

Recognition of H_2PO_4^- and Cu^{2+} in Water by Luminescent Terbium Silica Xerogel

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Abstract Terbium silica hybrid material with imidazole ring that can be emissive in water has been designed and showed host-guest interactions with specific ions (cations and anions). In detail, we studied the sensing abilities of this material by addition of the anions H_2PO_4^- , HSO_4^- , F^- , Cl^- , Br^- and I^- to water suspension of the derived powders. Only dihydrogen phosphate resulted in the quenching of the lanthanide luminescence (detection limit 10^{-5} M). The same way was found in Cu^{2+} ions which also gave rise to luminescence quenching (detection limit 10^{-5} M). More interestingly, luminescent sol-gel films were successfully prepared by the same materials and exhibited emission responses to H_2PO_4^- and Cu^{2+} . For the sake of improving its mechanical property, the robust and flexible inorganic/PMMA hybrid material with sensing capability was also developed for future use.

Keywords Luminescent · Dihydrogen phosphate · Copper ion · PMMA

Introduction

The detection of cations or anions is essential to life science, biological processes and industrial treatment for harmful pollutants or diagnostic analysis [1–4]. Especially

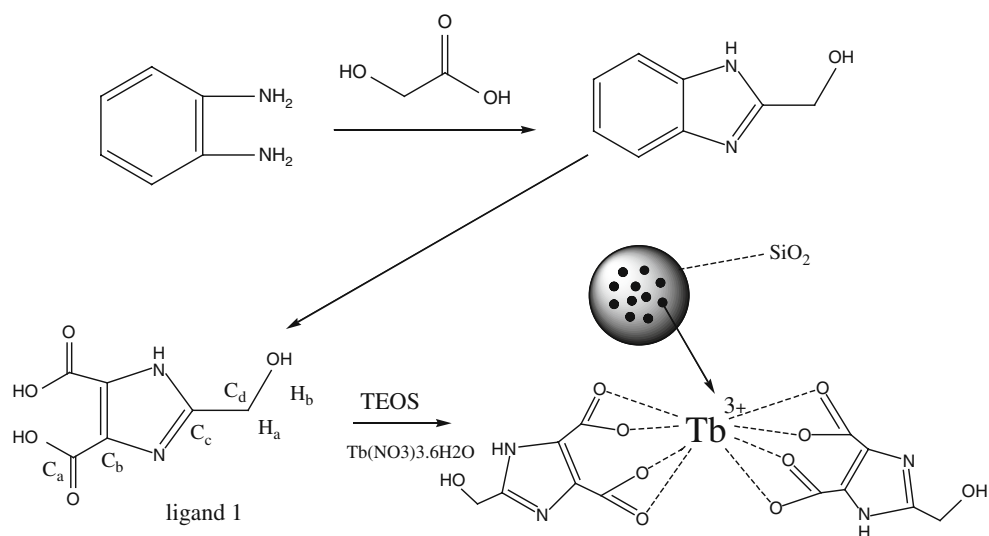
sensors for dihydrogen phosphate which is utmost important in health and environmental protection have been extensively explored [5, 6]. In the field of cation chemistry, copper ion that is terribly deleterious to human health and environment has also attracted much attention, consequently, several specially designed ion sensors have been reported [7, 8].

Most of the published results concerning the sensors were focused on fluorescent organic molecules or polymers [9]. As an innovative way to be readily distinguished by time-gated image, lanthanide complexes were chosen as they show several excellent properties such as long lifetimes, sharp emission peaks and large Stokes shifts. Moreover, the luminescence of lanthanide complexes is very sensitive to the environment factors, including the temperature, oxygen and pH [10]. Particularly some complexes exhibited highly selectivity to specific ions, this luminescence signaling effects have paved the way for the development of chemical sensors. A series of papers have been reported by Parker [11], Gunnlaugsson [12, 13] and Tsukube [14–16] et al. However, lanthanide complexes are very easily deactivated by the O-H oscillator of water because of its high vibration energy. Recently, lanthanide-based organic-inorganic hybrid materials have been well studied and they show excellent properties in the competitive media [17, 18]. Consequently, in this paper, we used the 2-hydroxymethylimidazole-4,5-dicarboxylic acid as the chosen ligand, which only needs two steps of synthesis (Fig. 1). The selected ligand was coordinated to terbium ions and was encapsulated into the inorganic host tetraethoxysilane (abbreviated as TEOS). In view of the energy migration process, aromatic acids and their derivatives were extensively studied and corresponding terbium coordination polymers were constructed [19]. However, here we designed the light-harvest ligand using the imidazole-ring and prepared the strong green emission material. It is

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Fig. 1 Synthesis processing of hybrid material



interesting to find that the luminescent hybrid material was not influenced by the vibration of hydroxyl groups, which means that it can be applied in aqueous environment. More importantly, upon addition of different anions such as H₂PO₄⁻, HSO₄⁻, F⁻, Cl⁻, Br⁻ and I⁻, it can recognize dihydrogen phosphate anion by quenching in water. We considered that the hydrogen bonding interaction between the dihydrogen phosphate anion and ligand resulted in the quenching of the luminescence. Moreover, green emission quenching can be observed due to copper ion addition. Additionally, sol-gel derived films and polymeric based transparent thin films that give rise to luminescent response in the presence of dihydrogen phosphate and copper ion were also fabricated.

Experimental Section

Tb₄O₇ (99.9%) was purchased from Shanghai yuelong company. Glycolic acid (99%), Tetraethoxysilane and o-phenylenediamine (AR) were provided by Shanghai chemicals. Spectrophotometric grade dimethyl sulfoxide (DMSO ≥ 99.9%) was purchased from Sigma-Aldrich. All the other reagents were used as received and without further purification. ¹H-NMR and ¹³C-NMR spectra were recorded at 293 K using Varian 400 (400 MHz) with tetramethyl silane (TMS) as an internal standard. Excitation and emission spectra were measured using a Agilent 8453 spectrophotometer with a 150 W xenon lamp as the light source. The scan speed was fixed at 300 nm/min. Both excitation and emission slit widths were 5.0 nm. The fluorescence images were taken by a Nikon Eclipse TS100 inverted fluorescence microscope system (Japan), equipped with a 50 W mercury lamp source. Liquid chromatography-mass spectrometry (LC-MS) was measured by Thermo

Finnigan Deca XP Max equipment. Thermogravimetric analysis was carried out by a STA409PC system under air at a rate of 10° C/min, Fourier transform infrared (FT-IR) spectra were collected by Perkin-Elmer 2000 spectrophotometer in the range of 4000–400 cm⁻¹ using the KBr pellet technique. Nitrogen adsorption/desorption isotherms were measured at the liquid nitrogen temperature, using an ASAP2020 analyzer. Surface areas were calculated by the Brunauer–Emmett–Teller (BET) method and pore size distributions were evaluated from the desorption branches of the nitrogen isotherms using the Barrett–Joyner–Halenda (BJH) model. The synthetic and preparation details were given in supporting information.

Results and Discussion

In Fig. S2, the IR spectra for ligand **1** (a), TbL₂ (b) and the hybrid material containing TbL₂ (c) can be observed. The intense band at 1920 cm⁻¹ is attributed to C=O vibration in COOH groups. The broad band located between 2400 to 2800 cm⁻¹ may be due to the intermolecular hydrogen bonding interactions. The strong bands at 3535 and 3446 cm⁻¹ correspond to –OH stretching vibrations (Fig. S2a) [20]. In Fig. S2b, the formation of coordinated bonds between the carboxylic groups and the terbium ion is evidenced by the bands located at 1581 and 1384 cm⁻¹ originating from the asymmetric (ν_{as}) and symmetric (ν_s) stretching vibrations of carboxylate. In addition, the previous COOH signal at 1920 cm⁻¹ for free ligand completely disappeared. This fact firmly indicated that the ligand takes part in the coordination with terbium ions. The difference between ν_{as} and ν_s is 197 cm⁻¹, showing that the ligand was coordinated with Tb³⁺ through oxygen atoms of carboxyl

groups [18, 20]. Due to the sol-gel hosts, it can be observed that the formation of the Si-O-Si framework is supported by the bands situated at 1066 cm^{-1} in Fig. S2c [19].

$^1\text{H-NMR}$ spectroscopy was applied to investigate anions binding affinity to ligand **1**. Based on addition of 2 equiv. dihydrogen phosphate ions, the H_a protons shifted to upfield (from 4.56 to 4.32 ppm) (Fig. 2), suggesting that **1** binded to dihydrogen phosphate ions in terms of hydrogen interactions to the imidazole-ring NH. Similarly, we also found the proton shifted to upfield while addition of 2 equiv. fluoride and sulfate hydrogen anions (Fig. S3), again proving the H-bonding might exist between imidazole moiety and fluoride anion. We tried analogous NMR experiments of Cl^- , Br^- and I^- , but **1** did not give rise to signal changes in each proton (data not shown).

The luminescent binary complex TbL_2 show very strong green color emission, its emission spectra can be seen in Fig. 3. But when it was dispersed into water, the light will be completely quenched by the O-H oscillator of the water. Hence, in order to improve the photo-stability of the complex, we incorporated the complex into the inorganic host (TEOS), developed a more stable hybrid material, which also have an intense green color emission (Fig. 3). When emission wavelength was fixed at 545 nm, the excitation spectrum shows a broad band covering from 250 to 320 nm with two peaks at 275 and 300 nm (Fig. S4).

As demonstrated in Fig. 4, once the hybrid powders were diffused in water (1 $\mu\text{g/ml}$), they could be very sensitive to ion interactions. When emission wavelength was fixed at 545 nm, the excitation spectrum shows a sharp peak at 289 nm, which was not similar to the solid state (Fig. S5). The emission spectra can be interpreted as follows: the excited $^5\text{D}_4 \rightarrow ^7\text{F}_J$ transitions exhibit five main components for $J=6, 5, 4$ and 3 respectively. After addition of 10^{-6} mol/L dihydrogen phosphate anions, green emission from terbium ions decreased a little. When $5 \times 10^{-6}\text{ mol/L}$ dihydrogen phosphate anions were added, the characteristic emission of the terbium complex was quenched half. Further quenching was seen in the fluorescence emission spectra upon $8 \times 10^{-6}\text{ mol/L}$ of dihydrogen

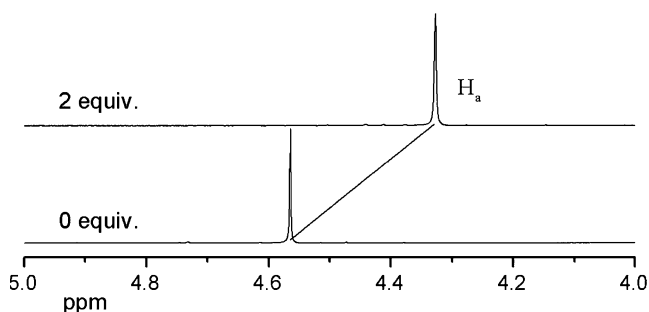


Fig. 2 $^1\text{H-NMR}$ spectra measured by titration of a $\text{DMSO-}d_6$ solution of pure **1** (1 mM) with 2 equiv. of $[\text{Bu}_4\text{N}] \text{H}_2\text{PO}_4$

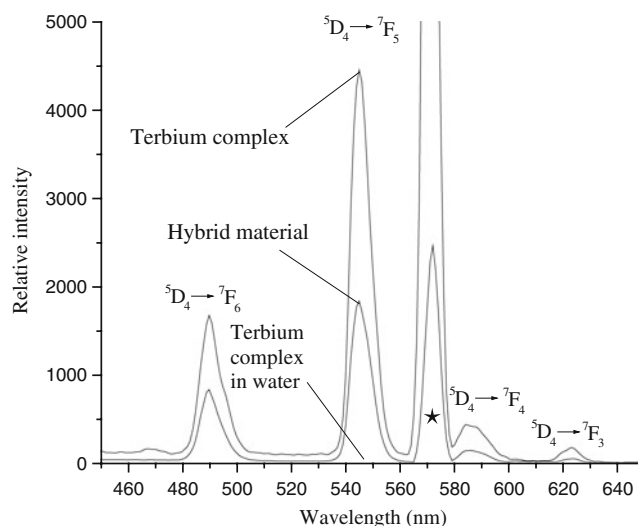


Fig. 3 Emission spectra of TbL_2 and the hybrid material powder excitation at 289 nm (★: second order effect)

phosphate anions addition. When the concentration of the dihydrogen phosphate ions increased to 10^{-5} mol/L , the luminescence of the hybrid material was almost completely quenched (Fig. 4). Interestingly, the terbium emission decreases at a rate that follows the linear function upon the addition of H_2PO_4^- (Fig. S6). Analogous experiments were applied by HSO_4^- , F^- , Cl^- , Br^- , I^- and 10^{-4} mol/L titration of corresponding $[\text{Bu}_4\text{N}]$ salts were measured by emission spectroscopy (Fig. S7). Less than 20% reduction in intensities could be observed in the emission spectra by halogen anions. The hydrogen sulfate anions could decrease the luminescence to 40%, but we still can detect the remaining green luminescence by naked eyes. Therefore, the emission investigations confirmed that the present hybrid material can

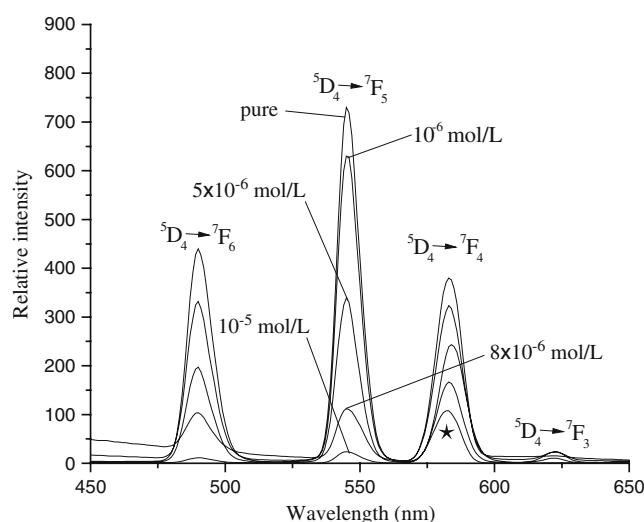


Fig. 4 Emission spectra of hybrid material (1 $\mu\text{g/ml}$ in water) excited at 289 nm upon addition of $0\text{--}10^{-5}\text{ M}$ of $[\text{Bu}_4\text{N}] \text{H}_2\text{PO}_4$ (★: second order effect)

be applied as a chemical sensor specific for dihydrogen phosphate anions. Compared to fluoride anions, it is estimated that the bulky tetrahedral anion (H_2PO_4^-) is acidic and may occur deprotonation with NH group of adjacent imidazole rings, thus making the luminescence quenching effect was more sensitive for H_2PO_4^- .

We also investigated its sensing abilities to ion by addition of Cu^{2+} , Pd^{2+} , Cd^{2+} , Co^{2+} and Mn^{2+} . After addition of 10^{-6} mol/L copper ion, the luminescence of hybrid material decreased a little. Green emission from terbium ions decreased with the addition the concentration of Cu^{2+} . When the concentration of the copper ion increased to 10^{-5} mol/L, its luminescence almost completely quenched (Fig. S8). As a consequence, we could see the quenching of the green luminescence by naked eyes (Fig. S9). The terbium emission also decreases at a rate that follows the linear function upon the addition of Cu^{2+} (Fig. S10). Analogous experiments were applied by Pd^{2+} , Cd^{2+} , Co^{2+} , Mn^{2+} and 10^{-5} mol/L titration of corresponding inorganic salts were measured by emission spectroscopy (Fig. S11). Almost no changes could be observed in the emission spectra. Therefore, the fluorescence investigations proved that the present hybrid material can be also applied as a chemical sensor to copper ion.

According to the description of reference [7], we regard that the addition of the dihydrogen phosphate not only can give rise to hydrogen bonding to the imidazole-ring NH, which have been proved by the NMR spectra above, but also can destroy the coordination interaction by expanding the distance between the ligand and metal ion to a great extent. Furthermore, it can neutralize the NH because of its acidity. In this case, it resulted in the quenching process. In terms of the reference [8], we regarded that the copper ion,

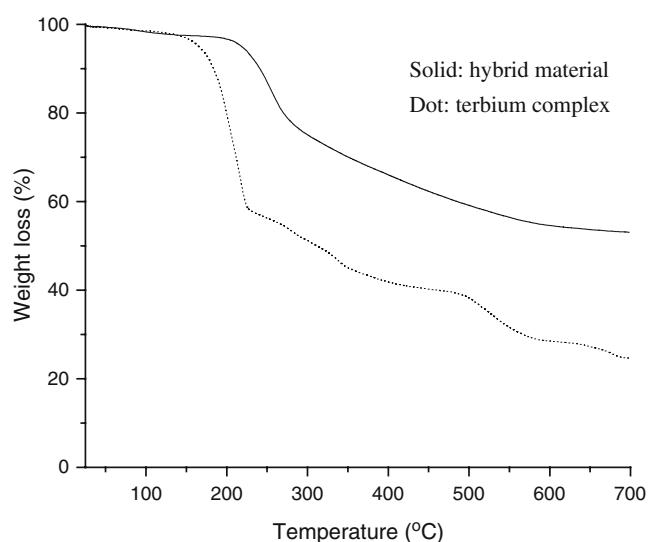


Fig. 5 Thermogravimetric analysis traces of terbium complex and hybrid material

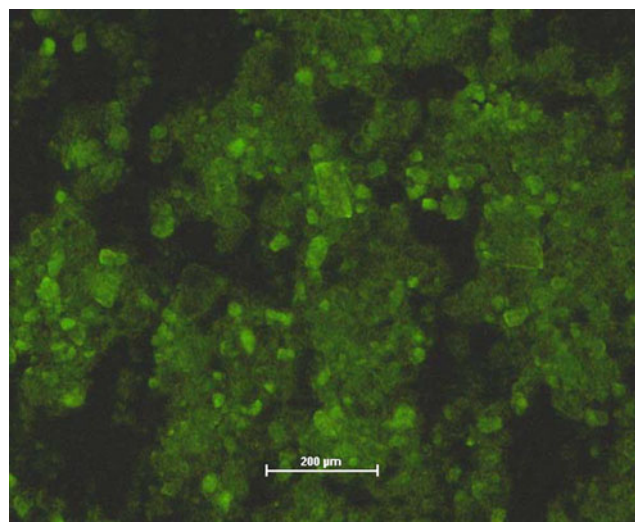


Fig. 6 Fluorescence microscope of hybrid material

because of the coordination between copper ion and imidazole-N, could give rise to the fluorescence quenching of the complex. The copper ion could dissipate terbium luminescence due to the overlap between the emission spectra of terbium ions and the absorption spectrum of Cu^{2+} .

Unfortunately, we found that this material just can recycle use for 2–3 times, the luminescence was almost entirely disappeared and can hardly be recovered. We notice that the powder is not very easy to recollect for recycle use. We therefore set out to develop more convenient devices by coating the sol-gel material on the glass substrate and prepared the thin film as an efficient tool as anion sensor. As show in the Fig. S12, strong green luminescence can be observed by naked eyes when excitation at 254 nm by ultraviolet lamp (the left one). We can see obviously that the luminescence quenched when it is dipped in 10^{-5} M dihydrogen phosphate or copper ion solution for 1–2 h. Similarly to the powder, it has no responses when immersed by the other anions at the same concentration (Fig. S13). This film can be re-used nearly ten times as a tool in real life, such as environmental analysis (Fig. S14). It is a significant progress for the ion sensor in practical use. But the responsive time of the thin film (1 h) to the dihydrogen phosphate anion was longer than the powder material (2 s). We thought that it is mainly due to the thickness of the film, when immersed into the ion solution, the surface luminescence of the thin film was quenched immediately. However, the inside thin film still gives rise to green emission. And it needs some time for the ions penetrated into the inside.

However, the above sol-gel film was easy cracked in terms of the fragile properties of the inorganic matrices. In order to overcome this shortcoming, we introduced the hybrid material powder into the polymeric host (PMMA) and developed a novel transparent thin film for ions sensor.

Within our expectation, this thin film also can give rise to emission quenching by dihydrogen phosphate and copper ion. In Fig. S15, strong green luminescence can be observed by naked eyes when excitation at 254 nm by ultraviolet lamp (the left one). We can see obviously that the luminescence turn-off when it was dipped in 10^{-5} M dihydrogen phosphate and copper ion solution for 3–5 min (the middle and right one respectively), which is more sensitive than the sol-gel thin film. The recycle experiments can be conducted at least eight times. To the best of our knowledge, it is the first time that this kind thin film was designed and used as sensing material. But, we discovered that it is easy to aggregate together and has to work in mixed solvent (DMSO and water) because of its hydrophobicity. The excellent materials for ion recognition that can combine various advantages of organic and inorganic hosts are still in progress.

Figure 5 shows the variation in the mass of the samples over temperature. We could clearly observe that terbium complex containing hybrid materials gave a much higher thermal stability based on pure complex. We recognized that when the complex incorporated into the TEOS, the inorganic host matrix will protect the complex and increased its decomposition temperature, so the inorganic host matrix is more stable than the coordination complex.

N_2 adsorption-desorption isotherms were recorded to assess the textural properties of the hybrid material (Fig. S16). The specific area and the pore size are calculated by the Brunauer-Emmett-Teller (BET) method and Barrett-Joyner-Halenda (BJH) model, respectively. It displays a surface area (S_{BET} 102.65 m^2/g , pore volume 0.387 cm^3/g , pore diameter 15.10 nm) without the construction of the amphiphilic surfactant template such as hexadecyl trimethylammonium bromide. The above small pores might be useful for the carrier of particular substances.

In addition, in order to determine the complex loading within the hybrid materials, we studied its localization through fluorescence microscopy (Fig. 6). The characteristic green luminescence image clearly demonstrates the distribution of terbium complex in SiO_2 matrices. These results strongly suggest the green emissive species were widely dispersed in the host. The dense packing of the granules were very homogenous over the entire range and assembled into large aggregates with diameter about 10–30 μm .

Conclusions

With the aim of developing luminescent sensor work in water, we developed novel hybrid materials as solid chemical sensor used in the heterogeneous solid–liquid phase specific to dihydrogen phosphate and copper ion. Because of the inorganic host well protected the terbium

complex from water, which made it more possible for practical use. The unique green emission peak of the present terbium complex was significantly quenched through the hydrogen-bonding interaction between ligand **1** and H_2PO_4^- . And upon addition of copper ion, the quenching of the luminescence of hybrid material also can be observed. However, the addition of excess amounts of HSO_4^- , F^- , Cl^- , Br^- and I^- or Pd^{2+} , Cd^{2+} , Co^{2+} and Mn^{2+} respectively exhibited minor changes of terbium emission bands. Sol-gel thin film and hybrid material containing polymeric thin film were designed and prepared for ions sensor. We found that both of them could detect dihydrogen phosphate and copper ion and used as convenient sensing tool respectively. Although the detection limit is considered as not so satisfied in the competitive media under the current situation, this new structural motives and preliminary attempt are still to be extensively explored.

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