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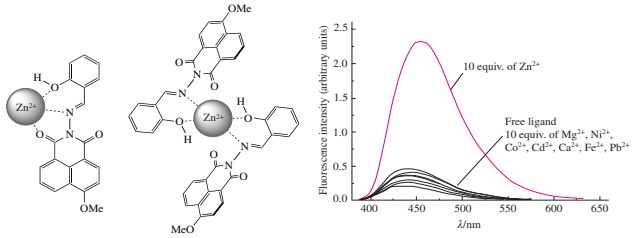
New 4-methoxy-1,8-naphthalimide derivative containing a salicylideneamino receptor group at the imide nitrogen atom demonstrated selective fluorescent response to Zn^{2+} cations due to the formation of 1 : 2 and 2 : 1 ligand–metal complexes.



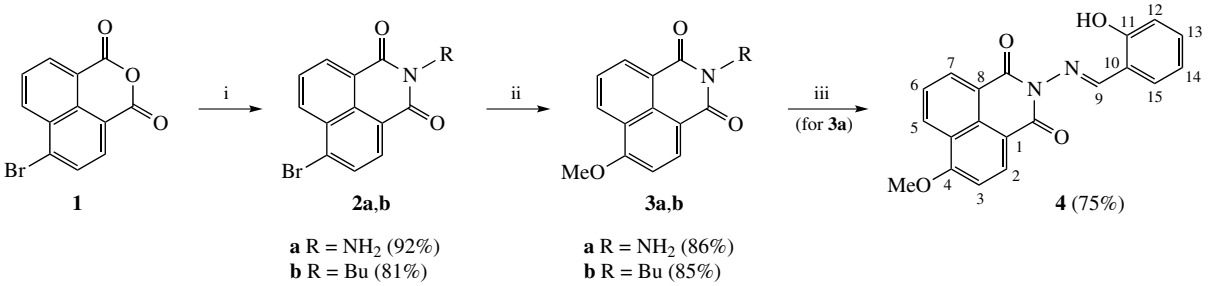
Keywords: sensor, zinc cation, fluorescence, photoinduced electron transfer (PET), 1,8-naphthalimide, Schiff base, salicylidene.

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



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