Fluorescent Calix[4]arene-appended Silica Nanotubes as Selective Chemosensor and Adsorbent for Pb^{2+} Ion

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Functionalized silica nanotube (FSNT) possessing a calix[4]arene moiety as a fluorescent receptor is fabricated by sol–gel reaction. The FSNT suspension in water selectively adsorbs 98% of Pb^{2+} over other metal ions (Li^+, Na^+, K^+, Cs^+, Mg^{2+}, Ca^{2+}, Ba^{2+}, Zn^{2+}, and Ag^+) and shows quenched fluorescence emission in both pyrene monomer and excimer bands.

Chemical sensors are molecular receptors that transform their chemical information into analytically useful signals upon binding to specific guests. These sensors are attracting attention owing to their potential for easy detection and quantification of the pollutant species in many fields of application, such as waste management, environmental chemistry, clinical toxicology, and bioremediation of radionuclides.[1–6] Among these, the sensitive detection of heavy-metal ion, such as lead and mercury, is critical for monitoring the environmental as they are highly toxic and common environmental pollutants.

In general, the development of most chemosensors is based on molecular-level host–guest concept in solution.[7–9] On the other hand, it is clear that the receptor-immobilized nanotubes have some important advantages as a solid chemosensor in heterogeneous solid–liquid phases. First, such nanotubes as a chemosensor can repeatedly utilize with suitable treatment. Second, the nanotube would be useful as selective and efficient adsorbent for specific guest molecules in environmental pollutants because of larger surface and well-defined pore in comparison to spherical structure of nanomaterials. This fact has attracted our attention in connection with the creation of new hybrid species based on the fusion of specific receptors and inorganic nanomaterials such as SiO_2, Al_2O_3, or TiO_2 as a solid supporting medium. We herewith, therefore, report the immobilization of a fluorescent receptor onto the surface of silica nanotubes and examine its specific adsorption behavior for Pb^{2+} over other metal ions. Silica nanotube and calix[4]arene derivative were introduced as solid support and binding site for Pb^{2+} ion, respectively.

Pyrene-appended, 1,3-alternate calix[4]arene **2** was prepared by the adaptation of procedures reported earlier.[10] Subsequently, treatment with **2** and aminoethyltriethoxysilane in the presence of DCC and DMAP in THF afforded the desired product **1** (Chart 1) as a yellow powder in Scheme S1 (Supporting Information).[12]

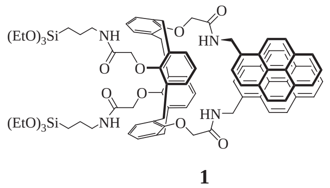

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Chart 1.

The silica nanotube with immobilized **1** (FSNT) was prepared by Scheme S2.[12] After immobilization of fluorescent **1** onto the silica nanotube, we took both SEM and TEM of the resultant silica. As illustrated in Figure 1, the silica product shows a well-defined nanotube with a diameter of ca. 260 nm and several micrometers in length (Figure 1a).

The TEM image of the fluorescent silica displays a hollow structure with uniform size dimensions, i.e., inner diameter of ca. 210 nm and wall thickness of 25 nm (Figure 1b), indicating that the fluorescent receptor **1** is covalently bound to the surface of the SNT by the post sol–gel reaction. Besides, for further proof of the new bond formation, we also took IR spectra of the SNT and the FSNT, respectively. IR peaks of SNT appeared at 3450, 1635, and 1085 cm^{-1} whereas the FSNT did at 3445, 2935, 2858, 1632, and 1560 cm^{-1} (Figure S1).[12] Among peaks appeared from FSNT, the peaks of 2935, 2858, and 1560 cm^{-1} originate from calixarene group, indicating that calixarene group is attached onto the surface of FSNT. The elemental analysis and TGA resulted in approximately 14 wt % FSNT of the receptor **1** (Figure S2).[12] In addition, the strong fluorescence of FSNT was observed when visible lamp at 350 nm irradiated to the FSNT. This material, called functionalized silica nanotube (FSNT), is then tested for its abilities for detection and separation for specific metal ions from aqueous and organic solvents.

We examined the binding abilities of FSNT for metal ions based on fluorescence changes upon the addition of Li^+, Na^+, K^+, Cs^+, Mg^{2+}, Ca^{2+}, Ba^{2+}, Zn^{2+}, Ag^+, and Pb^{2+} (all as perchlorates) in water (Table S1[12] and Figure 2a). In the absence of metal ions, two pyrene units of **1** attached to the SNT exhibit both strong monomer ($\lambda_{em} = 381$ nm) and excimer ($\lambda_{max} = 470$ nm) emissions. Formation of the excimer emission is attrib-

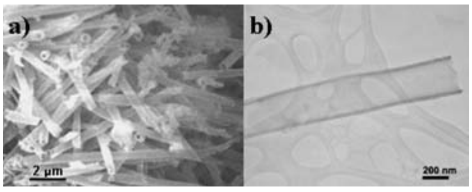

Figure 1. (a) SEM and (b) TEM images of FSNT obtained from sol–gel reaction.

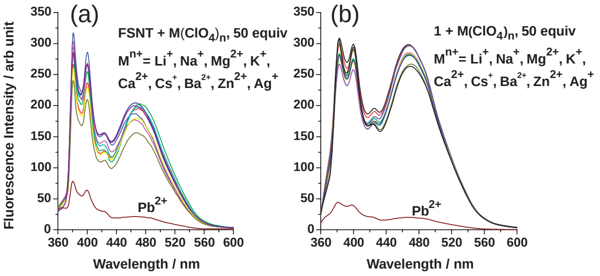

Figure 2. Fluorescent spectra of (a) FSNT and (b) **1** (0.30 mM) upon the addition of perchlorate salts (50 equiv) in (a) water and (b) MeCN.

uted to the two pyrene units of the amide pendants being in the face-to-face π-stacked.[10] With this dynamic excimer emission, the relative ratio of excimer to monomer ($I_{\text{excimer}}/I_{\text{monomer}}$) emissions of the FSNT is found to be 0.95.

Both pyrene monomer and excimer bands of the FSNT suspension in water are markedly quenched by the addition of Pb^{2+} ion (Table S1).[12] Ignorable or no change was observed with other metal ions such as Li^+, Na^+, K^+, Cs^+, Mg^{2+}, Ca^{2+}, Ba^{2+}, Zn^{2+}, and Ag^+ ions. Quenched excimer emission of the FSNT is rationalized by a conformational change of two outward-facing amide carbonyl groups turning inward to bind the Pb^{2+} ion.[10] The monomer emission was also quenched because the photoinduced electron transfer (PET) is executed when the Pb^{2+} is bound to amide carbonyl oxygen atoms.[10]

In control experiment, the fluorescence changes of the SNT alone without calixarene unit were investigated. As shown in Figures 2b and S3,[12] the fluorescence of **1** dramatically decreased by the addition of Pb^{2+} but did not change with the addition of any other metal ions. Also, no fluorescence changes were observed upon the addition of any metal ions to SNT without the attached the calix[4]arene moiety. The findings indicate that Pb^{2+} is selectively bound to carbonyl oxygen atoms of the calix[4]arene unit on the surface of FSNT. Also, the association constant for complexation of Pb^{2+} by FSNT in water calculated to be $4.7 \times 10^5\,M^{-1}$. The detection limitation of FSNT was $\approx 30\,\mu m$ sensitivity for Pb^{2+} ion.

We also measured the binding selectivity of the FSNT for the Pb^{2+} ion in multicomponent system in the presence of other metal ions such as Li^+, Na^+, K^+, Mg^{2+}, and Ca^{2+} ions (Figure S4).[12] In the addition of other metal ions to the FSNT–Pb^{2+} solution, fluorescence intensity of the FSNT did not change (Figure S4).[12] It is sure that the FSNT we have developed is very promisingly useful as a selective adsorbent in separation of Pb^{2+} ion in the mixture with other metal ions.

We took FT-IR spectra of both free FSNT and Pb^{2+}-bound FSNT. The characteristic peak of –C=O in **1** appearing at $1626\,cm^{-1}$ was found to shift to $1620\,cm^{-1}$ in the event of complexation with Pb^{2+} ion (Figure S5).[12] The shift results from the coordination of the Pb^{2+} to the oxygen atoms of amide groups.[11] Furthermore, FAB-MS of [**1**]–Pb^{2+} (851 *m*/*z*) as shown in Figure S6 gave a clue of 1:1 complex of **1**–Pb^{2+}.[12] These results are in good consistency with our previous report that the pyrene amide group of calix[4]arene acts as the selective binding site for Pb^{2+}.[10]

The adsorption capacity of FSNT for metal ions in solid–liquid phase was measured by IC (ion chromatography) and ICP (Figure 3 and Figure S7).[12] The results for solid–liquid extraction using FSNT are given in Figure 3. In single-ion extraction, 98.5% of Pb^{2+} in liquid phase was adsorbed onto the surface of FSNT. In contrast, less than 2.5% of other metal ions (Li^+, Na^+, K^+, Mg^{2+}, and Ca^{2+}) except Ag^+ ion was extracted into the solid phase. Thus, the FSNT can be potentially useful as a Pb^{2+} ion adsorbent in solid–liquid extraction. In addition, adsorption capacity of the FSNT measured through the solid extraction in the solutions of multicomponent metal system (Li^+, Na^+, K^+, Mg^{2+}, Ca^{2+}, Zn^{2+}, Ag^+, and Pb^{2+}) resulted in 95.6% of Pb^{2+} adsorption (Figure 3). In contrast, other metal ions were extracted into the solid phase only 0.7–7.5% in the competitive adsorption system.

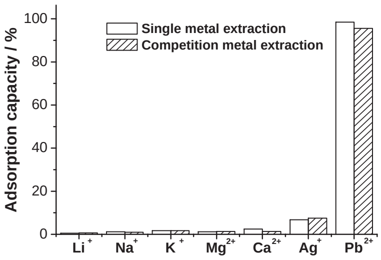

Figure 3. Adsorption capacity (%) of FSNT upon the addition of metal ions.

The present study has demonstrated that FSNT, a new type of chemosensor and adsorbent was fabricated by sol–gel reaction. The FSNT interestingly reveals a selective change in fluorescence monomer and excimer emission only for Pb^{2+} ion over other metal ions mainly because the two oxygen atoms of the two amides bind the Pb^{2+} ion, which remotes the conformational changes of the two amides to provide the decreased excimer emission.

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12 Supporting Information is available electronically on the CSJ-Journal Web site, http://www.csj.jp/journals/chem-lett/index.html.

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