Selective fluoride sensing using organic–inorganic hybrid nanomaterials containing anthraquinone†

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Anthraquinone-based fluorescent receptor **1** was immobilized on mesoporous silica (**AFMS**) or on silica particles (**AFSP**) *via* a sol–gel reaction. The sensing abilities of **AFMS** and **AFSP** were studied by addition of the anions F^-, Cl^-, Br^-, I^- and HSO_4^- to water suspensions of the assayed solid. The addition of fluoride ions to a suspension of **AFMS** resulted in a large decrease in the fluorescence intensity of the anthraquinone of **AFMS**. Thus, fluoride ions bind to two urea N–H protons of receptor **1** in **AFMS**. In contrast, the addition of Cl^-, Br^-, I^- or HSO_4^- did not reduce the fluorescence of **AFMS**. In the case of **AFSP**, the sensitivity for fluoride ions was 10 times lower than that of **AFMS** due to the immobilization of smaller amounts of receptor **1** on the silica particles. A linear response of **AFMS** upon the addition of fluoride ions was observed between 0.50 μM and 10.0 μM, with a detection limit of ~0.50 μM. These results suggest that mesoporous silica with its large surface area is useful as a supporting material. Furthermore, receptor **1** was also immobilized on a glass slide surface by a sol–gel reaction. The fluorescence of **1** immobilized on a glass slide was quenched when dipped into F^- solution. On the other hand, no fluorescence change was observed in Cl^- solution. These results imply that **1** immobilized on a glass slide is applicable as a portable fluorescent sensor for detection of fluoride ions in the biological and environmental fields.

Introduction

Molecular receptors with optical properties that change upon binding to specific guest ligands are of great interest due to their potential applications as molecular sensing devices. The detection of anionic guest molecules is of particular importance due to the widespread roles played by negatively charged species in biological, chemical and environmental processes.[1–7] Because most anionic species are found in aqueous media, receptors with large binding constants for anions in water are needed. The development of such receptors is impeded by the fact that anions typically have very large energies of solvation. Thus, in aqueous media strong competition exists between receptor binding and solvation.[8–10]

In recent years, a new method has been developed that is based on the change in fluorescence of an anion sensor. This type of sensor usually consists of three moieties: fluorophore, space and receptor. The fluorescence signal of the sensor changes upon binding of the guest species. The most common mechanism for fluorescence signal changes in the sensor is an intramolecular photo-induced electron transfer (PET) process.[11–14] The Czarnik group described the first example of this type of chemosensor for anionic species recognition, *i.e.*, for the detection of phosphate and pyrophosphate.[15,16] Urea and thiourea groups can interact effectively with anionic species by hydrogen bonding,[17–19] and several sensors containing these functional groups have been reported. Also, it is well known that the anthraquinone in these sensors acts as a fluorescence source.[19]

Recently organic–inorganic materials have been investigated in the search for new methodologies for ion recognition and sensing. Receptors immobilized on inorganic materials such as SiO_2, Al_2O_3 and TiO_2 have important advantages as solid chemosensors in the heterogeneous solid–liquid phase.[10,20–27] First, immobilized receptors on an inorganic support can liberate the organic guest molecules (metal ions or anions) from the pollutant solution. Second, the organic–inorganic hybrid nanomaterials can be recycled by suitable chemical treatment. Lastly, functionalized nanomaterials combined with fluorophores or chromophores display highly selective, sensitive fluorescence or absorption changes compared with spherical structures because of their larger surface areas and well-defined pores.

The homogeneous porosity and large surface area of mesoporous silica make it a promising inorganic support.[27,28] However, only limited examples of such heterogeneous sensors have been reported,[10,24–27] despite the fact that they take advantage of the independent solubility properties of the

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receptor in water and organic solvents. Herein, we report a novel heterogeneous system for the chromogenic detection of anions. Anthraquinone-based fluorescent receptor **1** was immobilized on a mesoporous silica surface by covalent bonding. We demonstrate that this approach provides a convenient solid material anion-sensing system that combines the highly sensitive and selective anion sensing of the molecular receptor with the reusability achieved by immobilization of the receptor on a solid support.

Experimental

Characterization

^{1}H and ^{13}C NMR spectra were recorded on a Bruker 300 apparatus. IR spectra of silica powder pellets were obtained using a Shimadzu FT-IR 8400S and the MS spectrum was obtained with a JEOL JMS-700 mass spectrometer. Powder X-ray diffraction (PXRD) patterns were recorded on a Siemens D8 Advance diffractometer using Cu Kα radiation and a secondary monochromator. Transmission electron microscopy (TEM) images were captured with a JEOL JEM-2100 F microscope. EDX analysis was conducted with a JEOL ultra-thin window (UTW)-type EDX detector capable of detecting boron and an OXFORD EDS system for signal processing in a 180 s live time. Nitrogen-adsorption isotherms were measured at 78 K on a Micromeritics ASAP 2010 analyzer. Thermal gravimetry analysis (TGA) was conducted on a TA SDT Q600 with a heating rate of 10 °C min^{-1} using a Pt pan in air. Heating temperature was scanned from 25 °C to 900 °C.

Preparation of the mesoporous silica

The silica precursor, tetraethyl orthosilicate (TEOS), was added as a surfactant to an aqueous solution of octadecyltrimethylammonium bromide (ODTMA) under strong acidic conditions at room temperature, with the molar ratio of 100 H_2O (360 mL) : 7 HCl (142 mL) : 0.02 ODTMA (1.6 g) : 0.03 TEOS (1.3 mL). The mixture was then covered and moved into an isothermal oven set at 80 °C, where it was kept without stirring for 3 days. Spontaneous growth of suspended flocculates and precipitated particles was observed. They were washed with distilled water three times and dried at 100 °C in air. To remove cationic surfactants, dried fiber-like flocculates and particles were calcined in a box furnace in air at 500 °C for 5 h, with a ramp rate of 1 °C min^{-1}.

Fabrication of anthraquinone-based fluorescent: receptor 1 immobilized on mesoporous silica (AFMS) or 1 immobilized on silica particles (AFSP)

Compound **1** (100 mg) was dissolved in toluene (10 mL). The mesoporous silica (100 mg) or commercial silica particles (100 mg) were added as a solid. The suspension of mesoporous silica or commercial silica particles was stirred under reflux conditions for 24 h in toluene. Then, the collected solid was washed copiously with toluene (50 mL) to rinse away any surplus **1** and dried under vacuum.

Fluorescence changes in AFMS or AFSP upon addition of anions

AFMS (5 mg) or **AFSP** (5 mg) was added to the anion solution (all anions as tetrabutylammonium (TBA) salts, 0.1–20.0 equiv. with respect to **1** anchored to the mesoporous silica). The mixture was stirred for 1 min. Then, fluorescence changes in **AFMS** and **AFSP** were measured by a luminescence spectrometer (Perkin Elmer). In addition, the fluorescence change in AFMS was observed by addition of fluoride ions in the presence of other anions (20.0 equiv. of Cl^-, I^-, Br^- and HSO_4^-).

Fluorescence reversibility of AFMS

Reversibility experiments were performed by dipping **AFMS** (5 mg) in a 5×10^{-4} M anion solution. After dipping, the fluorescence spectrum was measured. The sample was dipped in acidic solution (pH 2) for 5 min to remove the fluoride ions. Then, the sample was washed with a basic solution (pH 9) and finally with a neutral solution.

Preparation of activated glass slides

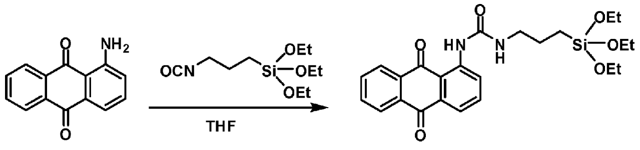
Glass slides were cleaned for 1 h in 1M HCl, followed by an immersion in H_2SO_4 and H_2O_2 for 12 h. The glass slides were then rinsed in distilled water and dried with Ar gas.

Receptor 1 immobilization on activated glass slides

Receptor **1** was dissolved in DMSO. A solution of receptor **1** (100 μL, 10 mM) was dropped on the activated glass slide. Then, the glass slide was maintained at 90 °C for 12 h. After thoroughly washing with THF and distilled water, the slides were dried for 1 h at 100 °C.

Synthesis of receptor 1

Under nitrogen, a solution of 1-aminoanthraquinone (100 mg, 0.45 mmol), 3-(triethoxysilyl)propyl isocyanate (0.11 mL, 0.45 mmol) and NaH (10 mg, 0.45 mmol) in THF (10 mL) was stirred for 24 h. After cooling to room temperature, the solvent was evaporated *in vacuo*. CH_2Cl_2 (100 mL) and water (200 mL) were added and the organic layer was separated. The CH_2Cl_2 layer was washed twice with water followed by drying over anhydrous Na_2SO_4. After filtration of sodium sulfate, removal of the solvent *in vacuo* gave a reddish crude sample that was further purified by column chromatography on silica gel (ethyl acetate–hexane, 1 : 2) to provide 180 mg of orange solid **1** in 85% yield. ^{1}H NMR ($CDCl_3$, 200 MHz): δ 9.03–8.98 (d, 1 H, NH_{Ar}, J = 8.79 Hz), 8.29–8.25 (t, 2 H, ArH, J = 4.39 Hz), 7.96–7.92 (d, 2 H, ArH, J = 7.79 Hz), 7.81 (m, 3 H, ArH), 5.2 (br s, 1 H, NH), 3.91–3.81 (q, 6 H, $–OCH_2CH_3$, J = 6.79 Hz), 3.42–3.32 (q, 2 H, $–NHCH_2CH_2$, J = 5.79 Hz), 1.80–1.72 (t, 2 H, $–CH_2CH_2CH_2$, J = 7.19 Hz), 1.28–1.22 (t, 9 H, $–CH_2CH_3$, J = 6.79 Hz), 0.78–0.70 (t, 2 H, $–CH_2CH_2Si–$, J = 8.19 Hz). ^{13}C NMR ($CDCl_3$, 50 MHz): δ 187.1, 182.9, 154.9, 144.4, 135.6, 134.1, 133.8, 132.9, 128.2, 128.1, 127.1, 126.9, 126.3, 125.3, 120.8, 58.5, 42.9, 28.7, 18.3, 7.8 ppm. FAB MS m/z (M^+) calcd 470.5, found 471.0.



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Scheme 1 Synthetic route to receptor **1**.

Results and discussion

Fabrication of AFMS and AFSP

Receptor **1**, possessing anthraquinone and urea components as the fluorescent unit and fluoride ion-binding site, respectively, was synthesized as shown in Scheme 1. The synthesis of the mesoporous silica as a solid support material was performed according to the procedure of Stucky and co-workers,[29] as detailed in the experimental section. Then, the fluorescent receptor **1** was attached to the mesoporous silica or silica particle support by a sol–gel reaction in toluene.

TEM images of both the mesoporous silica and the anthraquinone-based fluorescent receptor **1** immobilized on mesoporous silica (**AFMS**) clearly reveal the formation of ordered mesostructures with a hexagonal arrangement of mesoporous channels (Fig. 1). These results indicate that the ordered mesoporous structure of the silica was maintained after attachment of the functional unit.

We examined the effects of the immobilized fluorescent receptor **1** on the pore diameter of the silica solid support material. The nitrogen adsorption–desorption isotherms and the Barrett–Joyner–Halenda (BJH) pore diameters of the periodic mesoporous silica materials and **AFMS** were determined (Fig. 2). In the absence of immobilized receptor **1**, the mesoporous silica had a Brunauer–Emmett–Teller (BET) surface area of 1460 $m^2\ g^{-1}$ and a pore volume of 0.73 $cm^3\ g^{-1}$. In contrast, **AFMS** had ~2-fold lower values of BET surface area (731 $m^2\ g^{-1}$) and pore volume (0.36 $cm^3\ g^{-1}$). Both materials had narrow BJH pore diameters: 7.50 nm for the mesoporous silica material and 6.57 nm for **AFMS**. The smaller surface area and pore diameter for **AFMS** confirm the attachment of receptor **1**. Thermogravimetric analysis indicated that receptor **1** was attached to 22.1 wt% of the **AFMS** (Fig. S1, ESI†).

New bond formation was confirmed by obtaining IR spectra of the mesoporous silica and of **AFMS**. In the mesoporous silica without receptor **1**, IR peaks appeared at 3480, 1633 and 1080 cm^{-1}. In **AFMS**, new peaks appeared at 3241, 2980, 2933, 1670, 1640 and 1540 cm^{-1} (Fig. S2, ESI†). These peaks originated from receptor **1**, indicating that receptor **1** is attached to the surface of the mesoporous silica by a covalent bond.[10,24,25] In addition, strong fluorescence was observed when **AFMS** was irradiated with 420 nm light. As a reference compound, the anthraquinone-based fluorescent receptor **1** immobilized silica particles (**AFSP**) were prepared by the same method. Receptor **1** was found attached to less than 5.3 wt% of the silica particles, due to the small surface area (250 $m^2\ g^{-1}$) of the particle (Fig. S3, ESI†).

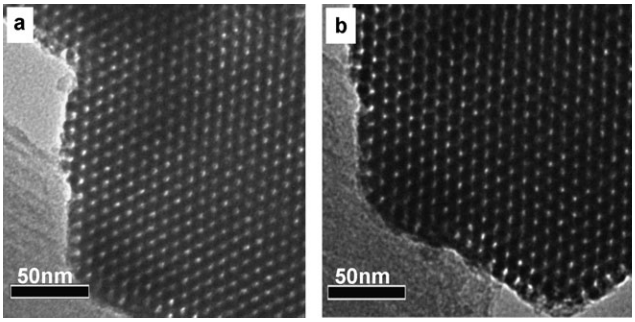

Fig. 1 TEM images of (a) mesoporous silica and (b) **AFMS**.

Anion-binding abilities of AFMS and AFSP

We probed the anion-binding abilities of **AFMS** by monitoring changes in fluorescence upon the addition of F^-, Cl^-, Br^-, I^- or HSO_4^- in water at pH = ~7 (Fig. 3A). In the absence of anions, the anthraquinone moiety attached to the surface of **AFMS** exhibits a strong fluorescence emission band (λ_{max} = 545 nm) when excited at 420 nm. Interestingly, the addition of fluoride ions to a suspension of **AFMS** in water produced the largest decrease in fluorescence intensity (Fig. 3A and Table S1, ESI†). As shown in Fig. 3B, fluoride ions bind to urea N–H protons.[18,19] The fluorescence quenching effect can be explained by reverse photoinduced electron transfer (PET), with one fluoride ion bound to the urea N–H protons behaving as a PET donor.[11–14] The fluorescence emission of the suspension of **AFMS** in water gradually decreased with increasing fluoride anion addition (Fig. 3C). However, as shown in Fig. 3D, the emission was nearly constant above the molar

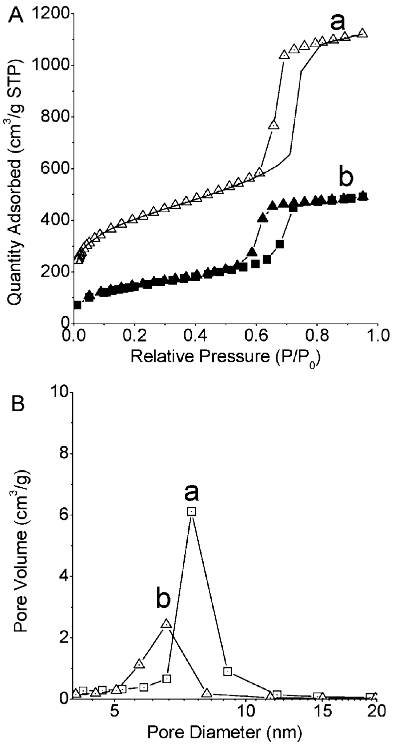

Fig. 2 (A) The nitrogen adsorption–desorption isotherms and (B) Barrett–Joyner–Halenda (BJH) pore diameters of (a) mesoporous silica and (b) **AFMS**.

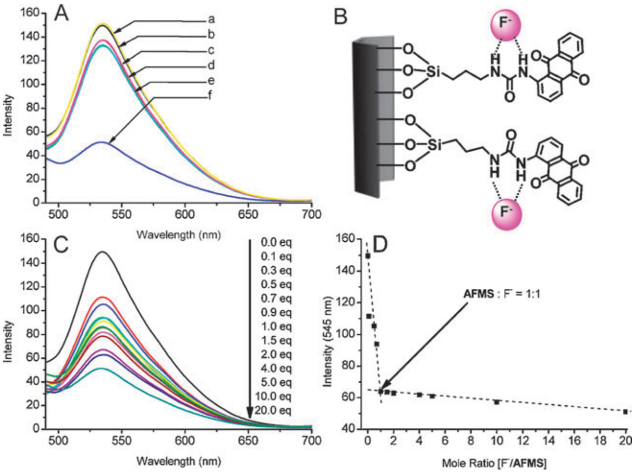

Fig. 3 (A) Fluorescent emission changes in **AFMS** (5.0 mg) upon the addition of (a) no anion, (b) Br^-, (c) HSO_4^-, (d) I^-, (e) Cl^- and (f) F^- ions (20 equiv.) in H_2O (pH = ~7). (B) Binding mode of receptor **1** attached to **AFMS** with fluoride ions. (C) Fluorescent changes in **AFMS** (5.0 mg) upon addition of TBA^+F^- in H_2O. (D) Plot of molar ratios [F^-/**AFMS**] against fluorescent intensity of **AFMS**.

ratio of 1 (fluoride ion : receptor **1**), indicating a 1 : 1 stoichiometry between receptor **1** attached to the mesoporous silica and the fluoride ions. On the other hand, no significant fluorescence changes were observed upon addition of Cl^-, I^-, Br^- or HSO_4^- (Fig. 3A and Table S1, ESI†), suggesting that those anions did not bind to the urea N–H protons of **AFMS**.

In control studies, fluorescence changes in **1** and in mesoporous silica alone (without receptor **1** covalently attached) were measured by the addition of anions. As shown in Fig. S4 and Table S2 (ESI†), the fluorescence of **1** dramatically decreased with the addition of fluoride ions but did not change with the addition of any other anion (Fig. S4a, ESI†). Also, no fluorescence change was observed upon the addition of any anion to mesoporous silica lacking the attached receptor **1** (Fig. S4b, ESI†). In addition, fluorescence changes in anthraquinone was observed by the addition of anions in acetonitrile. As expected, no significant fluorescence changes in anthraquinone were observed by the addition of fluoride ions as well as other anions (Fig. S5, ESI†). These findings indicate that the fluoride ion is selectively bound to the urea group of the receptor **1** unit on the surface of **AFMS**.

The anion-binding abilities of **AFSP** were determined based on changes in fluorescence upon the addition of F^-, Cl^-, Br^-, I^- or HSO_4^- in water (Fig. S6, ESI†). The fluorescence intensity of **AFSP** was 10 times less than that of **AFMS** due to the immobilization of smaller amounts of receptor **1** on silica particles by covalent bonding. This result implies that mesoporous silica with its large surface area is useful as a support material. Although the sensitivity of **AFSP** was much lower than that of **AFMS**, the selectivity of **AFSP** for anions was similar to that of **AFMS**, indicating that the receptor in the solid–liquid phase plays an important role for the selective sensing of specific guest anions.

To explore the interactions of fluoride ions with **1** in the solid state, the FT-IR spectra of free and F^--bound **AFMS** were determined (Fig. S7, ESI†). In both spectra, the characteristic peak of –NH in free **AFMS** appeared at 1540 cm^{-1}. This –NH peak shifted to 1555 cm^{-1} upon complexation with the F^- ion (Fig. S6, ESI†). The intermolecular hydrogen bonding interaction between the fluoride ion and receptor **1** in **AFMS** was further confirmed with the EDX technique (Fig. S8, ESI†). The material contained silicon, carbon, oxygen and fluoride components, supporting the idea that fluoride ions are adsorbed by intermolecular hydrogen bonding interactions with **1**, which is covalently attached to **AFMS**. Also, to confirm the mechanism for the fluorescence change in **AFMS** with fluoride ions, fluorescence changes in **AFMS** were observed upon the addition of OH^-, acetate or benzoate ions as basic anions in water. No fluorescence change was observed upon the addition of any of these anions to **AFMS** (Fig. S9, ESI†). These results indicate that the fluorescence changes in **AFMS** with fluoride ions were induced by intermolecular hydrogen bonding between the urea moiety of receptor **1** and a fluoride ion, but not deprotonation.

Immobilization of receptor 1 on glass slides

To extend the applications of the above-described fluoride-sensing device to a portable chemosensor kit, receptor **1** was immobilized on a glass slide by a sol–gel reaction as shown in Fig. S10 (ESI†). Fig. 4 shows fluorescence images of receptor **1** immobilized on glass plates before and after immersion into solutions of F^- and Cl^-. The fluorescence of receptor **1** immobilized on glass was strong before immersion in a F^- solution (Fig. 4a). As observed for **AFMS** suspensions in the solution studies, the fluorescence of receptor **1** immobilized on a glass slide was quenched when dipped into a F^- solution (Fig. 4c). On the other hand, no significant change in fluorescence was observed in a Cl^- solution (Fig. 4d). This result implies that supported **1** is applicable as a portable fluorescent sensor for detection of F^- in the biological and environmental fields.

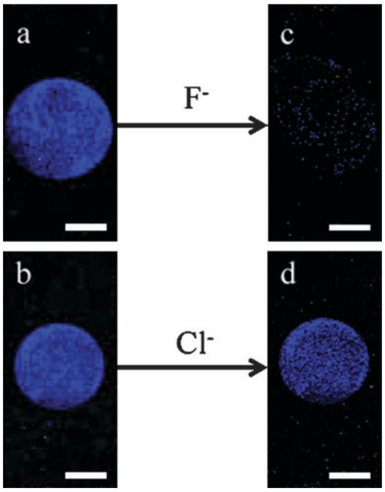

Fig. 4 Fluorescence images of **1** immobilized on a glass slide (a and b) before and after immersion in (c) F^- (10.0 mM) and (d) Cl^- (10.0 mM) solutions.

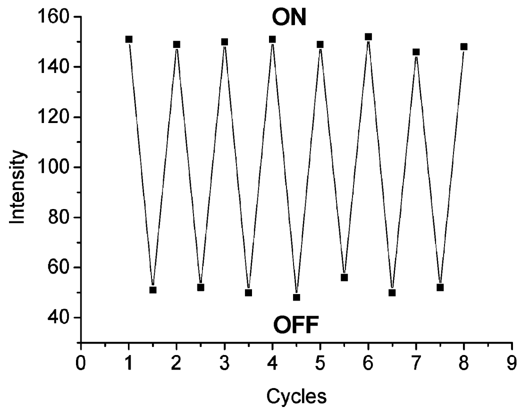

Fig. 5 Plot of the fluorescence of **AFMS** with alternated dipping in 5.0×10^{-5} M aqueous solution of fluoride ions ("OFF") and distilled water ("ON"). The cyclic index is the number of alternating dipping–rinsing cycles, with the vertical axis showing the position of the λ_{max} for the **AFMS** fluorescent maximum.

Fluorescence changes in AFMS with fluoride ions in the presence of other anions such as Cl^-, Br^-, I^- and HSO_4^-

As expected, the fluorescence intensity of **AFMS** gradually decreased with increasing addition of fluoride ions in the presence of other anions, indicating the quantitative binding of the fluoride ion to the urea moiety attached to **AFMS** in the presence of other anions (Fig. S11, ESI†).

Fig. S12 (ESI†) shows standard calibration data (intensity *vs.* [**AFMS**]) for concentrations of fluoride ions. A linear response was observed between 0.50 μM and 10.0 μM with a detection limit of ~0.50 μM. This sensitivity is much higher than that of previously reported spectrophotometric sensors anchored to mesoporous aluminosilicates.[10]

The fluorescence change observed following dipping of **AFMS** into a fluoride ion solution was found to be fully reversible when **AFMS** was rinsed thoroughly with distilled water. Reusability was evaluated by repeated dipping–rinsing cycles, with the **AFMS** fluorescence spectrum being recorded after each step. Typical data are shown in Fig. 5. It is apparent that **AFMS** exhibits excellent reusability because almost no loss in **AFMS** sensitivity was observed after eight repeated dipping–rinsing cycles. Furthermore, the rapid response time of the system, with the fluorescence change being complete within several seconds, allows rapid turnover of sensing function.

Conclusions

The present study has demonstrated that mesoporous silica is an attractive substrate for the development of heterogeneous anion sensors. The pore diameters of mesoporous silica are sufficiently large to allow rapid anion diffusion, resulting in sensing response times of <10 s. The strong binding of receptor **1** to the mesoporous silica prevents the interference of the anion-sensing function by anion ions. The **AFMS** system exhibited excellent sensitivity and selectivity for the fluoride ion. Furthermore, receptor **1** immobilized on a glass slide by a sol–gel reaction showed strong fluorescence. Receptor **1** immobilized on the glass slide only recognized fluoride ions. These results suggest that 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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