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Highly Selective and Sensitive Phosphane Sulfide Derivative for the Detection of Hg^{2+} in an Organoaqueous Medium

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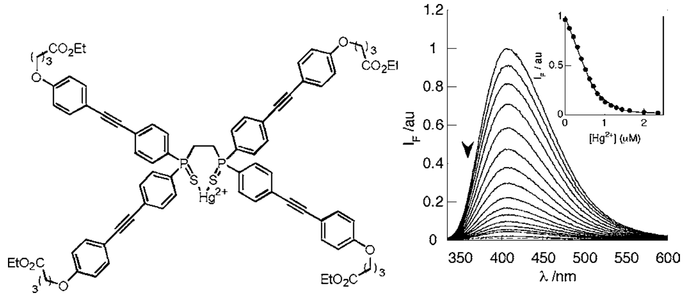
ABSTRACT



A new fluorescent molecular sensor for Hg^{2+} based on the phosphane sulfide derivative exhibits a very low detection limit in an aqueous medium (3.8 nM) with a very high selectivity over other interfering cations. The reversibility of the complexation process was also examined and was found to be successful.

Hg^{2+} is considered a highly toxic heavy metal ion causing environmental and health problems.[1] A wide variety of symptoms are observed upon exposure including digestive, kidney, and especially neurological diseases.[1] The level of this ion was therefore the object of strict regulation and should not exceed 1 μg L^{-1}.[2] Although sophisticated analytical techniques (atomic absorption, atomic emission, and inductively coupled plasma spectroscopy) are currently used in the environment, there is a strong demand to develop inexpensive and real-time monitoring methods for the detection of Hg^{2+} and other heavy metals. In this context, the methodology based on fluorescent molecular sensors has attracted considerable interest because of their intrinsic sensitivity and selectivity.[3] Considerable efforts have been devoted to the design of fluorescent molecular sensors for mercury;[4] however, only a few of them are very competitive[5] in terms of sensitivity, selectivity, and measurements in

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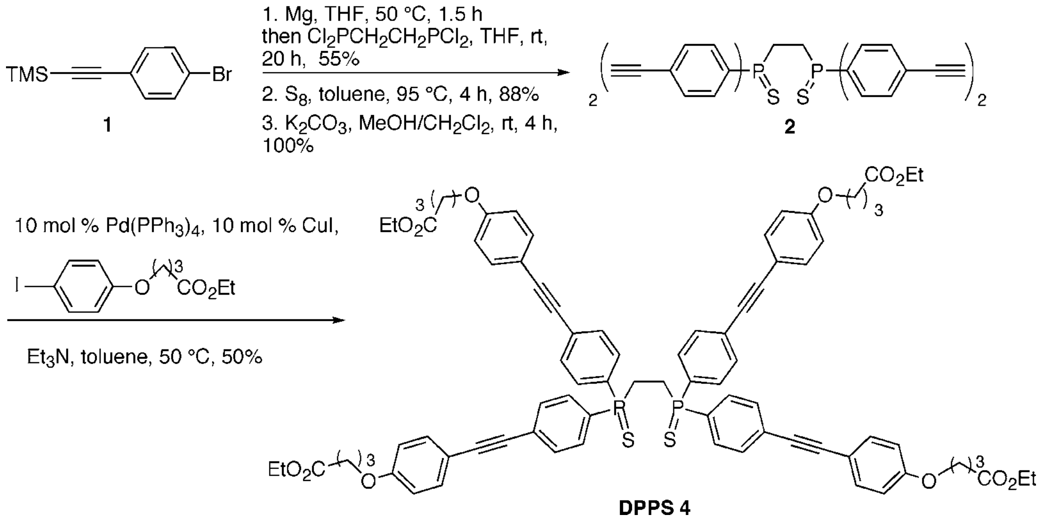
Scheme 1



aqueous media, and there still is a need for alternative systems. In the course of our recent ongoing program directed toward the production of novel fluorophores[6] and on the basis of recent work from Lobana et al.,[7] we envisaged that phosphane sulfide derivatives might be excellent candidates for complexation and detection of Hg^{2+}. Because there is no precedent on such a fluorescent family, we therefore wish to describe our preliminary results on the synthesis and applications of a novel sensor.

An issue for the success was the design and the easy preparation of the fluorescent molecule. Anticipating that 1,2-bis(diphenyl thiophosphinophenyl)ethane could form a strong complex with mercury, we decided to prepare diphosphane-bearing polyphenylethynyl fluorophores substituted by an ether group and to study their complexing and photophysical properties.[8] Scheme 1 outlines the synthesis of the DPPS ligand **4**. The reaction between the 1,2-bis(dichlorophosphano)ethane and the Grignard derivative of the commercially available 4-bromotrimethylsilylphenyl acetylene led to the diphenylphosphanoethane (dppe) derivative in 55% yield. Treatment with elemental sulfur (1:2 mole ratio) in toluene gave the thiophosphano product in 88% yield, which was then engaged in the desilylation step using K_2CO_3 in a mixture of CH_2Cl_2/MeOH. The corresponding phosphane sulfide **2** was obtained in 100% yield. The Sonogashira coupling between the thiophosphano product **2** and the iodide **3**[9] was then performed and afforded the corresponding DPPS **4** in 50% yield. This methodology is particularly interesting, as it would allow the synthesis of analogues.

The DPPS derivative **4** shows an intense absorption band in the UV region ($\epsilon = 1.5 \times 10^5$ L mol^{-1} cm^{-1}) and a fluorescence quantum yield (Φ_F) of 0.1 in acetonitrile. The emission maxima are indeed strongly dependent on the

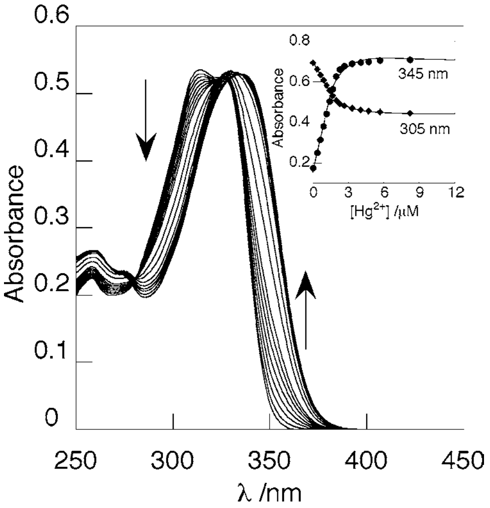


Figure 1. Absorption of DPPS **4** (3.3 μM) in the presence of an increasing concentration of Hg^{2+} in CH_3CN-H_2O (80:20 v/v) at pH = 4. Inset: titration curves at 305 and 345 nm.

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solvent polarity. The unresolved vibronic structure and the large Stokes shift observed in the polar solvent suggest the formation of an intramolecular charge transition (see Supporting Information).[10] In view of practical applications, the effect of cation complexation was then studied in CH_3CN/H_2O (80:20 v/v) at pH 4, and the DPPS **4** exhibits still the same fluorescence quantum yield ($\Phi_F = 0.1$). Figure 1 and Figure 2 display the evolution of the absorption and emission spectra of DPPS **4** upon complexation with Hg^{2+}, respectively.

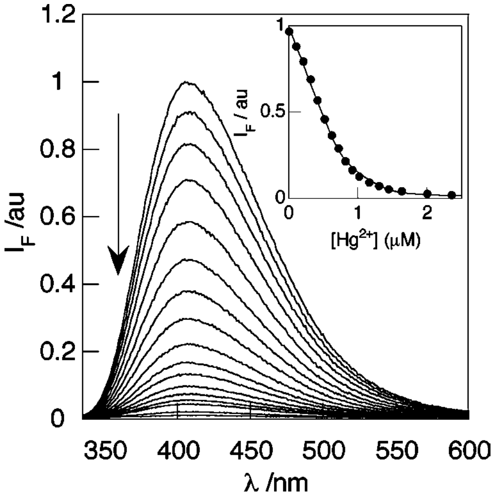

Figure 2. Corrected emission spectra of DPPS **4** (1.1 μM) in the presence of an increasing concentration of Hg^{2+} in CH_3CN-H_2O (80:20 v/v) at pH = 4. λ_{exc} = 350 nm. Inset: titration curve at 410 nm.

Addition of mercury induces a 15 nm bathochromic shift of the absorption spectra, which may be rationalized by an enhancement of the electron-withdrawing character of the thiophosphano group due to the interaction of the sulfur atom with the Hg^{2+}.

A strong decrease of the fluorescence is observed upon mercury complexation, which can be explained in terms of electron transfer between the excited fluorophore to the complexed mercury cation. The electrochemistry of the excited state of DPPS ($E(\text{DPPS}^{\bullet+}/\text{DPPS}^*) = -3$ V/SCE)[11] clearly shows that the excited state of DPPS is able to reduce Hg^{2+} ($E = 0.68$ V/SCE). A linear response of the fluorescence intensity as a function of the mercury complexation was observed from 0 to 140 μg L^{-1}.

The detection limit calculated as three times the standard deviation of the background noise was found to be 0.75 μg L^{-1} (3.8 nM) which is lower than the level defined by the World Health Organization.[2]

Careful analysis of the absorption spectra and the emission spectra upon mercury addition by means of the SPECFIT program reveals that a 1:2 complex, a 1:1 complex, and a 2:1 complex (metal−ligand) are successively formed with very high stability constants, which is in complete agreement with the work from Lobana's group.[7a]

The titration curves by considering the following complexes are shown in the insets of Figure 1 and Figure 2, respectively. The stability constants were found to be log $K_{12} = 15.4 \pm 0.5$, log $K_{11} = 8.4 \pm 0.3$, and log $K_{21} = 13.8 \pm 0.4$, respectively.

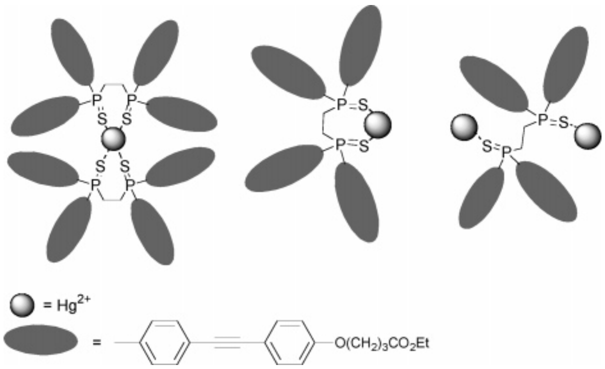

Figure 3. Binding model of DPPS **4** with Hg^{2+} leading to the formation of the complex ML_2, ML, and M_2L.

Figure 3 shows the possible structures of the formed complexes. The formation of these different complexes is in good agreement with the different possible coordination numbers in the case of the mercury complexation.[12] Considering the value of the stability constants, the linear coordination with the two sulfur atoms is clearly favored in the case of the mercury complex.

The selectivity of DPPS **4** over other cations such as Ca^{2+}, Na^+, K^+, Mg^{2+}, Pb^{2+}, Cd^{2+}, Cu^{2+}, Ag^+, and Zn^{2+} was evaluated. No significant change of the fluorescence was observed upon addition of a large excess of these interfering cations. Except for Ag^+, the stability constants of the complexes of these ions are too low to be determined. The stability constants obtained in the case of the Ag^+ complexes were log $K_{11} = 4.6 \pm 0.5$ and log $K_{21} = 8.6 \pm 0.5$. The selectivity toward Hg^{2+}, expressed as the ratio of the stability constants, was found to be higher than 6800.

Moreover, the competition-based fluorescence effect profiles for these cations are shown in Figure 4. No significant change of the response of the sensor is observed upon addition of a large excess of interfering cations at concentrations compatible with that obtained in the real medium. The

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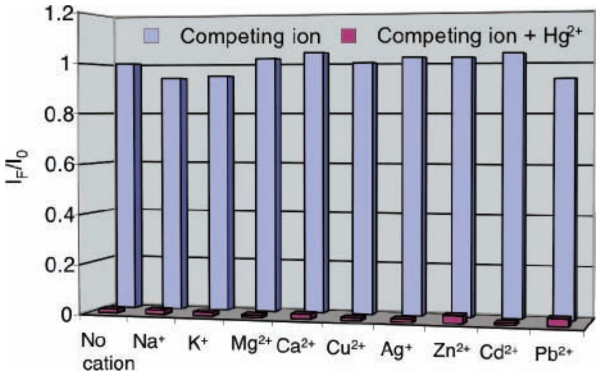

Figure 4. Response I_F/I_0 of DPPS **4** (0.88 μM) in CH_3CN-H_2O (80:20 v/v) at pH = 4 in the presence of Hg^{2+} (1.4 μM) and interfering ions K^+, Na^+, Mg^{2+}, Zn^{2+}, Cu^{2+}, and Cd^{2+} at 1 mM, Pb^{2+} at 0.1 mM, and Ag^+ at 1.5 μM (λ_{exc}= 324 nm, λ_{em} = 408 nm).

reversibility of the complexation process was also examined. After addition of 1 equiv of Hg^{2+}, the fluorescence was quenched immediately, and a switch on of the fluorescence was observed after addition of 50 equiv of a heavy metal ion chelator (2,3-dimercapto-1-propanol) (see Supporting Information).

In conclusion, we have described the synthesis and the photophysical and complexing properties of a new fluorescent molecular sensor DPPS for Hg^{2+} in an aqueous medium. The obtained detection limit (3.8 nM) is compatible with the level defined by the World Health Organization. This fluorescent molecular sensor displays reversible response upon mercury complexation and exhibits a very high selectivity for the mercury ion over other interfering cations. In view of practical application, this new fluorescent molecular sensor can be incorporated into a microfluidic flow-injection analysis device with fluorometric detection. A device that works in the case of potassium detection has been already developed in our group,[13] and work is in progress to apply it in the case of the DPPS **4** to detect Hg^{2+} directly in water.

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Supporting Information Available: Experimental procedures for the synthesis, full analyses of the synthesized products, and the photophysical measurements are described. This material is available free of charge via the Internet at http://pubs.acs.org.

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