Structure-Dependent Photoluminescence of Europium(III) Coordination Oligomeric Silsesquioxane: Synthesis and Mechanism

Ming Li, Chengyu Wang, Di Wang,* and Jian Li*

ABSTRACT: The coordination environment of Eu$^{3+}$ is a crucial factor in the optical performance of the complex. Herein, a new kind of oligomeric silsesquinoxane was employed to improve the coordination environment of central ions, the luminescence intensity of which was greatly enhanced with an efficient emission peak at 619 nm. More importantly, the photoluminescent properties of the product will be altered because of the formation of the Si–O–Si structure. The relevant mechanism has also been investigated and proposed by a series of characterization analyses. Additionally, the fluorescence lifetime, intrinsic quantum yield, and energy transfer efficiency were calculated. In addition, the observed trend of Judd–Ofelt intensity parameters was used to justify the coordination environment of Eu$^{3+}$ ions. The experimental results reveal that the sol–gel reaction can effectively promote intramolecular energy transfer. In addition, we introduced four theory modules of ligands (LSi, LSi-1, LSi-2, and LSi-3) with certain rules of formation of Si–O–Si, and density functional theory (DFT) and time-dependent DFT (TD-DFT) were used to explore their excited electron transfer process and their electronic absorption spectra, combined with Marcus theory. The calculated results show that the sol–gel reaction will induce the separation of the distribution of excited holes and electrons, leading to an efficient charge-transfer (CT) process. The predictable results were in good accordance with the experimental findings. Consequently, the sol–gel reaction occurring among ligands will be attributed to an efficient CT process, leading to a strong luminescence intensity, as observed experimentally.

1. INTRODUCTION

Lanthanide ions$^1$ have attracted research interest because of their unique photophysical properties.$^2$ These properties are based on the emission of the f–f forbidden transitions, including their narrow emission bandwidths, high color purities, and high quantum efficiency, as well as rare-earth ions' special electronic structure. Consequently, these ions have been used in various areas.$^1$ For instance, europium(III) has been used extensively as a probe because of the well-documented sensitivity of its luminescence. However, the absorption coefficients of the optical transitions for lanthanide ions are so low because of their parity-forbidden 4f–4f transitions, leading to a low luminescence intensity that limits their practical application considerably. This drawback can be improved through the use of an oligomeric silsesquioxane ligand strongly bonded to the 4f metal center, which acts as a sensitizer and provides a higher efficiency of the energy transition from the ligand to the lanthanide ions.$^{15,16}$ This can, in turn, enhance the luminescence intensity of rare-earth ions controllably.

As an environmentally friendly material, oligomeric silsesquioxane has attracted significant attention because of its unique nanoscale cage-shaped structure and good two-phase compatibility.$^{17}$ Furthermore, according to a previous report, oligomeric silsesquioxane shows high thermal and chemical stability in the environment.$^{18}$ It is usually added to conjugated polymer luminescent materials to improve solubility and maintain the luminescence of the polymer in the aggregate state.$^{21}$ This is attributed to the ability of the rigid silicon and oxygen framework to greatly enhance the stability and luminescence intensity of the resulting materials.$^{22}$ Although physical doping, such as mechanical blending or melt blending, can enhance the luminescence effect,$^{30}$ the mechanical properties of the material and the nucleophilic properties of the polymer are weak, and the concentration quenching easily occurs. In addition, the luminescence intensity cannot be linearly controlled. Therefore, complexes utilizing oligomeric silsesquioxane as ligands$^{33,34}$ have been synthesized. Oligomeric silsesquioxane can not only improve the solubility of complexes with other organic phases, as well as the stability and biocompatibility of the resulting compounds, but can also easily control the luminescence intensity by changing its structure by altering its reaction time or temperature.

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Although the application of oligomeric silsesquioxane-containing fluorescent materials is mainly attributed to how the rigid silicon and oxygen framework greatly enhances the stability and luminescence intensity of the resulting materials, few researchers have completely explored the theory. Thus, in the work reported herein, experimental and theoretical studies were carried out on the effects of the structure of ligands on the electronic properties. Density functional theory (DFT) calculations and time-dependent DFT (TD-DFT) were combined to analyze the electronic properties of the ligand with different degrees of sol-gel reactions, including frontier molecule orbitals, excited states, hole-electron recombination, and reorganization energy analysis. These properties suggest that the sol-gel reaction among ligands can affect the electronic character of the ligand, thereby improving the energy-transfer process and the luminescence of the resulting complexes.

In this work, a series of europium(III) coordination oligomeric silsesquioxanes was synthesized successfully. The structure and optical properties of the products were analyzed separately to determine the nature underlying the luminescence, which can be enhanced by the formation of the Si−O−Si structure through the sol-gel reaction. In addition, to understand the nature behind Eu$^{3+}$ coordination, electron and hole theory was used, demonstrating that the formation of the Si−O−Si structure among the ligands changes the electron-transfer mechanism, in accordance with the calculated absorption spectrum. Furthermore, a combination of excited-state dynamics studies and Marcus model theoretical calculations suggest that the formation of the Si−O−Si bonds between the ligands will result in a more efficient charge-transfer procedure, attributed to a more valid intersystem crossing process, and the enhanced luminescence efficiency observed in the experiment.

2. RESULT AND DISCUSSIONS

2.1. Structural Characteristics of Compounds. The IR spectrum of the europium(III) coordination oligomeric silsesquioxane (MP) reveals the characteristic Si−O−Si absorption band at 1063 cm$^{-1}$ appearing after the sol-gel reaction, as shown in Figure 1. The band at 3426 cm$^{-1}$ is assigned to the stretching vibration (V$_{N-H}$) of the amide groups. The stretching-vibration absorption (V$_{C=O}$) ascribed to amide I appears at 1707 cm$^{-1}$ and the N−H bending vibration belonging to amide II at 1604 cm$^{-1}$, indicating that the secondary amide group remains in the products. These results indicate the successful formation of MP.

$^{29}$Si NMR studies of M and MP at the optimal luminescent intensity (50 °C, 84 h) are used to explore the predominant environment of the silicon atom connectivity. The two signals of M due to T$^2$ [(SiO)$_2$Si(C(OH))] and Q$^4$ [(SiO)$_4$Si] were located at −47 and −110 ppm, respectively, and two peaks of MP can be seen at −62 and −110 ppm, assigned to T$^3$ [(SiO)$_3$SiC] and Q$^4$ [(SiO)$_4$Si], respectively. As shown in Figure 2, Q$^4$ species were predominant and were favored with the sol-gel reaction going on while T$^2$ intensity decreases. These results proved that the sol-gel reaction promotes the conversion of silicon species, which was still in the hydrolyzed form in linear structures, to fully condensed silicon site formation. The results show that the silicon nuclei are mostly presented as a Q$^4$ environment, indicating the presence of Si−O−Si structure formation originated from the sol-gel reaction of M.

To gain further insight into the reaction scheme, X-ray photoelectron spectroscopy (XPS) measurements were performed to characterize the functional groups on the surface. It was observed that the complex shows two typical peaks corresponding to C and O, as shown in Figure 3a,c. The C 1s spectra of the complexes coordinated with Eu$^{3+}$ are deconvoluted into four peaks positioned at 284.80, 285.50, 286.192, and 288.744 eV, which are attributed to C−H, the second peak is due to C−O, the third peak is the C−N bond, and the fourth peak is the carbon in C≡O, which has a higher oxidation state in this structure along with higher electron binding energies. In addition, the O 1s at around 530 eV$^{31}$ exhibit three peaks positioned at 531.39, 532.28, and 532.31 eV, which are attributed to O−C, O−Si, and C≡O bonds, respectively.

In comparison with the complex, changes were located in the XPS spectra of the europium(III) coordination oligomeric silsesquioxane, exhibiting two predominant peaks for C and O, as shown in Figure 3b,d. C 1s spectra consist of four peaks at 284.80, 285.10, 286.192, and 288.744 eV, which are attributed to C−C, C−O, C−N, and C≡O bonds, respectively. The increase in the binding energy of the C≡O bond reveals that the coordinate bond between Eu$^{3+}$ and the ligand is stronger because of the formation of Si−O−Si bonds, which improves the rigidity of system, resulting in a higher energy-transfer efficiency. Furthermore, the O 1s spectra of the modified gel...
centered with Eu$^{3+}$ is deconvoluted into three peaks located at 531.53, 532.38, and 533.34 eV, which are attributed to the oxygen in O-C, O-Si, and C=O, respectively. The increase of the binding energy in the oxygen of C=O indicates that the coordinate bond between Eu$^{3+}$ and the ligand is stronger, in accordance with the C spectrum. The result reveals that the sol–gel reaction between the ligands will make the coordination relation between the ions and ligands more robust, leading to an efficient energy transfer (ET) process.

2.2. Optical Properties of Compounds. The UV–vis absorption spectra of the complex (M) and europium(III) coordination oligomeric silsesquioxane (MP) were measured, as shown in Figure 4. MP has stronger ultraviolet absorption in the range of 230–290 nm than M. The absorption peaks at 270 nm are mainly attributed to the π → π$^*$ electron transition of the benzene ring belonging to the B-band absorption of the benzene ring from the ground state to the first excited state, indicating the variation of the conjugate system of M, proving the successful preparation of MP from M. The absorption at 324 nm belongs to the n → π$^*$ electron transition of amide unshared electron pairs of methacrylic acid. These results are consistent with the IR spectra, indicating the successful preparation of MP.

In order to explore the luminescence enhancement effect of the formation of the Si–O–Si structure on the luminescent properties of the products, the emission spectra of the complex (M) and europium(III) coordination oligomeric silsesquioxane shown in Figure 5 was obtained at the excitation wavelength of 395 nm. The products obtained with different sol–gel reaction conditions exhibit the emission peaks of the Eu$^{3+}$ ions, and the relevant characteristic emission bands are attributed to 5D$_0$ → 7F$^1$ (593 nm), 5D$_0$ → 7F$^2$ (619 nm), 5D$_0$ → 7F$^3$ (652 nm), and 5D$_0$ → 7F$^4$ (697 nm) (Figure S2a). When the reaction time is kept the same at 84 h, the emission intensity will increase greatly with an increase in reaction temperature and reaches maximum when the sol–gel reaction temperature is 50°C. In addition, when the sol–gel reaction temperature is kept the same, the emission intensity increases greatly with rising reaction time (Figure S3). The luminescence enhancement can account for the bonding behavior, which will strengthen the luminescence intensity because the formation of the Si–O–Si bond among the ligands will exhibit a certain rigid structure that will restrict the intramolecular rotations to block the nonradiative pathway and enhance the radiative channel.

To gain a deeper insight into the triplet state energy of the ligand, we replaced the trivalent europium ions (Eu$^{3+}$) with the trivalent gadolinium ions (Gd$^{3+}$) to obtain the phosphorescence spectrum at 77 K ($\lambda_{ex} = 395$ nm). From the spectra shown in Figure 6, it clearly appears that the emission maxima of the complex (M-Gd$^{3+}$) and gadolinium(III) coordination oligomeric silsesquioxane (MP-Gd$^{3+}$) obtained at 50°C for 84 h are quite similar and characterized by a single band at 535 nm, assigned to the triplet state of the ligand. The corresponding triplet state energy is 18692 cm$^{-1}$, which is higher than the excited state of Eu$^{3+}$ ($D_0$) (17300 cm$^{-1}$),
proving an effective ET pathway between the ligand and central ions, and the sol–gel reaction among the ligands did not have too much influence on their triplet state.

The most intense emission line corresponding to the hypertensive $^5D_0 \rightarrow ^7F_2$ transition sensitive to the coordination environment is regarded as an ultrasensitive transition, and the $^5D_0 \rightarrow ^7F_1$ transition belongs to the magnetic dipole transition less affected by the coordination environment.44,49 Thus, the ratio of the $^5D_0 \rightarrow ^7F_2$ to $^5D_0 \rightarrow ^7F_1$ transition could be used to predict the symmetry of the environment of Eu$^{3+}$, and a larger ratio stands for a lower chemical environment symmetry around the Eu$^{3+}$, leading to luminescence intensity enhancement affected by reaction condition perturbations.50,51 Before any further chemical reactions, the intensity ratio (5D0→7F1/5D0→7F2) of Eu$^{3+}$ in M is 0.775 (Table 1). After further modification, the obtained europium(III) coordination oligomeric silsesquioxane has a lower ratio with the increase of reaction temperature when the reaction time is 84 h. The intensity ratio (5D0→7F1/5D0→7F2) of Eu$^{3+}$ emission was on a decrease from 0.448 and 0.414 to 0.37, as shown in Figure S2b, which is lower than that in europium chloride solution,52 indicating that an initial interaction between Eu$^{3+}$ and ligands and the Eu$^{3+}$ environment changed from high symmetry to low symmetry. Therefore, the explanation is that the formation of the Si–O–Si structure during the sol–gel reaction has made the change of the symmetry of the Eu$^{3+}$ ion coordination environment from high to low, away from the center of inversion. This phenomenon of luminescence enhancement is directly attributed to the symmetry deviation-induced transition effect.53

In order to further explore the influence of the formation of the Si–O–Si structure on the coordination environment of Eu$^{3+}$ ions, the Judd–Ofelt theory54,55 was introduced, which allows for the calculation of the manifold transition probabilities that can predict the important radiative properties of lanthanide ions. The $\Omega_i$ parameters depend on the local geometry, bonding atoms, and polarizability of the first coordination sphere of lanthanide ions. Acccording to the theory, the $\Omega_i$ values are the most sensitive to small angular changes in the chemical environment around the Eu$^{3+}$ ion.56 However, it is difficult to obtain the refractive index. Thus, we decided to correct the emission intensity by the decay lifetime to obtain the refractive index as follows57

$$I = a \sum_{j=0}^{6} A_{\eta_j}$$

where $a$ is the scale factor, $A_{\eta_j}$ is electric dipole transition probabilities, and $I$ is the emission intensity from $^5D_0 \rightarrow ^7F_j$ ($j = 0 \rightarrow 6$). In addition, $A_{\eta_j}$ and decay time $\tau_0$ are inversely proportional

$$\sum_{j=0}^{6} A_{\eta_j} = \frac{1}{\tau_0}$$

From 1 and 2, we could obtain the value of $a$ and magnetic dipole transition probabilities $A_{\eta_j}$ could be acquired by the following formula

$$A_{\eta_j} = \frac{64\pi^4 \nu_{md}^3}{3h(2j+1)} n^2 S_{md}$$

where $\nu_{md}$ is the barycenter of $^5D_0 \rightarrow ^7F_j$ transitions, $S_{md}$ is the magnetic dipole transition line strength, which is independent

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Table 1. Intensity Ratio ($^5D_0 \rightarrow ^7F_1/^5D_0 \rightarrow ^7F_2$) of Eu$^{3+}$ Emission of M and MP (MP-1, MP-2, MP-3)

|     | M     | MP-1  | MP-2  | MP-3  |
|-----|-------|-------|-------|-------|
| $^5D_0 \rightarrow ^7F_1$/$^5D_0 \rightarrow ^7F_2$ | 0.775 | 0.448 | 0.414 | 0.367 |

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![Figure 5.](https://dx.doi.org/10.1021/acsomega.0c04365)

Figure 5. Emission spectra of the complex (M) and europium(III) coordination oligomeric silsesquioxane (MP) with different sol–gel reaction temperatures [MP-1 (40 °C), MP-2 (45 °C), MP-3 (50 °C) (optimum condition)] for 84 h.

![Figure 6.](https://dx.doi.org/10.1021/acsomega.0c04365)

Figure 6. Phosphorescence spectra of M and MP coordinated with gadolinium ions (Gd$^{3+}$) (50 °C 84 h).
from the host and equals to 7.83 × 10^{−42} \text{(dimensionless)},^{58} \hbar is Planck’s constant (\hbar = 6.626 \times 10^{−27} \text{ erg} \cdot \text{s}), J is the total angular momentum quantum number of the ground number of the ground state, and \eta is the refractive index of the medium. Having brought the values of the constants and the transition rate into formula (4), we could obtain the refractive index. Furthermore, phenomenological Judd—Ofelt intensity parameters could be determined by applying the following formula

\[ A_{\gamma_j} = \frac{64\pi^4 e^3}{3h(2J + 1)} \left( \frac{n(n^2 + 2)^2}{9} \right) S_{ed} \]

where \( S_{ed} \) means the area under the bands corresponding to 3D_{0} \rightarrow 7F_j transitions (J = 0–6) and \||U^{(i)}|| are the matrix elements which have been obtained. \(^{54}\)

The value of \( \Omega_j \) corresponds to the transition intensity ratio \( R \). The relationship between \( \Omega_j \) and the transition ratio \( R \) can be obtained from the following formula

\[ \frac{I_{j}(v)}{I_{v}(v)} = \frac{A_{\gamma_j}}{A_{\gamma_i}} = \frac{2n^3}{9S_{md}g_{i}} \sum_{i=2,4,6} \Omega_j \text{||}[L, S][U^{(i)}||[L', S'][J']|^2 \]

From formula (5), the transition intensity ratio \( R \) of M and MP could be obtained from the ratio of the transition intensity of the electric dipole and magnetic dipole according to the emission spectrum, and we could obtain the values of \( \Omega_j \) of M and MP as 0.6 \times 10^{−20} and 1.22 \times 10^{−20} respectively. \( \Omega_2 \) reflects the local microenvironment where Eu^{3+} is located, and a larger \( \Omega_2 \) is attributed to a stronger covalent effect of the Si−O bond. \(^{39}\) Through comparison, it could be found that the value of \( \Omega_2 \) of Eu^{3+} in MP is larger than that of M. It shows that the Eu−O bond formed after the formation of the Si−O−Si structure of MP has higher covalency, reflecting its lower local symmetry and larger polarization compared to M.

In order to explore the photophysical properties of lanthanide complexes deeply, the decay curves of the complex and europium(III) coordination oligomeric silsesquioxane under the optimal conditions were measured. The luminescent lifetime can be used to explain the variation of the microenvironment of the system. The decay curves of the 3D_{0} \rightarrow 7F_{2} transformation of Eu^{3+} were recorded at 395 nm in the microenvironment of the system. The decay curves of the lifetime can be used to explain the variation of the luminescent intensities, and we could obtain the values of the electric dipole and magnetic dipole according to the formula (4). Having brought the values of the constants into formula (4), we could obtain the refractive index.

Furthermore, phenomenological Judd—Ofelt intensity parameters could be determined by applying the following formula

\[ \tau = \frac{A_{i}r_{i}^2 + A_{f}r_{f}^2}{A_{i}\tau_{i} + A_{f}\tau_{f}} \]

where \( A_{i} \) and \( A_{f} \) are fitting constants and \( \tau_{i} \) and \( \tau_{f} \) are short and long decay components, respectively.

The photoluminescence quantum yield (PLQY) of MP (4.5%) is three times higher than that of M (1.10%). As shown in Figure 7, the decay time of 3D_{0} \rightarrow 7F_{2} of Eu^{3+} in MP (0.513 ms) is shorter than that in M (0.561 ms) suggesting that the luminescence lifetime of the complex after the formation of the Si−O−Si structure has a rapid decrease because the polarization of the Ln−L bond is increased, leading to more orbital mixing. Based on the changes of lifetimes and quantum yield, from the complexes to the europium(III) coordination oligomeric silsesquioxane, the radiative rate constants \( (k_{r}) \) are calculated according to the formula as follows \(^{60}\)

\[ k_{r} = \Phi/\tau \]

where \( k_{r} \) refers to the radiative rate constants and \( \Phi \) and \( \tau \) refer to the quantum yield and luminescence lifetime, respectively.

The photophysical properties and ET efficiency between the ligand and central ions, the luminescent efficiency of Eu^{3+} ions can also depend on the intensity of ligand absorption and the energy state of Gd^{3+}, which was coordinated with Eu^{3+} and Gd^{3+} under the same reaction conditions was performed, while the high excited energy state of Gd^{3+} forbids the ET from the ligand to Gd^{3+}, which is suitable for selection as a reference. The analysis of decay profiles allows for the deeper exploration of the Eu^{3+} ET process and for establishing.

Figure 7a,b, for which the curves are well-fitted to the double-exponential functions given by

\[ I(t)/I_0 = A_1 e^{-t/\tau_1} + A_2 e^{-t/\tau_2} \]

where \( \tau_1 \) is the decay time of a short lifetime component, \( \tau_2 \) is the delay time of a long component, and the \( A_1 \) and \( A_2 \) parameters are amplitudes at \( t = 0 \). To estimate the ET efficiencies, we used the average luminescence lifetime for the complex. The decay curves of (a) M and (b) MP.
the relation between luminescence lifetimes and the sol–gel reaction of the ligand of europium(III) coordination oligomeric silsesquioxane. First, we compared the luminescence lifetimes of the ligand in the complex (M) and europium(III) coordination oligomeric (MP) with the sol–gel reaction under the optimal conditions and the product coordinated with Gd3+ under the same conditions. The decay curves were recorded upon ultraviolet excitation (λex = 395 nm) and monitoring a blue emission related to the ligand (λem = 440 nm), for which the curves are well-fitted to double-exponential functions given as formula (6) and the average fluorescence lifetime of the ligand for the complex and oligomeric silsesquioxane coordinated with Eu3+ and Gd3+ ions calculated from the eq 7. The luminescence process of rare-earth complexes can be described as an ET process where after the formation of singlet excited state molecules attributed to energy absorption through the irradiation of excitation light, the singlet excited state energy is transferred to the triplet state by nonradiative transition, after which the triplet energy is transferred to rare-earth ions’ excited state without radiation, together with the radiation process from the excited state of metal ions to the ground state resulting in light emission.62 Consequently, a ligand useful for sensitizing the ions must have a higher excited triplet state, and ET must be efficient in the complex. The ET efficiency (ET) between Eu3+ ions and the ligand could be expressed by the following equation63,64

\[
\eta_{\text{ET}} = \left(1 - \frac{\tau}{\tau_0}\right) \times 100\%
\]

where \(\tau\) and \(\tau_0\) correspond to the decay lifetime of the donor in M and MP in the presence and absence of the acceptor (Eu3+), respectively. The ET process from the ligand to Gd3+ cannot happen because of the higher excited triplet state of Gd3+. Therefore, the fluorescence lifetime of the ligand in the complex coordinated with Gd3+ was chosen to be the reference (\(\tau_0\)). The calculated efficiencies of the ligand to Eu3+ ET for MP (50 °C 84 h) (18%) is higher than that of M (14%), suggesting that the formation of the Si–O–Si structure of the ligand optimizes the ET process as a certain rigid Si–O–Si structure restricts intramolecular rotations of the ligand and opens up the radiative channel, thus enhancing the ET efficiency between the ligand and central ions.64 In addition to the ET efficiency, the intrinsic quantum yield of the \(3D_0\) emitter level of the Eu3+ ion is defined as the ratio between the radiative transition rate (\(A_{\text{rad}}\)) and nonradiative transition rate (\(A_{\text{nrad}}\)).53,63 The calculation formula is shown below.

\[
\Phi = \frac{A_{\text{rad}}}{A_{\text{rad}} + A_{\text{nrad}}}
\]

\[
\tau = \frac{1}{A_{\text{rad}} + A_{\text{nrad}}}
\]

\[
A_{\text{rad}} = \sum A_{\gamma_j} = A_{\gamma_0} + A_{\gamma_1} + A_{\gamma_2} + A_{\gamma_3}
\]

The \(\tau\) in eq 11 stands for the luminescence lifetime of M and MP, which has been calculated. The value of \(A_{\gamma_j}\) has been obtained according to formula (1). The luminescence intrinsic quantum yield of MP is 0.984, which is larger than that of M, which is 0.916. The result confirms that the emission efficiency of MP is higher than that of M.

### Table 2. Absorption Spectrum with TD-DFT for Complexes

| sample | \(\lambda\) (nm) |
|--------|-----------------|
| M      | 224.99          |
| M1     | 230.84          |
| M2     | 234.65          |
| M3     | 211.57          |
| M4     | 226.38          |
| M5     |                 |

To explore the optical performance of the complexes more directly, the ligands shown in Figure S5 were examined. All of the ligand geometries were optimized by the Dmol3 module and DFT and TDDFT calculations at the level of B3LYP/6-31G* in the Gaussian 09 package,70 providing a prediction of the singlet excitation energy and triplet emission energy as well as the absorption spectrum shown in Figure 9. The products exhibit strong absorption at 222.44, 218.66, 257.46, and 273.24 nm, which are mainly attributed to \(S_0 \rightarrow S_1\) \((f = 0.1208), S_0 \rightarrow S_2\) \((f = 0.0749), S_0 \rightarrow S_3\) \((f = 0.0461),\) and \(S_0 \rightarrow S_1\) \((f = 0.0461),\) respectively. LSi-1 exhibits the largest shift among all ligands shown in Figure 9, suggesting that it leads to the greatest energy gap for the \(\pi \rightarrow \pi^*\) transition. This is because of the enlargement of the energy gap between the occupied molecular orbital and unoccupied molecular orbital, leading to the absorption peak having a blue shift.71 The variation of the absorption spectra was in good accordance with that of the complexes. This suggests that the excitation states of the compounds are mostly influenced by the ligands, which was illustrated by charge decomposition analysis (CDA).72–74

### Figure 8. Electronic absorption spectrum of compounds calculated by \(V_{\text{amp}}\)

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The D index of LSi is the lowest, indicating a small gap from that of LSi-2 and LSi-3, both having obvious separation. Compared with LSi, LSi-1 has a lower Sr index, which means that the formation of Si–O–Si induces the electron and hole overlap and the excitation because of the unidirectional charge-transfer (CT) excitation because there was no significant change in the electron distribution before and after excitation, as shown in Table 3. The ligands LSi-2 and LSi-3 have a higher D index, indicating that they are due to the unidirectional CT excitation. The overlap between the electron and hole of LSi-3 is more than that of LSi-2, as shown in Table 4.

Table 4. Holes and Electrons, $C_{\text{hole}}$ and $C_{\text{ele}}$, and Sr Function Diagrams of the Singlet Excitation of L, LSi, LSi-1, LSi-2, and LSi-3

| Hole & Electron | $C_{\text{hole}}$ & $C_{\text{ele}}$ | $S_r(t)$ |
|---------------|----------------|----------|
| LSi           |                |          |
| LSi-1         |                |          |
| LSi-2         |                |          |
| LSi-3         |                |          |

From the above discussion, it can be concluded that the self-condensation reaction of the ligand can increase the overall average distribution of electrons and holes to affect the energy excitation from $S_0$. From the data, the excitation can be clearly confirmed. The LSi and LSi-1 excitations belong to the spin-allowed $\pi \rightarrow \pi^*$ localized excitation transition, and LSi-2 and LSi-3 are both unambiguously assigned to single-direction CT excitation $\pi \rightarrow \pi^*$ transitions, as reported in Table 4. However, the shape of the absorption band in the ultraviolet (UV) region is not completely similar. The LSi band is shifted hypsochromically relative to others, which demonstrates the impact of the reaction between phthaloyl chloride and aminopropyl triethoxy silane (APTES). The extended $\pi$ electron system of phenanthroline leads to a greater energy gap for the $\pi \rightarrow \pi^*$ transition.

Absorbing photons is the first step in releasing luminescence from fluorescent molecules. By analyzing the frontier molecular orbitals shown in Figure S6, which are involved in the absorption peaks, the luminescence properties could be
HOMO→7 → LUMO (27.82%) (HOMO denotes highest occupied MO, and LUMO denotes lowest unoccupied MO), HOMO→4 → LUMO (19.01%), and HOMO→2 → LUMO (18.45%) transitions. The absorption maximum of LSi-1 appears at 218.66 nm because of the HOMO→2 → LUMO→1 (20.38%) and HOMO→6 → LUMO→1 (15.10%) transitions. Furthermore, the absorption of LSi-2 and LSi-3 are located at 257.46 nm because of the HOMO→1 → LUMO (69.04%) transition and at 273.24 nm, attributed to the HOMO→2 → LUMO→1 (65.37%) transition, respectively. In addition, LSi-1 has a larger blue shift than the others, indicating that it leads to the greatest energy gap for the π → π* transition. It is worth noting that the extra amide as well as the Si–O–Si bond in the ligand results in greater π-electron delocalization, confirming that changes in the spectra are mainly caused by the sol–gel reaction.

3.2. Charge Transfer. Charge transfer (CT) in Marcus theory will occur among the most fundamental and ubiquitous chemicals, which is critical to energy conversion and storage processes. To discuss the specific causes of the different ET rates for the ligand, the following Marcus expression is introduced

\[ k = \frac{(4\pi^2/\hbar)^2(4\pi\lambda k_B T)^{-0.5}}{\exp[-\lambda/(4k_B T)]} \]  

where \( k_B \) is the Boltzmann constant, \( \hbar \) is Planck’s constant, \( T \) is the absolute temperature, \( \lambda \) is the reorganization energy, and \( V \) is the CT matrix element. The ET rate strongly depends on two parameters: \( \lambda \) and \( V \).

To predict the ET rates of the ligand with different structures, the inner-sphere contribution (\( \lambda_i \)) of different ligands was calculated according to the following formula

\[ \lambda_i = \left[ E^\ast/E - E^\ast/E\right] + \left[E/E^\ast - E/E\right] \]  

where \( E/E^\ast \) and \( E^\ast/E \) are the energies of the neutral molecule and the optimized anion calculated with the optimized structure of the neutral molecule and the optimized anion structure, respectively. \( E/E^\ast \) and \( E/E^\ast \) are the energies of the neutral molecule calculated in the anionic state and at the ground state, respectively. The \( \lambda_i \) of all ligands are given in Table 6. From the table, one can see that \( \lambda_i \) varies greatly with different structures. The \( \lambda_i \) for all five targeted ligands follows the order of LSi > LSi-1 > LSi-2 > LSi-3 > LSi-2. According to formula (17), it can be predicted that the CT rates were in the order LSi-3 > LSi-2 > LSi-1 > LSi. Based on this observation, it is demonstrated that the formation of Si–O–Si among the ligands can be beneficial to charge transitions.

4. CONCLUSIONS

The coordination environment around Eu\(^{3+}\) plays an important role in the optical properties of the complex. Consequently, we modified the coordination environment of the central ions by introducing the oligomeric silesiquioxane, thereby significantly improving the photoluminescence of the complex. In addition, the photoluminescent properties of the complex will be modified by the formation of the Si–O–Si structure. The Judd–Ofelt intensity parameters and radiative properties were estimated, from which it could be found that Eu\(^{3+}\) was surrounded by asymmetric ligand environments after the sol–gel reaction among ligands. The experimental results reveal that the sol–gel reaction of the ligands can effectively promote the intramolecular ET. To further determine the mechanism, we designed a series of theory models of ligands to explore their excited electrons transfer process and their electronic absorption spectra at the DFT and TD-DFT level combined with Marcus theory. The calculated results show that the sol–gel reaction will induce the separation of the distribution of excited holes and electrons, leading to an efficient CT process. The theoretically calculated results were in good accordance with the experiment results. In conclusion, this work will be conducive to the control of luminescent materials and has potential for theoretical calculation application.

5. EXPERIMENT SECTION AND THEORETICAL METHODS

5.1. Materials. Ethanol (99.7%) and dichloromethane (analytical grade) were obtained from Tianjin Fuyu (Tianjin, China). Phthaloyl chloride (99%), phthaloyl chloride (98%), and europium nitrate hexahydrate (Eu(NO\(_3\))\(_3\)·6H\(_2\)O) were purchased from Sigma (Shanghai, China), and hydrochloric acid was obtained from Aladdin (Shanghai, China).

5.2. Synthesis of Modified Complexes. Phthaloyl chloride (0.01 mol, 2.03 g) dissolved in dichloromethane (10 mL) was added to a solution of (3-aminopropyl) triethoxysilane (0.02 mol, 4.43 g) in dichloromethane (10 mL) drop-by-drop in ice water to obtain a mixture. The solution was then...
placed in a magnetic stirrer (300 rpm) to react at room temperature for 2 h. Next, the solution was placed in a vacuum drying oven at 45 °C to evaporate the solvent in order to obtain a pure colorless ligand. The ligand, mixed with europium nitrate hexahydrate, was then dissolved in ethanol and reacted in a 70 °C water bath for 4 h to acquire the modified complex (M), after drying in a vacuum oven at the temperature of 50 °C.

5.3. Synthesis of Europium(III) Coordination Oligomeric Silsesquioxane. The appropriate amount of distilled water and 4−8 drops of 1 mol/L dilute hydrochloric acid were added to the complex’s solution above. After stirring magnetically in a water bath at 50 °C for 20 min, the mixture was placed in an ultrasonic wave cleaner for 30 min to remove all bubbles. The solution was then placed in a water bath at different temperature (40, 45, 50 °C) with the same reaction time (84 h) and different reaction time (48, 60, and 72 h) with the same temperature (40 °C). Finally, it was placed in an oven at 50 °C until the solvent was dried to obtain the europium(III) coordination oligomeric silsesquioxane (MP). The entire reaction process is shown in Scheme 1.

5.4. Characterization Techniques. A PerkinElmer infrared (IR) spectrometer was used to analyze characteristic group functions expected for the complex and europium(III) coordination oligomeric silsesquioxane. XPS analysis (PHI Thermo Fisher Scientific Company QuantERA) was used to determine the element compositions of the samples. 29Si NMR spectra were measured using an AVANCE III 600M spectrometer (BrukerCorp, Karlsruhe, Germany). The photoluminescence excitation (Figure S1) and emission spectra excited by 395 nm of samples were recorded at room temperature using an LS55 fluorescence spectrometer. The excitation and emission monochromator slit widths were 10 and 2.5 nm, respectively, and the speed was set at 1000 nm/min. The PLQY and decay curves were obtained using a steady-state time-resolved fluorescence spectrofluorometer (FLS920, Edinburgh).

5.5. Theoretical Studies. DFT calculations, based on semiempirical methods using the ZINDO Hamiltonian with the parameterized element CNDO/1, were carried out to further understand the effect of the electronic structures of the complexes. The Dmol³ code was used to perform all calculations related to DFT-based geometry optimizations at the level of gradient-corrected functionals (GGA/BP). All of the ligand geometries were optimized by the Dmol³ module and DFT and TDDFT calculations at the level of B3LYP/6-31G* in the Gaussian 09 package, providing a prediction of the singlet excitation energy and triplet emission energy and the absorption spectrum. To further understand the electronic properties of these ligands, hole and electron theory was used. Dₜ, S₀, Hₜ, and Δσ values calculated with the Multiwfn software package were used to explore the distribution between the holes and electrons.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.0c04365.

Excitation spectra of the europium(III) coordination oligomeric silsesquioxane; emission spectra of M and MP and the intensity ratio value of 5D0 → 7F1 and 5D0 → 7F2; emission spectra of M and MP (1:4) with different sol−gel reaction times (48 h (MP1), 60 h (MP2), and 72 h (MP3) (optimum condition)) at 40 °C; theoretical geometry structures of complexes; theoretical geometry structures of ligands; and the occupied and unoccupied orbitals contributing mostly to the singlet excitation of L, LSi, LSi-1, LSi-2, and LSi-3 (PDF)

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