

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 $(\text{L})\cdot\text{Zn}^{2+}$ and $(\text{L})_2\cdot\text{Zn}^{2+}$ 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 $[\text{Zn}(\text{L} - \text{H})\text{MeCN}]^+$ (m/z , found: 449.82; calculated: 450.03) and $[\text{Zn}(\text{L} - \text{H})\text{L}]^+$ 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 $(\text{L})\cdot\text{Zn}^{2+}$ 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 $(\text{L})\cdot\text{Zn}^{2+}$ 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 $(\text{L})_2\cdot\text{Zn}^{2+}$.

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.____.

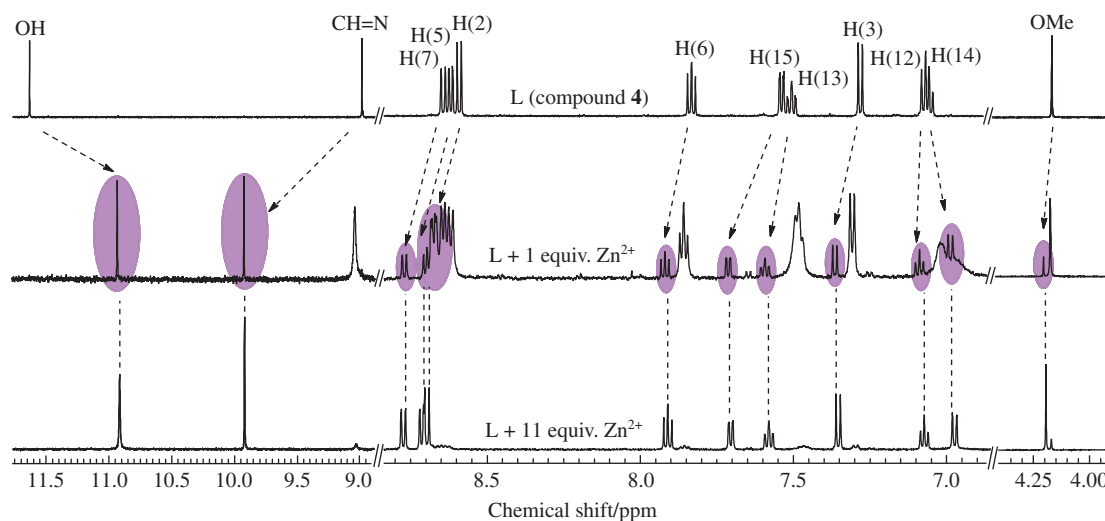


Figure 4 The ^1H NMR spectra of compound **4** in CD_3CN in the presence and in the absence of zinc perchlorate. The atom numbering in compound **4** used in the assignment of signals is shown in Scheme 1. The dashed arrows indicate proton signal shifts on going from the free ligand to the $(\text{L})\cdot\text{Zn}^{2+}$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