

Luminescent Cu^{2+} Probes Based on Rare-Earth (Eu^{3+} and Tb^{3+}) Emissive Transparent Cellulose Hydrogels

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Abstract Cellulose hydrogels are biodegradable materials that can be applied as accommodating hosts for various species. Here we report the preparation of novel thin films based on luminescent cellulose hydrogels. The spectroscopic behavior of these soft materials and their sensing effects are investigated. Interestingly, we found that these films only give selective signal changes in the presence of Cu^{2+} in water in comparison with Na^+ , K^+ , Ag^+ , Mn^{2+} , Co^{2+} , Ca^{2+} , Cd^{2+} , Hg^{2+} , Pd^{2+} , Mg^{2+} , Ni^{2+} , Fe^{2+} , and Fe^{3+} . High visible-light transmittance and good flexibility for these films can be observed. More importantly, the thermal stability of rare-earth complexes could be significantly enhanced in aqueous solution as result of the protection by hydrogel matrix.

Keywords Copper · Luminescent · Cellulose · Films · Probe

Introduction

Cellulose is one of most abundant natural, bio-renewable and environmentally friendly material on earth [1, 2]. Products derived from it have been widely applied in our daily

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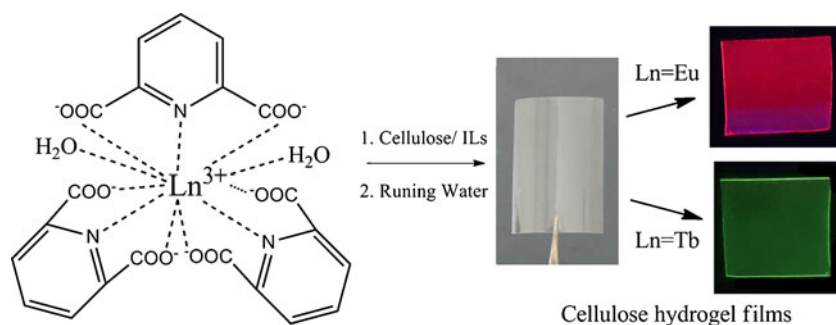
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life, such as fiber, paper, membrane, polymer, and paints industries. Cellulose hydrogels, a kind of biodegradable polymers, have attracted increasingly attention as the result of the environmental contamination caused by synthetic polymers [3–5]. Therefore, several methods for preparing hydrogels from cellulose have been developed [6–8].

The design and synthesis of fluorescence probes capable of showing signal response to specific metal ions has gained a great deal of interests due to the essential roles they played in life science, biological processes and industrial treatment in last decades [9, 10]. More specifically, it has been found that rare-earth luminescence-based complexes have many potential applications as optical sensors for detection of various analytes [11–16]. Hence, the development of lanthanide luminescence-based sensors for cations measurement has become a newly emerging field in recent years [17, 18]. However, most of these works were focused on lanthanide complexes. Recently, emissive complexes were introduced into host matrix, such as silica or polymer [19–21], and their potential applications can be significantly enhanced. However, most of these materials are non-biodegradable and toxic to human being. These weaknesses strictly restricted their practical usages in real life.

As a consequence, cellulose hydrogel was used as a new carrier to accommodate lanthanide complexes owing to their outstanding properties mentioned above. Two luminescent rare-earth complexes ($\text{Eu}(\text{DPA})_3$ and $\text{Tb}(\text{DPA})_3$) were assembled into cellulose hydrogel and two transparent thin films with characteristic emission were synthesized as metal ions receptors (Fig. 1). The target materials are transparent films and possess nice flexibility. Interestingly, characteristic lanthanide luminescence of the two films were quenched upon exposure them to Cu^{2+} but not Na^+ , K^+ , Ag^+ , Mn^{2+} , Co^{2+} , Ca^{2+} , Cd^{2+} , Hg^{2+} , Pd^{2+} , Mg^{2+} , Ni^{2+} , Fe^{2+} , and Fe^{3+} . Moreover, enhanced thermal

Fig. 1 Synthetic Scheme for rare-earth complexes loaded cellulose hydrogel thin films. Photo: Gel-1 (Eu) and Gel-2 (Tb) excited by UV light at 254 nm



stabilities of these materials can be observed compared with the complexes. To our knowledge, it has not been reported that luminescent cellulose films presented emission responses towards copper ions.

Experimental Section

General All the starting materials were obtained from commercial suppliers and used as received. Fluorescence spectra were measured on Agilent 8453 spectrophotometer and Edinburgh FLS920 spectrometer. Fourier transform infrared (FT-IR) spectra were collected through Perkin-Elmer 2000 spectrophotometer in the range of 4000–400 cm^{-1} by grinding potassium bromide (KBr) and samples (the concentration of the sample in KBr is 1 %) as transparent pellets. Thermogravimetric analysis was carried out on a STA409PC system under air at a rate of 10 $^{\circ}\text{C}/\text{min}$. SEM was measured using a ZEISS Ultra 55 scanning electron microscope.

Synthesis of $\text{Eu}(\text{DPA})_3 \cdot 2\text{H}_2\text{O}$ and $\text{Tb}(\text{DPA})_3 \cdot 2\text{H}_2\text{O}$ Dipicolinic acid (DPA, 50.1 mg) and $\text{Eu}(\text{ClO}_4)_3 \cdot 6\text{H}_2\text{O}$ (55.9 mg) or $\text{Tb}(\text{ClO}_4)_3 \cdot 6\text{H}_2\text{O}$ (56.3 mg) were dissolved in 10 ml ethanol, and the whole mixture was titrated by 3–5 drops of aq. $\text{NH}_3 \cdot \text{H}_2\text{O}$ and was refluxed for 1 h and cooled to room temperature. The resulting precipitate was collected and washed twice with water to give the titled complexes as white powder respectively. EA found for $\text{C}_{21}\text{H}_{13}\text{EuN}_3\text{O}_{14}(\text{Eu}(\text{DPA})_3 \cdot 2\text{H}_2\text{O})$: C, 37.05; H, 1.98; N, 6.03 %, Anal. Calcd: C, 36.91; H, 1.92; N, 6.15 %. EA found $\text{C}_{21}\text{H}_{13}\text{TbN}_3\text{O}_{14}(\text{Tb}(\text{DPA})_3 \cdot 2\text{H}_2\text{O})$: C, 36.74; H, 2.02; N, 5.89 %, Anal. Calcd for: C, 36.54; H, 1.90; N, 6.09 %.

Synthesis of Cellulose Hydrogel Films: Gel-1 (for Eu), Gel-2 (for Tb) and Gel-3 (Pure) The mixture of microcrystalline cellulose (2 g) and $\text{Eu}(\text{DPA})_3 \cdot 2\text{H}_2\text{O}$ (1 mg) or $\text{Tb}(\text{DPA})_3 \cdot 2\text{H}_2\text{O}$ (1 mg) in 1-butyl-3-methylimidazolium chloride (BMIMCl, 10 g) was heated at 80 $^{\circ}\text{C}$ to obtain a homogeneous transparent viscous material. The hot viscous material was coated onto glass plates carefully to be a thin layer. After the thin layer cooled to room temperature, the excluded BMIMCl was removed by washing with water to

form the hydrogel films. Synthesis of Gel-3 is similar with Gel-1, except without adding the complex. These target films were stored at freezing condition for future test.

Results and Discussion

The FT-IR spectra of Gel-1 (a), Gel-2 (b) and Gel-3 (c) are shown in Fig. 2. As shown in Fig. 2a, after incorporating complexes into cellulose hydrogel, the bands assigned to the stretching vibrations of carboxylate that located at 1571 and 1394 cm^{-1} still can be observed in the spectrum of Gel-1. In addition, the broad bands at 3391, 2906 and 1637 cm^{-1} , which can be attributed to characteristic bands of cellulose hydrogel (see the spectrum of Gel-3 in Fig. 2c), also can be detected [6]. We can observe similar results from the spectrum of Gel-2 in Fig. 2b. These evidences proved that these rare-earth complexes have been successfully assembled into cellulose hydrogel.

The binary complexes $\text{Eu}(\text{DPA})_3$ and $\text{Tb}(\text{DPA})_3$ displayed very strong characteristic luminescence. Their emission and excitation spectra can be seen in the Figure S1 ($\text{Eu}(\text{DPA})_3$) and S2 ($\text{Tb}(\text{DPA})_3$) respectively. However, these complexes are not stable in aqueous solution. Since cellulose hydrogels are promising soft matter for tactile pattern

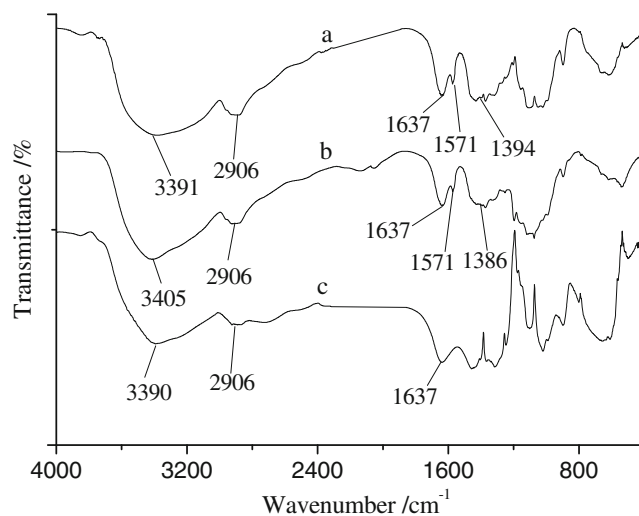


Fig. 2 IR spectra of a Gel-1, b Gel-2, and c Gel-3

sensing in environmental or biological applications, we therefore introduced the two complexes, Eu(DPA)₃ and Tb(DPA)₃, into cellulose hydrogels and two novel composite thin films (Gel-1 for Eu and Gel-2 for Tb) were fabricated as sensory materials for detection of cations.

The overall europium luminescence changes of Gel-1 upon titration of copper ions were demonstrated in Fig. 3. The excitation spectrum of Gel-1 exhibits a broad band covering from 250 to 290 nm with a maximum peak at 273 nm when recording excitation spectra with emission wavelength set at 617 nm (insert in Fig. 3). Its fascinating red luminescence can be detected by naked eyes under the excitation of the ultraviolet light (insert photo in Fig. 1). Narrow-width emission bands with maxima at 580, 595, 617, 652, and 699 nm are recorded in its emission spectrum. These bands are attributed to the ⁵D₀ → ⁷F₀, ⁵D₀ → ⁷F₁, ⁵D₀ → ⁷F₂, ⁵D₀ → ⁷F₃ and ⁵D₀ → ⁷F₄ transitions of Eu³⁺ ions, respectively. Upon exposure of Gel-1 to Cu²⁺ with concentration changing from 0.1 to 1 μM, the emission of europium ion went down gradually and almost disappeared at last. We performed analogous experiments upon addition of 10⁻⁵ molL⁻¹ of Na⁺, K⁺, Ag⁺, Mn²⁺, Co²⁺, Ca²⁺, Cd²⁺, Hg²⁺, Pd²⁺, Mg²⁺, Ni²⁺, Fe²⁺, and Fe³⁺ by emission spectroscopy (Fig. 4) and no extraordinary changes were detected (less than 20 %).

Similarly, the sensing ability of Gel-2 to cations was also studied through fluorescence spectroscopy (Fig. 5). A broad band covering from 250 to 300 nm with the maximum at 273 nm was recorded in the excitation spectrum of Gel-2 by fixing the emission wavelength at 545 nm (insert in Fig. 5). In its emission spectrum, Tb³⁺ emission in both cases was evident from the appearance of line-like emission bands at 491, 545, 585, and 623 nm, respectively, corresponding to the deactivation of the Tb³⁺ excited states ⁵D₄ → ⁷F_J (J=6, 5, 4 and 3) (excited at 273 nm). We could see its

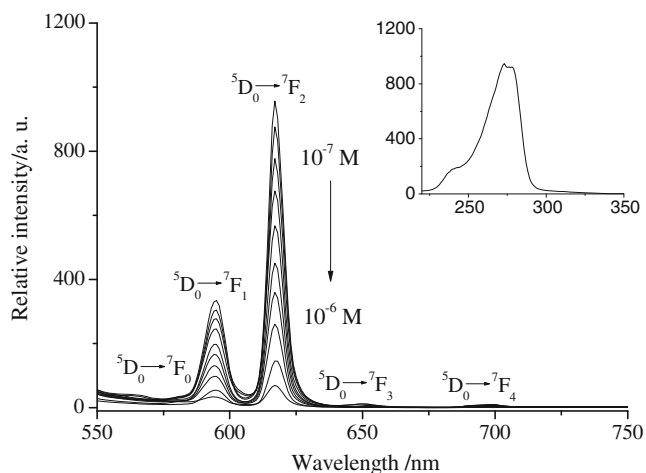


Fig. 3 Emission spectra of Gel-1 ($\lambda_{ex}=273$ nm) upon addition of 0.1 to 1 μM Cu²⁺ in water. Inset: excitation spectrum of Gel-1 ($\lambda_{em}=617$ nm)

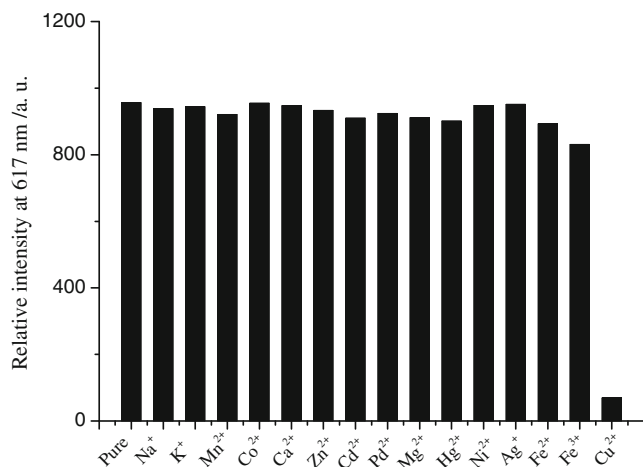


Fig. 4 Fluorescence intensity at 617 nm of Gel-1 excited at 273 nm in the presence of 10⁻⁵ mol/L of Na⁺, K⁺, Ag⁺, Mn²⁺, Co²⁺, Ca²⁺, Cd²⁺, Hg²⁺, Pd²⁺, Mg²⁺, Ni²⁺, Fe²⁺, and Fe³⁺ or 10⁻⁶ mol/L of Cu²⁺

characteristic green emission by naked eyes under the excitation of the ultraviolet light (insert photo in Fig. 1). In a similar fashion, the gradual quenching effects of Gel-2 can be detected upon addition of copper ions from 0.1 to 1 μM. No distinguished changes of its luminescence in present of 10⁻⁵ molL⁻¹ of other ions, such as Na⁺, K⁺, Ag⁺, Mn²⁺, Co²⁺, Ca²⁺, Cd²⁺, Hg²⁺, Pd²⁺, Mg²⁺, Ni²⁺, Fe²⁺, and Fe³⁺ (Figure S3).

Moreover, interference studies were conducted upon exposure the two probes to 10⁻⁵ molL⁻¹ of other ions as well as containing 10⁻⁵ molL⁻¹ of the copper cation. As shown in Figure S4, fluorescence spectroscopy results displayed that none of these cations had obvious affects on the quenching effects of copper ions to these sensing materials. As a consequence, based on all the results above, we could propose that the present films can be applied as highly selective

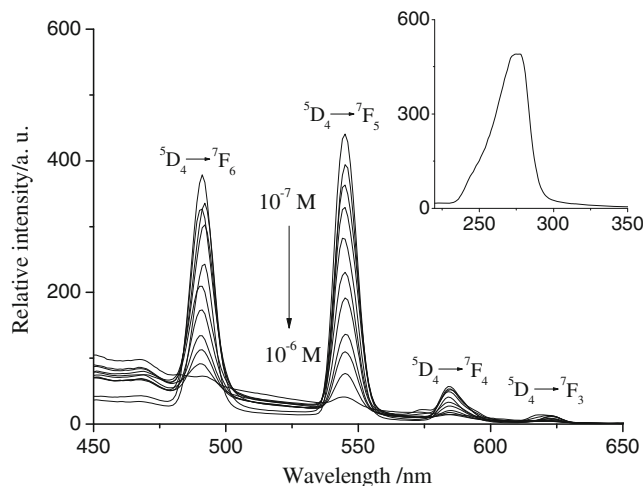


Fig. 5 Emission spectra of Gel-2 ($\lambda_{ex}=273$ nm) upon addition of 0.1 to 1 μM Cu²⁺ in water. Inset: excitation spectrum of Gel-2 ($\lambda_{em}=545$ nm)

chemical sensors specific for copper ions measurement in aqueous solution. However, we believed that it is the competitive coordination interactions between copper ions and lanthanide ions that resulted in the quenching effects.

The response times of these films toward Cu^{2+} were explored by fluorescence spectroscopy. The time-dependent emission response of Gel-1 to $1\ \mu\text{M}$ Cu^{2+} was measured at 617 nm with an excitation wavelength of 273 nm (Fig. 6). A rapid quenching of the luminescence intensity with the first 5 s (5~10 s in Fig. 6) can be observed after addition of copper ions. It presented a slower decrease over the next 5 s (10~15 s in Fig. 6), which indicated that the recognition process is complete within 10 s, thus enabling a rapid detection of copper ions. We performed the same experiment to Gel-2 and similar phenomena can be observed (Fig. 6).

The thermal- and photochemical stabilities of rare-earth complexes in aqueous media is very essential for their practical application [22]. However, most of the complexes do not have good thermal-photoluminescence. It has been found that their thermal stabilities can be improved by encapsulating rare-earth complexes into different matrix, such as silica and polymers [20]. Therefore, in this article, we also investigated the temperature-dependent photophysical properties of these novel materials compared with the corresponding complexes. As shown in Fig. 7a, the emission intensity of Gel-1 declined about 30 % with temperature changing from 10 to 50 °C in water. However, more than 60 % luminescence decrease can be detected under the same conditions for the solution of the complex in water (Fig. 7b). Analogous phenomena between $\text{Tb}(\text{DPA})_3$ and Gel-2 could be detected (Figure S5). In this case, we can conclude that the introduction of cellulose hydrogel can significantly enhance the thermal stability of rare-earth complexes in water.

Moreover, the thermal stabilities of complexes and these novel sensing materials in air condition were investigated by thermogravimetric analysis (TGA) experiment. Three steps

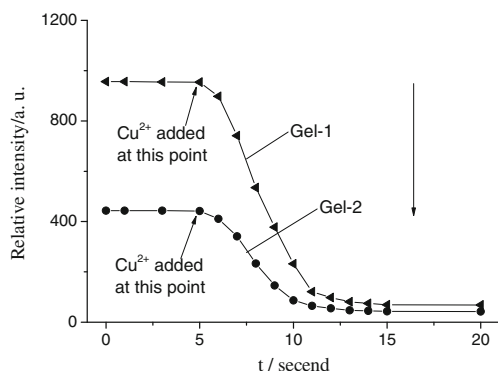


Fig. 6 Plot of emission intensity versus time for Gel-1 at 617 nm and Gel-2 at 545 upon addition of $1\ \mu\text{M}$ Cu^{2+} in water

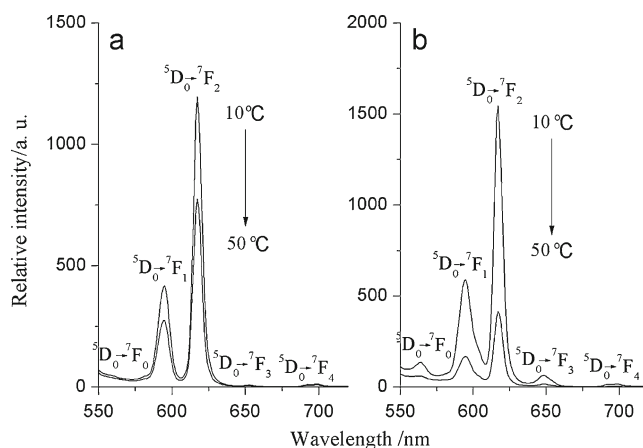


Fig. 7 Emission spectra of **a** Gel-1 and **b** $\text{Eu}(\text{DPA})_3$ in water excited at 273 nm respectively from 10 to 50 °C

of weight loss for $\text{Eu}(\text{DPA})_3$ was clearly displayed in Fig. 8. The first weight loss of 2.6 % in the range of 30–180 °C may generate by the removal of the free and coordinated water molecules in this complex. However, in the second and third steps, we can observe two major weight losses, which may be attributed to the collapse of the coordination structures. This curve shows that the complex started to decompose at 180 °C. In contrast, the result of thermogravimetric analysis of Gel-1 only has a tiny mass change before 250 °C. Similar experiments was conducted towards $\text{Tb}(\text{DPA})_3$ and Gel-2, analogous results and relationship between $\text{Tb}(\text{DPA})_3$ and Gel-2 were recorded (Fig. 8). All these data proved that the incorporation of rare-earth complexes into cellulose hydrogel matrix also can lead to their significant enhanced thermal stabilities especially under 250 °C.

The morphology of the two films was examined by scanning electron microscopy (SEM) (Fig. 9). We dried the present films under vacuum environment in order to remove all the solvents away. Smooth surface of Gel-1 was clearly described in Fig. 9a, which is very different from the previous reported reference [7]. All the cellulose and complexes were homogeneously dissolved together and

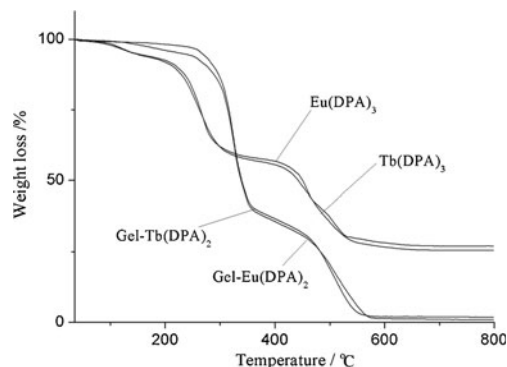
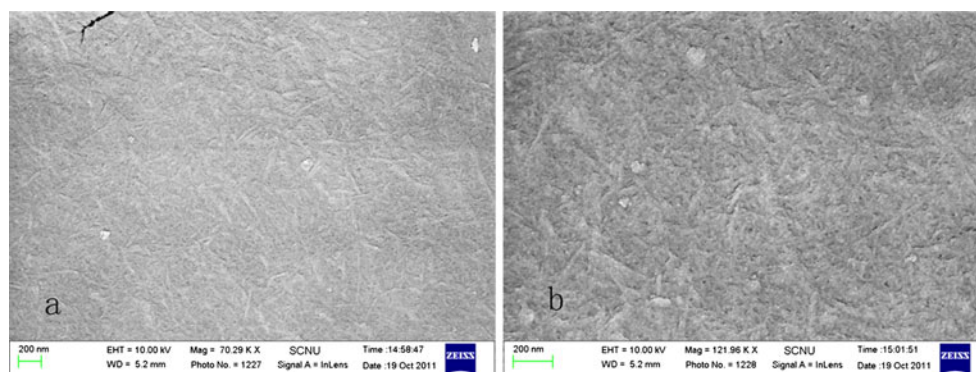


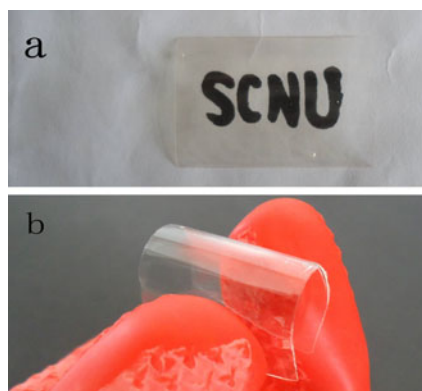
Fig. 8 Thermogravimetric analysis traces of $\text{Eu}(\text{DPA})_3$, $\text{Tb}(\text{DPA})_3$ Gel-1 and Gel-2

Fig. 9 SEM images of **a** Gel-1 and **b** Gel-2

no aggregation can be observed. More specifically, the image shows the presence of dendritic fibers with diameter in the range of nanoscale (Fig. 9a). Gel-2 possessed similar morphology with Gel-1, which is clearly presented in Fig. 9b.

In addition, we also simply examined the light transmittance and flexibility of the sensing films. Fig. 10a shows the photo that Gel-1 covered the letters SCNU (the abbreviation of South China Normal University) on a paper. It is worthy pointing out that these letters can be clearly seen through Gel-1, which indicated that this film is highly transparent. In Fig. 10b, we found that Gel-1 can bend over like a cycle under proper pressure. This gave the evidence that this thin film also has nice flexibility. Gel-2 exhibited similar performance with Gel-1. These advantages provided them more potential in practical applications.

Previously, silica or silica/polymer based hybrids have been reported as solid sensors for detecting metal ions [19–21]. However, our novel sensing films had several distinguished advantages in comparison with these previous references. These thin films had higher selectivity only for Cu^{2+} over more than ten other ions. More interestingly, this hydrogel films are biodegradable and environmentally friendly soft matter, which can be applied as portable tools in real life. Therefore, these probes could be more promising materials as optical sensors for recognition of copper ions.

**Fig. 10** Photos of **a** light transmittance and **b** flexibility for Gel-1

Conclusions

In summary, we have demonstrated the design and synthesis of lanthanide-based cellulose hydrogel films as sensing materials for the rapid and selective detection of copper ions in aqueous solution. We noticed that only exposure to Cu^{2+} , luminescence quenching effects of these thin films can be rapidly observed. More importantly, the host of these novel sensors, cellulose hydrogel, is a biodegradable and environmentally friendly material, which endows them with potential in practical applications. Overall, these transparent and flexible thin films provided a new idea for fabrication of chemical sensors specific for copper ions recognition in environmental and biological analyses.

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References

- Vogl O, Jaycox GD (1999) Polymer science in the 21 st century. *Prog Polym Sci* 24:3–6
- Finkenstadt VL, Millane RP (1998) Crystal structure of Valonia cellulose I β . *Macromolecules* 31:7776–7783
- Chandra R, Rustgi R (1998) Biodegradable polymers. *Prog Polym Sci* 23:1273–1335
- Kuo YN, Hong J (2005) Investigation of solubility of microcrystalline cellulose in aqueous NaOH. *Polym Adv Technol* 16:425–428
- Klemm D, Heublein B, Fink HP, Bohn A (2005) Cellulose: Fascinating biopolymer and sustainable raw material. *Angew Chem Int Ed* 44:3358–3394
- Chang CY, Peng J, Zhang LN, Pang DW (2009) Strongly fluorescent hydrogels with quantum dots embedded in cellulose matrices. *J Mater Chem* 19:7771–7776
- Swatloski RP, Spear SK, Holbrey JD, Rogers RD (2002) Dissolution of cellulose with ionic liquids. *J Am Chem Soc* 124:4974–4975
- Murakami M, Kaneko Y, Kadokawa J (2007) Preparation of cellulose-polymerized ionic liquid composite by in-situ polymerization of polymerizable ionic liquid in cellulose-dissolving solution. *Carbohydr Polym* 69:378–381
- Quang DT, Kim JS (2010) *Chem Rev* 110:6280–6301
- Zheng YJ, Orbulescu J, Ji XJ, Andreopoulos FM, Pham SM, Leblanc RM (2003) Development of fluorescent film sensors for the detection of divalent copper. *J Am Chem Soc* 125:2680–2686

11. Bunzli J-CG (2010) Lanthanide luminescence for biomedical analyses and imaging. *Chem Rev* 110:2729–2755
12. Stich MIJ, Schaeferling M, Wolfbeis OS (2009) Multicolor fluorescent and permeation-selective microbeads enable simultaneous sensing of pH, oxygen, and temperature. *Adv Mater* 21:2216–2220
13. Montgomery CP, Murray BS, New EJ, Pal R, Parker D (2009) Cell-penetrating metal complex optical probes: Targeted and responsive systems based on lanthanide luminescence. *Accounts Chem Res* 42:925–937
14. Comby S, Gunnlaugsson T (2011) Luminescent lanthanide-functionalized gold nanoparticles: exploiting the interaction with bovine serum albumin for potential sensing applications. *ACS-Nano* 5:7184–7197
15. Tan CL, Wang QM, Zhang CC (2011) Optical and electrochemical responses of an anthrax biomarker based on single-walled carbon nanotubes covalently loaded with terbium complexes. *Chem Commun* 47:12521–12523
16. Tan CL, Wang QM (2011) Reversible terbium luminescent poly-electrolyte hydrogels for detection of H_2PO_4^- and HSO_4^- in water. *Inorg Chem* 50:2953–2956
17. Nonat AM, Harte AJ, Senechal-David K, Leonard JP, Gunnlaugsson T (2009) Luminescent sensing and formation of mixed f-d metal ion complexes between a Eu(III)-cyclen-phen conjugate and Cu(II), Fe(II), and Co(II) in buffered aqueous solution. *Dalton Trans* 24:4703–4711
18. Orcutt KM, WS Jones, A McDonald, D Schrock, KJ Wallace (2010) A lanthanide-based chemosensor for bioavailable Fe^{3+} using a fluorescent siderophore: an assay displacement approach sensors. 10:1326–1337.
19. Tan CL, Zheng YH, Wang QM, Hang ZWG, Zheng SR, Cai SL (2011) Recognition of H_2PO_4^- and Cu^{2+} in water by luminescent terbium silica serogel. *J Fluoresc* 21:1117–1122
20. Wang QM, Tan CL (2011) Terbium hybrid particles with spherical shape as luminescent probe for detection of Cu^{2+} and Fe^{3+} in water. *Anal Chim Acta* 708:111–115
21. Blair S, Katakly R, Parker D (2002) Sol-gel-immobilised terbium complexes for luminescent sensing of dissolved oxygen by analysis of emission decay. *New J Chem* 26:530–535
22. Pagnot T, Audebert P, Tribillon G (2000) Photostability study of europium dibenzolymethide embedded in polystyrene thin films with high concentration. *Chem Phys Lett* 322:572–578