Applications of Fluorescent Sensor Based on 1H-pyrazolo[3,4-b]quinoline in Analytical Chemistry

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Abstract Fluorescent dye 2-[(2-Hydroxyethyl)-(1,3-diphenyl-1H-pyrazolo[3,4-b]quinolin-6-ylmethyl)-amino]ethanol (LL1) was examined for its efficiency in the detection of small inorganic cations (lithium, sodium, barium, calcium, magnesium, cadmium, lead and zinc). The dye was synthesized in the laboratory and investigated by means of both, steady-state and time-resolved fluorescence techniques. This compound acts as a fluorescent sensor suitable for detection of small inorganic cations (lithium, sodium, barium, calcium, magnesium, cadmium, lead and zinc) in strongly polar solvent (acetonitrile). An electron transfer from the electro-donative part (receptor) of the molecule to the acceptor part (fluorophore) is thought to be the main mechanism that underlies functionality of the compound as a sensor. This process can be retarded upon complexation of the receptor moiety by inorganic cations. Relatively high sensitivity but poor selectivity of the aminoalcohol that contains indicator towards the two-valued cations was observed. However, upon addition of some amounts of water the selectivity of this sensor has been enhanced (especially towards lead cation). The preliminary results in analytical application of the sensor are discussed.

Keywords Fluorescent molecular probes · Photoinduced electron transfer · Time resolved fluorescence · Pyrazolo[3,4-b]quinoline

Introduction

Measurements of the cation concentration are of considerable interest and the subject of various investigations conducted by chemists, biologists, clinical biochemists and environmentalists. Some of the cations play a crucial role in biological processes (Na⁺, K⁺, Ca²⁺, Mg²⁺, Zn²⁺). In medicine some diagnostics are based on the detection of certain cations and monitoring their concentration in blood and urine. In psychiatry the control of the lithium concentration is important for patients who are under the treatment for manic depression. Some cations are toxic (Pb²⁺, Cd²⁺, Hg²⁺) and early detection of their presence in organism is of uttermost importance.

Among other sensors the fluorescent molecular sensors (known also as indicators) are of considerable interest for the detection of small amounts of cations such as H⁺, Li⁺, Na⁺, K⁺, Ca²⁺, Mg²⁺, Zn²⁺, Pb²⁺, Al³⁺, Cd²⁺, etc. These are the molecular compounds that fluorescence emission can be strongly affected by the presence of inorganic cations. Their high detection sensitivity permits the investigation of non-fluorescent cations with the concentrations down to 10⁻⁶ M [1, 2]. Nevertheless, searches for new fluorescence materials capable of extended sensitivity are still underway.

The principles underlying functionality of fluorescence sensors are presented in several publications including monographs and original papers [3, 4]. Beneath, only the basic information necessary to understand the performance of the sensors is briefly reviewed.

A general principle of operation of many PET fluorescent indicators is based on significant enhancement of fluorescence emission upon addition of cations into fluorescing medium. Molecule-cation complexes of various stoichiometry
can be formed in this process. Their high stability in both, the
ground and excited states is desired to permit fluorescence
emission followed the electronic excitation of the complex
(see Scheme 1). To understand fluorescence emission en-
hancement a detailed mechanism of the process has to be
understood. For the purpose of current investigation we recall
the mechanism determined for the molecular sensors based on
pyrazoloquinoline skeleton. The mechanism underlying func-
tionality of molecular sensors that are constructed on the basis
of pyrazoloquinoline skeleton was discussed in the previous
papers [5, 6]. It involves an electron transfer process, i.e. after
excitation, the pyrazoloquinoline derivative accepts one elec-
tron from the lone pair located at the nitrogen atom of the
donor receptor moiety, being simultaneously a cation receptor
subunit. It was found that previously constructed fluorescent
cation indicators are more sensitive to the presence of bivalent
cations such as Mg$^{2+}$, Ca$^{2+}$, Zn$^{2+}$ than to monovalent cations
such as Li$^+$ and Na$^+$. Additionally, the binding constants
estimated from the concentration profiles of the fluorescence
changes are related to the charge density of the cations, so that
larger was the cation charge density, greater was the complex-
formation equilibrium constant.

We chose 1,3-diphenyl-1H-pyrazolo[3,4-b]quinoline as a
fluorophore because of its good emissive properties. The fluo-
rescence quantum yields and lifetimes are relatively independent
on solvent polarity and reach values up to 88 % and 25 ns,
respectively [7]. This fact results in effective photoinduced
electron transfer quenching in pyrazoloquinoline compounds
with electronically decoupled amino-recognition group and in
consequence easily detectable ON-OFF green fluorescence.
Another reason for selecting the pyrazoloquinoline is a relatively
simple synthesis. 1,3-diphenyl-1H-pyrazolo[3,4-b]quinoline is
received from the respective pyrazole and aniline precursors
[11]. The resulting compound 2 was brominated with NBS
(N-bromosuccinimide) in the presence of catalytic amount of
AIBN (2,2′-azoisobutyronitrile). The nucleophilic substitu-
tion of the bromomethyl group with diethanolamine in ace-
tonitrile gave the compound LL1. A more detailed descrip-
tion of the synthesis of this sensor was given in previous
publication [12].

Experimental

Synthesis of 2-[(2-Hydroxyethyl)-(1,3-Diphenyl-1H-Pyrazolo
[3,4-b]Quinolin-6-ylmethyl)-Amino]Ethanol (LL1)

The synthesis reaction steps of LL1 are depicted in Scheme 2.
6-methyl-1,3-diphenyl-1H-pyrazolo[3,4-b]quinoline 1 was
obtained from the respective pyrazole and aniline precursors
[11]. The resulting compound 2 was brominated with NBS
(N-bromosuccinimide) in the presence of catalytic amount of
AIBN (2,2′-azoisobutyronitrile). The nucleophilic substitu-
tion of the bromomethyl group with diethanolamine in ace-
tonitrile gave the compound LL1. A more detailed descrip-
tion of the synthesis of this sensor was given in previous
publication [12].

Apparatus and Measuring Procedures

The solvents: dibutyl ether (DBE), butyl chloride (BuCl),
tetrahydrofuran (THF), acetone (ACE), acetonitrile (ACN),
and dimethylformamide (DMF) were of spectroscopic grade
and were used as received (all from Aldrich). All the solvents
used in this study did not show any traces of fluorescence.
For fluorescence quantum yield and fluorescence lifetime
measurements the solutions of the dye were degassed using
multiple freeze-pump-thaw cycles. The sample concentra-
tion of the dyes (LL1 and fluorophore) for spectroscopic

Scheme 1 Principle underlying metal ion sensing by fluorescent
PET (photoinduced electron transfer) indicators
measurements was ca. $4 \times 10^{-5}$ M (this corresponds to absorbance of ca. 0.2 at the excitation wavelength used for the fluorescence investigations). Lithium, sodium, barium, magnesium, calcium (tetrahydrate) lead (x-hydrate), cadmium, zinc (hexahydrate) perchlorate, and zinc chloride, tetrabutylammonium chloride (TBACl) (Aldrich) were used as received. In an independent measurement it was found that a small addition of deionised water could not influence significantly the fluorescence of the dye alone in acetonitrile solution. The fluorescence titration experiments were not proceeded by the degassing procedure.

The fluorescence measurements of the titration between LL1-Pb$^{2+}$ complex and tetrabutylammonium chloride (TBACl) were carried out on ultracentrifuged samples. The others fluorimetric titrations were performed in situ.

The absorption spectra were recorded using a Shimadzu UV-2101 PC spectrometer and the emission spectra (with the correction for spectral sensitivity) were measured by means of Hitachi F7000 fluorometer. For time-resolved fluorescence measurements (time-correlated single photon counting technique) a picosecond diode laser ($\lambda$=400 nm, 70 ps pulse duration) (IBH-UK) was used as the excitation source. For steady-state fluorescence measurements a 365 or 380 nm line was used. The fluorescence quantum yield measurements were carried out with quinine sulphate in water ($\Phi_{\text{H}}=0.51$) [13] as an actinometer.

**Joe-Jones Method**

The equilibrium constants ($K_1$) for complexation of the ligand by alkali cations are calculated by fitting Eq. 1 to the relative fluorescence intensities in the presence of different concentration ($c_M$) of the employed alkaline metal perchlorates [14],

\[
\Phi(c_M) = \Phi(0) + \frac{\Phi(\infty) - \Phi(0)}{2c_L} \left[ c_L + c_M + 1/K_1 - \sqrt{(c_L + c_M + 1/K_1)^2 - 4c_Lc_M} \right]
\]  
(1)

where $\Phi(0)$, $\Phi(\infty)$ and $\Phi(c_M)$ is the fluorescence intensity of the dye alone, with a large concentration of the salt and with the $c_M$ concentration of the salt, respectively, $c_L$ indicates the analytical concentration of the ligand.
For 2:1 complexation the binding constant $K_2$ is defined by Eq. 2 [1]:

$$K_2 = \frac{[ML^+_2]}{[L]^2[M^+]} \tag{2}$$

The Eq. 1 converts into more complex one for 2:1 complexation scheme [3, 4]:

$$\Phi_c(c_M) = \Phi_0 + \frac{2x}{c_L} (\Phi_\infty - \Phi_0) \tag{3}$$

where $x$ denotes the concentration of the complex $ML^+_2$. This quantity can be obtained numerically by solving the third degree polynomial:

$$ax^3 + bx^2 + cx + d = 0$$

with the following parameters:

$$a = -4K_2$$
$$b = 4K_2(c_L + c_M)$$
$$c = -(K_2c_L^2 + 4K_2c_Lc_M + 1)$$
$$d = K_2c_L^2c_M \tag{3b}$$

The meaning of the parameters which appeared in Eq. 4a has been explained in the previous section, except of $\Phi_0(1-x)$ defined as the fluorescence intensity measured in the absence of cation at every concentration of the sensor.

The values of the binding constants $K_1$ and $K_2$ were obtained from the fluorescence intensities using a nonlinear least-square fitting routine coded in FORTRAN.

**Results and Discussion**

UV–vis Absorption and Fluorescence Emission Spectroscopy Studies

The absorption spectrum of LL1 in acetonitrile consists of two separate bands located between 250 and 325 nm and above 350 nm, respectively (Fig. 1). The first one is a structured band with a maximum at 260 nm ($\epsilon=57400$ dm$^3$mol$^{-1}$cm$^{-1}$) while the second one is a Gaussian-like band having maximum at 397 nm (molar absorption coefficient $\epsilon=7400$ dm$^3$mol$^{-1}$cm$^{-1}$). A simple comparison of the absorption spectra of LL1 and the parent molecule 1,3-diphenyl-1H-pyrazolo[3,4-b]quinoline (fluorophore of LL1) reveals a negligible effect of the electron-donating macrocyclic recognition unit on the energetics of the optical transitions within the fluorophore. For instance, the maxima of the absorption and fluorescence bands of LL1 in acetonitrile were found at 397 nm and 481 nm, whilst those of the fluorophore are centred at 395 nm and 476 nm (see Fig. 1). It can

![Fig. 1 Room absorption and fluorescence (inset) spectra of 1,3-diphenyl-1H-pyrazolo[3,4-b]quinoline (solid), LL1 (dash), LL1+Mg(ClO$_4$)$_2$ (dash dot dot) in acetonitrile. The concentration of Mg(ClO$_4$)$_2$ is equal to 4.10$^4$ M](image-url)
also be inferred that the absorption spectra of LL1 are rather insensitive to the solvent polarity.

Polarity of the solvents strongly influences the fluorescence lifetimes and quantum yields of LL1, likewise the previously investigated other dyes containing pyrazoloquinoline skeleton [3, 4]. Such dependences of the above mentioned fluorescence quantities on the dielectric permittivity parameter (\(\varepsilon_s\)) are tabulated in Table 1.

The reduced quantum yield of LL1 in acetonitrile (\(\Phi_{\text{fl}}=0.04\)) as compared to the fluorophore part (\(\Phi_{\text{fl}}=0.75\) determined experimentally) and simultaneous decrease of \(\Phi_{\text{fl}}\) and \(\tau_{\text{fl}}\) with increasing solvent polarity suggest the existence of quenching via an electron-transfer process from the electron-ically decoupled nitrogen atom, located at diethanolamine, to the fluorophore.

The fluorescence decays are monoexponential in nonpolar and medium polar solvents. However, in highly polar solvents the decays are clearly biexponential which may indicate the existence of two different ground-state conformers, related to the endo/exo isomerism [15]. The differences in position and direction of the lone pair at the nitrogen atom and its degree of pyramidalization can be responsible for various electron transfer quenching activities.

A small bathochromic shift of the fluorescence maximum of LL1, observed during the solvatochromic studies, points to a partial charge-transfer character of the transition within the pyrazoloquinoline fragment.

### Table 1

| Solvent | \(\lambda_{\text{abs}}\) [nm] | \(\lambda_{\text{fl}}\) [nm] | \(\Phi_{\text{fl}}\) | \(\tau_{\text{fl}}\) [ns] | \(\varepsilon_s\) |
|---------|------------------|------------------|----------------|-----------------|----------------|
| DBE     | 403              | 456              | 0.61           | 19.09           | 3.08           |
| BuCl    | 402              | 464              | 0.59           | 17.96           | 7.37           |
| THF     | 401              | 472              | 0.34           | 19.89           | 7.52           |
| ACE     | 398              | 478              | 0.051          | 0.63            | 21.01          |
| ACN     | 397              | 481              | 0.040          | 0.76            | 36.63          |
| DMF     | 400              | 482              | 0.049          | 0.52            | 38.25          |

Stability of the Fluorescent Complex (LL1\(\text{Men}^+\)) in Acetonitrile

Because of the large reduction of the fluorescence lifetime and quantum yields reduction, there is an opportunity to apply the molecule LL1 as a PET fluorescent probe in highly polar solvents (dielectric permittivity larger than 7). Acetonitrile was chosen as a solvent for all measurements conducted in this investigation owing to its high dielectric constant, lack of hydrogen bond formation and good solubility of the inorganic salts used in the experiments. Thus, all the results described in this paper are related to the acetonitrile solutions.

Upon addition of cations to the acetonitrile solution of LL1, the absorption spectrum does not change significantly (Fig. 1). The structured band in the UV region (250–325 nm) turns now into a relatively broad band.

However, the addition of cations changes the fluorescence properties considerably (Fig. 2). The locations of the band maximum in the fluorescence spectra of solutions containing and not containing inorganic cations are only slightly different (shifted bathochromically in the presence of the cations by ca. 10 nm, see inset in Fig. 1) but upon addition of the cations the intensity of the fluorescence rises dramatically (Fig. 2). For example, in the presence of 10 equivalent of \(\text{Mg}^{2+}\), the mixture shows an intense green fluorescence and a 10-fold enhancement in the fluorescence intensity at 490 nm.

Similar behaviour has been observed in the experiments when other cations were added. The examples of the titration curves are presented in Fig. 3.

It can be noticed that the bivalent cations have stronger influence on the fluorescence than the monovalent ones. The values of the binding constants that were calculated from the salt concentration dependencies of the integrated fluorescence

![Fig. 2](image-url)
intensities, are collected in Table 2. The stoichiometry of the complexes have been established by the analysis of the Job’s plots obtained from the fluorimetric titration of the mixtures of the acetonitrile solutions of the dye (LL1) and that of perchlorates (Fig.3b). It has been found that in the case of Mg or Zn cation the 2:1 complexes are formed in the ground state. For the other cations the LL1 forms complexes with 1:1 stoichiometry. One important conclusion emerges from the data collected in Table 2: the compound LL1 in acetonitrile exhibits a great sensitivity but poor selectivity to the presence of bivalent cations such as Mg$^{2+}$, Zn$^{2+}$, Cd$^{2+}$ and Pb$^{2+}$. Moreover, the equilibrium constants is found in good agreement with charge density of the cation by taking into account the complexes with alkaline and transition metals separately. For practical applications, the detection limit for this sensor evaluated by fluorescence titration was estimated at $4 \times 10^{-7}$ M, and is 100 times lower than that of the ligand concentration.

Stability of the Fluorescent Complex (LL1Me$^{n+}$) in Acetonitrile-Water Mixtures

The selectivity of the LL1 can be improved by performing fluorimetric measurements in acetonitrile-water mixtures. By adding small amounts of water to the acetonitrile solution of the complex LL1 with magnesium cation can quench fluorescence of the complex almost completely (Fig.4). The fluorescence of the magnesium complex was immediately quenched in the mixture containing 0.1 molar fraction of water (B), while the complexes with other bivalent cations are almost unaffected and the fluorescence intensity stays the same as in pure acetonitrile (A). However, a systematic increase of water concentration quenches fluorescence of other complexes except of the Pb$^{2+}$-LL1 complex (C). This is probably the result of different ability of the cations to hydrate. Hence, a simple addition of water to the mixture of the cations can change the selectivity of the dye making it more prone to form complex only with Pb$^{2+}$ cation.

Application of LL1 to the Fluorimetric Titration of Cations

The fluorimetric titration of LL1-Pb$^{2+}$ complex by tetrabutylammonium chloride (TBACl) was performed in acetonitrile. Addition of TBACl to the solution of Pb(ClO$_4$)$_2$ causes a precipitation of PbCl$_2$ with a residue that is hardly soluble in

\[
\text{Table 2} \quad \text{Binding constants i.e. equilibrium constants for the reaction between different inorganic cations and the compound LL1 in ACN determined from fluorimetric titrations.}(a) \quad \text{Obtained from the Job’s method.}
\]

| Cation(X) | Radius (Å) [16] | Charge density of cation [17] | $K_l$(LL1M$^{n+}$)/M$^{-1}$ or $K_l$(LL12M$^{n+}$)/M$^{-2}$ |
|-----------|-----------------|-----------------------------|--------------------------------------------------|
| Li$^+$    | 0.59            | 1.47                        | $K_l=12.7$                                      |
| Na$^+$    | 1.02            | 1.03                        | $K_l=2.8$                                      |
| Ca$^{2+}$ | 1.0             | 2.02                        | $K_l=1.2 \times 10^4$ (a) $K_l=1.6 \times 10^3$ (a) |
| Ba$^{2+}$ | 1.33            | 1.49                        | $K_l=1.7 \times 10^3$ (a) $K_l=1.6 \times 10^3$ (a) |
| Mg$^{2+}$ | 0.66            | 3.03                        | $K_l=2.7 \times 10^9$ (a) $K_l=1.4 \times 10^{10}$ (a) |
| Zn$^{2+}$ | 0.74            | 2.7                         | $K_l=3.3 \times 10^5$ (a) $K_l=4.2 \times 10^3$ (a) |
| Cd$^{2+}$ | 0.97            | 2.06                        | $K_l=1.0 \times 10^5$ (a) $K_l=2.1 \times 10^3$ (a) |
| Pb$^{2+}$ | 1.2             | 1.67                        | $K_l=84.1$                                      |
| Ag$^{+}$  | 1.29            | 0.78                        |                                                  |
acetonitrile. Further addition of Cl\(^{-}\) anions dissolves the precipitate due to formation of the anion complex Pb(Cl\(_4\))\(^{2-}\) [18]. The titration process can be monitored by fluorescence techniques in the presence of nonfluorescent LL1 dye (Fig. 5). Both PbCl\(_2\) and Pb(Cl\(_4\))\(^{2-}\) cannot form a fluorescent complex with LL1.

As shown in Fig. 5, up to the equivalence point the chloride anions consume mostly the lead cations that are non-bonded to the sensor (being in an excess), thus the fluorescence intensity remains nearly constant. In the vicinity of the equivalence point, the fluorescent complex reacts with the excess of chloride anions as follows:

\[
PbLL^2+ + 2Cl^- \rightleftharpoons PbCl_2 + 2LL
\]

Due to the progressive reaction, the concentration of the fluorescent complex LL1-Pb\(^{2+}\) decreases which results in the reduction of fluorescence intensity. Hence, the concentration of the lead cations may be calculated from the equivalence point, that can be determined by analysis of the first derivative of titration curve (Fig. 5 - inset).

Another example of the fluorimetric titration is the reaction of zinc perchlorate (Zn(ClO\(_4\))\(_2\)) with TBACl in acetonitrile. In this system a precipitation of the zinc chloride, that is soluble in acetonitrile, is not observed but the product reacts with an excess of chloride anions to form an anion complex (ZnCl\(_4\))\(^{2-}\) [19]. Again, this anion does not form a fluorescent complex with the LL1 dye. The fluorimetric titration profile is displayed in Fig. 6.

In this case, the titration curve illustrating the reaction between Zn(LL1)\(_2\)\(^{2+}\) and chlorides is more complex. Up to the equivalence point chloride anions reacts only with free zinc cations non-bonded to the LL1 dye (being in excess). Thus the fluorescence intensity remains nearly constant. At the equivalence point it is very likely that the following reaction occurs:

\[
Zn(LL1)_2^{2+} + 2Cl^- \rightleftharpoons ZnLL1Cl_2 + LL
\]

and the fluorescence intensity is reduced up to c.a. 50% of the initial level. This assumption was proven in the independent titration of LL1 by ZnCl\(_2\). It was found out that ZnCl\(_2\) can be effectively bound to a chelate (\(K_1\) is equal 2.28 x 10\(^4\))
M$^{-1}$) and likewise in the first equivalence point (Fig. 6), the intensity of the fluorescence (at the high ZnCl$_2$ concentration) is almost twice lower than the maximal intensity of the Zn(LL1)$_2^{2+}$ complex (both experiments were performed at the same concentration of the dye).

Further addition of chloride anions leads to the formation of an anion complex (ZnCl$_4$)$_2^{-}$ and weakly fluorescent LL1 dye. The process has been depicted in scheme 3.

Again, this hypothesis was confirmed by the reaction of ZnCl$_2$ with TBACl in the presence of LL1 dye (Fig. 7). The present investigation show analytical capabilities of applied fluorescence technique. It can be used for instance for monitoring of a simple exchange reaction where product could be traced by the fluorimetric method. Moreover, the fluorimetric titration experiment shows also that the binding of Zn$^{2+}$ or Pb$^{2+}$ to the investigated sensor is reversible in the presence of Cl$^{-}$ anions, which is of particular importance if the sensor will be widely employed in the detection of specific analysis.
Conclusions

The photophysical properties of 2-[(2-Hydroxyethyl)-(1,3-diphenyl-1H-pyrazolo[3,4-b]quinolin-6-ylmethyl)-amino]ethanol (LL1) relevant to that of fluorescent indicator of inorganic cations were investigated. It was found that this dye exhibits a large sensitivity with respect to bivalent cations such as Mg$^{2+}$, Zn$^{2+}$, Cd$^{2+}$ and Pb$^{2+}$ and its selectivity to detection of bivalent cations can be easily improved by addition of a small amount of water.

The fluorimetric titration (precipitation of hardly soluble lead chloride) using the LL1 dye was performed. The results of the investigation show that this fluorimetric method can be promising for sensitive and selective analysis of cationic species. Its potential importance for application in analytical chemistry and in a range of environmental analyses shall be stressed as well.

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