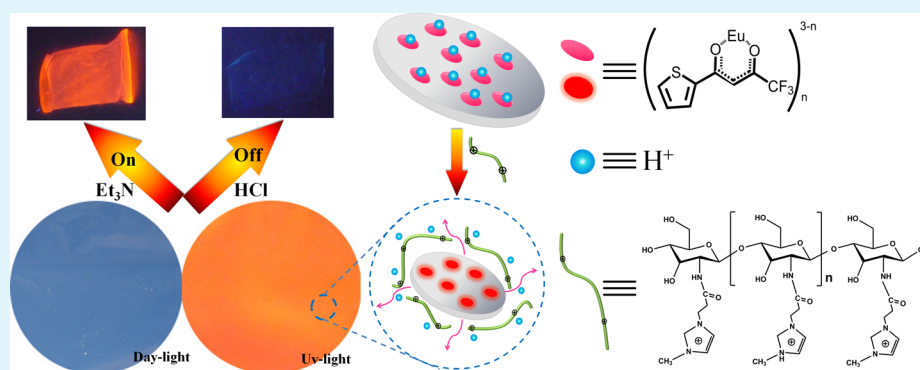


Carboxyl-Functionalized Ionic Liquid Assisted Preparation of Flexible, Transparent, and Luminescent Chitosan Films as Vapor Luminescent Sensor

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S Supporting Information



ABSTRACT: Herein we present a novel method to synthesize flexible self-standing films consisting of europium(III) complexes in nanoclay and chitosan, which are transparent and luminescent. Preparation takes place under aqueous conditions assisted by a carboxyl-functionalized ionic liquid (IL). The latter is used not only as a replacement for acetic acid to dissolve chitosan but, surprisingly, also to enhance the luminescence efficiency of the final films. A brighter luminescence is observed for the films prepared assisted with the ionic liquids compared to those by using acetic acid. The reason is that the ionic liquid used to dissolve chitosan can decrease proton strength on embedded platelets primarily through ion-exchange process and thus can increase the coordination number of europium(III) complexes. Exposure of the films to Et₃N vapors can cause a further remarkable luminescence enhancement, while significant luminescence quenching occurred upon exposure to HCl vapors. The films are promising for applications in areas such as optoelectronics and vapor-sensitive luminescent sensors.

KEYWORDS: chitosan, lanthanide complex, self-standing film, ionic liquid, vapor luminescent sensor

1. INTRODUCTION

Luminescent films consisting of lanthanide complexes and polymers have been receiving increasing attention in recent years for their great potential in various application fields such as sensing and optoelectronic devices.^{1–8} This family of films show obvious advantages of unique optical properties such as sharp emission bands, long decay times, strong UV-light absorbing abilities, and large Stokes shift from lanthanide complexes, and high transparency as well as excellent processability from the polymer matrices.^{9–12} The currently prevailing polymer used in preparing such luminescent films is a polymer such as PVA^{13,14} or PMMA.^{15–17} Their preparation usually demands the use of environmentally hazardous solvents.^{18–20} It is desirable to use environmentally friendly polymers as an alternative and to prepare them under greener conditions, e.g., by using water as the (main) solvent.

Low-cost and environmentally friendly biopolymers are considered ideal alternatives to petroleum-derived polymers for preparing luminescent hybrid materials.²¹ Among them,

chitosan (CS) derived from crab shells or shrimp is a promising candidate for this purpose by combining with luminescent centers due to the obvious advantage of transparency in UV–vis spectral region, ability to form films, nontoxicity, and so forth.^{22–26} However, reports on luminescent films of doping lanthanide complexes to CS prepared from aqueous solutions are rarely seen.^{27,28} In fact, preparation of them remains a challenge because (i) most of lanthanide complexes show poor solubility in water and (ii) the luminescence of lanthanide complexes can be effectively quenched by water molecules.²⁹ In addition, the luminescent films based on lanthanide complexes have advantages over conventional fluorescent dyes, which can be widely investigated as advanced “smart” materials in fields such as smart devices and sensors.^{30,31}

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Scheme 1. Schematic of the Mechanism for Preparing Luminescent Films and Using As Vapor Luminescent Sensor

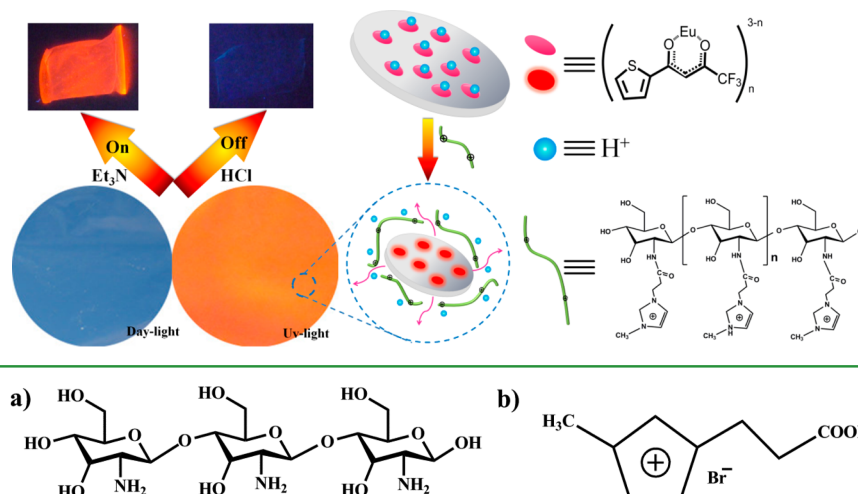


Figure 1. Structure of (a) chitosan and (b) carboxyl-functionalized IL.

In this work, we report a novel method to prepare flexible and transparent free-standing films exhibiting high luminescence efficiency by embedding luminescent hybrid nanocomposites (HN) consisting of europium(III) complexes in nanoclay within CS films under aqueous experimental conditions in the presence of a carboxyl-functionalized IL (Scheme 1). The key to success in obtaining such films is the utilization of the carboxyl-functionalized IL, playing a dual role of acting both as an additive in replacement of the conventional acid used for dissolving CS^{24,32,33} and as the ideal additive for increasing the luminescence efficiency of the films remarkably.^{34,35} Moreover, the CS films can be used as a vapor luminescent sensor; exposure of the films to Et_3N vapors causes a further remarkable luminescence enhancement, while significant luminescence quenching can be observed when treating the films with HCl vapors.

2. RESULTS AND DISCUSSION

A stable homogeneous CS solution was first obtained by dissolving CS powder (Figure 1a) in an aqueous carboxyl-functionalized IL (Figure 1b) solution, to which an aqueous suspension of luminescent nanocomposite was then added, and the mixture was further sonicated for a while. The luminescent films were finally obtained by a solution casting method and can be easily peeled from the substrate and denoted as HN@CS-IL. For comparison, we also prepared films by dissolving CS powders in acetic acid aqueous solution that was denoted as HN@CS-AA. Both the carboxyl-functionalized IL and acetic acid used can disrupt inter- and intramolecular hydrogen bonding in the biopolymers effectively.^{24,32,36} All the obtained films exhibit high transparency and flexibility (Figure 2a). A much brighter red-emission light is observed for HN@CS-IL compared to that for HN@CS-AA under illumination with a UV light (Figure 2b), attributed to the presence of IL that can boost the luminescence efficiency remarkably as we will discuss later.

FTIR analysis was performed to study the structure of the films. The absorption peak of chitosan powder in Figure 3a, with a broad band at 3700 to 2900 cm^{-1} centered at around 3400 cm^{-1} attributing to the overlap of N–H stretching vibration and O–H stretching vibration; and two absorption bands at 2924 and 2868 cm^{-1} corresponding to C–H

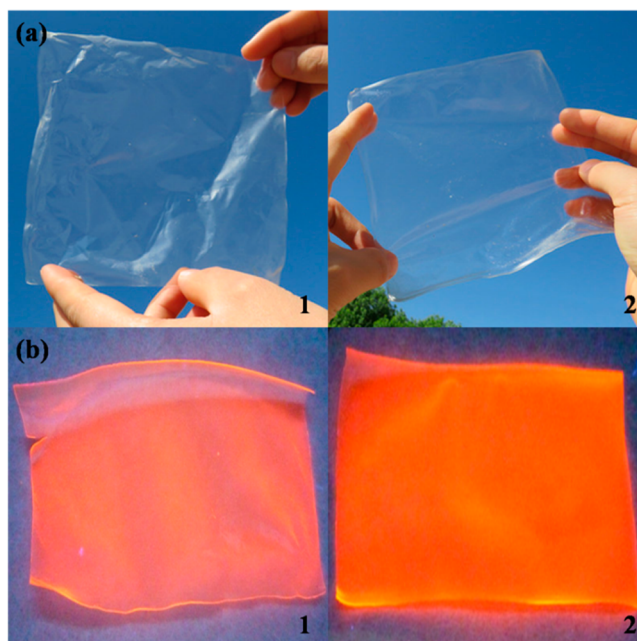


Figure 2. Photographs of films under daylight (a) and 365 nm UV lamp (b): HN@CS-AA (1), HN@CS-IL (2).

stretching bands.³⁷ The strong bands at 1651 and 1080 cm^{-1} can be observed in CS, which can be ascribed to the N–H stretching and dissymmetry stretching vibration of the C–O–C, respectively. The band at 1651 cm^{-1} becomes weaker and shifts to 1638 cm^{-1} as shown in Figure 3b and c, which is attributed to the formation of amide bonds,¹⁸ indicating that the –COOH group of acetic acid and IL can break the high density of hydrogen bonds in polymer chains during the dissolution process and leads the peak at 1080 cm^{-1} to broaden. The absorption band at 1570 cm^{-1} is assigned to the stretching vibration of ligand in HN, indicating that the luminescent nanocomposites were embedded well in CS film. The band at 896 cm^{-1} in CS indicated the presence of β -(1–4) stretching^{32,38} and also observed in two films. No obvious change or shift of 896 cm^{-1} means that the dissolution process does not change the carcass construction of CS. Generally, the

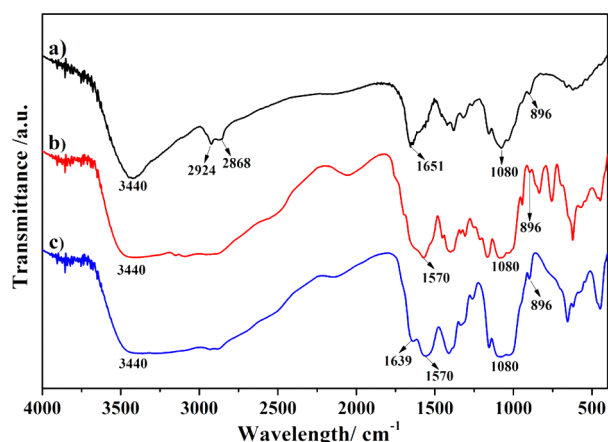


Figure 3. FT-IR spectra of chitosan (a), HN@CS-AA (b), and HN@CS-IL (c).

transparency of films is a very important issue for composites for practical application, which can be measured by UV-vis transmittance spectra and are shown in Figure 4. Absorption

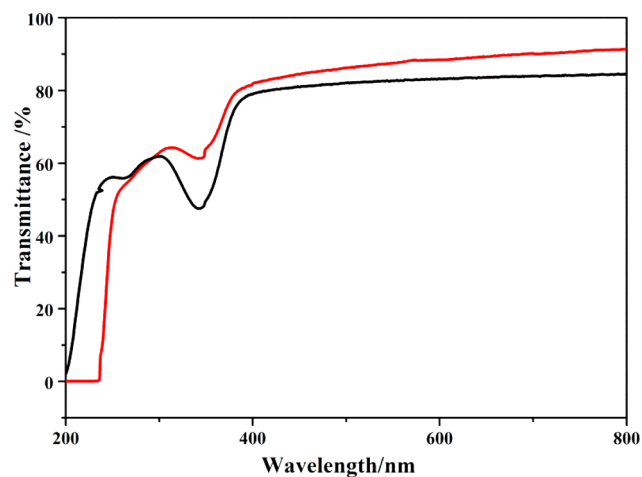


Figure 4. UV-vis transmittance spectra of HN@CS-AA (black line) and HN@CS-IL (red line).

bands at 340 nm are clearly observed in two films, which can mainly be attributed to the absorption of the tta (2-thenoyltrifluoroacetate) ligand¹³ (Supporting Information, Figure S1). The spectra shown in Figure 4 demonstrate that

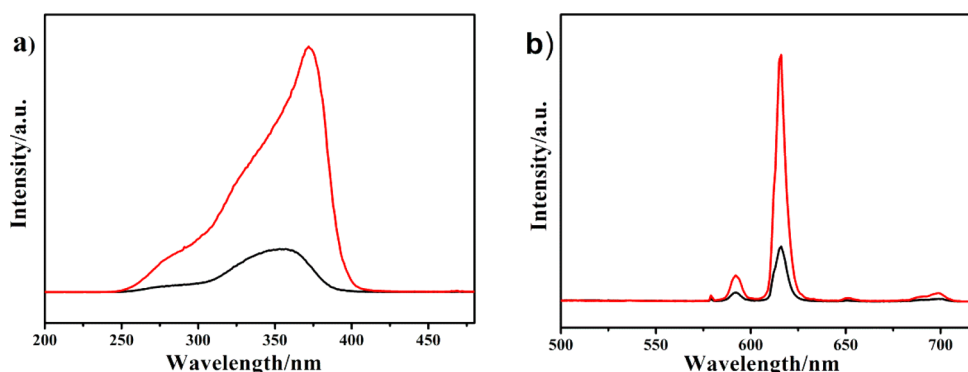


Figure 5. Excitation spectra (a) and emission spectra (b) of HN@CS-AA (black line) and HN@CS-IL (red line).

the film obtained using IL is more transparent than that prepared by acetic acid solution.

The luminescence data are recorded at r.t. and shown in Figure 5. The excitation spectra are dominated by a broad band ranging from 200 to 400 nm, which can be attributed to the absorption of the diketone moieties of the tta ligand. Excitation at 360 nm leads to five sharp emission lines peaking, which correspond to the $^5D_0 \rightarrow ^7F_J$ ($J = 0 \rightarrow 4$) transitions of Eu^{3+} , of which the $^5D_0 \rightarrow ^7F_2$ transition at 612 nm is the most intense and responsible for the fluorescence red light as shown in Figure 2b. The film HN@CS-IL displays much stronger luminescence intensity than that of HN@CS-AA, which is in good agreement with the photos shown in Figure 2b. The 5D_0 emission decay curves for both films are fitted by mono-exponential functions (Supporting Information, Figure S2). The 5D_0 lifetime value of HN@CS-IL (0.60 ms) is much longer than that of HN@CS-AA (0.22 ms). Furthermore, the absolute quantum yield of HN@CS-IL is determined to be 0.38, a much larger value compared to that of HN@CS-AA (0.07) where no IL molecules are present. The results imply that the use of carboxyl-functionalized IL for dissolving CS powder in water can also remarkably boost the luminescence of the film. The luminescence enhancement of HN resulting from the IL introduction has been reported in our previous reports.^{13,34} We believe that the IL molecules can remove the protons on the surface of HN platelets primarily through the ion-exchange process, which can favor the complete coordination between $\text{Eu}(\text{III})$ and β -diketonate.^{13,39–41}

In order to further prove this claim, we also carried out the following experiment that is directly adding carboxyl-functionalized IL to the luminescent hybrid nanocomposite. An appropriate amount of the carboxyl-functionalized IL aqueous solution was directly added to the aqueous suspension of HN, and the product HN-IL was recovered by sonication and centrifugation. As expected, the IL addition leads to a remarkable luminescence enhancement of HN, which can be easily observed by the naked eye (Figure 6 inset). The excitation spectra monitored at 612 nm (Supporting Information, Figure S3) consisting of a broad band ranging from 250 to 450 nm are also due to the tta ligand (Figure 5a). The emission spectra (Figure 6) excited at 360 nm leads to the same $^5D_0 \rightarrow ^7F_J$ emission line as observed in Figures 5b with the $J = 2$ line as the most intense feature. Compared with bare HN, HN-IL exhibited a higher value in absolute quantum yield (50.2% for HN-IL versus 9.64% for HN). Moreover, the luminescence lifetimes are determined from the single-exponential decay curves under excitation at 360 nm. Figure

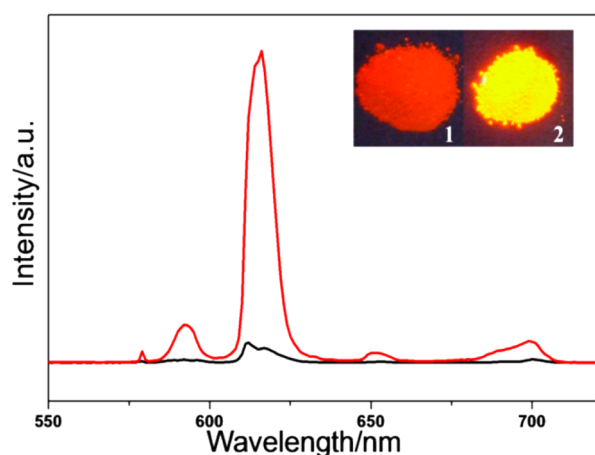


Figure 6. Emission spectra of HN (black line) and HN-IL (red line). (Inset) Photographs of HN (1) and HN-IL (2) under UV-light irradiation ($\lambda = 365$ nm).

S4 (Supporting Information) exhibits that the luminescence lifetime of HN is apparently increased from 0.25 to 0.76 ms caused by the IL modification. The formation of HN-IL can be verified by FT-IR spectra in Figure 7. The vibration bands at

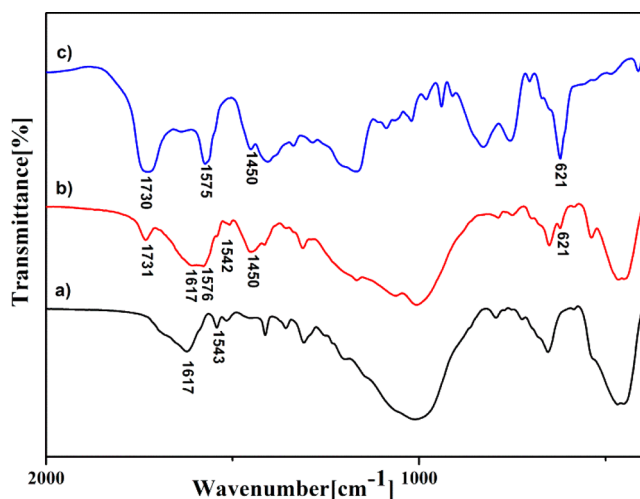


Figure 7. FT-IR spectra of HN (a), HN-IL (b), and IL (c).

1617 and 1543 cm^{-1} of HN (Figure 7a) can be assigned to the stretching vibrations of the C=O and C=C of tta ligand, respectively,⁴² which is not shifting in the IR spectrum of HN-IL shown in Figure 7b. Carboxyl-functionalized IL was clearly observed, which can be verified by the appearance of band at 1575 cm^{-1} assigned to the ring stretching of the imidazolium ring and those at 1731 and 1450 cm^{-1} attributed to the carboxylate group of the IL (Figure 7c).⁴³ No obvious shift of these bands upon the modification of HN with IL can be observed, indicating that the carbonyl group does not coordinate with Eu^{3+} ions in the obtained luminescent nanocomposite HN-IL. The increase in luminescence is primarily due to the complexes formed with high coordination number between Eu(III) and β -diketonate driven by the IL molecules that decrease the proton strength on platelets via ion exchange process^{13,44} rather than through coordination of the oxygen atoms of the carboxylic acid groups from the ILs as we reported previously.⁴⁵

The obtained films are highly luminescent, transparent, and flexible; these merits can make them promising candidates for fabrication into flexible optical devices. Interestingly, we also observed that the films can be used as vapor luminescent sensors. We used triethylamine (Et_3N) and hydrochloric acid (HCl) as the operating base/acid pair to generate the remarkable change, which is well demonstrated by photography under UV lamp (inset of Figure 8a), luminescence intensity (Figure 8a), and luminescence decay time (Supporting Information, Figure S5). When the film was exposed to Et_3N -gas enriched environment for 10 s, the emission spectra display a pronounced increase, while upon exposure to HCl vapor for 10 s, the red light of the film disappeared. The luminescence responses of the flexible film exposed to Et_3N and HCl vapor are shown in Figure 8a, which reveals a remarkable increase in emission intensity for Et_3N vapor and an obvious decrease in emission intensity for HCl vapor. The sensing reversibility was examined by the luminescence emission intensity at 612 nm, we treated HN@CS-IL film with HCl vapor and Et_3N gas alternately for several HCl- Et_3N cycles, and the results are shown in Figure 8b. This film displays good reversibility after 5 cycles. We believe that Et_3N can neutralization the acidic sites on pellets of HN embedded within CS films and thus can favor the complete coordination of complexes between Eu(III) and β -diketonate as previously reported (Supporting Information, Figure S6).^{13,46,47} On the contrary, HCl vapor can increase the acidity of the resulting flexible films; the high proton strength in the luminescent

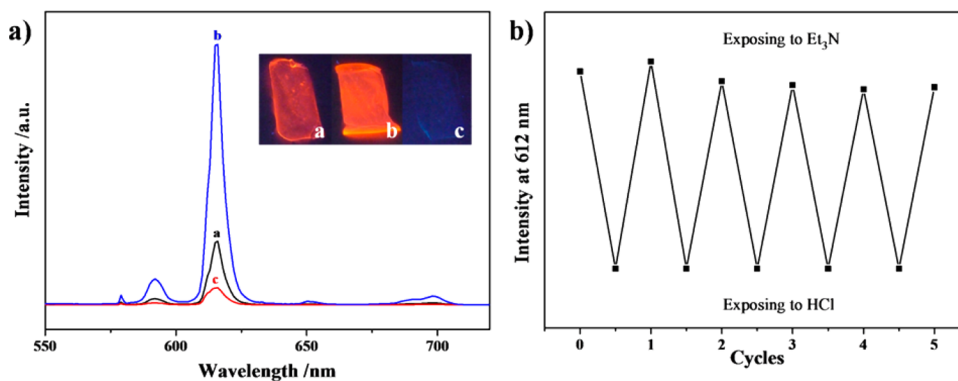


Figure 8. (a) Photographs (inset) and emission spectra by 360 nm UV excitation of HN@CS-IL before (a) and after exposure to Et_3N (b) and HCl (c); (b) response of luminescent intensity of HN@CS-IL at 612 nm during HCl- Et_3N exposure cycles.

nanocomposites makes the Eu^{3+} - β -diketonate complexes unstable and then transform to single protonated tta ligand with enol or ketone form.^{30,46,48} Furthermore, this mechanism can be further supported by IR spectra shown in Figure 9. The

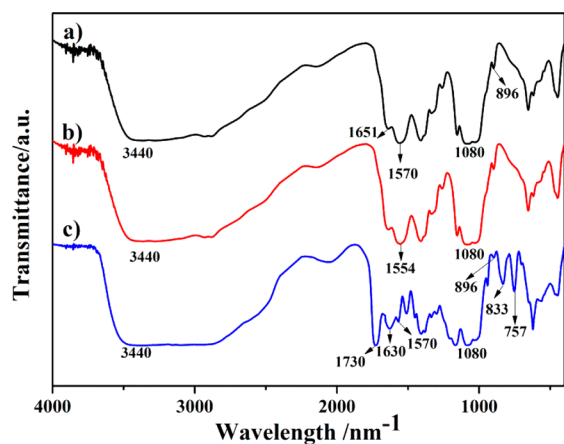


Figure 9. FT-IR spectra of film HN@CS-IL before (a) and after exposure to Et_3N (b) and HCl (c).

β -diketonate of tta stretching vibrations at 1570 cm^{-1} (Figure 9a) shifts to ca. 1554 cm^{-1} when the film is treated with Et_3N vapor (Figure 9b), indicating the more effective coordination of the ligand tta to Eu^{3+} . However, the band becomes weaker when the films were treated with HCl vapors as shown in Figure 9c; we therefore can reason that Eu^{3+} - β -diketonate complexes become unstable after the film exposed to a HCl-gas enriched environment, i.e., tta ligand, was protonated and transformed to the enol or ketone form. Further information observed in Figure 9c could be supported as follows: (1) the absorption band at 1725 cm^{-1} observed is assigned to the vibration of $\text{C}=\text{O}$ of tta ligand; (2) bands at 1630 , 833 , and 757 cm^{-1} are attributed to the $\text{C}=\text{C}$ stretching vibration and $\text{C}-\text{H}$ bending vibration of the vinyl groups of tta ligand.

3. CONCLUSION

We have demonstrated a novel method to prepare transparent, flexible, and free-standing film with high luminescent quantum efficiency (38%) under aqueous experimental conditions assisted by a carboxyl-functionalized IL. The IL used as a replacement of the acetic acid for dissolving CS in aqueous solution can simultaneously boost the luminescence of the final films by decreasing the proton strength on the platelets, thus leading to the formation of Eu^{3+} - β -diketonate complexes with high coordination number. The films are highly sensitive to both base and acid vapors, the emission intensity increases remarkably when the film are exposed to Et_3N vapors and decreases significantly when treated with HCl vapors. Our study demonstrates that the luminescent CS films prepared will be a more appropriate choice for the replacement of conventional petroleum-based films, and will find great potential in various areas such as luminescent solar concentrators, optoelectronics, and vapor luminescent sensors.

4. EXPERIMENTAL SECTION

Materials. CS with a deacetylation degree of 75–85% was obtained from J&K and used as received. The hybrid nanocomposites HN was obtained according to the previously procedure reported in ref 13. IL

in this work was obtained according to the previously procedure reported in ref 49.

Dissolution of Chitosan in Acetic Acid and IL. The stable homogeneous CS-AA aqueous solution (1 wt %) was prepared by dissolving 1 g of CS in 99 g water (with 1 g acetic acid, 16.7 mmol) and stirring constantly at $60\text{ }^\circ\text{C}$ for 1 d. The stable homogeneous CS-IL aqueous solution (1 wt %) was prepared by dissolving 1 g of CS in 99 g water (with 3.96 g IL, 16.7 mmol) and stirring constantly at $60\text{ }^\circ\text{C}$ for 1 d.

Fabrication Procedures of Luminescent Films. The homogeneous aqueous suspension of luminescent materials were obtained by dispersing HN (20 mg) in water (5 mL), then adding 5 mL aqueous solution of CS-AA or CS-IL and sonicating for half on hour. Dropping the homogeneous aqueous suspension on glass and drying in air overnight, the flexible and luminescent films (HN@CS-AA, HN@CS-IL) can be easily peeled from the substrate.

Modification of HN with IL. The preparing process was according to the previously procedure reported in ref 13 and the product was denoted as HN-IL.

Exposure to Et_3N /HCl vapor. For each experiment, a piece of film ($1 \times 2\text{ cm}^2$) HN@CS-IL or HN@CS-AA was put in a cuvette for vapor treatments. $\sim 4\text{ mL}$ Et_3N or HCl solvent was added to a 100 mL sealed container, and then the cuvette placed into a container with equilibrated vapor for 10 min.

Characterization. Fourier transform infrared (FT-IR) spectra were recorded in the spectral range from 4000 to 400 cm^{-1} with a Bruker Vector 22 spectrophotometer by using pressed KBr pellets for solid samples and films. Light transmittance of the CS films were measured using a UV–vis spectrometer (Agilent cray100) from 200 to 800 nm. The luminescence measurements (excitation spectra, emission spectra, luminescence decay time, and absolute quantum yield) of solid state powder and films were measured on an Edinburgh Instruments FS920P.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsami.6b06325.

UV–vis absorption spectra, excitation spectra, luminescence decay curves, Formation of Eu^{3+} - β -diketonate complexes (PDF)

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Notes

The authors declare no competing financial interest.

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