

A new fluorosensor based on bis-1,8-naphthalimide for metal cations and protons

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Abstract

The paper reports on the synthesis and spectral characteristics of a new fluorescent bis-1,8-disubstituted naphthalimide linked by a diethylenetriamine bridge (NI2TEA). The ability of the new compound to detect cations has been evaluated by monitoring spectrophotometrically the changes in the fluorescence intensity performed on its *N,N*-dimethylformamide (DMF) solution. The behaviour of the new compound has been tested in the presence of different metal cations: Fe³⁺, Cr³⁺, Mn²⁺, Sr²⁺, Ni²⁺, Zn²⁺, Cu²⁺ and Co²⁺. The results show clearly that only Fe³⁺ and Cr³⁺ cations are effectively detected. Besides, in *N,N*-di-methylformamide solution the NI2TEA can be used as a naked eye sensor for hydroxyl anions. © 2007 Published by Elsevier B.V.

Keywords: Naphthalimides; Sensors; Photophysics; Fluorescence; PET; Metal cations

1. Introduction

In the last decade, much attention has been paid to supramolecular fluorescent systems for the sensing and reporting of analytes which may be of importance for chemical, biological and environmental sciences. Variations of the fluorescence intensity of such devices can be used for evidencing and quantitatively measuring the concentrations of ions or molecules with high sensitivity [1–3]. Many of these fluorescent chemosensors are based on a photoinduced electron transfer (PET) process occurring under certain conditions. The multicomponent sensor is designed, as far as possible, in such a way that the electron transfer process originates, in the excited state, from an electron donating receptor separated from the electron acceptor by a short spacer. In this situation, the fluorescence of the signalling fluorescent unit will be quenched while guests (metal ions or protons) capable of binding with the receptor of the molecule when available in the medium, will cut off PET process and switch on the fluorescence of the system. The 1,8-naphthalimide derivatives, comprising a substituent with electron donating receptor

have proved to be good PET sensors for metal cations and protons [4–14].

Based on our previous research on the PET systems, a new bis-1,8-naphthalimide derivative (NI2TEA) has been synthesized. Its two 1,8-naphthalimides are substituted with a *N,N*-dimethylaminoethylamino group as receptor while a triethyleneamine linker is used to connect the two chromophores. The basic photophysical properties were investigated in organic solvents of different polarity and the influence of metal cations on the fluorescence intensity is reported.

2. Experimental

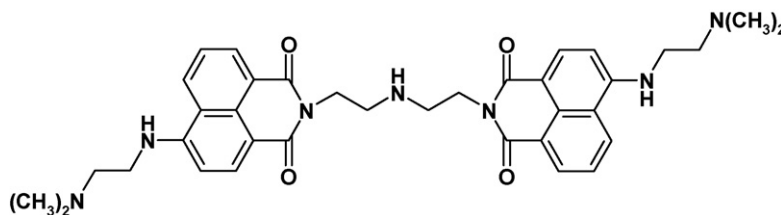
The synthesis of the nitro precursor of the NI2TEA derivative was already described [15]. The structure of NI2TEA is presented in Scheme 1.

2.1. Synthesis of NI2TEA

Bis-4-nitro-1,8-naphthalimide (0.01 M) was reacted with 0.006 M of *N,N*-dimethylethylenediamine in 50 ml of *N,N*-dimethylformamide (DMF) 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 under

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Scheme 1. Chemical structure of NI2TEA.

vacuum at 40 °C. Yield: 80%. FT-IR (KBr) cm^{-1} : 3103, 2950, 2825, 1665, 1645, 1581, 1530, 1348, 1243, 779, 759; ^1H NMR (CDCl_3 (ppm), 250 MHz): 8.37 (dd, $J=1.0$, 8.2 Hz, 2 H), 8.36 (dd, $J=1.0$, 7.3 Hz, 2 H), 8.25 (d, $J=1.1$, 8.3 Hz, 2 H), 7.48 (m 4H), 6.35 (1 H, NH), 6.56 (2 H, NH); ^{13}C NMR (CDCl_3) δ (ppm): 164.8, 164.2, 149.5, 132.5, 130.9, 129.6, 128.7, 126.7, 1143, 104.2, 56.6, 47.5, 44.9, 39.4; analysis: $\text{C}_{36}\text{H}_{41}\text{O}_4\text{N}_7$ (635.2); Calcd (%): C 68.01, H 6.45, N 15.45; found (%): C 68.12, H 6.59, N 15.76.

3. Materials and methods

All organic solvents were of spectroscopy grade and used without special treatment. $\text{Zn}(\text{ClO}_4)_2$, $\text{Cu}(\text{ClO}_4)_2$, $\text{Mn}(\text{ClO}_4)_2$, $\text{Sr}(\text{ClO}_4)_2$, $\text{Ni}(\text{ClO}_4)_2$, $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ and $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$, salts were the sources for metal cations. Sulphuric acid was used as a source of protons.

UV–vis spectrophotometric investigations were performed on a Varian Cary-50 instrument and the fluorescence spectra on a Varian Cary Eclipse at 10^{-5} M l^{-1} . Fluorescence quantum yield was determined by comparison with Rhodamine 101 used as a reference ($\Phi_F = 1.00$). 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 a tetramethylsilane standard. Experiments with 30° pulses, 1 s relaxation delays, 16 K time domain points, zero-filled to 64 K for protons and 32 K for carbons were performed. The distortion less enhancement by polarisation transfer (DEPT) spectra were recorded under the conditions used for the ^{13}C NMR spectra at $\tau = (2 \ ^1J_{\text{CH}})^{-1} = 3.45 \ \mu\text{s}$. The 2D $^1\text{H}/^1\text{H}$ correlated spectra (COSY) were performed with spectral width 2200 Hz, relaxation delay 2 s, number of increments 512, and

size $1\text{K} \times 1\text{K}$. The 2D $^1\text{H}/^{13}\text{C}$ heteronuclear multiple quantum coherence (HMQC) experiments were carried out with a spectral width of 2200 Hz for ^1H and 9000 Hz for ^{13}C , relaxation delay 1.5 s, FT size $1\text{K} \times 256 \text{ W}$. 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 [16].

4. Results and discussion

It is well known that the light absorption properties of the 1,8-naphthalimide derivatives are basically related to the polarization of the chromophoric system. Light absorption in this molecule generates a charge transfer (CT) interaction between the substituents at C-4 position and the imide functionality. This interaction strongly depends on the medium, especially, on the polarity of organic solvents. Organic solvents with different dielectric constants were used to investigate this effect on the photophysical properties of NI2TEA. Table 1 summarizes the spectral characteristics of the NI2TEA in the organic solvents used: the absorption (λ_A) and fluorescence (λ_F) maxima, the extinction coefficient ($\log \epsilon$), Stokes shift ($\nu_A - \nu_F$) and quantum yield of fluorescence (Φ_F).

The NI2TEA compound has yellow-green colour with absorption maxima at 422–435 nm and fluorescence emission maxima at 509–526 nm in all organic solvents under study at room temperature.

Fig. 1 presents the normalized absorption and fluorescence spectra of NI2TEA in *N,N*-di-methylformamide solution as an example. In the long-wavelength region, the fluorescence spectrum is the mirror image of the absorption one. This is indicative for the preserved planarity of the molecular structure of the NI2TEA in the excited state. The overlap of the absorption and flu-

Table 1
Photophysical properties of NI2TEA in organic solvents of different polarity

	λ_A (nm)	ϵ ($\text{l mol}^{-1} \text{ cm}^{-1}$)	λ_F (nm)	$\nu_A - \nu_F$ (cm^{-1})	Φ_F
Toluene	423	20,600	509	3974	0.313
Chloroform	429	21,400	510	3702	0.280
Ethyl acetate	422	20,600	510	4008	0.196
Tetrahydrofuran	424	22,400	511	4015	0.106
Di-chloromethane	428	22,200	513	3871	0.094
Acetone	426	22,700	520	4243	0.022
Ethanol	433	22,300	526	4083	0.013
Methanol	433	23,800	528	4155	0.010
<i>N,N</i> -di-methylformamide	435	21,000	526	3977	0.014
Acetonitrile	428	21,300	522	4207	0.012

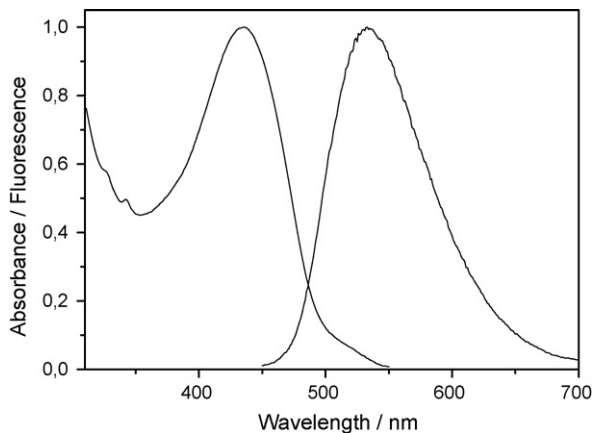


Fig. 1. Normalized absorption and fluorescence spectra of NI2TEA in DMF solution ($10^{-5} \text{ mol l}^{-1}$).

orescence spectra is small and an aggregation effect has not been observed at the studied concentration ($c = 1 \times 10^{-5} \text{ mol l}^{-1}$) of the NI2TEA.

In the visible region, the molar extinction coefficients (ϵ) of NI2TEA are high (between 20,600 and 22,700 $\text{l mol}^{-1} \text{ cm}^{-1}$). It is a very good range of values since they are twice larger than the one of the analogous monomeric 1,8-naphthalimide having the same substituent at C-4 ($\epsilon = 11,200 \text{ l mol}^{-1} \text{ cm}^{-1}$). This suggests that no important ground state interaction occurs between the 1,8-naphthalimide chromophoric units [17]. The fact that the molar extinction coefficients are higher than 10,000 indicates that the long-wavelength band of the absorption spectra is a band of charge transfer (CT) which occurs as a result from a $\pi \rightarrow \pi^*$ electron transfer during the $S_0 \rightarrow S_1$ transition.

Stokes shift ($\nu_A - \nu_F$) indicates the difference in the properties and the structure between the ground S_0 state, and the first excited S_1 state. The values of Stokes shift for NI2TEA are in the 3871–4243 cm^{-1} region, which is in accordance with other investigations on similar 1,8-naphthalimide derivatives.

The fluorescent quantum yield (Φ_F) of NI2TEA has been calculated using Eq. (1):

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

where Φ_F is the emission quantum yield of the sample, Φ_{st} 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} the solvent refractive index of the standard and sample, u and s refer the unknown and standard, respectively.

As seen from Table 1, the quantum yield of NI2TEA shows large variations depending strongly on the polarity of the solvent, with values situated in the 0.010–0.313 range. Fig. 2 presents the dependence of the quantum fluorescence yield on the di-electric constant of the solvents. The great difference in the quantum yields in polar and non-polar solvents is due to the fact that, in non-polar medium PET no longer takes place, due to the absence of stabilisation of the charge separated state which may survive in polar medium. This behaviour has also been exhibit by the

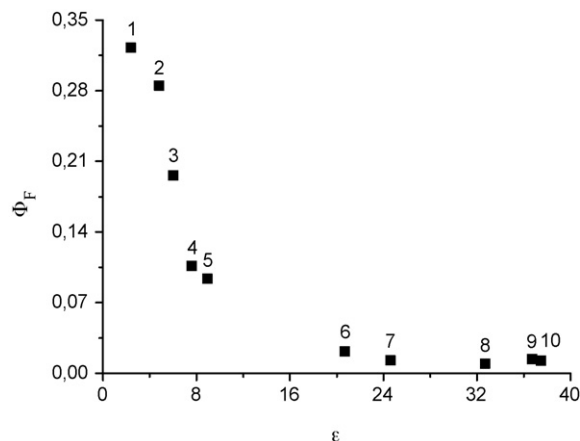


Fig. 2. Relative quantum fluorescence yields (Φ_F) of NI2TEA vs. the solvent dielectric constant toluene (1), chloroform (2), ethyl acetate (3), tetrahydrofuran (4), di-chloromethane (5), acetone (6), ethanol (7), methanol (8), DMF (9), acetonitrile (10).

corresponding monomeric 4-*N,N*-di-methylaminoethylamino-*N*-alkyl-1,8-naphthalimides [18,19].

4.1. Influence of metal cations on the photophysical properties

The investigation of photophysical properties of NI2TEA as a ligand in the presence of different metal cations has been of particular interest. Its functional properties signalling the presence of transition metal cations have been investigated in DMF with regard to potential applications as a PET sensor. DMF 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.

The fluorescence spectra show that the nature of the metal cations (Fe^{3+} , Cr^{3+} , Mn^{2+} , Sr^{2+} , Ni^{2+} , Zn^{2+} , Cu^{2+} and Co^{2+}) determines the behaviour of NI2TEA in the complex formation process. The dependence of the metal cations on the fluorescence enhancement (FE) is presented in Fig. 3 The $\text{FE} = I/I_0$ was determined from the ratio of maximum fluorescence inten-

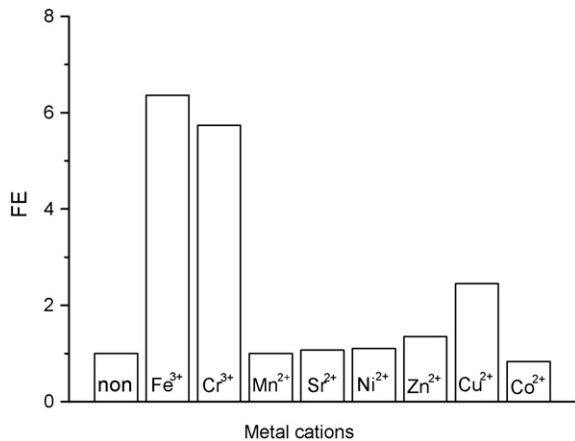
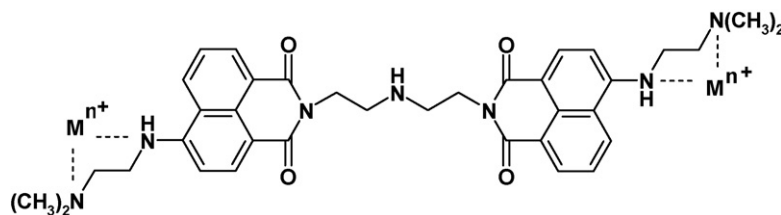


Fig. 3. Fluorescence enhancement factor (FE) of bis-4-*N,N*-di-methylaminoethylamino-1,8-naphthalimide ($c = 1 \times 10^{-5} \text{ mol l}^{-1}$) in the presence of different metal cations ($c = 1.8 \times 10^{-4} \text{ M}$) in DMF solution.

Scheme 2. Schematic presentation of complex of NI2TEA and metal cations (M^{n+}).

sity I (after addition of metal cations) and minimum fluorescence intensity I_0 (before metal cations addition). The highest fluorescence enhancement has been determined in the presence of Fe^{3+} and Cr^{3+} cations ($FE = 6.35$ and 5.74 , respectively). In the case of Mn^{2+} , Sr^{2+} , Ni^{2+} , Zn^{2+} and Co^{2+} the changes in the fluorescence intensity is negligible. This effect can be explained by the presence of the electron donating nitrogen atom in the bridge between the two naphthalimide fluorophores. The nature of this atom weakens the electron accepting strength of the carbonyl groups, hence the electron density of NI2TEA is lowered. As Fe^{3+} and Cr^{3+} cations are of higher acidity, they benefit from the latter phenomenon to form complexes with the NI2TEA.

Fig. 4 presents the sensor capacity of NI2TEA in DMF solution ($1 \times 10^{-5} \text{ mol l}^{-1}$) at different concentrations of the Fe^{3+} cations as an example. The increase in fluorescence intensity occurs after the addition of Fe^{3+} cations in the $(0-1.8) \times 10^{-4} \text{ mol l}^{-1}$ concentration range. The addition of Fe^{3+} at concentration $1.66 \times 10^{-5} \text{ mol l}^{-1}$ produces 40% enhancement in the fluorescence intensity which proves the good sensitivity. Raising the concentration of the cation up to $8.3 \times 10^{-5} \text{ mol l}^{-1}$ also induces an increase in the fluorescence. Further higher concentrations in the range 8.3×10^{-5} to $1.8 \times 10^{-4} \text{ mol l}^{-1}$ have a small impact on the variation of fluorescence intensity. As mentioned above, the fluorescence intensity increases due to the formation of a complex between the NI2TEA and Fe^{3+} cations. The stoichiometry of

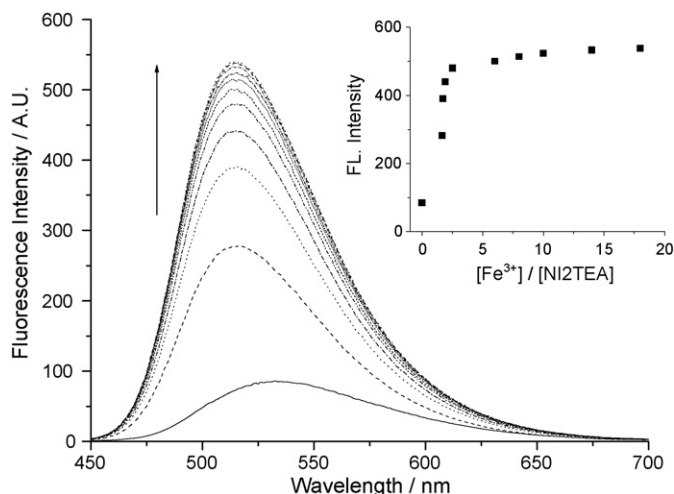


Fig. 4. Fluorescence spectra of NI2TEA ($1 \times 10^{-5} \text{ mol l}^{-1}$) in DMF at various concentrations of Fe^{3+} . The concentrations of Fe^{3+} cations are in order of increasing intensity from 0 to $1.8 \times 10^{-4} \text{ mol l}^{-1}$. The inset shows the plot obtained monitoring changes in the fluorescence maxima upon addition of Fe^{3+} cations.

the NI2TEA- Fe^{3+} complex system has been determined by the enhancement in the fluorescence intensity of NI2TEA in the three presence of varying concentrations of Fe^{3+} cations. Titration plots (Fig. 4, inset) show that a 2:1 metal/ligand complex is formed. A hypsochromic shift in the fluorescence spectra ($\Delta\lambda_F = 8-12 \text{ nm}$) in the presence of these metal cations has been observed, which indicates that the switch might bind metal cations via a bidentate chelation to nitrogen atoms both from the receptor and from the aromatic amine (Scheme 2).

This chelation has two different effects: (i) the photoinduced electron transfer from the receptor amine to the fluorophore is inhibited causing a fluorescence enhancement; (ii) weakening the electron donating ability of the aromatic amine at C-4 position leading to a shift of the spectra to the shorter wavelength.

Fig. 5 presents the fluorescence spectra of the newly synthesized bis-1,8-naphthalimide taken in the presence of metal cations (Mn^{2+} , Sr^{2+} , Ni^{2+} , Zn^{2+} , Cu^{2+} and Co^{2+}) each at concentration $4.10^{-5} \text{ mol l}^{-1}$. The fluorescence intensity in the case is slightly higher ($FF = 1.1$) than that of the solution free of metal cations. The addition of Fe^{3+} at concentration of $4.10^{-5} \text{ mol l}^{-1}$ to the same solution causes a drastic increase in fluorescence intensity ($FF = 5.1$). Most probably Fe^{3+} is more competitive in the complex forming reaction and eliminates the complexation ability of the other cations present. The fluorescence maxima are shifted with 15 nm as a result of a complex formed between the cations and the naphthalimide ligand. Similar spectral characteristics have been obtained running the experiment with Cr^{3+} cations. The data prove the selectivity of the new NI2TEA and its high prospects to be used as a reliable detector of Fe^{3+} and Cr^{3+} cations.

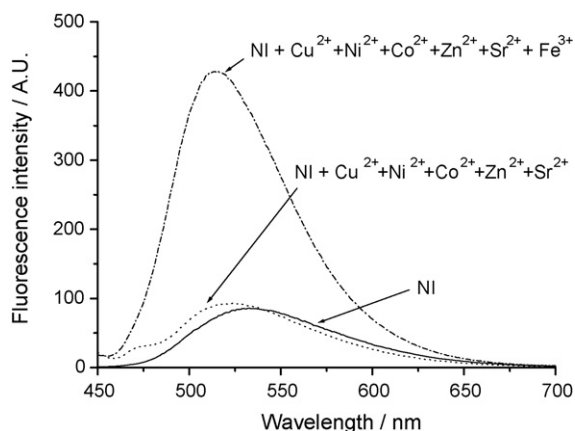


Fig. 5. Fluorescence spectra of NI2TEA ($1 \times 10^{-5} \text{ mol l}^{-1}$) in DMF at various metal cations. The concentrations of metal cations are $4.10^{-5} \text{ mol l}^{-1}$.

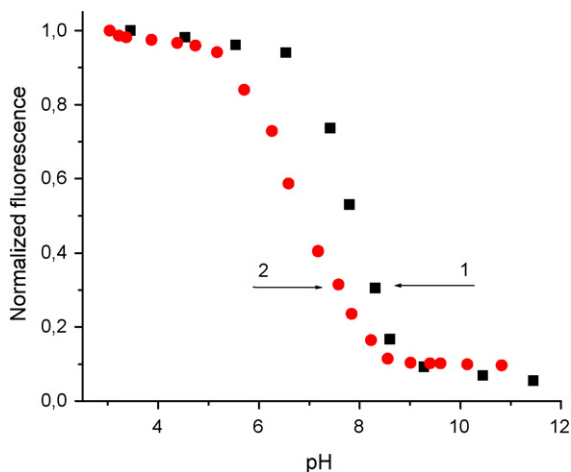


Fig. 6. The influence of pH on the fluorescence intensity at the fluorescence maxima of MD [9] (1) and NI2TEA ($c = 10^{-5} \text{ mol l}^{-1}$) (2) investigated in a of methanol–water (1:4, v/v) solution.

4.2. Influence of protons on the fluorescence intensity

In the recent years some 1,8-naphthalimide derivatives have been used as supramolecular models to design pH sensors based on the PET [1–3]. The pH intensity of NI2TEA has been investigated in the 3–11 pH range in a methanol–water mixed solvent (1:4, v/v). Though the profiles of the fluorescence spectra do not vary at different pH values, the intensity of the fluorescence varies significantly. As shown in Fig. 6, NI2TEA exhibits high sensitivity to the presence of protons. As seen the increase in pH up to 5.0 does not change the fluorescence intensity. Higher pH values cause its drastic decrease and finally at pH 8.5 the curve reaches again a plateau. The pattern of the curve is due to fact that in alkali solution the PET suppresses the fluorescence emission which becomes very weak. The protonation of the distal tertiary nitrogen atoms $[\text{NHCH}_2\text{CH}_2\text{N}(\text{CH}_3)_2]$ in the NI2TEA stops the PET process and the fluorescence increases. Therefore, the fluorescence intensity at pH 3.0 is 10 times higher than that at pH 10.8. The pH dependence of fluorescence intensity has been analyzed with Eq. (2) and the calculated $\text{p}K_a$ value is 6.85. The $\text{p}K_a$ value of the monomer 1,8-naphthalimide whit $\text{NHCH}_2\text{CH}_2\text{N}(\text{CH}_3)_2$ substituent is 7.78 [11]:

$$\text{pH} - \text{p}K_a = \log \left(\frac{I_{F_{\text{max}}} - I_F}{I_F - I_{F_{\text{min}}}} \right) \quad (2)$$

These results reveal that the newly synthesized NI2TEA has the capacities of a pH sensor, hence can be used as a detector of aqueous media pollution. A maximum of its sensitivity has been observed at pH 5.

4.3. Influence of hydroxyl anions on the absorption and fluorescence intensity

Upon titration of NI2TEA in DMF with NaOH the absorbance at 435 nm is substantially reduced and marked by the formation of new bands at 339 and 536 nm and concomitant formation of three isobestic points at ca. 296, 382 and 474 nm (Fig. 7). The formation of the new bands can be

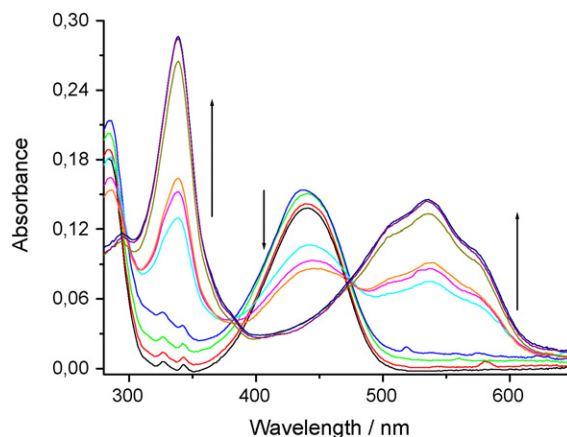


Fig. 7. Absorption spectra of NI2TEA ($c = 10^{-5} \text{ mol l}^{-1}$) in DMF at different concentrations of NaOH.

explained by de-protonation of the amino moiety at C-4 position caused by OH^- anions and the two new peaks appearing at 339 and 536 nm are attributed to the negatively charged 1,8-naphthalimide rings. This increases the electron density at nitrogen atoms C-4 position, hence the respective absorption maximum is bathochromically shifted with ca. 100 nm and the solution colour changes from yellow to red. As seen from Fig. 7, the newly formed band assigned to the charge transfer is of vibronic structure having maxima at 507, 536 and 570 nm. The deprotonated form of the NI2TEA has been found to emit red fluorescence. The fluorescence spectrum of the NI2TEA solution excited at 339 and 536 nm has a broad fluorescence band in the 500–700 nm region with a maximum at 611 nm (Fig. 8). In this case during the titration, the yellow solution of NI2TEA became red, as shown in Fig. 9. Upon re-protonation with chlorhydric acid the colour changes from red to yellow evidencing the reversibility of the process and a pH dependent response. In this case the acidic protons interact with the deprotonated nitrogen atoms at C-4 position thus restoring their electron donating ability. Respectively, a hypsochromic shift of the fluorescence and absorption maxima is observed.

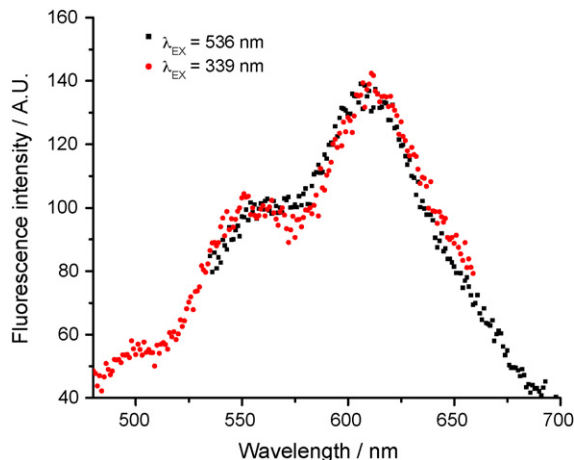


Fig. 8. Fluorescence spectra of NI2TEA ($c = 10^{-5} \text{ mol l}^{-1}$) in DMF on addition of NaOH.



Fig. 9. The colour change of NI2TEA in DMF ($c = 10^{-5} \text{ mol l}^{-1}$) on addition of NaOH.

Our results are in a very good agreement with those reported recently by Gunnlaugsson et al. [20] and Liu and Tian [12], though these authors have performed the titration with $(\text{C}_4\text{H}_9)_4\text{NF}$. This allows the assumption that 1,8-naphthalimide derivatives have great prospects as naked eye sensors for wide range of hydroxyl ions. Till now the reaction has been observed only in DMF solution.

5. Conclusions

A new NI2TEA has been synthesized and investigated. The results from the investigations on PET and photophysical properties of the new compound performed in organic solvents of different polarity reveal the strong dependence of the fluorescence intensity on the polarity of the solvents. The influence of metal cations (Fe^{3+} , Cr^{3+} , Mn^{2+} , Sr^{2+} , Ni^{2+} , Zn^{2+} , Cu^{2+} and Co^{2+}) and protons on the fluorescence intensity has been studied to test the capacities of the newly synthesized naphthalimide as a fluorescence sensor for these ions in the environment. The data obtained allow the assumption that the new NI2TEA is capable of detecting selectively Fe^{3+} and Cr^{3+} cations protons. The detection is based on the quenching of PET processes in the 1,8-

naphthalimide fluorophore. In *N,N*-dimethylformamide solution this compound is potential as a naked eye sensor for hydroxyl anions.

Acknowledgments

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