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A fluorescent PET chemosensor for Zn^{2+} cations based on 4-methoxy-1,8-naphthalimide derivative containing salicylideneamino receptor group

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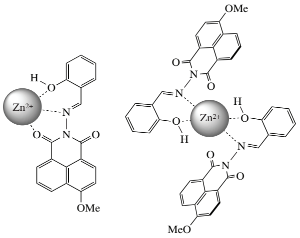
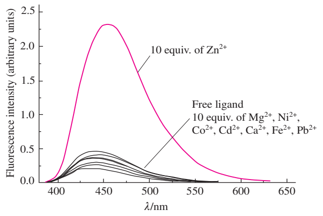
New 4-methoxy-1,8-naphthalimide derivative containing a salicylideneamino receptor group at the imide nitrogen atom demonstrated selective fluorescent response to Zn^{2+} cations due to the formation of 1 : 2 and 2 : 1 ligand–metal complexes.





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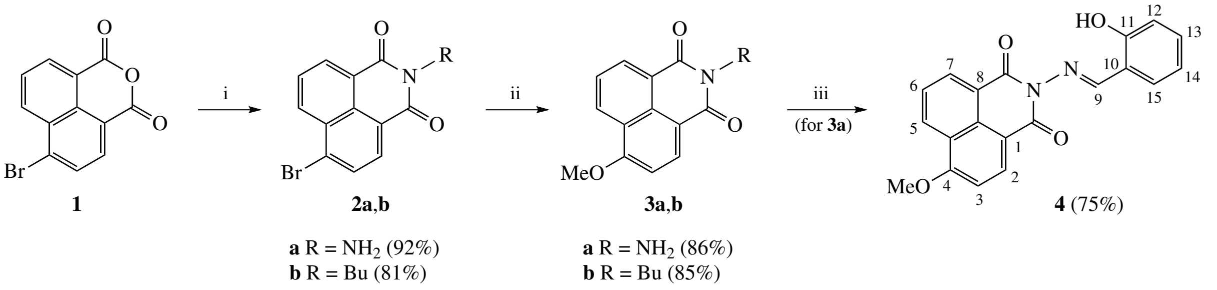
The determination of the content of metal cations in environmental objects and biological systems is an important problem for industry, ecology and medicine. Among the variety of physico-chemical methods suitable for this purpose, optical electron spectroscopy has become very popular due to the relative simplicity of the experiment and relatively high sensitivity.[1] Significant progress has been made in the field of cationic analysis in recent years due to the development of optical chemosensors whose molecules contain a receptor responsible for binding to an ion and a chromophore signal element capable of changing its spectral characteristics upon complexation.[2]

1,8-Naphthalimide derivatives belong to main types of organic luminophores and are of great practical importance. They have found application as dyes for natural and synthetic fibers,[3] optical brighteners,[4] laser dyes,[5] reagents for fluorescent crack detection,[6] fluorescent photochromes,[7] components of organic light emitting diodes[8] and as fluorescent labels in biological studies.[9] Considerable attention has been paid to the development of 1,8-naphthalimide-based fluorescent chemosensors for cations, anions and neutral molecules.[10]

In the present work, compound **4** (Scheme 1), which is a Schiff base derived from 4-methoxy-*N*-amino-1,8-naphthalimide **3a** and salicylaldehyde, was suggested as a fluorescent chemosensor for metal cations. Salicylideneamino group presenting in the structure of **4** quite often acts as a receptor in molecular fluorescent chemosensors.[11] This receptor is known to form chelate complexes with transition metal cations. The combination of a naphthalimide chromophore and a salicylideneamino group as a receptor has been described,[12] however, in most cases, the optical response involves either changes in the characteristics of absorption spectra upon binding with a cation (without the capability of fluorimetric determination)[12(*a*),(*b*)] or fluorescence quenching.[12(*c*),(*d*)] The latter is less preferable for the analysis due to poorer signal-to-noise ratio (in comparison with fluorescence enhancement).

To obtain a system demonstrating an increase in emission signal intensity upon complexation, a combination of a salicylideneamino receptor group with a 4-methoxy-1,8-naphthalimide moiety was used. The way of combining the two molecular fragments in the structure **4** is typical of PET (photoinduced electron transfer) sensors based on naphthalimide derivatives; it consists in the introduction of an ionophore unit into a substituent attached to the imide nitrogen atom.[13] The choice of the



Scheme 1 *Reagents and conditions*: i, RNH_2, EtOH, Δ; ii, MeONa, MeOH, Δ; iii, 2-HOC_6H_4CHO, MeCN, TsOH, Δ.

chromophore element was due to the relatively high electron-deficient character of 4-methoxy-1,8-naphthalimide in the excited state, which provides a higher contrast of fluorescence switching by the PET mechanism in comparison with more frequently used 4-amino derivatives.[10(*b*)] In addition, an increase in the electron-acceptor properties of the chromophore on going from 4-amino- to 4-methoxy-1,8-naphthalimide hampers the donor–acceptor d,π-interactions between the metal cation and the photoactive moiety that reduce the efficiency of radiative deactivation.[14]

Compound **4** was synthesized by the reaction of 4-methoxy-*N*-amino-1,8-naphthalimide **3a** with salicylaldehyde (see Scheme 1) by the procedure suggested for the preparation of 4-chloro-*N*-salicylideneamino-1,8-naphthalimide.[12(*a*)] Intermediate compound **3a** was readily available from 4-bromonaphthalic anhydride **1**, which was subjected to imidiation with hydrazine hydrate[15] followed by introduction of methoxy group *via* nucleophilic substitution of the 4-positioned bromine atom. 4-Methoxy-*N*-butyl-1,8-naphthalimide **3b** described previously[16] was used for a comparative analysis of spectral characteristics. Synthetic protocols for the preparation of derivatives **3a** and **4** as well as the data confirming their structure and composition are given in Online Supplementary Materials.

The long wavelength band in the absorption spectrum of compound **4** in acetonitrile at 363 nm is associated with intramolecular charge transfer (ICT) from the methoxy group at position 4 to the carbonyl groups of the dicarboximide moiety (Figure S1 in Online Supplementary Materials). The fluorescence band of **4** is observed at 437 nm. Comparison of the $\lambda_{\text{max}}^{\text{abs}}$ and $\lambda_{\text{max}}^{\text{fl}}$ values for **4** and *N*-butyl derivative **3b** ($\lambda_{\text{max}}^{\text{abs}}$ = 362 nm, $\lambda_{\text{max}}^{\text{fl}}$ = 432 nm) allows us to conclude that incorporation of a receptor moiety into a molecule does not significantly affect the charge transfer in the naphthalimide chromophore that occurs upon light absorption/emission. However, the fluorescence intensities of **4** and **3b** differ substantially: the quantum yield of **3b** (φ^{fl} = 0.41) was more than one order of magnitude higher as compared to the φ^{fl} of **4** (0.0096).

To explain the weak fluorescence of compound **4**, quantum-chemical calculations of its frontier molecular orbitals using the PM6 method were carried out. As shown in Figure 1, the HOMO of **4** is localized on the salicylidene receptor moiety, while the HOMO(–1) and the LUMO belong to the naphthalimide chromophore. Such an arrangement of the local MO energy levels indicates the possibility of non-irradiative electron transfer from the HOMO of the salicylidene amino group to the singly occupied HOMO(–1) of the naphthalimide residue in excited state that competes with the fluorescence.

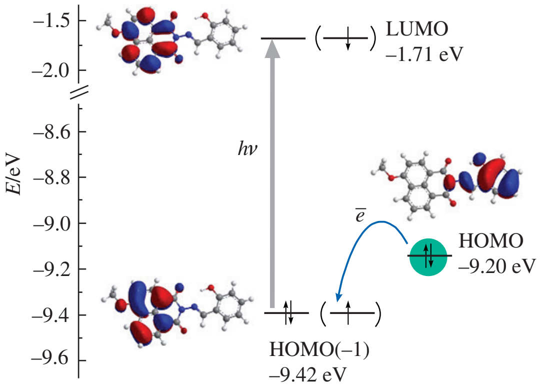


Figure 1 Energy diagram of the frontier molecular orbitals of compound **4**. The local MO of the receptor group is marked green. The vertical arrow shows the electronic transition corresponding to the long wavelength band in the absorption spectrum.

Since the fluorescence of the naphthalimide fragment in **4** is quenched to a considerable extent due to electron transfer, the binding of metal cations leading to a decrease in the electron-donating character of the receptor group should result in the fluorescence enhancement. Sensor properties of compound **4** was studied with respect to divalent heavy and transition metal cations such as Ni^{2+}, Cd^{2+}, Co^{2+}, Fe^{2+}, Zn^{2+} and Pb^{2+} as well as alkaline earth metal cations Ca^{2+} and Mg^{2+}. Within this series, only Zn^{2+} caused a significant increase in the intensity of the emission band [Figure S2(*b*) in Online Supplementary Materials]. Figure 2 shows the degree of fluorescence enhancement (FE) calculated as the ratio of fluorescence intensity at 455 nm after the addition of 10 equivalents of an ion to the intensity before the addition. It should be noted that in some cases small FE values do not imply the absence of complex formation. In fact, binding of Ni^{2+} and Co^{2+} with **4** was indirectly indicated by the changes in the absorption spectrum exhibiting the bathochromic shift of the long wavelength band maximum [see Figure S2(*a*)]. The fluorescent response to Zn^{2+} was rather selective, as follows from the weak effect of the addition of competitive ions (Mg^{2+}, Ca^{2+}, Cd^{2+}, Co^{2+}, Fe^{2+}, Pb^{2+}) to a solution containing **4** and Zn^{2+} on its fluorescence intensity (see Figure 2). At the same time, it was found that the presence of Ni^{2+} interfered with the detection of Zn^{2+} since it decreased the FE value.

The complexation of **4** with Zn^{2+} cations was studied in more detail using the spectrofluorimetric titration method. The fluorescence spectra of **4** were recorded upon gradual addition of zinc perchlorate to the acetonitrile solution [Figure 3(*b*)]. It was found that the experimental data on fluorescence intensity at 461 nm *vs*. Zn^{2+} concentration [shown as dots in the upper inset in Figure 3(*b*)] best fit the calculation results obtained using the SPECFIT/32 program [shown as a red curve in the upper inset in Figure 3(*b*)] if the formation of two types of complexes according to the equations (1) and (2) is taken into account:

$$\mathrm{L} + \mathrm{Zn}^{2+} \rightleftarrows (\mathrm{L})\cdot\mathrm{Zn}^{2+}, \qquad (1)$$

$$2\,\mathrm{L} + \mathrm{Zn}^{2+} \rightleftarrows (\mathrm{L})_2\cdot\mathrm{Zn}^{2+}, \qquad (2)$$

where L designates the ligand (compound **4**). The calculated logarithms of the stability constants of complexes with the ligand to metal ratios 1:1 and 2:1 [$\lg K_{(\mathrm{L})\cdot\mathrm{Zn}^{2+}}$ and $\lg K_{(\mathrm{L})_2\cdot\mathrm{Zn}^{2+}}$] were found to be as 2.63±0.15 and 8.20±0.29, respectively. Similar values of constants [$\lg K_{(\mathrm{L})\cdot\mathrm{Zn}^{2+}} = 2.75\pm0.15$, $\lg K_{(\mathrm{L})_2\cdot\mathrm{Zn}^{2+}} = 7.77\pm0.26$] were found from spectrophotometric titration data [see Figure 3(*a*)]. Spectrophotometric and spectrofluorimetric titration curves [see insets in Figure 3(*a*),(*b*)] were obtained at 379 and 461 nm because the most significant changes in the absorption and fluorescence spectra upon binding with Zn^{2+}

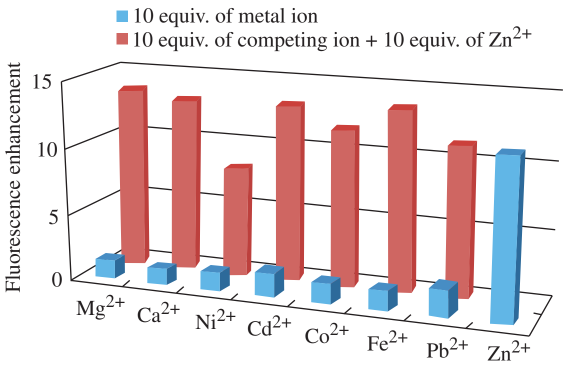


Figure 2 The degree of fluorescence enhancement (FE) of compound **4** (4×10^{-6} M in MeCN) in the presence of various metal cations. The excitation wavelength was 375 nm.

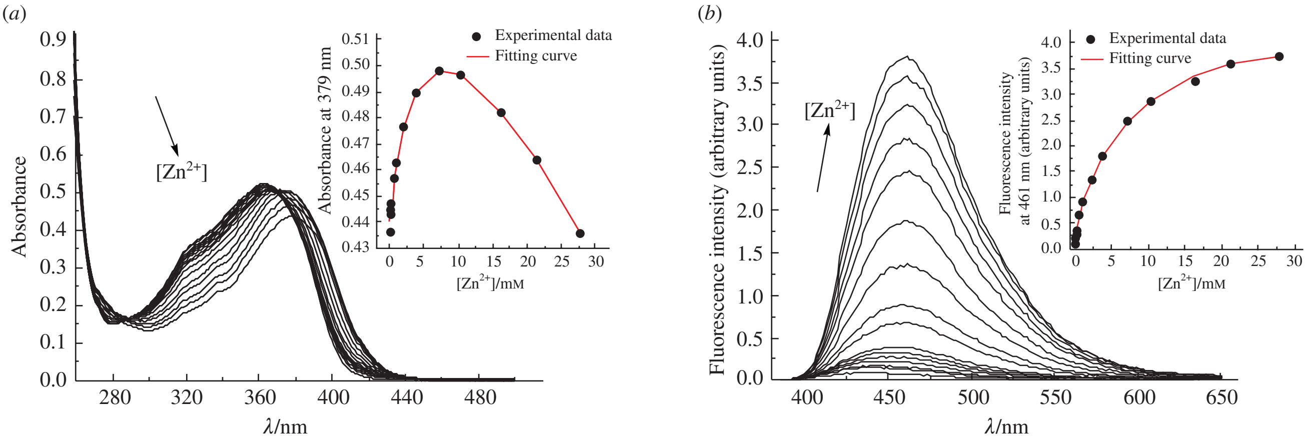


Figure 3 Changes in the (*a*) absorption spectrum and (*b*) fluorescence of a solution of compound **4** (4×10^{-5} M in MeCN) upon addition of zinc perchlorate. The excitation wavelength was 375 nm. The insets show the dependences of (*a*) optical density at 379 nm and (*b*) fluorescence intensity at 461 nm on Zn^{2+} concentration.

cation occur at these wavelengths. The complex dependence of the optical density at 379 nm [see Figure 3(*a*)] on Zn^{2+} concentration is due to the simultaneous formation of $(L)\cdot Zn^{2+}$ and $(L)_2\cdot Zn^{2+}$ complexes and the difference in their absorption spectra (Figures S4 and S5). The formation of two types of complexes was also confirmed by the data of the ESI-mass spectrum (Figure S3), which contained peaks corresponding to the $[Zn(L-H)MeCN]^+$ (*m*/*z*, found: 449.82; calculated: 450.03) and $[Zn(L-H)L]^+$ species (*m*/*z*, found: 755.03; calculated: 755.11).

The addition of 1 equiv. of zinc perchlorate caused a significant downfield shift in the signals for the protons of the naphthalimide moiety and salicylideneamino group in the ^1H NMR spectrum of ligand **4** in CD_3CN (Figure 4). It presumably can be associated with the formation of the $(L)\cdot Zn^{2+}$ complex, in which the metal cation is involved in coordination both with the receptor moiety and with the oxygen atom of one of the carbonyl groups of the chromophore. Such mode of cation coordination is consistent with the bathochromic shift of the long wavelength band maximum in the absorption spectrum upon Zn^{2+} addition [see Figure 3(*a*)]. At the same time, the second set of signals with the lower chemical shift values than in the case of $(L)\cdot Zn^{2+}$ was also found in the ^1H NMR spectrum in the presence of 1 equiv. of Zn^{2+}. The second set of signals disappeared at 11 equiv. of Zn^{2+} in the solution. Hence, it could be assigned to the resonances of protons in $(L)_2\cdot Zn^{2+}$.

To conclude, a novel derivative of 4-methoxy-1,8-naphthalimide **4** has been obtained. The observed increase in its fluorescence intensity upon Zn^{2+} binding is due to suppression of the PET process in the free ligand. Using mass spectrometry, optical and NMR spectroscopy, the possibility of formation of the two complexes with different compositions has been demonstrated. The study revealed that compound **4** exhibits the properties of a selective fluorescent PET chemosensor for the Zn^{2+} cation.

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Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.1016/j.mencom.2020.01.018.

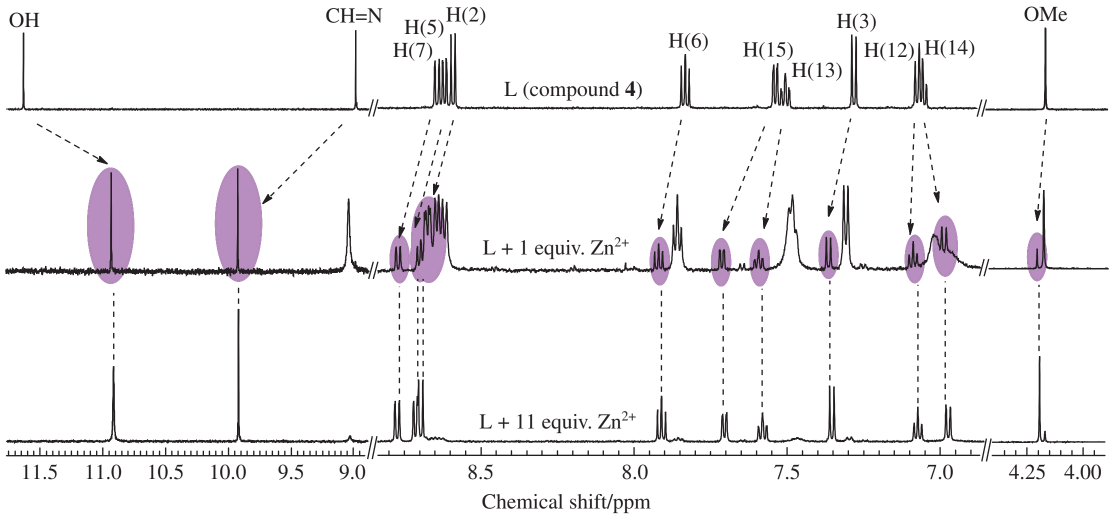

Figure 4 The ^1H NMR spectra of compound **4** in CD_3CN in the presence and in the absence of zinc perchlorate. The atom numbering in compound **4** used in the assignment of signals is shown in Scheme 1. The dashed arrows indicate proton signal shifts on going from the free ligand to the $(L)\cdot Zn^{2+}$ complex. The signals of $(L)\cdot Zn^{2+}$ are marked by pink color.

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