Research Article

Multiligand Europium Complexes Incorporated Polyvinylpyrrolidone for Enhanced Solar Cell

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Intense reddish-orange fluorescence of Eu^{3+} is observed in multiligand europium complexes $\text{Eu}(\text{BA})(\text{TTA})_2$ and $\text{Eu}(\text{BA})(\text{T-TA})_2\text{Phen}$ doped polyvinylpyrrolidone (PVP). Under 367 nm UVA-LED pumping with 708.5 μW , the net emission powers are as high as 204.8 and 243.2 μW , and the total emission photon numbers are derived to be 635.9×10^{12} and 754.9×10^{12} cps for $\text{Eu}(\text{BA})(\text{TTA})_2$ and $\text{Eu}(\text{BA})(\text{T-TA})_2\text{Phen}$ doped PVP thin films, respectively. It is incredible that the quantum yield (QY) is up to 57.87% in the former; furthermore, as the introduction of Phen, the QY of Eu^{3+} is increased to 62.03%, verifying the effectiveness of multiligands in photon conversion. Conclusive photon quantification and efficient fluorescence emission reveal the potential of europium complexes/PVP as UV-visible conversion layers for enhanced solar cells.

1. Introduction

Energy harvesting by means of the photovoltaic system has attracted extensive attention, while the inadequate utilization of ultraviolet (UV) radiation restricts application and development for solar cells [1–3]. In order to solve this problem, the photoluminescence materials are introduced into solar cells as photonic conversion layers [4–10]. As is well known, the fluorescent materials are able to absorb the short-wavelength photons and convert them into long-wavelength photons with better spectral responsiveness for solar cells [11–13]. Proceeding from this angle, rare-earth europium complexes can be introduced into solar cells with a significant impact on the photoelectric conversion efficiency [14–17]. Consequently, the optical conversion materials are capable of absorbing UV radiation effectively, which are worthy of further research and development.

Compared to other photoluminescence materials, rare-earth complexes have high fluorescence quantum efficiency and extremely narrow emission bands [18–20]. Moreover, the fluorescence of rare-earth complexes can be enhanced by synthesizing a stable complex with a suitable organic ligand. In the rare-earth organic complexes, the composite of

β -diketone and carboxyl possesses better stability and higher fluorescence efficiency than those of single-ligand complexes [21–23]. Furthermore, the combination of europium complexes and organic polymers has good thermal properties, which is favorable in solar cells [24–27]. Herein, as a typical amphiprotic organic polymer, polyvinylpyrrolidone (PVP) is introduced into rare-earth complexes with low toxicity, excellent chemical stability, and good compatibility [28–31]. Hence, europium complexes/PVP as the emitters in organic photoluminescence devices is a potential candidate as an UV-visible conversion layer for enhanced solar cells, and the schematic diagram is proposed and depicted in Figure 1.

In this work, the europium complexes/PVP luminescence films with high absorption efficiency and intense fluorescence emission have been synthesized. The brilliant reddish-orange fluorescence indicates the validity of energy transfer from multiligands to Eu^{3+} through intramolecular energy transfer. Under UVA-LED radiation, the absorption and emission photon numbers are obtained, and the quantum yields are estimated as high as 57.87% and 62.03% for $\text{Eu}(\text{BA})(\text{TTA})_2/\text{PVP}$ and $\text{Eu}(\text{BA})(\text{T-TA})_2\text{Phen}/\text{PVP}$, respectively. The multiligand europium complexes doped PVP thin film protects the solar cells components on the one hand

FIGURE 1: Schematic diagram of UV-visible conversion layer for enhanced solar cells.

and improves the photon conversion efficiency on the other hand, which is prospective as UV-visible conversion layers for enhanced solar cells.

2. Experimental

Ternary complex $\text{Eu}(\text{BA})(\text{TTA})_2$ and quaternary complex $\text{Eu}(\text{BA})(\text{TTA})_2\text{Phen}$ were prepared by the chemical synthesis using benzoic acid (BA), thenoyltrifluoroacetone (TTA), and 1,10-phenanthroline (Phen). For example, according to $\text{Eu}(\text{BA})(\text{TTA})_2\text{Phen}$ chemical formula, initially, EuCl_3 , BA, TTA, and Phen with the molar ratio of 1:1:2:1 were dissolved in 30 ml 99.7% ethanol and placed in a water bath at 50°C , and then, sodium hydroxide (NaOH) solution was dripped to the pH value of 6-7. Instantaneously, the white precipitate of $\text{Eu}(\text{BA})(\text{TTA})_2\text{Phen}$ was formed, which was filtered, washed, and dried at room temperature. In the fabrication process of europium complexes doped PVP, 1 g PVP powder was dissolved in 0.95 g *N,N*-dimethylformamide (DMF) solution and 10 ml ethyl alcohol solution followed by the addition of 0.01 g $\text{Eu}(\text{BA})(\text{TTA})_2$ and 0.01 g $\text{Eu}(\text{BA})(\text{TTA})_2\text{Phen}$, respectively. The well-mixed solutions were heated at 50°C for 1 hour using a thermostat water bath, and the samples were obtained by evaporating the solvent slowly. Finally, the resultant solution was deposited on the quartz sheet and dried to obtain transparent films.

Fourier-transform infrared (FT-IR) spectra were measured at room temperature by a PerkinElmer FT-IR/NIR spectrometer in the range of $4000\text{--}400\text{ cm}^{-1}$. The elemental analysis was carried out by energy dispersive X-ray spectroscopy (EDS) at an accelerating voltage of 5 kV. The emission and excitation spectra were taken on a Hitachi F-7000 fluorescence spectrophotometer equipped with a photomultiplier tube (PMT) as a detector and a commercial CW Xe-lamp as a pump source. Transmittance spectra were recorded by a UV-1600 spectrophotometer. The differential scanning calorimetry (DSC) and the thermogravimetric analysis (TGA) were carried out by the American TA

company SDT 600 at a heating rate of $20^\circ\text{C}/\text{min}$ under a dynamic nitrogen atmosphere. By the Metricon 2010 prism coupler, the refractive indices of the $\text{Eu}(\text{BA})(\text{TTA})_2$ and $\text{Eu}(\text{BA})(\text{TTA})_2\text{Phen}$ doped PVP were measured to be 1.5215 and 1.5256 at 635.96 nm, and 1.5091 and 1.5115 at 1546.9 nm, respectively. The refractive indices of other wavelengths can be reckoned by Cauchy equation $n = (A + B)/\lambda^2$ with $A = 1.5066$ and $B = 6035.2\text{ nm}^2$ for $\text{Eu}(\text{BA})(\text{TTA})_2$ doped PVP, and $A' = 1.5086$ and $B' = 6862.6\text{ nm}^2$ for $\text{Eu}(\text{BA})(\text{TTA})_2\text{Phen}$ doped PVP. All of the spectral power distributions of $\text{Eu}(\text{BA})(\text{TTA})_2/\text{PVP}$ and $\text{Eu}(\text{BA})(\text{TTA})_2\text{Phen}/\text{PVP}$ were carried out in an integrating sphere of 25 cm inner diameter (Labsphere) which was connected to a QE65000 and a USB4000 standard CCD detector (Ocean Optics) with a $600\text{ }\mu\text{m}$ -core optical fiber. The currents of the exciting 308 nm UVB and 367 nm UVA light emitting diode were fixed at 20 mA with reference voltages 5.780 and 3.607 V, respectively. The samples covered the upper part of LED completely, and the measurement system is calibrated with a standard halogen lamp (Labsphere, SCL-050).

3. Results and Discussion

3.1. Structural Analysis of Multiligand Europium Complexes.

The structures of $\text{Eu}(\text{BA})(\text{TTA})_2$, $\text{Eu}(\text{BA})(\text{TTA})_2\text{Phen}$, $\text{Eu}(\text{BA})(\text{TTA})_2/\text{PVP}$, $\text{Eu}(\text{BA})(\text{TTA})_2\text{Phen}/\text{PVP}$, and PVP are measured in the $4000\text{--}400\text{ cm}^{-1}$ region by FT-IR spectroscopy, as shown in Figure 2. Such as the case of $\text{Eu}(\text{BA})(\text{TTA})_2\text{Phen}$ (curve 2), after the coordination formation between organic ligand and Eu^{3+} , the carbonyl group ($\text{C}=\text{O}$) stretching vibration absorption peak of TTA has a redshift from 1680 to 1605 cm^{-1} [32, 33], which is caused by the reduction of bond length and bond energy of the covalent bond because the isolated electrons transfer from part of the oxygen to the outer layer of a hollow orbit in Eu^{3+} . In addition, carbonyl is conjugated with Eu^{3+} after the deprotonation, subsequently forming a stable chelating ring, and then the conjugate effect of the system makes the density of π -electron cloud more uniform; therefore, absorption frequency is decreased, and polarity of the covalent bonds is weakened [34, 35]. The peaks located in the range of $1304\text{--}1357$ and $1538\text{--}1569\text{ cm}^{-1}$ belong to symmetric and antisymmetric stretching vibrations of carboxyl, respectively, indicating the carboxylic acid of BA removes the proton and coordinates with the Eu^{3+} ions. Compared with $\text{Eu}(\text{BA})(\text{TTA})_2$ (curve 1), the absorption peak shifts from 1545 to 1538 cm^{-1} due to the introduction of the third ligand suggesting the energy required for vibration is higher, and the group is more stable. And the noncharacteristic absorption $\text{C}=\text{N}$ stretching vibration peak of Phen appears a slight redshift from 1422 to 1415 cm^{-1} , demonstrating that the lone pair of electrons on the two N atoms of the Phen coordinates with the Eu^{3+} to form the chelate ring [33]. Moreover, the spectra of PVP-loaded composite films have changed significantly in contrast to powders, and the corresponding absorption peaks of the complex powders are weakened due to the overlapping of PVP vibration peaks. Besides, the blue shift of $\text{C}=\text{O}$ stretching vibration in $\text{Eu}(\text{BA})(\text{TTA})_2/\text{PVP}$ (1660 cm^{-1}) and $\text{Eu}(\text{BA})(\text{TTA})_2\text{Phen}/$

FIGURE 2: FT-IR spectra of $\text{Eu}(\text{BA})(\text{TTA})_2$ (curve 1), $\text{Eu}(\text{BA})(\text{TTA})_2\text{Phen}$ (curve 2), $\text{Eu}(\text{BA})(\text{TTA})_2\text{PVP}$ (curve 3), $\text{Eu}(\text{BA})(\text{TTA})_2\text{Phen/PVP}$ (curve 4), and PVP (curve 5), respectively.

PVP (1663 cm^{-1}) occurs remarkably in contrast to pure-phased PVP (1648 cm^{-1}), which further confirms the effects of dopants on the FT-IR spectra of PVP.

For the sake of examining the elemental composition in the films, the EDS spectra of $\text{Eu}(\text{BA})(\text{TTA})_2\text{PVP}$ and $\text{Eu}(\text{BA})(\text{TTA})_2\text{Phen/PVP}$ are obtained, as shown in Figures 3(a) and 3(b), respectively. Both of them show that the C, O, N, Eu, S, and F elements existed in europium complex originate from BA, TTA, and Phen ligands, which provides a basis for the synthesis of the europium complexes doped PVP composites. Meanwhile, the schematic diagram based on the molecular formula of $\text{Eu}(\text{BA})(\text{TTA})_2$ and $\text{Eu}(\text{BA})(\text{TTA})_2\text{Phen}$ is illustrated in Figure 3. In $\text{Eu}(\text{BA})(\text{TTA})_2\text{Phen}$, the center Eu^{3+} connects to three ligands (BA, TTA, and Phen), among which Phen as a synergic shielding ligand enhances the luminescence intensity of the complexes [36, 37]. The presence of the surrounding ligand acts as a physical buffer between the Eu^{3+} and other ions.

3.2. Fluorescence Behaviors of Multiligand Europium Complexes/PVP. Figures 4(a) and 4(b) show the emission spectra of $\text{Eu}(\text{BA})(\text{TTA})_2$ and $\text{Eu}(\text{BA})(\text{TTA})_2\text{Phen}$ powders under the excitation of 278 and 366 nm, both of them exhibit the typical emission peaks of Eu^{3+} located at 578, 591, 615, 651, and 701 nm, which are ascribed to the Eu^{3+} transitions from the 5D_0 to 7F_J ($J=0-4$) [38, 39], respectively. Among them, the $^5D_0 \rightarrow ^7F_2$ electric dipole transition has the strongest relative fluorescence intensity, which reveals the better monochromaticity of europium complexes. The excitation spectra of multiligand europium complexes monitored at

615 nm are depicted in Figure 4(c), and a broad band almost covers the whole ultraviolet region, which mainly corresponds to $\pi \rightarrow \pi^*$ electronic transition of the ligands. Meanwhile, the excitation of coligand Phen exists in the long-wavelength region, indicating that the introduction of the Phen enlarges the range of conjugated $\pi \rightarrow \pi^*$ and facilitates energy transfer.

In order to facilitate the application in solar cells, the preparation of $\text{Eu}(\text{BA})(\text{TTA})_2$ and $\text{Eu}(\text{BA})(\text{TTA})_2\text{Phen}$ doped PVP films is carried out, and the emission and excitation spectra are shown in Figure 5, respectively. The broad band from ligand at about 310 nm is mainly attributed to the transition of $\pi \rightarrow \pi^*$ of the BA under 278 nm excitation. Simultaneously, the larger emission intensity of $\text{Eu}(\text{BA})(\text{TTA})_2\text{Phen/PVP}$ at 366 nm can be explained in accordance with the introduction of Phen as a synergistic screening ligand for BA and TTA. Bright red fluorescence is observed, and the effect of Phen is reconfirmed upon enhanced emission, indicating the availability of conversion from UV to visible photons. Figure 5(c) reveals the excitation spectra of $\text{Eu}(\text{BA})(\text{TTA})_2\text{PVP}$ and $\text{Eu}(\text{BA})(\text{TTA})_2\text{Phen/PVP}$ by monitoring the ligand emission at 381 nm, respectively. It can be effectively activated within the scope of 200–360 nm, and the optimum excitation wavelength locates at 278 nm. As shown in Figure 5(d), an excited broad band of europium complexes/PVP in the UV region indicates the effective absorption of the organic ligands.

Taking an example of quaternary complex, in order to clearly show the crosslink interaction between the europium complexes and PVP, the normalized excitation spectra of $\text{Eu}(\text{BA})(\text{TTA})_2\text{Phen}$ and $\text{Eu}(\text{BA})(\text{TTA})_2\text{Phen/PVP}$ monitored at 615 nm are depicted in Figure 6. It can be seen that the excitation peak located at 373 nm shows a slight blue shift and the width of excitation peak narrows in the $\text{Eu}(\text{BA})(\text{TTA})_2\text{Phen/PVP}$ films. Moreover, the fluorescence intensity decreases significantly in the short-wavelength range, which indicates the strong interaction between PVP and rare-earth complex with the occurrence of energy transfer. Meanwhile, the two broad bands further confirm that both $\text{Eu}(\text{BA})(\text{TTA})_2\text{PVP}$ and $\text{Eu}(\text{BA})(\text{TTA})_2\text{Phen/PVP}$ can be stimulated under the entire UV range, and the latter is more efficient. The reason for the intensity increment is that the cooperative ligand Phen improves the conjugation and the electron delocalization of the whole system, which facilitates the absorption and the utilization of UV radiation [40–42].

In rare-earth complexes, energy transfer efficiency mainly depends on the energy level matching between the excited state of rare-earth ions and the triplet state of the ligand, and the better the energy level matching, the stronger the fluorescence emitting [43]. The possible energy transfer mechanisms of $\text{Eu}(\text{BA})(\text{TTA})_2\text{PVP}$ and $\text{Eu}(\text{BA})(\text{TTA})_2\text{Phen/PVP}$ are portrayed in Figure 7. In $\text{Eu}(\text{BA})(\text{TTA})_2\text{Phen/PVP}$, the ligands absorb the energy from the ground state to the first two lowest energy singlet excited states $S_0 \rightarrow S_1$ and $S_0 \rightarrow S_2$ under 278 and 366 nm excitation. As shown in Figure 7(b), the energy flows from BA- S_1 to Phen- S_1 , then to TTA- S_2 , and internal conversion to TTA- S_1 under 278 nm excitation. Because the energy levels of Phen- S_1 and TTA- S_2 are close, the

FIGURE 3: EDS spectra of Eu(BA)(TTA)₂/PVP (a) and Eu(BA)(TTA)₂Phen/PVP (b).

FIGURE 4: Emission (a, b) and excitation (c) spectra of Eu(BA)(TTA)₂ (curve 1) and Eu(BA)(TTA)₂Phen (curve 2). Insets: fluorescence of Eu(BA)(TTA)₂ (I) and Eu(BA)(TTA)₂Phen (II), respectively.

resonance is allowed to transit from S_1 to S_2 , and vice versa. Subsequently, partial energy of TTA is released in the form of fluorescence (FL), and the other is transferred to its triplet excited state through intersystem crossing (ISC) and then released FL. In addition, under the excitation of 366 nm, TTA gets directly excited to S_1 due to changes in the circumstance, and some energy is transferred to TTA- T_1 through ISC and others to Phen- T_1 . Finally, the energy transfers from the ligands to the resonantly excited level 5D_2 of Eu^{3+} ion [11, 44–48]. The 5D_0 level is populated by the nonradiative relaxation (NRR); afterward, the radiative transition takes place accompanying the release of visible emissions.

3.3. Absolute Spectra and Radiometric Flux Quantitation. To accurately reflect the fluorescence performance of multiligand europium complexes/PVP thin films, the absolute spectral parameters were determined which provides an external quantum yield to assess luminescence and laser materials. Spectral power distributions of Eu(BA)(TTA)₂/PVP and Eu(BA)(TTA)₂Phen/PVP are recorded using an integrating sphere with a 367 nm UVA-LED as the pump source when the sample on the quartz sheet is located on the top of the LED pump source. By removing the influence of the quartz sheet, the net spectral power distributions of europium complexes/PVP are obtained, as depicted in

FIGURE 5: Emission (a, b) and excitation (c, d) spectra of Eu(BA)(TTA)₂/PVP (curve 1) and Eu(BA)(TTA)₂Phen/PVP (curve 2). Insets: fluorescence of Eu(BA)(TTA)₂/PVP (I) and Eu(BA)(TTA)₂Phen/PVP (II), respectively.

FIGURE 6: Normalized excitation spectra of Eu(BA)(TTA)₂Phen and Eu(BA)(TTA)₂Phen/PVP.

Figure 8, and the net emission powers are calculated to 204.8 and 243.2 μW , respectively. Subsequently, the bright reddish-orange fluorescence is observed, and the CIE coordinates of Eu(BA)(TTA)₂/PVP and Eu(BA)(TTA)₂Phen/PVP are calculated to (0.670, 0.330) and (0.671, 0.329), respectively, verifying the effectiveness of multiligands in photon conversion and providing the theoretical basis for the application in enhanced solar cells.

The photon distribution provides the fundamental information in optical field and relevant applications. Based on the net spectral power distributions, the photon distributions can be derived by

$$N(\nu) = \frac{\lambda^3}{hc} P(\lambda), \quad (1)$$

where ν , λ , h , c , and $P(\lambda)$ represent wavenumber, wavelength, Planck constant, vacuum light velocity and spectral power distribution, respectively. The net absorption and emission photon distributions of Eu(BA)(TTA)₂/PVP and Eu(BA)(TTA)₂Phen/PVP are calculated by equation (1) and depicted in Figure 9, and the integrated values are listed in Table 1. Meanwhile, the total emission photon numbers are derived to be 635.9×10^{12} and 754.9×10^{12} cps for Eu(BA)(TTA)₂ and Eu(BA)(TTA)₂Phen doped PVP thin films, respectively.

Quantum yield (QY) is used to reflect the utilization of luminescent materials to the absorption of photons and is defined as the photon number ratio of emission and absorption [49]. Namely,

$$\text{QY} = \frac{\text{emitted photons}}{\text{absorbed photons}} = \frac{N_{\text{em}}}{N_{\text{abs}}}. \quad (2)$$

All the QY values for different emission peaks of europium complexes/PVP under the excitation of the 367 nm UVA-LED are listed in Table 1. The total QYs of Eu(BA)(TTA)₂/PVP and Eu(BA)(TTA)₂Phen/PVP are derived to be 57.87% and 62.03%, respectively, which are far

FIGURE 7: Schematic energy level diagram: energy transfer processes and different transitions in $\text{Eu(BA)(TTA)}_2/\text{PVP}$ (a) and $\text{Eu(BA)(TTA)}_2\text{Phen}/\text{PVP}$ (b). ISC, intersystem crossing, IC, internal conversion, ET, energy transfer, S, singlet, T, triplet, and NRR, nonradiative relaxation.

FIGURE 8: Net spectral power distributions of $\text{Eu(BA)(TTA)}_2/\text{PVP}$ (a) and $\text{Eu(BA)(TTA)}_2\text{Phen}/\text{PVP}$ (b) under 367 nm UVA-LED excitation. Insets: fluorescence of $\text{Eu(BA)(TTA)}_2/\text{PVP}$ (a) and $\text{Eu(BA)(TTA)}_2\text{Phen}/\text{PVP}$ (b) in an integrating sphere under 367 nm UVA-LED excitation.

higher than those of 9.34% in $\text{Eu(DBM)}_3\text{Phen}/\text{PMMA}$ [50], 18% in $\text{Eu(DBM)}_3\text{PIP}/\text{PVP}$ [51], and 36% $\text{Eu(DBM-D)}_3(\text{Bath})/\text{PMMA}$ [52]. The large QYs reflect the effectiveness of the photon utilization in the multiligand europium complexes. In the table, the absolute quantum efficiency is

accordingly changed with the introduction of Phen. Due to the low inversion symmetry at Eu^{3+} ion sites, the mixture of uneven ligand field components and the electric dipole transitions is no longer strictly forbidden in the ligand fields, resulting in faster electron transition radiation rates.

FIGURE 9: Net photon distributions of Eu(BA)(TTA)₂/PVP (a) and Eu(BA)(TTA)₂Phen/PVP (b) under 367 nm UVA-LED excitation. Insets: details of the absorption photon distributions.

TABLE 1: Absorption, emission photon number, and quantum yield in Eu(BA)(TTA)₂/PVP and Eu(BA)(TTA)₂Phen/PVP fibers under 367 nm UVA-LED excitation.

Samples	Absorption photon number (10 ¹⁴ cps)	Emission transition	Wavenumber (cm ⁻¹)	Emission photon number (10 ¹² cps)	Quantum yield (%)	Total quantum yield (%)
Eu(BA)(TTA) ₂ /PVP	10.988	⁵ D ₀ → ⁷ F ₀	17276	3.674	0.33	57.87
		⁵ D ₀ → ⁷ F ₁	16894	33.021	3.01	
		⁵ D ₀ → ⁷ F ₂	16301	520.958	47.41	
		⁵ D ₀ → ⁷ F ₃	15379	11.985	1.09	
		⁵ D ₀ → ⁷ F ₄	14275	56.805	5.17	
		⁵ D ₀ → ⁷ F ₆	12416	9.480	0.86	
Eu(BA)(TTA) ₂ Phen/PVP	12.168	⁵ D ₀ → ⁷ F ₀	17276	4.217	0.35	62.03
		⁵ D ₀ → ⁷ F ₁	16916	39.581	3.25	
		⁵ D ₀ → ⁷ F ₂	16301	611.108	50.22	
		⁵ D ₀ → ⁷ F ₃	15379	13.809	1.13	
		⁵ D ₀ → ⁷ F ₄	14275	73.404	6.03	
		⁵ D ₀ → ⁷ F ₆	12336	12.753	1.05	

Luminous flux refers to the amount of radiant flux that is evaluated according to the international standard of human visual characteristics [53]. The total luminous flux Φ_V of the luminescence can be calculated by

$$\Phi_V = K_m \int_{380}^{780} V(\lambda) P(\lambda) d\lambda, \quad (3)$$

where $V(\lambda)$ is the relative eye sensitivity and K_m is the maximum luminous efficacy at 555 nm (683 lm/W). The luminous efficacy is obtained by dividing total luminous flux Φ_V by the electric power (W) on the LED. Thereupon, the luminous flux distributions of the Eu(BA)(TTA)₂/PVP and Eu(BA)(TTA)₂Phen/PVP films can be obtained under the excitations of 308 nm UVB-LED and 367 nm UVA-LED, as presented in Figure 10, and the relevant total luminous fluxes Φ_V and luminous efficacy in the whole visible spectral region are listed in Table 2.

Under the excitation electric power of 115.61 mW for 308 nm UVB-LED, the total luminous fluxes Φ_V of Eu(BA)(TTA)₂/PVP and Eu(BA)(TTA)₂Phen/PVP are integrated to be 13.20 and 16.60 mlm by equation (3) and luminous efficacy get 11.4% and 14.4% lm/W, respectively, which are higher than 2.63 mlm and 2.27% lm/W in TAH/PMMA [54]. Under the excitation electric power of 72.14 mW

for 367 nm UVA-LED, the luminous fluxes of residual LEDs are 0.33×10^{-2} and 0.25×10^{-2} mlm, and its role is negligible in Eu(BA)(TTA)₂/PVP and Eu(BA)(TTA)₂Phen/PVP, respectively. The total luminous fluxes of Eu(BA)(TTA)₂/PVP and Eu(BA)(TTA)₂Phen/PVP are as high as 44.55 and 52.34 mlm, and luminous efficacy are calculated to 61.8% and 72.6% lm/W when excited by 367 nm UVA-LED, respectively. As the excitation wavelength changes, both of luminous flux values and luminous efficacy show upward tendency due to the enhancement of conversion fluorescence intensity. Moreover, the 367 nm UVA-LED is confirmed as a more effective excitation device for the sample, and the higher luminous efficacy reveals that the multiligand europium complexes have good luminescence ability under UV radiation.

Judd–Ofelt (J–O) intensity parameters Ω_t ($t = 2, 4, 6$) are used to evaluate rare-earth ion interaction with the substrate, which reflect some characteristics of the local coordination field and estimate the population of odd parity electron transitions [55, 56]. Since the Eu³⁺ has limited absorption transitions and the special energy level structure, radiative transition properties of Eu³⁺ in Eu(BA)(TTA)₂/PVP and Eu(BA)(TTA)₂Phen/PVP are derived from their emission behaviors [57]. The Ω_t ($t = 2, 4$, and 6) are determined based on emission photon numbers and listed in Table 3, and the

FIGURE 10: Luminous flux distributions of luminescence of Eu(BA)(TTA)₂/PVP (a) and Eu(BA)(TTA)₂Phen/PVP (b) under 308 nm and 367 nm excitations.

TABLE 2: Total luminous fluxes of Eu(BA)(TTA)₂/PVP and Eu(BA)(TTA)₂Phen/PVP films under 308 and 367 nm UV-LEDs excitations.

Samples	Excitation wavelength (nm)	Excitation electric power (mW)	Luminous flux (mlm)	Luminous efficacy (lm/W)
Eu(BA)(TTA) ₂ /PVP	308	115.61	13.20	0.114
	367	72.14	44.55	0.618
Eu(BA)(TTA) ₂ Phen/PVP	308	115.61	16.60	0.144
	367	72.14	52.34	0.726

TABLE 3: Photon number ratio, reduced matrix, and J-O intensity parameters (Ω_2 , Ω_4 , and Ω_6) of Eu³⁺ in Eu(BA)(TTA)₂/PVP and Eu(BA)(TTA)₂Phen/PVP under 367 nm UVA-LED excitation.

Samples	Emission transition	Wavenumber (cm ⁻¹)	$\ U^{(2)}\ ^2$	$\ U^{(4)}\ ^2$	$\ U^{(6)}\ ^2$	Photon number ratio	J-O intensity parameter (10 ⁻²⁰ cm ²)
Eu(BA)(TTA) ₂ /PVP	⁵ D ₀ → ⁷ F ₁ (N ₁)	16894	0	0	0	—	—
	⁵ D ₀ → ⁷ F ₂ (N ₂)	16301	0.0032	0	0	N ₂ /N ₁ = 15.777	Ω ₂ = 30.221
	⁵ D ₀ → ⁷ F ₄ (N ₄)	14275	0	0.0023	0	N ₄ /N ₁ = 1.720	Ω ₄ = 6.880
	⁵ D ₀ → ⁷ F ₆ (N ₆)	12416	0	0	0.0002	N ₆ /N ₁ = 0.287	Ω ₆ = 20.192
Eu(BA)(TTA) ₂ Phen/PVP	⁵ D ₀ → ⁷ F ₁ (N ₁)	16916	0	0	0	—	—
	⁵ D ₀ → ⁷ F ₂ (N ₂)	16301	0.0032	0	0	N ₂ /N ₁ = 15.439	Ω ₂ = 29.579
	⁵ D ₀ → ⁷ F ₄ (N ₄)	14275	0	0.0023	0	N ₄ /N ₁ = 1.854	Ω ₄ = 7.426
	⁵ D ₀ → ⁷ F ₆ (N ₆)	12336	0	0	0.0002	N ₆ /N ₁ = 0.322	Ω ₆ = 23.158

Ω_2 values of Eu³⁺ in Eu(BA)(TTA)₂/PVP and Eu(BA)(TTA)₂Phen/PVP are derived to be 30.221×10^{-20} and $29.579 \times 10^{-20} \text{ cm}^2$, respectively. In particular, Ω_2 is more sensitive to the asymmetry and the sequence of ligand fields, which strongly depends on the local environments of rare-earth ions, such as high inversion asymmetrical and strong covalent environments. In addition, the Ω_2 of Eu(BA)(TTA)₂Phen/PVP is smaller than that of Eu(BA)(TTA)₂/PVP, which confirms that the covalence degree of Eu³⁺ in the first coordination shell tiny decreases after the addition of Phen [58, 59].

The J-O intensity parameters Ω_b , spontaneous transition probabilities A_{ij} , branching ratios β_{ij} , and calculated radiative lifetimes τ_{rad} are calculated and listed in Table 4. The A_{ij} of ⁵D₀ → ⁷F₂ transition are up to 954.7 s^{-1} and 942.6 s^{-1} in

Eu(BA)(TTA)₂/PVP and Eu(BA)(TTA)₂Phen/PVP, respectively, and the β_{ij} are also found as high as 83.99% and 82.94%, respectively, which are stronger than other transitions indicating that the ⁵D₀ → ⁷F₂ transition is efficient and dominant in europium complexes doped PVP thin films. These results further confirm the suitability of multiligand europium complexes/PVP as UV-visible conversion layers for enhanced solar cells.

Stimulated emission cross section σ_{em} is one of the most basic physical quantities to evaluate the energy extraction efficiency from rare-earth doped optical materials, not only for a fundamental understanding of the excitation and depopulation process but also for the optimization of laser materials, which is determined through the Fuchtbauer-Ladenburg equation [60]:

TABLE 4: Spontaneous transition probabilities A_{ij} , branching ratios β_{ij} , and calculated radiative lifetimes τ_{rad} of 5D_0 in $\text{Eu}(\text{BA})(\text{TTA})_2/\text{PVP}$ and $\text{Eu}(\text{BA})(\text{TTA})_2\text{Phen}/\text{PVP}$.

Samples	Transition	Energy (cm^{-1})	A_{ij} (s^{-1})	β_{ij} (%)	τ_{rad} (μs)
$\text{Eu}(\text{BA})(\text{TTA})_2/\text{PVP}$	$^5D_0 \rightarrow ^7F_1$	16894	60.51	5.32	879.7
	$^5D_0 \rightarrow ^7F_2$	16301	954.71	83.99	
	$^5D_0 \rightarrow ^7F_4$	14275	104.10	9.16	
	$^5D_0 \rightarrow ^7F_6$	12416	17.37	1.53	
$\text{Eu}(\text{BA})(\text{TTA})_2\text{Phen}/\text{PVP}$	$^5D_0 \rightarrow ^7F_1$	16916	61.05	5.37	879.9
	$^5D_0 \rightarrow ^7F_2$	16301	942.55	82.94	
	$^5D_0 \rightarrow ^7F_4$	14275	113.22	9.96	
	$^5D_0 \rightarrow ^7F_6$	12336	19.67	1.73	

$$\sigma_{\text{em}} = \frac{A_{\text{rad}}}{8\pi cn^2} \times \frac{\lambda^5 N(\lambda)}{\int \lambda N(\lambda) d\lambda}, \quad (4)$$

where n , A_{rad} , and $N(\lambda)$ represent the refractive index, spontaneous transition probability, and emission photon distribution, respectively. As is clearly seen in Figure 11, there are four visible emission bands, whose peaks are located at 592, 615, 701, and 810 nm corresponding to the $^5D_0 \rightarrow ^7F_J$ ($J=1, 2, 4, 6$) transitions of Eu^{3+} , respectively. The maximum values $\sigma_{\text{em-max}}$ for $^5D_0 \rightarrow ^7F_2$ transitions of Eu^{3+} in $\text{Eu}(\text{BA})(\text{TTA})_2/\text{PVP}$ and $\text{Eu}(\text{BA})(\text{TTA})_2\text{Phen}/\text{PVP}$ peaking at 615 nm both are derived to be $7.90 \times 10^{-21} \text{ cm}^2$, indicating both of them have approximate emission capability. As for the increment of fluorescence intensity, which can be interpreted that the addition of Phen leads to the combination of the heterogeneous ligand field and the antiparity of the 4f configuration levels, resulting in the intense absorption property and the prominent radiation behavior [61]. The large emission cross section enables the europium complexes/PVP to be a promising material for photon conversion materials.

3.4. Optical Absorbability and Thermal Stability. The transmission spectra and the images of $\text{Eu}(\text{BA})(\text{TTA})_2/\text{PVP}$ and $\text{Eu}(\text{BA})(\text{TTA})_2\text{Phen}/\text{PVP}$ are depicted in Figure 12(a), respectively. Both of them show up to 95% transparency at 350–800 nm and the broad band at 200–350 nm exhibits an intense absorbability of ligands, indicating the PVP is a suitable matrix for doping rare-earth complexes into photon conversion materials. The optical absorption exhibits excellent absorption properties for multiligand europium complexes/PVP upon UV radiation, as depicted in Figure 12(b). As for the $\text{Eu}(\text{BA})(\text{TTA})_2/\text{PVP}$, the absorption of BA at 234 and 273 nm is primarily attributed to the $n \rightarrow \sigma^*$ transitions of E absorption band and $\pi \rightarrow \pi^*$ transitions of B absorption band [62, 63], respectively, and the strong absorption of TTA at 350 nm is assigned to the $n \rightarrow \pi^*$ electron transition. With the addition of Phen, the energy transfer is more effective; meanwhile, the effect of Phen is reconfirmed; that is, Phen has no contribution in increasing the emission section while enhances the absorption of the UV. The absorption coefficient curve is nearly unchangeable after 400 nm, which implies that the ligands can effectively transfer the excited state energy to the

FIGURE 11: Emission cross-sectional profiles of Eu^{3+} in $\text{Eu}(\text{BA})(\text{TTA})_2/\text{PVP}$ (a) and $\text{Eu}(\text{BA})(\text{TTA})_2\text{Phen}/\text{PVP}$ (b) under 367 nm UVA-LED excitation. Insets: emission cross-sectional profiles of $^5D_0 \rightarrow ^7F_6$ transition of Eu^{3+} in $\text{Eu}(\text{BA})(\text{TTA})_2/\text{PVP}$ and $\text{Eu}(\text{BA})(\text{TTA})_2\text{Phen}/\text{PVP}$, respectively.

emission state of Eu^{3+} through the nonradiated transition, thus sensitizing luminescence and making up for the small absorption coefficient of Eu^{3+} in the UV region [64]. And the multiligand europium complexes are put into a dark room with a hole for guiding sunlight through a glass tube and attached with foil in the inner wall to avoid energy losses. Meanwhile, the bright red fluorescence of $\text{Eu}(\text{BA})(\text{TTA})_2/\text{PVP}$ and $\text{Eu}(\text{BA})(\text{TTA})_2\text{Phen}/\text{PVP}$ exhibits an effective response to the sunlight, as shown in Figure 12(b).

FIGURE 12: UV-Vis transmission spectra (a) and absorption spectra (b) of $\text{Eu(BA)(TTA)}_2/\text{PVP}$ (curve 1) and $\text{Eu(BA)(TTA)}_2\text{Phen/PVP}$ (curve 2). The thickness of $\text{Eu(BA)(TTA)}_2/\text{PVP}$ and $\text{Eu(BA)(TTA)}_2\text{Phen/PVP}$ is 0.160 mm and 0.198 mm, respectively. The insets are the samples without (I) and with (II) Phen under direct sunlight, respectively.

Thermodynamic property is essential to europium complexes/PVP for practical applications as optical materials; therefore, the DSC-TGA analyses of $\text{Eu(BA)(TTA)}_2/\text{PVP}$ and $\text{Eu(BA)(TTA)}_2\text{Phen/PVP}$ have been carried out to explore their degradation behavior, as illustrated in Figure 13. The TGA curves of $\text{Eu(BA)(TTA)}_2/\text{PVP}$ and $\text{Eu(BA)(TTA)}_2\text{Phen/PVP}$ are similar, and both of them show 5% weightlessness at 100°C , which is ascribed to the water detach from the samples with an obvious endothermic peak. Furthermore, in the $200\text{--}400^\circ\text{C}$ temperature ranges, an exothermic peak appears due to the sample melting. Besides, the curve reveals that the major weightlessness events occur at the temperature interval ($400\text{--}500^\circ\text{C}$), implying the thermal decomposition behavior of PVP appears with the emergence of endothermic peaks as well. The DSC curve tends to a constant at $470\text{--}600^\circ\text{C}$, indicating the decomposition of the coordination compound is complete. The results further confirm that the composition of the Eu(BA)(TTA)_2 and $\text{Eu(BA)(TTA)}_2\text{Phen}$ doped PVP has excellent thermal stability for the research and development of electronic devices.

4. Conclusions

The films of Eu(BA)(TTA)_2 and $\text{Eu(BA)(TTA)}_2\text{Phen}$ doped polyvinylpyrrolidone (PVP) have been synthesized, and the bright red fluorescence is observed under ultraviolet radiation. Absorption and emission spectra confirm that the composite material with good thermodynamic stability can convert ultraviolet radiation into visible light efficiently and suggest the interaction between PVP and Eu^{3+} . Under 367 nm UVA-LED pump source, the highest emission powers, emission photon numbers, and luminous efficacy are derived to be 204.8 and $243.2\ \mu\text{W}$, 635.9×10^{12} and 754.9×10^{12} cps, and 61.8% and 72.6% lm/W for $\text{Eu(BA)(TTA)}_2/\text{PVP}$ and $\text{Eu(BA)(TTA)}_2\text{Phen/PVP}$ thin films, which verifies the effective utilization of UVA radiation by introducing multiligands. Simultaneously, the quantum yields are up to 57.87% and 62.03% for without and with Phen, respectively. Meanwhile, the J-O intensity

FIGURE 13: DSC-TAG analyses of $\text{Eu(BA)(TTA)}_2/\text{PVP}$ (a) and $\text{Eu(BA)(TTA)}_2\text{Phen/PVP}$ (b).

parameter Ω_2 of $\text{Eu(BA)(TTA)}_2/\text{PVP}$ is higher than $\text{Eu(BA)(TTA)}_2\text{Phen/PVP}$, confirming that the local asymmetry around Eu^{3+} increases after the addition of Phen. Efficient photon emission demonstrates the availability of multiligand europium complexes as an attractive UV radiation conversion material for enhanced solar cells.

Data Availability

The data used to support the findings of this study are available from the corresponding author upon request.

Conflicts of Interest

The authors declare that there are no conflicts of interest regarding the publication of this paper.

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