Luminescent Lanthanide (Eu³⁺, Tb³⁺) Hybrids with 4-Vinylbenzeneboronic Acid Functionalized Si-O Bridges and Beta-Diketones

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ABSTRACT

4-Vinylphenylboronic acid ligand (VPBA) is functionalized with two crosslinking reagents (3-(triethoxysilyl)-propylisocyanate [TEPIC] and 3-(trimethoxysilyl) propyl methacrylate [TMPMA]) to achieve the two special molecular bridge VPBA-TEPIC and VPBA-TMPMA. Meanwhile, beta-diketone ligands (2-thenovltrifluoroacetone [TTA], acetyl acetone [ACAC]) as the second ligands play the role of the main energy donor, which absorb abundant energy in ultraviolet-visible extent and then transfer the energy to the corresponding lanthanide ions (Eu³⁺, Tb³⁺) to sensitize their emission of them. Eight binary and ternary Eu³⁺, Tb³⁺ hybrids with VPBA-TEPIC (VPBA-TMPMA) and TTA (ACAC) have been constructed, whose photoluminescence properties are studied in depth and suggest that the ternary hybrids show the favorable characteristic luminescent properties (longer lifetime and higher quantum efficiency).

INTRODUCTION

Due to their unique photophysical properties that aid in shielding 4f electrons from interactions with their surroundings by the filled $5s^2$ and $5p^6$ orbital, lanthanide ions have been well known as important components in phosphors, lasers and optical amplifiers (1-3). However, the direct Ln^{3+1} photoexcitation is not very efficient, with the low molar absorption coefficients limiting the light output. Some organic ligands such as aromatic carboxylic acids etc. are well known to be efficient sensitizers for the luminescence of lanthanide ions, whose organic chromophores typically present effective absorption and a much broader spectral range than the corresponding Ln^{3+} ions can absorb energy to be transferred to nearby Ln³⁺ ions by an effective intramolecular energy transfer process. This process is called lanthanide luminescence sensitization or antenna effect (4-7). These chelates possessing the effective emission in the near-UV, visible and NIR spectral regions are of great interest for a wide range of optical applications, such as tunable lasers, amplifiers for optical communications, components of the emitter layers in multilayer organic light-emitting diodes (OLEDs), light concentrators for photovoltaic devices and so on (8–10).

However, concerning the technological applicability, there exist somewhat low thermal and photochemical stability, together with the poor mechanical properties of lanthanide complexes that represent some disadvantages. In order to overcome these drawbacks, lanthanide complexes have been encapsulated into polymers (11-13), liquid crystals (14,15) and sol-gel-derived organic-inorganic hybrids (mostly siloxanebased ones) (16-18). Organic-inorganic hybrid materials have been developed in the past two decades affording materials with desired properties, for they combine some advantages of organic compounds (easy processing with conventional techniques, elasticity and organic functionalities) with properties of inorganic oxides (hardness, thermal and chemical stability, transparency) and thus have attracted considerable attention (19,20). These kinds of hybrids can be classified according to the interaction established between organic and inorganic components: the physically doping hybrids and chemically bonding one (21). Carlos et al. and Binnemans both give overview of the different types of lanthanide-based hybrid materials and compared their respective advantages and disadvantages (22,23). Our research team has presently done extensive work on covalently grafting the ligands to the inorganic networks in which the luminescent centers of lanthanide complexes are bonded with a siloxane matrix through Si-O linkage and we have realized six paths to construct the functional silvlated precursors. In addition, after the modification, we assembled the above modified bridge ligands with lanthanide ions and tetraethoxysilane (TEOS) to compose hybrid systems with covalent bonds and obtained a series of stable and efficient molecular hybrid materials in optical areas (24-31).

The special covalent linkage, named as functional molecular bridge, is the key to construct these kinds of organometallic hybrid systems. Based on the former work, 4-vinylphenylboronic acid (VPBA) containing a hydroxyl group and a carboxyl group (32) can realize the hydrogen-transfer nucleophilic addition reaction through the hydroxyl group with 3-(triethoxysilyl) propyl isocyanate (TEPIC) and 3-(trimethoxysilyl) propyl methacrylate (TMPMA) to achieve two kinds of molecular bridge (VPBA-TEPIC and VPBA-TMPMA) and coordinate to lanthanide ions (Eu³⁺ and Tb³⁺) through carboxyl groups. Under this consideration, we construct eight chemically binary and ternary bonded lanthanide organometallic hybrids (RE-VPBA-RSi and L-RE-VPBA-RSi: RE = Euor Tb, RSi = TEPIC, TMPMA, L = TTA or ACAC), whose physical characterization and photophysical properties are reported in detail.

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MATERIALS AND METHODS

Materials. VPBA, TEPIC and TMPMA were purchased from Lancaster Synthesis Ltd. 2-thenoyltrifluoroacetone (TTA) and acetyl acetone (ACAC) were purchased from Shanghai chemical plant. Benzoyl peroxide (BPO) and TEOS were supplied by China National Medicines Group. Ln (NO₃)₃ (Ln = Eu, Tb) aqueous solution was prepared by dissolving their respective oxides (Eu₂O₃ and Tb₄O₇) in concentrated nitric acid (HNO₃). The solvents were purified according to literature procedures. All reagents were analytically pure.

Synthesis of molecular bridge precursors VPBA-TMPMA and VPBA-TEPIC linkages. For VPBA-TMPMA: VPBA (1 mmol, 0.148 g) was first dissolved in 20 mL of tetrahydrofuran (THF) solvent with stirring. Then, 2.0 mmol (0.496 g) of TMPMA was added drop-wise. Then the mixtures were heated to reflux at 65°C in a covered flask for about 12 h under nitrogen atmosphere. The coating liquid was concentrated to remove the solvent THF using a rotary vacuum evaporator, and a colorless viscous liquid sample was obtained. The colorless viscous sample was then dissolved in solvent N,N-dimethylformamide (DMF) 20 mL and acrylic acid was added with initiator BPO to the solution, and the polymers were then constructed through addition polymerization under nitrogen atmosphere for approximately 14 h. The solvent DMF was then removed using a rotary vacuum evaporator. After isolation and purification, a yellow viscous liquid was obtained. The ¹H NMR data of VPBA-TMPMA are as follows: 0.57(2H, t), 0.68(4H, t) 1.22(6H, d) 1.70 (4H, m), 2.61(2H, m), 3.18(4H, t), 3.35 (9H, m), 3.74(4H, t), 3.58(18H, s), 6.83(1H, t), 7.2(2H, s), 7.1(2H, s).

For VPBA-TEPIC (32): VPBA (1 mmol, 0.148 g) was first dissolved in 20 mL of THF solvent with stirring. Then, 2.0 mmol (0.495 g) of TESPIC and hydrochloric acid (0.11 mmol) were added drop-wise. Further steps were similar to those of VPBA-TMPMA (32). The ¹H NMR data of VPBA-TEPIC are as follows: $\delta 0.58(2H, t)$, 0.64(4H, t), 1.244(18H, t), 1.56(4H, m), 3.2(2H, t) 3.35(9H, m) 3.78(12H, q), 3.83(12H, m), 6.76(2H, t), 7.2(2H, s), 7.1(2H, s).

Synthesis of eight kinds of hybrids with lanthanide complexes imbedded into Si-O networks and organic carbon chains through chemical bonds. The organic cross-linking precursor VPBA-TE-PIC/TMPMA was dissolved in DMF solvent and a stoichiometric amount of Ln (NO₃)₃·6H₂O (0.33 mmol, 0.149 g [Ln = Eu], 0.150 g [Ln = Tb]) was added to the solution while stirring. After 6 h, a stoichiometric amount of TEOS and H2O was added to the mixed solution after completion of the coordination reaction between the organic cross-linking precursor VPBA-TEPIC/TMPMA and the europium ion, which accompanied the addition of one drop of dilute hydrochloric acid to promote hydrolysis. The molar ratio of Ln (NO₃)₃·6H₂O:VPBA-TÉPIC/TMPMA:TEOS:H₂O was 1:3:6:24. After hydrolysis, an appropriate amount of hexamethylenetetramine was added to adjust the pH to 6-7. The mixture was agitated magnetically to achieve a single phase in a covered Teflon beaker, and then it was aged at 65.5° C until the onset of gelation in about 5 days. The gels VPBA-TEPIC/TMPMA-Eu and VPBA-TEPIC/TMPMA-Tb were collected as monolithic bulks and were ground into powdered samples for photophysical studies.

TTA-Eu-VPBA-TEPIC (TMPMA) and ACAC-Tb-VPBA-TEPIC (TMPMA): The precursor VPBA-TEPIC (TMPMA) was dissolved in DMF solvent and a stoichiometric amount of Ln(NO₃)₃·6H₂O (0.33 mmol, 0.149 g [Ln = Eu], 0.150 g [Ln = Tb]) was added to the solution while stirring. After 2 h, the terminal ligand TTA (or ACAC) (0.33 mmol, 0.0734 g [or 0.033 g]) was added to the mixture, and then another 6 h later, a stoichiometric amount of TEOS and H₂O was added to the mixed solution, after completion of the coordination reaction between precursors and europium ions, which accompanied the addition of one drop of dilute hydrochloric acid to promote hydrolysis. The molar ratio of Ln (NO₃)₃:6H₂O:VPBA-TE-PIC/(TMPMA):TTA(ACAC):TEOS:H₂O is 1:3:1:6:24 (TEOS 1:3:1:6:24 (TEOS 2 mmol, 0.417 g, and H₂O 0.144 g). After hydrolysis, an appropriate amount of hexamethylenetetramine was added to adjust the pH to 6-7. The mixture was agitated magnetically to achieve a single phase in a covered Teflon beaker, and then it was aged at 65.5°C until the onset of gelation in about 6 days. The gels TTA-Eu-VPBA-TEPIC (TMPMA) and ACAC-Tb-VPBA-TEPIC (TMPMA) were collected as monolithic bulks and were ground into powdered samples for photophysical studies.

Physical measurements. Infrared spectroscopy (FT-IR) were obtained in KBr pellets and recorded on a Nexus 912 AO446 FT-IR spectrophotometer in the range of 4000-400 cm⁻¹. Ultraviolet absorption spectra of these samples $(5 \times 10^{-4} \text{ mol}^{-1} \text{ DMF solution})$ and the ultraviolet-visible diffuse reflection spectra of the powder samples were recorded on an Agilent 8453 spectrophotometer and a BWS003 spectrophotometer, respectively. Differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) were performed on a NETZSCH STA 449C with a heating rate of 10 K min⁻¹ under a nitrogen atmosphere (flow rate: 40 mL min⁻¹). Scanning electronic microscope (SEM) images were obtained with a Philips XL-30. The Xray diffraction (XRD) measurements were carried out on powdered samples via a BRUKER D8 diffractometer (40 mA/40 kV) using monochromated CuK α 1 radiation (λ) 1.54 Å over the 2 θ range 10–70°. Luminescence excitation and emission spectra are obtained on a Perkin-Elmer LS-55 spectrophotometer with different excitation and emission slits. Luminescent lifetimes were recorded on an Edinburgh FLS 920 phosphorimeter using a 450 W xenon lamp as excitation source (pulse width, 3 μ s). ¹H NMR spectra were recorded on a Bruker AVANCE-500 spectrometer with tetramethylsilane (TMS) as internal reference.

RESULTS AND DISCUSSION

Figure 1 shows the scheme for the synthesis of the precursors and the basic composition of the hybrid systems. The main composition and coordination effect of the precursors can be predicted according to the lanthanide coordination chemistry principle and the functional groups of organic units. Considering the structure of the molecular bridge ligands VPBA-TEPIC (TMPMA) with two modified carbonyl groups in this article, it can be assumed that there exist two chelated oxygen atoms of C = O groups and so the molar ratio of 1:3 between RE^{3+} and VPBA-TEPIC (TMPMA) will occupy the six coordination position around RE³⁺. For the binary hybrid system, the remaining coordination space can be filled with two or three H₂O molecules to form the common eight or nine coordination structure. For ternary hybrid systems, one betadiketone ligand (TTA or ACAC) can provide the two chelated oxygen atoms to replace the two H₂O molecules without influence on the coordination behavior of RE³⁺; besides this there still may exist coordinated water molecules. These predictions have also been confirmed by the infrared spectra and the estimation of the coordination water molecules from the luminescent lifetimes and quantum efficiency afterward.

Figure 2A shows the Fourier transform infrared spectra of the precursor VPBA and the two modified molecular bridges VPBA-TEPIC (TMPMA). For the IR spectrum of VPBA-TEPIC, the peak at 2275 cm⁻¹ to the O = C = N group of TEPIC disappears while the peaks at 2965, 2930 and 2890 cm⁻¹ corresponding to the stretching vibration of methylene groups of VPBA-TEPIC appear, suggesting that TEPIC has been grafted onto VPBA. Furthermore, the peaks located at 1082 and 465 cm⁻¹ derived from the stretching and bending vibrations of the Si-O group have not been changed to the broad band at 1150-1000 cm⁻¹, which indicates that the molecular precursor has not hydrolyzed to form the siliconoxygen network, consistent with the ¹H NMR data. The peaks at 1330 and 1260 cm⁻¹ corresponding to the stretching and bending vibrations of the Si-C group reveal that no siliconcarbon bond (Si-C) cleavage occurred during the synthesis of the precursor (33). The absorption peak for stretching vibration of the carbonyl group is located at 1690 cm⁻¹, and the broad peak at 3345 cm⁻¹ has accounted for the existence of the



Figure 1. The selected scheme for the synthesis of linkage VPBA-TMPMA (A) and the predicted composition and structure of binary and ternary lanthanide hybrids (B).

stretching vibration of the grafted -NH- group and the residual-associated hydroxyl group, both of which have proved the formation of the group O = C-NH- through the hydrogen-transfer nucleophilic addition reaction (34). For the IR spectrum of VPBA-TMPMA, the absorption band in the 3010–3050 cm⁻¹ range for double C = C group of TMPMA is not observed, which is due to the addition reaction of it and hydroxyl group of VPBA. Besides, the absorption peaks within the 1000–1500 cm⁻¹ range become complicated, suggesting that the ester group exists in the product VPBA-TMPMA. The other feature is similar to the IR spectrum of VPBA-TEPIC.

Figure 2B illustrates the ultraviolet absorption spectra of VPBA and linkages VPBA-TEPIC and VPBA-TMPMA. From the spectra, it is observed that VPBA has the characteristic absorption peak of an aromatic ring at 248 nm. After the completion of the hydrogen-transfer nucleophilic addition



Figure 2. The FT-IR spectra (A) and UV–visible absorption spectra (B) of VPBA and the two linkages VPBA-TEPIC and VPBA-TMPMA.

reaction between VPBA and TEPIC, the hydroxyl group of VPBA is modified to ester group O-C=O and the ultraviolet absorption peak of VPBA is redshifted to 271 nm, which indicates that major π - π^* electronic transitions occurred and the formation of VPBA decreases the energy level difference among electron orbits, and enlarges the planar conjugated effect of double bonds. A difference can be observed when comparing the ultraviolet absorption spectra of VPBA and VPBA-TMPMA. The ultraviolet absorption spectrum of VPBA-TMPMA shows the blueshift to 242 nm for the completion of the addition polymerization reaction between VPBA and the TMPMA, suggesting that the planar conjugated effect has been further decreased and the blueshift at wavelength 7 nm has been found. It is indicated from the figure that the two precursors have been synthesized as they have different electron distribution from the raw materials, which can be reflected by the ultraviolet spectra.

The IR spectra of binary and ternary lanthanide hybrids with VPBA-TEPIC linkage can be seen in Fig. 3A. The spectra



Figure 3. The IR spectra of binary and ternary lanthanide hybrids with VPBA-TEPIC linkage (A) and VPBA-TMPMA linkage (B).

of these hybrid materials with different lanthanide ions are similar. After coordination of Eu³⁺ and Tb³⁺ ions in the hybrid system, the v (C=O) vibrations are shifted to lower frequencies ($\Delta v = 10-16 \text{ cm}^{-1}$) compared with that of the VPBA-TEPIC linkage, which indicates the coordination interaction between Ln^{3+} with the oxygen atom (16). Besides, the spectra of the hybrid material indicate the formation of the Si-O-Si framework, which is evidenced by the broad bands located at about 1110–1065 cm⁻¹ (v_{as} , Si-O). It is attributed to the achievement of hydrolysis and condensation reactions (16). The v (O-H) vibration at around 3200 cm⁻¹ can be observed, which means the existence of the H₂O molecule. And the ρ_{α} (H₂O) stretching vibration at 425 cm^{-1} is further evidence of participation of water molecules in coordination in these hybrids. Figure 3B shows the IR spectra of binary and ternary lanthanide hybrids with VPBA-TMPMA linkage, which shows a character similar to that of Fig. 3A. The shifts in the v (C=O) vibrations compared with that of the VPBA-TEPIC linkage reveal that the coordination interaction takes place between Ln³⁺ with the oxygen atom of carbonyl groups.



Figure 4. Select X-ray diffraction patterns of binary and ternary lanthanide hybrids.

Certainly, strong absorption to the Si-O-Si framework also can be found at about 1100–1200 cm⁻¹ (v_{as} , Si-O) for the hydrolysis and condensation reactions. In addition, the introduction of TTA and ACAC ligands in the ternary hybrid systems of both linkages produces some absorption peaks in their IR spectra.

The room-temperature X-ray diffraction patterns of the hybrid materials in Fig. 4 reveal that all the materials with $10^{\circ} \le 2\theta \le 70^{\circ}$ are totally amorphous, suggesting the noncrystalline state of the hybrids. All diffraction curves show similar broad peaks centered around 22°, which is attributed to the "amorphous hump" and it is a typical characteristic of amorphous silica backbone materials (35). For amorphous solids, the position of the first sharp diffraction peak can be related, via a reciprocal relation, to a distance in the real space between the structural units (Bragg law: $2d\sin\theta = n\lambda$). So the structural unit distance is approximately 4.04 Å, similar to the 4.2 Å reported for vitreous SiO_2 (36). The small narrow peaks are weak, suggesting the contents of the simple Si-O components are less for the incompleteness of hydrolysis-condensation reactions between the excessive TEOS molecule. Besides, the formation of the true covalent-bonded molecular hybrid system proves that none of the hybrid materials contains measurable amounts of phases corresponding to the pure organic compound or free lanthanide nitrate.

Figure 5 presents select TG diagraphs of binary and ternary lanthanide hybrids conducted at a heating rate of 5.0°C min⁻¹. The three hybrids have lost the mass from 70°C to 200°C, corresponding to the loss of the solvent ethanol and DMF. The mass changes of three hybrids are about 4.8% for TTA-Eu-VPBA-TMPMA and TTA-Eu-VPBA-TEPIC and 5.5% for Eu-VPBA-TEPIC, respectively. Furthermore, the second weight losses for the three hybrids are about 14.5% for TTA-Eu-VPBA-TMPMA, 24.9% for TTA-Eu-VPBA-TEPIC and 25.2% for Eu-VPBA-TEPIC beyond 350°C, which is related to the decomposition of ligands. In addition, ternary hybrids show higher thermal stability than binary ones.

SEM of the lanthanide hybrid materials demonstrate that the homogeneous materials are obtained (Fig. 6). On the



Figure 5. Select TG diagraphs of binary and ternary lanthanide hybrids.

surface of the materials, there are many linear stripes. Moreover, new small branches emerge at the end of each trunk stripe and the stripes continue to grow according to the direction of these branches to form the final structure. In the sol-gel process between the linkage and TEOS, the cohydrolysis and copolycondensation reaction is not equivalent for the influence of organically modified groups, which influence the hydrolysis and polycondensation of TEOS to form the Si-O host. After the introduction of lanthanide ions, the coordination reaction between Ln³⁺ and ligands or linkage also affects the sol-gel process, resulting in the dominant tendency to special direction (trunk or stripe). Subsequently, a huge complicated molecular system is obtained containing a functional bridge ligand with strong covalent bonds between the inorganic and organic phases. In addition, there still exists some purity over the surface of the hybrids, which may be the sole product of TEOS.

Figure 7A shows select excitation spectra of binary and ternary europium hybrids. All these excitations are obtained by monitoring the maximum emission of the Eu^{3+} ions at



Figure 6. Select scanning electron microscope images of the lanthanide hybrids.

Figure 7. Select excitation spectra of europium hybrids (A) and terbium hybrids (B).

400

616 nm and appear as a dominant broad band from 300 to 400 nm except for the distinct maximum excitation peaks, which can be due to the absorption of photoactive VPBA unit in the organically modified Si-O network. The strong absorption of photoactive VPBA unit behaves as the main energy absorption for the whole hybrid systems. With the introduction of beta-diketones (TTA), the whole excitation bands become stronger, suggesting that the energy absorption of the whole ternary system is more effective for the energy transfer to Eu³⁺. The sharp excitation bands corresponding to the f-f transition of Eu³⁺ cannot be observed for they are too weak. Undoubtedly, the broad band excitation is favorable for sensitizing the luminescence of Eu³⁺. The excitation spectra for the selected terbium hybrid materials show a similar feature (Fig. 7B at 545 nm emission wavelength). The wide excitation bands in the 300-400 nm range are attributed to the absorption of VPBA-TMPMA-modified Si-O host. The excitation bands of the ternary hybrid system ACAC-Tb-VPBA-TMPMA become wider and stronger than that of the binary one. ACAC is beneficial for the luminescence of Tb^{3+} . Here, it needs to be mentioned that the organically modified VPBA Si-O networks play a dual role for the luminescence of Ln^{3+} in the hybrid systems: one is the host for which Ln³⁺ are immobilized in it through the covalently bonded linkage, and the other is the ligand for they are coordinated to Ln^{3+} through the oxygen atoms.

Figure 8A,B presents the emission spectra of binary europium and terbium hybrids with two linkages. Both of them show the weak characteristic emission of europium and terbium ions within the four hybrid systems. For binary europium hybrids (Fig. 8A), only two emission bands can be observed, 590 and 616 nm, corresponding to the ${}^{5}D_{0} \rightarrow {}^{7}F_{1}$ and ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$ transition, respectively. Besides, there exists the high baseline in the short wavelength < 575 nm, which can be ascribed to the emission of the organically modified host (or ligand). For binary terbium hybrids (Fig. 8B), two weak emission bands can also be observed: 488 nm (${}^{5}D_{4} \rightarrow {}^{7}F_{6}$) and 545 nm (${}^{5}D_{4} \rightarrow {}^{7}F_{5}$). Here, the emissions of the organically modified host (or ligand) become clear (especially Tb-VPBA-TESPIC): a broad emission band covering the 400-650 nm range, which is overlapped with the characteristic emission of terbium ions. There are three distinct energy transfer pathways that can be figured out (37): (1) the emitting centers of the hybrid host transfer energy to the ligand excited states (hybridto-ligand energy transfer) or (2) directly to the Ln^{3+} ions (hybrid-to- Ln^{3+} energy transfer), and (3) the excited ligand states transfer energy to the Ln³⁺ ions (ligand-to-Ln³⁺ energy transfer). Here, a broad band in the blue/green spectral region to extensive visible region, which is ascribed to the emitting levels of the hybrid host and already observed in similar organic-inorganic hybrids, results from a convolution of the emission that originates in the NH/C=O groups of the urea bridges with electron-hole recombination occurring in siloxane nanoclusters. From the luminescence of the binary hybrids, it can be predicted that the energy transfer to Eu^{3+} or Tb^{3+} is not effective within these systems. The two linkages VPBA-TEPIC (TMPMA) are not suitable for the luminescence of Eu^{3+} (Tb³⁺). So the introduction of secondary ligands such as beta-diketones may be necessary.

The emission spectra of the ternary europium and terbium hybrid materials are displayed in Fig. 9. In Fig. 9A for



Figure 8. Emission spectra of binary europium hybrids (A) and terbium hybrids (B).

europium hybrids, the very sharp peaks of the lines are located at 578, 590, 616, 652 and 695 nm for TTA-Eu-VPBA-TEPIC (578, 590, 615, 650 and 697 nm for TTA-Eu-VPBA-TMPMA), assigned to the ${}^{5}D_{0} \rightarrow {}^{7}F_{J}$ (J = 0, 1, 2, 3, 4) transitions of Eu³⁺, respectively. The ternary hybrids exhibit much stronger luminescence intensity than the binary ones, suggesting that the introduction of a second TTA ligand improves the sensitization degree of Eu³⁺ greatly. Furthermore, among these emission peaks of each material, the red emission peak at 616 (615) nm corresponding to the electric dipole transition of ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$, which is hypersensitive to the coordinative environment around Eu³⁺, shows higher intensities than the orange emission peak at 590 nm, which is the magnetic dipole transition of ${}^{5}D_{0} \rightarrow {}^{7}F_{1}$ and independent of the environment around. The domination of electric dipole transition demonstrates that Eu³⁺ occupies the coordination environment site without inversion symmetry (38) and the asymmetric microenvironment will induce the polarization of Eu³⁺ due to the influence of the electric field of the ligand with the probability for electric dipole transition. The nonsymmetry and the intensities of the electric dipole transition ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$

will increase as the interaction of the rare-earth complex with its local chemical environment is completed more entirely, so the relative intensity ratio (I_{02}/I_{01}) of ${}^{5}D_{0} \rightarrow {}^{7}F_{2}/{}^{5}D_{0} \rightarrow {}^{7}F_{1}$ transition is widely used as an indicator of Eu³⁺ site symmetry. The relative intensity ratio (I_{02}/I_{01}) of ${}^{5}D_{0}{}^{-7}F_{2}/{}^{5}D_{0}{}^{-7}F_{1}$ transition for these europium hybrids is summarized in Table 1 and TTA-Eu-VPBA-TEPIC possesses the largest value, indicating Eu³⁺ is located in the most



Figure 9. Emission spectra of ternary europium hybrids (A) and terbium hybrids (B).

 Table 1. Photoluminescence data for binary and ternary lanthanide hybrids.

Hybrids	I ₀₂ /I ₀₁	τ (μs)	$A_{\rm rad}$ (s ⁻¹)	A_{nrad} (s ⁻¹)	η (%)	n _w
Eu-VPBA-TEPIC	2.52	298	181	3180	5.4	~ 3
Eu-VPBA-TMPMA	4.35	303	279	3020	8.5	~ 3
TTA-Eu-VPBA-TEPIC	15.9	321	922	2200	29.5	~ 2
TTA-Eu-VPBA-TMPMA	14.3	313	887	2380	27.1	~ 2
Tb-VPBA-TEPIC		247				
Tb-VPBA-TMPMA		289				
ACAC-Tb-VPBA-TEPIC		329				
ACAC-Tb-VPBA-TMPMA		347				

asymmetric environment. In addition, the I_{02}/I_{01} value of both the ternary hybrids is much larger than those of the binary ones. Therefore, the introduction of TTA is beneficial for the improvement of the I_{02}/I_{01} value, from which it can be expected that the ternary hybrids will obtain higher luminescent quantum yields.

The peaks of the lines for ternary terbium hybrids in Fig. 9B are assigned to the ${}^{5}D_{4} \rightarrow {}^{7}F_{I}$ (J = 6, 5, 4, 3) transitions at about 488 (488), 545 (544), 582 (583) and 619 nm, respectively, for Tb³⁺. The green emission at 545 (544) nm possesses the strongest intensity among all the emissions. It can be found that the emission intensity of ACAC-Tb-VPBA-TMPMA is stronger than that of ACAC-Tb-VPBA-TEPIC, whereas the emission intensity of TTA-Eu-VPBA-TMPMA weaker than that of TTA-Eu-VPBA-TEPIC. This can be explained by the energy match and energy transfer mechanism between the ligands and lanthanide ions (39-41). The intramolecular energy transfer efficiency from ligands to lanthanide ions mainly depends on the energy match between them. The energy match for Eu^{3+} and Tb^{3+} is different and generally opposite for the difference of the two ions, resulting in the different luminescence order for their hybrids (39-41).

The typical decay curves of the Eu and Tb hybrid materials are measured and they can be described as a single exponential $(\operatorname{Ln}(S(t)/S_0) = -k_1t = -t/\tau)$, indicating that all Eu^{3+} and Tb³⁺ ions occupy the same average coordination environment. The resulting lifetime data of Eu and hybrids are given in Table 1. It is found that the lifetimes of all binary and ternary hybrids show no apparent distinction. The luminescent lifetimes of ternary hybrids are slightly longer than those of binary ones. And the luminescent lifetimes of binary europium hybrids are a bit longer than those of binary terbium. These facts agree with the corresponding luminescent intensities. But the difference is not apparent and the luminescent quantum vields will be determined with the luminescent intensity ratio. Furthermore, we selectively determined the emission quantum yields of the ${}^{5}D_{0}$ excited state of europium ion for Eu³⁺ hybrids on the basis of the emission spectra and lifetimes of the ${}^{5}D_{0}$ emitting level; the detailed luminescent data are shown in Table 1. To investigate the luminescence efficiency of these hybrids, we selectively determined the emission quantum efficiencies of the ⁵D₀ excited state of europium ion on the basis of the emission spectra and lifetimes of the ⁵D₀ emitting level for Eu³⁺ hybrids. The detailed principles and methods are adopted from references (42-45).

$$\tau_{\rm exp} = \left(A_{\rm r} + A_{\rm nr}\right)^{-1} \tag{1}$$

$$\eta = A_{\rm r} \tau_{\rm exp} \tag{2}$$

$$A_{\rm r} = \Sigma A_{0J} = A_{00} + A_{01} + A_{02} + A_{03} + A_{04} \tag{3}$$

$$A_{0J} = A_{01} (I_{0J} / I_{01}) (v_{01} / v_{0J})$$
(4)

As shown in Table 1, the quantum yields of the europium hybrid materials can be determined in the order: Eu-VPTA-TEPIC < Eu-VPTA-TMPMA < TTA-Eu-VPTA-TEPIC. The luminescent quantum yields of ternary hybrids (29.5%, 27.1%) are much higher than those of

binary ones (5.37%, 8.46%) in that TTA is in a better position to sensitize the emission of the Eu³⁺ ions.

To study the coordination environment surrounding lanthanide ions, according to Horrocks' previous research (46,47), it is therefore expected that probable number of coordinated water molecules (n_w) can be calculated according to following equation:

$$n_{\rm w} = 1.05(A_{\rm exp} - A_{\rm r})$$
 (5)

On the basis of the results, the coordination number of water molecules in the binary and ternary europium hybrids can be estimated to be about 3 and 2, respectively. So the total coordination number for Eu^{3+} in the binary and ternary hybrids is around 9 and 10, which correspond to the coordination chemistry behavior of lanthanide ions. Besides, the coordinated water molecules produce the vibration of the hydroxyl group, resulting in nonradiative transition and decreased luminescent efficiency.

CONCLUSIONS

In summary, eight binary and ternary luminescent lanthanide organometallic hybrid material systems are assembled through two novel bridge molecules and covalent linkages (VPBA-TEPIC and VPBA-TMPMA). These hybrids have been characterized in detail, especially the photophysical properties. Within the hybrid systems, the connection of inorganic and organic parts on a molecular level is to exhibit homogeneous microstructures. The binary hybrids show weak luminescence and the introduction of beta-diketone ligands (TTA and ACAC) in the ternary hybrid systems shows the greatest improvement in luminescence (intensity, red/orange ratio, quantum yields).

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