Forced Solid-State Interactions for the Selective “Turn-On” Fluorescence Sensing of Aluminum Ions in Water Using a Sensory Polymer Substrate

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Supporting Information

ABSTRACT: Selective and sensitive solid sensory substrates for detecting Al(III) in pure water are reported. The material is a flexible polymer film that can be handled and exhibits gel behavior and membrane performance. The film features a chemically anchored salicylaldehyde benzoylhydrazone derivative as an aluminum ion fluorescence sensor. A novel procedure for measuring Al(III) at the ppb level using a single solution drop in 20 min was developed. In this procedure, a drop was allowed to enter the hydrophilic material for 15 min before a 5 min drying period. The process forced the Al(III) to interact with the sensory motifs within the membrane before measuring the fluorescence of the system. The limit of detection of Al(III) was 22 ppm. Furthermore, a water-soluble sensory polymer containing the same sensory motifs was developed with a limit of detection of Al(III) of 1.5 ppb, which was significantly lower than the Environmental Protection Agency recommendations for drinking water.

KEYWORDS: sensory polymer, aluminum sensing, fluorescence chemosensor, fluorescence turn-on

INTRODUCTION

Aluminum is ubiquitous in nature, is the most abundant metallic element in the Earth’s crust, and occurs in our everyday lives in metallic, alloy, and trivalent ion derivative forms. In fact, the importance of aluminum to humans is evidenced by its use as a preservative in food and drugs and as an additive in personal hygiene products, housewares, and technological devices. However, despite the tremendous impacts of aluminum on the socioeconomic development of mankind, the extensive application of aluminum results in environmental hazards, including the acidification of soils and aqeous media and toxicity toward aquatic biota.1−3 Furthermore, aluminum presents an important health concern for humans because it is believed to be a causative factor for Alzheimer’s and other diseases, such as dementia, encephalopathy, Parkinson’s disease, and different types of cancer.4−14

Accordingly, detection and quantification devices for Al(III) are needed to mitigate medical and environmental risks, especially devices that could perform measurements cheaply, in situ, and in real time. On the basis of these considerations, optical chemosensors could play a vital role in developing these devices. However, few optical chemosensors systems based on the sensitive fluorescence technique have been reported,15−27 and even fewer systems have been reported for sensing in pure water (the main medium of interest).28−30

Thus, we report a water-soluble polymer chemosensor that exhibits fluorescence “turn-on” for Al(III). Moreover, we describe a chemosensing polymer film substrate for the fluorescence detection and quantification of Al(III) and a new methodology for quantifying Al(III) within minutes at the ppb level that only uses a few microliters of the solution to be measured. Specifically, a drop of water containing Al(III) is absorbed by the solid hydrophilic sensory material. The absorption forces the solvated cations into the film, and the water is evaporated by applying heat. Consequently, the bare cations are forced to interact with the sensing motifs in the polymer structure, which increases the sensitivity and dramatically decreases the response time. The sensory materials were prepared through the copolymerization of a hydrophilic acrylic monomer with a novel methacrylic monomer featuring a salicylaldehyde benzoylhydrazone moiety as a sensing core for Al(III).

EXPERIMENTAL SECTION

Materials. All materials and solvents were commercially available and used as received unless otherwise indicated. The following materials and solvents were obtained: 2,2-dimethoxy-2-phenylacetophenone (Aldrich, 99%), 2,2′-azobis(2-methylpropionitrile) (AIBN) (Aldrich, 98%), hydrazine monohydrate (Aldrich, 98%), 1-(4-amino-phenyl)-1-propanone (Aldrich, 99%), triethylamine (Aldrich, 98%), methacryloyl chloride (Alfa Aesar, 97%), vinyl-2-pyrrolidone (VP) (Aldrich, 99%), 2-hydroxyethyl acrylate (2HEA) (Aldrich, 96%), ethylene glycol dimethacrylate (EGDMA) (Aldrich, 99%), aluminum nitrate nonahydrate (Aldrich, 98%), ammonium nitrate (Aldrich, 98%), barium chloride dehydrate (LabKem, 99%), cadmium nitrate tetrahydrate (Alfa Aesar, 98.5%), cerium(III) nitrate hexahydrate (Alfa

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The quantum yields (Φ) were measured in DMA using quinone sulfate in sulfuric acid (0.05 M) as a reference standard. The water-swelling percentage (WSP), which is the weight percentage of water taken up by the film after soaking and until equilibrium was reached, in pure water was calculated based on the weights of a dry sample film (w0) and a water-swelled sample film (w1) (the membranes were immersed in pure water at 20 °C until the swelling equilibrium was achieved) as follows: 100[(w1 - w0)/w0]. The mechanical properties of the membranes were measured using a Shimadzu EZ Test Compact Table-Top Universal Tester at 20 °C.

**Monomer Synthesis.** The methacrylamide monomer (E)-N-(2-(2-hydroxybenzylidene)hydrazine-carbonyl)phenyl methacrylamide (3) was synthesized from inexpensive and readily available chemicals using proven and high-yield organic reactions, beginning with ethyl 4-aminobenzoate. Details regarding the synthesis process are described below and are schematically depicted in Scheme 1.

**Intermediate Synthesis.** 4-Aminobenzohydrazide (1). First, 72 mL (1.5 mol) of hydrazine monohydrate and 20 g (121 mmol) of ethyl 4-aminobenzoate were added to a 500 mL pressure tube that was fit with a magnetic stirrer. The solution was stirred at 130 °C for 45 min and cooled to rt. Next, 130 mL of absolute ethanol was added, and the solution was stirred at 100 °C for 1 h. Finally, the solution was cooled and filtered, and the product was washed with water (the product was recrystallized in ethanol). Yield (after recrystallization): 12 g (65%). 1H NMR (399.94 MHz; DMSO-d6): δ (ppm), 9.41 (s, 1H), 7.66 (d, 2H, 8.6 Hz), 7.64 (d, 2H, 8.6 Hz), 5.64 (s, 2H), 4.44 (s, 2H). 13C NMR (100.58 MHz; DMSO-d6): δ (ppm), 167.8, 129.6, 121.0, 113.8. Electron impact mass spectrometry (EI-MS), m/z: 151 (M+, 7), 121 (7), 120 (100), 93 (5), 92 (54), 91 (5), 78 (11), 69 (6), 65 (34), and 63 (14). FTIR (wavenumber, cm⁻¹): ν(3400, 3340, 3300, and 3236); ε(C=N): 1660. ESI-HRMS calcd for C10H10N2O1: 151.0746, found 151.0745.

(E)-4-amino-N’-(2-hydroxybenzylidene)benzohydrazide (2). First, 1 g (6 mmol) of compound (1), 803 mg (6 mmol) of salicylaldehyde, and 20 mL of ethanol were added to a 100 mL pressure tube. The mixture was stirred at 120 °C for 5 h. Next, the reaction was allowed to occur at rt, and a pale-yellow precipitate was filtered off and washed with a small amount of cool ethanol. Yield: 1.32 g (86%). 1H NMR (399.94 MHz; DMSO-d6): δ (ppm), 11.69 (s, 1H), 8.60 (s, 1H), 7.74 (d, 2H, 8.6 Hz), 7.51 (d, 1H, 7.6 and 1.3 Hz), 7.34-7.28 (m, 1H), 6.99-6.91 (m, 2H), 6.66 (d, 2H, and 8.7 Hz), and 5.88 (s, 1H). 1C NMR (100.58 MHz; DMSO-d6): δ (ppm), 163.58, 158.36, 153.48, 147.84, 131.82, 130.58, 130.34, 120.13, 119.69, 119.66, 117.31, and 113.59. EI-MS, m/z: 255 (M⁺, 9.14), 151 (5), 136 (8), 121 (8), 120 (100), 92 (19), 78 (10), 65 (12), and 63 (10). FTIR (wavenumber, cm⁻¹): ν(C=O): 1664. ESI-HRMS calcd for C15H12N2O4: 255.0108, found 255.0108.

**Monomer Synthesis.** (E)-N-(4-(2-(2-Hydroxybenzylidene)hydrazinecarbonyl)phenyl) methacrylamide (3). First, 1.55 mmol (0.5 g) of product (2), 2.32 mmol (0.334 mL) of triethylamine, and 15 mL of NMP were added to a pressure tube. Subsequently, 2.01 mmol (0.197 mL) of methacryloyl chloride was added to the tube, and the solution was stirred for 12 h at 50 °C under a nitrogen atmosphere. Finally, the solution was added to water, and the product (3) was obtained.

**Scheme 1. Monomer (3) Synthesis and Structure**

The high-resolution mass spectrometry (HRMS) data were obtained in an API QSTAR XL Hybrid spectrometry system (Applied Biosystems) using an electrospray ionization (ESI) with a high-resolution or a fast atom bombardment (FAB) with DMSO as solvent.
The photograph of the membrane on a notebook shows the aspect ratio and the transparency of the sensory material; the holes correspond to the areas where the 5 mm discs were removed for the sensory kits.

**RESULTS AND DISCUSSION**

To improve the performance of chemosensors, we addressed the task of designing a material that can be handled and exhibits improved fluorescence "off–on" sensing capabilities for Al(III). Thus, we synthesized a novel methacrylic monomer featuring a...
salicylaldehyde hydrazone moiety as the sensing core for Al(III) (Scheme 1).

This monomer was used to prepare solid sensory films (M\text{sen}). In addition, this monomer was used to synthesize a water-soluble sensory film (L\text{sen}) as a sensing material and to characterize the interactions between the Al(III) and the polymer structure (Scheme 2).

**Preparation and Characterization of the Sensory Materials.** The monomer containing the salicylaldehyde benzoylhydrazone sensory motif (3) was prepared in a straightforward manner from widely available commercial chemicals. First, hydrazine and ethyl 4-aminobenzoate were used, followed by two further reaction steps (as shown in Scheme 1). The overall yield was 40%. The NMR spectra of (3) obtained at rt is relatively simple (Figure S3, Supporting Information (SI)), and the assignment of all peaks via conventional NOESY and COSY experiments was straightforward (Figures S4 and SS, SI). However, heating the NMR sample revealed the more complex nature of (3) in the solution, and splitting the signals at a higher temperature indicated equilibria between the associated and nonassociated species (Figure 1), with a clear domination of the associated species at rt. In addition, unique \textsuperscript{13}C NMR signals were observed for each nucleus. This feature was also observed in the \textsuperscript{1}H NMR spectra (Figures S3–SS, SI).

![Figure 1](https://example.com/figure1.png)  
**Figure 1.** 100.58 MHz \textsuperscript{13}C NMR spectra of monomer (3) in DMSO-d\textsubscript{6} at different temperatures (from top to bottom: 80, 60, 40, and 25 °C).

The sensory core is an excellent Al(III) chelator for different organic molecules in organic or aqueous/organic solutions.\textsuperscript{24–29} Thus, we designed monomer (3) and prepared organic sensory materials to function in pure water. The conventional thermally initiated radical polymerization of (3) with the inexpensive commercial comonomers VP and 2HEA resulted in the water-soluble linear copolymer (L\text{sen}), and the addition of a cross-linker (EGDMA) yielded the membrane (M\text{sen}) (Scheme 2). Regarding the envisioned application, only approximately 1% of the synthetic sensory monomer (3) is needed for preparing the L\text{sen} and M\text{sen} as sensory materials. The \textsuperscript{1}H NMR spectrum of L\text{sen} agrees with the feed monomer ratio of the polymerization reaction, including the small monomer (3) content, as depicted in Figure S11, SI.

The dense polymer membrane or film (see the surface and cross-section appearance in the SEM images, Figure S13, SI) was mechanically ceasable and flexible, exhibiting a Young’s modulus (MPa)/tensile strength (MPa)/elongation at breakage (%) under ambient conditions of 100/6/34. Drying the membranes at 60 °C for 30 min resulted in a significant increase in the Young’s modulus and tensile strength, with a concomitant decrease in the elongation at break (394/31/23), demonstrating the influence of membrane hydration due to the humidity in the air.

Furthermore, the materials exhibited reasonably good thermal stability according to TGA. The decomposition temperature associated with a 10% weight loss under a nitrogen atmosphere was approximately 350 °C for both L\text{sen} and M\text{sen}. However, the char yield at 800 °C was slightly higher for the cross-linked material (9% for M\text{sen} and 6% for L\text{sen}). The TGA curves and full data are shown in Figure S12 in the SI. The material was designed to be hydrophilic to provide water solubility to the linear copolymer L\text{sen}and gel behavior of the membrane. The latter is a prerequisite because solvated Al(III) must enter the membrane to reach and interact with the receptor motifs. The water-swelling percentage (WSP) was 63% (between 40 and 100%), which is suitable for both the rapid diffusion of chemicals into the membrane and for maintaining tractability of the mechanical properties of the water-swelled materials.

**Depicting the Sensory Mechanism.** Salicylaldehyde benzoylhydrazone derivatives form complexes with Al(III) with published Al(III)/salicylaldehyde-derivative stoichiometries of 1:1\textsuperscript{24} and 1:3.\textsuperscript{25–29} Unlike organic ligands, these coordination complexes are highly fluorescent in solution. The stoichiometry of the published complexes remains unclear or are dependent on the salicylaldehyde derivative. Thus, we studied the complex stoichiometry to determine the sensory mechanism.

A complex (C\textsubscript{1:3}) was prepared by reacting Al(NO\textsubscript{3})\textsubscript{3} with (3) at a molar ratio of 1:3.

The C\textsubscript{1:3} complex has a molecular weight of 994.00, and the analysis of its HR-ESI-MS spectrum is coherent with the suggested stoichiometry of 1:3 (Figures S6 and S7, SI). In the DMSO-d\textsubscript{6} solution, complex C\textsubscript{1:3} reaches equilibrium with complex C\textsubscript{1:2} (or [Al(3)\textsuperscript{3+}]) and deprotonated (3) ([(3)-H\textsuperscript{–}])\textsuperscript{–}, C\textsubscript{1:3} = C\textsubscript{1:2} + [(3)-H\textsuperscript{–}], as observed in the COSY experiments (Figures S8 and S9, SI).

This equilibrium was analyzed using \textsuperscript{1}H NMR at different temperatures. At 30 °C, four peaks corresponding to the methyl groups were observed, one signal for the symmetric C\textsubscript{1:3} complex, another signal for deprotonated ([3]-H\textsuperscript{–}) and two signals for the nonsymmetric C\textsubscript{1:2} complex. At 80 °C, two peaks corresponding to C\textsubscript{1:2} were merged into one (Figure S8, SI).

Thus, the formation of the complex could be monitored using \textsuperscript{27}Al NMR (Figure 2),\textsuperscript{29} for which two main signals were obtained. The sharper signal at approximately 19 ppm corresponds to the symmetric C\textsubscript{1:3} species, and the broader signal centered at approximately 16 ppm corresponds to the nonsymmetric C\textsubscript{1:2} species. The small peak at approximately 5 ppm is derived from aluminum in the glass substrate of the reference material.

After analyzing the sensory mechanism ascribed to the formation of complexes with the monomer and Al(III), the same behavior is expected to be responsible for the sensing characteristics of the sensory polymer materials. Accordingly, we found evidence of the formation of complexes with an Al(III)/salicylaldehyde derivative with a stoichiometry of 1:3 in the Job’s plot obtained from the fluorescence titration curves.
of Al(III) with solutions of \( \text{L}_{\text{sen}} \) in pure water. In this plot, a maximum was observed for a salicylaldehyde derivative molar fraction of 0.75 (Figure S10, SI).

**Sensing Behavior of the Sensory Materials.** As previously discussed, nonfluorescent pure aqueous solutions of \( \text{L}_{\text{sen}} \) became highly fluorescent in the presence of aluminum.
ions (i.e., following an off−on pattern, as shown in Figure 3), which allowed us to draw a titration curve.

Following a similar off−on pattern, 5 mm discs cut from the Msen film resulted in a large increase in their fluorescence intensities upon immersion in water containing aluminum ions, as discussed below. In contrast, a manageable and highly fluorescent hybrid organic−inorganic film-shaped material (Al-Msen) was prepared after immersing Msen in a water solution of Al(III).

After preparing the sensory materials, critical parameters such as response time, interfering chemicals, selectivity, and sensitivity were measured, as discussed below. In addition, a short study of the performance of the hybrid film as a luminescent material was performed.

Response Time. The response time was significantly short (approximately 5 min) for the sensory system composed of an aqueous Lsen solution at micromolar and millimolar Al(III) concentrations (Figure 4). The response time was not dependent on the Al(III) concentration.

However, the most interesting sensory solid system, Msen showed a much longer response time, especially at a low Al(III) concentration. Moreover, this time was highly dependent on the Al(III) concentration. These trends were observed because the sensing phenomenon relies on two concomitant factors, namely, the relatively slow physical diffusion of the target species (Al(III)) into the membrane and the rapid chemical interactions of the species with the sensory motifs chemically anchored to the membrane polymer network. Thus, the response time for a submillimolar concentration of Al(III) was approximately 1 h, as shown in Figure 4.

Nevertheless, the response time of the Msen could be reduced to 20 min for the concentration of the target cation Al(III), achieving the goal of attaining a short measurement time. This reduction was accomplished by forcing the interaction to occur in the solid state (i.e., a known quantity of the aqueous solution containing Al(III)) was dropped on the surface of a dry membrane disc and allowed to stand for 15 min, resulting in the immediate absorption of the Al(III) by the hydrophilic membrane structure, before drying the disc in an oven at 100 °C for 5 min). On one side, the rapid absorption of the aqueous drop by the membrane drags the solvated Al(III) ions into the material. On the other side, the simultaneous drying of the material forces the previously hydrated Al(III) ions to interact with the membrane sensory motifs (3).

Hybrid Materials Al-Msen. The addition of Al(III) to the DMA solutions of (3) caused the fluorescence to turn on, transforming the formerly weakly fluorescent solution into a highly fluorescent solution due to the formation of Al(3)\(^{3−}\)n complexes with Al(III)/(3) stoichiometries of 1:1, 1:2, and 1:3.

The quantum yield of the solution containing (3) in DMA was negligible (Φ = 0.02) when using quinine sulfate in sulfuric acid (0.05 M) as a reference standard. Furthermore, the addition of Al(III) to this solution at molar ratios of 1:1, 1:2, and 1:3 (with respect to (3)) resulted in quantum yields of Φ = 0.59, 0.53, and 0.59, respectively, indicating a high fluorescence efficiency, as previously outlined.

After determining that the high quantum yield of the organometallic complexes resulted from the interaction of (3) with Al(III), which was determined in organic media because (3) is water-insoluble, and based on the potential of the materials derived from (3) as luminescent converters (LUCO), the Al-Msen hybrid membrane was prepared (please see the SEM images in Figure S13 in the SI. The Al(III) content in the cross section of the membrane obtained from EDS analysis was 0.22%, which agreed well with the theoretical value of 0.20%). Furthermore, the color of the materials upon irradiation was determined in terms of the CIE chromaticity coordinates (x and y) that were calculated from the fluorescence spectra using the corresponding CIE 1931 color matching functions (Figures 5). Figure S13 in the SI contains an image of membrane Al-Msen strips under UV light. These types of materials are promising for luminescence conversion applications because of their high quantum yields and the blue emissions observed upon irradiation under conventional 365 nm UV. The CIE chromaticity coordinates were x = 0.14 and y = 0.26 for Al-Msen and were x = 0.15 and y = 0.16 for the monomer in the organic solution. Both systems showed blue emissions.

Substrate Selectivity and Interference Study. Preliminary interference studies regarding the sensory monomer (3) were conducted in organic/aqueous solutions due to the lack of the solubility of (3) in water. A broad set of cations was added to the sensing solutions at a high concentration (10 times the concentration of (3)), and only five cations significantly enhanced the fluorescence. A 24-fold enhancement occurred for Al(III) and 1- to 4-fold enhancements occurred for Zr(IV), Cd(II), Zn(II), and La(III), as shown in Table S1 in the SI. The greater response toward Al(III) was accompanied by a higher selectivity because the emission and excitation spectra are both characteristic of these cations, as shown in the 2D and
of detection (LOD) and the limit of quantitations ranging from 0.3 ppb to 2.8 ppm (Figure 4). The limit achieved with the sensory disc cut from provided the benefit of sensitivity, whereas the solid system presented the advantage of selectivity. Thus, a cocktail of higher, 22 and 36 ppm, respectively. Thus, the solution system depicted a different scenario. From a practical viewpoint, Zr(IV) is considered as a unique interferent. However, to test the performance of the sensory system, a competitive experiment was conducted (Figure 6). Thus, a cocktail of cations was added to the solution, and the results were compared with those obtained from an experiment in which only Al(III) was added. The cocktail included the cations that caused interference to (3), and no significant effects due to these cations were observed regarding fluorescence enhancement and the fluorescence pattern, as shown in the inset of Figure 6. The same behavior was observed for the solid sensory substrate MSen in which the spectral patterns of the membrane with and without Al(III) differed from that of the solutions of (3) and LSen due to the solid swollen state, as illustrated in the 2D and 3D fluorescence spectra shown in Figures S21 and S22 (SI).

**Substrate Sensitivity.** Water solutions of LSen were used as off−on fluorescence probes for detecting Al(III) at concentrations ranging from 0.3 ppb to 2.8 ppm (Figure 4). The limit of detection (LOD) and the limit of quantification (LOQ) were 1.5 and 4.7 ppm, respectively, below the Environmental Protection Agency (EPA) Secondary Drinking Water Regulations (SDWR, 50 to 2000 ppb). In contrast, the LOD and LOQ achieved with the sensory disc cut from MSen were much lower, 22 and 36 ppm, respectively. Thus, the solution system presented the advantage of sensitivity, whereas the solid system provided the benefit of a short response time and simplicity.

**CONCLUSIONS**

In summary, we designed an innovative solid material for the fluorescence off−on detection of Al(III). In addition, we developed a new method for measuring the concentration of Al(III) using one drop of the measuring solution that can be conducted within minutes and measure concentrations at the ppb level, which is significantly lower than the EPA-recommended concentrations for drinking water. The sensory material was a flexible polymer film that could be handled and exhibited gel behavior. The film was prepared using a novel fluorescence aluminum ion sensory salicylaldehyde benzoylhydrazine derivative and other comonomers to impart hydrophilicity and good mechanical properties. The measurement method consisted of depositing a drop of the solution to be measured onto the surface of the sensory film, which allowed it to enter the hydrophilic material. This process was followed by a drying period that forced the Al(III) to interact with the sensory motifs within the membrane. Overall, this process required approximately 20 min to complete. After this process, the fluorescence of the system was measured using conventional methods. In addition, a water-soluble sensory polymer using the sensory monomer was prepared, and its performance in detecting aluminum was characterized, which yielded results that were similar to those obtained for the films. However, the measurements involving solutions were much less labor-intensive and time-consuming.

**ASSOCIATED CONTENT**

Supporting Information

1D and 2D NMR and mass spectra of monomer (3) and complexation studies of (3) with Al(III). The 1H NMR spectra of LSen, TGA of LSen, and MSen; SEM images of MSen and Al−MSen; 2D and 3D fluorescence spectra of (3) and the MSen with and without different cations in the media, and the interference study. This material is available free of charge via the Internet at http://pubs.acs.org.

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**Notes**

The authors declare no competing financial interest.

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