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Fluorimetric detection of Ag^+ cations in aqueous solutions using a polyvinyl chloride sensor film doped with crown-containing 1,8-naphthalimide

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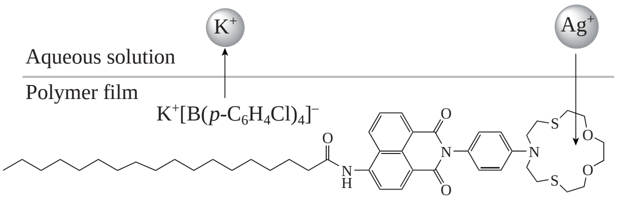
A composite material based on polyvinyl chloride and a 1,8-naphthalimide derivative containing an azadithia-15-crown-5 ether receptor showed a fluorescent response to silver cations in an aqueous solution at low concentrations.



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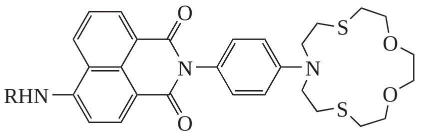
The development of sensor systems capable of changing their spectral characteristics upon binding metal ions is of current interest in supramolecular chemistry.[1] The variety of optical chemosensors can be tentatively divided into two types: one of them includes molecular optical sensors[2] and the other includes heterogeneous sensor materials in which a fluoroionophore component is either incorporated into a polymer matrix[3] or immobilized on the surface of an organic or inorganic substrate by covalent binding, adsorption, or formation of Langmuir–Blodgett films.[4] The incorporation of fluoroionophoric groups into a polymer matrix is promising since it allows one to avoid the contamination of a test solution with toxic reagents[5] and a decrease in fluorescence intensity characteristic of many organic luminophores in water and aqueous-organic media,[6] to analyze aqueous solutions without chemical modifications of the ion-active compound required to make it soluble, and to miniaturize and automate analytical methods.[7] Heterogeneous fluorescent sensors can be used in the development of sensor arrays based on the electronic nose and electronic tongue principles.[8]

The derivatives of naphthalic acid imide (1,8-naphthalimide) are organic luminophores widely used as laser dyes,[9] optical brighteners,[10] imaging agents for biology and medicine,[11] antitumor drugs,[12] photoactive components of electroluminescent devices,[13] and photochromic materials with switchable fluorescent characteristics.[14] The optical platform of 1,8-naphthalimide is very popular in the creation of fluorescent chemosensors for metal cations.[15]

In this work, we used 4-(acyl)amino-1,8-naphthalimide derivative **1** to obtain a polymer sensor based on plasticized polyvinyl chloride (PVC). As shown previously for a structurally similar compound containing a methoxy group rather than an (acyl)amino group at position 4 of the naphthalene ring, the presence of an azadithia-15-crown-5-ether receptor in the *N*-aryl moiety at the imide nitrogen atom provides the properties of a fluorescent sensor demonstrating a selective optical response (fluorescence enhancement) upon formation of a complex with a silver cation with 1 : 1 metal to ligand ratio in an aqueous solution.[16(*a*)] On the other hand, fluoroionophore **1** contains a lipophilic moiety, a stearic acid residue, which increases the solubility in the polymer matrix and prevents the sensor from passing to an aqueous solution.

Compound **1** was obtained as described previously.[17] We also used derivative **2** without lipophilic groups (see Online Supplementary Materials) for a comparative analysis of spectral characteristics.



1 R = *n*-$C_{17}H_{35}CO$
2 R = Ac

The absorption band of compound **2** [Figure 1(*a*)] in acetonitrile at 365 nm is due to intramolecular charge transfer from an electron-donating (acetyl)amino group to the carbonyl groups of the dicarboxyimide residue. The fluorescence of **2** is characterized by a low-intensity band (quantum yield, 0.0007) at 455 nm [Figure 1(*b*)]. The weak fluorescence of **2** can be due to photoinduced electron transfer (PET) from the *N*-aryl group bearing a macrocyclic receptor to the photoexcited naphthalimide chromophore, as confirmed by quantum chemical calculations (Figure S3, see Online Supplementary Materials).

The addition of Ag^+, Cu^{2+}, Ca^{2+}, Pb^{2+}, Cd^{2+}, Ni^{2+}, Zn^{2+} or Mg^{2+} cations to a solution of **2** in acetonitrile had almost no effect on the position and intensity of a long-wavelength absorption band. However, in the case of Ag^+ and Cu^{2+}, it was accompanied by a considerable fluorescence enhancement associated with the suppression of PET upon the coordination of a cation with the crown ether moiety. A similar cation-dependent spectral behaviour was observed in naphthalimide derivatives containing a *N*-phenylazadithia-15-crown-5 ether receptor in the *N*-aryl substituent.[16] Taking into account similar structure and mutual

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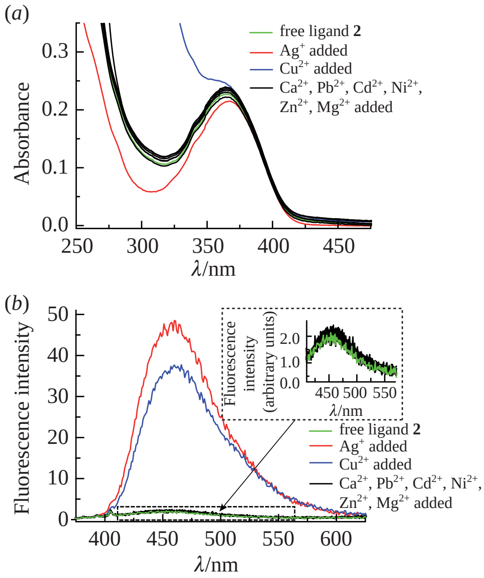

Figure 1 (*a*) Absorption and (*b*) fluorescence spectra of compound **2** (2×10^{-5} mol dm^{-3}) in the absence and in the presence of 10 equiv. of metal (Ag^+, Cu^{2+}, Ca^{2+}, Pb^{2+}, Ni^{2+}, Zn^{2+}, Mg^{2+}) perchlorates in acetonitrile. The excitation wavelength is 360 nm.

arrangement of the chromophore and receptor moieties in derivatives **1** and **2** and, hence, their close sensor properties toward Cu^{2+} and Ag^+, we made a polymer composite based on fluoroionophore **1** and tested its sensor properties.

In addition to fluoroionophore **1**, the polymer composite contained PVC, a dioctyl sebacate plasticizer, and potassium *tetra*(*p*-chlorophenyl)borate ($K[B(p\text{-}C_6H_4Cl)_4]$) – an additive for the ion-exchange extraction of cations from a solution into the film. On binding a cation, the polymeric material acquires a positive charge, which inhibits the further extraction. The resulting positive charge decreases due to the passage of potassium ions from the film to the solution, while the hydrophobic tetra(para-chlorophenyl)borate anion is strongly retained in the organic phase. Note that only compound **1** was suitable for the preparation of polymeric sensor membranes because it is soluble in the polymer and, unlike naphthalimide **2**, is not washed out from the film into an aqueous solution.

The plasticized PVC sensor membranes with dimensions of $35 \times 11 \times 0.1$ mm were prepared by applying a solution of the components in tetrahydrofuran onto the surface of an inert substrate followed by solvent evaporating (see Online Supplementary Materials). The resulting composite was a polymer network of PVC molecules containing a ~10^{-3} mol dm^{-3} solution of fluoroionophore **1** in the plasticizer.

Keeping the sensor based on derivative **1** in an aqueous solution of $AgClO_4$ for 30 min resulted in an enhancement of fluorescence (Figure 2). Visible changes were observed up to 10^{-5} mol dm^{-3} of cations in the solution. However, similar treatment in a solution of Cu^{2+} did not cause fluorescence, probably, due to the fact that a relatively high concentration of Cu^{2+} cations (~10^{-3} mol dm^{-3})† was created in the composite, and fluorescence was quenched upon contact with the paramagnetic ion. A decrease in the fluorescence intensity of the naphthalimide chromophore in a fluorescent PET sensor in the presence of excess of Cu^{2+} in a solution is well known.[18]

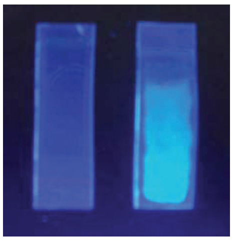

Figure 2 Sensor films doped with compound **1** and treated for 30 min (left) with water and (right) with an aqueous solution of $AgClO_4$ (10^{-2} mol dm^{-3}). The picture was taken under UV light.

We used a slightly acidic aqueous buffer solution for studying the optical response of the sensor membrane since it excludes an increase in the sensor fluorescence due to the protonation of aza nitrogen in the crown ether moiety upon the acid hydrolysis of metal perchlorate. A plot of the fluorescence intensity of compound **2** *versus* the pH of solution is shown in Figure S4. As one can see from Figure S4, the protonation of ligand **2** resulting in the enhancement of fluorescence intensity begins at pH 4.5. Since the hydrolysis of silver salts is efficiently suppressed in weakly acidic solutions, an acetate buffer with pH 6.0 (1 mM, prepared by mixing AcOH and AcONa solutions) was chosen for further experiments. The fluorescence spectrum remained unchanged

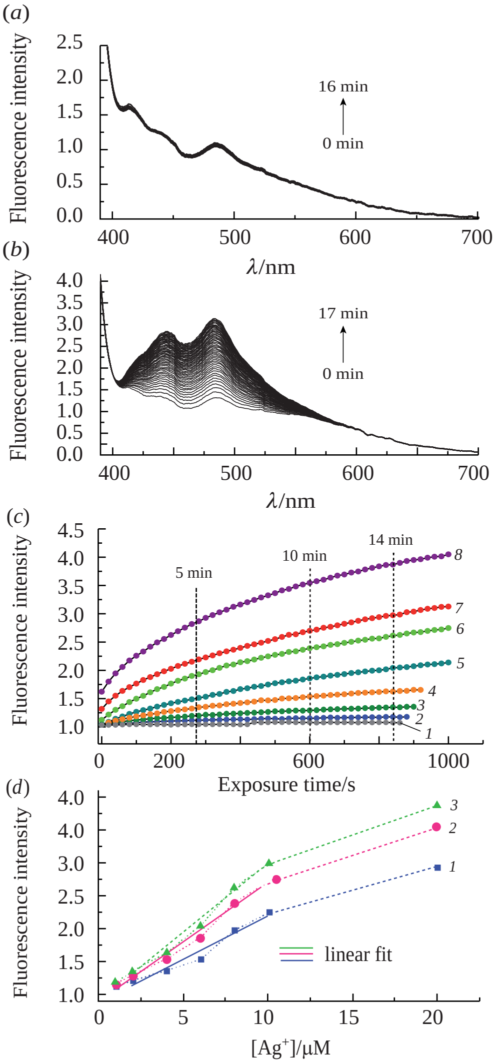

Figure 3 Sensor properties of a polymer film based on compound **1**. Changes in the fluorescence spectrum upon exposure to an acetate buffer solution (1 mM, pH 6.0) (*a*) in the absence and (*b*) in the presence of $AgClO_4$ (1×10^{-5} μM). Plots of the membrane fluorescence intensity at 485 nm (*c*) *versus* time at various concentrations (μM) of $AgClO_4$: (*1*) 0, (*2*) 1, (*3*) 2, (*4*) 4, (*5*) 6, (*6*) 8, (*7*) 10 and (*8*) 20 and (*d*) *versus* concentration of $AgClO_4$ at various exposure times (min): (*1*) 5, (*2*) 10, (*3*) 14. Solid lines correspond to the linear least squares fit. The correlation coefficients are 0.949, 0.980 and 0.983 for times of 5, 10 and 14 min, respectively. The excitation wavelength is 365 nm.

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† Provided that the film is completely saturated with Cu^{2+} ions and a 1 : 1 ligand–metal complex is formed.

after keeping a film in this buffer solution [Figure 3(*a*)]. It should be noted that in a more acidic medium at pH 4.8 (acetate buffer, 1 mM), a pronounced enhancement of the film fluorescence due to the protonation of ligand **1** was observed (Figure S5). The complex shape of the emission spectrum was due to the fluorescence of the substrate underlying the polymer membrane (Figure S6).

Figure 3(*b*) shows changes in the fluorescence spectrum of the film upon exposure to a 10 μM aqueous solution of silver perchlorate at pH 6.0 for 17 min. At 485 nm, the emission signal intensity in the spectrum increased by a factor of 2.4. To determine an optimum exposure time, we measured the kinetics of fluorescence intensity at various silver concentrations [Figure 3(*c*)]. As expected, more contrast changes (especially at the initial time instants) were observed at higher Ag^+ concentrations. Nevertheless, the extraction of Ag^+ into the film was incomplete even after 14–17 min, as follows from the absence of a plateau in the kinetic curves. At exposure times of 5, 10 and 14 min, a good linear correlation between the signal intensity and the analyte concentration in a range of 2.0–10.0 μM was observed [Figure 3(*d*)]. Based on the slopes (r) of the straight lines in Figure 3(*d*) and the standard deviation of the analytical signal (s), the detection limits of silver cations ($[Ag^+]_{DL}$) were calculated using equation (1).[19] The obtained values of $[Ag^+]_{DL}$ were 3.4, 2.5 and 2.1 μM for exposure times of 5, 10 and 14 min, respectively. Thus, an optimal exposure time for the detection of Ag^+ ions was 14 min. The detection limit found under these conditions is close to the secondary maximum contaminant level of silver(I) in drinking water (0.1 mg dm^{-3} or 0.93 μM) established by the US Environmental Protection Agency.[20]

$$[\mathrm{Ag}^+]_{\mathrm{DL}} = 3s/r \qquad (1)$$

As a result of this work, we suggested an original sensor material based on an azacrown-containing derivative of naphthalimide **1** and optimized its production method. A study on the cation-dependent fluorescent properties of the material showed that it can detect silver ions in aqueous solutions at low concentrations. The optimal conditions for practical use include a 14-min exposure of the membrane in a solution with pH 6.0 followed by recording a spectrum.

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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.2021.07.027.

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