Organic–inorganic hybrid nanomaterial as a new fluorescent chemosensor and adsorbent for copper ion†

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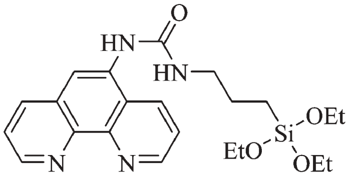
Functionalized silica nanotube (FSNT) possessing the phenanthroline moiety as a fluorescent receptor was fabricated by sol–gel reaction, and the binding ability of FSNT with metal ions was evaluated by fluorophotometry.

The synthesis of nanotubes has greatly expanded the possibilities for the design of open pore structures. Because of their large surface area and their well-defined pore size and pore shape, these materials have great potential in environmental and industrial processes.[1–4] However, many applications including adsorption, ion exchange, catalysis and sensor require materials possessing specific attributes such as binding sites, stereochemical configuration, charge density and acidity.[5,6]

In general, the development of most chemosensors is based on molecular-level host–guest concept in solution.[7–10] On the other hand, it is clear that receptor-immobilized nanotubes have some important advantages as solid chemosensors in heterogeneous solid–liquid phases. First, such nanotubes as chemosensors can be repeatedly utilized with suitable treatment. Second, nanotubes would be useful as selective and efficient adsorbents for specific guest molecules in environmental pollutants due to their larger surface and well-defined pores in comparison to spherically structured nanomaterials. Third, nanotubes can be easily isolated from pollutants by simple filtration. Fourth, the single nanotube is advantageously applicable as sensing material for the development of nano-scaled devices. Fifth, if receptors can be immobilized onto the inner-wall of silica nanotubes, such well-ordered silica nanotubes could be expected to act as nanofilters to separate specific guest molecules from a mixture by size inclusion. 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 solid supporting media. Here we report the immobilization of a fluorescent receptor onto the surface of silica nanotubes and examine its specific adsorption behavior for Cu^{2+}.

Compound **1** as a fluorescent receptor was synthesized by the synthetic route depicted in Scheme S1 (hereafter S denotes: Electronic Supplementary Information†). The nitrogen atoms in the phenanthroline moiety would act as the binding site for specific metal ions. Also, the triethoxylsilyl group of **1** was introduced to facilitate covalent attachment of the receptor onto the surface of the silica nanotube (SNT) by sol–gel reaction.



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Based on our new concept of developing a selective fluorescent chemosensor and adsorbent for Cu^{2+}, the phenanthroline derivative **1** was covalently attached onto the SNT by sol–gel reaction. The details of the preparative procedure are depicted in Scheme S2. The high yield of SNT (>97%) was obtained by sol–gel reaction of tetraethyl orthosilane (TEOS) using organogel **2** as a template by a previously reported method.[11] The unreacted TEOS and the organogel template were completely removed by calcination followed by washing with THF, and a white solid was obtained. Immobilization of the fluorescent receptor **1** into the SNT was conducted under reflux for 24 h in toluene. In this process, the triethoxylsilyl group of **1** undergoes hydrolysis and attaches covalently to the surface of SNT. After cooling to room temperature, the slightly yellow solid product was filtered, washed with THF, and then dried. Also, we used the commercial silica-gel as a supporting material for receptor **1**. These products were characterized by scanning electron microscopy (SEM), transmission electron microscopy (TEM), fluorophotometry and thermogravimetric analysis (TGA).

The silica product showed a well defined nanotube possessing a diameter of *ca.* 260 nm and several micrometers in length (Fig. 1a). The TEM image of the fluorescent silica displayed a hollow structure with uniform size dimensions, *i.e.*, inner diameter of *ca.* 210 nm and wall thickness of 25 nm (Fig. 1b), indicating that the fluorescent receptor **1** was covalently attached onto the surface of SNT by post sol–gel reaction. This material, called functionalized silica nanotube (FSNT), was evaluated for its ability to detect and separate specific metal ions from aqueous and organic solutions.

To confirm that the fluorescent receptor **1** was immobilized onto the surface of SNT, we performed elemental mapping of silicon (Si), carbon (C), nitrogen (N) and oxygen (O) by energy dispersive X-ray spectroscopy (EDX) technique coupled with TEM measurements.[12] After complete removal of template with THF, the material (Fig. S1a) contained silicon (Fig. S1b), oxygen (Fig. S1c), nitrogen (Fig. S1d) and carbon (Fig. S1e) components.†

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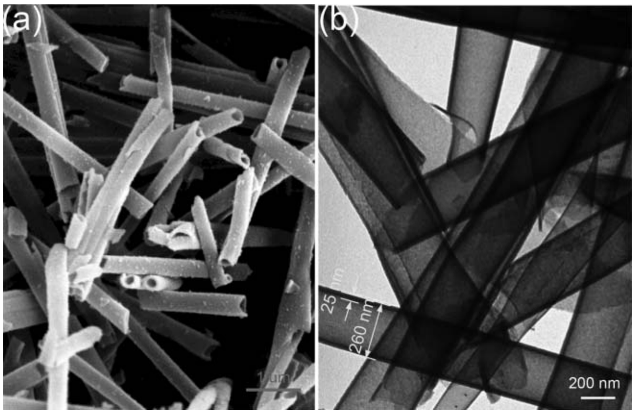

Fig. 1 (a) SEM and (b) TEM images of FSNT.

Table 1 Fluorescence changes ($I - I_0$) for FSNT, **1** and SNT upon addition of metal ions

	Fluorescence changes ($I - I_0$)									
	λ_{em}/nm	Ag^+	Cd^{2+}	Co^{2+}	Pb^{2+}	Hg^{2+}	Ni^{2+}	Zn^{2+}	Fe^{3+}	Cu^{2+}
FSNT	451	−30	0	0	−5	−12	−21	−21	−5	−340
1	411	−42	0	−6	−9	−21	−30	−21	−14	−306
SNT	370	−4	−3	−4	−2	−1	0	0	−2	−2

These findings strongly support the view that the fluorescent receptor **1** was immobilized onto the surface of the SNT. In addition, elemental analysis and TGA indicated that the FSNT contained approximately 32 wt% of the receptor **1** (Fig. S2†). In contrast, only 9 wt% of the receptor **1** was immobilized onto the surface of the commercial silica-gel, which has an irregular structure (Fig. S3†). The lower content of receptor **1** attached in the commercial silica-gel is due to its lower surface area.

We probed the binding abilities of FSNT for metal ions based on changes in fluorescence upon the addition of Ag^+, Co^{2+}, Cd^{2+}, Pb^{2+}, Zn^{2+}, Fe^{3+}, Ni^{2+}, Cu^{2+} and Hg^{2+} (all as nitrates) in acetonitrile (Table 1). In the absence of metal ion, the phenanthroline moiety attached onto the surface of FSNT exhibits a strong fluorescence emission band (λ_{max} = 451 nm) when excited at 275 nm. Interestingly, addition of Cu^{2+} to a suspension of FSNT in acetonitrile markedly diminished the fluorescence intensity of phenanthroline in FSNT (Fig. 2a and Fig. S4†), suggesting that Cu^{2+} forms a complex with the nitrogen atoms of the phenanthroline unit, and strongly quenched the emission intensity. The fluorescence quenching can be explained as reverse photoinduced electron transfer (PET) when Cu^{2+} is bound to nitrogen atoms of the phenanthroline unit behaving as a PET donor.[7,13–15] The fluorescence emission of the suspension of FSNT in acetonitrile gradually decreases with increasing Cu^{2+} concentration (Fig. S5†), indicating that Cu^{2+} is quantitatively bound to the phenanthroline moiety attached to FSNT. In contrast, the fluorescence of FSNT did not change by addition of Ag^+, Co^{2+}, Cd^{2+}, Pb^{2+}, Zn^{2+}, Fe^{3+}, Ni^{2+} and Hg^{2+}. These results support the view that those metal ions did not bind to the phenanthroline moiety of FSNT.

On the other hand, the fluorescence selectivity of metal ions with the commercial silica gel with immobilized receptor **1** was almost same as that of FSNT (Fig. S6†). However, the fluorescence sensitivity of commercial silica-gel was lower than that of FSNT due to the lower content of receptor immobilized.

In control studies, the fluorescence changes of **1** and of SNT alone, without the phenanthroline unit covalently attached, were measured by the addition of metal ions. As shown in Fig. 2b and 2c, the fluorescence of **1** dramatically decreased by the addition of only Cu^{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 phenanthroline moiety. The findings indicate that Cu^{2+} is selectively bound to nitrogen atoms of the phenanthroline unit on the surface of FSNT.

In efforts to understand the coordination behaviors between receptor **1** attached in FSNT and Cu^{2+}, our repeated attempts to obtain the crystal structures of the related complexes were not successful. As an alternative, we measured FT-IR spectra of both free-FSNT and Cu^{2+}-bound FSNT to confirm the binding site of Cu^{2+}. The characteristic peak due to –N–C groups in **1** at 1385 cm^{-1} shifted to 1377 cm^{-1} when in complex with Cu^{2+} (Fig. S7†). The resulting shift to shorter wavenumber is attributed to the coordination of the Cu^{2+} to the nitrogen atoms in the phenanthroline moiety. Furthermore, the molecular weight of **1**-Cu^{2+} complex was measured by FAB mass spectroscopy. As shown in Fig. 3, evidence for the 3 : 1 complex was indicated by the FAB mass spectrum of the $[\mathbf{1}]_3$–Cu^{2+} complex (694. *z*/*e*). The coordination between Cu^{2+} and the phenanthroline receptor **1** attached in SNT was further confirmed by EDX technique (Fig. S8†). The material contained silicon, carbon, nitrogen and copper components, supporting the idea that Cu^{2+} ions are homogeneously adsorbed by electrostatic interaction to **1** which is covalently attached in FSNT.

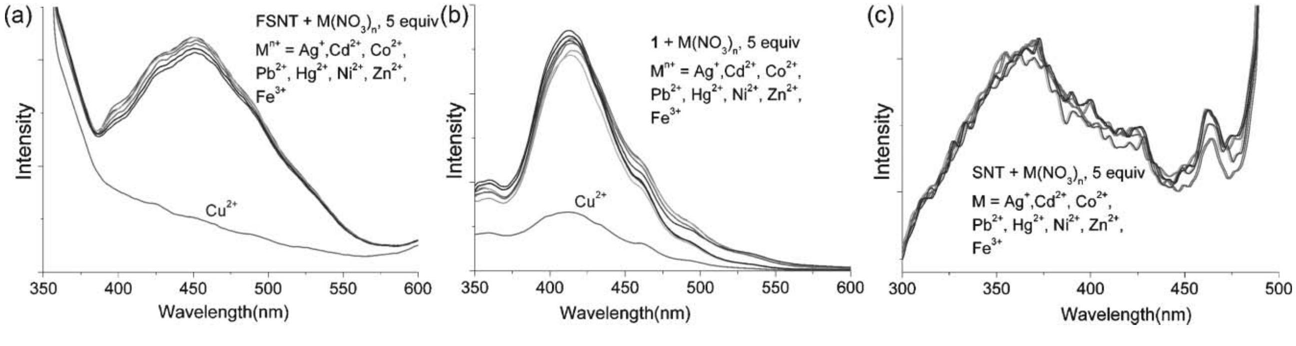

Fig. 2 Fluorescent spectra of (a) FSNT(0.30 mM), (b) **1**(0.30 mM) and (c) SNT(0.30 mM) upon the addition of metal nitrates (5.0 equiv.) in acetonitrile.

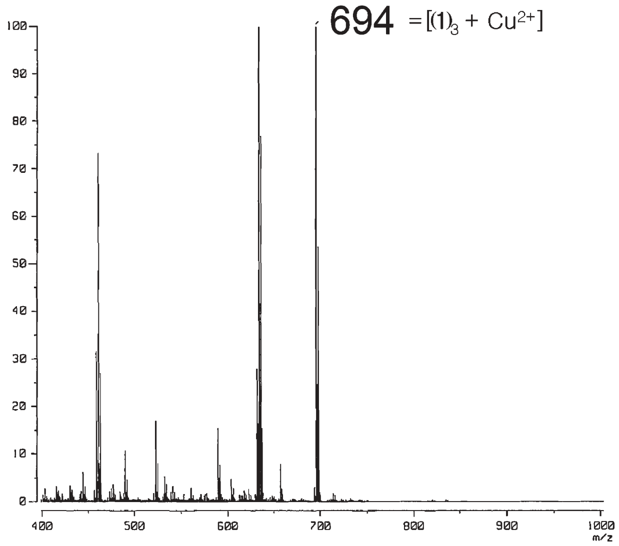

Fig. 3 FAB-MS spectrum of **1** + Cu^{2+}.

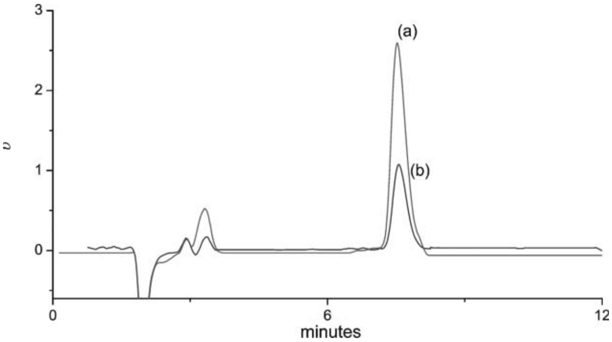

Fig. 4 Ion chromatograms of Cu^{2+} (a) before and (b) after extraction with FSNT in water.

We examined the ability of FSNT to absorb metal ions in solid–liquid phase. The adsorption capacity of FSNT was also measured by ion chromatography and ICP (Fig. 4). The results for solid–liquid extraction by using FSNT are shown in Table S1†. In single-ion extraction, only 75% of Cu^{2+} in liquid phase was adsorbed onto the surface of FSNT. On the other hand, the spherical silica-gel showed much lower (25%) extractability for Cu^{2+} than that of FSNT in the solid extraction experiment. In contrast, in single ion systems, less than 3% of other metal ions (Zn^{2+}, Cd^{2+}, $Co^{2+}$and Pb^{2+}) were extracted into the solid phase. Furthermore, the spherical silica-gel showed much lower (20%) extractability for Cu^{2+} than that of FSNT. Thus, FSNT is potentially useful as a metal-adsorbent for Cu^{2+} in solid–liquid extraction.

In conclusion, FSNT, a new type of chemosensor was fabricated by sol–gel reaction. The FSNT selectively detected and separated Cu^{2+}. Beyond its immediate applications in environmental clean-up, FSNT provides a unique opportunity to introduce molecular binding sites and to rationally design the surface properties of inorganic nanomaterials. We believe the combination of well-defined inorganic nanomaterials and functionalized organic receptors can play a pivotal role in the development of a new generation of hierarchical structures and functionalized composites.

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