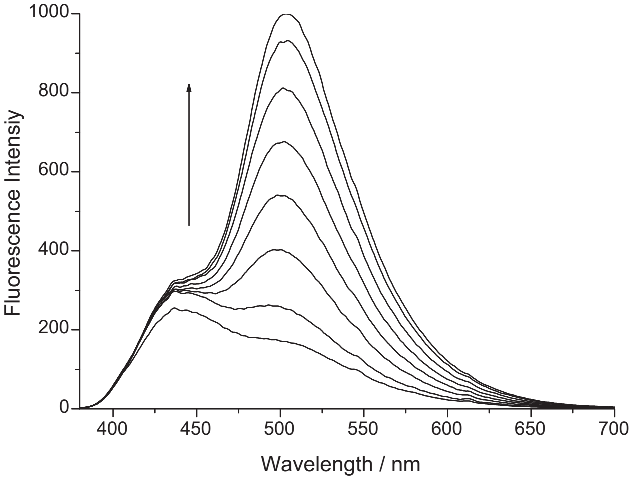


Fig. 6. Fluorescence spectra of D2 in acetonitrile solution ($c = 1 \times 10^{-6}$ mol l^{-1}, $\lambda_{EXT} = 365$ nm) in the presence of Zn^{2+} at concentration 1.0×10^{-7}–1.4×10^{-6} mol l^{-1}.

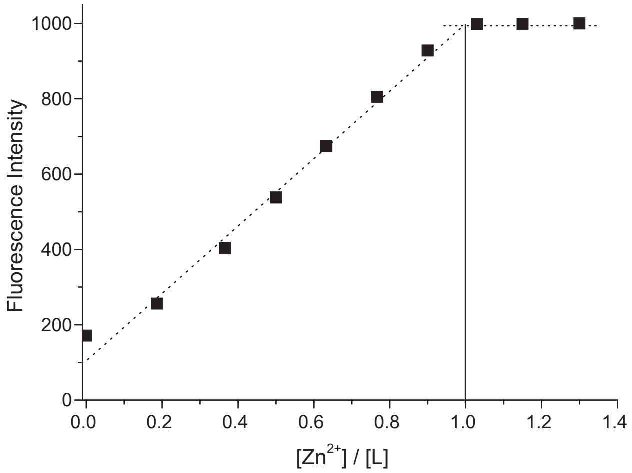


Fig. 7. Dependence between the fluorescence intensity of D2 and Zn^{2+} concentration.

indicates that the complex formed takes part in the energy transfer which results into the emission of yellow–green fluorescence. At a low Cu^{2+}concentration (1×10^{-7} mol l^{-1}) the enhancement of fluorescence intensity is 8.5%, which demonstrates good fluorescence sensitivity and a low threshold for sensing this cation. In this case the detection limit is 1×10^{-7} mol l^{-1} which is higher than the results obtained by excitation at $\lambda_{EXT} = 365$ nm.

It has been established that a metal ion forms a complex with D2 at a schematic 1:1 ratio as illustrated in Fig. 7.

4. Conclusion

A new effective antenna dendron containing two differently substituted 1,8-naphthalimide fluorophores has been synthesized. Its photophysical characteristics have been investigated in organic solvents of different polarity. The quantum fluorescence yield depends strongly on the solvent polarity and exhibits high values in non-polar media. The light energy transfer from the donor 4-ethoxy-1,8-naphthalimide units to the acceptor 4-*N*,*N*-dimetialmoethilenidamino-1,8-naphthalimide units shows the excellent energy transfer capacities of the dendron (99%).

The influence of metal cations (Cu^{2+}, Co^{2+}, Zn^{2+}, Ni^{2+}, and Pb^{2+}) on the fluorescence intensity has been investigated at two different excitation wavelengths: $\lambda_{EXT} = 365$ nm and $\lambda_{EXT} = 435$ nm. It has been shown that in acetonitrile solution the new dendron increases its fluorescence in the presence of the cations studied. The highest effect is observed in the presence of Zn^{2+}. It has been established that one metal ion forms a complex with D2 at a 1:1 stoichiometric ratio. The newly synthesized antenna dendron is a much better detector than the low molecular weight 1,8-naphthalimide ones having a 4-*N*,*N*-dimetialmoethilenidamino residue as a receptor fragment at C-4 position of the 1,8-naphthalimide. The light harvesting system enhances the PET effect thus improving the capacity of D2 detector. Its combined mechanism facilitates effective detection of metal cations even at a very low concentration.

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