

# Molecularly Imprinted Fluorescent Polymers as Chemosensors for the Detection of Mercury Ions in Aqueous Media

Orhan Güney,<sup>1</sup> Fevzi Ç. Cebeci<sup>2</sup>

<sup>1</sup>Department of Chemistry, Istanbul Technical University, Istanbul 34469, Turkey

<sup>2</sup>Department of Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139

Received 28 July 2009; accepted 8 January 2010

DOI 10.1002/app.32077

Published online 13 April 2010 in Wiley InterScience (www.interscience.wiley.com).

**ABSTRACT:** This article describes the investigation of molecularly imprinted fluorescent polymer membranes as sensing receptors for Hg<sup>2+</sup> detection by an optical approach. The polymers were synthesized with 4-vinylpyridine as a functional monomer and Hg<sup>2+</sup> as a template; 9-vinylcarbazole was used as both a complex-forming agent and a fluorescence probe. The free-radical polymerization was performed within a semicylindrical Teflon mold and was initiated by 2,2'-azobisisobutyronitrile at 60°C. The template, ion-bonded to pyridine and carbazole groups in the polymer membrane, was removed by acid treatment. Attenuated total reflectance–Fourier transform infrared (FTIR) spectroscopic measurements and scanning electron microscopy images were used to compare the

chemistry and surface morphology, respectively, of both imprinted and nonimprinted polymer materials. The final polymer membranes with semicylindrical shapes were used directly to determine Hg<sup>2+</sup> concentration in aqueous solutions by the monitoring of the fluorescence intensity of the carbazole groups quenched upon complex formation with metal ions. The values of the Hg<sup>2+</sup> binding ratio for the imprinted and nonimprinted polymeric membranes were compared, and the results indicate the superior sensitivity and selectivity of the imprinted membranes. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 117: 2373–2379, 2010

**Key words:** fluorescence; metal–polymer complexes; molecular imprinting; sensors; templates

## INTRODUCTION

Mercury is considered a human health hazard because it may cause kidney toxicity, neurological damage, paralysis, chromosome breakage, and birth defects.<sup>1</sup> The long atmospheric residence time of mercury vapor and its oxidation to soluble inorganic mercury ions provides a pathway for the contamination of vast amounts of water and soil.<sup>2</sup> The detection of mercury has long held the attention of the analytical community, and as such, a large number of protocols have arisen.<sup>3–5</sup> However, the toxicity of mercury at lower and lower concentrations is being realized, and the direct determination of mercury at submicrogram-per-liter levels has been limited by matrix interference problems. It is evident that the use of separation and preconcentration procedures is still often necessary before the determina-

tion step, despite recent advances in analytical instrumentation.<sup>6</sup>

Current techniques for mercury screening including atomic absorption spectroscopy, atomic emission spectroscopy, and inductively coupled plasma mass spectrometry and usually require expensive and sophisticated instrumentation. The fluorescent detection of Hg<sup>2+</sup> has become an attractive approach in the development of chemical detectors because of its simple instrumentation and its high selectivity and sensitivity.<sup>7–12</sup> Fluorescent devices for the sensing and reporting of chemical species are currently of significant importance in chemistry, biology, and environmental science.<sup>9,13–15</sup> The design and synthesis of a sensitive and selective fluorescent sensor is a fundamental goal for organic and analytical chemists.<sup>7,16–18</sup> Fluorescence spectroscopic sensing represents an attractive means of creating an effective chemosensor because of its ease of use and its capability of detecting submicromolar concentrations; thus, the incorporation of chromophoric reporter molecules into molecularly imprinted sensors has been researched to a considerable extent.<sup>19,20</sup> As molecularly imprinted materials are inherently versatile, a variety of methods have been used to attain the optical transduction of specific binding events via fluorimetry.

Correspondence to: O. Güney (oguney@itu.edu.tr).

Contract grant sponsor: Research Funds of Istanbul Technical University; contract grant number: Bilimsel Araştırma Projesi (BAP) project number 31472.

Template polymerization, also known as *molecular imprinting*, is a method for synthesizing host molecules to recognize targeted guest species.<sup>21–27</sup> Upon removal of the template species, cavities that recognize the spatial features and binding preferences of the template are produced.<sup>28,29</sup> Metal-ion-templated polymers could be designed as recognition receptors for *in situ* measurements of the concentration of metal ions in solutions. Fluorescent indicators that are sensitive to metal ions and exhibit changes in fluorescence intensity depending on the metal-ion concentration can be used as molecular-recognition materials in common optical sensors.<sup>30</sup> Immobilization of the indicators in the supports has significant effects on the performance of the optical sensors in terms of selectivity, sensitivity, and stability.

In this study, mercury(II)-ion-imprinted fluorescent polymers, which contained 4-vinylpyridine (VP) as a functional monomer, 9-vinylcarbazole (VCz) as a fluorescent monomer, and ethylene glycol dimethacrylate (EGDM) as a crosslinker, were synthesized and used to determine  $\text{Hg}^{2+}$  by the monitoring of the fluorescence intensity of the carbazole groups. The imprinted polymers were synthesized in a Teflon mold and used directly as recognition elements in sensors without the destruction of the imprinted pores.

## EXPERIMENTAL

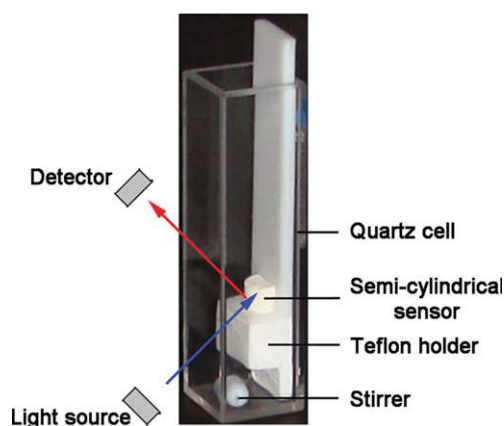
### Materials

VP, VCz, 2,2-azobisisobutyronitrile (AIBN), and EGDM (Taufkirchen, Germany) were supplied by Aldrich. The other chemicals were supplied by Merck (Darmstadt, Germany), and all of the chemicals were used as received. The organic solvents were high performance liquid chromatography (HPLC) grade.

### Methods

#### Equipment

A Jasco FP-750 spectrofluorimeter (Tokyo, Japan) was used to acquire the fluorescence spectra and to perform all fluorescence measurements. The slits for the excitation and emission monochrometers were 5 nm, and the spectral scan rate was 50.0 nm/min. Fluorescence experiments were carried out in a custom-built cell with a Teflon holder (Fig. 1). As shown in the figure, a semicylindrical sensor with a radius of 3 mm was mounted on the Teflon holder in a quartz cell, and excited light and emitted light were perpendicular each other. Attenuated total reflectance (ATR)–Fourier transform infrared (FTIR) spectra of the samples were recorded on a PerkinElmer Spectrum v5.0.1 FTIR spectrometer. The morphology of the imprinted and nonimprinted polymer surfaces was investigated with a field emission scanning electron



**Figure 1** Configuration of the semicylindrical sensor in the Teflon holder in a quartz cell for fluorescence measurements. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

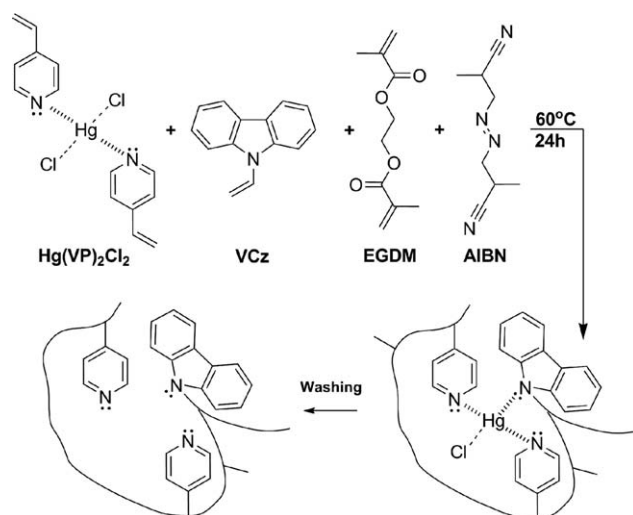
microscope (FEI/Philips XL30 FEG ESEM (Field Emission Gun Environmental Scanning Electron Microscope) instrument) Philips, Eindhoven, The Netherlands at an acceleration voltage of 5 kV. Samples were mounted on sample disk pucks and were coated with a 10-nm layer of gold by a K-550x sputter coater (Emitech, Ashford, U.K.) to prevent charging.

### Procedure

Synthesis of the imprinted and nonimprinted polymeric membranes

Mercury-ion imprinted polymeric membranes were synthesized with a molar ratio of 1 : 1 : 2 : 40 ( $\text{HgCl}_2$  : VCz : VP : EGDM). We prepared a prepolymer complex of mercury(II) ions with VP by stirring a mixture of 0.1 mmol of mercury chloride and 0.1 mmol of VP in 5 mL of ethoxyethanol for 2 h. The prepolymer solution was transferred into a Teflon mold covered by glass plates to obtain a semicylindrical material. Then, the solution was polymerized with the fluorophore monomer (VCz) and crosslinking monomer (EGDM) with AIBN as the initiator (Fig. 2). After the solution was degassed *in vacuo*, the polymerization was carried out at 60°C over 24 h. The mercury(II) ions were leached from the synthesized polymer membrane by stirring with 100 mL of 50% (v/v) HCl for 18 h.<sup>30,31</sup> The polymer membranes were then obtained after washing with water and dried in a vacuum desiccator at room temperature.

The synthesis of the corresponding control polymer membrane (nonimprinted polymer), where VP was randomly distributed within the polymer matrix, was carried out under the same conditions as used for the mercury-ion-imprinted polymers except without the mercury ions. The control polymers were also subjected to the same pretreatments as those used for the mercury-ion-imprinted material.



**Figure 2** Scheme for the preparation of mercury-ion-imprinted polymeric membranes with 1 : 1 complexation of  $\text{Hg}^{2+}$  with VP.

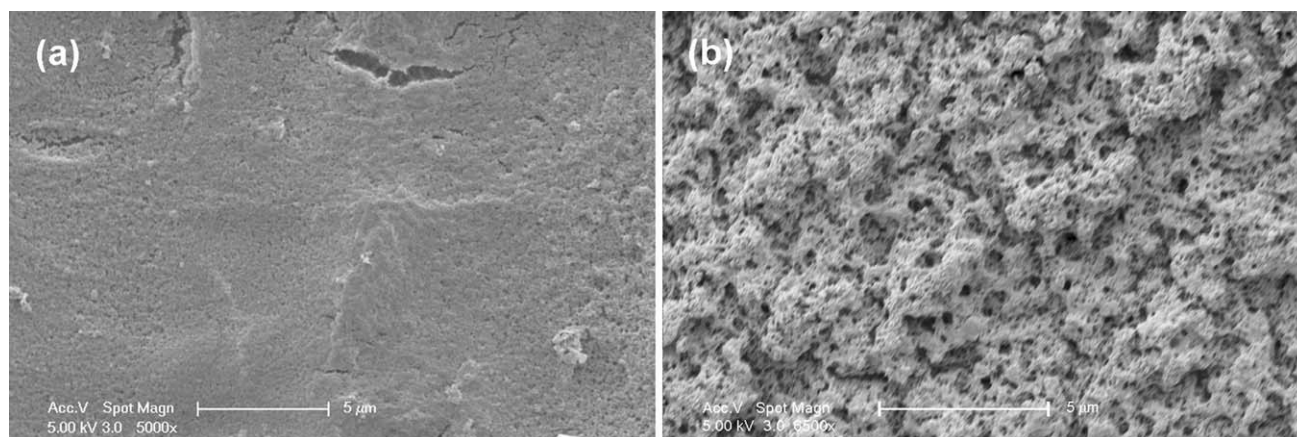
## RESULTS AND DISCUSSION

The surface morphology and internal structure of  $\text{Hg}(\text{II})$ -imprinted and nonimprinted particles are shown in the scanning electron microscopy (SEM) micrographs in Figure 3. As clearly shown in the Figure, the  $\text{Hg}(\text{II})$ -imprinted polymer membrane had a rougher surface than the nonimprinted material because of the presence of pores. We concluded that the imprinted polymer had a nanoporous interior surrounded by a reasonably rough surface. Pores created by the imprinting approach on the particle surface served to increase the surface area of the material. The surfaces of the imprinted and nonimprinted materials were analyzed by ATR-FTIR spectroscopy to elucidate the whether the imprinted material was chemically identical to the nonimprinted material after the mercury ions were removed from

the polymer membrane. Figure 4 shows the ATR-FTIR spectra of EGDM and the polymer membranes prepared under the same reaction conditions in the absence and presence of mercury ions. The peaks at 2951 and 2928  $\text{cm}^{-1}$  were characteristic of the stretching vibration modes of aliphatic C—H groups. The peaks at 1722 and 1716  $\text{cm}^{-1}$  were attributable to the stretching vibration modes of ester carbonyl groups. The peak signifying the C=C bond (used in the free-radical polymerization) at 1635  $\text{cm}^{-1}$  decreased; this indicated that the polymerization was completed at the specimen surface. Figure 4 furthermore reveals bands at 1453 and 1387  $\text{cm}^{-1}$ , which originated from C—H bendings and plane bendings. The bands at approximately 1244 and 1141  $\text{cm}^{-1}$  were assigned to the symmetric and asymmetric stretching modes of the C—O—C bonds in ester groups. The IR spectra of the imprinted and nonimprinted polymers showed similar characteristic peaks; this indicated the chemical similarity in the backbone structure of the polymer membranes.

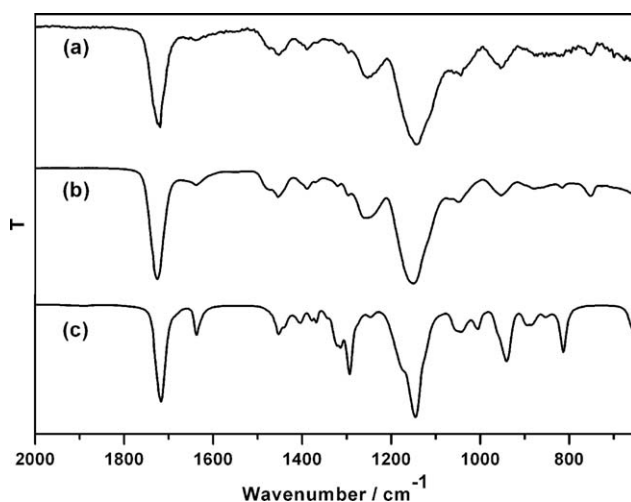
### Effect of pH

The plot of fluorescence intensity versus pH (Fig. 5) for the imprinted polymeric membrane was obtained by adjustment of the solution pH with hydrochloric acid or sodium hydroxide at a fixed  $\text{Hg}^{2+}$  ion concentration of  $1.0 \times 10^{-5}$  mol/dm<sup>3</sup>. At a pH value of lower than 5, the fluorescence intensity of the imprinted membrane increased with decreasing pH value. This phenomenon might have been caused by both the weak interaction of  $\text{Hg}^{2+}$  ions with VCz at high acidity and the restricted resonance structure of VCz in the imprinted membrane due to the protonation on the nitrogen atom of the carbazole group.<sup>29</sup> In the basic pH range, an increase in the fluorescence intensity of the imprinted membrane was



**Figure 3** (a) SEM image of nonimprinted poly(VP-VCz-EGDM) and (b) SEM image of  $\text{Hg}(\text{II})$ -imprinted poly(VP-VCz-EGDM).



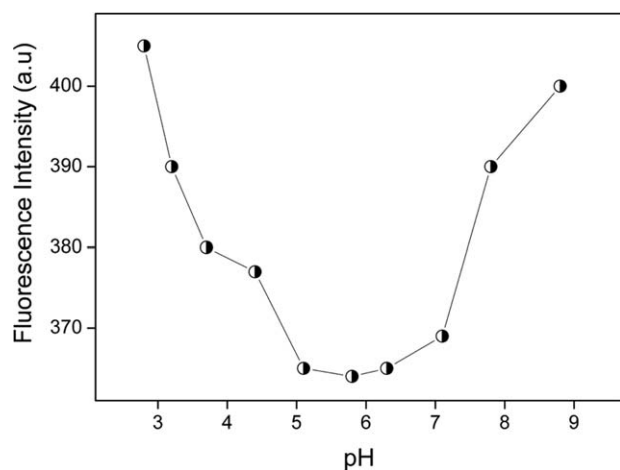


**Figure 4** ATR-FTIR spectra of (a) imprinted and (b) non-imprinted polymers and (c) EGDM.

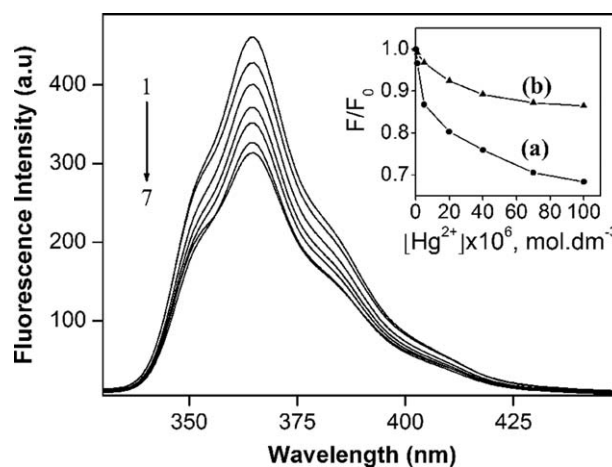
possibly induced by both the deprotonation of the nitrogen atom on the carbazole ring and the partial precipitation of  $\text{Hg}^{2+}$  ion, which was expected to reduce actual concentration of the  $\text{Hg}^{2+}$  ions in the sample solution.

#### Response characteristics and mechanism

We investigated the metal-ion-binding capabilities of the imprinted and randomly synthesized polymer membranes by obtaining fluorescence emission spectra in the presence of different concentrations of  $\text{Hg}^{2+}$  in aqueous acetate buffer solutions at pH 5.5 (Fig. 6). As shown in Figure 6, the fluorescence of the imprinted fluorescent polymers was significantly quenched by the addition of different concentrations of  $\text{Hg}^{2+}$  in aqueous solution. The emission intensity of VCz in the nonimprinted polymer, which was synthesized in the absence of template ions, was



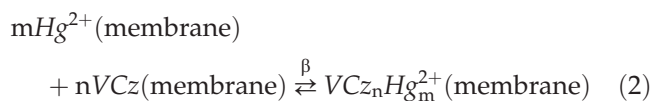
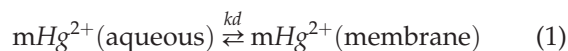
**Figure 5** Effect of pH on the determination of  $\text{Hg}^{2+}$  ions with proposed imprinted membrane. The concentration of  $\text{Hg}^{2+}$  ions was fixed at  $1.0 \times 10^{-5}$  mol/dm<sup>3</sup>.



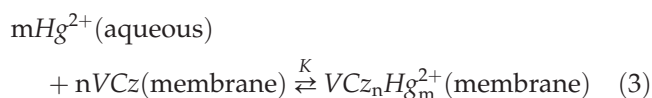
**Figure 6** Fluorescence emission spectra of the imprinted polymeric membrane in the presence of different concentrations of  $\text{Hg}^{2+}$  in acetate buffer at pH 5.5 : (1) 0, (2)  $1 \times 10^{-6}$ , (3)  $5 \times 10^{-6}$ , (4)  $2 \times 10^{-5}$ , (5)  $4 \times 10^{-5}$ , (6)  $7 \times 10^{-5}$ , and (7)  $1 \times 10^{-4}$  mol/dm<sup>3</sup> (Excitation wavelength;  $\lambda_{\text{ex}} = 330$  nm). The spectra were obtained after 30 min after treatment with  $\text{Hg}^{2+}$  ions. Inset:  $F/F_0$  values versus concentration for (a) imprinted and (b) nonimprinted sensors.

also quenched, depending on the  $\text{Hg}^{2+}$  ion concentration. Importantly, we concluded that the emission intensity of VCz in the imprinted polymer was more greatly quenched than that of VCz in the nonimprinted polymer (Fig. 6, inset). The increase in the quenching effect showed the additional  $\text{Hg}^{2+}$  ion binding ability of the imprinted polymeric membrane.

While in contact with VCz in the polymer,  $\text{Hg}^{2+}$  in the aqueous sample solutions was extracted into the polymer membrane. We supposed that a complexation equilibrium between  $\text{Hg}^{2+}$  in the aqueous sample solution and VCz in the polymer was established with the formation of a complex described by a complexing ratio  $m : n$ , such that  $m$  and  $n$  are stoichiometric coefficients of  $\text{Hg}^{2+}$  ion and VCz, respectively.

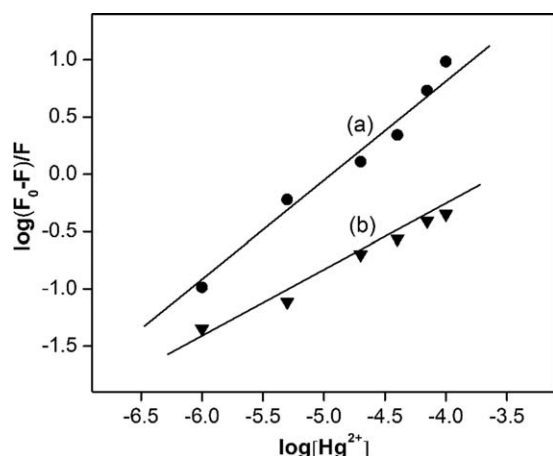


That is



where  $k_d$ ,  $\beta$ , and  $K$  are the distribution coefficient, apparent complex formation constant of  $\text{VCz}_n\text{Hg}_m^{2+}$ , and overall equilibrium constant of the reaction, respectively.

When the difference between the activities and concentrations was neglected for simplification, the



**Figure 7** Plots of  $\log(\Delta F/F)$  versus  $\log(\text{Hg}^{2+})$  obtained with (a) imprinted and (b) nonimprinted polymeric membranes.

corresponding  $K$  could be expressed by the law of mass action:

$$K = k_d x \beta = \frac{\text{VCz}_n \text{Hg}_m^{2+} (\text{membrane})}{[\text{VCz}(\text{membrane})]^n [\text{Hg}^{2+}(\text{aqueous})]^m} \quad (4)$$

According to the modified Stern–Volmer equation, the relationships among the change in fluorescence intensities, the concentration of  $\text{Hg}^{2+}$  in aqueous solution, and the total concentration of VCz(membrane) in the polymer membrane could be expressed as follows:

$$\frac{F_0 - F}{F} = K[\text{VCz}]_{(\text{membrane})}^{n-1} [\text{Hg}^{2+}]_{(\text{aqueous})}^m \quad (5)$$

With the assumption that difference in the fluorescence intensities ( $\Delta F$ ) can be defined as  $\Delta F = F_0 - F$

$$\log\left(\frac{\Delta F}{F}\right) = \log K + (n-1) \log\{[\text{VCz}]_{(\text{membrane})}\} + m \log\{[\text{Hg}^{2+}]_{(\text{aqueous})}\} \quad (6)$$

where  $F_0$  and  $F$  denote the fluorescence intensities of the polymer membrane in the absence and presence of  $\text{Hg}^{2+}$ , respectively. It is evident from eq. (6) that  $m$  is the slope of the plot of  $\log(\Delta F/F)$  versus  $\log(\text{Hg}^{2+})$  (shown in Fig. 7), which was calculated to be 0.91 and 0.52 for the imprinted and nonimprinted polymer membranes, respectively. The high value of  $m$  showed the higher metal-ion-binding capacity of the imprinted polymer membranes compared to that of the nonimprinted ones.

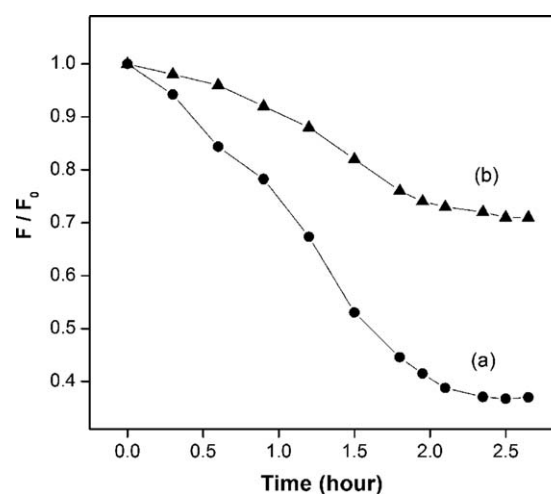
#### Dynamic response time

The response time curve of the Hg(II)-imprinted and nonimprinted polymeric membranes is shown in

Figure 8. The linear response range spanned from  $5 \times 10^{-7}$  to  $1 \times 10^{-4}$  mol/dm<sup>3</sup>  $\text{Hg}^{2+}$  in acetate buffered solution at pH 5.5. Figure 8 shows the fluorescence intensity response versus time recordings for the mercury-ion optical sensing polymer when it was exposed to a concentration of  $5 \times 10^{-5}$  mol/dm<sup>3</sup>  $\text{Hg}^{2+}$ . The response time of the sensor depended on the thickness of the membrane, the flow rate of the sample solution, and the change in the concentration of mercury ions. When the thickness of the membrane reached the order of millimeters, the response time could reach 3 h.

#### Selectivity and stability

The effects of a number of common alkaline, alkaline earth, and transition-metal ions on the fluorescence emission of the proposed imprinted polymeric membrane were investigated. Selectivity, which reflects the relative response of the sensor for primary ions over divers ions present in solution, is a crucial characteristic of a chemical sensor, so a selectivity experiment was carried out with a fixed  $\text{Hg}^{2+}$  concentration of  $1.0 \times 10^{-5}$  mol/dm<sup>3</sup>. The fluorescence intensity changes were monitored before ( $F$ ) and after another interferent was added ( $F_i$ ) in the mercury solution, which was buffered at pH 5.5. The calculation of the resulting relative error was defined as  $\%RE = [(F - F_i)/F] \times 100\%$ . The experimental results of the selectivity studies are summarized in Table I and indicate that some alkali, alkaline earth metal, and metal cations, such as  $\text{Sr}^{2+}$ ,  $\text{Ba}^{2+}$ ,  $\text{Mn}^{2+}$ , and  $\text{Zn}^{2+}$ , existing at concentrations lower than  $1.0 \times 10^{-2}$  mol/dm<sup>3</sup>, did not show an interfering effect on the  $\text{Hg}^{2+}$  assay. Transition-metal cations, such as  $\text{Fe}^{2+}$ ,  $\text{Ni}^{2+}$ , and  $\text{Cu}^{2+}$ , did not interfere with the



**Figure 8** Time-dependent fluorimetric responses of (a) imprinted and (b) nonimprinted polymeric membranes to mercury ions ( $5 \times 10^{-5}$  mol/dm<sup>3</sup>) in acetate buffer at pH 5.5. (Emission wavelength;  $\lambda_{\text{em}} = 367$  nm).

**TABLE I**  
Effect of Different Interferents on the Fluorescence Emission of the Imprinted Polymeric Membrane

Interferent	Concentration (mol/dm <sup>3</sup> )	Fluorescence change ( $\Delta F = F - F_i$ ) <sup>a</sup>	RE% ( $\Delta F/F_i \times 100\%$ )
Na <sup>+</sup>	$1.0 \times 10^{-1}$	$-5.4 \pm 0.2$	-1.47
K <sup>+</sup>	$1.0 \times 10^{-1}$	$-3.1 \pm 0.1$	-0.84
Mg <sup>2+</sup>	$5.0 \times 10^{-2}$	$6.4 \pm 0.2$	1.75
Ca <sup>2+</sup>	$5.0 \times 10^{-2}$	$8.3 \pm 0.3$	2.27
Sr <sup>2+</sup>	$1.0 \times 10^{-2}$	$-6.2 \pm 0.2$	-1.69
Ba <sup>2+</sup>	$1.0 \times 10^{-2}$	$-7.7 \pm 0.3$	-2.10
Mn <sup>2+</sup>	$1.0 \times 10^{-2}$	$7.2 \pm 0.2$	1.97
Zn <sup>2+</sup>	$1.0 \times 10^{-2}$	$9.9 \pm 0.3$	2.71
Fe <sup>2+</sup>	$1.0 \times 10^{-3}$	$15.2 \pm 0.5$	4.16
Ni <sup>2+</sup>	$1.0 \times 10^{-3}$	$13.6 \pm 0.3$	3.72
Cu <sup>2+</sup>	$1.0 \times 10^{-3}$	$17.8 \pm 0.7$	4.87
Pb <sup>2+</sup>	$5.0 \times 10^{-4}$	$16.7 \pm 0.5$	4.57

<sup>a</sup>  $F$  and  $F_i$  are the emission intensities of the imprinted fluorescent polymeric membrane in the presence of a fixed concentration of  $1.0 \times 10^{-5}$  mol/dm<sup>3</sup> Hg<sup>2+</sup> ions without and with interferents, respectively.

Hg<sup>2+</sup> assay at a concentration of less than  $1.0 \times 10^{-3}$  mol/dm<sup>3</sup>. However, the existence of Pb<sup>2+</sup> at the same concentration showed an interfering effect on the Hg<sup>2+</sup> assay. Further examination revealed that Pb<sup>2+</sup> caused slight interference when its concentration was above  $5.0 \times 10^{-4}$  mol/dm<sup>3</sup>. The relative error of all interferents was less than  $\pm 5\%$ , which was considered an acceptable range.

As shown in Table I, the interference effect caused by the ionic charge of metal ions was inhibited because we designed the fluorescent polymeric membranes on the basis of a coordination interaction. Therefore, only metal ions that had the ability to interact with the membrane through coordination bonding could cause interference. Furthermore, pores created by the imprinting approach also limited the interaction. Hence, both the size of the cavities in the imprinted polymer and the coordination-complex-forming capability of Hg<sup>2+</sup> made the imprinted polymer membranes more specific and sensitive to mercury ions.

On the basis of the results of the stability test, we concluded that the fluorescent polymer membrane could be stored in wet conditions without substantial changes to the fluorescence intensity; this implies that the fluorescence probe, PVCz (poly(9-vinylcarbazole)) in the polymer membrane, was stable in contact with water.

## CONCLUSIONS

Mercury(II)-imprinted and nonimprinted polymeric membranes with mercury chloride (or without it) were prepared by the free-radical polymerization of VCz as a fluorescence probe and VP as a coordina-

tion-complex-forming monomer with EGDM as a crosslinker in the presence of AIBN as an initiator. ATR-FTIR spectroscopic measurements clarified that both the imprinted and nonimprinted polymer membranes had similar chemical structures after the washing procedure; this indicated the complete removal of metal ions from the imprinted polymers. The SEM images clearly showed that Hg<sup>2+</sup>-imprinted resins had a rougher surface because of the pores, which provided an increase in the surface area. The fluorescence measurements showed that the greater quenching of the fluorescence intensities of the imprinted resin could be accounted for by the increase in mercury-ion complexation with PVCz in the imprinted polymer membrane. The higher value of  $m$ , the Hg<sup>2+</sup> binding ratio, for the imprinted polymeric membranes substantiated that definite metal-ion binding sites were formed and provided evidence of the imprinting properties conferred to the polymer membrane. The Hg<sup>2+</sup>-imprinted copolymers had some drawbacks, including long equilibration and elution times because of the thickness of the polymer membrane. This may make it difficult to apply the imprinted membranes for immediate practical use and should be a subject of further investigations.

The authors thank Hulya Cebeci of Massachusetts Institute of Technology (MIT) for taking the SEM images and for stimulating discussion and Daniel J. Schmidt of MIT for invaluable contributions.

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