

Research Article

Detection of Metal Ions and Protons with a New Blue Fluorescent Bis(1,8-Naphthalimide)

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The synthesis of a new blue fluorescent bis(1,8-naphthalimide) has been described and its basic photophysical characteristics have been investigated in organic solvents of different polarity. The detection of protons and different metal cations (Ag^+ , Cu^{2+} , Co^{2+} , Ni^{2+} , Fe^{3+} and Zn^{2+}) with the new compound has been investigated by the use fluorescence spectroscopy.

1. Introduction

Metal ions pollution in the environment has received significant attention because of its toxicity and adverse biological effects. In this respect, environmental monitoring is important to ensure ecosystem health and humanity. Of particular interest are the optical fluorosensors, which are molecular devices able to detect the presence of environmental pollutants via the changes in their fluorescence intensity [1, 2]. In this sense, sensors are of great importance to chemistry, biology, and medicine because they allow rapid detection of different compounds in the living organisms and environment. Most of the known fluorescent sensors are based on the photoinduced electron transfer (PET) [3, 4]. The fluorescent PET sensors are of great interest because of their various applications. Under appropriated conditions, the fluorophore emission is quenched by the distal amino group by means of electron transfer from the substituent to the fluorophore ring. If the PET process is "switched off" by, for example, protonation of the amino group or complexation with metal ions, the emission of the fluorophores is restored. Due to their excellent photophysical properties, 1,8-naphthalimide derivatives are unsurpassed as a signal fragment in the design of fluorescent chemosensors [5–10]. Various other mechanisms and fluorophores are used in the design of molecular devices with sensory properties [11–14].

In this work, the study is focused on the synthesis and photophysical investigation of a blue fluorescent compound (Bis2) having *N,N*-dimethylaminoethyl group in C-4 position at the 1,8-naphthalimide structure as a receptor for metal ions and protons. The functional properties of Bis2 have been investigated in organic solvents of different polarity. Its photophysical and supramolecular properties have been also studied in the presence of some metal cations.

2. Experimental

2.1. Materials and Methods. UV-Vis spectrophotometric investigations were performed using "Thermo Spectronic Unicam UV 500" spectrophotometer. Emission spectra were taken on a "Cary Eclipse" spectrofluorometer. All spectra were recorded using 1 cm pathlength synthetic quartz glass cells (Hellma, Germany). All organic solvents (dimethyl sulfoxide, *N,N*-dimethylformamide, acetonitrile, dichloromethane, and chloroform) used in this study were of spectroscopic grade. Fluorescence quantum yield was determined on the basis of the absorption and fluorescence spectra, using anthracene as reference ($\Phi_{\text{st}} = 0.27$ in ethanol [15]). The effect of metal cations upon the fluorescence intensity was examined by adding a few microliters of the metal cations 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 [16]. $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$, $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, AgNO_3 , $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Fe}(\text{NO}_3)_3$ and $\text{Zn}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ were used as source of metal cations. 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 CD_3Cl solution at ambient temperature. The chemical shift was referenced to tetramethylsilane (TMS). Thin layer chromatographic (TLC) analysis of the dyes was followed on silica gel (Fluka F₆₀ 254 20 × 20; 0.2 mm) using the solvent system n-heptane/acetone (1 : 1) as an eluent.

2.2. Synthesis of Bis(4-Bromo-N-ethyl-1,8-naphthalimide) Amine (Bis1). 0.01 M diethylenetriamine was added to solution of 0.02 M 4-bromo-1,8-naphthalic anhydride in 50 mL of absolute ethanol and heated in reflux for 60 min. After cooling to room temperature, the precipitate was filtered, washed with diethyl ether, dried, and recrystallized with ethanol. Yield was 84%.

FTIR (cm^{-1}): 3067, 2960, 2831, 1701, 1660, 1557, 1438, 1345, 1233, 779.

^1H NMR (CDCl_3 , δ , ppm): 8.52 (d, 2H, HAr), 8.38 (d, 2H, HAr), 8.11 (d, 2H HAr), 7.69 (m, 4H HAr), 7.26 (s, 1H, NH), 4.34–4.27 (m, 4H, $-\text{CH}_2-$), 3.10 (t, 4H, $-\text{CH}_2-$).

^{13}C -NMR (CDCl_3 , δ , ppm): 163.7, 163.4, 132.9, 131.7, 130.9, 129.9, 128.8, 127.9, 125.4, 122.9, 121.1, 104.6, 47.0, 39.6.

Analysis: $\text{C}_{28}\text{H}_{19}\text{N}_3\text{O}_4\text{Br}_2$ (620.9 g mol^{-1}).

Calculated (%): C 54.11, H 3.06, N 6.76.

Found (%): C 54.39, H 3.10, N 6.89.

2.3. Synthesis of Bis(4-N,N-dimethylaminoethoxy-N-ethyl-1,8-naphthalimidyl) Amine (Bis2). A solution of 0.01 mol of Bis1 in 50 mL 2-(dimethylamino)ethanol was refluxed in the presence of 0.03 M KOH for 6 hours. The process was controlled by thin-layer chromatography. After cooling to room temperature, the liquor was poured into water and the resulting precipitate was washed with water, and then dried in vacuum at 40°C. Yield was 98%.

FTIR (cm^{-1}): 3064, 2946, 2822, 1698, 1657, 1590, 1439, 1385, 1349, 1268, 1236, 1170, 1031, 779.

^1H NMR (CDCl_3 , δ , ppm): 8.49 (dd, $J = 1.0, 8.4$ Hz, 2H, HAr), 8.37 (dd, $J = 1.0, 7.2$ Hz, 2H, HAr), 8.16 (d, $J = 8.3$ Hz, 2H HAr), 7.65 (m, 4H HAr), 6.96 (1H, NH), 4.32 (m, 8H, $-\text{CH}_2-$), 3.2–2.8 (m, 8H, $-\text{CH}_2-$), 2.43 (s, 12H, CH_3).

^{13}C -NMR (CDCl_3 , δ , ppm): 164.7, 164.4, 159.8, 133.7, 133.4, 131.5, 131.1, 129.4, 128.6, 128.1, 126.8, 125.8, 122.6, 105.8, 67.4, 57.9, 47.4, 46.1, 39.7.

Analysis: $\text{C}_{36}\text{H}_{39}\text{N}_3\text{O}_6$ (609.1 g mol^{-1}).

Calculated (%): C 70.92, H 6.40, N 6.90.

Found (%): C 70.74, H 6.59, N 6.92.

3. Results and Discussion

3.1. Synthesis of Bis2. 4-Bromo-1,8-naphthalic anhydride has been used as starting material for Bis1 synthesis. Bis1 was synthesized by the condensation of diethylentriamine and 4-bromo-1,8-naphthalic anhydride in boiling ethanol solution [17].

TABLE 1: Photophysical characteristics of Bis2.

Solvent	λ_A nm	λ_F nm	$\nu_A - \nu_F$ cm^{-1}	ϵ $\text{L mol}^{-1} \text{cm}^{-1}$	Φ_F
Dimethyl sulfoxide	351	443	5917	20090	0.004
<i>N,N</i> -dimethylformamide	349	438	5822	20169	0.008
Acetonitrile	347	435	5670	19175	0.008
Ethanol	346	435	5913	20773	0.002
Acetone	347	430	5563	20773	0.09
Dichloromethane	350	425	5042	21199	0.19
Chloroform	351	423	4849	23684	0.29

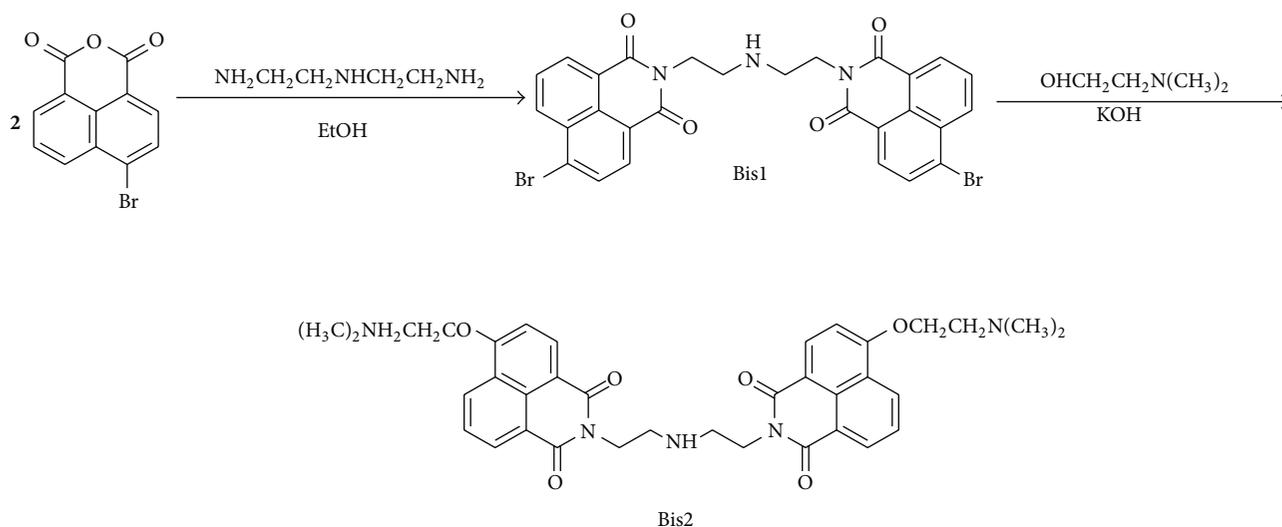
The final product Bis2 has been obtained in high yields and purity by nucleophilic substitution of the bromine atom in Bis1 with *N,N*-dimethylaminoethyl group. In this case, the electron accepting carbonyl groups of the 1,8-naphthalimide molecule favors the reaction of nucleophilic substitution wherein the bromine atom is replaced by the alkoxy group. It is well known that this substituent is widely used in the design of molecular sensor devices which are able to coordinate with metal ions and protons [18–20].

The route employed for the synthesis, according to the method described is presented in Scheme 1.

3.2. Photophysical Properties of Bis2. The photophysical properties of the 1,8-naphthalimides depend basically on the polarization of naphthalimide molecule due to the electron donor-acceptor interaction occurring between the substituents at C-4 and the carbonyl groups from the imide structure of the chromophoric system. Table 1 presents the spectral characteristics of Bis2 in seven organic solvents with different polarity: the absorption (λ_A) and fluorescence (λ_F) maxima, the extinction coefficient (ϵ), Stokes shift ($\nu_A - \nu_F$), and quantum yield of fluorescence (Φ_F).

The solvent polarity was characterized by the dielectric constant. As can be seen from the data in Table 1, the polarity of organic solvents play a significant role on the photophysical properties of Bis2. In all organic solvents, the new compound absorbs in the ultraviolet region with maxima in the near UV range of 346–351 nm and emitting blue fluorescence with maxima in the range of 423–443 nm. The molar extinction coefficients at λ_A maximum are at the range of $\epsilon = 19175$ – $23684 \text{ l mol}^{-1} \text{ cm}^{-1}$, indicating that the long wavelength band in the spectrum is a band of charge transfer, due to $n \rightarrow \pi^*$ electron transfer at $S_0 \rightarrow S_1$ transition. The extinction coefficients for a monomeric 1,8-naphthalimide having the same substituent at C-4 determined in our previous studies are 12000–14000 $\text{mol L}^{-1} \text{ cm}^{-1}$ [21, 22]. As can be seen from the data presented in Table 1, the molar extinction coefficient for the new bis-chromophoric compound is approximately 2-fold higher than that of the monomeric 1,8-naphthalimide derivative. That suggests a lack of ground state interaction between the 1,8-naphthalimide units [23].

Figure 1 plots the fluorescence maxima of Bis2 in different media. As it can be seen there is correlation between



SCHEME 1: Synthesis of Bis2.

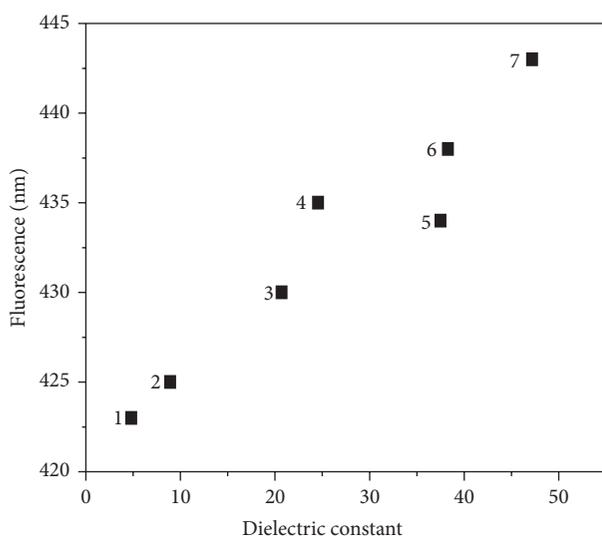


FIGURE 1: Dependence of fluorescence maxima of Bis2 on the dielectric constant: (1) chloroform, (2) dichloromethane, (3) acetone, (4) ethanol, (5) acetonitrile, (6) *N,N*-dimethylformamide, (7) dimethyl sulfoxide.

the media polarity and fluorescence maxima ($\Delta\lambda_F = 20$ nm). Moreover it is seen that Bis2 has a positive solvatochromism.

Figure 2 presents an example of absorption and fluorescence spectra of Bis2 in DMF solution. It is seen that the fluorescence spectrum has an emission band with a single maximum, without vibrational structure. The overlap between absorption and fluorescence spectra is low and an aggregation effect for the concentration at about 10^{-5} mol L⁻¹ has not been observed.

Stokes shift is an important parameter of the fluorescent compound indicating the difference in the properties and structure of the fluorophore between the ground state S_0 ,

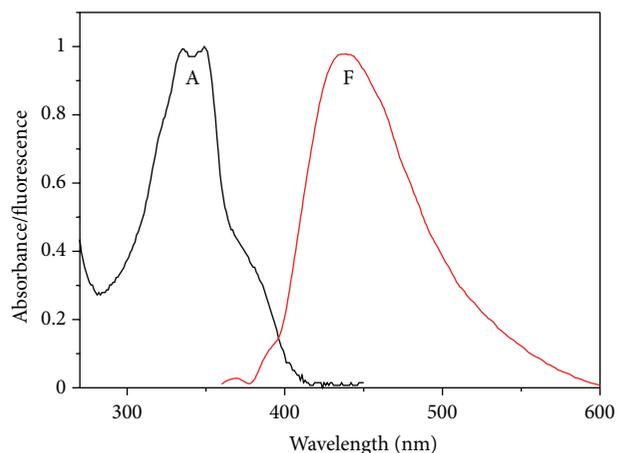


FIGURE 2: Normalized absorption (A) and fluorescence (F) spectra of Bis2 in DMF solution.

and the first excited state S_1 . The Stokes shift is found by the following equation:

$$(\nu_A - \nu_F) = \left(\frac{1}{\lambda_A} - \frac{1}{\lambda_F} \right) \times 10^{-7}. \quad (1)$$

The Stokes shift values range obtained in this work is $\nu_A - \nu_F = 4849 - 5917$ cm⁻¹. They depend on the polarity of the organic solvents used. It is seen that in the nonpolar media the values of Stokes shift are lower, if compared to those obtained in polar media (Table 1 and Figure 3).

The molecules ability to emit the absorbed light energy is characterized quantitatively by the fluorescence quantum yield. The fluorescence quantum yield has been calculated on

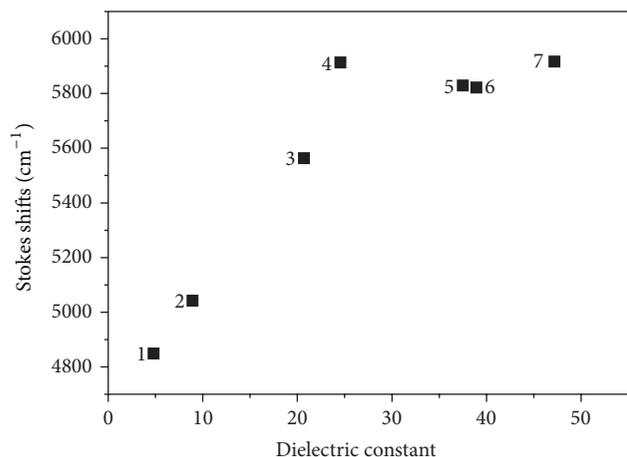


FIGURE 3: Dependence of Stokes shift of Bis2 on the dielectric constant: (1) chloroform, (2) dichloromethane, (3) acetone, (4) ethanol, (5) acetonitrile, (6) *N,N*-dimethylformamide, (7) dimethyl sulfoxide.

the basis of the absorption and fluorescence spectra by the following equation:

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

where the 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 excited wavelength, respectively, while S_{st} and S_u are the integrated emission band areas of the standard and sample respectively, n_{Dst} and n_{Du} are the solvent refractive index of the standard and sample, and u and st refer to the unknown and standard, respectively.

The calculated Φ_F is in the region 0.002–0.29. As it can be seen from Table 1 the fluorescence quantum yield values depend strongly on the solvent polarity. The lowest Φ_F has been observed in ethanol ($\Phi_F = 0.002$) and its value increases more than 145 times in chloroform solution ($\Phi_F = 0.29$). This great difference in the quantum yield values is due to the photoinduced electron transfer that is quenched in nonpolar media. In this case, the quenching leads to restored fluorescence emission of the fluorophore. Such behavior has also been exhibited by similar monomeric 4-*N,N*-dimethylaminoethoxy-*N*-allyl-1,8-naphthalimide having a small Φ_F in polar organic solvents and higher in non-polar solvents [18, 19].

3.3. Effect of Protons and Metal Cations on the Spectral Properties of the Bis2. In the presence of protons, the absorption and fluorescence maxima of Bis2 do not change their position. However, the fluorescence intensity in an ethanol/water (v/v 1:4) solution is pH dependent, as can be seen from Figure 4. This correlation has been investigated in the 3.5–11.0 pH value range and gives evidence that Bis2 responds to pH changes due to its high sensitivity to proton concentration. The constant value of the fluorescence intensity decreases

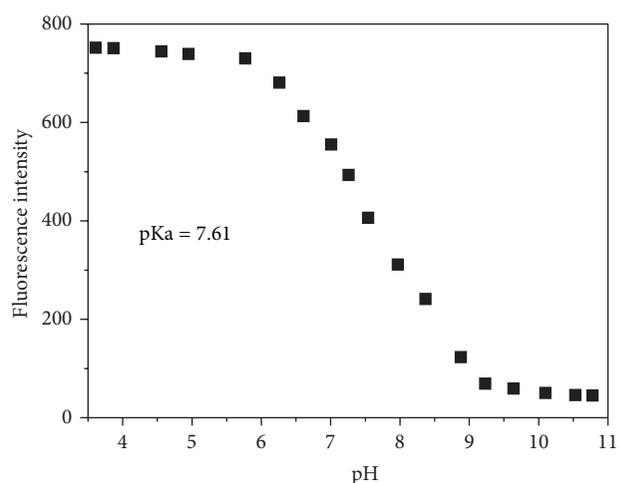


FIGURE 4: The influence of pH upon fluorescence intensity of Bis2 in ethanol-water solution (1:4, v/v).

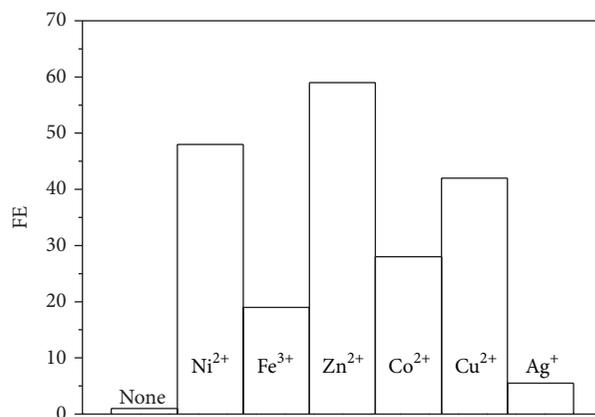


FIGURE 5: Fluorescence enhancement factor (FE) of Bis2 in acetonitrile solutions ($c = 10^{-5} \text{ mol L}^{-1}$) in presence of metal cations ($c = 8.10^{-5} \text{ mol L}^{-1}$) at excitation wavelength 350 nm.

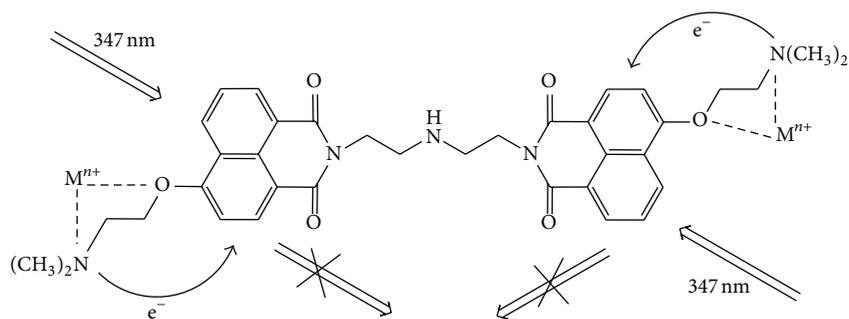
after reaching pH 5.0–5.5 and at values higher than pH 9.5 the curve forms also a plateau. A 9-fold fluorescence quenching is observed for the pH range investigated.

The pH dependence of fluorescence intensity has been analyzed using the following equation:

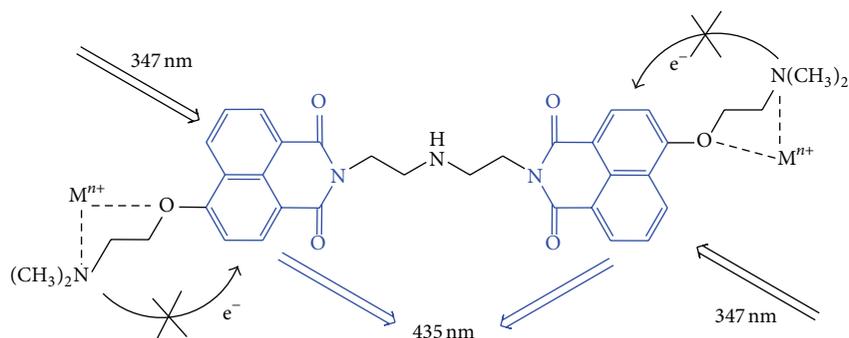
$$\text{pH} - \text{pKa} = \log \left(\frac{(I_{F \max} - I_F)}{(I_F - I_{F \min})} \right). \quad (3)$$

The calculated pKa value for Bis2 is 7.61. This value is smaller than that of the monomer fluorophore, having the same substituents at C-4 position (pKa = 8.40) [18].

The investigation of photophysical properties of Bis2 as a ligand in the presence of different metal cations has been of particular interest. Its properties signaling the presence of transition metal cations have been investigated in acetonitrile with regard to potential applications as a PET sensor. Acetonitrile has been chosen as the solvent for all the measurements since it guarantees a good solubility of the used metal salts, ligand, and the respective complexes.



SCHEME 2: Proposed mechanism of photoinduced electron transfer of Bis2.



SCHEME 3: Proposed mechanism of photoinduced electron transfer of Bis2.

In acetonitrile, Bis2 has a very weak fluorescence emission as expected for a good PET fluorescence switch. A dramatic enhancement in the fluorescence intensity in presence of the different metal cations has been observed. The influence of the metal cations on the fluorescence enhancement (FE) is presented in Figure 5. The $FE = I/I_0$ has been determined from the ratio of maximum fluorescence intensity I (after addition of metal cations) and minimum fluorescence intensity I_0 (before metal cations addition). Upon the addition of metal cations the enhancements of the fluorescence emission is determined by the nature of the cations added. The highest values have been observed in the presence of Zn^{2+} cations ($FE = 59$) and a rank can be given as follows:



The 1,8-naphthalimide under study is subjected to a PET proceeding from the distal amino groups of *N,N*-dimethylaminoethoxy moieties at C-4 position to the 1,8-naphthalimide units. The interaction between the 1,8-naphthalimide as a fluorophore and the *N,N*-dimethylamino group as a receptor provoking PET leads to a quenching of the fluorescence emission (Scheme 2). The presence of transition metal cations in the solution changes the photophysical properties of Bis2 since in this case the system fluoresces intensively (Scheme 3). The enhancement of fluorescence intensity confirms the existence of coordination interaction between the metal cations and oxygen at C-4 position of the naphthalene ring and the *N,N*-dimethylamino group [19].

4. Conclusion

The synthesis and the photophysical characteristics of a new bis-1,8-naphthalimide have been described. The strong dependence of the fluorescence intensity on the solvent polarity has been observed and was explained by means of possible photoinduced electron transfer. In the presence of protons and metal cations, the fluorescence intensity of the bis-1,8-naphthalimide is higher than that in acetonitrile solution free of metal cations. The relative affinity of the bis-1,8-naphthalimide to form metal complexes increases in the range $Zn^{2+} > Ni^{2+} > Cu^{2+} > Co^{2+} > Fe^{3+} > Ag^+$. On the basis of the present investigation, it can be assumed that the new bis-1,8-naphthalimide is suitable for detecting of metal cations and protons based on the quenching of photoinduced electron transfer processes at concentration ranges from 0 to $8.10^{-5} \text{ mol L}^{-1}$.

Acknowledgments

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