

Functionalized Ni@SiO₂ Core/Shell Magnetic Nanoparticles as a Chemosensor for Fluoride Ion

Minsung Park, Ki-Young Kwon,* and Jong Hwa Jung*

Department of Chemistry and Research Institute of Natural Sciences, Gyeongsang National University, Jinju 660-701, Korea

*E-mail: jonghwa@gnu.ac.kr (J. H. Jung); kykwon@gnu.ac.kr (K.-Y. Kwon)

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Molecular receptors with optical properties that can be changed upon binding to specific guest ligands are of great interest due to their potential application as molecule-based sensor devices. The detection of anionic guest molecules is of particular significance due to the fact that negatively charged species play a critical role in biological, chemical, and environmental processes.¹⁻⁷ Since most anionic species are found in aqueous media, the need to develop receptors with large binding constants for anions in water is important. Since anions typically have very large energies of solvation, there is strong competition between receptor binding and solvation in aqueous media.⁸⁻¹⁰

In recent years, a new method based on the change in fluorescence of an anionic sensor has been developed. This kind of sensor usually consists of three moieties: fluorophore, spacer, and receptor. The fluorescence signal of this sensor changes when the guest species is bound by the receptor. The most common mechanism for fluorescence signal changes in this kind of sensor results from an intramolecular photo-induced electron transfer (PET) process.¹¹⁻¹⁴ The first example of kind of chemosensor for anionic species recognition was described by the Czarnik group for the detection of phosphate and pyrophosphate.^{15,16} It is well known that urea and thiourea groups can interact with anionic species effectively *via* hydrogen bonding.¹⁷ Several sensors containing these functional groups have been reported.

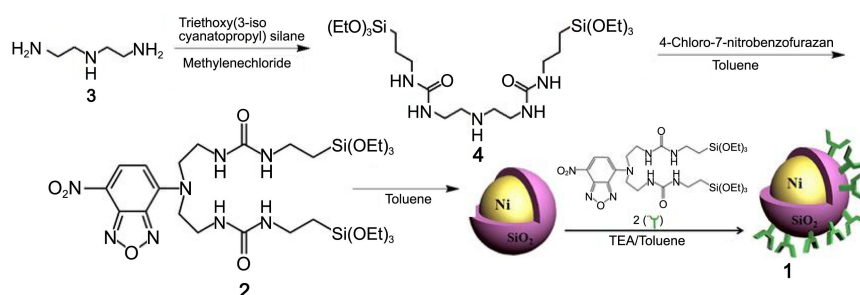
Until recently, anion sensing studies have focused upon single phase systems, in which the molecular receptors are fully dissolved in a specific solvent.^{8-10,18,19} Heterogeneous anion sensors, based upon the immobilization of molecular anion receptors to solid supports, are technologically attractive due to their potential easiness of use and reusability.

However, only limited examples of such heterogeneous sensors have been reported,^{10,20-23} even though they take advantage of the independent solubility properties of the receptor in both water and organic solvents.

In this context, magnetic nanoparticles used as solid supports coupled with supramolecular structures are important for the development of hybrid nanomaterials with improved functionalities. Such materials offer simple and efficient separation and detection of specific ions for biological, toxicological and environmental usage.²⁸⁻³³ Herein, we describe the preparation of nitrobenzofuran-functionalized Ni@SiO₂ core/shell magnetic nanoparticles **1** and their ability to detect F⁻ ion. We find that the Ni@SiO₂ core/shell nanoparticle **1** have a highly selective chemosensor for F⁻ ion.

Compound **2** was synthesized by two steps as shown in Scheme 1. Nickel nanoparticles were prepared by a modified polyol process. Then the particles were coated with silica shells through the Stöber method using tetraethyl orthosilicate (TEOS) as a silica source in water to yield Ni@SiO₂ core/shell particles.³⁴ The Ni@SiO₂ core/shell nanoparticles were then reacted with **2** in toluene under vigorous stirring overnight to covalently link **2** to the surface of the Ni nanoparticles *via* a sol-gel reaction (Scheme 1). The synthetic **1** was characterized by transmission electron microscopy (TEM), FTIR spectroscopy, time-of-flight secondary ion mass spectrometry (TOF-SIMS) and fluorophotometry.

The TEM image of **1** revealed a spherical structure with a narrow size distribution (*ca.* 35 nm) with a 30 nm Ni core (Figure 1(a)). The particles maintained the magnetic properties of Ni (Figure 1(b)). For further proof of the new bond formation between silica and link **2**, we acquired FT-IR and TOF-SIMS spectra of **1**. In the FT-IR spectrum of **1**, in



Scheme 1. Preparation of nitrobenzofuran-functionalized Ni@SiO₂ core/shell magnetic nanoparticles **2** by sol-gel reaction.

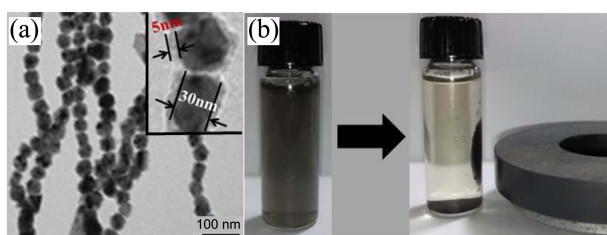


Figure 1. (a) TEM image of the **1**. (b) Photograph of a magnet attracting **1** in aqueous solution.

addition to the bands attributed to the Ni@SiO₂ core/shell nanoparticles themselves, strong new bands at 3393, 2969, 2932, 1639, 1566, 1278 and 1051 cm⁻¹ appeared, originating from the receptor **2**. This result is consistent with **2** residing on the Ni@SiO₂ core/shell nanoparticle surface. The TOF-SIMS spectrum of **1** displayed the characteristic fragments of **2** ($m/z = 136$ and 291), also provide that **2** was anchored onto the surface of the Ni@SiO₂ core/shell nanoparticles.

We probed the binding abilities of **1** for several anions based on changes in fluorescence upon the addition of F⁻, Cl⁻, Br⁻, I⁻ and HSO₄⁻ in water (Figure 2). In the absence of anions, the nitrobenzofuran moiety attached onto the surface of **1** exhibits a strong fluorescence emission band ($\lambda_{\text{max}} = 530$ nm) when excited at 460 nm. Interestingly, among all of the anions tested, addition of fluoride ion to a suspension of **1** in water produced the largest decrease in the fluorescence

intensity (Figure 2(a)). As shown in Figure 2(b), fluoride ions are bind to four urea N-H protons. The fluorescence quenching effect can be explained as reverse photoinduced electron transfer (PET) when one ion is bound to the urea N-H protons behaving as a PET donor.^{11-14,27} The fluorescence emission of the suspension of **1** in acetonitrile/water (1:1 v/v) gradually decreased with increasing additions of fluoride anion (Figures 2(c) and 2(d)), indicating the quantitative binding of fluoride ion to the urea moiety attached to **1**. On the other hand, fluorescent intensities of **1** by addition of Cl⁻, I⁻, Br⁻ and HSO₄⁻ slightly decreased, suggesting that those anions did not bind to the urea N-H protons of **1**.

To confirm the binding site of receptor **2** attached onto **1** with fluoride ion, solid ¹⁹F NMR technique was applied to explore the interactions of **2** attached onto **1** with fluoride ion in the solid state. Before addition of fluoride ion to **1**, no peak corresponding to fluoride appears, whereas peaks at -118 ppm appeared in the spectrum after addition of fluoride anion. These results indicate that fluoride ion was bound to the receptor **2** attached onto **1** by the intermolecular hydrogen bonding interaction. In FT-IR spectra of both free-**1** and F⁻-bound **1**, the characteristic peak of N-H bend in free **1** appeared at 1565 cm⁻¹, and was found to shift to 1578 cm⁻¹ in the event of complexation with F⁻ ion. The intermolecular hydrogen bonding interaction between fluoride ion and the receptor **2** in **1** was further confirmed by EDX technique. The material contained silicon, carbon, nitrogen,

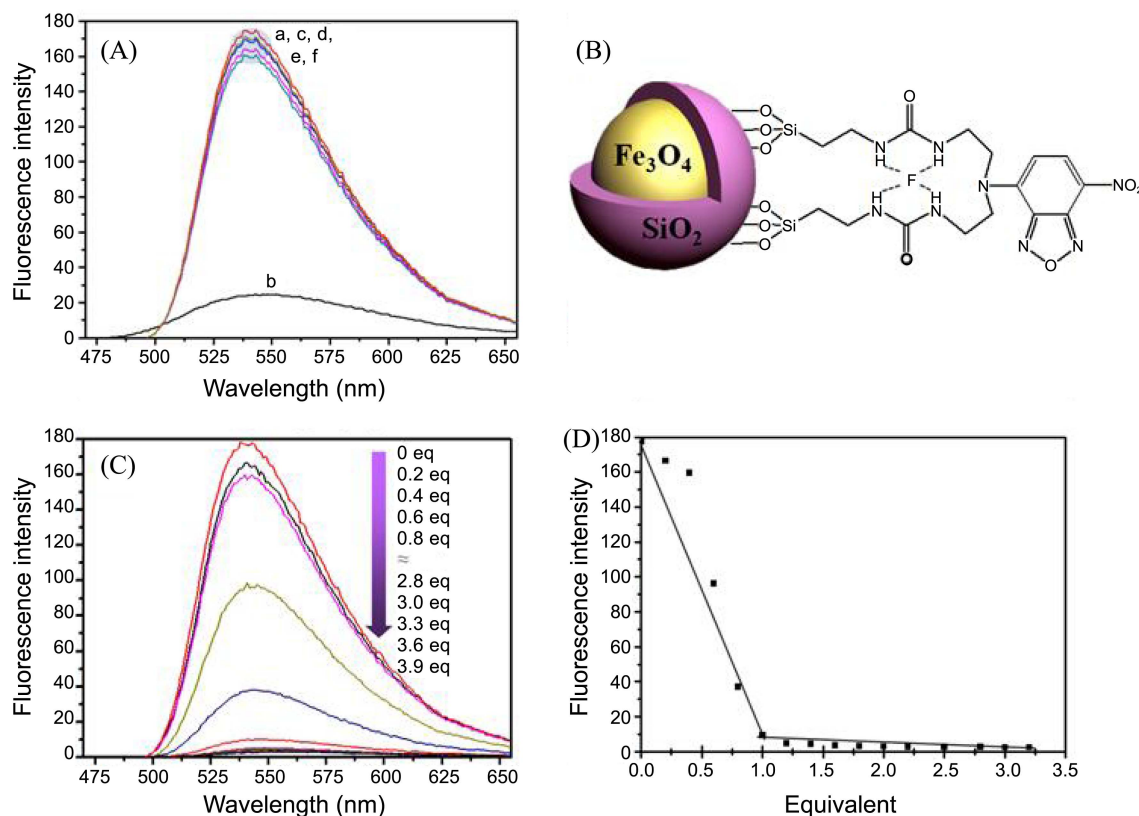


Figure 2. (A) Fluorescent emission changes in **1** (5.0 mg) without (a) anion and with, (b) F⁻, (c) HSO₄⁻, (d) I⁻, (e) Cl⁻ and (f) Br⁻ ions (20 equiv.) in H₂O/acetonitrile (1:1 v/v). (B) Binding mode of **2** attached to Ni@SiO₂ core/shell nanoparticle with fluoride ions. (C) Fluorescent changes in **1** (5.0 mg) upon addition of 1+F⁻ in H₂O/acetonitrile (1:1 v/v). (D) Plot of molar ratios [F/1] against fluorescent intensity of **1**.

nickel, and fluoride components, supporting the idea that fluoride ions are adsorbed by intermolecular hydrogen bonding interaction to **1** which is covalently attached onto **1**.

The fluorescence change observed following dipping in fluoride ion solution was found to be fully reversible when **1** was well rinsed with distilled water. Reusability was evaluated by repeated dipping/rinsing cycles, with the **1** fluorescence spectrum being recorded after each step. It is apparent that the **1** exhibits excellent reusability since almost no sensitivity loss in **1** was observed after 8 repeated dipping/rinsing cycles. Furthermore, the rapid response time of the system, with the fluorescent change being complete within several seconds, allows rapid turnover of sensing.

For a biological or environmental fluorescence sensor, the sensing should be effective over a wide pH range. The effect of pH on probe **1** in the absence of F⁻ was examined. At pH=3, the fluorescence emission is largely quenched, probably due to the protonation of the nitrogen atoms of the nitrobenzofurane group. However, minimal or no significant fluorescence changes were observed between pH 4-11. Thus, **1** can be used in physiological environments with pH > 3. Also, upon addition of F⁻, a large quenching effect occurred in the range of pH 4-11, indicating that the nanoparticle **1** can be successfully applied as a chemosensor for F⁻ at pH > 3.

In conclusion, we have prepared nitrobenzofurane-functionalized Ni@SiO₂ core/shell magnetic nanoparticles that act as a new type of a fluorogenic chemosensor for the efficient sensing F⁻ in aqueous solution over the pH range of 4-11. Chemosensor **1** exhibits a high affinity and high selectivity for F⁻ over a number of other anions tested, and successfully detected F⁻. These are promising findings for the development of a new category of biocompatible sensing systems built by immobilizing appropriate fluorogenic receptors on the surfaces of other novel magnetic nanomaterials for detection of other anions.

Experimental Section

Chemicals. Unless otherwise stated, all reagents were purchased Aldrich and used without further purification.

Preparation of Compounds 1-4. Compounds **1-4** were synthesized as described previously.³⁵

Characterization. ¹H and ¹³C NMR spectra were measured with a Bruker ARX 300 MHz spectrometer. MS spectra were obtained with a JEOL JMS-700 mass spectrometer. Transmission electron microscopy (TEM) images were taken with a JEOL JEM-2100 F instrument operated at 150 keV. IR spectra were obtained for KBr pellets, in the range 400-4000 cm⁻¹, with a Shimadzu FTIR 8400S instrument, and the MS spectrum was obtained with a JEOL JMS-700 mass spectrometer. Time-of-flight Second Ion Mass Spectrometer (TOF-SIMS) was analyzed on Model PHI 7200 equipped with Cs and Ga ion guns for positive and negative ion mass detection.

Photospectroscopy. Fluorescence emission spectra were recorded with a Shimadzu RF-5301-PC instrument. Stock

solutions (0.01 M) of the hydrated metal perchlorate salts were prepared in H₂O at pH 7. Stock solutions of **1** were prepared in H₂O. For all measurements, excitation was at 350 nm, with excitation and emission slit widths of 1.5 nm. The pH value was adjusted by using 0.2 M MOPS.

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