Hybrid Eu(III) Coordination luminophore Standing on Silica Nanoparticles By Two Legs for Enhanced Luminescence

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Abstract: In this study, we demonstrated a two-legs standing-up molecular design method for mono-chromatic and bright red luminescent Ln(III)-silica nanomaterials. A novel Eu(III)-silica hybrid nanoparticle using double binding TPPO-Si(OEt)\(_3\) (TPPO: triphenyl phosphine oxide) linker were developed. The TPPO-Si(OEt)\(_3\) was determined by \(^1\)H, \(^{31}\)P, \(^{29}\)Si NMR spectroscopy and single-crystal X-ray analysis. Luminescent Eu(hfa)\(_3\) and Eu(tf)\(_3\) parts (hfa: hexafluorooxacetelactonate, tfc: (trifluoromethylhydroxymethylene)camphorate) were fixed on the TPPO-Si(OEt)\(_3\) modified silica nanoparticles, producing in Eu(hfa)\(_3\)(TPPO-Si)\(_2\)-SiO\(_2\) and Eu(tf)\(_3\)(TPPO-Si)\(_2\)-SiO\(_2\), respectively. The Eu(hfa)(TPPO-Si)\(_2\)-SiO\(_2\) exhibited higher intrinsic luminescence quantum yield (93%) and longer emission lifetime (0.98 ms), which is much larger than those of previously reported Eu(III)-based hybrid materials. Eu(tf)(TPPO-Si)\(_2\)-SiO\(_2\) also showed extra-large intrinsic emission quantum yield (54%), although the emission quantum yield for the precursor Eu(tf)(TPPO-Si(OEt))\(_2\) was found to be 39%. These results confirmed that the TPPO-Si(OEt)\(_3\) linker is a promising candidate for development of Eu(III)-based luminescent materials.

Introduction

Luminescent molecular materials attract considerable attention not only due to their practical applications in lamps, lasers and displays,[1] but also widely used in biomedicine, optoelectronic devices, and sensors.[2-5] Thus, various types of luminescent Ln(III)-based materials have been developed in the field of material chemistry. To improve physical properties and chemical stabilities of the luminescent molecular materials, many research efforts have focused on hybrid nanostructures decorated with luminescent molecules.[13-15] The hybrid luminescent nanomaterial can combine both advantages of the solid matrix (rigidity and thermal stability) and the molecular compound (flexibility for molecular design). Their physicochemical properties depend on nature of the substrate (silica, zirconia and zinc oxide) and the surface conditions. Nanomaterial attached with noble metals (gold, silver, platinum, ruthenium, and/or iridium) represent a class of hybrid luminescent material that have been well studied.[16-19] and applied in probes, bioimaging, and catalysis.[20-22] In addition, organic ligand-functionalized nanomaterials for enhancing luminescence were also investigated recently, such as upconversion nanoparticles, quantum dots, and the nanoMOFs.[23-25] Here, we focus on the lanthanide(III)-coordinated nanomaterial as a bright luminophore. The Ln(III)-coordinated based materials show characteristic luminescence with sharp spectral shape (FWHM < 10 nm), large stokes shift and long emission lifetime (> micro seconds) originated from 4f-4f forbidden transitions.[10,26] In the last decade, various types of Ln(III)-based materials such as sol-gel materials, polymers, and mesoporous materials have been developed.[27-30] Binnemans and Gunnlaugsson reported on Ln(III) complex-based sol-gel and polymer derived luminescent materials.[31,32] An Eu/Tb(III) complex-based sol-gel material with reversible stimuliresponsive properties was also achieved.[33] The Ln(III)-modified mesoporous materials were obtained by grafting Ln(III) complex onto a mesoporous matrix, for example, immobilizing lanthanide β-diketone or pyridine complexes onto the SBA-15, MCM-41, and silica hosts were fully investigated.[30,34,35] Even though their thermal stability enhanced, the emission quantum yields of previous Ln(III)-coordinated materials are smaller than those of corresponding pure Ln(III) complexes. In this context, novel conceptual design for Ln(III)-based luminescent materials is required.

In previously reported Ln(III)-based materials, the Ln(III) complexes were functionalized on the inorganic matrix surface with one binding site (Figure 1a: L\(_2\) joint),[36-38] in this case, the flexible vibration of the organic ligands can decrease of Ln(III) emission quantum yield. Here, we demonstrate a novel fixation method, taking advantage of an Eu(III) complex with organic ligand covalently bonded to the silica nanoparticles through two binding sites as support (Figure 1b: L\(_2^\prime\) joints). Fixation of Eu(III) complex on the covalent rigid Si-O-Si polymeric network structures of the silica nanoparticles surface with two binding sites, can promote effective suppression of the vibrational relaxation process of the excited organic ligand, resulting in enhanced luminescence performance. As reported in our previous work, the hfa has low vibrational frequency for decreasing the non-radiative rate constant,[39] and TPPO can formation of antisymmetric structure for increasing of the radiative rate constant.[40,41] Therefore, in this study, we synthesized a new triphenylphosphine oxide compound TPPO-Si(OEt)\(_3\), and identified by \(^1\)H, \(^{31}\)P, \(^{29}\)Si NMR spectroscopies and single-crystal X-ray analysis. Using Eu(hfa)\(_3\) complex with TPPO-Si(OEt)\(_3\) ligand covalently bonded to the silica nanoparticle through two binding sites, we developed a nano-luminophore Eu(hfa)\(_3\)(TPPO-Si)\(_2\)-SiO\(_2\) (Figure 1c). It exhibited higher intrinsic luminescence quantum yield (93%) and longer emission lifetime (0.98 ms), which is much larger than...
those of previous Eu(III)-based hybrid materials. Furthermore, the synthesized Eu(tfc)3(TPPO-Si)2-SiO2 also showed extra-large intrinsic emission quantum yield (54%), although for the precursor Eu(tfc)3[TMPO-Si(OEt)3]2 was found to be 39%. In the present work, conceptual two-legs standing-up molecular design for bright luminescent Ln(III)-silica nanomaterials is demonstrated for the first time.

Results and Discussion

Preparation of nano-luminophore Eu(hfa)3(TPPO-Si)2-SiO2.

The linker ligand for fixation on the SiO2 nanoparticles, triphenylphosphine oxide compound, TPPO-Si(OEt)3, was synthesized according to the procedure in Scheme S1. We used diphenyl(p-tolyl)phosphine as a starting compound and oxidized it with potassium permanganate, the achieved 4-(diphenylphosphino) benzoic acid can be isolated as white crystals from ethanol solution (Figure S1). Then, reaction of 4-(diphenylphosphino) benzoic acid in thionyl chloride with 3-aminopropyl triethoxysilane results in the product of TPPO-Si(OEt)3. The structure was characterized using 1H, 31P, and 29Si NMR spectroscopies, respectively (Figure S2).

Characterizations

Dynamic light scattering (DLS) detection showed average size of the prepared silica nanoparticles is 36 nm (Figure 4a), which is in agreement with previously reported result.47 After modification with Eu(III) complexes, the resulting nano-luminophore 3 displayed an average size of 53 nm (Figure 4b). To get a further understanding of 3 at the nanometre scale, we performed the transmission electron microscopy (TEM) investigation. TEM images revealed particle size of the pure silica nanoparticles (average size around 36 nm, Figure 4c) well-agrees with the DLS result, and energy dispersive X-ray spectroscopy (EDS) confirmed the presence of oxygen and silicon element in the nanoparticles (Figure S3).

Significantly different from the pure silica nanoparticles, TEM images of nano-luminophore 3 contained numerous dark objects (Figure 4d). The objects with large size attribute to the Eu(hfa)3(TPPO-Si)2 aggregates on the SiO2 surface, the others are too small to see clearly belong to the Eu(hfa)3(TPPO-Si)2 dispersion functionalized on the silica nanoparticles (Figure S4). Compared with pure SiO2, EDS showed the presence of additional europium, phosphorus and fluorine element in the nano-luminophore 3 (Figure S5), indicated it was constructed by both Eu(hfa)3(TPPO-Si)2 and silica nanoparticles. In the EDS, europium exhibited different species, due to the outer shell electron can come from different shells with different energy. Furthermore, we measured X-ray photoelectron spectroscopy (XPS) of nano-luminophore 3 (Figure S6). In the XPS spectrum, the Eu 3d (5/2) bands corresponding to Eu(III) was observed at 1135 and 1165 eV, which is similar to previously reported simple Eu(III) compounds48 confirmed the Eu(hfa)3 is one component of nano-luminophore 3, consistent with the EDS result.
exhibited one broad 31P NMR signal at -90.5 ppm (Figure S7), modified SiO2 nanoparticles. In deuterated chloroform, the displays a P=O stretching vibration at 1184 cm -1 (Figure 5, TPPO-Si(OEt)3 modified SiO2 nanoparticles, we carried out nano-luminophore dehydration Eu(hfa)3(H2O)2, the resulting Eu(III) complex 29.4 ppm (Figure S6). However, after it reacted with the paramagnetism of the central Eu(III), consistent with free TPPO-Si(OEt)3 displayed a sharp 31P NMR signal at -28.5 ppm due to the elimination of ethyl groups for connection on SiO2 surface.

To investigate the tight-binding between Eu(hfa)3 and TPPO-Si(OEt)3 modified SiO2 nanoparticles, we carried out IR measurements. The P=O stretching vibration bands of TPPO-Si(OEt)3(Eu)3 displays a P=O stretching vibration at 1184 cm -1 (Figure 5, black line).[49] However, for complex 2 and nano-luminophore 3 the P=O bands were observed at 1142 cm -1 (Figure 5, red and blue lines). The P=O stretching vibrational energy in metal coordination compound is generally smaller than that in non-coordinated organic ligand,[50] indicating the P=O group in nano-luminophore 3 is directly connected with the Eu(hfa)3 unit. In addition, we observed the disappearance of characteristic -CH3 vibrational bands at around 3000 cm-1 in nano-luminophore 3 due to the elimination of ethyl groups for connection on SiO2 surface.

Photophysical Properties

Emission spectra of Eu(III) complex 1, 2 and nano-luminophore 3 were excited at 350 nm (Figure 6), which at the end absorption of the hfa ligand (Figure S10), indicate the hfa can transfer energy efficiently to the central Eu(III). The emission bands observed at 579, 593, 614, 652, and 699 nm, attributed to the Eu(III) ion 5D0 → 7Fj (j = 0 - 4) transitions. Emission spectra are normalized with respect to the magnetic dipole transition intensities at 593 nm (Eu: 5D0→7F1), which is known to be insensitive to the surrounding environment of the lanthanide ions.[40] The characteristic of Eu(III) red luminescence is corresponding to the strongest sharp emission band at 614 nm (5D0 → 7F2) due to the electric dipole transition, and shape of this transition band is generally affected by coordination environment of the central Eu(III).[55] Relative emission intensity of nano-luminophore 3 is larger than the precursor Eu(III) complex 1 and 2. The effective large transition band of nano-luminophore 3 is linked with a large radiative rate constant based on the asymmetric coordination structure on the SiO2 surface. According to the emission spectrum, the splitting shape of the band at 614 nm for complex 2 is similar to nano-luminophore 3, but significantly different from complex 1, and the transition intensity is depended on the electric transition probability. Based on these photophysical findings, we consider that in the nano-luminophore 3 Eu(hfa)3 units are attached by two TPPO units linked with SiO2 surface.

Further NMR spectroscopy also reveals the evidence for connection between Eu(hfa)3 unit and the TPPO-Si(OEt)3 modified SiO2 nanoparticles. In deuterated chloroform, the free TPPO-Si(OEt)3 displayed a sharp 31P NMR signal at 29.4 ppm (Figure S6). However, after it reacted with the dehydrated Eu(hfa)3(H2O)2, the resulting Eu(III) complex 2 exhibited one broad 31P NMR signal at -90.5 ppm (Figure S7), due to the NMR signal is strongly affected by the paramagnetism of the central Eu(III), consistent with previously reported phosphate oxide Eu(III) complex.[51-53]

Furthermore, 1H NMR signals of the free ethyl groups come from TPPO-Si(OEt)3 modified SiO2 nanoparticles in CD2OD were also detected (Figure S8), consistent with the IR result that showed disappearance of characteristic -CH3 vibrational bands. Based on the TEM, IR and NMR results, unambiguously indicate that Eu(hfa)3 units were tight-fixed on the TPPO-Si-modified SiO2 nanoparticles.

To estimate the thermal stability of complex 2 and nano-luminophore 3, we performed the thermogravimetric analysis (TGA). TGA curve showed the decomposition temperature of complex 2 was 191 °C (Figure S9). On the other hand, decomposition temperature for the nano-luminophore 3 was 282 °C. Significant covalent rigid Si-O-Si polymeric network structures between Eu(hfa)3(TPPO-Si)2 units and the silica nanoparticles promote thermo-stable structure under heat-treatment.[54]
The nano-luminophore 3 exhibited an extra-large intrinsic emission quantum yield (Φff, 93%), higher than the precursor Eu(III) complex 1 and 2. This Φff is based on a large radiative rate constant (κr, 9.5 × 10^2 s^-1) and an extremely small non-radiative rate constant (κnr, 6.9 × 10^-1 s^-1). The κr is smaller than those previously reported Eu(III) complex with phosphine oxide, naphthalene, and pyridine ligand (10^2 s^-1).[57-59] The large κr for nano-luminophore 3 should be due to tight and antisymmetric aggregations of the Eu(hfa)3(TPPO-Si(OEt)3)2 ligand bonded on the silica nanoparticles. It can be attributed to the following reasons: (i) the organic ligand TPPO-Si(OEt)3 has a three-dimensional antisymmetric structure that promotes faster radiative rate and suppresses non-radiative rate; (ii) in the nano-luminophore 3, the covalent rigid Si-O-Si polymeric network structures restrict the thermal-vibrations of TPPO-Si(OEt)3 ligand.[54] The Φff of nano-luminophore 3 is significantly higher than previously reported Eu@Si-OH (38%)[60] (which is the Eu(TPPO)2 with one bidentate anchored on the silica nanoparticles), and Eu(III)-based materials such as Eu(III)-SBA-15 (29%),[34] Eu(III)-MCM-41 (81%),[35] Ddp-ePMO-Eu(tta)3 (7.5%)[37] and even larger than the pure Eu(III) complex with phosphine oxide and pyridine ligand.[61-63] In addition, the photosensitized energy transfer efficiency ηsens for nano-luminophore 3 was estimated to be 29%, which is smaller than that of Eu(III) complex 1 and 2. The ηsens might be related to excited-triplet-state lifetime. To get a further understanding of the energy transfer efficiency observed for complex 2 and 3, we investigated lifetime of the corresponding gadolinium complex at 90K (Table S5). The average triplet-state lifetime of hfa ligand in Gd(hfa)3(TPPO-Si-OEt)3-SiO2 is 15 ms, which is smaller than those of in the Gd(hfa)3(TPPO-Si(OEt)3)2 (47 ms), in agreement with their energy transfer efficiency in complex 2 and nano-luminophore 3.

Using organic ligand TPPO-Si(OEt)3 as support, we developed a nano-luminophore 3, which shows larger emission quantum yield than those of previous reported Eu(III)-coordinated materials, suggesting TPPO-Si(OEt)3 is a promising candidate for the development of Eu(III)-based luminescent nanomaterials. To verify this supposition, we prepared the Eu(III) complex Eu(tfc)3(TPPO-Si(OEt)3)2 (4), Eu(tfc)3(TPPO-Si(OEt)3)2-SiO2 (5) and hybrid nano-luminophore Eu(tfc)3(TPPO-Si-SiO2)2 (6) (Figure 2). The relative emission intensity of the 5D0 → 7F2 transition for nano-luminophore 6 is higher than Eu(III) complex 4 and 5 (Figure S13), in agreement with their observed luminescence lifetimes (Table S6). Furthermore, the nano-luminophore 6 provides larger Φff (54%) than complex 5 (39%) and 4 (9%) (Table 1). This large Φff is also based on a higher radiative rate constant (κr, 1.07 × 10^3 s^-1) and a lower non-radiative rate constant (κnr, 9.20 × 10^-2 s^-1). Compare with complex 5, the nano-luminophore 6 has a lower photosensitized energy transfer efficiency. The low ηsens for nano-luminophore 6 (9%) and 3 (29%) might be related to the stabilization of the excited triplet states of tfc and hfa ligand. Depending on the phoshorescence lifetime of Gd(hfa)3(TPPO-Si-OEt)3-SiO2 (ave. lifetime = 15 ms) is smaller than that of Gd(hfa)3(TPPO-Si(OEt)3)2 (ave. lifetime = 47 ms), we consider that the unstable excited-triplet-state of hfa and tfc ligand in nano-luminophore 3 and 6 promote their lower photosensitized energy transfer efficiency.

According to the above results, the triphenylphosphine oxide compound TPPO-Si(OEt)3 can act as a support covalent on the silica nanoparticles. In the case of hfa and tfc as photosensitization ligand, the achieved Eu(III) coordinated nano-luminophore 3 and 6 exhibit large intrinsic

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**Table 1. Photophysical properties of Eu(III) complexes in solid.**

<table>
<thead>
<tr>
<th>Samples</th>
<th>τobs / ms</th>
<th>kr / s⁻¹</th>
<th>κnr / s⁻¹</th>
<th>Φff / %</th>
<th>Φnr / %</th>
<th>ηsens / %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Eu(hfa)3(H₂O)₂</td>
<td>(1)</td>
<td>0.42</td>
<td>5.9 × 10²</td>
<td>1.8 × 10³</td>
<td>25</td>
<td>9</td>
</tr>
<tr>
<td>Eu(hfa)3(TPPO-Si(OEt)₃)₂</td>
<td>(2)</td>
<td>0.74</td>
<td>7.8 × 10²</td>
<td>5.8 × 10²</td>
<td>58</td>
<td>31</td>
</tr>
<tr>
<td>Eu(hfa)3(TPPO-Si)₂-SiO₂</td>
<td>(3)</td>
<td>0.98</td>
<td>9.5 × 10²</td>
<td>6.9 × 10</td>
<td>93</td>
<td>27</td>
</tr>
<tr>
<td>Eu(tfc)₃(H₂O)₃</td>
<td>(4)</td>
<td>0.16</td>
<td>5.93 × 10²</td>
<td>5.78 × 10³</td>
<td>9</td>
<td>-</td>
</tr>
<tr>
<td>Eu(tfc)₃(TPPO-Si(OEt)₃)₂</td>
<td>(5)</td>
<td>0.42</td>
<td>9.40 × 10²</td>
<td>1.46 × 10³</td>
<td>39</td>
<td>9</td>
</tr>
<tr>
<td>Eu(tfc)₃(TPPO-Si-SiO₂)</td>
<td>(6)</td>
<td>0.50</td>
<td>1.07 × 10³</td>
<td>9.20 × 10²</td>
<td>54</td>
<td>5</td>
</tr>
</tbody>
</table>

[a] λex = 356 nm. [b] Calculation method is shown in experimental section. [c] λex = 320 nm. [d] The photosensitized energy transfer efficiency ηsens = Φsens / Φtot. [e] The value is too low to collect.

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Figure 6. Emission spectra of Eu(hfa)₃(H₂O)₂ (1) (black line), Eu(hfa)₃(TPPoS-Si(OEt)₃)₂ (2) (red line) and Eu(hfa)₃(TPPO-Si-SiO₂) (3) (blue line), which were excited at 350 nm in solid state at room temperature.
A novel triphenylphosphine oxide compound TPPO-Si(OEt)_3 was synthesized for fixation of Eu(III) complexes and silica matrices (mesoporous silica materials, nanomaterials can apply to other lanthanide (Tb, Dy) complexes and silica matrices (mesoporous silica materials, micro silica particles, silica glass materials), opening their corresponding application as luminescent materials.

Deposition Numbers 2045883 (for TPPO-Si(OEt)_3) contain the supplementary crystallographic data for this paper. These data are provided free of charge by the joint Cambridge Crystallographic Data Centre and Fachinformationszentrum Karlsruhe Access Structures service www.ccdc.cam.ac.uk/structures.

Acknowledgements

This work was supported by Grant-in-Aid for Grant Number JP20K21201, JP20H05197, JP20H04653, JP20H02748, JP19H04556, JP18H04497 and JP18H02041. This work was also supported by the Institute for Chemical Reaction Design and Discovery (ICReDD), established by the World Premier International Research Initiative (WPI) of MEXT, Japan.

Keywords: europium complex • nanoparticles • luminescence
A novel method for development of lanthanide-based hybrid nanomaterials, taking advantage of an Eu(III) complex with organic ligand covalently bonded to the silica nanoparticles through two binding sites as support was demonstrated. The developed hybrid nanoluminophore exhibited higher intrinsic luminescence quantum yield (93%) and longer emission lifetime (0.98 ms), which is much larger than those of previous Eu(III)-based hybrid materials.