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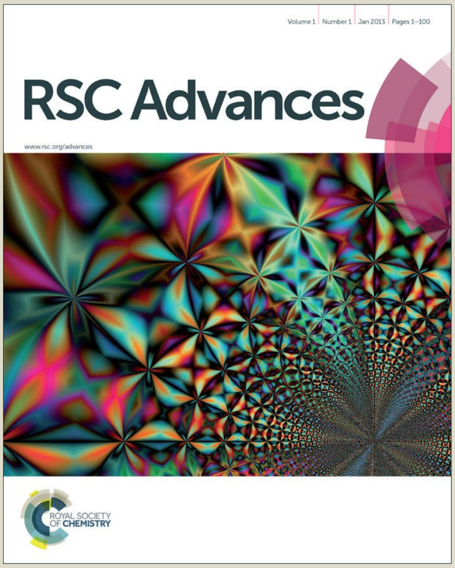

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ARTICLE

Aqueous Synthesis of Stable and Luminescent Flexible Non-covalently Assembled Europium (III) Complexes-organoclay Films

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In this paper, we report a novel lanthanide luminescent hybrid material that prepared by simple supramolecular co-assembly of aminoclay (AC), $Eu(TTA)_3·2H_2O$ and deprotonated 4'-para-phenylcarboxyl-2,2':6',2''-terpyridine (Na-Carb-Terpy) in aqueous system at room temperature. Bright red luminescence dominated by $^5D_0 \rightarrow {}^7F_2$ transition (λ_{em} = 614 nm) of Eu^{3+} can be observed under appropriate UV light illumination. The hybrid material exhibits optimal luminescent properties coupled with good water dispersibility when the initial addition amount of AC and Terpy moieties is 4:1 in molar ratio. A consequence is that flexible, transparent and strong red-light-emitting thin film based on water-soluble polymer poly(vinyl alcohol) (PVA) has been successfully prepared, showing better luminescent properties than the hybrid material, as well as improved photo- and thermo-stability compared with pure $Eu(TTA)_3·2H_2O$.

1. Introduction

Lanthanide organic complexes have been of great interest in decades due to their excellent photo-luminescent properties such as narrow emission bands, long decay time as well as large ligand-induced Stokes' shift, with a promising prospect as candidates for light-emitting diodes (LEDs), luminescent solar concentrators (LSCs), laser materials or sensors for biological applications. [1-11] Nowadays numerous researches are concentrated on the lanthanide(III)-β-diketonate complexes (LnDCs) since this type of complexes show high luminescence intensity, good color purity and high quantum efficiency, such as the $[Eu(TTA)_3(phen)]$ (TTA = 2-thenoyltrifluoroacetonate), a well-known LnDCs, which has a high quantum efficiency of 36.5%. [12, 13] Unfortunately, low photo- and thermo-stability severely limit their further application. A frequently-used method for solving this problem is doping LnDCs into organic/inorganic matrices like polymers, ionic liquids (ILs), polysilsesquioxanes, zeolite L or laponite [13-18], giving rise to hybrid materials with improved photo- and thermo-stability as well as good processibility. However, high cost, long time-consuming and complicated procedure are still the main drawbacks of this method. Therefore, a simple, low cost and environmentally friendly procedure for preparing LnDCs-doped hybrid materials with excellent luminescent properties as well as good photo- and thermo-stability is highly desirable.

We previously prepared multicolored luminescent hybrid materials by simple supramolecular co-assembly of aminoclay (AC), organic sensitizer and Ln^{3+} cations in aqueous medium at room temperature[19, 20], where AC (see Scheme 1) is an aminopropyl-functionalized layered magnesium phyllosilicate, with an approximate chemical composition of $R_8Si_8Mg_6O_{16}(OH)_4$ (R = -$(CH_2)_3NH_2$), which has been recognized as an excellent scaffold in aqueous system [21-29]. Tunable emission colors from red to blue and white light can be observed under UV light illumination. Moreover, luminescent thin films on quartz substrate can also be prepared using water suspension of the materials, with high transparency and good color purity. These indicate that AC is an ideal scaffold for preparing lanthanide-based luminescent hybrid materials, which may also be suitable for LnDCs. However, the luminescence quenching effect of coordinated water molecules on LnDCs is still a barrier for preparing hybrid materials in aqueous system [17]. Therefore, our target is to prepare luminescent hybrid materials in aqueous system by introducing LnDCs into AC substrate, with good luminescent performance and excellent aqueous processibility.

Herein we report a novel lanthanide hybrid luminescent material, with AC, $Eu(TTA)_3·2H_2O$ and deprotonated 4'-para-phenylcarboxyl-2,2':6',2''-terpyridine (Na-Carb-Terpy) as the starting materials (denoted as AC-Terpy-$Eu(TTA)_3$ (n:1), where n is the initial addition amount of AC and Terpy in molar ratio, n = 2, 4, 10, 20, 50 and 100. The initial addition amount of Terpy moieties and $Eu(TTA)_3$ was maintained at 1:1 in molar ratio). The Na-Carb-Terpy acts as a linker between AC and $Eu(TTA)_3$ molecules, since the carboxyl anions of which can be non-covalently connected with the protonated AC layers while the terpyridine groups are able to coordinate with

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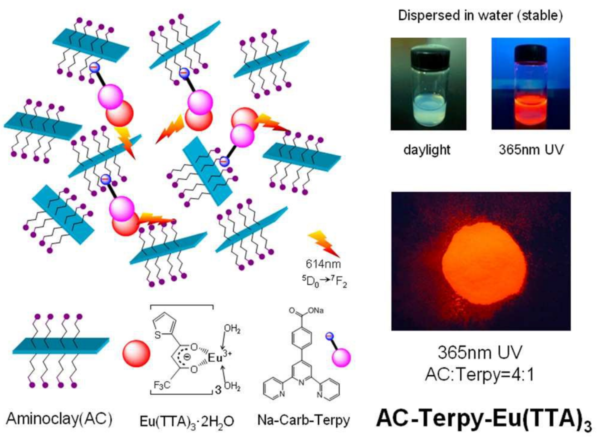
Eu(III) of $Eu(TTA)_3·2H_2O$. Interestingly, the hybrid material exhibits good water dispersibility, since the protonation on the free aminopropyl moieties can guarantee partial exfoliation of AC layers in water and result in a stable dispersion finally. [23] Both the powder and water dispersion of the material are able to emit bright red luminescence under 365 nm UV lamp illumination (see Scheme 1). In addition, transparent and flexible luminescent thin film with remarkably improved photo- and thermal-stability was obtained by simply casting aqueous suspension of the hybrid material with a small amount of water-soluble organic polymer.



Scheme 1. Predicted microstructure of AC-Terpy-Eu$(TTA)_3$ together with its powder (under 365 nm UV illumination) and water dispersion.

2. Results and discussion

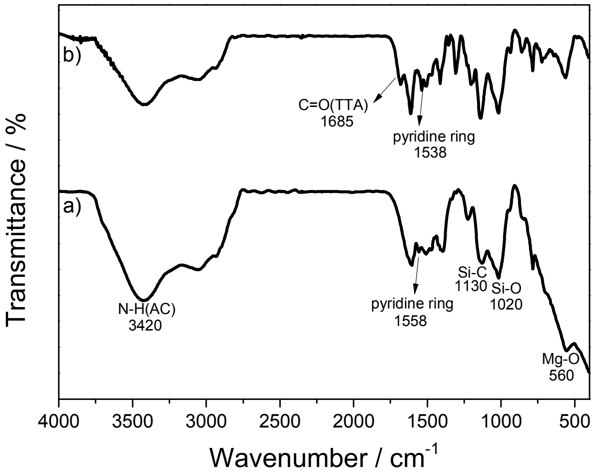


Figure 1. FT-IR spectra of a) AC-Terpy and b) AC-Terpy-Eu$(TTA)_3$ (4:1).

The formation of the hybrid materials can be confirmed by FT-IR spectra, as shown in Figure 1. Figure 1a displays the characteristic absorption bands of AC:3420 cm^{-1} (N-H of aminopropyl), 1130 cm^{-1} (Si-C), 1020 cm^{-1} (Si-O) as well as 560 cm^{-1} (Mg-O), while a weak band at 1558 cm^{-1} due to the C=N stretching reveals the existence of pyridine ring. In Figure 1b, the sharp peak located at 1685 cm^{-1} can be assigned to the C=O vibration of TTA molecules. Compared Figure 1b with 1a, it can be observed that the C=N stretching of the pyridine ring experiences a downshift from 1558 cm^{-1} to 1538 cm^{-1} (Δv = 20 cm^{-1}) upon the introduction of Eu$(TTA)_3$, indicating that at least partial Terpy moieties are coordinated with Eu$(TTA)_3$ molecules. [13]

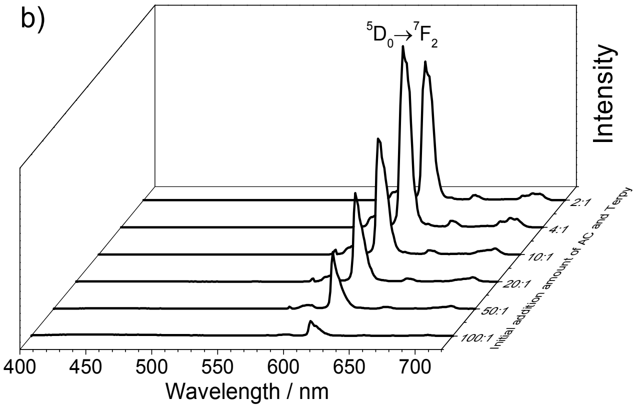


Figure 2. a) Excitation spectrum of AC-Terpy-Eu$(TTA)_3$ ($\lambda_{monitored}$ = 614 nm); b) emission spectra of AC-Terpy-Eu$(TTA)_3$ (λ_{ex} = 385 nm).

The luminescence data of AC-Terpy-Eu$(TTA)_3$ were measured and displayed in Figure 2. A broad absorption band peaking at 385 nm (Figure 2a) is attributed to the $\pi \rightarrow \pi^*$ electronic transition of the ligands TTA and Terpy. The weaker sharp band at 465 nm ($^7F_0 \rightarrow {}^5D_2$ transition) is assigned to intra-configurational excitation of Eu(III), from which we can conclude that the Eu^{3+} are essentially excited by ligand-induced process rather than the self-absorption of themselves. After excitation within the ligands' excited state (385 nm), five sharp emission bands at 578, 592, 614, 650 and 700 nm ($^5D_0 \rightarrow {}^7F_J$ transition of Eu^{3+}, J = 0, 1, 2, 3 and 4) can be observed (Figure 2b), where the $^5D_0 \rightarrow {}^7F_2$ transition acts as the dominant feature, resulting in bright red luminescence (see Scheme 1). Besides, the relatively weaker absorption from 400 to 460 nm (Figure 2a) suggests that the hybrid material can also be excited by visible light, affording it potential candidate for designing optoelectronic conversion devices like photovoltaic (PV) cells. [30, 31]

The initial addition amount of AC and Terpy moieties highly affects the luminescent properties of the resulting materials, as shown in Figure 2b. The intensity of the $^5D_0 \rightarrow {}^7F_2$ transition reaches the maximum when the initial addition amount of AC and Terpy is 4:1 in molar ratio (AC-Terpy-Eu(TTA)$_3$ (4:1)) and decreases gradually with the further increase of the initial AC addition amount. The same situation for the $^5D_0$ lifetime of Eu(III) in AC-Terpy-Eu(TTA)$_3$ (τ_{Eu}) is observed (Figure 3). The AC-Terpy-Eu(TTA)$_3$ (4:1) shows the longest $^5D_0$ lifetime of Eu(III) (0.45 ms), which is higher than that of pure Eu(TTA)$_3$·2H$_2$O (0.37 ms). [32] This phenomenon might be attributed to the displacement of the water molecules coordinated to Eu^{3+} after the introduction of Terpy moieties since water molecules provide an efficient route for the radiationless deactivation. [16] In order to prove this point, we roughly calculated the number of water molecules coordinated to Eu^{3+} (n_w). The n_w can be estimated by using the following empirical equation [33]:

$$n_w = 1.11(k_{exp} - k_r - 0.31) \quad (1)$$

where k_{exp} is the reciprocal value of τ_{Eu} (ms^{-1}) and k_r is the radiative probabilities (ms^{-1}). The value of k_r can be estimated as follow [34]:

$$k_r = \frac{A_{0-1}E_{0-1}}{S_{0-1}} \sum_{J=0}^{4} \frac{S_{0-J}}{E_{0-J}} \quad (2)$$

where A_{0-1} is the Einstein's coefficient of spontaneous emission between the $^5D_0$ and the $^7F_1$ Stark levels, which is approximately 50 s^{-1}, and E_{0-J} and S_{0-J} are the energy and the integrated intensity of the $^5D_0 \rightarrow {}^7F_J$ (J = 0-4) transitions, respectively. The corresponding luminescent parameters of Eu(TTA)$_3$·2H$_2$O and AC-Terpy-Eu(TTA)$_3$ (4:1) were listed in Table 1. The k_r here is 0.81, thus the n_w is 1.22 and is lower than that of Eu(TTA)$_3$·2H$_2$O. This provides a satisfactory explanation for the reason why AC-Terpy-Eu(TTA)$_3$ (4:1) exhibits higher τ_{Eu} value than that of Eu(TTA)$_3$·2H$_2$O. We also measured the absolute $^5D_0$ quantum efficiency of Eu^{3+} (Φ_{tot}) in AC-Terpy-Eu(TTA)$_3$ (4:1) by using an integrating sphere according to the reported method [35]. The value of Φ_{tot} is 39.2% (± 2.6%) and is much higher than that of Eu(TTA)$_3$·2H$_2$O (25%) [36]. We therefore conclude that hybridization of Eu(TTA)$_3$·2H$_2$O and aminoclay through Terpy moieties affords the pure complex higher $^5D_0$ lifetime and quantum efficiency, and the AC-Terpy-Eu(TTA)$_3$ (4:1) can be regarded as the optimal one.

Table 1. Luminescent parameters of Eu(TTA)$_3$·2H$_2$O and AC-Terpy-Eu(TTA)$_3$ (4:1).

Luminescent materials	τ_{Eu}/ms	k_r/ms^{-1}	n_w	Φ_{tot}
Eu(TTA)$_3$·2H$_2$O	0.37	0.59	2	25%
AC-Terpy-Eu(TTA)$_3$ (4:1)	0.45	0.81	1.22	39.2%

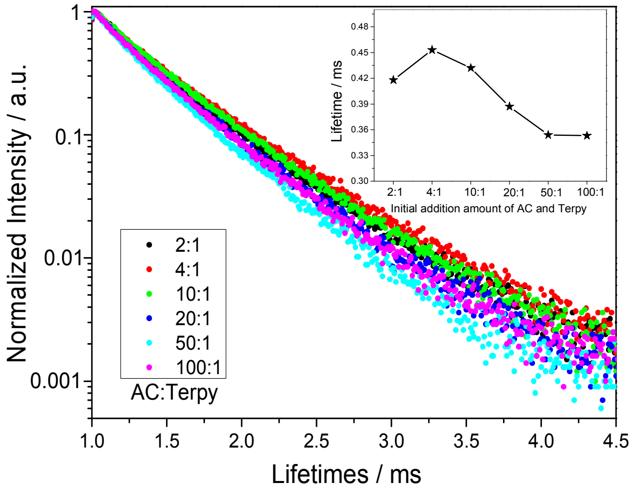


Figure 3. $^5D_0$ lifetimes of Eu(III) in AC-Terpy-Eu(TTA)$_3$ (n:1), λ_{ex} = 385 nm, $\lambda_{monitored}$ = 614 nm. The inner figure shows the variation curve of the lifetimes *versus* the molar ratio of AC and Terpy.

Flexible luminescent thin films typically show great advantages in fabricating collapsible optoelectronic devices owing to their advantages of foldability and crack resistance[37], we therefore prepared the thin film by using AC-Terpy-Eu(TTA)$_3$ (4:1) as the building blocks via a very simple process: casting aqueous suspension of the material with a small amount of water-soluble organic polymer like poly(vinyl alcohol) (PVA). The as-obtained thin film (named as AC-Terpy-Eu(TTA)$_3$-PVA) exhibits high flexibility, transparency and can emit bright red luminescence under 365 nm UV illumination (see Figure 4a). Figure 4b shows the UV-Visible transmittance spectrum of the thin film. The broad band from 320 to 450 nm can be attributed to the absorption of the organic ligands. Furthermore, the value of transmittance is more than 80% from 450 to 800 nm, indicating that the thin film is fairly transparent in the visible region. The $^5D_0$ lifetime and absolute $^5D_0$ quantum efficiency of Eu^{3+} in AC-Terpy-Eu(TTA)$_3$-PVA were measured as 0.55 ms (Figure 4c) and 42.5% (± 3.2%), respectively, and both of them are higher than those of AC-Terpy-Eu(TTA)$_3$ (4:1) (0.45 ms and 39.2%, respectively). We speculate that the molecular motion and bond vibration of the europium complexes were restrained when the AC-Terpy-Eu(TTA)$_3$ (4:1) was introduced into PVA matrices, which could decrease the non-radiative transition.[38]

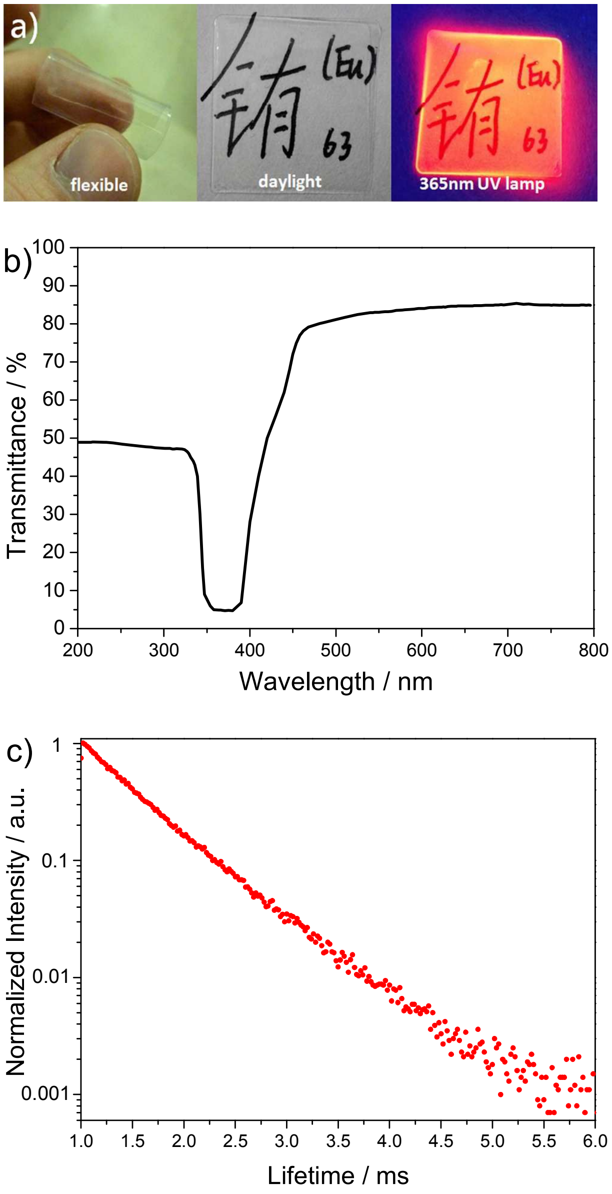


Figure 4. Digital photos (a) and UV-Visible transmittance spectrum (b) of AC-Terpy-Eu(TTA)$_3$-PVA, c is the $^5D_0$ lifetime of Eu^{3+} in AC-Terpy-Eu(TTA)$_3$-PVA (λ_{ex} = 385 nm, $\lambda_{monitored}$ = 614 nm).

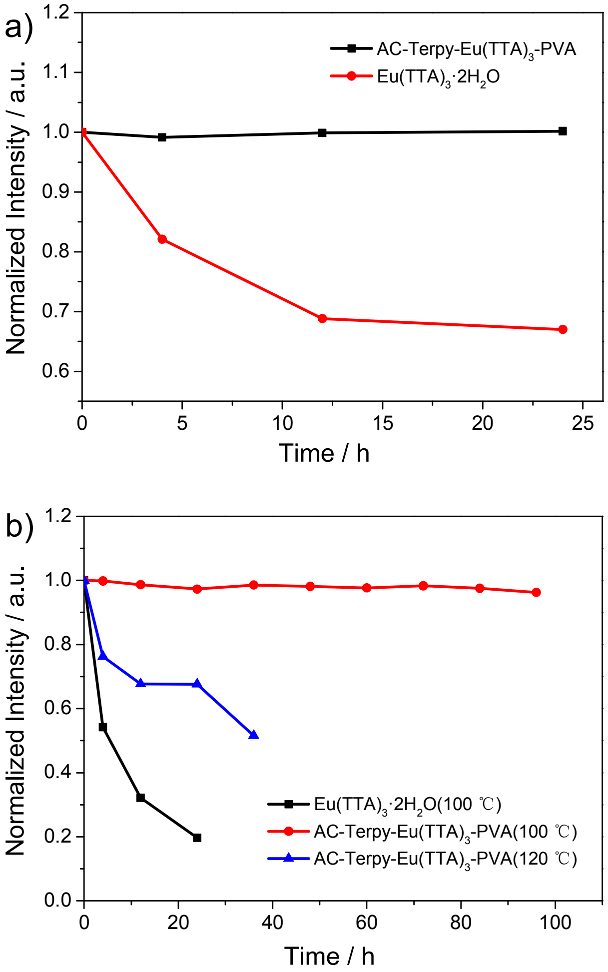


Figure 5. Variations of the emission intensity at $^5D_0 \rightarrow {}^7F_2$ transition of AC-Terpy-Eu(TTA)$_3$-PVA and Eu(TTA)$_3$·2H$_2$O under 365 nm UV lamp illumination (a) and after heating at different temperatures in air (b).

Since the photo- and thermo-stability are significant criteria of lanthanide-based luminescent materials, we therefore investigated the photo- and thermo-stability of AC-Terpy-Eu(TTA)$_3$-PVA as well as the precursor Eu(TTA)$_3$·2H$_2$O, and the results were shown in Figure 5. In Figure 5a, after 24 hours of 365 nm UV lamp illumination, no obvious emission intensity loss of $^5D_0 \rightarrow {}^7F_2$ transition can be observed for the PVA thin film, whereas the emission intensity of Eu(TTA)$_3$·2H$_2$O decreases about 1/3 compared with its initial value. The instability of LnDCs towards UV irradiation has already been reported elsewhere [13, 39]. Apparently, the PVA thin film exhibits much better UV light-resistance stability than Eu(TTA)$_3$·2H$_2$O. The thermo-stability of the PVA thin film and Eu(TTA)$_3$·2H$_2$O was investigated by measuring the $^5D_0 \rightarrow {}^7F_2$ emission intensity after heating at 100 ℃ in air (Figure 5b). It reveals that more than 80% emission intensity loss can be found for $Eu(TTA)_3\cdot 2H_2O$ after 24 hours' heating. However, the film retains its emission intensity even after heating for 4 days. As a comparison, we heated the film at 120 ℃ for 36 h, and 50% emission intensity loss was found in the end. The experimental data suggests that the thermo-stability of PVA thin film is also better than the pure complex, and 100 ℃ can be treated as the highest working temperature for the film. Therefore, the polymer thin film AC-Terpy-$Eu(TTA)_3$-PVA has improved photo- and thermo-stability with respected to the pure complex $Eu(TTA)_3\cdot 2H_2O$, maybe because of the protection effect of the PVA surface as well as AC substrates.[18, 40]

Conclusions

In summary, a novel hydrophilic red-light-emitting hybrid material that composed of aminoclay (AC), deprotonated 4'-para-phenylcarboxyl-2,2':6',2''-terpyridine (Na-Carb-Terpy) and $Eu(TTA)_3\cdot 2H_2O$ has been successfully prepared through a very simple and green procedure. The material exhibits optimal luminescent properties when the initial addition amount of AC and Terpy is 4:1 in molar ratio, with the $^5D_0$ lifetime (τ_{Eu}) and the absolute $^5D_0$ quantum efficiency (Φ_{tot}) of Eu(III) of 0.45 ms and 39.2%, respectively, as well as excellent water dispersibility. Flexible, transparent and luminescent thin film based on poly(vinyl alcohol) (PVA) has also been prepared under aqueous condition at room temperature, exhibiting higher τ_{Eu} (0.55 ms) and Φ_{tot} (42.5%) value than those of the hybrid material. In addition, compared with $Eu(TTA)_3\cdot 2H_2O$, the photo- and thermo-stability of the thin film are remarkably improved. These characteristics afford the thin film potential candidate for fabricating collapsible optoelectronic devices.

Experimental

Materials

Aminoclay (AC), $Eu(TTA)_3\cdot 2H_2O$ and 4'-para-phenylcarboxyl-2,2':6',2''-terpyridine (Carb-Terpy) were synthesized by the methods reported previously.[19, 41, 42] Poly(vinyl alcohol) (PVA) was used as purchased. $Eu(TTA)_3$ ethanol solution (0.01 M) was obtained by dissolving $Eu(TTA)_3\cdot 2H_2O$ into absolute ethanol. Na-Carb-Terpy aqueous solution (0.01 M) was obtained by dissolving Carb-Terpy into NaOH aqueous solution. 5% (mass ratio) PVA aqueous solution was obtained by dissolving PVA into double distilled water at 90-100 ℃.

Preparation of AC-Terpy-$Eu(TTA)_3$

AC was dissolved in an appropriate amount of double distilled water, then the Na-Carb-Terpy aqueous solution was added and a light-yellow emulsion (named as AC-Terpy) was obtained after sonication for 5 minutes, with the initial addition amount of AC and Terpy being n:1 (n = 2, 4, 10, 20, 50 or 100) in molar ratio. Afterwards, we added the $Eu(TTA)_3$ ethanol solution to the emulsion (the initial addition amount of Terpy moieties and $Eu(TTA)_3$ was maintained at 1:1 in molar ratio), and the mixture was sonicated for 5 minutes and dried at 80 ℃ for several hours followed by fine grind, resulting in the final material (light-yellow powder, named as AC-Terpy-$Eu(TTA)_3$ (n:1)).

Preparation of the luminescent polymer thin film (AC-Terpy-$Eu(TTA)_3$-PVA)

0.05 g AC-Terpy-$Eu(TTA)_3$ (4:1) was dispersed in 4.95 g double distilled water and 10 g PVA aqueous solution was then added followed by sonication for 5 minutes, resulting in a translucent suspension. The PVA thin film was obtained by drop-casting 1.5 g the suspension onto a 2.5 cm × 2.5 cm quartz substrate and drying in air at 40 ℃ for several hours.

Characterization

The Fourier transform infrared spectrum (FT-IR) spectra were obtained on a Bruker Vector 22 spectrometer using KBr pellets for the powder samples, from 4000 to 400 cm^{-1} at a resolution of 4 cm^{-1} (16 scans collected), about 2 mg of each compound were mixed with KBr (Merck, spectroscopic grade) finely ground and pressed into pellets. The UV-Visible transmittance spectrum was obtained on an Agilent Carry 100 UV-vis spectrometer, from 200 to 800 nm. The solid-state luminescence spectra and the lifetimes were measured on an Edinburgh Instrument FS920P spectrometer, with a 450 W xenon lamp as the steady-state excitation source, a double excitation monochromator (1800 lines mm^{-1}), an emission monochromator (600 lines mm^{-1}), a semiconductor cooled Hamamatsu RMP928 photomultiplier tube. Powder samples and films on quartz substrate were directly put in the chamber of the instrument, for the photophysical measurements. A microsecond flash lamp (pulse length: 2 μs) was used as the excitation source for the lifetime measurements. Photons were collected up to 10 ms until maximum of 104 counts. Decay curves were fitted according to the single-exponential function ($I = I_0 + A * exp(- (t-t_0) / \tau)$).

Acknowledgements

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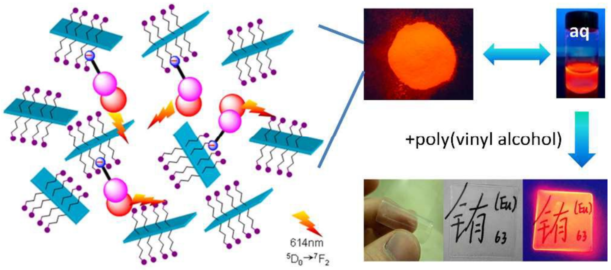
Graphic Abstract



Flexible, transparent and red-light-emitting luminescent polymer thin film derived from Eu(TTA)$_3$-doped Hydrophilic Hybrid Material.