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Optical detection of pentachlorophenol in water using thin films of octa-tosylamido substituted zinc phthalocyanine

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ABSTRACT

In this work, thin films of eight octasubstituted zinc(II) phthalocyanine derivative ($ZnPcR_8$) with tosylamido substituents $R = -NHSO_2(C_6H_4)CH_3$ were investigated as active layer of optical sensors for the detection of pentachlorophenol. Using total internal reflection ellipsometry (TIRE) technique response characteristics of $ZnPcR_8$ films to pentachlorophenol were studied in the concentration range from 0.1 to 20 μg/l. This was also validated for natural river and wastewater samples. It was demonstrated that the specific binding of pentachlorophenol molecules causes substantial shift of $\Delta(\lambda)$ spectrum. The minimum registered concentration of pentachlorophenol was 0.7 μg/l. For the river water and wastewater samples the detection limits as well as a working concentration ranges showed no significant difference with respect to those found in distilled water.

1. Introduction

The worldwide use of pesticides and herbicides for agricultural practices is considered a global environmental pollution problem. Herbicides used in agriculture can be transported to surface or ground waters, possibly causing adverse ecotoxicological effects on aquatic life and affecting drinking water quality [1].

These compounds and their residues may produce severe negative effects in natural flora and fauna, biodiversity, water resources, ecosystem functioning, and can disturb the equilibrium of agricultural systems. The most hazardous herbicides for living organisms which are in daily use are chlorinated derivatives, such as organochlorine pesticides, polychlorinated biphenyls, chlorotriazines (atrazine, simazine), and chlorinated phenylureas (diuron) because of their very strong resistance to microbial, photochemical, chemical, and thermal degradation [2].

Pentachlorophenol (PCP) is a xenobiotic causing great environmental concern. It has been commonly applied for many years as bactericide, fungicide, defoliant, herbicide and preservative [3,4]. This biocide is slightly soluble in water, up to 12–14 mg/l, and very resistant to biotic and abiotic attack, which leads to a constant increase in its concentration in soil, water sediments and living organisms. PCP has relatively low absorption in soil and would migrate along the food chains. Pentachlorophenol is considered to have carcinogenic activity in mammals [5,6]. In addition to having immunosuppressive effects (similar to atrazine-like herbicides) highly chlorinated phenols are nephrotoxic and interfere with blood formation [7,8].

Monitoring of pesticides and herbicides in comparatively low concentrations, especially in drinking and natural waters is a complicated and expensive task. The European Union has limited the maximum allowable concentration for a single pesticide to 0.1 μg/l [9], and their presence in different foods and drinks is limited by legislation.

Different analytical procedures based on liquid chromatography–mass spectrometry (LC–MS) [10–12], LC–tandem mass spectrometry (LC–MS/MS) [13], high performance liquid chromatography (HPLC) [14], and gas chromatography–mass spectrometry (GC–MS) [15] have been reported to provide efficient determination of these pesticides, according to the present legislation. However these methods, although highly sensitive and specific, are quite laborious, time-consuming, and expensive. In this context, the need for cost-effective and rapid methods of screening is evident.

Surface plasmon resonance (SPR)-based detection techniques have also been used for the determination of individual organophosphorus and carbamate insecticides in water samples [16,17]. Identification of some phenols by SPR technique with the use of polyviologen and other sensoring compounds was described in the literature [18]. The possibility of using SPR-based

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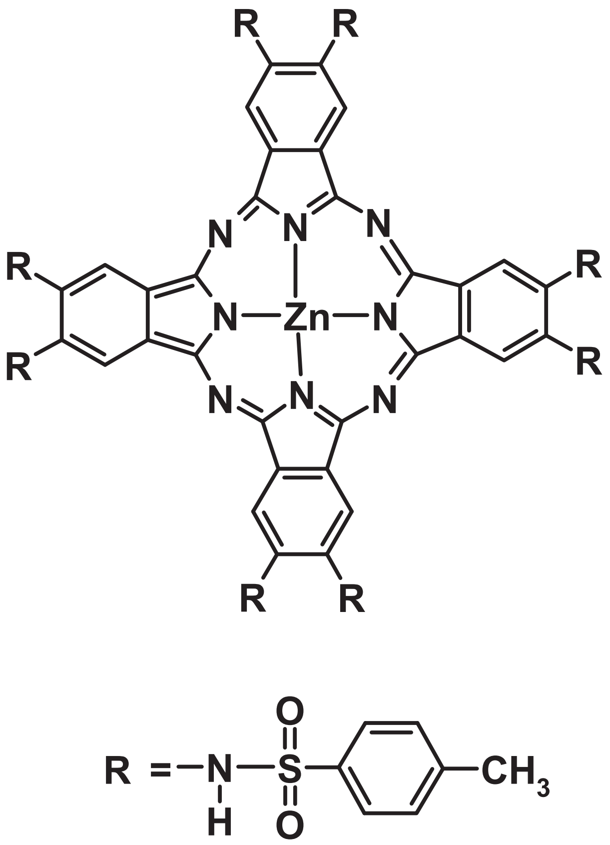

Fig. 1. Schematic representation of the zinc(II) phthalocyanine with eight tosylamido substituents.

immunosensors for detection of very low concentrations (up to 20 ng/l) of simazine and atrazine in natural water samples was also studied [19]. However, immunosensors as active layers are very expensive and they need quite complicated procedure of sample preparation for measurements.

It was established in some works that ellipsometry can be used in total internal reflection mode and in combination with the surface plasmon resonance phenomenon [20]. This technique is known as total internal reflection ellipsometry (TIRE). There has been an extensive work in applying TIRE as a technique for the detection of biomolecules [21–23]. It has been established that TIRE is a more suitable technique than SPR method for the registration of low molecular weight toxins such as simazine, atrazine and T2 mycotoxin [24].

The main advantage of TIRE over standard ellipsometry is its ability of performing measurements in non-transparent media. The simultaneous spectroscopic measurements of the two ellipsometric parameters Ψ and Δ constitutes the main advantage over the conventional Kretschman SPR technique, where only one parameter (reflection intensity) was measured at a certain wavelength of incident light [25].

In our previous paper [26] response characteristics of octa-substituted zinc phthalocyanine films to PCP was studied in the concentration range 0.5–50 μg/l using TIRE technique. The study showed that a clear recovery was only observed for low concentrations (<6 μg/l) of PCP solution with a minimum registered concentration of 0.8 μg/l. Treatment of ZnPcR$_8$ films with higher concentrations of PCP has resulted in irreversible response.

In this work, thin films of octa-tosylamido Zn(II) phthalocyanines (ZnPcR$_8$, R = –NHSO$_2$(C$_6$H$_4$)CH$_3$) (Fig. 1) are investigated as active layers of optical sensors for the detection of pentachlorophenol in water solutions. TIRE method is applied for the registration of PCP in the concentration range 0.1–20 μg/l in Millipore water and was also validated for natural river and wastewater samples. These results are compared with our recently published data of PCP detection using another octasubstituted zinc phthalocyanine derivative [26].

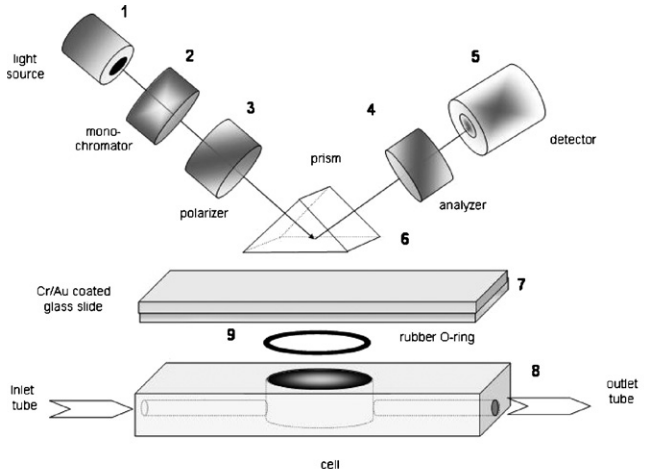

Fig. 2. Total internal reflection ellipsometry experimental set-up.

2. Experimental details

The synthesis of zinc(II) phthalocyanine with eight groups in peripheral positions (Fig. 1) and the absorption and emission based spectral characterization of octa-tosylamido Zn(II) phthalocyanine and detailed spectroscopic probing of the acid–base properties have already been reported in Refs. [27,28], respectively.

Thin films of ZnPcR$_8$ were produced by spin coating of its solution (1 mg/ml) in chloroform using a photoresist spinner (Microsystem model 4000) at a spin speed of 3000 rpm. UV–vis spectra of films spun onto quartz substrates were recorded with a UV–vis scanning spectrophotometer (UV–vis-3101PC "Shimadzu") in the range from 300 to 900 nm.

An in-house built TIRE experimental attachment was fixed on the base of a commercial M2000, J.A. Woollam Co., spectroscopic rotating analyzer ellipsometer, operating in the 370–1000 nm wavelength range, as shown in the schematic diagram presented in Fig. 2. The set-up includes a white light source (1), monochromator (2), polarizer (3), analyzer (4) and a photodetector array (5). Additional elements, which allow performing TIRE measurements, are a 68° prism (6) with a gold-coated glass slide (7) brought into optical contact via index matching fluid, and the reaction cell (8) sealed by the glass slide through a rubber O-ring (9). The choice of the prism was dictated by conditions of total internal reflection of light on the glass/water interface. Further details of TIRE method and the experimental set-up are found in previous publications [24,25]. The measurements were performed in situ in a specially designed 1.5 cm^3 reaction cell attached to the bottom of the 68° glass prism (BK7, $n = 1.515$) with the gold-coated glass slide attached to it via index matching fluid. The cell has inlet and outlet tubes allowing the injection of different aqueous solutions into the cell.

The spectra of the two ellipsometric parameters Ψ and Δ, were recorded with the M2000V instrument in the spectral range 350–1000 nm using the rotating analyzer principle. Ψ and Δ, respectively represent the amplitude ratio $\mathrm{tg}(\Psi) = A_p/A_s$ and the phase shift $\Delta = \varphi_p - \varphi_s$ between the p- and s-components of the polarised light. Optical parameters of the reflection system, i.e. thickness, refractive index and extinction coefficient of the substrate and the adsorbed layers, can be obtained by solving the