Fixed-Component Lanthanide-Hybrid-Fabricated Full-Color Photoluminescent Films as Vapoluminescent Sensors

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Abstract: Full-color lanthanide (Ln) photoluminescent materials have attracted considerable interest owing to their potential applications in display systems and lighting technologies. Herein, full-color photoluminescent films have been designed and fabricated facilely with a fixed-component Lnbased (Ln=Tb and Eu) polymer hybrid doped with a proton-sensitive amide-type β -diketonated photosensitizer, *N*-(2-pyridinyl)benzoylacetamide (HPBA). The tunable photolumines-

cence emissions of the films are achieved by changing the amounts of OH⁻ in the hybrid rather than varying the relative concentrations of the lanthanide ions and photosensitizers, thus representing a new paradigm for fullcolor displays. The emission color can also be finely tuned through the varia-

Keywords: energy transfer · lanthanides · luminescence · sensors · white-light emission tion of the excitation wavelength, and white-light emission can be achieved when the given film is excited at the visible region (405 nm). The photophysical properties and the mechanisms of the intra- and intermolecular energy transfer before and after deprotonation have been investigated in detail. Meanwhile, the films might find application as vapoluminescent sensors due to their good stability, sensitivity, reversibility, and quick response when triggered by a base–acid vapor.

Introduction

Full-color photoluminescent materials, especially those with white-color emissions, have attracted increased attention in recent years because they are known for their potential applications in various important devices such as color-tunable phosphors,^[1] white-light-emitting devices,^[2] and multicolor light-emitting diodes (LEDs).^[3] One of the promising components in the design of full-color materials are lanthanide (Ln)-based hybrids,^[4] which possess distinct advantages over organic chromophores, such as their sharp and intense line-

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like emissions as well as their wide range of lifetimes.^[5] Ideally, white-color emissions should consist of relative red, green, and blue luminescent components with suitable intensities. Therefore, doping Eu³⁺ (red-light emission) and Tb³⁺ (green-light emission) complexes accompanied by an excess amount of blue-light-emitting ligand in the materials results in three primary colors and offers full-color photoluminescence, including white emission.^[6]

Known for more than one hundred years, β -diketones continue to draw considerable interest because of their effectiveness in energy transfer to Ln ions.^[7] However, most β-diketones are not good ligands for sensitizing the luminescence of Tb^{3+} because of their triplet levels below the ${}^{5}D_{4}$ resonance level of Tb³⁺.^[5a] Our group recently designed and assembled functional amide-type β-diketone-based Ln inorganic-organic hybrid materials.^[8] The introduction of an amide group increases the triplet levels of the β-diketone architecture, and energy transfer to Tb³⁺ was attempted. It is well known that β-diketones coordinated to metal ions usually exist as an enol tautomer (deprotonated form). A pyridine ring is condensed to the amide-type β -diketone block because of its acceptance of the residual proton.^[9] This amide-type β -diketone architecture N-(2-pyridinyl)benzoylacetamide (HPBA) is assumed to possess the ability to transfer energy to Tb³⁺ under neutral conditions because of the proton accepted by its own pyridyl nitrogen atom. In addition, when the proton is removed completely under alkaline conditions, the negatively charged architecture might efficiently transfer energy to Eu^{3+} , similar to classic β -diketone ligands.^[5a] This phenomenon offers a prerequisite for the realization of multicolor photoluminescent materials. The in-

CHEMISTRY

FULL PAPER

corporation of Ln complexes within matrices should be the megatrends for practical applications. Poly(vinyl pyrrolidone) (PVP) polymer can firmly encapsulate Ln complexes and is apparently a good candidate to increase the strength of the hypersensitive transitions of Ln ions; therefore, PVP is preferred for application in optical devices.^[10]

We then designed novel full-color photoluminescent films fabricated with the use of a new fixed-component specific Ln-based (Ln=Tb and Eu) PVP hybrid (Scheme 1). The



Scheme 1. Synthesis of multicolor emission polymer films.

films reported here realize tunable photoluminescence emissions from green to red (from films A to K) depending on the changes of OH^- concentrations in the hybrid, which is more facile than the traditional methods that typically rely on tuning the ratios of Ln^{3+} and organic ligands. The emission color can also be finely tuned through variation in the excitation wavelength, and white-light emission can be achieved when the given film is excited at the visible region (approximately 405 nm). To the best of our knowledge, it is the first example of Ln-based materials that can emit fullcolor photoluminescence, including white-color emission, as a function of OH^- concentrations and excitation wavelength. It is worth noting that the luminescence of the film can efficiently transform from green to red even after several cycles when the film is exposed to base–acid vapor.

Results and Discussion

Characterization of the multicolor photoluminescence polymer films: The FTIR spectra of films A and K are similar to those of pure PVP (Figure S1 in the Supporting Information). A few small characteristic vibrational modes of pyridine in the corresponding Tb–HPBA or Eu–PBA complex (Figure S2 in the Supporting Information) emerge in the spectra of film A or film K, thereby suggesting that PVP can firmly encapsulate Ln complexes and confine the vibrations of the ligands. The powder X-ray diffraction (PXRD) patterns of the complex-doped PVP films (Figure S3 in the Supporting Information) show only amorphous peaks of PVP, and the crystalline peaks of the complex molecules could not be detected, which confirms that the complex molecules are homogeneously distributed in the PVP matrices.

Luminescence properties

Photophysical properties of the multicolor photoluminescence polymer films: Interestingly, when the OH⁻ concentration in the hybrid was increased, the fabricated films display the various color luminescent emissions under UV excitation listed in Figure 1a (films A, E, F, G, H, and K); Figure 1b illustrates the photoluminescence spectra of the corresponding films at room temperature. To deduce whether deprotonation alters sensitization to Ln ions, the room-temperature excitation and emission spectra of films A and K were examined (Figures S4 and S5 in the Supporting Information). The excitation spectrum of film A displayed an intense and broad band with a maximum at approximately 371 nm, and a bathochromic shift was observed in film K. Upon optimal excitation, film A only displayed emission peaks at 488, 545, 581, and 620 nm, which can be assigned to the ${}^{5}D_{4} \rightarrow {}^{7}F_{J}$ (J= 6, 5, 4, 3, respectively) transitions of Tb^{3+} . Upon excitation at 387 nm, film K exhibited emissions at 579, 592, 611, 653, and 703 nm, which can be attributed to the ${}^{5}D_{0} \rightarrow {}^{7}F_{J}$ (J=0, 1, 2, 3, 4, respectively) transitions of Eu³⁺. These results indicate that HPBA is an excellent antenna chromophore for Tb³⁺. However, after deprotonation, PBA⁻ becomes a comparatively good organic chelator to transfer energy to Eu^{3+} . The films evidently exhibited distinct chromaticity coordinates observed in the CIE chromaticity diagram (Figure 1c).^[11] The detailed integrated intensities of the ${}^{5}D_{4} \rightarrow {}^{7}F_{J}$ (Tb³⁺; 545 nm) and ${}^{5}D_{0} \rightarrow {}^{7}F_{J}$ (Eu³⁺; 611 nm) transitions of the deprotonated films are shown in Figure S6 in the Supporting Information. As the OH⁻ concentrations increase, the emission intensity of Tb3+ decreases, whereas that of Eu³⁺ increases, which is consistent with the above observation by the naked eye. The luminescence lifetimes and quantum yields of the complexes and the films, which are two important parameters for the estimation of the luminescence efficiency, have also been determined (Table S1 in the Supporting Information). Films A and K have longer luminescence lifetimes and higher overall quantum yields than the corresponding Tb-HPBA and Eu-PBA complexes, thus indicating that PVP chains could firmly encapsulate Ln complexes and inhibit the vibration of the ligands around Ln^{III} and intermolecular collisions of the complex.^[10]

Energy-transfer studies: To clarify the effect of deprotonation of the photosensitizer HPBA on luminescence color tunability, the mechanism of the most probable inter- and intramolecular energy-transfer (ET) processes demonstrated in Figure 2 were examined on the basis of experimental data (Table S2 in the Supporting Information). The singlet energy levels of the photosensitizers were estimated for solutions in methanol with the use of their UV-visible absorbance edges. The triplet excited energy level (T_1) data of the ligands were calculated by the low-temperature (77 K) phosphorescence spectra of the corresponding Gd³⁺ complexes



Figure 1. a) Fluorescence microscopy images and b) emission spectra of films A, E, F, G, H, and K. c) CIE chromaticity diagram showing the (x, y) photoluminescence emission color coordinates from films A to K with increasing OH⁻ concentrations from 0.0 to 1.0 equiv (the step increment was 0.1 equiv) relative to the photosensitizer HPBA.

in 1:1 methanol/ethanol mixture (Figure S7 in the Supporting Information). From the experimentally observed triplet energy, the sensitizing properties of the ligands were readily evaluated in terms of the so-called energy-gap law.^[12] The triplet excited energy level of HPBA was located approximately 3858 cm⁻¹ (0.48 eV) higher than the ⁵D₄ level of Tb³⁺. Therefore, efficient intramolecular energy transfer was facilitated. For Eu³⁺, the energy level of HPBA was ap-



Figure 2. Energy-level diagram of the $Tb^{3+}:Eu^{3+}:HPBA:PBA^{-}@PVP$ hybrid. The dashed arrows represent nonradiative decays and the most probable inter- and intramolecular energy-transfer processes.

proximately 7058 cm⁻¹ (0.88 eV) higher than the corresponding ${}^{5}D_{0}$ level. Such a large energy gap resulted in the nonradiative deactivation of the europium emitting state and the quenching of the luminescence of the complex. By contrast, the triplet excited energy level of PBA⁻ was approximately 3590 cm⁻¹ (0.45 eV) higher than the corresponding ${}^{5}D_{0}$ level of Eu³⁺, and only slightly higher than the corresponding ${}^{5}D_{4}$ level in Tb³⁺. Therefore, the efficient sensitization of Eu³⁺ was promoted. Therefore HPBA is a good photosensitizer for Tb³⁺. After deprotonation, the triplet-state energy levels T_{1} of PBA⁻ changed, thus resulting in the efficient transfer of energy to Eu³⁺.

In addition, ET mechanisms might occur not only between organic photosensitizers and Ln ions, but also between Tb³⁺ and Eu³⁺. For all luminescence dopants incorporated in PVP, the distance between these molecules was short enough to promote intermolecular ET.^[13] To understand the mechanism of intermolecular ET, the average lifetimes of the excited state ${}^{5}D_{4}$ (Tb³⁺) of the films were monitored in the presence and absence of Eu³⁺ at different OH⁻ concentrations (Figure 3), and the experimental data are listed in Tables S3 and S4 in the Supporting Information. The decreasing lifetime values of the ${}^{5}D_{4}$ emitting level of Tb³⁺ were observed along with the increase of the OH⁻ concentrations both in the presence and absence of Eu³⁺. At the same OH⁻ concentration, the film doped with both Tb^{3+} and Eu^{3+} exhibited a shorter ${}^{5}D_{4}$ lifetime than that of the film doped only with Tb³⁺. This result indicates the transfer of energy from Tb³⁺ to Eu³⁺.^[14] Theoretically, the ET efficiency (E) between the donor and the acceptor can be determined by Equation (1):^[14]

$$E = 1 - \frac{\tau_{\rm da}}{\tau_{\rm d}} \tag{1}$$

in which τ_{da} and τ_d are the 5D_4 lifetimes of the films in the presence and absence of Eu³⁺, respectively. The ET efficien-





Figure 3. a) The average excited-state ${}^{5}D_{4}$ lifetimes for films D to H. b) The ${}^{5}D_{4}$ lifetimes for Tb-based PVP films with varying OH⁻ concentrations from 0.3 to 0.7 equiv (the step is 0.1 equiv) of the hybrid.

cy of Tb^{3+} to Eu^{3+} displays a stable enhancement with an increase in OH⁻ concentrations (Figure S8 in the Supporting Information). The detailed ET mechanism might be mainly supported by the phonon-assisted Förster transfer mechanism.^[15]

To further understand the effect after deprotonation, the molecular geometry and the highest-occupied molecular orbital (HOMO) and the lowest-unoccupied molecular orbital (LUMO) energy levels of the free ligands HPBA and PBA⁻ were optimized with density functional theory (DFT) at the B3LYP/6-31G* level by Gaussian 03 (Figure 4).^[16] The estimated $S_0 \rightarrow S_1$ transition (E_g) can be calculated principally by a HOMO \rightarrow LUMO excitation. The energy levels of the lowest triplet excited state can be calculated with the time-dependent DFT approach (Table S5 in the Supporting Information),^[17] which matched well with the above experimental data.

A potential white-light-emitting device: Furthermore, the tuning of photoluminescence color can also be obtained by



Figure 4. The optimized geometries and calculated spatial distributions (DFT, B3LYP/6-31G*, Gaussian 03) of HOMOs and LUMOs of the photosensitizers HPBA and PBA $^-$.

the change of the excitation wavelength. Upon selective excitations, tunable luminescence emission is then achieved. For film G, the broad-band emission with a maximum at approximately 490 nm emerged when the film was excited at 390 nm. To determine the source of this broad band, the emission spectra of the ligands and the complexes were examined. The first excited level $({}^{6}P_{7/2})$ of Gd³⁺ was far above the T_1 state of the ligands; therefore, the emission spectra of the Gd³⁺ complexes provided information on the energy levels of the ligands.^[18] Consequently, the emission spectra of Gd-HPBA, Gd-PBA, Tb-HPBA, and Eu-PBA in the solid state were determined (Figure 5a). The broad band at approximately 490 nm of film G is attributed to the emission of PBA⁻ (Figure 5a). When the excitation wavelength was altered from 390 to 430 nm, the emission of PBA- increased steadily, thus indicating a lower and less efficient energy transfer from the ligand to Ln³⁺ (Figure S9 in the Supporting Information). When film G was excited at 405 nm, the CIE chromaticity diagram established white-light chromaticity coordinates at (0.351, 0.380) (Figure 5b). This white-color emission (the white line in Figure 5a) consists of relative red (Eu³⁺), green (Tb³⁺), and blue (PBA⁻) luminescent components with suitable intensities. The detailed emission spectra and the CIE chromaticity diagrams of films A, E, F, H, and K through the change of the excitation wavelength are illustrated in Figures S10 to S14 in the Supporting Information.

To research the possibility of practical applications, the stabilities of the films and absolute complexes were investigated. To compare photoluminescence stability, kinetic scans of the luminescence induced by light in the different samples were performed (Figure 6). Less fluorescence quenching was noted in all the films, and this result implies a better photostability than that of the Tb-HPBA complex. It is observed that Eu-PBA did not show a clear fluorescence decrease, thus indicating that the ligand becomes more effective in protecting europium ions from photobleaching after deprotonation. The TG curves of films A and K demonstrate profiles similar to that of PVP (Figure S15 in the Supporting Information). However, absolute Tb-HPBA and Eu-PBA generally begin thermal decomposition at around 200 °C (Figure S16 in the Supporting Information), thus indicating that the films were stable relative to absolute Tb-HPBA and Eu-PBA. These good luminescent properties

CHEMISTRY

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Figure 5. a) Emission spectra of Gd–HPBA (blue line), Gd–PBA (cyan line), Tb–HPBA (green line), Eu–PBA (red line), and film G excited at 405 nm (white line) in the solid state at room temperature. b) CIE chromaticity diagram showing the (x, y) emission color coordinates of Tb–HPBA (dot a), Eu–PBA (dot b), Gd–HPBA (dot c), Gd–PBA (dot d), and film G excited from 390 to 430 nm (dashed arrow, the step is 10 nm) and irradiated at 405 nm (dot e). Inset: white emission behavior of film G coated on clean quartz glass irradiated at 405 nm by a laser source.

and stabilities enable the films to be used in potential optical applications.

Application of the film as a vapoluminescent sensor: The color-tunable mechanism can also be applied to a vapoluminescent sensor. Some reports have described the vapoluminescent switch of materials triggered by the presence of base–acid vapors,^[19] but such reports are scarce for vapoluminescent color-tunable materials. Interestingly, we found



Figure 6. Photoluminescence stabilities of Tb–HPBA, film A, film E (normalized intensities of the ${}^{5}D_{4} \rightarrow {}^{7}F_{5}$ transition as a function of time); and Eu–PBA, film H, film K (normalized intensities of the ${}^{5}D \rightarrow {}^{7}F_{2}$ transition as a function of time).

that the photoluminescence of the film could be changed from green to red and back to green when the film was exposed to a base-acid vapor. To present this characteristic graphically, film A that contained laser-etched Olympic fiveringed flags was used (Figure 7). As expected, the exposure



Figure 7. Fluorescence microscopy images of the laser micropatterned film A: a) as obtained on a silicon slice, b) upon brief exposure with Et_3N , c) treated with continuous-flow Et_3N , and d) upon treatment with HCl vapor shifting the luminescence back to the pristine one.

of the film to Et₃N vapor resulted in an intensification of the red emission, which could serve as a signal. The luminescence of the film shifted back to the green emission when treated with HCl gas (see Movie S1 in the Supporting Information). Such a mixed Ln-based film exhibited higher sensitivity than the single Tb-based luminescent switch, as demonstrated in its larger slope of the luminescence decay rate (Figure S17 in the Supporting Information). From the standpoint of device applications, the reversibility and the response time of the sensor are also important. The spectral changes at 545 and 612 nm of the films were monitored over several base–acid vapor cycles (Figure 8). The films exhibit-

FULL PAPER



Figure 8. Responses of luminescence intensities at 545 nm (squares) and 612 nm (triangles) of film A during acid–base vapor exposure cycles.

ed good reversibility even after eight cycles. In addition, the response time of the film was also rapid. After exposure to Et_3N vapor for 10 s, the red emission appeared completely. After exposure to HCl gas for approximately 10 s, the green emission reappeared (see Movie S1 in the Supporting Information). The films also maintained their luminescence for a few weeks without any degradation. Therefore, such a colortunable solid-state luminescence sensor by external stimuli would be of importance in a variety of applications.^[20]

Conclusion

In conclusion, we have demonstrated for the first time the realization of tunable photoluminescence films by changing OH^- concentrations of a designed fixed-component Lnbased hybrid. The emission color of the films can also be finely tuned by varying the excitation wavelength, and white-light emission can be achieved in the visible region. This novel approach to tuning emission color is a promising strategy in the development of lanthanide-based full-color photoluminescent displays. At the same time, base–acid vapor-responsive luminescent films with good stability, sensitivity, reversibility, and quick response might provide access to sensor materials. The results of this work might have great theoretical and practical significance for the design of multifunctional materials. Further investigations of these materials and other candidates are still ongoing in our lab.

Experimental Section

Materials: All reagents and solvents were obtained from commercial sources and used without further purification. Terbium ($Tb(NO_3)_3$ - $6H_2O$) and europium nitrates ($Eu(NO_3)_3$ - $6H_2O$) were obtained by dissolving Tb_4O_7 and Eu_2O_3 (99.99%, Shanghai Yuelong) in nitric acid followed by

successive fuming to remove excess amounts of acid. PVP K-30 and 2aminopyridine were purchased from Alfa Aesar. Ethyl benzoylacetate was purchased from Lanzhou Aihua Corporation.

Synthesis of HPBA: The photosensitizer *N*-(2-pyridinyl)benzoylacetamide (HPBA) was prepared by the reaction of 2-aminopyridine with ethyl benzoylacetate.^[21] Yield: 70%; m.p. 104–108°C; ¹H NMR (CDCl₃, 400 MHz): δ =4.21 (s, 2H), 7.23 (t, 1H), 7.71 (t, 1H), 8.26 (d, 1H), 8.61 (d, 1H), 7.46 (t, 2H), 7.50 (t, 1H), 8.17 (d, 2H), 9.99 ppm (s, 1H); elemental analysis calcd (%) for C₁₄H₁₂N₂O₂: C 69.79, H 4.68, N 11.38; found: C 69.99, H 5.03, N 11.66.

Synthesis of the films: PVP K-30 powder (1 g) was dissolved in DMF (40 mL) that contained distilled water (10 mL), followed by the addition of the constant amount of photosensitizer HPBA (1 mmol) and Ln^{3+} (Ln = Eu, Tb) ions to acquire the hybrid. The molar ratio of HPBA/Eu-(NO₃)₃·6H₂O/Tb(NO₃)₃·6H₂O was 10:1:2. Subsequently, the hybrid was spin-coated on clean quartz glasses and finally dried at 80°C under vacuum for 8 h. The polymer film was obtained after the total evaporation of the solvent. The tunable photoluminescence films (A–K) were fabricated after the addition of the varied OH⁻ (NaOH) concentrations from 0.0 to 1.0 equiv (the step is 0.1 equiv) relative to the photosensitizer into the hybrid.

Measurements: NMR spectra were recorded using a Bruker 400 MHz spectrometer. Chemical shifts (δ) are given in parts per million. The compositions of HPBA, 1, and 2 were determined by CHN elemental analyses using an Elementar Vario EL analyzer. Mass spectra were recorded using a Bruker UHR-TOF maXis 4G mass spectrometer. FTIR spectra of the materials were conducted within the 4000-400 cm⁻¹ wavenumber range by using a Nicolet 360 FTIR spectrometer with the KBr pellet technique. PXRD were determined using a Rigaku-Dmax 2400 diffractometer with $Cu_{K\alpha}$ radiation over the 2θ range of 3-60°. Thermogravimetric analyses (TGA) were performed using a Perkin-Elmer thermal analyzer up to 800 $^{\circ}\mathrm{C}$ at a heating rate of 10 $^{\circ}\mathrm{C\,min^{-1}}$ under a nitrogen atmosphere. The phosphorescence spectra of Gd-HPBA and Gd-PBA were measured at 77 K in a methanol/ethanol mixture (1:1 v/v) using a Hitachi F-4500 spectrophotometer. The steady-state luminescence spectra and the lifetime measurements were measured using an Edinburgh Instruments FSL920 fluorescence spectrometer with a 450 W Xe arc lamp as the steady-state excitation source and an Nd-pumped OPOlette laser as the excitation source for lifetime measurements. In the experiments of photoluminescence stability, the 450 W Xe arc lamp was used as the irradiation source, with a slit of 0.4 nm and a shutter opening after 10 s for 800 s. The overall quantum yields of the samples were determined by an absolute method with an integrating sphere^[22] (150 mm diameter, BaSO₄ coating) using an Edinburgh Instrument FLS920. Three parallel measurements were carried out for each sample, so that the presented value corresponds to the arithmetic mean value. The errors in the quantum-yield values associated with this technique were estimated to be within 10%.[23] The micropatterned films were prepared by laser micromachining using a LUCE laser source ($\lambda = 1064$ nm, Bright Solution, Italy).

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4562 -