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# Sensor potential of 1,8-naphthalimide and its dyeing ability of cotton fabric

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## ABSTRACT

A new 4-(2-*N*,*N*-dimethylamino)ethylamino-*N*-2-hydroxyethyl-1,8-naphthalimide has been synthesized. The photophysical characteristics have been determined in aqueous and acetonitrile solutions. The influence of metal cations ($Ni^{2+}$, $Zn^{2+}$, and $Cu^{2}$) and protons on the fluorescence intensity has been studied to evaluate the capacities of the newly synthesized 1,8-naphthalimide as a fluorescence sensor. The 1,8-naphthalimide dye has been chemically bonded to a cotton textile fabric in order to obtain a heterogeneous fluorescent sensor for detecting of metal cations and protons.

## 1. Introduction

In the recent years the development of new materials which can detect and react to external stimuli providing important information on chemical, biological, medical and physical change occurring in the environment have been studied intensively [1].

Textile materials have some specific physicomechanical properties making them favored matrixes for immobilizing different substances. They are particularly suitable for the design of chemosensors or biosensors indicating biological functions and when they should be constantly worn by an individual without hampering their daily routine. The advantages of textile materials are their large specific surface, the good mechanical and exploitation properties (flexibility, softness, strength, lightness, ability to permeate gases) [2–5]. The large contact surface of textiles in general enables efficient contact with the detected substances compared to other polymer materials used for the same purpose.

Derivatives of 1,8-naphthalimide have been extensively studied owing to their interesting photophysical and biological properties and the wide range of their applications in different chemical and biochemical areas [6–8]. Amongst the fluorescent compounds utilized as sensors 1,8-naphthalimide derivatives have emerged as quite appropriate for the purpose. The 1.8-naphthalimides moiety has also been used to design fluorescent molecular probes sensitive to variations of pH or metal ions concentrations [9–15].

In this paper we present the synthesis and properties of a new 4-(2-*N*,*N*-dimethylamino)ethylamino-*N*-(2-hydroxyethyl)-1,8-naphthalimide designed to act as a fluorescence sensor. The influence of biologically important metal cations and protons on the fluorescence intensity of acetonitrile and aqueous solutions has been discussed with regard to its potential application as a detector for these ions. The dyeing of cellulose textile fibers with the new 1,8-naphtalimide under different conditions has also been investigated.

## 2. Experimental

### 2.1. Materials and methods

Bleached and unmercerized cotton fabrics were used throughout the work. Cotton fabric with a surface weight of about 140 g/m$^2$ has been used. Chloroacetyl chloride, 4-nitro-1,8-naphthalic anhydride, 2-hydroxyethylamine and *N*,*N*-dimethylaminoethylendiamine were used without further purification as obtained from (Aldrich). $Cu(NO_3)_2 \cdot 3H_2O$, $Ni(NO_3)_2 \cdot 6H_2O$, and $Zn(NO_3)_2 \cdot 4H_2O$, used as source for metal cations.

#### 2.1.1. Synthesis of 4-nitro-N-(2-hydroxyethyl)-1,8-naphthalimide

4-Nitro-1,8-naphthalic anhydride (2.43 g, 0.01 mol) was reacted with 2-hydroxyethylamine (0.61 mL, 0.01 mol) in 2-methoxyethanol

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(60 mL) for 3 h at 100 °C. After cooling the precipitate was filtered off, washed with water, and then dried in vacuum at 40 °C. Yield: 86%.

FT-IR (KBr) $cm^{-1}$: 3456, 2940, 1700, 1662, 1567, 1457, 1373, 1342, 1236, 1000, 931, 779. $^{1}H$ NMR (DMSO, 250 MHz) ppm: 3.62 (m., 2H, $CH_2C\underline{H}_2OH$); 4.13 (t. 2H, $J = 6.4$ Hz, $NC\underline{H}_2CH_2OH$); 4.82 (t., 1H, $J = 6.1$ Hz, $CH_2CH_2O\underline{H}$); 8.05 (dd., 1H, $J = 7.5$ Hz, 8.5 Hz, ArH-4); 8.5–8.7 (m., 4H, ArH).

$^{13}C$ NMR (DMSO, 62 MHz) ppm: 42.2, 57.6, 122.7, 122.8, 124.3, 126.7, 128.3, 128.7, 129.5, 130.1, 131.6, 149.0, 162.2, 163.0.

Analysis: $C_{14}H_{10}N_2O_5$ (286.14 g $mol^{-1}$): Calc. (%): C-58.74, H 3.50, N 9.79. Found (%): C-58.49, H 3.58, N 9.64.

### 2.1.2. *Synthesis of 4-(2-N,N-dimethylamino)ethylamino-N-(2-hydroxyethyl)-1,8-naphthalimide (NI)*

4-Nitro-*N*-(2-hydroxyethyl)-1,8-naphthalimide (1.43 g, 0.005 mol) was reacted with *N,N*-dimethylaminoethylendiamine (0.55 mL, 0.0005 mol) in *N,N*-dimethylformamide (60 mL) for 24 h at room temperature. After that the liquor was added to the 600 mL of water. The precipitate was collected by filtration, washed with water, and then dried in vacuum at 40 °C. Yield: 94%.

M.p. 93–95 °C.

FT-IR (KBr) $cm^{-1}$: 3383, 3064, 2964, 2881, 1676, 1637, 1567, 1469, 1388, 1342, 1248, 1024, 775.

$^{1}H$ NMR (DMSO, 250 MHz) ppm: 2.86 (s., 6H, $CH_3$); 3.43 (t. 2H, $J = 5.9$ Hz, $C\underline{H}_2N(CH_3)_2$); 3.56 (t., 2H, $J = 6.7$ Hz, $CH_2C\underline{H}_2OH$); 3.78 (q., 2H, $J = 5.6$ Hz, $NHC\underline{H}_2CH_2N(CH_3)_2$); 4.07 (t., 2H, $J = 6.7$ Hz, $NC\underline{H}_2CH_2OH$); 6.84 (d., 1H, $J = 8.6$ Hz, ArH-2); 7.62 (dd., 1H, $J = 7.5$ Hz, 8.2 Hz, ArH-4); 8.06 (t., 1H, $J = 5.1$ Hz, $N\underline{H}CH_2CH_2N(CH_3)_2$); 8.19 (d., 1H, $J = 8.5$ Hz, ArH-1); 8.35 (d., 1H, $J = 7.2$ Hz, ArH-3); 8.85 (d., 1H, $J = 8.5$ Hz, ArH-5).

$^{13}C$ NMR (DMSO, 62 MHz) ppm: 37.8, 41.4, 42.2, 54.4, 57.9, 104.2, 108.8, 120.4, 121.8, 124.4, 129.1, 129.2, 130.6, 133.9, 149.8, 163.0, 163.8.

Analysis: $C_{18}H_{21}N_2O_3$ (313.18 g $mol^{-1}$): Calc. (%): C-69.01, H 6.71, N 8.95. Found (%): C-68.76, H 6.62, N 8.89.

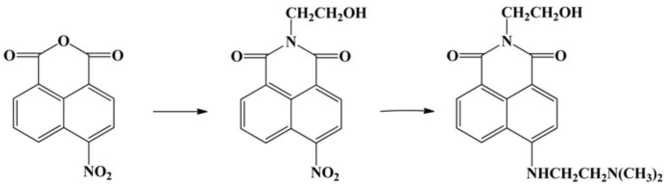
### 2.2. *Analysis*

UV–Vis spectrophotometric investigations were performed using “Thermo Spectronic Unicam UV 500” spectrophotometer at concentrations of $1 \times 10^{-5}$ mol $l^{-1}$. The fluorescence spectra were taken on a “Cary Eclipse” spectrophotometer at concentrations of $1 \times 10^{-5}$ mol $l^{-1}$. IR analysis of compounds and both treated and untreated cotton was carried out using the Infrared Fourier transform spectrometer (IRAffinity-1 “Shimadzu”) with the diffuse-reflectance attachment (MIRacle Attenuated Total Reflectance Attachment). The color characteristics of the fabrics were determined on a Texflach ACS/DATACOLOR with spectrophotometer Spectraflash 600 using D65 illuminant and 10°observer.

The quantum fluorescence yield has been calculated on the basis of the results obtained from the absorption and fluorescence spectra using Equation (1):

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

where $\Phi_{st}$ is the quantum yield of the reference, $A_{st}$ and $A_u$ 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. Fluorescein was used as reference ($\Phi_{st} = 0.85$) [16] All spectra in organic solvents were recorded using 1 cm path length synthetic quartz glass cells. The NMR spectra were obtained on a Bruker DRX-250 spectrometer, operating at 250.13 and 62.90 MHz for $^{1}H$ and $^{13}C$, respectively using a dual 5 mm probe head. The measurements were carried out in DMSO-$d_6$ 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 $F_{60}$ 254 20 × 20; 0.2 mm) using the solvent system n-heptane/acetone (1:1) as an eluent.



1 2 NI

**Scheme 1.** Synthesis of 4-(2-*N,N*-dimethylamino)ethylamino-*N*-(2-hydroxyethyl)-1,8-naphthalimide.

## 3. Results and discussion

4-Nitro-1,8-naphthalic anhydride, was reacted at an equimolar ratio with 2-hydroxyethylamine for 3 h in 2-methoxyethanol at 100 °C until 4-nitro-*N*-(2-hydroxyethyl)-1,8-naphthalimide was obtained. The final 4-(2-*N,N*-dimethylamino)ethylamino-*N*-(2-hydroxyethyl)-1,8-naphthalimide (NI) was obtained in good yield by nucleophilic substitution of the nitro group in 4-nitro-*N*-(2-hydroxyethyl)-1,8-naphthalimide with *N,N*-dimethylethylendiamine in DMF solution at room temperature according to Scheme 1. In this case the electron accepting carbonyl groups of the 1,8-naphthalimide molecule favors the nucleophilic substitution reactions wherein the nitro group is displaced by the aliphatic *N,N*-dimethylaminoethylamino group.

### 3.1. *Photophysical properties of NI*

The photophysical properties of 4-substituted-1,8-naphthalimides depend mainly on the polarization of the naphthalimide molecule. Upon irradiation the polarization occurs resulting from the donor substituents at a C-4 position and the carbonyl groups from the imide structure of the chromophoric system. In general the derivatives with amino groups are yellow in color and emit a green fluorescence. Table 1 presents the spectral characteristics of the NI under study in acetonitrile and water solution at two different pH values: the absorption ($\lambda_A$) and fluorescence ($\lambda_F$) maxima, the extinction coefficient (log $\varepsilon$), Stokes shift ($\nu_A$–$\nu_F$), and quantum yield of fluorescence ($\Phi_F$).

In acetonitrile and aqueous solutions the NI exhibits yellow–green color with absorption maxima $\lambda_A = 430$–432 nm. The fluorescence maxima is situated at $\lambda_F = 520$–540 nm. From the data in Table 1 it is seen that in alkaline aqueous medium (pH = 10) a batochromic shift has been observed of the fluorescence maximum compared to the acidic environment (pH = 5). An example of the absorption and fluorescence spectra of the NI in aqueous solution is shown in Fig. 1. As seen the fluorescence spectra has a fluorescence band with a single maximum, without vibrational

**Table 1**
Photophysical properties of NI in acetonitrile and aqueous solutions.

| | $\lambda_A$ nm | $\varepsilon$ mol $l^{-1}$ $cm^{-1}$ | $\lambda_F$ nm | $\nu_A$–$\nu_F$ $cm^{-1}$ | $\Phi_F$ |
|---|---|---|---|---|---|
| $CH_3CN$ | 432 | 10 430 | 520 | 3917 | 0.011 |
| $H_2O$ at pH = 5.0 | 432 | 16 400 | 530 | 4280 | 0.883 |
| $H_2O$ at pH = 10.2 | 430 | 14 600 | 540 | 4668 | 0.071 |

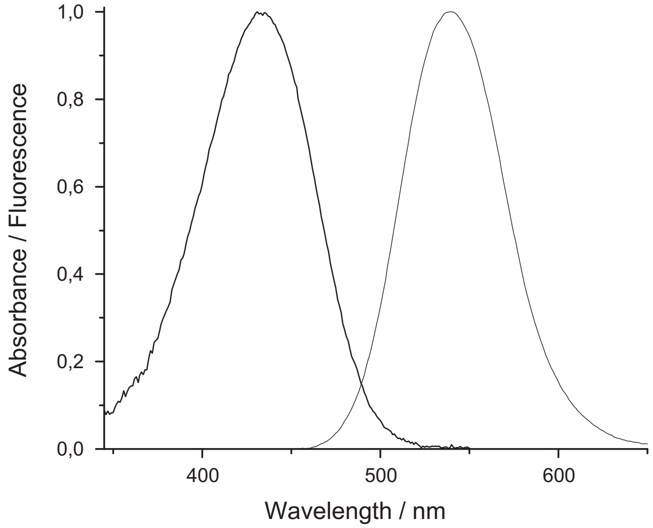


**Fig. 1.** Normalized absorption and fluorescence spectra of NI in aqueous solution at pH = 7.0.

structure. The fluorescence curve is an approximate mirror image of the absorption one. This is an indication of the prevailing fluorescence emission and of the unchanged molecular structure of the 1,8-naphthalimide fluorophore in the exited state.

In all cases the extinction coefficients $\varepsilon$ are higher than 10,000 mol $l^{-1}$ $cm^{-1}$, indicating that the long-wavelength band of the absorption spectra is a band of charge transfer/CT/, electron transfer on $S_0 \rightarrow S_1$ transition. The Stokes shift is a parameter which indicates the difference in the properties and structure of the dyes between the ground state $S_0$ and the first exited state $S_1$. The Stokes shift values are in the 3917–4668 $cm^{-1}$ region, which is in accordance with our previous investigations on the 1,8-naphthalimide derivatives [17,18]. The fluorescence efficiency of NI is estimated by measuring its quantum yield $\Phi_F$ on the basis of the absorption and fluorescence spectra. As seen from the data in Table 1, the NI studied has low quantum yield $\Phi_F = 0.011–0.071$ at polar solvents as acetonitrile and alkali water solution. In an acidic environment (pH = 5) the fluorescence intensity dramatically increases ($\Phi_F = 0.883$).

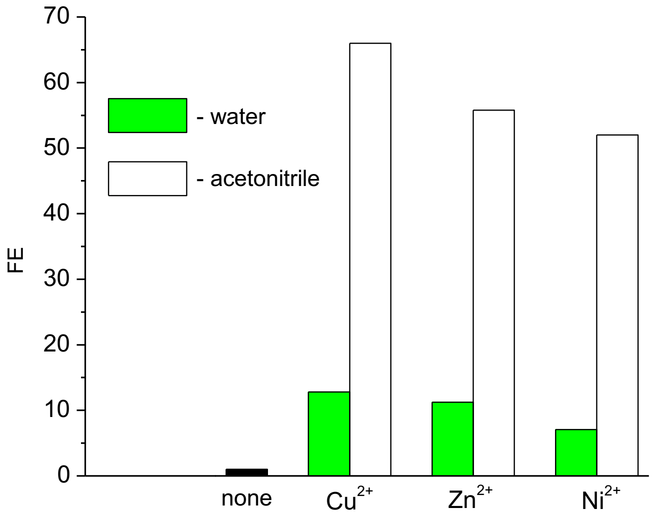
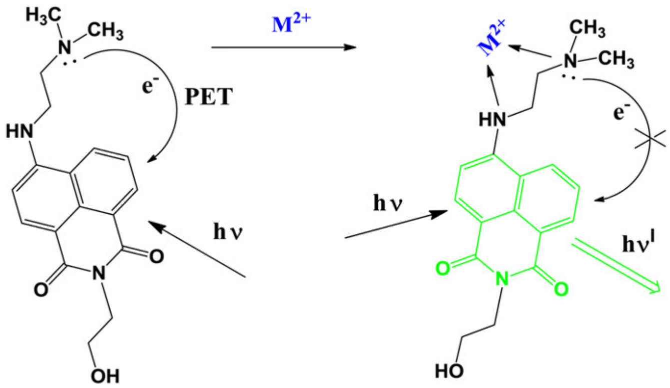


**Fig. 2.** Fluorescence enhancement factor (*FE*) of NI ($c = 1 \times 10^{-5}$ mol $l^{-1}$) in the presence of different metal cations ($c = 5 \times 10^{-5}$ mol $l^{-1}$) in acetonitrile and aqueous (pH = 7.0) solutions.



**Scheme 2.** Schematic presentation of coordination of NI with metal cations ($M^{2+}$).

### 3.2. Influence of biologically important metal cations on the fluorescence intensity of NI

We stated in our previous papers that in organic solvents some transition metal cations can quench or the enhance fluorescence intensity of the 1,8-naphthalimide [19–21]. Their fluorescent characteristics have been studied in different media viewing their practical application as fluorescent sensors able to detect metal ions.

In this work the ability of a NI to detect metal cations has been tested in acetonitrile and water solutions by monitoring the changes in their absorption and fluorescent spectra in the presence of tree biologically important metal cations ($Cu^{2+}$, $Zn^{2+}$ and $Ni^{2+}$). The influence of these metal cations and their concentration upon the fluorescence intensity has been investigated spectrophotometrically with regard to its application as photoinduced electron transfer (PET) sensors for these cations.

Also for the practical applications the investigation in water is very important. In this case, the fluorescence intensity (fluorescence quantum yields) is of particular importance in the absence of the metal cations.

The influence of the metal cations on the fluorescence intensity of NI alone has been measured in both acetonitrile and buffered

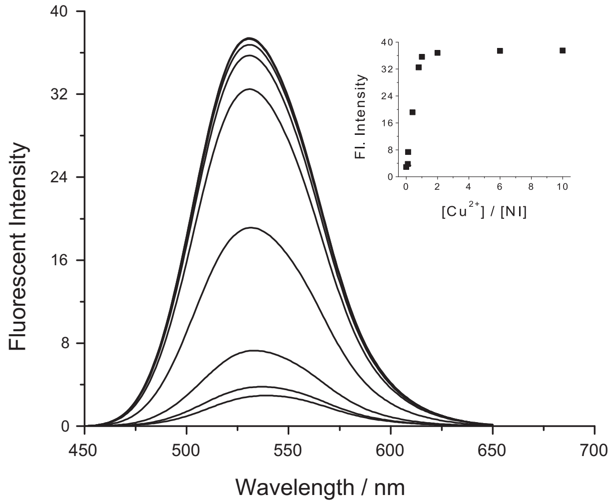


**Fig. 3.** Fluorescence spectra of NI in aqueous solution (pH = 7.0) at various concentrations of $Cu^{2+}$ cations. The concentrations of $Cu^{2+}$ cations are in order of increasing intensity from 0 to $1 \times 10^{-4}$ mol $l^{-1}$. The concentration of NI is $1 \times 10^{-5}$ mol $l^{-1}$. The inset displays the relationship between the fluorescence intensity and cation concentration.

**Table 2**
Photophysical characteristics of NI in acetonitrile in the presence of metal cations (see text).

| | $\lambda_A$ nm | $\lambda_F$ nm | $\nu_A$–$\nu_F$ cm$^{-1}$ | $\Phi_F$ |
|---|---|---|---|---|
| $CH_3CN$ | 432 | 520 | 3917 | 0.011 |
| $Cu^{2+}$ | 432 | 511 | 3578 | 0.793 |
| $Zn^{2+}$ | 432 | 509 | 3502 | 0.727 |
| $Ni^{2+}$ | 430 | 511 | 3686 | 0.589 |

water (pH = 7.0) solutions. A dramatic enhancement in the fluorescence intensity in presence of the guest metal cations has been observed in acetonitrile. The influence of the metal cations on the fluorescence enhancement (*FE*) is presented in Fig. 2. The *FE* = *I/Io* has been determined from the ratio of maximum fluorescence intensity *I* (after addition of metal cations) and fluorescence intensity *Io* (before metal cations addition). Upon the addition of metal cations the enhancements of fluorescence emission is determined by the nature of the cations added. The highest values have been observed in the presence of $Cu^{2+}$ cations (*FE* = 66.5).

Similar results have been obtained in aqueous solution, but the *FE* values are less than in acetonitrile solution. Probably in this case the water molecules coordinate the metal cations before their ability to coordinate with the diamine receptor fragment.

In both cases the effect of metal cations on the fluorescence intensity of NI can be ranked as follows:

$$Cu^{2+} > Zn^{2+} > Ni^{2+}$$

In the absence of metal cations, NI emits a very weak fluorescence emission which can be attributed to an efficient PET process that takes place between the photoexcited 1,8-naphthalimide and the lone-pair electrons of the free amine at the substituent at C-4 position. In the presence of metal cations, the lone-pair electron of the free tertiary amine quencher is engaged in coordination with metal cations (Scheme 2). Accordingly, when a metal cation engages the lone electron pair of the receptor nitrogen atom in coordination, it reduces the donor potential and consequently leads to a deceleration or a complete “switching off” of the electron transfer. The result is a fluorescence emissive complex and the fluorescence of the system is “switched on” (Scheme 2).

The typical change in the fluorescence intensity of NI induced by $Cu^{2+}$ is plotted in Fig. 3. As seen the addition of $Cu^{2+}$ leads to an increase in the fluorescence intensity of NI solution ($c = 10^{-5}$ mol l$^{-1}$), thought it depends on the concentration. Above the concentration of $10^{-5}$ mol l$^{-1}$ the change in fluorescence intensity is insignificant. $Cu^{2+}$ cations induce a hypsochromic shift $\Delta\lambda_F = 11$ nm of the fluorescence maximum ($\lambda_F = 531$ nm) which indicates that the switch might bind metal cations to the nitrogen atoms from the receptor via chelation [22].

The basic photophysical characteristics obtained for NI in acetonitrile and aqueous solutions in the presence of metal cations under study are presented in Tables 2 and 3: absorption ($\lambda_A$) and fluorescence ($\lambda_F$) maxima, Stokes shift ($\nu_A$–$\nu_F$) and quantum ($\Phi_F$) yield of fluorescence.

**Table 3**
Photophysical characteristics of NI in aqueous solution in the presence of metal cations (see text).

| | $\lambda_A$ nm | $\lambda_F$ nm | $\nu_A$–$\nu_F$ cm$^{-1}$ | $\Phi_F$ |
|---|---|---|---|---|
| $H_2O$ at pH = 7.0 | 430 | 541 | 4771 | 0.711 |
| $Cu^{2+}$ | 428 | 530 | 4496 | 0.864 |
| $Zn^{2+}$ | 430 | 529 | 4352 | 0.812 |
| $Ni^{2+}$ | 429 | 530 | 4442 | 0.792 |

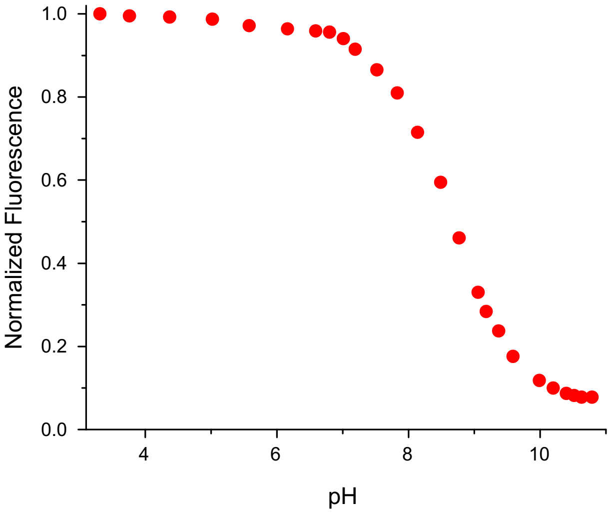


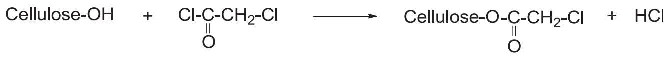
**Fig. 4.** pH dependence of fluorescence intensity of NI.

The data collected in Tables 2 and 3 evidence no change in the absorption maxima in comparison with the NI free from the metal ions. In both cases the metal cations induce a hypsochromic shift of the fluorescence maxima ($\Delta\lambda_F = 9$–11 nm) indicating a possible the interaction between the NI and metal cations. The results also show the high increase in the fluorescence caused by the presence of metal cations. In acetonitrile solution the quantum yields ($\Phi_F = 0.58$–$0.79$) increase after adding of metal ions with concentration $10^{-5}$ mol l$^{-1}$, if compared to those of the ions free solution ($\Phi_F = 0.01$). The highest quantum yield values have been obtained in the presence of $Cu^{2+}$ cations ($\Phi_F = 0.79$). We suppose the higher quantum yield in the case to be on account of the better coordination ability of $Cu^{2+}$ cations as well as on the stabilization of the coplanar system of the complex formed. The spectrum of the NI complex with metal cations has a Stokes shift smaller than that of the spectrum of NI alone, which indicates the stabilized planarity of the chromophoric structure after the complexation. In this case the non-radiative emission during the transition from $S_1$ to the ground state $S_0$ is smaller and leads to higher fluorescence quantum yields.

Similar results have been obtained in water solution, but the *FE* values are less than in acetonitrile solution. Probably in this case the water molecules attack metal cations before their ability to coordinate with the receptor fragment (Fig. 2).

### 3.3. *Effect of pH on the spectral properties of NI*

It was of great interest to investigate the influence of pH on the fluorescence intensity of the 1,8-naphthalimide under study. The fluorescence intensity NI was investigated in a pH range of 3.2–11.0. The fluorescence intensity against pH is plotted in Fig. 4 and a sigmoidal dependence has been established. NI exhibit high sensitivity to the presence of protons due to the protonation of the distal tertiary nitrogen atoms [$NHCH_2CH_2N(CH_3)_2$] of the C-4substituents. At pH values up to 7.0 NI does not change its fluorescence intensity. At pH >7 a drastic decrease of the fluorescence intensity has been observed, and finally at pH = 10.2 the curve again plateaus. In the acidic medium the protonation of the distal tertiary



$$\text{Cellulose-OH} + \text{Cl-}\underset{\overset{\|}{O}}{C}\text{-CH}_2\text{-Cl} \longrightarrow \text{Cellulose-O-}\underset{\overset{\|}{O}}{C}\text{-CH}_2\text{-Cl} + \text{HCl}$$

**Scheme 3.** Modification of cellulose with chloroacetyl chloride.

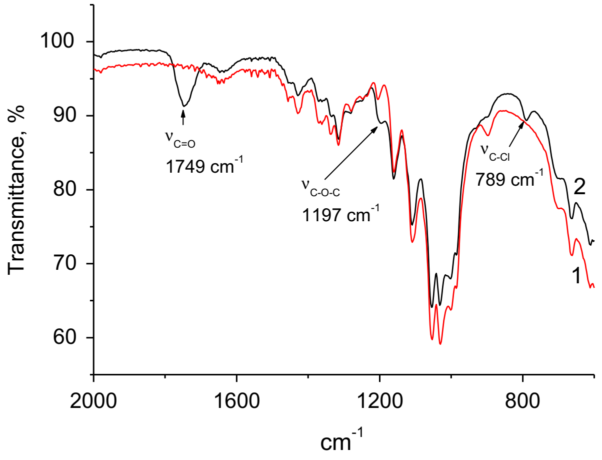


**Fig. 5.** Infrared spectra of cotton fabrics before (1) and after acylation with chloroacetyl chloride (2).

nitrogen atoms of the C-4 substituent stops the PET process and the fluorescence increases. The fluorescence intensity at pH = 7 is fourteen times higher than that at pH = 10.2.

The pH dependence of fluorescence intensity has been calculated according to Equation (2).

$$\mathrm{pH} - \mathrm{pK}_a = \log(I_{F\max} - I_F)/(I_F - I_{F\min}) \tag{2}$$

The calculated $\mathrm{pK_a} = 8.51$.

## 3.4. Dyeing of cellulose textile fabrics by NI

### 3.4.1. Chemical modification of cellulose textile fabrics by chloroacetyl chloride

As demonstrated NI has properties that make it suitable for detection of protons and metal cations in solution. Of interest was the immobilization of NI on the textile matrix. The NI does not have any affinity for the cotton fabric. One approach is to modify the dye with reactive groups and the other is to modify the matrix by introducing new functional groups capable of reacting readily with the hydroxyl group from the NI and to form a covalent bond [23]. In this work we have modified the cotton fabric with chloroacetyl chloride. It is a bifunctional compound having two different active chlorine atoms. Acyl chloride easily forms esters and amines by nucleophilic substitution reactions with alcohols or amines respectively.

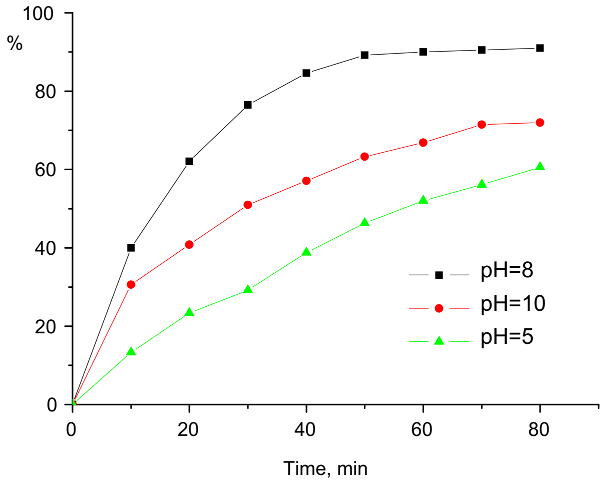


**Fig. 6.** NI dye bath exhaustion from the modified cotton fabric dyeing at pH = 5, pH = 8 and pH = 10 and 25 °C.

**Table 4**
CIELab color coordinates of cotton fabrics dyed at pH = 5, pH = 8 and pH = 10.

| | $L^*$ | $a^*$ | $b^*$ |
|---|---|---|---|
| at pH = 5 | 95.17 | −21.65 | 63.92 |
| at pH = 8 | 94.5 | −21.84 | 70.65 |
| at pH = 10 | 95.09 | −21.95 | 63.65 |

For this purpose cotton fabric was modified with 10% (v/v) chloroacetyl chloride ($\mathrm{ClCOCH_2Cl}$) in DMF solution at 60 °C for 2 h [24,25]. Thus the cellulose macromolecules have obtained active chlorine atoms, which can react with hydroxyl reactive groups from NI. The use of chloroacetyl chloride for the modification of cotton fabric is illustrated in Scheme 3.

IR spectra of the modified and none treated cotton fabrics with chloroacetyl chloride are plotted and are compared in Fig. 5. There is an appearance of new bands in the modified fabric which are characteristic of the ester carbonyl band at 1749 cm$^{-1}$ (C═O ester group) at 1197 cm$^{-1}$ (C—O ester group) and 789 cm$^{-1}$ (C—Cl bond).

### 3.4.2. Dyeing of modified cotton fabrics

The aim of this work is to find the conditions of dyeing in which NI reacts with the functional groups of the cotton fabrics, so that the sensor fragment responsible for the photoinduced electron is free.

In acidic media the hydroxyl group from NI is protonated, and in an alkaline media it is deprotonated, while at pH ≈ 8 ($\mathrm{pK_a} = 8.51$) there is balance between two forms. The dyeing of cotton fabric has been conducted at pH = 5, 8 and 10 and the concentration of NI 0.5 owf% by mass of fiber at 25 °C for 80 min. The dyeing process has been followed spectrophotometrically. At pH 5 the process takes place gradually with maximum extraction of the dye 60% and at pH = 10, this percentage increased up to 90%, the fastest and the largest percentage of exhaustion/fixation occurs at pH 8 as seen from Fig. 6.

Thus fluorescent cotton fabrics were received with intense yellow-green color. Their CIELab colorimetric parameters are presented in Table 4. A small difference has been observed at $L^*$, $a^*$ and $b^*$ coordinates of the dyed cotton fabric at pH 8.

### 3.4.3. Functional characteristics of dyed cotton fabric

The photophysical characteristics of dyed cotton fabric have been investigated with regard for its potential for heterogeneous

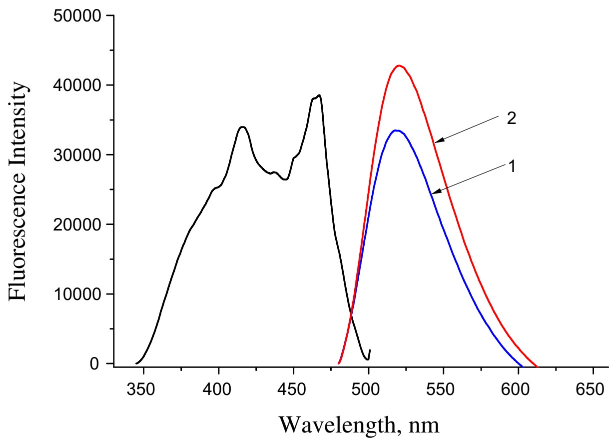


**Fig. 7.** Excitation and fluorescence spectra of dyed cotton fabrics with NI at pH = 5, ($\lambda_{ext}$ 1 = 410 nm, $\lambda_{ext}$ 2 = 467 nm and $\lambda_{em}$ = 520 nm).

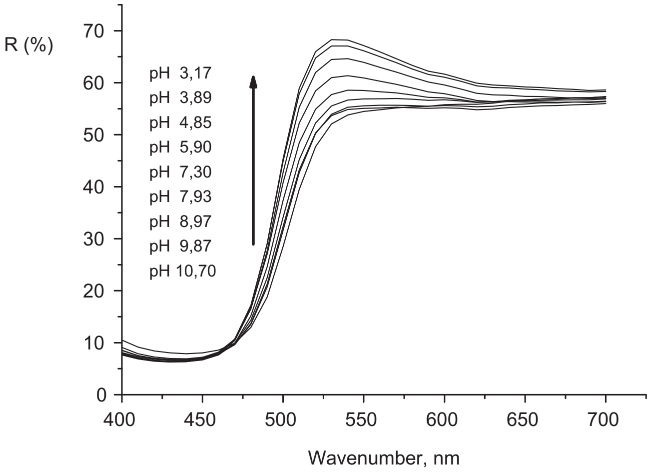


**Fig. 8.** pH influence on the reflectance R% of the cotton fabric dyed at pH = 5.

fluorescence sensor of biologically important metal cations ($Zn^{2+}$ and $Cu^{2}$) and protons in aqueous media.

Excitation fluorescence spectra of the dyed cotton are shown in Fig. 7. As can be seen the excitation spectrum has two well pronounced maxima. The maximum at 467 nm is with higher intensity compared to the first maximum at 410 nm. The fluorescence spectrum obtained with excitation at 467 nm is more intensive compared to that obtained at 410 nm without change in the fluorescence maximum ($\lambda_F = 520$ nm). Fluorescence spectra of dyed cotton fabrics at pH = 5, 8 and 10 have well pronounced maxima at 516–520 nm. This fact indicates that during the dyeing of cotton fabrics, there are no structural changes in the chromophore system of NI which maintaining its fluorescent characteristics.

The influence of pH on the fluorescence emission was followed with the change of the reflectance of the cotton fabric dyed at pH = 5. The reflectance curves after dipping in solutions with decreasing pH are plotted in Fig. 8. The higher proton concentration switches on the fluorescence emission and enhances the R% at 520–600 nm.

The cotton fabric dyed at pH = 5 has been treated with aqueous solution of two biologically important metal cations ($Zn^{2+}$ and $Cu^{2+}$ at concentration 0.15 mg/g cotton fabric) in order to determine its ability to detect these cations. The effect of the added metal cations on the cotton samples has been estimated by the difference of the reflectance (ΔR% at $\lambda = 530$ nm) after and before the addition of metal cations and are presented in Fig. 9. This reflection increase is cause by the fluorescence emission of the fabric. This confirms the statement that after dyeing the sensor fragment responsible for PET effect remain free for the metal ion detection. The immobilized on the textile matrix 1,8-naphthalimide dye as distinguished from its water solution shows selectivity to $Zn^{2+}$ ions compared to $Cu^{2+}$. Probably in this case important role play the cotton fabric matrix.

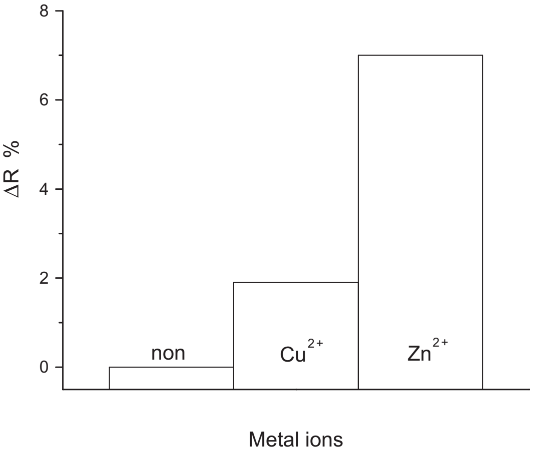


**Fig. 9.** Effect of metal ions on the reflectance difference ΔR% at $\lambda = 530$ nm of dyed cotton fabrics in the presence of $Zn^{2+}$ and $Cu^{2+}$ at concentrations 0.25 mg/g fabric.

## 4. Conclusion

The synthesis of a new 4-(2-*N*,*N*-dimethylamino)ethylamino-*N*-2-hydroxyethil-1,8-naphthalimide has been described and its functional properties have been investigated. The modification of cotton fabric by chloroacetyl chloride has been studied by IR spectroscopy. The cotton fabrics thus modified has been dyed with the new 1,8-naphthalimide dye. That resulted in a new textile material with promising properties as a heterogeneous fluorescence sensor of biologically important metal cations ($Zn^{2+}$ and $Cu^{2}$) and protons in aqueous media.

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