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A New Sensitive and Selective Off-On Fluorescent Zn^{2+} Chemosensor Based on 3,3′,5,5′-Tetraphenylsubstituted Dipyrromethene

Natalia A. Bumagina[1] · **Elena V. Antina**[1] · **Anna Yu. Nikonova**[2] · **Mikhail B. Berezin**[1] · **Alexander A. Ksenofontov**[1] · **Anatoly I. Vyugin**[1]

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Abstract 3,3′,5,5′-Tetraphenyl-2,2′-dipyrromethene was described as a highly sensitive and selective Off-on fluorescent colorimetric chemosensor for Zn^{2+} based on the chelation-enhanced fluorescence (CHEF) effect. The reaction of dipyrromethene ligand with Zn^{2+} induces the formation of the $[ZnL_2]$ complex, which exhibits the increasing fluorescence in 120 fold compared with ligand in the propanol-1/cyclohexane (1:30) binary mixture. The Zn^{2+} detection limit was 1.4×10^{-7} M. The UV-Vis and fluorescence spectroscopic studies demonstrated that the dipyrromethene sensor was highly selective toward Zn^{2+} cations over other metal ions (Na^+, Mg^{2+}, Co^{2+}, Ni^{2+}, Fe^{3+}, Cu^{2+}, Mn^{2+}, Cd^{2+} and Pb^{2+}), excluding Hg^{2+}.

Keywords Dipyrromethene · Fluorescent chemosensor · Zinc ion · Selectivity · Theoretical calculation

Introduction

Increasing sensitivity and availability of the detection methods of biologically important and toxic metal ions is one of the most important goals of research in the sensorics field. To achieve this purpose, various methods such as mass spectrometry, atomic absorption spectroscopy, high performance liquid chromatography were developed. At the same time, these methods include laborious procedures and requires of the using complex equipment. Among the numerous physical and chemical methods of analysis, the electron spectroscopy methods have a special place, of which the fluorescence method is the most sensitive. The fluorescence is a powerful tool due to its simplicity, easy implementation, high sensitivity and detection limit of the analyte. When adding fluorescent chemosensor to a solution of metal ion due to the reaction between them, a color change, which can be observed with the naked eye under visible light or under a UV lamp, and changes of the absorption and fluorescence characteristics are occurred.

Fundamental principles of chemosensorics and comprehensive understanding about fluorescent chemosensors were reflected in a series of major reviews, including [1–6]. A large number of organic compounds of different structures such as rhodamines, quinolines, pyridine derivatives, oligopyrroles, et al. were tested as fluorescent chemosensors [7–10].

Interaction of fluorescent chemosensor with detectable cation leads to the formation of the complex and is accompanied by a fluorescence buildup or quenching fluorescence. Thus, On-off and Off-on chemosensors are distinguished, respectively. Off-on chemosensors are a greatest interest.

✉ Natalia A. Bumagina
nad@isc-ras.ru

Elena V. Antina
eva@isc-ras.ru

Anna Yu. Nikonova
aynikonova@mail.ru

Mikhail B. Berezin
mbb@isc-ras.ru

Alexander A. Ksenofontov
ivalex.09@mail.ru

Anatoly I. Vyugin
aiv@isc-ras.rus

[1] G. A. Krestov Institute of Solution Chemistry of Russian academy of Sciences 1 Akademicheskaya St., Ivanovo, Russian Federation 153045

[2] Inorganic Chemistry Department, Ivanovo State University of Chemistry and Technology, 7 Sheremetevskij prosp, Ivanovo, Russian Federation 153000

Receptors in organic cation chemosensors can contain different functional groups, which are based on electron donor heteroatoms (nitrogen, oxygen, etc.).

Cation chemosensors with receptors based on the oxygen donor atoms exhibit the sensory properties predominantly towards of alkali, alkaline earth and rare earth ions. For example, fluorescence of chemosensors with crown ether substituents is effectively enhanced when coordination to potassium and magnesium cations [11–13]. Fluorescent chemosensors based on the nitrogen-containing heterocycles are widely used for the detection of the transition metal ions [7, 14, 15].

Despite the large arsenal of known chemosensors, an active search of new analytic agents with higher sensitivity, selectivity and detection limit of cation does not stop at the present time.

Over the past 10 years the acyclic oligopyrroles and their derivatives generated considerable interest. The hybrid molecules of chelating ligands, covalently bounded to BF_2-dipyrromethenes (BODIPY), have gained recognition due to the wide range of applications as fluorescent sensors of cations [16–19]. However, the synthesis of these hybrid molecules is very laborious. On the other hand, dipyrromethene ligands also possess useful properties, including strong absorption in the visible region of the spectrum and fluorescence buildup by the coordination with Zn(II), Al(III), Si(IV), Sn(IV) and some others cations [20–26].

Reaction of dipyrromethenes with zinc ions gives the largest fluorescent response compared to the other above listed cations. For example, upon detection of zinc cations using the meso-aryl dipyrromethenes, the fluorescent response reaches 72 [27]. Detection of zinc cations is particular interest because Zn^{2+} ions play an important role in many biological processes. However, studies of chemosensory activity of dipyrromethene ligands is extremely limited [27–32].

We have previously shown [33] that 3,3′,5,5′-tetraphenyl-2,2′-dipyrromethene (HL) with the Zn(II) forms homoligand complex of composition $[ZnL_2]$. Ligand HL is very weak fluorophore with fluorescence quantum yield (φ) less than $1{\cdot}10^{-3}$. The $[ZnL_2]$ complex gives intense fluorescence with a maximum in the region from 608 to 615 nm depending on the solvent properties. Moreover, the fluorescence quantum yield of $[ZnL_2]$ reaches 33 % in non-polar environments (cyclohexane, hexane, benzene, toluene) and is reduced with increasing solvent polarity (chloroform, alcohols, DMF). These presuppositions provide a basis for the study of HL as a new chemosensor for the zinc cations and selection of the medium optimal conditions for its maximum sensory activity.

In this paper the first results of a study of sensitivity and selectivity of the new fluorescent chemosensor of zinc cations on the basis of 3,3′,5,5′-tetraphenyl-2,2′-dipyrromethene HL (Fig. 1) were presented.

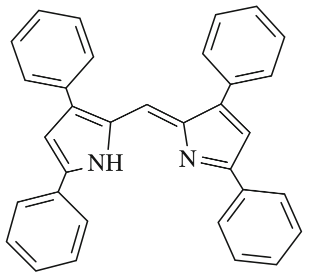

Fig. 1 Structure of 3,3′,5,5′-tetraphenyl-2,2′-dipyrromethene (HL)

Experimental

Reagents and Chemicals

The analysis of HL activity as fluorescent chemosensor towards Zn^{2+} cations and the influence of other cations (Na^{+}, Mg^{2+}, Mn^{2+}, Co^{2+}, Ni^{2+}, Fe^{3+}, Cu^{2+}, Cd^{2+}, Hg^{2+}, Pb^{2+}) was carried out in the propanol-1/cyclohexane (1:30) binary mixture.

Propanol-1 (UVIR-HPLC-HPLC preparative, PAI) and cyclohexane (Panreac, Barcelona) were used without further purification.

The 1,7-dibromine-2,6-dimethyl-3,5-diamyl-BODIPY in ethanol with fluorescence quantum yield 0.30 [34] was used as a standard for the determination of fluorescence quantum yield of HL.

Synthesis of the 3,3′,5,5′-Tetraphenyl-2,2′-Dipyrromethene

The 3,3′,5,5′-tetraphenyl-2,2′-dipyrromethene was prepared using procedure described in [35, 36].

A mixture of 0.44 g (2.02 mmol) of 3,5-diphenylpyrrole, 0.5 g (2.02 mmol) of 2-formyl-3,5-diphenylpyrrole, 10 ml of acetic acid, and 2.5 ml of acetic anhydride was heated at reflux

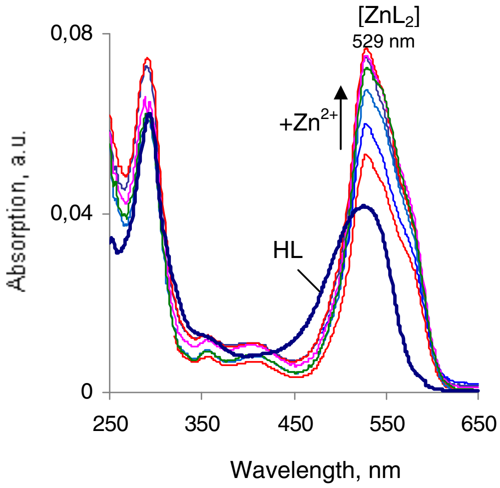

Fig. 2 UV − Vis spectral changes during a titration of HL (1.3×10^{-6} mol L^{-1}) by the 2–34-fold molar excess of $Zn(AcO)_2$ in propanol-1/cyclohexane (1:30) binary mixure

for 1 h. The solution became crimson and a precipitate formed. The resultant precipitate was separated by filtration, washed with methanol, and dried. The acetic acid solution was poured into 200 ml of water. The precipitate was separated by filtration, dried, and chromatographed on silica gel (L 100/250, chloroform as an eluent). Yield is 0.7 g (77.2 %).

Electronic Absorption Spectrum: λ_{max} at 532; 295 nm (Benzene)

^{1}H NMR (δ, ppm): 14.35 (br s, 1H, NH), 7.94–8.03 (m, 8H, *o*-H-Ph), 7.42–7.60 (m, 12H, *m,p*-H-Ph), 6.99 (s, 2H, 4,4′-H), 6.76 (s, 1H, *ms*-H).

For $C_{33}H_{24}N_2$ anal. Calcd. (%): C, 88.36; H, 5.39; N, 6.25. Found (%): C, 88.51; H, 5.18; N, 6.12.

Mass spectrum MALDI-TOF: calculated ($C_{33}H_{24}N_2$) m/z = 448.57, found m/z = 449.04.

Apparatus

UV/Vis and fluorescence (at λ_{ex} = 505 nm) spectra in the visible 250–700 and 350–750 nm range respectively were recorded on SM2203 (SOLAR) spectrofluorimeter.

^{1}H NMR (500 MHz) spectra of the dipyrromethene in $CDCl_3$, using TMS signal as an internal reference, were measured by a Avance-500 spectrometer (Bruker, Germany) in the "The upper Volga region centre of physico-chemical research" of G.A. Krestov Institute of Solution Chemistry of Russian academy of sciences.

Element analysis (C, H, N) of the dipyrromethene was performed on analyzer Flesh EA1112 (TermoQuest, Italy).

Mass spectrum (MALDI-TOF) of dipyrromethene HL was performed on AXIMA Confidence (Shimadzu) MALDI-TOF mass spectrometer.

General UV–Vis and Fluorescence Spectra Measurements

The spectrophotometric titration was performed using the method of molar ratios. The molar series of solutions with constant concentration of ligand (HL) and varying concentration of the zinc acetate $c_{Zn^{2+}}/c_{HL}$ from 0 to 34 were prepared by adding Zn(II) acetate solution to the HL solution (1.3 × 10^{-6} mol L^{-1}) in propanol-1/cyclohexane binary mixture. Registration of the absorption and fluorescence spectra before and after addition of a zinc salt or mixture of several metal salts was performed. Fluorescent response I_{609}/I^{o}_{594} was calculated as the ratio of the fluorescence intensity in the spectra after addition of the zinc acetate (I_{609}) to the fluorescence intensity in spectrum of the sensor (I^{o}_{594}).

Theoretical Calculations

All calculations were carried out using the PC GAMESS v.12 program package [37]. The geometries of all compounds were optimized by density functional calculations employing the hybrid B3LYP function and a mixed basis set, i.e., the 6-31G(d,p) basis set for non-metallic atoms and the Los Alamos effective core potential basis set (LANL2DZ) for zinc atom [38–40]. Frequency analyses were then performed to confirm that the optimized geometries are true minima on the potential energy surface. Subsequent single-point calculations were performed with the same method and basis sets but in a cyclohexane solvent environment represented by the polarizable continuum model.

Results and Discussion

Spectrophotometric Detection of Zn^{2+}

Electronic absorption spectrum (UV-Vis) of the molecular form of sensor HL in cyclohexane is characterized by band with a maximum at 526 nm (ε = 31,568 L·mol^{-1}·cm^{-1}). To investigate the binding ability of HL toward Zn^{2+}, UV/Vis spectra of HL (1.3 × 10^{-6} mol L^{-1}) in the presence of various concentrations of Zn^{2+} (0–4.4) × 10^{-5} mol L^{-1} in the 1-propanol/cyclohexane (1:30) binary mixture were recorded. This binary mixture of solvents was selected according to data on the highest fluorescent response of reaction and satisfactory solubility of reagents and the resulting helicates [41].

Observed in Fig. 2 changes in the electronic absorption spectra appear in a result of coordination of HL by the Zn^{2+} with the formation of homoligand [ZnL_2] complex (Fig. 3), the structure of which was confirmed previously [33].

As seen in Fig. 2, during the titration of ligand solution by the Zn^{2+} acetate solution in the electronic absorption spectra

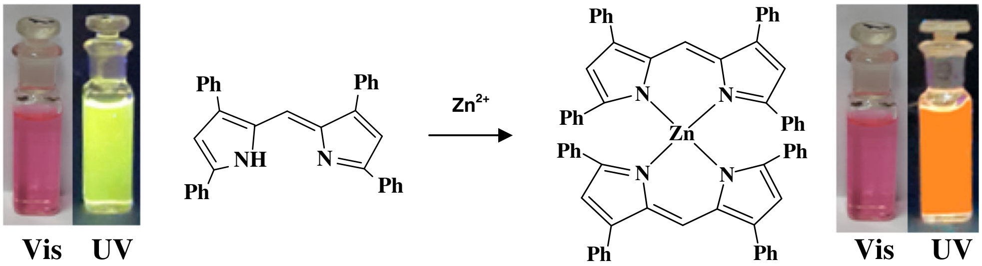

Fig. 3 Formation of the complex Zn(II) with dipyrromethene HL, and images of sensor in the absence (left) and presence (right) of 10-fold excess of Zn^{2+} under the visible and UV (λ_{ex} = 366 nm) light

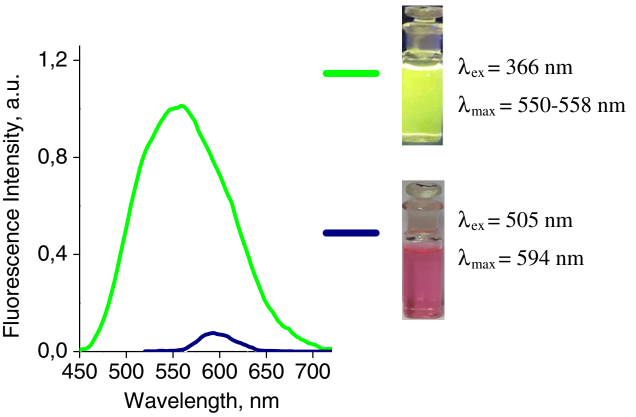

Fig. 4 Fluorescence spectra of 3,3′,5,5′-tetraphenyl-2,2′-dipyrromethene HL in the propanol-1/cyclohexane (1:30) binary mixure at excitation on 366 and 505 nm

the HL band with a maximum at 526 nm is transformed into a more intense band of complex with λ_{max} at 529 nm.

Fluorescent Detection of Zn^{2+}

The studied previously free dipyrromethenes exhibit very weak fluorescence independently of the wavelength of the exciting light, composition and properties of the medium [29]. We have found that the fluorescence of 3,3′,5,5′-tetraphenyl-2,2′-dipyrromethene depends on the wavelength of the exciting light. Thus, the HL in 1-propanol/cyclohexane (1:30) binary mixture upon excitation by visible light (λ_{ex} = 505 nm) gave a very weak fluorescence with low intense band at λ_{max} = 594 nm (Fig. 4) and quantum yield of less than 0.001. Upon excitation of HL by UV light with λ_{ex} from 300 to 400 nm in the same binary solvent, in the fluorescence spectrum more intense broadened band with λ_{max} in the range of 550–558 nm is registered, and the quantum yield is significantly increased (φ = 15 %) (Fig. 4).

Taking into account this feature, the chemosensory ability of dipyrromethene was evaluated with excitation at 505 nm, that allowed increasing dipyrromethene fluorescent response in analytical reaction with zinc ions. Titration of dipyrromethene HL solution (c_{HL}= 1.3 × 10^{-6} mol L^{-1}) by the zinc acetate solution was carried out before the molar ratio $c_{Zn^{2+}}/c_{HL}$ = 34. As shown in Fig. 5, during titration the red shift of the emission band maximum (λ_{max} from 594 to 609 nm) and the growth of fluorescence intensity were observed. In this case, the color change of the solution from yellow-green to bright orange can be seen by the naked eye.

The fluorescence intensity reaches a maximum value at a molar ratio $c_{Zn^{2+}}/c_{HL}$ = 10 (Fig. 5, insert). Further increasing zinc acetate(II) concentration ($c_{Zn^{2+}}/c_{HL}$ = 10–34) does not cause noticeable changes in fluorescence intensity (Fig. 5, insert). The maximum fluorescent response of reaction was 120. The fluorescence buildup of the dipyrromethene chromophore in the complex with Zn^{2+} can be attributed to the highly efficient chelation-enhanced fluorescence effect (CHEF-effect), associated with an increased rigidity of the sensor molecules due to chelation.

Theoretical Calculations

For theoretical justification the reasons of fluorescence enhancement of [ZnL_2] complex in comparison with HL the orbital energy analysis (E_{HOMO}, E_{LUMO}) and the width of the HOMO–LUMO energy gaps (E_g) analysis was carried out. The electron density distribution of HOMO and LUMO orbitals obtained by the PCM(cyclohexane)/B3LYP/6-

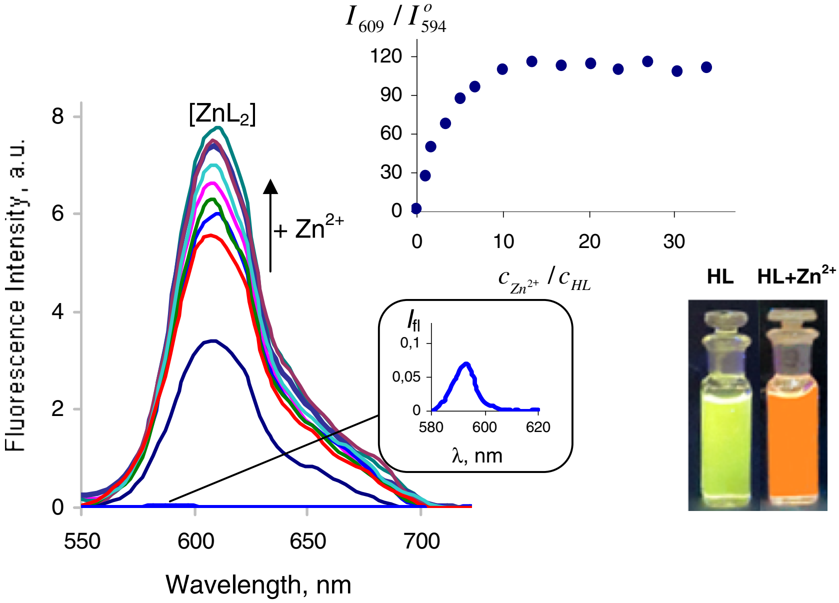

Fig. 5 Fluorescence emission spectral changes during a titration of the HL (1.3 × 10^{-6} mol L^{-1}) with $Zn(AcO)_2$ in the propanol-1/cyclohexane (1:30) at λ_{ex} fixed at 505 nm. *Insert*: Fluorescence spectrum of dipyrromethene HL, fluorescence intensity changes (at 609 nm) as a function of molar ratio$c_{Zn^{2+}}/c_{HL}$ and images of sensor in the absence and presence of 10-fold excess of Zn^{2+} under the UV light (λ_{ex} = 366 nm)

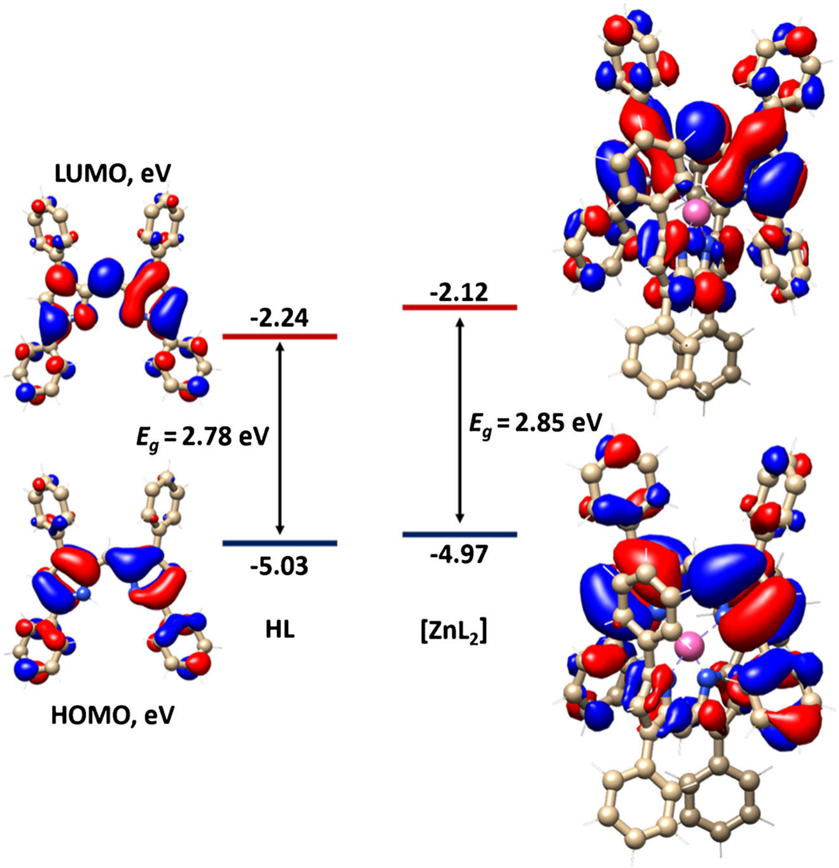

Fig. 6 The distribution of boundary molecular orbitals of HL and [ZnL_2] and the energy gap values ($E_g = E_{\mathrm{HOMO}}, E_{\mathrm{LUMO}}$), (PCM(cyclohexane)/B3LYP/6-31G(d,p) + LANL2DZ)

31G(d,p) + LANL2DZ and shown in Fig. 6. The quantum–chemical calculations showed that HOMO–LUMO transition makes major contribution to the fluorescence of the studied compounds. Figure 6 demonstrate the distribution of the electron density of molecular HOMO and LUMO orbitals in the HL and [ZnL_2] molecules.

Quantum-chemical calculations showed that complexing influences on the spectral-luminescent properties. At the transition from of the ligand HL to the corresponding Zn complex incremented the energy gap value (on 0.07 eV) (Fig. 6). The observed pattern in good agreement with experimentally observable trends of change of fluorescence of the dipyrromethene HL and the resulting Zn complex in during titration (fluorescent "off-on" response).

Detection Limit

The detection limit is one of the important indicators of analite sensitivity determination. For many practical purposes, including for biochemical studies, important to determine very low concentrations of cations. As a result of fluorescence measurements during titration of ligand solution by the zinc(II) acetate solution, the dependence of Log $[(I–I_o)/(I_{max}–I)]$ as function of Log $[Zn^{2+}]$ was obtained (Fig. 7) by analogy [42]. The detection limit of Zn^{2+} ions, using the ligand HL, was 1.4×10^{-7} mol L^{-1}, i.e. the sensor in sensitivity is not inferior by many the best analytical agents on zinc ions [43, 44].

Selectivity

Selectivity of detecting analyte is another important indicator of sensor. Figure 8 shows the differences in the color of HL solutions with 10-fold excess of different metal cations in the 1-propanol/cyclohexane (1:30) binary mixture when excited by UV light (λ_{ex} = 366 nm). Change of solution color from yellow-green to bright orange was visible to the naked eye only with addition of zinc ions. In the presence of other ions

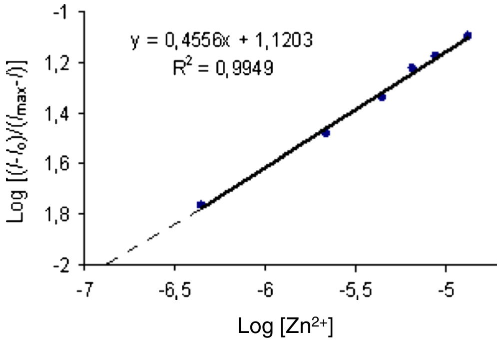

Fig. 7 Relative fluorescence intensity as a function of the logarithm of Zn^{2+} concentration

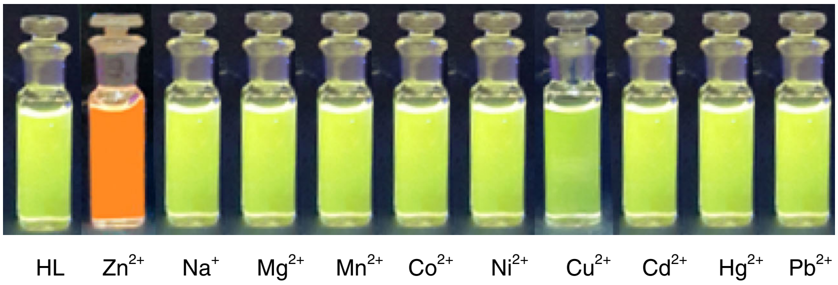

Fig. 8 The color of HL solutions with 10-fold excess of the cations of different metals in the 1-propanol/cyclohexane (1:30) binary mixture when excited by UV light (λ_{ex} = 366 nm)

the solution color practically unchanged, because the complexation with alkali (Na^{+}), alkaline earth (Mg^{2+}) and some d-metals (Mn^{2+}, Co^{2+}, Ni^{2+} and Cd^{2+}) does not occured, or non-fluorescent complexes with Cu^{2+}, Pb^{2+} are formed.

As can be seen from Fig. 9a, the dipyrromethene sensor HL gives maximum fluorescent response (I_{609}/I^{o}_{594} = 120) in the presence of Zn^{2+} cations. Also, Hg^{2+} ion enhances the fluorescence intensity of HL, but the effect was weaker compared with that of Zn^{2+} ion under similar concentration (Fig. 9a). Addition of 10-fold excess of individual Mn^{2+}, Co^{2+}, Ni^{2+}, Fe^{3+}, Cd^{2+}, Pb^{2+} ions or 10 and 100-fold excess of Na^{+} and Mg^{2+} to the sensor solution does not practically effect on the sensor fluorescence (Figs. 8 and 9a). The sensor fluorescence is completely quenched in the presence of Cu^{2+} cations, due to their paramagnetic nature and electron or energy transfer between the metal cations and the ligand [17, 45–47].

It is known that the presence of other metal cations, particularly Cu^{2+} [17, 46, 47], can negatively affect the Zn^{2+} ions determination. Therefore, to further evaluate the HL selectivity for Zn^{2+}, the dipyrromethene fluorescence spectra in the presence of Zn^{2+} mixed with various metal ions (Na^{+}, Mg^{2+}, Mn^{2+}, Co^{2+}, Ni^{2+}, Fe^{3+}, Cu^{2+}, Cd^{2+}, Hg^{2+} or Pb^{2+}) in the propanol-1/cyclohexane (1:30) binary mixure were recorded. Each of the cations was taken in a tenfold molar excess, or in 10 or 100-fold molar excess in the case of Na^{+} and Mg^{2+} ions relative to HL content. The Na^{+}, Mg^{2+}, Mn^{2+}, Ni^{2+}, Fe^{3+}, Cd^{2+} or Pb^{2+} ions did't interfere fluorescent detection of Zn^{2+} cations (Fig. 9b). If in the solution the Zn^{2+}/Co^{2+} or Zn^{2+}/Cu^{2+} cation mixtures are presented, the fluorescence intensity of sensor is significantly (3 and 4 times, respectively) decreased (Fig. 9b) compared with the sensor solution containing only Zn^{2+} ions. At the same time, the maximum position of the fluorescence band of formed $[ZnL_2]$ complex remains unchanged. Nevertheless, 3,3′,5,5′-tetraphenyl-2,2′-dipyrromethene sensor can also be successfully used for the Zn^{2+} detection in the presence of Co^{2+} and Cu^{2+} ions. The fluorescence of HL/Zn^{2+} system was significantly quenched (approximately 7 times) by Hg^{2+} that may be due transmetallation to form a more stable and weakly fluorescing complex of mercury with a fluorescence band maximum at 573 nm (Fig. 9a, b).

Conclusions

In summary, we developed fluorescent colorimetric chemosensor based on the 3,3′,5,5′-tetraphenyl-2,2′-

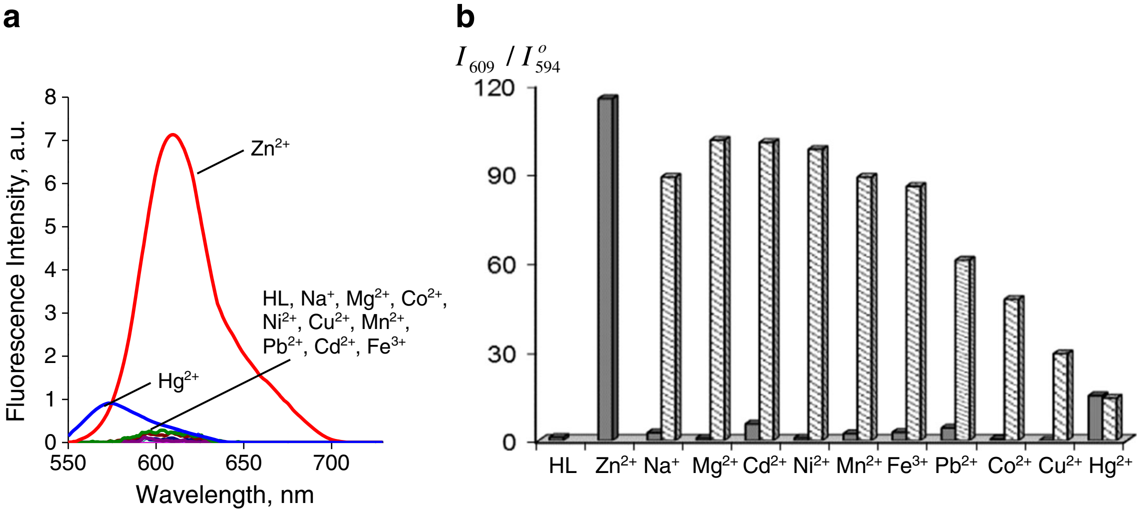

Fig. 9 Selectivity of HL (1.3×10^{-6} mol L^{-1}) towards Zn^{2+} ions in propanol-1/cyclohexane (1:30) upon excitation at 505 nm: (**a**) emission spectra of HL in the presence of 10-fold excess of various metal ions (Na^{+}, Mg^{2+}, Mn^{2+}, Co^{2+}, Ni^{2+}, Fe^{3+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, Hg^{2+} and Pb^{2+}); (**b**) graph with gray bars representing the addition to sensor solution of 10-fold excess of various metal ions and striped bars representing the addition to sensor solution of 10-fold excess of Zn^{2+} mixed with 10-fold excess of the indicated metal ions

dipyrromethene that exhibited high selectivity and sensitivity towards Zn^{2+} ions in organic media, imitating the lipid layers of biological membranes. This sensor exhibited significant Off-on fluorescence (at λ_{max} = 609 nm) upon binding to Zn^{2+}. Fluorescent response I_{609}/I^{o}_{594} of dipyrromethene reaction with $Zn(AcO)_2$ is 120 at a molar ratio $c_{Zn^{2+}}/c_{HL} \geq 10$. Under a UV lamp, the detection process leads to a color change from yellow-green to bright orange, which could easily be detected by the naked eye. The detection limit of the chemosensor for Zn^{2+} cations reached 1.4×10^{-7} mol L^{-1}. Dipyrromethene exhibited high selectivity toward Zn^{2+} over other alkali, alkaline-earth and transition-metal ions (Na^{+}, Mg^{2+}, Mn^{2+}, Co^{2+}, Ni^{2+}, Fe^{3+}, Cu^{2+}, Cd^{2+} and Pb^{2+}), excepting Hg^{2+}.

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