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Novel 4-(2,2,6,6-tetramethylpiperidin-4-ylamino)-1,8-naphthalimide based yellow-green emitting fluorescence sensors for transition metal ions and protons

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ABSTRACT

Two novel yellow-green emitting 1,8-naphthalimides, containing a 4-amino-2,2,6,6-tetramethylpiperidinyl moiety, were configured as "fluorophore–spacer–receptor" systems. The photophysical characteristics of the dyes were investigated in both DMF and water/DMF (4:1, v/v) solutions. The ability of the new compounds to detect cations was evaluated by means of the changes in their fluorescence intensity imparted by the presence of transition metal ions (Cu^{2+}, Pb^{2+}, Zn^{2+}, Ni^{2+}) and protons. The presence of metal ions and protons was found to disallow photoinduced electron transfer resulting in enhanced fluorescence intensity. The results clearly show that only Cu^{2+} ions and protons were effectively detected, indicating the potential of the novel compounds as highly efficient "*off–on*" switchers for Cu^{2+} ions and protons.

1. Introduction

In the last two decades, much attention has been paid to the design, synthesis and characterisation of photochemical molecular devices. The extension of the concept of a device to the molecular level is of interest, not only for basic research but also for the growth of nanoscience and the development of nanotechnology [1a]. Supramolecular devices that show large changes in their so-called "*off*" and "*on*" states are currently of great interest as these can be modulated, or tuned, by employing external sources such as ions, molecules, light, etc. [1]. The "*off*" and "*on*" states of the molecular-level devices refer to their luminescence, magnetic or electronic properties. Luminescence is one of the most useful techniques to monitor the operation of molecular devices. A part of this rapidly emerging field is the development of fluorescent sensors where the fluorescence is switched "*off*" or "*on*" as a function of the analyte [2].

The photoinduced electron transfer (PET) system using the "fluorophore–spacer–receptor" format, developed by de Silva et al. [3], is one of the most popular approaches to the design of fluorescent sensors and switchers [4]. In this model, the excited state of the fluorophore can be quenched by intermolecular electron transfer from the receptor to the fluorophore (or vice versa) prior recognition. Upon recognition of species such as cations, the oxidation potential of the receptor is increased and this causes the electron transfer to be "*switched off*" and in turn the emission to be "*switched on*" [5].

Environment-sensitive fluorophores are a special class of chromophores. Their spectroscopic behaviour is dependent on the physicochemical properties of surrounding environment. Particularly useful are solvatochromic fluorophores that display sensitivity to the polarity of the local environment, such as 4-amino-1,8-naphthalimide derivatives [5c,6]. Because of their strong yellow-green fluorescence and good photostability, the 1,8-naphthalimide derivatives have found application in a number of areas including colouration of polymers [7], laser active media [8], potential photosensitive biologically units [9], fluorescent markers in biology [10], analgesics in medicine [11], light emitting diodes [12], photoinduced electron transfer sensors [13], fluorescence switchers [14], electroluminescent materials [15], liquid crystal displays [16] and ion probes [17]. Moreover, these properties are essential when employing such devices in real-time and on-line analyses.

Series of 1,8-naphthalimide derivatives, containing different 4-aminoalkyl moieties, with good "*off–on*" switching of fluorescence upon encountering the correct target have been synthesized [5,6,13,14]. Owing to the basicity of the amine group, these serve as fluorescent sensors which are finding use in physiology research [18]. Recently, we have synthesized new yellow-green emitting 1,8-naphthalimides, containing differing in their action hindered amine and 2-hydroxyphenylbenzotriazole fragments, designed as

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highly photostabile additives for “one-step” fluorescent dyeing and photostabilization of polymers [19]. Therefore, it was of interest to see if 2,2,6,6-tetramethylpiperidine analogues of the 4-aminoalkyl-1,8-naphthalimide fluorophores would shed further light on this issue. This paper takes on added significance given the growing body of sensors and other optical devices which employ 4-amino-1,8-naphthalimide fluorophores [6]. Hence, compounds **1** and **2** were investigated by electronic absorption and emission spectroscopy as potential PET sensors for protons and transition metal ions (Scheme 1).

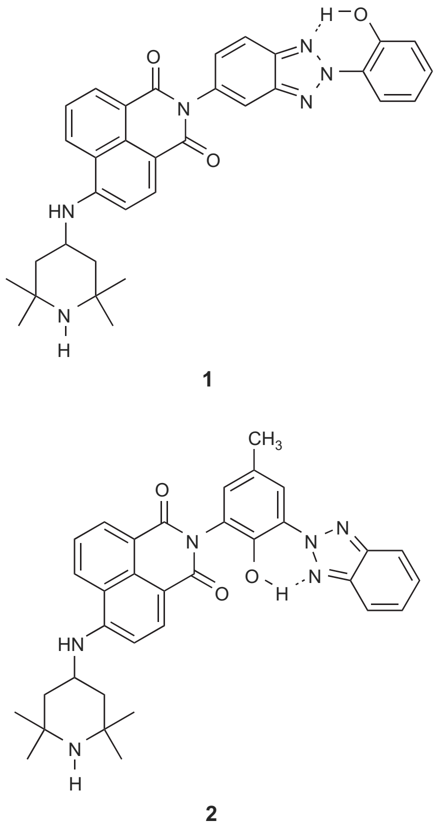
2. Experimental

2.1. Materials

1,8-Naphthalimides **1** and **2** were synthesized by consecutive reactions of 4-nitro-1,8-naphthalic anhydride first with 2-(5-amino-2*H*-benzotriazol-2-yl)phenol (compound **1**) or 2-amino-6-(2*H*-benzotriazol-2-yl)-4-methylphenol (compound **2**) in glacial acetic acid at 110 °C and then with 2,2,6,6-tetramethylpiperidin-4-ylamine in DMF at room temperature as described before [19]. All solvents (Fluka, Merck) were of p.a. or analytical grade. $Zn(NO_3)_2 \cdot 6H_2O$, $Cu(NO_3)_2 \cdot 2.5H_2O$, $Ni(NO_3)_2 \cdot 6H_2O$ and $Pb(NO_3)_2$ salts were the sources for metal cations. Sulphuric acid was used as a source of protons. The effect of the metal cations and protons upon the fluorescence intensity was examined by adding few microliters of stock solution (5 µl) of the metal cations to a known volume of the dye solution (3 ml). The addition was limited to 0.065 ml so that dilution remains insignificant.

2.2. Methods

UV/vis spectra were recorded on a Hewlett Packard 8452A spectrophotometer with 2 nm resolution at room temperature. The fluorescence spectra were taken on a Perkin Elmer LS 45 fluorescence spectrophotometer. The fluorescence quantum yields (Φ_F) were measured relative to Coumarin 6 ($\Phi_{ref} = 0.78$ in ethanol) [20].



Scheme 1.

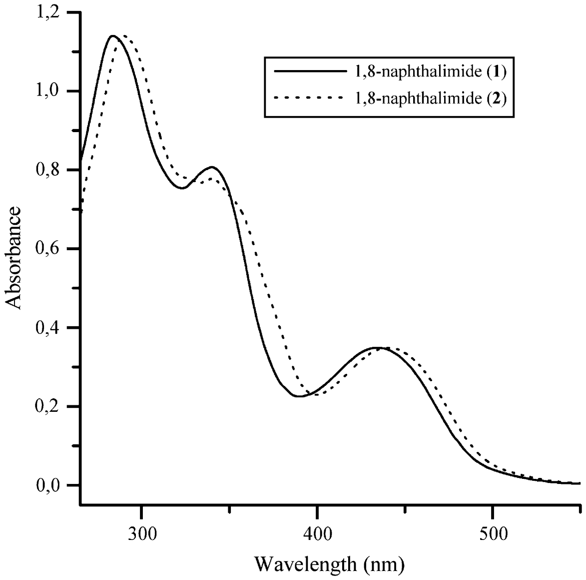


Fig. 1. Absorption spectra of 1,8-naphthalimides **1** and **2** in DMF solution at concentration 10^{-5} mol l^{-1}.

3. Results and discussion

3.1. Design of the dyes

The two dyes (**1** and **2**) were designed to act as sensitive detectors of environment pollution by transition metal cations and protons. They are based on the “fluorophore–spacer–receptor” model, where the 4-amino-1,8-naphthalimide moiety is the fluorophore and the 2,2,6,6-tetramethylpiperidine amine is the analyte receptor. The hydrocarbon part of the piperidine fragment serves as spacer that covalently separates the two units. In these particular cases, it was predicted that a PET process (an electron transfer from the receptor to the excited state of the fluorophore) would quench fluorescence emission of the 1,8-naphthalimide unit. This would represent the “*off-state*” of the system. The protonation or respective metal complex formation of the piperidine amine would increase the oxidation potential of the receptor, and as such, thermodynamically disallow the electron transfer [21]. Consequently the emission would be “*switched on*”. Thus, we expect the fluorescence to be strong in acidic media and transition metal cations’ environment.

3.2. Photophysical characterisation of the dyes

Photophysical properties of the 4-alkylamino-1,8-naphthalimides are basically related to the polarization of the 1,8-naphthalimide molecule and may be influenced by the environmental effect of the media.

The absorption spectra of the dyes **1** and **2** (Fig. 1) clearly show the participation of both UV absorber and 1,8-naphthalimide units

Table 1
Absorption and fluorescence characteristics of dyes **1** and **2** in DMF solution at concentration 10^{-5} mol l^{-1} ($\lambda_{A2} = \lambda_{ex}$)

Compound	λ_{A2} (nm)	log ε (l mol^{-1} cm^{-1})	λ_F (nm)	$\nu_A - \nu_F$ (cm^{-1})	f	Φ_F
1	436	4.541	532	4139	0.614	0.10
2	440	4.543	534	4001	0.581	0.11

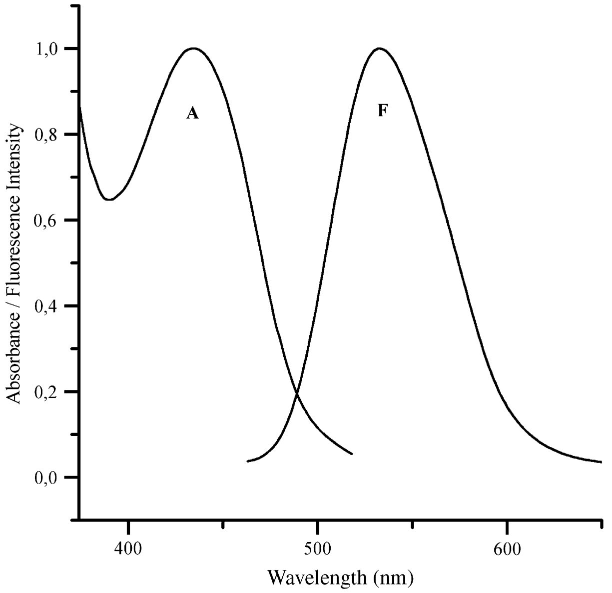


Fig. 2. Normalized absorption (λ_{A2}) and fluorescence (λ_F) spectra of dye **1** in DMF solution at concentration 10^{-5} mol l^{-1}.

in the combined molecules. Benzotriazole fragments absorb in the UV region at $\lambda_{A1} = 340 - 342$ nm, while the 1,8-naphthalimide absorption is shifted from UV to visible region at $\lambda_{A2} = 436 - 440$ nm.

The absorption maximum of 2-(5-amino-2*H*-benzotriazol-2-yl)phenol ($\lambda_{A1} = 360$ nm, precursor for dye **1**) was 36 nm bathochromically shifted than that of 2-amino-6-(2*H*-benzotriazol-2-yl)-4-methylphenol ($\lambda_{A1} = 324$ nm, precursor for dye **2**), which could be related to the difference in the intramolecular hydrogen bond strength due to the position effect of the electron-donating amino group in the benzotriazole moiety [19]. After acylation with 1,8-naphthalic anhydride the electron-donating activity of the amino group decreases strongly and the benzotriazole absorption of dye **1** was shifted hypsochromically, while that of dye **2** – bathochromically. As a result of such behaviour the benzotriazole absorption maxima of dyes **1** and **2** are brought closer to $\lambda_{A1} = 340 - 342$ nm as it is shown in Fig. 1.

Basic absorption and fluorescence characteristics such as 1,8-naphthalimide absorption (λ_{A2}) and fluorescence (λ_F) maxima, Stokes shift ($\nu_A - \nu_F$), oscillator strength (*f*) and quantum yield of fluorescence (Φ_F) of dyes **1** and **2** were measured in DMF solution and presented in Table 1.

In DMF solution compounds **1** and **2** displayed intense yellow-green fluorescence due to the charge transfer in the 1,8-naphthalimide moieties from the electron-donating alkylamino group at C-4 position to the carbonyl groups. Dyes' emission was observed in the visible region with well-pronounced maxima (λ_F) at 532–534 nm. Fig. 2 displays the absorption and fluorescence spectra of fluorescent dye **1** as a typical example for the spectra of compounds under study.

The Stokes shift and oscillator strength values [22] for dyes **1** and **2** (Table 1) were common for the 1,8-naphthalimide derivatives and are in agreement with previous investigations [23,24].

The ability of the molecules to emit the absorbed light energy is characterized quantitatively by the fluorescence quantum yield (Φ_F). The quantum yields of fluorescence were calculated relative to Coumarin 6 ($\Phi_{ref} = 0.78$) as a reference compound [20]. As seen from Table 1, the quantum yields of fluorescence of dyes **1** and **2** in DMF are vastly lower in respect to those in chloroform solution [19] and are lower in comparison with the data for other 1,8-naphthalimides [16c,24a]. This phenomenon might be caused by the possible photoinduced electron transfer (PET) from the piperidine nitrogen donor (receptor) to the 4-amino-1,8-naphthalimide fluorophore through the piperidinyl ring. Thus the fluorescence of the 4-amino-1,8-naphthalimide fluorophore is quenched (Scheme 2). 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 impossibility for stabilisation of the charge separated state which may survive in polar medium.

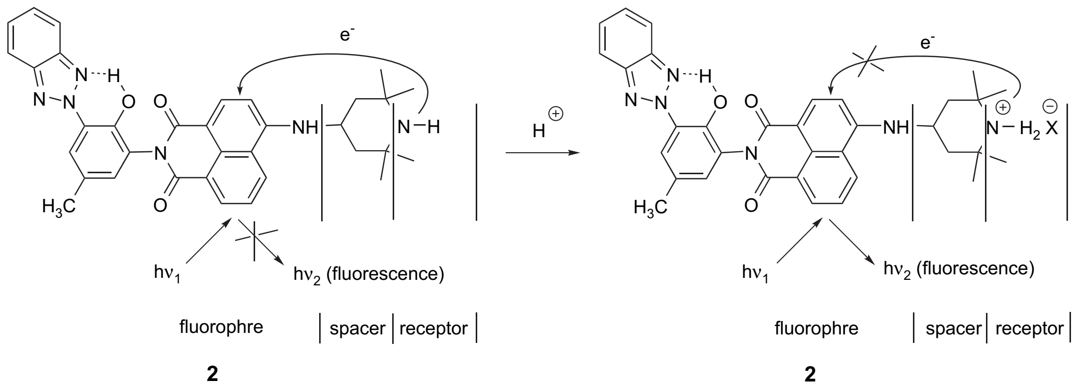
Upon recognition of the analyte (protons or transition metal ion) piperidine amine would increase the oxidation potential of the receptor, and as such, thermodynamically disallow the electron transfer and the emission would be "*switched on*" [21].

Furthermore, as demonstrated experimentally by de Silva et al. [21a] only the receptor that is directly attached to the 4-amino moiety (the 'lower' moiety) is capable of quenching the fluorophores' excited state. This is due to the fact that molecules like **1** and **2** have high exited state dipole moments that arise from their Internal Charge Transfer (ICT) excited state nature. In the case of **1** and **2**, the amino moiety is acting as an electron donor, whereas the imide functions as an electron acceptor. This could be the reason for the observed decrease of the quantum yield of fluorescence for combined dyes **1** and **2**, containing 4-aminopiperidine moiety at C-4 position of the 1,8-naphthalimide fluorophore.

The results obtained provide for PET sensor properties of the fluorescent dyes **1** and **2**, which was the reason to investigate their photophysical behaviour in water/DMF (4:1, v/v) at different pH values and in the presence of transition metal ions.

3.3. Influence of pH on the fluorescence properties of the dyes

The photophysical characteristics of dyes **1** and **2** in distilled water/DMF (4:1, v/v) solution (pH = 6.12) are represented in Table 2. Some bathochromic shift of the absorption and fluorescence



Scheme 2.

Table 2
Fluorescence characteristics ($\lambda_{ex} = \lambda_A$) of 1,8-naphthalimides **1** and **2** at concentration 10^{-5} mol l^{-1} in water/DMF (4:1, v/v)

Compound	λ_A (nm)	log ε (l mol^{-1} cm^{-1})	λ_F (nm)	Intensity[a]	$\nu_A - \nu_F$ (cm^{-1})	f
1	442	4.827	541	288.3	4140	0.687
2	444	4.724	542	280.9	4072	0.665

[a] Fluorescence intensity at λ_F, arbitrary units.

maxima of compounds was observed if compared the spectra to those recorded in DMF (Table 1). The oscillator strength values calculated in water/DMF (4:1, v/v) were higher than those in DMF which are well correlated with the increase in the extinction coefficient of the dyes in this medium.

In water/DMF (4:1, v/v) solution both compounds are highly coloured. However, the fluorescence intensity of compounds **1** and **2** is higher than that observed in DMF (Table 2, Fig. 3). The fluorescence enhancement (FE) of compounds **1** and **2** can be assigned to protonation of the basic piperidine amine in the weakly acidic medium (pH = 6.24), which disallows PET.

Family of fluorescence emission spectra of compounds **1** and **2** as a function of pH was recorded in water/DMF (4:1, v/v). As a typical example of the two dyes under the study, in alkaline solution for compound **2** only a week emission was observed between 460 and 650 nm (Fig. 4), with maximum at $\lambda_F = 550$ nm. However, upon acidification the emission was gradually increased as demonstrated in Fig. 4. After careful titration from pH 12 to 2.5, the emission maximal had shifted to 541 nm, and the emission intensity had enhanced practically five times (FE = 4.81). The fluorescence enhancement of compound **1** was FE = 4.68. These changes are of such magnitude that they can be considered as representing two different "states", where the fluorescence emission is "*switched off*" in alkaline solution and "*switched on*" in acidic solution. These changes are due to the protonation of the "lower" piperidine amino moiety of dye **2**. In alkaline solution this moiety is engaged in PET quenching of the 1,8-naphthalimide excited state, and upon protonation of this amine the quenching process is substantially removed.

Compounds **1** and **2** are thus highly efficient "*off–on*" switchers for pH. This switching process was also found to be reversible. Fig. 5 shows the changes in the fluorescence emission spectra of dyes **1** and **2** as a function of pH. From these changes the emission is switched "*off–on*" between *ca.* pH 6 and 8.5.

Taking the part of the graphs located between pH 5.5 and 9.0, the pH influence on the fluorescence intensity has been calculated by Eq. (1) [21b].

$$\log[(I_{Fmax} - I_F)/(I_F - I_{Fmin})] = \mathrm{pH} - \mathrm{p}K_a \qquad (1)$$

A pK_a value of 7.31 for dye **1** and 7.45 for dye **2** has been found. The results obtained are consistent with compounds of similar nature that were developed before [21a,25]. These pK_a values also indicate that the sensors **1** and **2** would be well suited to monitor changes in the physiological pH range.

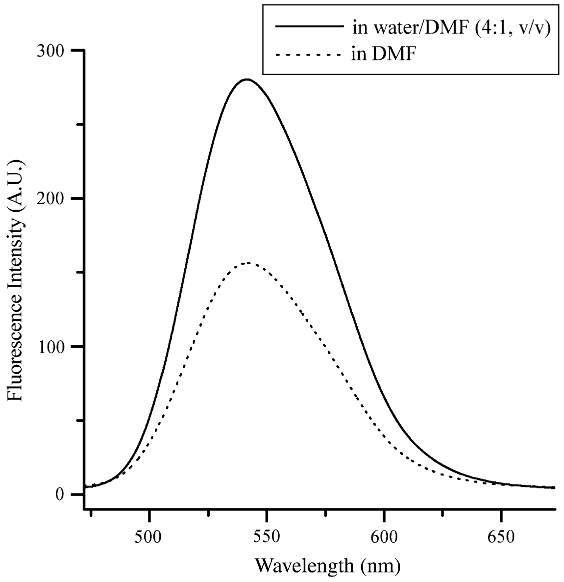


Fig. 3. Fluorescence spectra of 1,8-naphthalimide **2** in DMF and water/DMF (4:1, v/v) solutions.

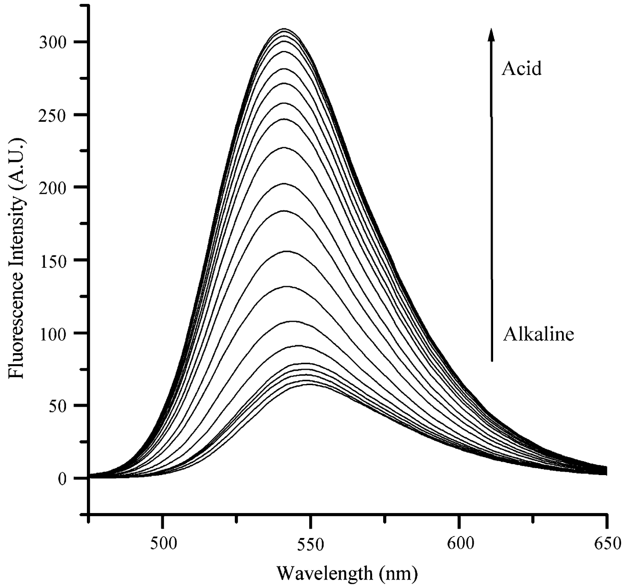


Fig. 4. Changes in the fluorescence spectra of **2** as a function of pH in water/DMF (4:1, v/v) solution. The pH range was from 11.70 to 2.82.

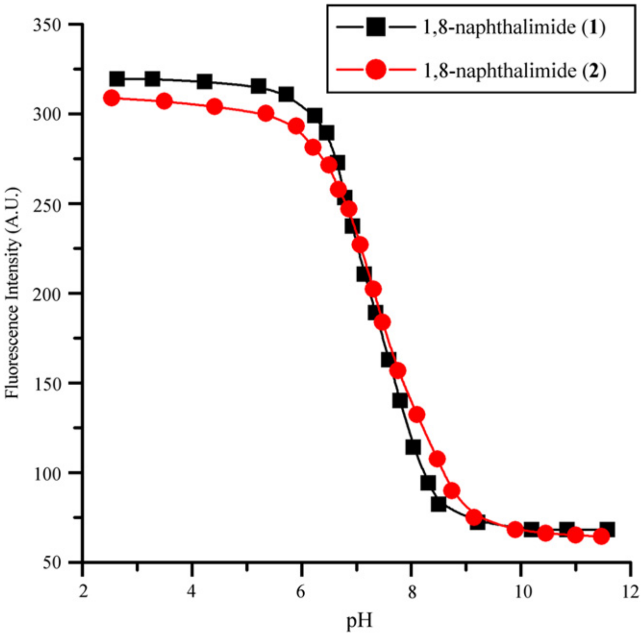


Fig. 5. Effect of pH on the fluorescence intensity ($\lambda_{ex} = 440$ nm) of **1** and **2** in water/DMF (4:1, v/v) solution.

3.4. Influence of metal cations on the fluorescence intensity of the dyes

The signalling fluorescent properties of dyes **1** and **2** in the presence of transition metal ions have been investigated in DMF with regard to their potential application as PET sensors. DMF has been chosen as a solvent in all measurements since it guarantees a good solubility of the used metal salts, ligands and the respective complexes.

The two 1,8-naphthalimide dyes (**1** and **2**) showed, as expected, approximately the same fluorescence behaviour in the complex formation process with different metal ions (Cu^{2+}, Pb^{2+}, Zn^{2+}, Ni^{2+}). The influence of the metal ions on the fluorescence enhancement (FE) of dye **2** is presented in Fig. 6. The $FE = I/I_0$ was calculated using minimal (I_0) and maximal (I) fluorescence intensities recorded before and after addition of metal ions, respectively. The highest fluorescence enhancement of dyes **1** and **2** has been observed in the presence of Cu^{2+} ions (FE = 3.74 and 3.80, respectively).

The sensor capacity of dye **1** in DMF solution (10^{-5} mol l^{-1}) at different concentrations of Cu^{2+} ions is represented in Fig. 7 as an example for the fluorescence behaviour of the two dyes under study.

The increase in fluorescence intensity was occurred after addition of Cu^{2+} ions in the concentration range of 1.667×10^{-6}–2.166×10^{-5} mol l^{-1}. Noticeable fluorescence intensity enhancement was observed at Cu^{2+} concentration of 6.667×10^{-6} mol l^{-1} which showed good sensitivity of the dyes (Fig. 8). Raising the cation concentration up to 1.333×10^{-5} mol l^{-1} also induced an increase in the fluorescence. Further augmentation of the metal ions' concentration up to 2.166×10^{-5} mol l^{-1} had a small impact on the alteration of fluorescence intensity.

As mentioned above, the fluorescence intensity increased due to the complexation between the piperidine amine and Cu^{2+} ions. However, titration plots (Fig. 8) provide for a 1:1 metal/ligand complex formation. In consent to this assumption, a hypsochromic shift ($\Delta\lambda_F = 8 - 9$ nm) of the dyes' fluorescence spectra in the presence of metal ions has been observed, which indicates a bidentate chelation to both piperidine and aromatic amine, as it can be seen in Scheme 3.

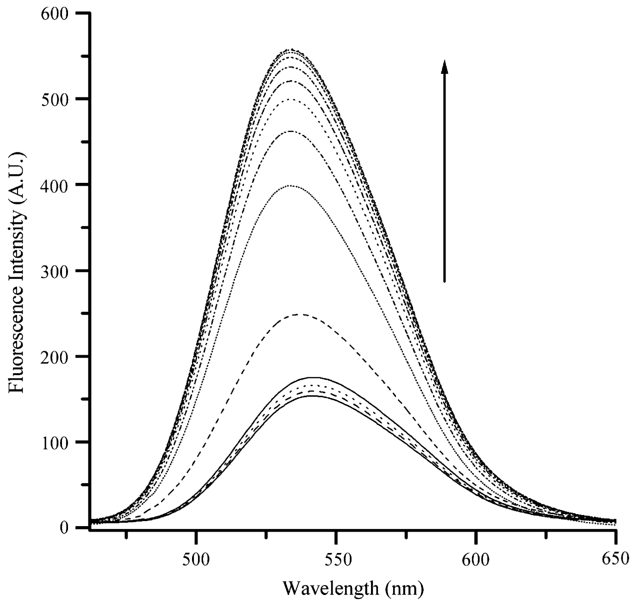


Fig. 7. Fluorescence spectra of dye **1** (10^{-5} mol l^{-1}) in DMF solution at various concentrations of Cu^{2+}. The concentrations of Cu^{2+} ions are in the order of increasing intensity from 0 to 2.166×10^{-5} mol l^{-1} with step of 1.667×10^{-6} mol l^{-1}.

This type of chelation has two different effects: (i) the photoinduced electron transfer from the receptor amine to the fluorophore is disallowed (see Scheme 2) causing a dye fluorescence enhancement; (ii) the electron-donating ability of the aromatic (donor) amine at 1,8-naphthalimide C-4 position is reduced, and as such, the fluorescence maxima of the dyes shift to the shorter wavelength.

Thus, the data obtained show a good sensor selectivity of the new dyes indicating their potential as highly efficient "*off–on*" switchers for Cu^{2+} ions.

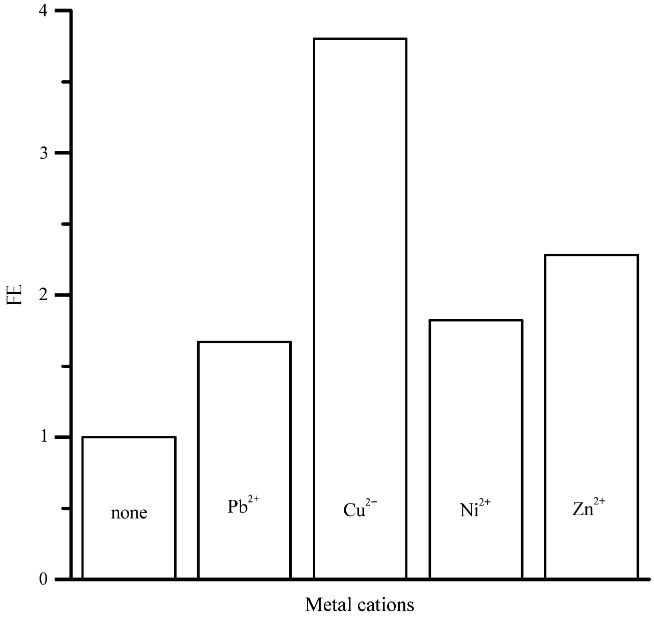


Fig. 6. Fluorescence enhancement (FE) of 1,8-naphthalimide **2** (10^{-5} mol l^{-1}) in the presence of different metal cations at concentration 2.166×10^{-5} mol l^{-1} in DMF solution.

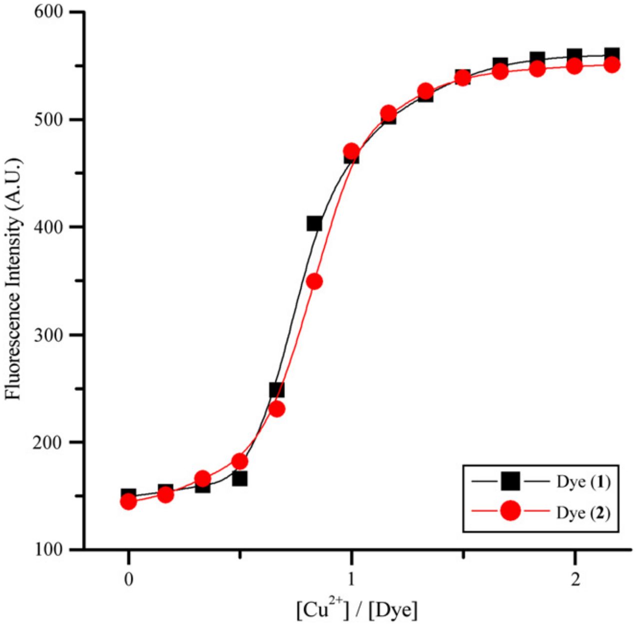
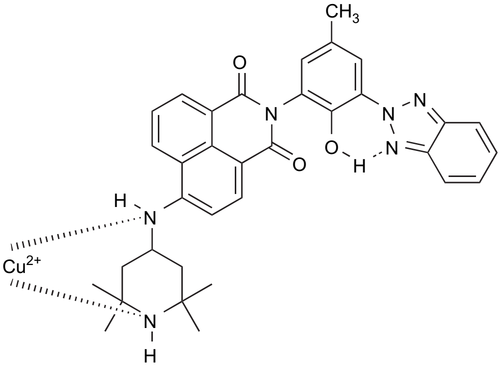


Fig. 8. Changes in the fluorescence maxima of dyes **1** and **2** upon addition of Cu^{2+} ions.



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Scheme 3.

4. Conclusions

In this paper we have given a comprehensive account of the design of two yellow-green emitting 4-amino-1,8-naphthalimide dyes, containing 2,2,6,6-tetramethylpiperidinyl moiety, as PET fluorescence sensors for transition metal ions and protons. Their photophysical properties were studied in both DMF and water/DMF (4:1, v/v) solutions. In the presence of transition metal ions (Cu^{2+}, Pb^{2+}, Zn^{2+}, Ni^{2+}) and protons both dyes sustained considerable changes in their fluorescence intensity. These changes can be attributed to the complexation or protonation, of the piperidine amino moiety of the fluorophores, whereupon the piperidine amine receptor increases its oxidation potential, and as such, thermodynamically disallow the electron transfer and the emission is "*switched on*". The results clearly showed that only Cu^{2+} ions and protons are effectively detected, indicating the potential of the novel compounds as highly efficient "*off–on*" switchers for Cu^{2+} ions and protons.

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