

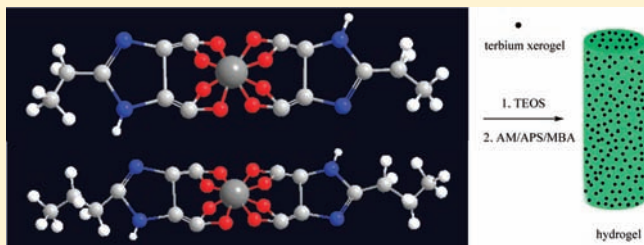
Reversible Terbium Luminescent Polyelectrolyte Hydrogels for Detection of H_2PO_4^- and HSO_4^- in Water

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Supporting Information

ABSTRACT: Polyelectrolyte gels are promising soft networks that can accommodate various guest species and retain liquid nature. The incorporation of two novel silica based terbium complexes ($\text{Tb}(\mathbf{a})_2$ and $\text{Tb}(\mathbf{b})_2$) in the poly(acrylamide) host can exhibit the characteristic green terbium emission in water. More interestingly, we noted that these target materials can selectively recognize H_2PO_4^- (detection limit 10^{-5} M) and HSO_4^- (detection limit 5×10^{-5} M) compared with other anions, such as F^- , Cl^- , Br^- , and I^- . The fluorescence intensity ratios against both anions (H_2PO_4^- and HSO_4^-) concentration all follow the simple linear equations by the least-squares fitting method.



INTRODUCTION

Anions are regarded as essential in various fields of physiology, process control, and environmental analysis.¹ It is urgent for us to design anion-sensitive dependent sensors to fulfill this demand.

In recent decades, lanthanide complexes have attracted a great deal of interest as novel sensing materials not only because of their distinguished photophysical properties but also the high sensitivity to environmental factor including ions, pH, temperature, pressure, and gas.² However, these complexes are very easily deactivated by the O–H oscillator of water because of the high vibration energy. In this sense, lanthanide-based organic–inorganic hybrid materials have been well studied³ and applied as potential anion sensors.⁴ However, the collection and reusability of these kinds of bulk materials, usually as powders, are rather complicated and troublesome. Moreover, it is not easy to retain their luminescence quantum yields during the repeated uses.

Therefore, we tried to develop a new carrier to extend the lifetimes of the sensor materials. Lately, the entanglement of numerous fibers and water molecules has led to the formation of a viscoelastic solid-like network, which is called hydrogel. Particularly the polyelectrolyte gels have attracted much attention in food science, biomedical engineering, pharmaceutical applications, and polymer material and biomaterials science because of their tunable chemical and physical structure, good mechanical properties, high water content, and biocompatibility.⁵ Accordingly, in this paper, the modified ligands 2-ethylimidazole-4,5-dicarboxylic acid (**a**) or 2-propylimidazole-4,5-dicarboxylic acid (**b**) can be easily prepared in two steps based on *o*-phenylenediamine (see the synthetic process of ligand **a** and **b** in Supporting Information Figure S1). These building blocks have been used for the formation of complexes with terbium ions. Then, we designed luminescent $\text{Tb}(\mathbf{a})_2$ or $\text{Tb}(\mathbf{b})_2$ containing xerogels (X_a and X_b) by incorporating terbium complexes to tetraethoxysilane

(TEOS), and the hybrid materials were formed through hydrolysis and poly condensation process. Finally, the xerogels were dispersed in acrylamide monomer, ammonium persulfate (APS), *N,N'*-methylenebisacrylamide and water. The above mixture was polymerized under nitrogen atmosphere, and we obtained novel terbium luminescent hydrogels with strong green luminescence, which are very sensitive to anions (Figure 1; further synthetic details were described in Supporting Information). They are elastic but with enough mechanical strength and can be recycled more than 10 times, in comparison with conventional luminescent powders. It was noticed that these smart materials not only gave unique quenching effects to H_2PO_4^- but also to HSO_4^- . We regarded that not just the hydrogen bonding interaction but also the neutralization between anions and ligands resulted in the “on-off” process.

RESULTS AND DISCUSSION

Crystal of ligand **a** was grown by recrystallization in water. The structure was elucidated by single-crystal X-ray diffraction and is shown in Supporting Information Figure S2a. Its bond lengths and angles information were presented in Supporting Information Table S1. We discovered that there is intramolecular hydrogen bonding between two carboxyl groups. It was found that it forms layer-like structure through the hydrogen bond together with water molecular and intermolecular hydrogen bonding interactions (Supporting Information Figure S2b). We also can observe intermolecular hydrogen bond between nitrogen of imidazole and hydrogen of carboxyl moiety. More importantly, the formation of 3D structure can be observed through intermolecular interaction (Supporting Information Figure S2c). All hydrogen

Received: November 27, 2010

Published: March 02, 2011

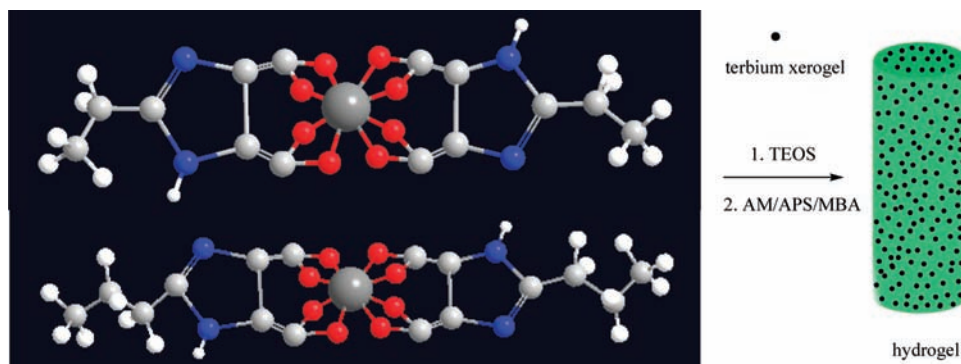


Figure 1. Design strategy for terbium luminescent hydrogels (AM, acrylamide; APS, ammonium persulfate; MBA, *N,N'*-methylenebisacrylamide; TEOS, tetraethoxysilane).

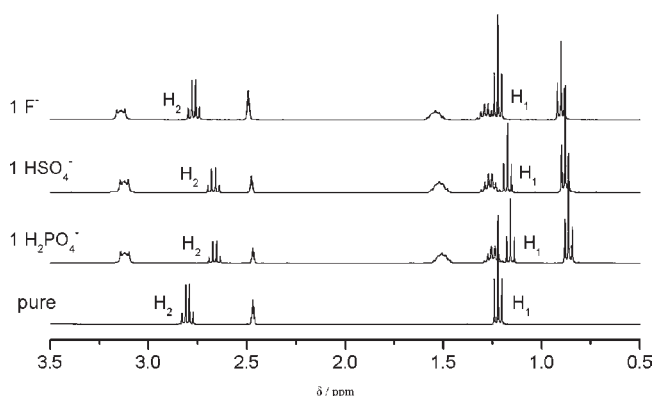


Figure 2. ^1H NMR spectra measured by titration of a DMSO- d_6 solution of pure **a** (1 mM) with 1 equiv of $[\text{Bu}_4\text{N}]^+\cdot\text{H}_2\text{PO}_4^-$, HSO_4^- , and F^- .

bonding data are given in Supporting Information Table S2. Unfortunately, we failed to prepare the single crystal of the terbium complexes.

^1H NMR spectroscopy was applied to investigate the guest–host interaction between ligands and anions. Addition of 1 equiv of dihydrogen phosphate, the protons (H_2 and H_1) of the ligand **a** gives rise to remarkable shifts toward upfield (from 2.80, 1.22–2.61, and 1.12 ppm) in Figure 2. Similar shifts can be observed by addition of 1 equiv of hydrogen sulfate ions, H_2 and H_1 shifted from 2.80 and 1.22 to 2.60 and 1.11 respectively (Figure 2). The change of proton signals is explained not only in terms of hydrogen-bonding but also of acid–base interaction between the imidazole-ring NH of **a** and anions. Additionally, we also found the proton signal shifted upfield while adding 1 equiv of fluoride ions, which suggests the existence of hydrogen-bonds between fluoride and ligand (Figure 2). We tried analogous NMR experiments of Cl^- , Br^- , and I^- , but signal changes in each proton (data not shown) do not occur when adding the previous ions to ligand **a**. Similar phenomenon can be seen when adding different anions to ligand **b** (Supporting Information Figure S3).

The luminescent binary complexes $\text{Tb}(\mathbf{a})_2$ and $\text{Tb}(\mathbf{b})_2$ exhibited very strong green emission (Supporting Information Figure S4). But the light will be completely quenched by the O–H oscillator of the water when dissolved in water (Supporting Information Figure S4). Consequently, to protect it from water, we used mild sol–gel technique to prepare two silica xerogels and their photo/thermal stabilities were improved. Their emission

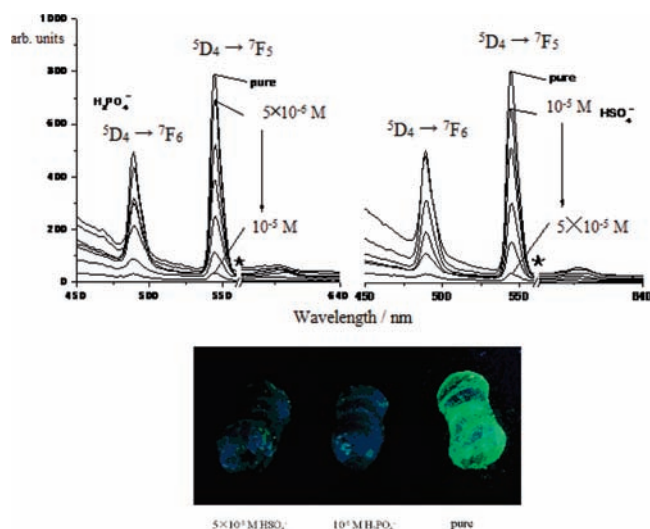


Figure 3. Emission spectra of CM_a and CM_b excited at 286 nm upon addition of $6\text{--}10 \times 10^{-6}$ M of $[\text{Bu}_4\text{N}]^+\text{H}_2\text{PO}_4^-$ (left) and $0\text{--}5 \times 10^{-5}$ M of $[\text{Bu}_4\text{N}]^+\text{HSO}_4^-$ in water. Photo of CM_a and after immersion in 10^{-5} M of $[\text{Bu}_4\text{N}]^+\text{H}_2\text{PO}_4^-$ and 5×10^{-5} M of $[\text{Bu}_4\text{N}]^+\text{HSO}_4^-$ (down). (★: There are multiple scattering artifacts around 572 nm and we have removed them.)

and excitation spectra in water can be seen in the Supporting Information Figure S4. Because hydrogels are promising for tactile pattern sensing in biomedical or environmental uses according to their excellent biocompatibility, with the aim of improving terbium materials sensing performance in water, we introduced those xerogel materials into polymeric hydrogel and fabricated two novel composite materials (CM_a and CM_b) as sensory materials to detect anions.

The overall terbium luminescence changes of CM_a upon titration of dihydrogen phosphate are demonstrated in Figure 3 (left). When emission wavelength was fixed at 545 nm (the excitation spectrum shows a broad band from 240 to 320 nm (Supporting Information Figure S5)). The emission spectra can be interpreted as follows: the excited $^5\text{D}_4 \rightarrow ^7\text{F}_j$ transitions exhibit four main components for $J = 6, 5, 4,$ and 3 respectively. Upon addition of dihydrogen phosphate from 5×10^{-6} to 10^{-5} mol/L, the luminescence of CM_a decreased gradually and quenched at last. Interestingly, the correlation of luminescence intensity at 545 nm versus dihydrogen phosphate concentration fit well with the simple linear function $y = -0.1685x + 1.6838$ by the least-squares fitting

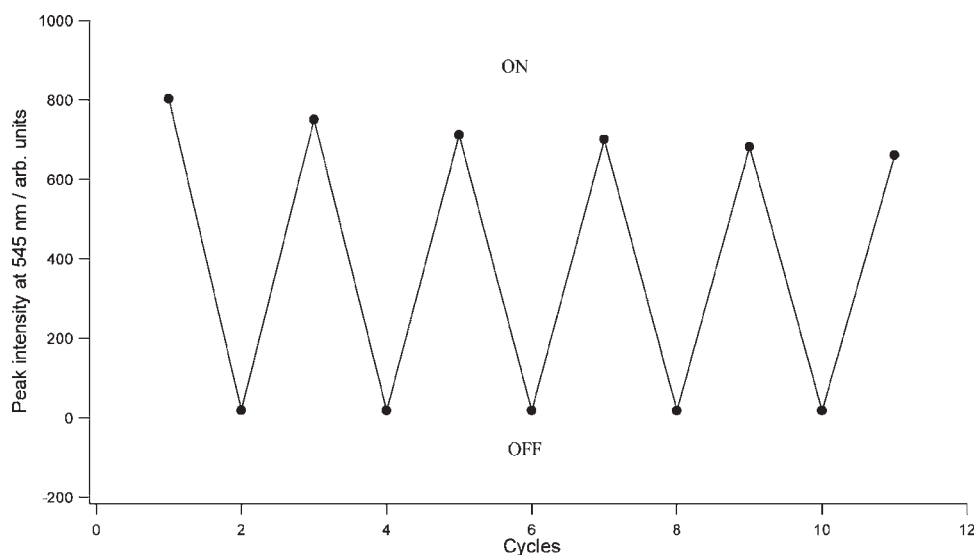


Figure 4. Graph of the fluorescence peak intensity of terbium (polymeric hydrogel containing xerogels X_a) with alternate dipping into 10^{-5} M of dihydrogen phosphate anions in water.

method and give a correlation coefficient (R^2) of >0.99 (Supporting Information Figure S6 left). In an analogous fashion, the luminescence of CM_a declined sharply with the concentration of hydrogen sulfate anions increasing from 10^{-5} to 5×10^{-5} (Figure 3 right). The relationship between the intensity of emission at 545 nm, and the concentration of hydrogen sulfate anions also follows the simple linear equation $y = -0.0199x + 1.007$ and the coefficient correlation $R^2 = 0.9952$ (Supporting Information Figure S6, right). Consequently, we could observe the sharp and distinguished changes by naked eyes under the excitation of the ultraviolet light (Figure 3). Similar experiments were titrated by F^- , Cl^- , Br^- , or I^- anions of corresponding $[Bu_4N]^+$ salts (10^{-3} mol/L) (Supporting Information Figure S7). No pronounced reduction (less than 20%) could be observed in the fluorescent spectra. We collected the emission spectra data of CM_b toward the above anions and discovered that the phenomenon was very similar to CM_a (Supporting Information Figure S8). Hence, we could conclude that this pattern of materials can be used as chemical sensors specific for $H_2PO_4^-$ and HSO_4^- . These sensing materials were a little more sensitive to dihydrogen phosphate than to hydrogen sulfate.

We studied the reusability of the luminescent materials for anion sensing (Figure 4). Repeated experiments were performed by rinsing the terbium luminescent hydrogels with plenty of water for three times. In this way, the characteristic emission of terbium ion was nearly recovered. So, it can be used again as sensing material as the original one. The composite materials exhibit only 10% luminescence intensity reduction after ten repeated cycles. Whereas $Tb(a)_2$ containing xerogel gave more than 85% reduction because of the repeated recognition processes (Supporting Information Figure S9). Therefore, this luminescence response opens a new possibility for rapid tetrahedral type anions recognition in aqueous environment.

Theoretically speaking, the changes of NMR signals proved the existence of hydrogen bond forces between $H_2PO_4^-$ (or HSO_4^-) and NH moieties of imidazole-ring. Furthermore, these two anions can neutralize the NH because of their acidity.⁶ In contrast to small anion such as fluoride, $H_2PO_4^-$ (or HSO_4^-) can break the coordination interaction by expanding the distance

between the ligand and metal ion in term of their tetrahedral structure and steric hindrance. In this way, they resulted in the fluorescence quenching of ligands, which led to the termination of the energy transfer between ligands and terbium ions.

CONCLUSIONS

In an effort to fabricate advance luminescent sensors, we encapsulated terbium luminescent silica xerogels into polymeric hydrogel, developed two novel composite materials specific to tetrahedron type anions. To the best of our knowledge, this is the first trial that the soft material exhibits high selective emission quenching to $H_2PO_4^-$ and HSO_4^- . It is worthy to point out that these materials could be used for more than ten times. Their excellent properties have paved the way for future practical use in biological and environment science as anions probes.

ASSOCIATED CONTENT

S Supporting Information. Experimental details, figures showing synthesis processing of a and b, crystal structure of ligand a, 1H NMR spectra, emission and excitation spectra, intensity ratio, fluorescence peak intensity, and ^{13}C NMR spectra, and tables showing bond lengths and angles and hydrogen-bonding interactions. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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ACKNOWLEDGMENT

Q.M. appreciates National Natural Science Foundation of China (21002035) and start funding of South China Normal University G21117. The authors thanks for the kind assistance provided by Dr Y. Liu (Kumamoto University, Japan) for the preparation of polyelectrolyte gels.

■ REFERENCES

- (1) (a) Anzenbacher, J. P.; Jursíková, K.; Sessler, J. L. *J. Am. Chem. Soc.* **2000**, *122*, 9350–9351. (b) Atkinson, P.; Bretonniere, Y.; Parker, D. *Chem. Commun.* **2004**, 438–439.
- (2) (a) Bunzli, J.-C. G.; Piguet, C. *Chem. Soc. Rev.* **2005**, *34*, 1048–1077. (b) Parker, D. *Coord. Chem. Rev.* **2000**, *205*, 109–130. (c) Murray, N. S.; Jarvis, S. P.; Gunnlaugsson, T. *Chem. Commun.* **2009**, 4959–4961. (d) Yamada, T.; Shinoda, S.; Tsukube, H. *Chem. Commun.* **2002**, 1218–1219. (e) Wang, Q. M.; Tamiaki, H. *J. Photochem. Photobiol. A* **2009**, *206*, 124–128. (f) Gulgas, C. G.; Reineke, T. M. *Inorg. Chem.* **2008**, *47*, 1548–1559.
- (3) (a) Binnemans, K. *Chem. Rev.* **2009**, *109*, 4283–4374. (b) Franville, A.-C.; Zambon, D.; Mahiou, R. *Chem. Mater.* **2000**, *12*, 428–435. (c) Dong, D. W.; Jiang, S. C.; Men, Y. F.; Ji, X. L.; Jiang, B. Z. *Adv. Mater.* **2000**, *12*, 646–649.
- (4) Wang, Q. M.; Tan, C. L.; Chen, H. Y.; Tamiaki, H. *J. Phys. Chem. C* **2010**, *114*, 13879–13883.
- (5) (a) Oha, J. K.; Drumright, R.; Siegwart, D. J.; Matyjaszewski, K. *Prog. Polym. Sci.* **2008**, *33*, 448–477. (b) Friedman, M. *J. Agric. Food Chem.* **2003**, *51*, 4504–4526.
- (6) dos Santos, C. M. G.; Fernandez, P. B.; Plush, S. E.; Leonard, J. P.; Gunnlaugsson, T. *Chem. Commun.* **2007**, 3389–3391.