Preparation, characterization and photophysical properties of layered zirconium bis(monohydrogenphosphate) intercalated with rare earth complexes

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Two kinds of rare earth (RE) complexes were intercalated into zirconium bis(monohydrogenphosphate) (α-ZrP) by exchanging the RE complexes into the p-methyoxyaniline (PMA) preintercalated compound $Zr(O_3POH)_2 \cdot 2PMA$ (α-ZrP$\cdot$2PMA). Powder X-ray diffraction patterns reveal that $Eu(DBM)_3phen$ (DBM: dibenzoylmethane, phen: 1,10-phenanthroline) and $Tb(AA)_3phen$ (AA: acetylacetone) intercalated into α-ZrP$\cdot$2PMA. This was confirmed by the UV-visible spectra of both the RE complexes and the assemblies. At the same time, the assemblies have better luminescent properties, and the fluorescent lifetimes of RE^{3+} in the excited state in the assemblies are much longer than those in the complexes. The stabilities of the assemblies under UV radiation are much better than those of the RE complexes.

As a base for luminescent materials, rare earth (RE) complexes have been mainly encapsulated in or adsorbed on host materials including Langmuir–Blodgett films,[1] sol–gels[2] and some kinds of zeolites.[3] The luminescence of RE complexes in supramolecular species was studied in 1991.[4] Later Hazenkamp studied the luminescence of [Eu⊂2.2.1] and [Ce⊂2.2.1] cryptates adsorbed on oxide surfaces.[5] Encapsulation of $[Eu(ppy)_2]^{3+}$ in zeolite Y was the earliest report of research into the luminescence of the RE complex in the channels of the zeolite.[6] Since zirconium bis(monohydrogenphosphate), $Zr(HPO_4)_2 \cdot H_2O$, referred to as α-ZrP, was first synthesized and its layer structure was confirmed in 1964,[7] studies on α-ZrP have been mainly focused on syntheses, ion exchange, thermal stability, adsorption and catalysis.[8] Intercalation into α-ZrP was mainly concentrated on the transition metal compounds,[9] and porphyrins.[10] However, there are no reports on RE complexes intercalated into layered α-ZrP.

As is well known, organized media can profoundly influence the photophysical and photochemical processes of guest molecules. These hosts provide a variety of interesting microenvironments for the guest molecules.[11] Inorganic layered phosphates, as host media, can provide unique microenvironments for the guests.[12] α-ZrP consists of a layer of Zr(IV) ions sandwiched between two layers of phosphate anions.[13] Each phosphate group in ZrP carries one ionizable hydroxyl group, making these materials highly acidic. They can be readily deprotonated and the resulting ionic sites serve to bind cations. Alkylamines react with α-ZrP via Brønsted acid–base reactions to give an intercalation compound $[Zr(O_3PO^-)_2(RNH_3^+)_2]$, which is composed of alternating layers of $Zr(O_3PO^-)_2$ and bilayers of RNH_3^+. Weakly basic or sterically hindered amines do not react directly with α-ZrP to give fully intercalated materials. Treatment of α-ZrP with PMA (p-methyoxyaniline) results in layered materials with methyoxy-anilinium ions preintercalated into the galleries of α-ZrP;[14] the increased interlayer spacing in the p-methoxyaniline-preintercalated complex is essential for the incorporation of large hydrophobic cations into the galleries.[10,13,14] The assembly of chromophores in the galleries of α-ZrP$\cdot$2PMA can build artificial light harvesting complexes.[15] By the use of appropriate substrates, the energy trapped by such assemblies may be stored as chemical potential.[16,17]

In this work, the photophysical properties of $Eu(DBM)_3phen$ (DBM: dibenzoylmethane, phen: 1,10-phenanthroline) and $Tb(AA)_3phen$ (AA: acetylacetone) intercalated into the layered compound α-ZrP are investigated. Attempts are being made to use these organized media to generate superamolecular assemblies that may function as antenna systems for light harvesting. It was found that the assemblies had very good luminescent properties, the lifetimes of RE^{3+} in the excited state in the assemblies are much longer than those of the unintercalated RE complexes, and the photostabilities of the assemblies under UV radiation are better than those of the corresponding pure RE complexes.

Experimental

Reactant sources and preparation procedures

The main starting materials for the synthesis of α-ZrP$\cdot$2PMA are $ZrOCl_2 \cdot 8H_2O$ (Shanghai chemical reagent factory) and p-methyoxyaniline (Fluka reagent).

(a) **α-ZrP, α-ZrP$\cdot$2PMA, $Eu(DBM)_3phen$ and $Tb(AA)_3$-phen.** These were synthesized according to references 7, 10 and 18, respectively.

(b) **Preparations of the assemblies.** $Eu(DBM)_3phen$ or $Tb(AA)_3phen$ was firstly dissolved into a small amount of dimethylformamide (1 mg RE complex to 0.1 ml dimethylformamide), and then diluted with chloroform. α-ZrP$\cdot$2PMA was added to the above solution with the mass ratio of α-ZrP$\cdot$2PMA to the RE complexes being 10/1. The mixture was stirred at room temperature for three weeks, filtered and washed with chloroform until the filtrate had no luminescence of the RE complexes under the UV radiation. The resultant powder was dried at room temperature.
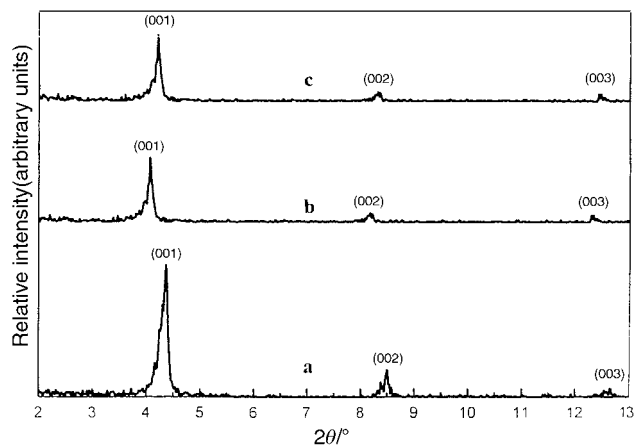
Fig. 1 X-Ray powder diffraction patterns for α-ZrP·2PMA (a), assemblies of Tb(AA)₃phen (b) and Eu(DBM)₃phen (c).

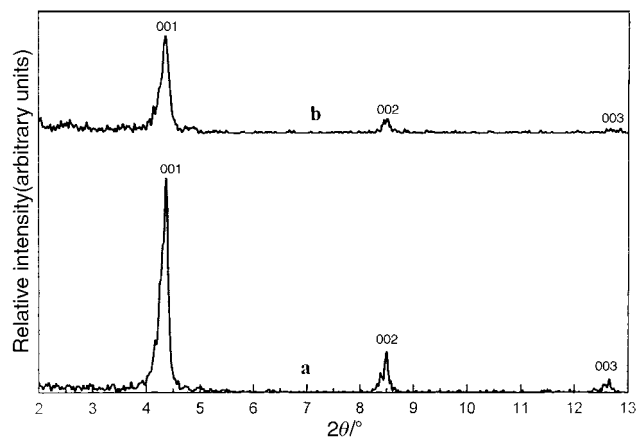**Fig. 2** X-Ray powder diffraction patterns for α-ZrP·2PMA (a), and α-ZrP·2PMA refluxed in chloroform for three weeks (b).

Characterization

X-Ray powder diffraction patterns of α-ZrP·2PMA with and without the RE complexes were recorded on a Rigaku D/MAX diffractometer with CuKα ($\lambda = 1.5418$ Å) radiation. The UV-visible absorption spectra were measured using a ZF-1 spectrometer. Fluorescence excitation and emission spectra were recorded on a SPEX Fluorolog-2T2 Spectrofluorometer equipped with a 450 W xenon lamp as the excitation source (the excitation state and the emission state slits are 5.0 nm and 1.5 nm, respectively. All the samples were measured under the same conditions). The luminescent lifetime measurements were performed on a SPEX 1934D phosphorimeter. For photo-stability experiments, the samples were irradiated using a 30 W high-pressure mercury lamp, the distance between the samples and the center of the lamp was 14 cm, parts of the samples were taken out at different irradiation times. The contents of Eu^{3+}, Tb^{3+}, C and N in the assemblies were measured on a PLASMA-SPEC (I) ICP-AES.

Results and discussion

XRD patterns

Fig. 1 shows XRD patterns of α-ZrP·2PMA and the RE complexes intercalated into α-ZrP·2PMA. The interlayer spacing (d_{001}) of α-ZrP·2PMA is 20.25 Å (Fig. 1a). As seen from the shift of the (001) peaks toward low 2θ angles, the interlayer spacing (d_{001}) increases from 20.25 Å to 21.02 Å and 20.25 Å to 21.22 Å for the assemblies of Eu(DBM)₃phen (Fig. 1c) and Tb(AA)₃phen (Fig. 1b), respectively. The former increases by 0.77 Å and the latter by 0.97 Å. The gallery height of the assembly (Eu(DBM)₃phen) is therefore estimated to be 14.62 Å by subtraction of the sheet thickness of α-ZrP, 6.40 Å, from this value, *i.e.*, $21.02 - 6.4 = 14.62$ Å (the diameter of Eu(DBM)₃phen is about 13.60 Å).[19] For the assembly of Tb(AA)₃phen, the gallery height was estimated to be 14.82 Å

(the diameter of Tb(AA)₃phen is about 13.40 Å).[19] The gallery heights of the assemblies are consistent with the diameters of the RE complexes, indicating that the RE complexes were probably intercalated into the layered compound.

On the other hand, compared to α-ZrP·2PMA, not only are the (001) peaks of the assemblies shifted to low 2θ angles, but the (002) and (003) peaks are also shifted to low 2θ angles at the same time, indicating that the changes of the XRD patterns have not arisen from the error of the measurements but from the guests in the layers.

In order to prove that the differences of the XRD patterns between the assemblies and α-ZrP·2PMA do not come from the rearrangement of PMA molecules in the interlayers during the course of the intercalations, the experiment of refluxing α-ZrP 2PMA in chloroform containing a very small amount of dimethylformamide for three weeks was performed. The XRD patterns of α-ZrP·2PMA (Fig. 2a) and α-ZrP·2PMA refluxed (Fig. 2b) are shown. Comparing the two patterns, it is found that there are no differences between them, indicating that the rearrangement of PMA does not happen in the chloroform, and the changes of the layer distance can only come from the intercalation of the RE complexes.

Chemical compositions

The contents of Eu^{3+}, Tb^{3+}, C and N in some samples are listed in Table 1. The percentage of PMA drived out by Eu(DBM)₃phen is 18.36 wt.%, which was calculated from the percentages of N in α-ZrP·2PMA, the Eu assembly, and in the Eu intercalated complex, *i.e.*, $3.15\% - (1.29\% - 0.23\%) = 2.09\%$ and $2.09\% \times 123/14 = 18.36\%$ (the molecular formula of PMA is C_7H_9NO). From the calculation above, 22.31 PMA molecules came out from the host per intercalated Eu(DBM)₃phen, suggesting that the formula composition of the assembly of Eu(DBM)₃phen is α-ZrP·0.27PMA·0.023Eu(DBM)₃phen (the coefficients in the formula come from the molar proportions of α-ZrP, PMA and

Table 1 Chemical analysis for Eu^{3+}, Tb^{3+}, C, N in the samples

	Calculated (%)				Found (%)			
	Eu^{3+}	Tb^{3+}	C	N	Eu^{3+}	Tb^{3+}	C	N
In α-ZrP·2PMA							19.06	3.15
In the Eu assembly					1.03		11.2	1.29
In Eu(DBM)₃phen intercalated			4.64[a]	0.19[a]	1.03		4.93	0.23
In the Tb assembly						2.33	8.17	1.01
In Tb(AA)₃phen intercalated			4.74[b]	0.41[b]		2.33	4.96	0.45

[a]Calculated from the content of Eu^{3+} in the Eu assembly, *i.e.*, $1.03\% \times 57 \times 12/152 = 4.64\%$ and $1.03\% \times 2 \times 14/152 = 0.19\%$. [b]Calculated from the content of Tb^{3+} in the Tb assembly with the same method. In the sheets in the Eu assembly and in the Tb assembly, the contents of elements C and N include C and N in the RE complex intercalated and in PMAs retained in the layered compound.
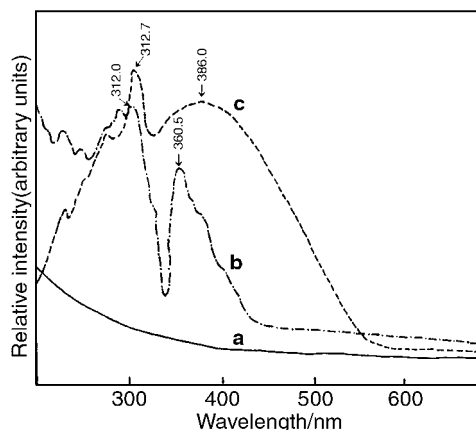
Fig. 3 UV-visible absorption spectra for α-ZrP·2PMA (a), Eu(DBM)₃phen in α-ZrP·2PMA (b), and Eu(DBM)₃phen (c).

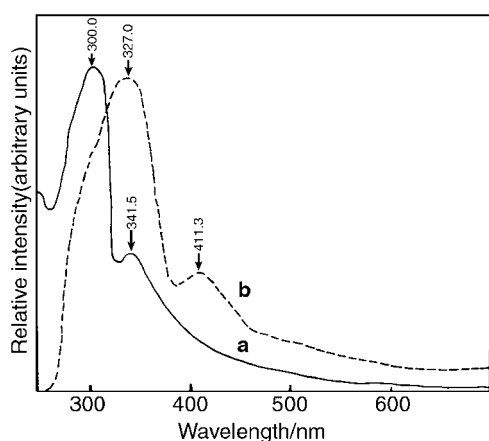**Fig. 4** UV-visible absorption spectra for Tb(AA)₃phen in α-ZrP·2PMA (a) and Tb(AA)₃phen (b).

Eu(DBM)₃phen in the Eu assembly). The molecular formula of Eu(DBM)₃phen is $EuC_{57}H_{41}N_2O_6$.

With the same method, it can be calculated that there are about 22.76 wt.% PMA removed from the layered compound. 12.73 PMA molecules were driven out from the host per Tb(AA)₃phen intercalated, suggesting that the formula composition of the assembly of Tb(AA)₃phen is α-ZrP·0.13PMA·0.048·Tb(AA)₃phen. The molecular formula of Tb(AA)₃phen is $TbC_{27}H_{29}N_2O_6$.

UV-visible spectra

The UV-visible absorption spectra of α-ZrP·2PMA with and without the RE complexes are shown in Fig. 3 and Fig. 4 respectively. It can be easily seen that no absorption peaks for α-ZrP·2PMA are visible over the range from 300 nm to 600 nm (Fig. 3a). The UV-visible spectrum of Eu(DBM)₃phen has two main absorption peaks located at 312.7 nm and 386.0 nm (Fig. 3c), while the assembly also has two main absorption at 312.0 nm and 360.5 nm (Fig. 3b). Tb(AA)₃phen has two main absorption located at 327.0 nm and 411.3 nm (Fig. 4b). For the assembly of Tb(AA)₃phen, the main UV-visible absorptions are located at $\lambda = 300.0$ nm and 341.5 nm (Fig. 4a). The UV-visible spectra can show the RE complexes loaded on the α-ZrP. The microenvironments in the interlayer of α-ZrP result in a blue shift of the RE complex absorptions.

Excitation and emission spectra

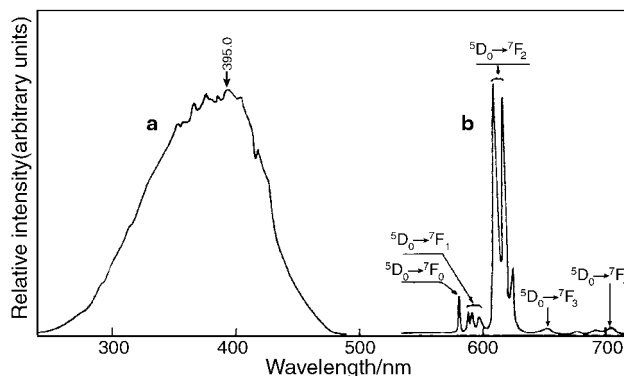The excitation and emission spectra of Eu³⁺ of Eu(DBM)₃phen powder and the assembly are shown in

Fig. 5 Excitation (a) and emission spectra (b) of the luminescence of Eu(DBM)₃phen.

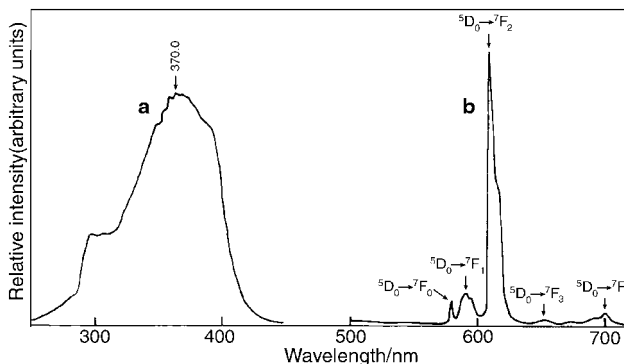**Fig. 6** Excitation (a) and emission spectra (b) of the luminescence of Eu(DBM)₃phen in α-ZrP·2PMA.

Fig. 5 and Fig. 6. Both of the excitation spectra are broad bands and the emission spectra exhibit the characteristic emission of Eu³⁺ arising from the transition ⁵D₀→⁷F_J ($J = 0,1,2,3,4$), with the transition ⁵D₀→⁷F₂ red emission as the dominant group. This strongly suggests that an efficient energy transfer from the ligands to Eu³⁺ can take place not only in the pure RE complex but also in the complex incorporated into α-ZrP.

Some differences in the excitation and emission spectra in Fig. 5 and Fig. 6 can be seen. For α-ZrP intercalated with the europium complex, the excitation spectrum consists of an asymmetric broad band ranging from 250 nm to 450 nm with a maximum intensity at 370 nm and no distinct splits are observed on the emission bands (Fig. 6a). For the pure complex, it becomes a symmetric broad band ranging from 250 nm to 480 nm. Compared to the corresponding pure RE complex (Fig. 5a), the maximum excitation wavelength for the assembly shows a blue shift, changing from 395 nm to 370 nm, fewer splits are exhibited in the emission spectrum.

The excitation and emission spectra of Tb³⁺ of Tb(AA)₃-phen powder and the assembly are shown in Fig. 7 and Fig. 8, respectively. Both of the emission spectra present the characteristic emission bands originating from the transition ⁵D₄→⁷F_J ($J = 6,5,4,3$), with the transition ⁵D₄→⁷F₅ green emission as the dominant group. Compared to the pure RE complex (Fig. 7a), the excitation of the assembly shows an asymmetric broad band and a blue shift, while fewer splits than that of the corresponding RE complex are shown in the emission spectrum (Fig. 8a).

The differences in the excitation spectra between α-ZrP intercalated with the RE complex and the pure complex powder can be interpreted as follows. Compared to the pure RE complex, when the complex was intercalated into α-ZrP, the polarity around the Eu³⁺ surrounding environment will

increase, according to the Lippert equation:[20]

$$hc\Delta v = 2\Delta f(\mu* - \mu)^2/a^3$$

where v is the frequency shift (in cm^{-1}) of the excitation state, f is the orientation polarizability, $\mu*$ and μ are the excited and ground state dipole moments, respectively, h is Planck's constant, c is the velocity of light and a is the cavity radius. Since the polarity of the RE complex in α-ZrP is increased, Δf is a positive value. Therefore, Δv is also a positive value. In other words, compared to the pure RE complex, the excitation wavelengths of the assemblies show blue shifts. These also agree with the results obtained from UV-visible spectra.

The intensity of the $^5D_0 \rightarrow {}^7F_2$ transition of Eu^{3+} is strongly dependent on the environment due to its electric-dipole character while the $^5D_0 \rightarrow {}^7F_1$ emission intensity is independent of the environment. The ratio of $^5D_0 \rightarrow {}^7F_2/{}^5D_0 \rightarrow {}^7F_1$ (0–2/0–1) emission intensities will give valuable information about environment changes around Eu^{3+}. The decrease of 0–2/0–1 from 14.0 in the pure RE complex to 8.8 in the complex intercalated into α-ZrP indicates that there is high symmetry around the Eu^{3+} ion in the assembly. Therefore, fewer emission lines were observed in the emission spectrum of the assembly.

Comparison of fluorescent lifetimes

The fluorescent decay curves of Eu^{3+} related to the transition $^5D_0 \rightarrow {}^7F_2$ emission and that of Tb^{3+} related to the transition $^5D_4 \rightarrow {}^7F_5$ were measured and the lifetimes are summarized in Table 2. It can be clearly seen that the RE complexes intercalated into α-ZrP have longer lifetimes than those of the corresponding pure complexes. It is well known that the luminescent lifetime of RE^{3+} is related to the vibration of the nearby ligands. The excitation energy of RE^{3+} can be absorbed by the vibration of the ligands, which leads to the decrease of the RE^{3+} lifetimes. The relatively rigid matrix structure limits
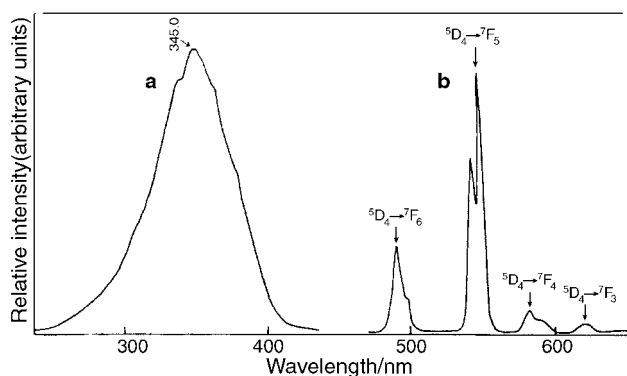

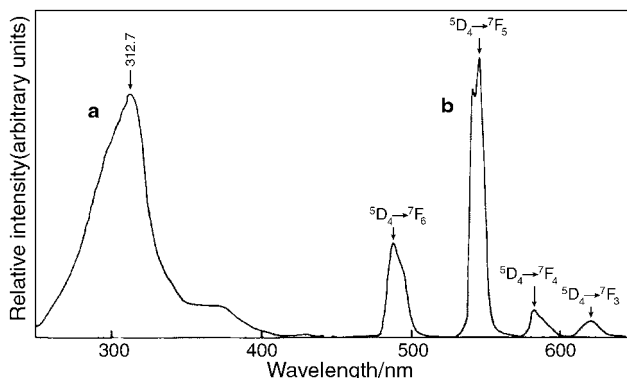**Fig. 7** Excitation (a) and emission spectra (b) of the luminescence of Tb(AA)$_3$phen.

Fig. 8 Excitation (a) and emission spectra (b) of the luminescence of Tb(AA)$_3$phen in α-ZrP·2PMA.
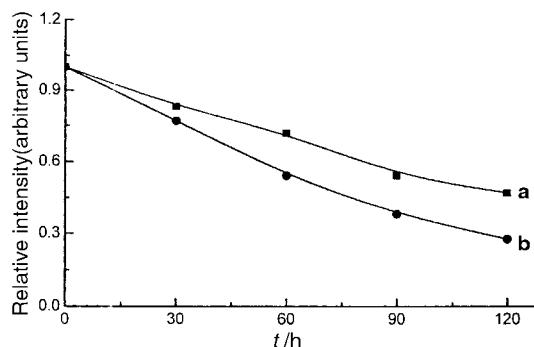
Fig. 9 Change of luminescent intensity of Eu(DBM)$_3$phen in α-ZrP·2PMA (a) and Eu(DBM)$_3$phen (b) with the irradiation time.
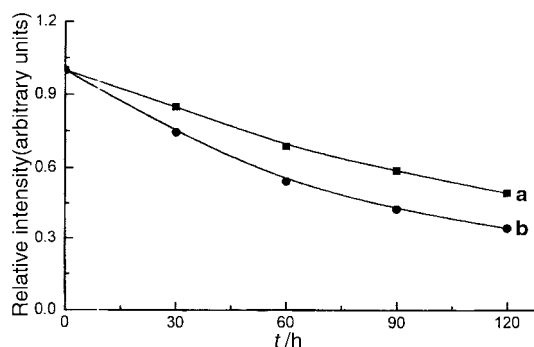
Fig. 10 Change of luminescent intensity of Tb(AA)$_3$phen in α-ZrP·2PMA (a) and Tb(AA)$_3$phen (b) with the irradiation time.

the vibration of the ligands around RE^{3+}, leading to longer luminescent lifetimes of RE^{3+} in the layered compounds than in the pure complexes.

Comparison of the photostability

The photostability of the RE complexes and the assemblies were measured and the results are presented in Fig. 9 and Fig. 10. Similar to the literature,[21] we employ the half-life $t_{1/2}$ to characterize the photostability, where $t_{1/2}$ denotes the time taken for the fluorescent intensity to decrease to 50% of the initial value after irradiation under UV light. The $t_{1/2}$ values of Eu(DBM)$_3$phen (Fig. 9b) and its assembly (Fig. 9a) are 62 h and 97 h, respectively, and those for Tb(AA)$_3$phen (Fig. 10b) and its assembly (Fig. 10a) are 66 h and 120 h, respectively. It is easily found that the fluorescent photostabilities of the RE complexes in the assemblies are higher than those of the corresponding pure RE complexes.

Relationship between the contents and the luminescent intensity

The contents of the RE complexes in the assemblies and their relative luminescent intensities are listed in Table 3. It can be clearly seen that the unit molecule of the RE complexes in their assemblies gives stronger luminescence than the corresponding pure complex.

Table 2 The luminescent lifetimes of RE ions in different materials

Materials	Lifetimes/μs
Eu(DBM)$_3$phen	608
Eu Assembly	768
Tb(AA)$_3$phen	960
Tb Assembly	1309

Table 3 Relationship between the contents and luminescent intensities

Materials	Rare earth complexes (wt%)	Relative intensities
Eu(DBM)$_3$phen	100	1.2×10^6
Eu Assembly	6.71	4.8×10^5
Tb(AA)$_3$phen	100	4.6×10^6
Tb Assembly	9.31	8.9×10^5

Conclusion

In this work, intercalation of RE complexes into α-ZrP has been performed, resulting in the first example of the insertion of a RE complex into bulk α-ZrP. α-ZrP·2PMA is a useful starting material for the intercalation of bulky and weakly basic guests, in that it combines a large interlayer spacing with easily exchanged groups.

Compared to the pure RE complexes, the excitation spectra of the intercalated complexes show a blue shift. The emission spectra for both the assemblies and the pure RE complex show the characteristic emission bands. The luminescent lifetimes of the assemblies are longer than those of the corresponding pure complexes. The photostabilities are improved after the RE complexes are intercalated into α-ZrP. The unit mass of the RE complexes in their assemblies can give stronger luminescence than the corresponding pure complexes.

Acknowledgements

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