Novel hybrid luminescent materials derived from multicarboxy cage silsesquioxanes and terbium ion

Liguo LI,* Shengyu FENG* and Hongzhi LIU**,†

*Key Laboratory of Special Functional Aggregated Materials, Ministry of Education; School of Chemistry and Chemical Engineering, Shandong University, Jinan, 250100, People’s Republic of China
**State Key Laboratory of Molecular Engineering of Polymers, Fudan University, Shanghai, 200433, People’s Republic of China

Multicarboxy (8, 16) functionalized cage silsesquioxanes were synthesized through the photochemical thiol-ene reaction of octavinylsilsesquioxane with 3-mercaptopropionic acid and mercaptosuccinic acid, respectively. These two cage precursors acted as ligands to coordinate with terbium ion (Tb3+) to obtain two novel hybrid luminescent materials, which exhibited fine luminescent properties and good thermal stabilities. Their morphologies were investigated by XRD, SAXS, SEM, TEM and DLS. And the results showed that self-assembly particle size of the hybrid complex with octacarboxyl cage was larger size than that of cage with 16 carboxyl groups.

©2015 The Ceramic Society of Japan. All rights reserved.

Key-words : Silsesquioxanes, Luminescence, Multicarboxy

1. Introduction

Researchers have been interested in the photoluminescence properties of lanthanide (Ln) compounds for decades.1–3) An attractive feature of luminescent lanthanide compounds is their line-like emission, which results in a high color purity of the emitted light. Because of the unique photophysical properties and great potential applications in optical amplifiers, phosphors, the lanthanide coordination complexes are of great interest.3–6) A lot of reports have focused on the luminescence and intramolecular energy transfer in the rare earth complexes, especially with aromatic carboxylic acids, β-diketones, and heterocyclic ligands.7–9)

Carboxylic acids have been studied in considerable detail as building blocks in designing various high-dimensional coordination polymers.10,11) The use of di- and multicarboxy can generate a large number of coordination complexes composed of chains, sheets and 3D networks with an enormous variety of intriguing structural topologies.12)

Materials with inimitable organic–inorganic hybrid structures belong to the most interesting classes of compounds, because they can be developed into organic–inorganic nanocomposites with unique properties, whereby the organic functionalization of an inorganic host can play an important role.13–16) Cage silsesquioxanes are a class of unique hybrid molecules with an inorganic silica core (SiO12), which is surrounded by eight organic corner groups.7–9) Due to their unique cage-like structure, the properties of cage silsesquioxanes have been widely studied for the last few decades, such as optical, electronic and optoelectronic properties, thermal stability and so on.20–22) Cage silsesquioxanes were used as precursors for the preparation of hybrid nanocomposites and as catalyst supports, as scaffolds for drug delivery.19,23–25) Among them, multicarboxy functionalized cages are of great significance because of their potential use in supramolecular chemistry and crystal engineering, which is currently being pursued.26,27) However, it should be mentioned that the preparation of multicarboxy cage as ligands for coordination with lanthanide ions was rarely investigated by far. Compared to those lanthanide-bridged cages with missing coordination with lanthanide ions was rarely investigated by far. Compared to those lanthanide-bridged cages with missing coordination,25–30) the multicarboxy functionalized cages and their corresponding hybrid materials in this report can be prepared easily and efficiently under mild conditions; in addition, intact cages make these hybrid lanthanides complexes more thermally stable. Based on our early study of hybrid lanthanide complexes derived from diketone functionalized cage silsesquioxane,3) herein, we described the design and synthesis of two multicarboxy (8, 16) functionalized cages through the photochemical thiol-ene reaction of octavinylsilsesquioxane with 3-mercaptopropionic acid and mercaptosuccinic acid, respectively. Then two novel hybrid luminescent materials were prepared in which two multicarboxy cages acted as ligands and Tb3+ as the joints. And Tb3+ was selected in this paper for its outstanding luminescent spectrum with comparatively good cost effectiveness. The obtained hybrid materials were investigated by TGA, XRD, SAXS, SEM, TEM and DLS.

2. Experimental

2.1 Materials

The 3-mercaptopropionic acid and mercaptosuccinic acid were purchased from Aladdin Chemistry Co. Ltd. and the solvents were purchased from commercial supplier and used without further purification. The catalyst of 2,2-Dimethoxy-2-phenylacetophenone (DMPA) was purchased from Aldrich and used as received. Terbium nitrates were obtained from their corresponding oxides in strong nitric acid. Octavinylsilsesquioxane (OVS) was prepared according to the literature procedures.21,32)

2.2 Measurements

The reaction was irradiated by high intensity ultraviolet (365 nm) on a Spectroline Model SB-100/FA lamp.1H NMR, 13C NMR and 29Si NMR spectra were recorded in CD3OD on Bruker Avance-300 spectrometer without internal reference.

* Corresponding author: H. Liu; E-mail: liuhongzhi@sdu.edu.cn
† Preface for this article: DOI http://dx.doi.org/10.2109/jcersj2.123.P9-1
Fourier transform infrared (FT-IR) spectra were measured within the 4000–400 cm⁻¹ region on a Brucker TENSOR-27 infrared spectrophotometer (KBr pellet). High-resolution mass spectra were obtained using positive mode on Agilent Technologies 6510 Q-TOF mass spectrometer. Elemental analysis was measured on a Vario EL III elemental analyzer. Photo luminescence (PL) (excitation and emission) spectra of these solid complexes were determined with a Hitachi F-4500 spectrophotometer. Ultraviolet absorption (UV) spectra of these samples were recorded using a UV-vis TU-1901 spectrometer. Thermal gravimetric analysis (TGA) was performed on a Mettler-Toledo TGA/DSC1 with heating rate of 10°C/min from 35 to 800°C under N₂ (100 mL/min) at ambient pressure. Powder X-ray Diffraction patterns were recorded on a Rigaku D/Max 2200PC diffractometer equipped with Cu Kα Radiation at 40 kV/20 mA (λ = 1.542 Å). The scanning rate was 10°/min from 2θ = 2θ = 6–80°. Small-angle X-ray scattering experiments were performed on a Anton Par Saxes mc2 with Cu Kα Radiation at 40 kV/50 mA (λ = 1.542 Å) at room temperature. Field emission scanning electron microscopy (FE-SEM) tests were performed with a Hitachi S-4800 high resolution SEM. The transmission electron microscopy (TEM) experiments were performed with a JEM-1011 electron microscopy. Dynamic light scattering (DLS) measurements were performed on a multiangle laser photometer equipped with a linearly polarized gallium arsenide (GaAs) laser (λ = 658 nm; Wyatt Technology Co. DAWN HELEOS), which were conducted at a scattering angle of 90°.

2.3 Preparation of octacarboxy substituted cage silsesquioxane (OCS) and hexadecycarbonyl substituted silsesquioxane (HCS)

OCS and HCS were prepared by the photochemical thiol-ene click reaction. In a typical procedure, to a 30 x 50 mm weighing bottle was added 0.52 g (0.8 mmol) OVS, 0.81 g (7.6 mmol) 3-mercaptopyrroline, 0.027 g (2 wt %) DMPA and 10 mL THF. After the solids were dissolved, the mixtures were irradiated by ultraviolet lamp for 30 min. Then the solvent was removed via vacuum rotation evaporation. The crude product was dissolved in methanol and dropped in n-hexane to remove excess DMPA and thiols. The resulting OCS and HCS were white solids and they were soluble in most common solvents.

The FT-IR spectra showed that –C=C– (1604 cm⁻¹) disappeared in the spectra of OCS and HCS after the reaction [Fig. S1(a)]. Subsequently, the characteristic absorption band of the carboxyl groups appeared at 1710 cm⁻¹, and a strong band was associated with the asymmetric stretching of a siloxane framework near 1116 cm⁻¹. In the ¹H NMR spectra [Fig. S1(b)], it was observed that the characteristic signal of vinyl group of OVS at around 6.0 ppm disappeared in OCS or HCS, indicating that the thiol-ene reaction was complete. Meanwhile, for example in ¹H NMR spectrum of OCS, it can be obviously observed that the characteristic signals of Si(–CH₂–) and –CH₂–CH₂– emerged at around 1.00 and 2.67 ppm, respectively. In the ¹³C NMR spectrum of OCS, it was observed that the signals of two carbons of vinyl group at 128.7 and 137.0 ppm disappeared and new signals at 12.41, 25.59, 26.48, 34.38 and 174.48 ppm appeared, corresponding to the carbon atoms in OCS, further confirming that the success of the thiol-ene reaction (Fig. S3). These results strongly suggested that the reaction was complete. In addition, only one peak (–68.5 and –68.6 ppm, respectively) was observed in the ⁴⁰Si NMR spectrum of OCS or HCS, indicating that the cage kept intact during the reaction (Figs. S4 and S8). In addition, the results of elemental analysis suggested that the desired compounds were formed. More importantly, the molecular ion peaks of OCS [1480.01] and HCS [1839.96] unambiguously appeared in MS-ESI spectra (Figs. S5 and S9), corresponding to [M+H⁺]⁺ and [M+2NH₄]⁺, which further indicated that OCS and HCS were successfully synthesized via the thiol-ene reaction.

To demonstrate that the OCS (and HCS) had coordinated with the Tb³⁺, FT-IR was performed at room temperature. Figure 1(a) showed the FT-IR spectra of multicarboxy cages and their complexes with Tb³⁺ in the region of 4000–400 cm⁻¹. As shown in the profiles, the band at 1720 cm⁻¹ referred to C=O stretching frequency in carboxyl groups and the intensity of C=O bond in their corresponding complexes decreased significantly, with new bands appeared at 1564 and 1445 cm⁻¹, suggesting that OCS and HCS had successfully coordinated with Tb³⁺. The new bands referred to antisymmetric and symmetric stretching vibrations of carboxylate, which were induced by coordination with Tb³⁺ [33,34]. The bands at 1483 and 1003 cm⁻¹ referred to N=O bond and N–O bond, respectively, indicating that NO⁻ participated in the coordination as well.

The band of OC–OH in OCS significantly shifted to a high wavenumber at 1310 cm⁻¹ in OCS–Tb by 29 cm⁻¹, implying that the Tb³⁺ not only coordinated with C=O but also with OC–OH. And the intensity of OC–OH bond in HCS was higher than OCS (0.20 g, 0.14 mmol), terbium nitrate (0.16 g, 0.36 mmol) and 10 mL THF. The mixtures stirred at 80°C for 24 h to obtain a white precipitation. The precipitation was separated by centrifugation and washed by THF, then dried in vacuum for 24 h to obtain a white powder (denoted as OCS–Tb). Similarly, the complex based on HCS (denoted as HCS–Tb) was also prepared by using HCS (0.20 g, 0.11 mmol) and terbium nitrate (0.26 g, 0.56 mmol). Those precipitations were stable and insoluble in most common solvents, i.e. H₂O, methanol, ethanol, CHCl₃.

3. Results and discussion

As shown in Scheme 1, OCS and HCS were synthesized through the thiol-ene click reaction of OVS with corresponding thiols in THF under UV radiation for 30 min. Considering DMPA and thiols could dissolve in hexane, the crude product was dissolved in methanol and dropped in n-hexane to remove excess DMPA and thiols. The resulting OCS and HCS were white solids and they were soluble in most common solvents.

As shown in Scheme 1(a), OCS and HCS were synthesized through the thiol-ene click reaction of OVS with corresponding thiols in THF under UV radiation for 30 min. Considering DMPA and thiols could dissolve in hexane, the crude product was dissolved in methanol and dropped in n-hexane to remove excess DMPA and thiols. The resulting OCS and HCS were white solids and they were soluble in most common solvents.

As shown in Scheme 1(a), OCS and HCS were synthesized through the thiol-ene click reaction of OVS with corresponding thiols in THF under UV radiation for 30 min. Considering DMPA and thiols could dissolve in hexane, the crude product was dissolved in methanol and dropped in n-hexane to remove excess DMPA and thiols. The resulting OCS and HCS were white solids and they were soluble in most common solvents.
for more carboxyl groups. In the 4000–2000 cm⁻¹ region in HCS, it could be clearly observed that O–H stretching vibration appeared at 2546 cm⁻¹, indicating a strong intramolecular hydrogen bond formed between the gemini carboxyl groups;36)–38) however, the band could not be observed in OCS, which should be ascribed to the different spatial framework from HCS. The spectrum of HCS–Tb showed that the intensity of O–H stretching vibration at 2546 cm⁻¹ weakened remarkably, suggesting that the incorporation of Tb³⁺ destroyed the intramolecular hydrogen bond between the gemini carboxyl groups. Hence, HCS might coordinate with Tb³⁺ in two possible modes as shown in Fig. 1(b).

3.1 Morphology structures of the hybrid luminescent complexes

In many cases, the coordination bond between the central metal and peripheral ligand was a major driving force for their self-assembly behaviors in solid phases.39) In this study, the coordination bond between the center Tb³⁺ and the carboxyl groups was the driving force of the self-assembly of these hybrid complexes. The morphology structures of these complexes based on cages was investigated using PXRD, SAXS, TEM, and DLS. Figure 2 represented the PXRD patterns of OVS, OCS, HCS, OCS–Tb and HCS–Tb. It was observed that OVS was highly crystalline and some sharp peaks were also appeared in the patterns of OCS and HCS.40) However, PXRD results showed that the hybrid complexes were amorphous and exhibited no long-range order. All the samples exhibited broad diffraction peaks at 23°, which was typically observed in amorphous silica nanocomposites and associated with Si–O–Si linkage. It could be concluded that, the coordination of carboxyl groups with Tb³⁺ occurred and destroyed the hydrogen bond networks and led to amorphous morphology.41)

SAXS was also performed to investigate the self-assembly behaviors of the hybrid complexes. Figure 3 showed that there exist strong characteristic peaks in OVS, OCS and HCS, while no obvious peaks could be seen in the hybrid complexes, implying the amorphous structure were dominant. The OCS and HCS possessed apparent maximums at around q = 3.5 and 6.0 nm⁻¹,
which vanished in the hybrid complexes, demonstrating that the cage ligands were well-distributed without large-scale aggregation. The SAXS results were consistent with XRD analysis, further confirming that coordination occurred between the cage ligands and Tb³⁺.

To further investigate the self-assembly behaviors of the hybrid complexes, TEM and DLS were also performed. As shown in Figs. 4(A) and 4(B), it was interesting to observe that OCS-Tb was composed of some bigger size particles with diameter from about 100 to 500 nm; while HCS-Tb was composed of some smaller particles with diameter from about 60 to 100 nm in the TEM images.

The DLS results in Figs. 4(a) and 4(b) showed that the statistical hydrodynamic diameters of OCS-Tb and HCS-Tb are about 207.3 and 77.8 nm, respectively, which agreed with the TEM results.

3.2 The plausible formation mechanism of the hybrid complex particles

It was interesting to explore the formation mechanism of the particles derived from different cage ligands, i.e. OCS and HCS. There existed two coordination modes between multicarboxy cages and Tb³⁺, i.e. intermolecular and intramolecular coordination and Tb³⁺ acted as cross-linkers to combine the ligand (OCS or HCS) together. In OCS-Tb system, intermolecular coordination was dominant; consequently, more OCS monomers coordinated with Tb³⁺ and were connected together to form one large fundamental unit. However, in HCS-Tb system, intramolecular coordination is greatly enhanced for the existing gemini carboxyl groups in HCS. As a result, less HCS was connected and the fundamental unit, smaller than that of OCS-Tb, was formed. These two kind of fundamental units aggregated and gradually grew into the final morphology.

Based on the foregoing analysis, we proposed a possible mechanism (Fig. 5) for the formation process of the hybrid complex particles. It consisted of coordination, formation of fundamental units, aggregation and growth into particles. At the initiation, the cages and Tb³⁺ coordinated to form one large fundamental unit. However, in HCS-Tb system, intramolecular coordination is greatly enhanced for the existing gemini carboxyl groups in HCS. As a result, less HCS was connected and the fundamental unit, smaller than that of OCS-Tb, was formed. These two kind of fundamental units aggregated and gradually grew into the final morphology.

3.3 Optical and thermal properties

The luminescence behaviors of the hybrid complexes in solid
state were studied at room temperature. Figure 6 illustrated the typical photoluminescence spectra of OCS–Tb and HCS–Tb, respectively. It was observed that the characteristic narrow–width green emissions of Tb3+ located at 491, 546, 586, 623 and 652 nm, respectively. These bands belonged to the transitions between the different levels of Tb3+ and were attributed to the 5D4→7F6, 5D4→7F5, 5D4→7F4, 5D4→7F3 and 5D4→7F2 transitions of Tb3+,

43,45 which indicated that the effective intramolecular energy transfer between the cage ligands and the chelated Tb3+ had taken place. Among these transitions, the 5D4→7F2 transition exhibited the strongest emission, suggesting that the chemical environment around Tb3+ was in low symmetry.46 The symmetry of Tb3+ coordination was disordered by the existence of NO3− and H2O, which was in accordance with the results in FT-IR spectra. The low symmetry around Tb3+ might increase the energy transfer probability, thus resulted in the enhancement of the fluorescence intensity of the hybrid complexes.47 Considering the possible complexation modes, HCS–Tb can be excited at comparative low energy (λex = 287 nm), we infer that intramolecular coordination probably favors the luminescence of the complexes.

The ultraviolet absorption spectra of the hybrid complexes dispersed in methanol (Fig. S10) and in solid state (Fig. S11) were measured at room temperature, respectively. In Fig. S10, the absorption spectra of OCS, HCS, OCS–Tb and HCS–Tb revealed the maximum absorption at 265 nm and shoulder peaks appeared at around 265, 275 and 285 nm, which are assigned to the π→π* electronic transition of carbonyl group.47

TGA was used to evaluate the thermal stability of the hybrid complexes based on cage silsesquioxanes in N2 and air, respectively. (Fig. 7, S12). Initial thermal decomposition temperature (Td) was defined as the temperature at which the mass loss of 5 wt% occurred.48 The hybrid complexes exhibited similar thermal degradation behaviors, i.e., two main degradation steps could be clearly observed in the TGA curves. The first weight loss before 200°C (180°C for HCS–Tb) could be attributed to the loss of physically absorbed and chemically conjugated water. The second weight loss could be ascribed to the decomposition of the organic groups, the coordinated Tb(NO3)3, and the degradation of the main framework of cages. In addition, the residual mass increased with the incorporation of Tb3+. Meanwhile, the decomposition rates were clearly slower than those of cage ligands, suggesting that the hybrid complexes possessed good oxidative stability and flame resistance.

4. Conclusion

In conclusion, two multicarboxy (8, 16) functionalized cage silsesquioxanes were successfully prepared via the photochemical thiol–ene reaction. These two multicarboxy cages were used as ligands to coordinate with terbium (III) ion to obtain novel hybrid luminescent materials, which exhibited fine luminescent properties and good thermal stabilities.

The method in this paper represented an ideal approach to prepare multicarboxy molecules based on cages and this study extended cage silsesquioxanes applications in the field of luminescent materials. Considering the convenience of the route to multicarboxy cage silsesquioxanes, numerous multifunctional dendritic ligands based on cage silsesquioxanes and their hybrid complexes can be prepared in the future.

Acknowledgments: This research was supported by the National Natural Science Foundation of China (21274081).

References

41) P. Nagpure and S. Omanwar, J. Rare Earths, 30, 856–859 (2012).