

# Synthesis and Sensor Activity of a PET-based 1,8-naphthalimide Probe for $Zn^{2+}$ and pH Determination

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Received: 12 July 2014 / Accepted: 20 August 2014 / Published online: 9 September 2014  
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**Abstract** A novel blue-emitting 1,8-naphthalimide fluorophore designed as a molecular PET-based probe for determination of pH and detection of transition metal ions in the environment was successfully synthesized. Novel compound was configured on the “*fluorophore-spacer-receptor*” format. Due to the tertiary amine receptor the novel system showed “off-on” switching properties under the transition from alkaline to acid media (FE=3.2) and in the presence of  $Zn^{2+}$  ions (FE=2.5). The results obtained illustrate the high potential of the synthesized blue-emitting 1,8-naphthalimide fluorophore as an efficient pH chemosensing material and a selective probe for  $Zn^{2+}$  ions.

**Keywords** Blue-emitting 1,8-naphthalimide · Photoinduced electron transfer · Absorption · Fluorescence · Fluorescent pH probe · Selective fluorescent  $Zn^{2+}$  probe

## Abbreviations

PET Photoinduced electron transfer  
ICT Internal charge transfer  
FE Fluorescence enhancement

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## Introduction

The recognition and sensing of biologically and environmentally important species has emerged as a significant goal in the field of chemical sensors in recent years [1–4]. Because of the high sensitivity, high speed and cheap instrumentation, particularly the fluorescence sensors and switches have been actively investigated [5–7]. The photoinduced electron transfer (PET) system using the “*fluorophore-spacer-receptor*” format is one of the most popular approaches to the design of fluorescent sensors and switches [8–11]. A PET based fluorescent chemosensor involves a signal fragment (fluorophore) and a receptor, bound through a spacer. When the receptor is unbound, the so assembled molecule loses its fluorescence due to photoinduced electron transfer (PET) from receptor to the fluorophore. Upon recognition of guest, which binds to the receptor, engaging its lone-pair electrons, the PET process is no longer possible and the fluorescence of the system is recovered [12, 13].

$Zn^{2+}$  is the second most abundant transition metal ion in the human body after iron, and is an essential co-factor in many biological processes such as brain function and pathology, gene transcription [14], immune function, and mammalian reproduction [15]. This ion is also involved in pathological processes, such as Alzheimer’s disease, epilepsy, ischemic stroke, infantile diarrhea, apoptosis, enzyme regulation and neurotransmission [16–18] suggests that  $Zn^{2+}$  may be a major regulatory ion in the metabolism of cells [19]. This has been a concern of chemists which resulted in the emergence of considerable activities in the development of  $Zn^{2+}$ -specific molecular probes.

Determination of pH is one of the most important analytical methods in the chemical laboratories and in the industry. The pH is a key parameter in clinical analysis, food production, biotechnological processes, waste water treatment procedures, environmental and life sciences [20]. Recent reports discussed a relation between abnormal pH values and inappropriate cell function observed in some common disease types such as

cancer and Alzheimer's [21]. Although potentiometric pH sensor is well-established for routine pH measurements, it possess some limitations as regarding miniaturized and disposable devices, work in a strong electromagnetic field, high throughput screening, presence of organic matter or selectivity in high pH media [22]. Indeed in some applications pH electrode is irreplaceable, but in a number of research and technological tasks fluorescence probes could be an alternative to overcome the above mentioned limitations. However, one of the major drawbacks of fluorescence probe is photo-destruction (photo-stability) of the dye molecule, which limits their application for continuous and long-term use.

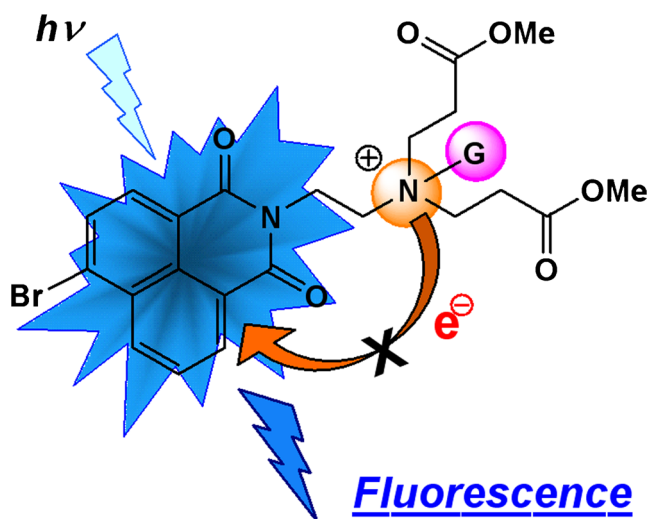
Because of their strong fluorescence and good photostability, the 1,8-naphthalimide derivatives have found application in a number of areas including coloration of polymers [23–25], laser active media [26], fluorescent markers in biology [20], antibacterial, antifungal [27] and anticancer agents [28], analgesics in medicine [29], fluorescent sensors and molecular switches [30–33], light emitting diodes [34], light-harvesting systems [35–38], electroluminescent materials [39], liquid crystal displays [40] and molecular logic devices [41–43]. Also 1,8-naphthalimide fluorophores have already found application as a signal fragment in fluorescent probes for protons [44], transition metal cations [45] and anions [46].

This work describes the synthesis and photophysical behavior of a new blue-emitting 1,8-naphthalimide-based PET probe (Scheme 1), which exhibits sensitivity and selectivity for recognition of protons and Zn(II) ions.

## Experimental

### Materials

The starting 4-bromo-1,8-naphthalic anhydride **1**, ethylenediamine and methyl acrylate (Fluka, Merck) were



**Scheme 1** Blue-emitting 1,8-naphthalimide-based PET probe **3**

used without purification. All solvents (Fluka, Merck) were pure or of spectroscopy grade. Commercial aqueous buffer solution HEPES (Fisher Chemical) was used. The pH values were adjusted by addition of NaOH and HCl aqueous solution.  $\text{Zn}(\text{NO}_3)_2$ ,  $\text{Cu}(\text{NO}_3)_2$ ,  $\text{Ni}(\text{NO}_3)_2$ ,  $\text{Co}(\text{NO}_3)_2$ ,  $\text{Pb}(\text{NO}_3)_2$ ,  $\text{Fe}(\text{NO}_3)_3$ ,  $\text{Hg}(\text{NO}_3)_2$ , and  $\text{AgNO}_3$  salts were the sources for metal cations and used as obtained from Aldrich. Double distilled water was used in all experiments.

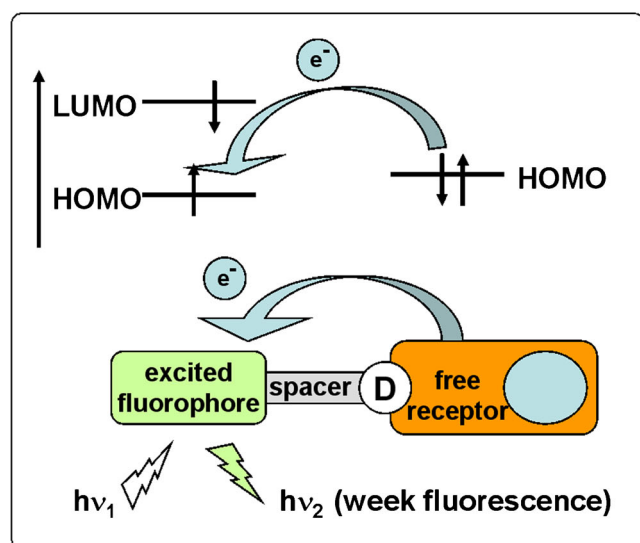
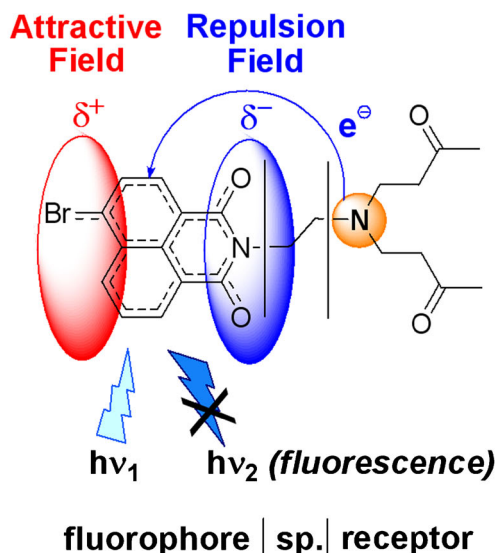
## Methods

FT-IR spectra were recorded on a Varian Scimitar 1,000 spectrometer. The  $^1\text{H}$  NMR spectra (chemical shifts are given as  $\delta$  in ppm) were recorded on a Bruker DRX-250 spectrometer operating at 250.13 MHz. TLC was performed on silica gel, Fluka F60 254,  $20 \times 20$ , 0.2 mm. The melting points were determined by means of a Kofler melting point microscope. The UV–vis absorption spectra were recorded on a spectrophotometer Hewlett Packard 8452A. The fluorescence spectra were taken on a Scinco FS-2 spectrofluorimeter. The excitation source was a 150 W Xenon lamp. Excitation and emission slits width were 5 nm. Fluorescence measurement was carried out in right angle sample geometry. All the experiments were performed at room temperature (25.0 °C). A  $1 \times 1$  cm quartz cuvette was used for all spectroscopic analysis. The fluorescence quantum yields ( $Q_F$ ) were measured relatively to 9,10-diphenylanthracene ( $Q_F=0.95$  in ethanol) [47]. The spectral data were collected using FluoroMaster Plus 1.3 and further processed by OriginPro 6.1 software. The effect of the metal cations and protons upon the fluorescence intensity was examined by adding portions ( $1 \times 10^{-6}$  mol  $\text{L}^{-1}$ ) of the metal cations stock solution to a known volume of the fluorophore solution (4 mL). The addition was limited to 60  $\mu\text{L}$  so that dilution remains insignificant.

### Synthesis of the Novel Blue Emitting 1,8-naphthalimide Sensor **3**

#### Synthesis of 4-bromo-*N*-(2-aminoethyl)-1,8-naphthalimide **2**

To a solution of 5.5 mL ethylenediamine (82.5 mmol) in 12.6 mL of water, a suspension of 4-bromo-1,8-naphthalic anhydride **1** (3.47 g, 12.5 mmol) in 5 mL of water was added portionwise at 75 °C under stirring over a period of 10 min. The resulting suspension was kept under these conditions for 40 min than filtered off. The precipitate was collected, washed with water and dried in vacuum. The crude solid was extracted with boiling chloroform to give after evaporation of the solvent in vacuum 2.04 g (51 %) of pure 4-bromo-*N*-(2-aminoethyl)-1,8-naphthalimide **2** as pale yellow crystals (m.p. 151–152 °C; lit. [48] 150–151 °C). FT-IR (KBr)  $\text{cm}^{-1}$ :



**Scheme 2** Feasible photoinduced electron transfer in the 1,8-naphthalimide **3**

3374 ( $\nu_{\text{NH}_2}$ ); 2920 ( $\nu_{\text{CH}}$ ); 1696 ( $\nu^{\text{as}}\text{N}-\text{C}=\text{O}$ ); 1659 ( $\nu^{\text{s}}\text{N}-\text{C}=\text{O}$ ).  $^1\text{H NMR}$  ( $\text{CDCl}_3-d$ , 250.13 MHz) ppm: 8.66 (dd, 1H,  $J=7.3$  Hz,  $J=1.1$  Hz, naphthalimide H-5); 8.57 (dd, 1H,  $J=8.5$  Hz,  $J=1.1$  Hz, naphthalimide H-7); 8.40 (d, 1H,  $J=7.9$  Hz, naphthalimide H-3); 8.05 (d, 1H,  $J=7.9$  Hz, naphthalimide H-2); 7.84 (dd, 1H,  $J=8.5$  Hz,  $J=7.3$  Hz, naphthalimide H-6); 5.18 (br.s, 2H,  $\text{NH}_2$ ); 4.27 (t, 2H,  $J=6.6$  Hz,  $\text{NCH}_2\text{CH}_2\text{NH}_2$ ); 3.07 (t, 2H,  $J=6.7$  Hz,  $\text{NCH}_2\text{CH}_2\text{NH}_2$ ).

**Scheme 3** Synthesis of 1,8-naphthalimide PET-based probe **3**

### Synthesis of 1,8-naphthalimide Probe **3**

To a solution of methyl acrylate (5.2 mL, 60 mmol) in 30 mL of methanol, 1.91 g of 4-bromo-*N*-(2-aminoethyl)-1,8-naphthalimide **2** (6 mmol) was added. The reaction mixture was stirred for 72 h at room temperature and the precipitate was filtered off, washed with water and dried to give 2.54 g (86 %) of the ester-functionalized 4-bromo-1,8-naphthalimide **3** as pale yellow solid (m.p. 90–92 °C,  $R_f=0.56$  in a solvent system: *n*-hexane/acetone=1:1). FT-IR (KBr)  $\text{cm}^{-1}$ : 2934 ( $\nu_{\text{CH}}$ ); 1728 ( $\nu_{\text{COOCH}_3}$ ); 1692 ( $\nu^{\text{as}}\text{N}-\text{C}=\text{O}$ ); 1640 ( $\nu^{\text{s}}\text{N}-\text{C}=\text{O}$ ).  $^1\text{H NMR}$  ( $\text{CDCl}_3-d$ , 250.13 MHz) ppm: 8.65 (dd, 1H,  $J=7.4$  Hz,  $J=1.0$  Hz, naphthalimide H-5); 8.59 (dd, 1H,  $J=8.5$  Hz,  $J=1.0$  Hz, naphthalimide H-7); 8.43 (d, 1H,  $J=7.8$  Hz, naphthalimide H-3); 8.01 (d, 1H,  $J=7.8$  Hz, naphthalimide H-2); 7.85 (dd, 1H,  $J=7.4$  Hz,  $J=8.5$  Hz, naphthalimide H-6); 4.25 (t, 2H,  $J=7.2$  Hz,  $(\text{CO})_2\text{NCH}_2$ ); 3.52 (s, 6H,  $2 \times \text{OCH}_3$ ); 2.88 (t, 4H,  $J=7.1$  Hz,  $2 \times \text{CH}_2\text{CH}_2\text{CO}$ ); 2.78 (t, 2H,  $J=7.2$  Hz,  $\text{NCH}_2\text{CH}_2$ ); 2.45 (t, 4H,  $J=7.1$  Hz,  $2 \times \text{CH}_2\text{CH}_2\text{CO}$ ). Elemental analysis: calculated for  $\text{C}_{22}\text{H}_{23}\text{BrN}_2\text{O}_6$  (MW 491.33) C 53.78, H 4.72, N 5.70 %; found C 54.14, H 4.63, N 5.81 %.

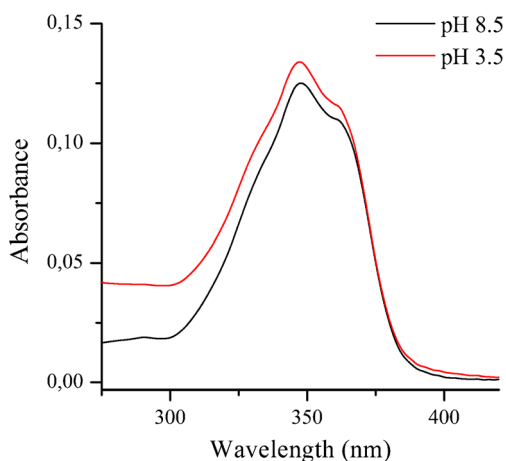
## Results and Discussion

### Design and Synthesis

The 1,8-naphthalimide chromophore under study was designed as a PET fluorescent probe for protons and transition metal ions determination based on “fluorophore-spacer-receptor” format. The 1,8-naphthalimide was chosen as a fluorophore unit because of its desirable properties, such as an excellent photostability, high luminescence efficiency, large Stoke’s shift and easy modification of the molecular structure [49–51]. It is well known that photophysical properties of the 1,8-naphthalimide derivatives depend mainly on the polarization of their chromophoric system [52, 53]. Light absorption in this molecule generates a charge transfer interaction between the substituents at C-4 position and the carbonyl groups. A large dipole moment in the excited state gives rise to a strong photogenerated electric field with positive charge at the substituent in C-4 position and negative one at

**Table 1** Photophysical characteristics of compound **3** in water/DMF (4:1, v/v) solution ( $C=10^{-5}$  mol L $^{-1}$ ) at different pHs

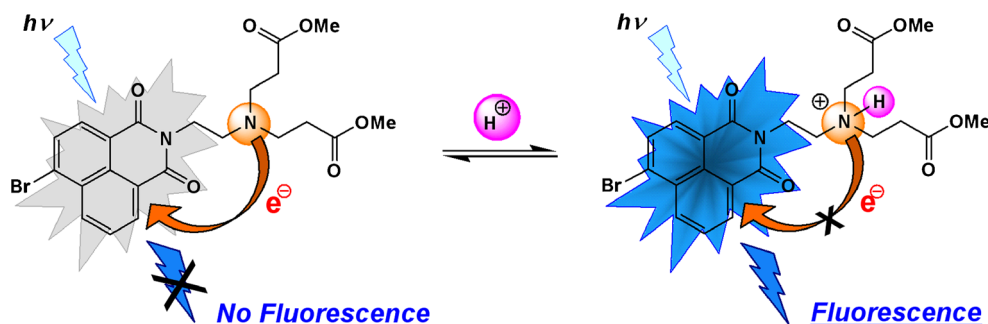
Compound	pH	$\lambda_A$ (nm)	$\epsilon$ (L mol $^{-1}$ cm $^{-1}$ )	$\lambda_F$ (nm)	$\nu_A-\nu_F$ (cm $^{-1}$ )	$Q_F$
<b>3</b>	8.5	342	12 100	440	6 500	0.003
	3.5	344	13 300	411	4 700	0.008

**Fig. 1** Absorption spectra of probe **3** in water/DMF (4:1, v/v) at pH 3.5 and pH 8.5 ( $C=10^{-5}$  mol L $^{-1}$ )

imide group (Scheme 2). Such a molecular electric field can, depending on its sign and magnitude, inhibit or accelerate a transiting electron in the 1,8-naphthalimide compounds [54]. Thus the bulk 1,8-naphthalimide PET systems are using “lower” receptor moiety (receptor is directly attached to the C-4-position) in which electron leaving the unprotonated amine receptor across the C-4 position with its attractive electric field.

The PET path from the “upper” receptor in *N*-position is just as feasible thermodynamically but requires the electron to enter the fluorophore across the imide moiety with its repulsive electric field and is observed in electron poor unsubstituted, 4-chalogeno- and 4-alkoxy- 1,8-naphthalimides [55, 56].

Recently we have synthesized some 1,8-naphthalimide derivatives, containing “lower” tertiary amine receptor, for cation recognition [57, 58]. The synthesized 1,8-naphthalimide derivatives were prepared using accessible materials in high yields and showed high sensing activity.

**Scheme 4** Photophysical behavior of 1,8-naphthalimide **3** as a function of pH

Therefore it was of interest to see if analogues of the 1,8-naphthalimide fluorophore, containing “upper” amine receptor would shed further light on this issue. The 4-bromo-1,8-naphthalimide was chosen as a fluorophore moiety in a view of its electron deficient nature, high singlet state energy and a weak repulsion field at the imide group. These properties are likely to make PET process much more efficient as compared to that in structurally similar systems involving electron-donating group in C-4 position [59].

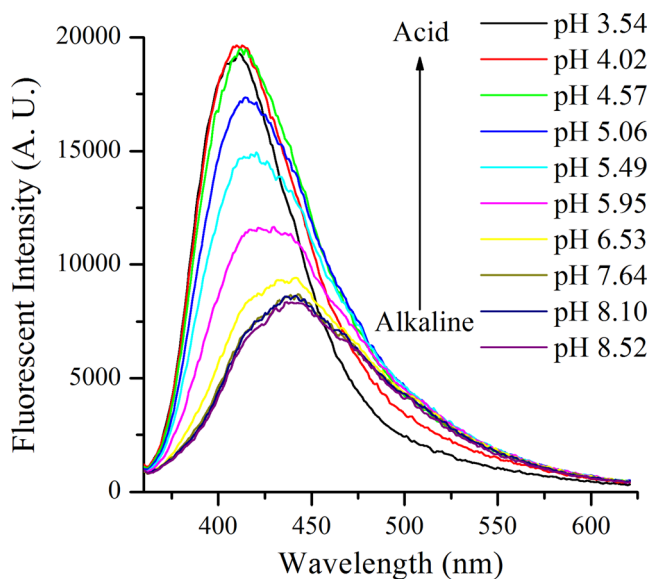
The synthesis of 1,8-naphthalimide sensor **3** was achieved in two steps according Scheme 3. As shown, first 4-bromo-1,8-naphthalic anhydride **1** was reacted with ethylenediamine in water solution at 75 °C for 5 h to give intermediate **2**. The desired ester-terminated 1,8-naphthalimide **3** was synthesized by initial Michael addition of 4-bromo-*N*-(2-aminoethyl)-1,8-naphthalimide **2** with methyl acrylate resulting in ester **3**. The synthesized compounds were characterized and identified by their melting points, TLC ( $R_f$  values), elemental analysis data, UV-vis, fluorescence, FT-IR and  $^1\text{H}$  NMR spectroscopy.

#### Photophysical Properties of Probe **3** as a Function of pH

The basic photophysical characteristics of the synthesized probe **3** were recorded in water/DMF (4:1, v/v) solution ( $C=10^{-5}$  mol L $^{-1}$ ) at different pHs (Table 1). In solution compound **3** shows absorption band in range 280–320 nm, which is attributed to the typical for the 4-bromo-1,8-naphthalimides ICT process [57]. The position of compound’s **3** absorbance remains almost constant at different pHs since the 1,8-naphthalimide fluorophore does not affect the ICT excited states (Fig. 1).

The molar absorptivity ( $\epsilon$ ) of probe **3** in the longest-wavelength band of the absorption spectra is higher than 10,000 L mol $^{-1}$  cm $^{-1}$  (Table 1), indicating that this is a charge transfer (CT) band, due to ( $\pi$ ,  $\pi^*$ ) character of the  $S_0 \rightarrow S_1$  transition. Also, as can be seen from the data presented in

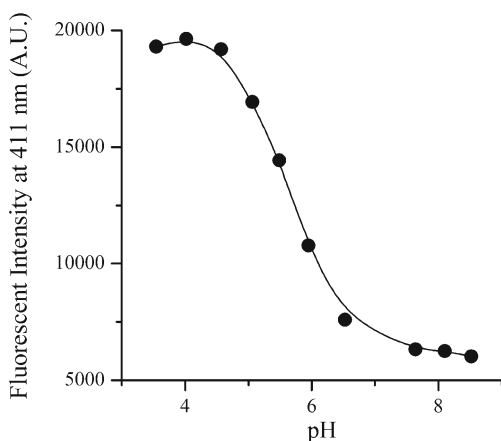




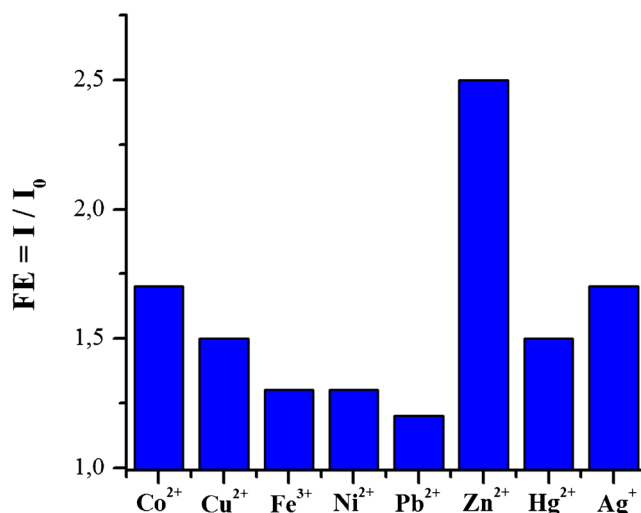
**Fig. 2** Fluorescent changes of probe **3** as a function of pH in water/DMF (4:1, v/v)

Table 1, at high pH values the molar absorptivity of **3** is lower in comparison with the molar absorptivity at low pHs. Obviously in basic solution compound **3** forms self-aggregates due to an intermolecular  $\pi$ - $\pi$  stacking which results in decreased absorbance. In acidic solution, the amino group in compound **3** is protonated and the electrostatic repulsion between cationic species counteracts the  $\pi$ - $\pi$  stacking action making the self-aggregates dissociable.

In acid solution (pH=3.5) probe **3** displays blue fluorescence with maximum at 411 nm which is usual for the 4-bromo-1,8-naphthalimides [60]. At alkaline conditions (pH=8.5) the emission band of **3** is centered at 440 nm and the Stoke's shift increased that supports the aggregation of **3**. This bathochromic shift of fluorescence is typical for 4-bromo-1,8-naphthalimide and indicates the formation of *J* aggregates which can be explained by molecular exciton theory [60]. According to this theory, a molecule is regarded as a point



**Fig. 3** Effect of pH on the fluorescence intensity at 411 nm of probe **3**



**Fig. 4** Effect of the metal cations at concentration  $C=1 \times 10^{-4} \text{ mol L}^{-1}$  on the fluorescence of **3** ( $C=1 \times 10^{-5} \text{ mol L}^{-1}$ ) in DMF solution buffered with 1 mmol HEPES

dipole and the excitonic state of the aggregate splits into two levels through the interaction of transition dipoles [61].

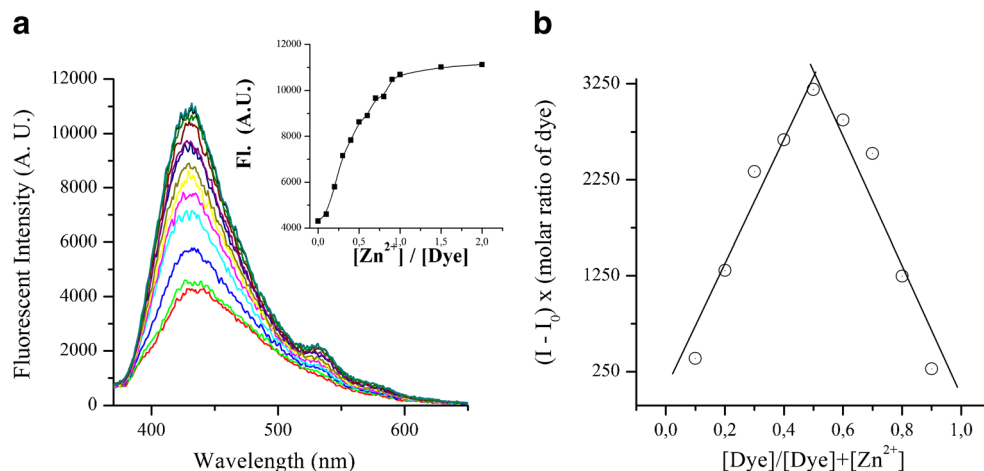
The ability of the molecules to emit the absorbed light energy is characterized quantitatively by the fluorescence quantum yield ( $Q_F$ ). The quantum yields of fluorescence were calculated using 9,10-diphenylanthracene ( $Q_F=0.95$  in ethanol) as a standard [47] according to Eq. (1), where  $A_{ref}$ ,  $S_{ref}$ ,  $n_{ref}$  and  $A_{sample}$ ,  $S_{sample}$ ,  $n_{sample}$  represent the absorbance at the excited wavelength, the integrated emission band area and the solution refractive index of the standard and the sample, respectively.

As can be seen from the data presented in Table 1, the quantum yield of fluorescence of compound **3** in basic solution is lower in comparison with the data for acid media. This indicates that the fluorescence of compound **3** is being quenched by PET process from the tertiary amino group to the fluorophore. Upon protonation the oxidation potential of the receptor is being increased thermodynamically thus disallowing PET process and the fluorescence of the compound is recovered (Scheme 4).

$$Q_F = Q_{ref} \left( \frac{S_{sample}}{S_{ref}} \right) \left( \frac{A_{ref}}{A_{sample}} \right) \left( \frac{n_{sample}^2}{n_{ref}^2} \right) \quad (1)$$

The effect of pH on the fluorescence intensity of probe **3** was further studied in a pH range *ca.* from pH 3 to pH 9, maintained by small portions of hydrochloric acid starting from alkaline solution of **3**. Family of fluorescent spectra of compound **3** at different pH values in water/DMF (4:1, v/v) solution are presented in Fig. 2. As can be seen, upon acidification the emission of **3** was gradually increased. The enhancement of the fluorescence intensity ( $FE=3.2$ ) have been used as a qualitative parameter. The  $FE=I/I_0$  is the ratio

**Fig. 5** Changes of fluorescent intensity of probe **3** in DMF solution buffered with 1 mmol HEPES upon addition of  $Zn^{2+}$  from 0 to 20  $\mu M$  (a) and Job's plot (b)



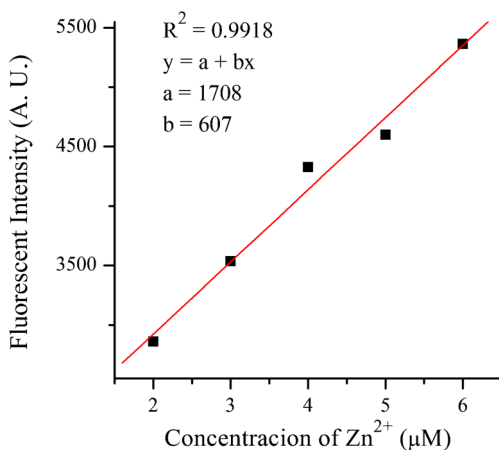
between the maximum fluorescence intensity  $I$  at pH 4 and the minimum fluorescence intensity  $I_0$  at pH 8.

Analysis of the fluorescence changes at 411 nm (Fig. 3) according to Eq. (2) gives the  $pK_a$  value of 5.61 which matches the typical pH values of acidic organelles (pH 4–6) [21], indicating that the novel compounds may be suitable for monitoring pH variations in the acidic environment in bio-samples.

$$\log \frac{(I_{Fmax} - I_F)}{(I_F - I_{Fmin})} = pH - pK_a \quad (2)$$

#### Influence of Metal Ions on the Fluorescence Intensity of Probe 3

Compound **3** was designed as a PET-based fluorescent probe for cation recognition. The signaling fluorescent properties of the compound in the presence of transition metal ions have been investigated by fluorescence spectroscopy in DMF



**Fig. 6** Linear relationship between the intensity of **3** and  $Zn^{2+}$  concentration in DMF solution buffered with 1 mmol HEPES

(Fig. 4). To maintain a constant pH of the environment, the examined solutions were buffered by addition of 1 mmol HEPES solution (pH=7.2). The HEPES buffer was chosen because it ensures pH value about pH=7 where the probe **3** is in its “off-state” and PET process is feasible. The experiments have been performed in the presence of different metal cations:  $Co^{2+}$ ,  $Cu^{2+}$ ,  $Fe^{3+}$ ,  $Ni^{2+}$ ,  $Pb^{2+}$ ,  $Zn^{2+}$ ,  $Hg^{2+}$  and  $Ag^+$ . As expected the presence of “guest” metal ions in the solution of 1,8-naphthalimide **3** was signaled by fluorescent enhancement (FE) due to the coordination of the receptor with the cations thus disallowing the PET quenching process. The  $FE = I/I_0$  is determined as the ratio between the maximum fluorescence intensity ( $I$  - after metal ions addition) and the minimum fluorescence intensity ( $I_0$  - free of metal cations solution). The value of FE depends on the nature of the metal ion.

As can be seen from Fig. 4, where the calculated FE values in the presence of different metal cations are presented, the examined compound exhibits sensor selectivity. In DMF solution of 1,8-naphthalimide **3**, stronger fluorescence enhancement ( $FE=2.5$ ) was observed only upon addition of  $Zn^{2+}$  (Fig. 5a).

The stoichiometry of the complex between  $Zn^{2+}$  cations and the ligands was determined using the method of continuous variations (Job's method). Job's plot analysis of the titrations revealed a maximum at about 0.5 mol fraction, indicating 1:1 binding stoichiometry (Fig. 5b).

The limit of detection (LOD) of probe **3** was calculated to be  $2.5 \times 10^{-7} \text{ mol L}^{-1}$  according to formula  $LOD = 3\sigma/b$  where  $\sigma$  is the standard deviation and  $b$  is the slope of the calibration plot (Fig. 6) [62].

#### Conclusions

A new blue-emitting molecular PET probe based on 1,8-naphthalimide fluorophore (**3**) was designed and synthesized. The photophysical behavior of the compound in water/DMF

(4:1, v/v) solutions as a function of pH as well as in DMF solutions in the presence of different transition metal ions was studied. In water/DMF (4:1, v/v) solution 1,8-naphthalimide **3** enhanced its fluorescence intensity more than three times ( $FE=3.2$ ) after acidification from pH *ca.* 9 to 3. In buffered with HEPES DMF solution (pH=7.2) in the presence of representative metal cations ( $Co^{2+}$ ,  $Cu^{2+}$ ,  $Fe^{3+}$ ,  $Ni^{2+}$ ,  $Pb^{2+}$ ,  $Zn^{2+}$ ,  $Hg^{2+}$  and  $Ag^{+}$ ), 1,8-naphthalimide **3** showed selectivity towards  $Zn^{2+}$  ions ( $FE=2.5$ ). These effects are attributed to the coordination of the tertiary amine receptor, which disallows photoinduced electron transfer in the molecule. The changes were of such magnitude that they can be considered as representing two different “states”, where the fluorescence emission is “switched off” in alkaline media and “switched on” in acid environment and in the presence of  $Zn^{2+}$  ions. The  $pK_a$  value of 5.61 which matches the typical pH values of acidic organelles (pH 4–6) and selectivity towards Zn(II) indicates that the novel compound may be suitable for monitoring pH variations in the acidic environment in bio-samples and for use as a molecular sensor for  $Zn^{2+}$  ions.

**Acknowledgments** This work was supported by the National Science Foundation of Bulgaria (project DDVU-02/97). Authors also acknowledge the Science Foundation at the University of Chemical Technology and Metallurgy (Sofia, Bulgaria).

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