Synthesis and investigation of 1,8-naphthalimide derivative with sensor activity

Polya Miladinova¹

¹Organic Synthesis Department, University of Chemical Technology and Metallurgy, Sofia, Bulgaria

ISSN 2712-1267 UDC: 66.091.3:542.913 https://doi.org/10.7251/JCTE2203006M Original scientific paper

Paper received: 21 Oct 2022 Paper accepted: 21 Dec 2022 Paper available from 30 Dec 2022 at https://glasnik.tf.unibl.org/

Keywords:

1,8-naphthalimide derivative, charge-transfer, selective pH sensor, sensor for Fe³⁺. The paper reports on the synthesis and fluorescence characteristics of novel 1,8-naphthalimide fluorophore. It was configured as a "fluorophore-spacer-receptor" system able to act as a pH-probe via PET (photoinduced electron transfer) fluorescence sensing mechanism. Due to the tertiary amine receptor the novel probe showed "off-on" switching properties under the transition from alkaline to acid media. Also, the ability of the probe to detect metal ions in water/dimethylformamide (1:1, v/v) has been evaluated by monitoring the changes of its fluorescence intensity. Among the tested metal ions (Cu²⁺, Pb²⁺, Zn²⁺, Ni²⁺, Hg²⁺, Fe³⁺) only the presence of Fe³⁺ was efficiently detected by fluorescence quenching mechanism.

INTRODUCTION

Analysis of pollutants of different origins in air, soil and water sources is a challenge for scientists on a global scale. A number of scientific laboratories are engaged in the development of new detectors for their detection. There is great interest in the development of highly efficient and selective sensors for the detection of heavy and transition metal ions. This has given rise to a drive to develop molecular devices capable of performing sensory functions, such as fluorosensors responding by a change in their fluorescence emission (Lieberzeit & Dickert, 2009; Saccomano et al., 2021; Thai & Lee, 2021; Wu et al., 2017). The measurement of pH is very important in biological, chemical and industrial fields. In recent years, the optical pH sensory technique based on the absorption or emission of certain organic compounds with structural diversity, has received increasing attention because it offers many advantages over the potentiometric method, such as fast response time and the absence of the otherwise requested reference electrode (Abu-Thabit et al., 2016; Martínez-Quiroz et al., 2016; Ozdemir, 2020; Qi et al., 2015; Ye et al., 2019; Wang et al., 2010).

Two common principles for fluorescence sensors are used: photoinduced electron transfer (PET) and

*Corresponding author:

internal charge transfer (ICT) (Jinbo et al., 2020; Panchenko et al., 2014; Prasanna de Silva et al., 2009; Valeur & Leray, 2000; Wu et al., 2019).

different Among fluorescent chemosensors, naphthalimidederivativesareattractingmuchattention due to their excellent stability, photophysical, thermal, electrochemical and electroluminescence properties, which can be modulated by introduction of different substituents at the 4th position of the naphthalimide ring. Despite the many naphthalimides synthesized, the design of new fluorescent sensors which exhibit high selectivity and sensitivity fluorescence, lowtoxicity and stability are still challenging (Geraghty et al., 2021; Gudeika, 2020; Lee, 2016; Li et al., 2012; Oshchepkov et al., 2021; Pablos et al., 2022; Poddar et al., 2019; Shaki et al., 2010; Tian et al., 2010; Zhang et al., 2019).

This paper reports on the design and synthesis of novel PET based 1,8-naphthalimide fluorophore (1). Also, the photophysical properties of the new compound in presence of protons and metal cations are presented.



Polya Miladinova, Organic Synthesis Department, University of Chemical Technology and Metallurgy, Sofia, Bulgaria; email: ppolya@uctm.edu

MATERIALS AND METHODS

N-allyl-4-nitro-1,8-naphthalimide as a precursor for the synthesis of the target dye has been synthesized according to a method described previously (Konstantinova et al., 1993). 1-(2-Aminoethyl) piperazine was product of Sigma Aldrich (Merck). Solvents are of p.a or analytical grade (Fluka). Commercial HEPES (Fisher Chemical) was used. Zn(NO₃)₂, Cu(NO₃)₂, Ni(NO₃)₂, Pb(NO₃)₂, Fe(NO₃)₃ and Hg(NO₃)₂, and salts were the sources for metal cations (all Aldrich salts at p.a. grade).

The melting point was recorded on a Büchi 535 apparatus (Switzerland). Thin-layer chromatography (TLC) measurements were performed on silica gel plates (Merck, 60 F 254, 20x20 cm, 0.2 mm thickness, ready-to-use). pH values were monitored using a 704 pH-meter (Metrohm, Swiss). Electronic spectra were recorded on a Hewlett Packard 8452A UV/vis spectrophotometer; IR - on a Varian 660 instrument (Varian, USA); ¹H-NMR spectra - on DRX-250-Brucker equipment and fluorescent spectra – on spectrometer FS-2 (Scinco).

The fluorescence quantum yields ($\Phi_{\rm F}$) were measured relatively to Coumarin 6 ($\Phi_{\rm F}$ = 0.78 in ethanol) as standards. All fluorescence measurements were performed at 25.0°C. A 1×1 cm quartz cuvette was used for all spectroscopic analysis. To adjust the pH, very small volumes of hydrochloric acid and sodium hydroxide were used. The effect of the metal cations upon the fluorescence intensity was examined by adding portions of the metal cations stock solution (fresh prepared aqueous solutions) to a known volume of the fluorophore solution (10 mL dimethylformamide buffered with HEPES buffer). The addition was limited to 100 µL so that dilution remains insignificant.

RESULTS AND DISCUSION

The synthetic route used for the preparation of 1,8-naphthalimide fluorophore (1) is outlined in Scheme 1.

N-allyl-4-nitro-1,8-naphthalimide as a precursor for the synthesis of the target dye has been synthesized according to a method described previously (Konstantinova et al., 1993).

For the synthesis of 1,8-naphthalimide fluorophore (1) N-allyl-4-nitro-1,8-naphthalimide (1.41 g, 0.005 mol) was dissolved in 25 ml dioxane, then 0.66 ml (0.005 mol) of 1-(2-Aminoethyl)piperazine was added and the solution was stirred for 3 h while boiling. The reaction was monitored by TLC (system heptane:acetone = 1:1 on silica gel). After cooling to room temperature, the reaction mixture was poured into 50 ml water. The precipitate of N-allyl-4-((2-(piperazin-1-yl)ethyl) amino)-1,8-naphthalimide (1) was filtered off, washed with water till pH 7 and dried in vacuum at 40 °C. Yield 95%. The product obtained was purified with column chromatography (above mentioned system). The dye (1) was characterized and identified by TLC (system heptane:acetone = 1:1 on silica gel) - Rf = 0.49; UVvis spectrum - λ max (DMF) = 430 nm; fluorescent spectrum - λ max (DMF) = 517 nm and ¹H NMR (CDCl₂, ppm): 8.54-8.53 (d, 1H, -CH- from ArH); 8.36-8.35 (d, 1H, -CH- from ArH); 8.05-8.04 (d, 1H, -CH- from ArH); 7.59 (t, 1H, -CH- from ArH); 6.82-6.81 (d, 1H, -CH- from ArH); 5.93 (m, 1H, -CH=); 5.24-5.21 (d, 2H, =CH₂); 5.13-5.11 (d, 2H, -NCH₂CH=CH₂); 4.92 (bs, 4H, 2 x -CH, from piperazine); 4.72 (bs, 5H, 2 x -CH, from piperazine, ArNH-); 2.89 (bs, 2H, -NHCH,-CH₂);2.82 (bs, 2H, -NHCH₂-CH₂-); 0.81(bs, 1H, -NH from piperazine). Elemental analysis: calculated for C₂₁H₂₄N₄O₂ (MW 364.4) C 69.21, H 6.64, N 15.37%; Found C 69.33, H 6.61, N 15.42 %.



Table 1. Basic spectral characteristics of (1	Table	ctral character	istics of (1)
---	-------	-----------------	---------------

I	1.	·					
Compound	Yeild,%	Rf	Melting point, °C	λ _A , nm	λ _բ ,nm	V _A - V _{F,} cm ⁻¹	${\Phi_{\scriptscriptstyleF}}^*$
N-allyl-4-nitro-1,8- naphthalimide	97	0.65	109-112	348	-	-	-
1	95	0.49	> 280	430	517	3868	0.357

* $\Phi_{\rm F}$ was measured relatively to Coumarin 6 ($\Phi_{\rm F}$ = 0.78 in ethanol) (Reynolds, Drexhage, 1975)

Characteristics of the compound (1)

The photophysical properties of the compound (1) were investigated in dimethylformamide at a concentration of 1 x 10⁻⁵ mol l⁻¹. Table 1 summarizes the basic spectral characteristics of (1): the values of absorption (λ_A) and fluorescence (λ_F) maxima, Stokes shift ($v_A - v_F$) and the quantum yield of fluorescence (Φ_F).

The absorption maximum of (1) is shifted bathochromically in comparison with N-allyl-4-nitro-1,8-naphthalimide (430 nm) due to the electron donating ability of the amino group. The presence of the last one leads to the availability of fluorescence. The value of the Stokes shift is within the range typical for the naphthalimide dyes. The low quantum yield is a result of the PET present in the molecule.

The synthesized naphthalimide (1) is based on the "fluorophore-spacer-receptor" architecture, where aminonaphthalimide acts as a fluorophore and the electrondonating piperazine tertiary amino group is the cation receptor, while the ethylene group in between serves as a spacer separating covalently the two units.

In the absence of a bound cation or proton, the highest occupied molecular orbital (HOMO) of the unbound receptor has higher energy than that of the halffilled HOMO of the excited fluorophore. This energy difference drives a rapid electron transfer from the receptor to the excited-state fluorophore resulting in quenched or "switched off" fluorescence. When the receptor is bound to a cation or proton, the energy level of the receptor is lower than that of the HOMO of the excited fluorophore. Hence, the receptor is stabilized and the electron transfer is not energetically favored. Thus the fluorescence is "switched on". In the presence of an anion deprotonation of the nitrogen atom connected to the naphthalimide part occurs leading to fluorescence increment and bathochromic movement of λ max (as shown in Scheme 2).

Influence of pH on absorption and fluorescent properties of compound (1)

The compound under study was designed as a fluorescence sensor for determining pH changes over a wider pH scale. This was the reason to investigate the photophysical behavior of probe (1) in water/DMF (1:1, v/v) solution at different pH values.

The UV-VIS spectrum of compound (1) was recorded. It revealed the longest-wavelength absorption band in the range between 375 nm and 475 nm (Figure 1).

This absorption band is typical for the naphthalimide dyes and it is attributed to the internal charge transfer (ICT). It is well known that the photophysical properties of the naphthalimide derivatives are basically related to the polarization of their chromophoric system. Light absorption in this molecule generates a charge transfer interaction between the electron-donor substituent at C-4 position and the electron-acceptor carbonyl groups within the naphthalimide molecule. The absorption spectra of compound (1) shifted bathocromically in the 2-14 pH window in the course of the transition from acid to alkaline media (Figure 1).



Scheme 2. Mechanism of compound (1) action

The changes in the fluorescence spectra of compound (1) in water/DMF (1:1, v/v) solution at different pH values are depicted in Figure 2.

In alkaline media (pH 7.9 - 14) naphthalimide (1) showed fluorescence in the range between 450 nm and 650 nm with a maximum at 533 nm (Figure 3).

The addition of HCl to compound (1) (pH 8.4 – 5.6) converts the imino group of piperazine fragment in quaternary ammonium cations which strongly decreases the electron donating ability of the nitrogen atom. As a result, the PET transfer is terminated and the fluorescence of the molecule is "switched on". The quantum yield of fluorescence $\Phi_{\rm F}$ = 0.357 was calculated using Coumarin 6 ($\Phi_{\rm F}$ = 0.78 in ethanol) as a standard (Reynolds, Drexhage, 1975) according to Eq. (1) (Grabchev et al., 2006), where $A_{\rm ref}$, $S_{\rm ref}$, $n_{\rm ref}$ and $A_{\rm sample}$, $S_{\rm sample}$, $n_{\rm sample}$ represent the absorbance at the excitation wavelength, the integrated emission band area and the solvent refractive index of the standard and the sample, respectively.

$$\Phi_{\rm F} = \Phi_{\rm ref} \left(\frac{S_{\rm sample}}{S_{\rm ref}} \right) \left(\frac{A_{\rm ref}}{A_{\rm sample}} \right) \left(\frac{n_{\rm sample}^2}{n_{\rm ref}^2} \right)$$
(1)

Upon further acidification of the medium (pH 5.6-2), the fluorescence intensity decreases and compound (1) goes into the "off" state. This is explained by the protonation of the imino group attached to the naphthalimide nucleus. Confirmation of the fact is that the compound ceases to fluoresce and a hypsochromic shift is observed in the absorption spectra (Figure 1).

In an alkaline media (pH 8.4-13), a hump is observed in the fluorescence spectrum, which could be explained as follows: in the pH range 8.4-10.5, the deprotonation of the imino group connected to the naphthalimide nucleus begins and the fluorescence of the compound increases more slightly in comparison with that in the pH range 8.4-5.6. In the pH range 10.5-14, the deprotonation of the nitrogen atoms from the 2-piperazine-1-ylethylamine part begins. This is confirmed by the fact that the molecule does not produce fluorescence as PET is regenerated.

The sensory activity observed in the pH range 14 - 2 is "off₁-on₁-off₂-on₂-off₃".

To evaluate compound (1) for pH sensing purposes, the calibration curve was constructed (Figure 2) and acidity constant was determined. The pK_a values of compound (1) has been calculated by the Eq. (2) (Qian et al., 2008).

$$\log\left(\frac{\text{IFmax} - \text{IF}}{\text{IF} - \text{IFmin}}\right) = \text{pH} - \text{pKa}$$
(2)



Figure 1. Absorption spectra of fluorophore (1) in water/ DMF (1:1, v/v) solution at different pH values



Figure 2. Fluorescence spectra of fluorophore (1) in water/DMF (1:1, v/v) solution at different pH values

Four values were obtained for pK_a : 2.9 - corresponding to the protonation of the nitrogen atom connected to the naphthalimide part, 7.32 - corresponding to the protonation of the nitrogen atom from the piperazine part, 8.75 - corresponding to the deprotonation of the nitrogen atom connected to the naphthalimide part and 13.2 - corresponding to the deprotonation of the nitrogen atom from the piperazine moiety.

The enhancement of the fluorescence emission $FE_1 = 1.38$ and $FE_2 = 1.33$ have been used as a qualitative parameter. The $FE_1 = I/I_0$ is determined as the ratio between the maximum fluorescence intensity I at pH 5.6 and the minimum fluorescence intensity I₀ at pH 2. The $FE_2 = I/I_0$ is determined as the ratio between the maximum fluorescence intensity I at pH 10.5 and the minimum fluorescence intensity I at pH 10.5 and the minimum fluorescence intensity I at pH 14.

Influence of metal cations on the fluorescence intensity of compound (1)

The signaling fluorescent properties of compound (1) in the presence of transition metal cations (Cu^{2+} , Fe^{3+} , Ni^{2+} , Pb^{2+} , Zn^{2+} and Hg^{2+}) were investigated. In order to avoid the aggregation process and more complicated equilibrium, the influence of the metal cations was studied in organic solvent. The investigation was carried out in DMF using 0.5, 1, 5 and 10 metal equivalents. Figure 3 shows the fluorescence quenching FQ of compound (1) in the presence of various metal cations.

As can be seen from the figure, the novel compound (1) exhibits sensor selectivity, a strong fluorescence quenching was observed only upon the addition of Fe^{3+} , while the remaining ions produce a weaker effect. Possibly the well pronounced quenching effect of Fe^{3+} is due to the better complexation and paramagnetic properties of Fe^{3+} which are resulting unspecific fluorescence quenching by energy or electron transfer (Fabbrizzi et al., 1996; Yordanova et al., 2014).





To maintain a constant pH values, the experiments have been performed in DMF in presence of HEPES buffer (pH 7.2). The HEPES buffer was chosen, because it ensures pH in the physiological range which is assumption for applications in living organisms. In Figure 4a and 4b presents the fluorescence spectra in DMF describing the behavior of sensor (1) towards the transition metal Fe^{3+} without and with a presence of a buffer.

It was found that upon addition of an equivalent of Fe³⁺ cations without addition on buffer (Figure 4a) results FQ = 1.53 while the addition 10 equivalent of Fe³⁺ quenches the emission with FQ = 2.31. After the addition of 10 μ l of buffer HEPES (pH = 7.2) a bigger fluorescence quenching was observed (FQ=2.33 at using of an equivalent of Fe³⁺ and 2.65 at using of 10 equivalent of Fe³⁺).

Therefore, we can conclude that both in the presence as well as in the absence of buffer coordination of the metal with the ligand is observed, as a result of which, however, PET is not interrupted.

CONCLUSIONS

The synthesis and characterization of new N-allyl-4-((2-(piperazin-1-yl)ethyl)amino)-1,8-naphthalimide, has been described. Novel compound was designed as a "fluorophore-spacer-receptor" format, making the compound capable to act as a molecular fluorescence PET-based pH probe. The photophysical properties of the novel compound were studied in water/DMF (1:1, v/v) solution and discussed. The determined pK values indicate that it would be able to act as efficient "off-on" switches for pH. Also, the novel probe showed sufficient sensor selectivity towards metal ions. In the presence of Fe³⁺ the synthesized compound quenched its fluorescence intensity (FQ = 2.65). These results demonstrate the potential of the novel naphthalimide derivative to detect metal ions with pronounced selectivity towards Fe³⁺.



Figure 4. Change in fluorescence signal at different concentration of Fe³⁺ without (a) and using 10 μ l of buffer (b)

REFERENCES

- Abu-Thabit, N., Umar, Y., Ratemi, E., Ahmad, A., & Abuilaiwi, F. (2016). A Flexible optical pH sensor based on polysulfone membranes coated with pH-responsive polyaniline nanofibers. *Sensors (Basel)*, *16*(7), 986. <u>https://</u> doi.org/10.3390/s16070986
- Fabbrizzi, L., Licchelli, M., Pallavicini, P., Perotti, A., Taglietti, A., & Sacchi, D. (1996). Fluorescent sensors for transition metals based on electron-transfer and energytransfer mechanisms. *European Journal of Chemistry*, 2, 75-92. <u>https://doi.org/10.1002/</u> CHEM.19960020114
- Geraghty, C., Wynne, C., & Elmes, R. (2021). 1,8-Naphthalimide based fluorescent sensors for enzymes. *Coordination Chemistry Reviews*, 437, 213713. <u>https://doi.org/10.1016/j.</u> ccr.2020.213713
- Grabchev, I., Chovelon, J-M., & Nedelcheva, A. (2006). Green fluorescence poly(amidoamine) dendrimer functionalized with 1,8-naphthalimide units as potential sensor for metal cations. *Journal of Photochemistry and Photobiology*, 183, 9-14. <u>https://doi.org/10.1016/j.jphotochem.2006.02.012</u>
- Gudeika, D. (2020). A review of investigation on 4-substituted 1,8-naphthalimide derivatives. Synthetic Metals, 262, 116328. <u>https://doi.org/10.1016/j.synthmet.2020.116328</u>
- Jinbo, D., Ohira, K., Imato, K., & Ooyama, Y. (2020). Development of fluorescent sensors based on a combination of PET (photo-induced electron transfer) and FRET (Förster resonance energy transfer) for detection of water. *Materials Advances*, 1(3), 354-362. <u>https://doi. org/10.1039/DOMA00139B</u>
- Konstantinova, T., Meallier, P., & Grabchev, I. (1993). The synthesis of some 1,8-naphthalic anhydride derivatives as dyes for polymeric materials, *Dyes and Pigments*, 22(3), 191-198. <u>https://doi.org/10.1016/0143-7208(93)87006-Z</u>
- Lee, M. (2016). Bis(naphthalimide-piperazine)-based off-on fluorescent probe for acids, *Journal* of *Fluorescence*, *26*(3), 807-811. <u>https://doi.</u> org/10.1007/s10895-016-1767-6
- Li, C., Zhou, Y., Xu, F., Li, Y., Zou, C., & Weng, C. (2012). A fluorescent pH chemosensor based on functionalized naphthalimide in aqueous solution. *Analytical Sciences*, *28*(8), 743-747. https://doi.org/10.2116/analsci.28.743
- Li, P., Zhang, D., Zhang, Y., Lu, W., Zhang, J., Wang, W., He, Q., Théato, P., & Chen, T. (2019). Aggregation-caused quenching-type

naphthalimide fluorophores grafted and ionized in a 3d polymeric hydrogel network for highly fluorescent and locally tunable emission. *ACS Macro Letters*, 8(8), 937–942. <u>https://doi.org/10.1021/acsmacrolett.9b00337</u>

- Lieberzeit, P., & Dickert, F. (2009). Chemosensors in environmental monitoring: challenges in ruggedness and selectivity. *Analytical and Bioanalytical Chemistry*, 393(2), 467-472. https://doi.org/10.1007/s00216-008-2464-3
- Martínez-Quiroz, M., Ochoa-Terán, A., Pina-Luis, G., & Ortega, H. (2016). Photoinduced electron transfer in N,N-bis(pyridylmethyl) naphthalenediimides: study of their potential as pH chemosensors. *Supramolecular Chemistry*, *29*(1), 32-39. <u>https://doi.org/10.10</u> 80/10610278.2016.1162905
- Oshchepkov, A., Oshchepkov, M., Oshchepkova, M., Al-Hamry, A., Kanoun, O., & Kataev, E. (2021). Naphthalimide-based fluorescent polymers for molecular detection. *Advanced Optical Materials*, 11, 2001913-2001943. <u>https://doi.org/10.1002/adom.202001913</u>
- Ozdemir, M. (2020). Two colorimetric and fluorescent dual-channel chemosensors for the selective detection of pH in aqueous solutions. *Chemistry Select*, 5(45), 14340-14348. <u>https://</u> doi.org/10.1002/slct.202003627
- Pablos, J., Hernández, E., Catalina, F., & Corrales, T. (2022). Solid fluorescence pH sensors based on 1,8-naphthalimide copolymers synthesized by UV curing. *Chemosensors*, 10(2), 73. <u>https://</u> doi.org/10.3390/chemosensors10020073
- Panchenko, P., Fedorova, O., & Fedorov, Y. (2014). Fluorescent and colorimetric chemosensors for cations based on 1,8-naphthalimide derivatives: design principles and optical signalling mechanisms. *Russian Chemical Reviews*, 83(2), 155-182. <u>https://doi.</u> org/10.1070/RC2014v083n02ABEH004380
- Poddar, M., Sivakumar, G., & Misra, R. (2019). Donoracceptor substituted 1,8-naphthalimides: Design, synthesis, and structure-property relationship. *Journal of Materials Chemistry C*, 7(47), 14798-14815. <u>https://doi.org/10.1039/</u> C9TC02634G
- Prasanna de Silva, A., Moody, T., & Wright, G. (2009). Fluorescent PET (photoinduced electron transfer) sensors as potent analytical tools. *Analyst*, 134(12), 2385-2393. <u>https://doi.org/10.1039/B912527M</u>
- Qi, J., Liu, D., Liu, X., Guan, S., Shi, F., Chang, H., He, H., & Yang, G. (2015). Fluorescent pH sensors for broad-range pH measurement based on a single fluorophore. *Analytical Chemistry*,

87(12), 5897-5904. <u>https://doi.org/10.1021/</u> acs.analchem.5b00053

- Qian, J., Xu, Y., Qian, X., & Zhang, S. (2008). Molecular logic operations based on surfactant nanoaggregates. *ChemPhysChem*, 9(13), 1891-1898. <u>https://doi.org/10.1002/</u> cphc.200800009
- Reynolds, G., & Drexhage, K. (1975). New coumarin dyes with rigidized structure for flashlamp-pumped dye lasers. *Optics Communications*, 13(3), 222-225. <u>https://doi.org/10.1016/0030-4018(75)90085-1</u>
- Saccomano, S., Jewella, M., & Cash, K. (2021). A review of chemosensors and biosensors for monitoring biofilm dynamics. *Sensors and Actuators Reports*, *3*, 100043. <u>https://doi.org/10.1016/j.snr.2021.100043</u>
- Shaki, H., Gharanjig, K., Rouhani, S., & Khosravi, A. (2010). Synthesis and photophysical properties of some novel fluorescent dyes based on naphthalimide derivatives. Journal of Photochemistry and Photobiology A: Chemistry, 216(1), 44-50. <u>https://doi.org/10.1016/j.</u> jphotochem.2010.09.004
- Thai, D., & Lee, N. (2021). A paper-based colorimetric chemosensor for rapid and highly sensitive detection of sulfide for environmental monitoring. *Analytical Methods*, 13(11), 1332-1339. <u>https://doi.org/10.1039/D1AY00074H</u>
- Tian, Y., Su, F., Weber, W., Nandakumar, V., Shumway, B., Jin, Y., Zhou, X., Holl, M., Johnson, R., & Meldrum, D. (2010). A series of naphthalimide derivatives as intra and extracellular pH sensors. *Biomaterials*, 31(29), 7411-7422. <u>https://doi.org/10.1016/j.</u> biomaterials.2010.06.023

- Valeur, B., & Leray, I. (2000). Design principles of fluorescent molecular sensors for cation recognition. *Coordination Chemistry Reviews*, 205(1), 3-40. <u>https://doi.org/10.1016/S0010-</u> 8545(00)00246-0
- Wang, R., Yu, C., Yu, F., & Chen, L. (2010). Molecular fluorescent probes for monitoring pH changes in living cells. *Trends in Analytical Chemistry*, 29, 1004-1013. <u>https://doi.org/10.1016/J.</u> <u>TRAC.2010.05.005</u>
- Wu, D., Sedgwick, A.; Gunnlaugsson, T., Akkaya, E., Yoon, J., & James, T. (2017). Fluorescent chemosensors: The past, present and future. *Chemical Society Reviews*, 46(23), 7105-7123. <u>https://doi.org/10.1039/C7CS00240H</u>
- Wu, J., Jiang, L., Verwilst, P., An, J., Zeng, H., Zeng, L., Niu, G., & Kim, J. (2019). A colorimetric and fluorescent lighting-up sensor based on ICT coupled with PET for rapid, specific and sensitive detection of nitrite in food, *Chemical Communications*, 55(67), 9947-9950. https://doi.org/10.1039/C9CC05048E
- Ye, F., Liang, X., Wu, N., Li, P., Chai, Q., & Fu Y. (2019). A new perylene-based fluorescent pH chemosensor for strongly acidic condition. Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy, 216(5), 359-364. https://doi.org/10.1016/j.saa.2019.03.049
- Yordanova, S., Grabchev, I., Stoyanov, S., & Petkov, I. (2014). New detectors for metal cations and protons based on PAMAM dendrimers modified with 1,8-naphthalimide units. *Journal of Photochemistry and Photobiology A: Chemistry*, 283, 1-7. https://doi.org/10.1016/j. jphotochem.2014.03.002