Preparation, characterization and luminescence properties of core–shell ternary terbium composites SiO$_2$$(600)@Tb$(MABA-Si)$·L

Yang-Yang Ma$^1$, Wen-Xian Li$^1$, Yu-Shan Zheng$^2$, Jin-Rong Bao$^1$, Yi-Lian Li$^1$, Li-Na Feng$^1$, Kui-Suo Yang$^1$, Yan Qiao$^1$ and An-Ping Wu$^1$

$^1$College of Chemistry and Chemical Engineering, Inner Mongolia University, Hohhot 010021, People's Republic of China
$^2$Inner Mongolia Autonomous Region food inspection test center, Hohhot 010021, People's Republic of China

Two novel core–shell structure ternary terbium composites SiO$_2$(600)@Tb$(MABA-Si)$·L$(L$:dipy/phen) nanometre luminescence materials were prepared by ternary terbium complexes Tb$(MABA-Si)$·L$_2$·$(ClO_4)_3$·$2H_2O$ shell grafted onto the surface of SiO$_2$ microspheres. And corresponding ternary terbium complexes were synthesized using $(CONH(CH_2)_3Si(OCH_2CH_3)_3)_{2}$ (denoted as MABA-Si) as first ligand and L as second ligand coordinated with terbium perchlorate. The as-synthesized products were characterized by means of IR spectra, $^1$HNMR, element analysis, molar conductivity, SEM and TEM. It was found that the first ligand MABA-Si of terbium ternary complex hydrolysed to generate the Si–OH and the Si–OH condensate with the Si–OH on the surface of SiO$_2$ microspheres; then ligand MABA-Si grafted onto the surface of SiO$_2$ microspheres. The diameter of SiO$_2$ core of SiO$_2(600)@Tb$(MABA-Si)$·L$ was approximately 600 nm. Interestingly, the luminescence properties demonstrate that the two core–shell structure ternary terbium composites SiO$_2$(600)Tb$(MABA-Si)$·L(dipy/phen) exhibit strong emission intensities, which are 2.49 and 3.35 times higher than that of the corresponding complexes Tb$(MABA-Si)$·L$_2$$(ClO_4)_3$·$2H_2O$, respectively. Luminescence decay curves show that core–shell
structure ternary terbium composites have longer lifetime. Excellent luminescence properties enable the core–shell materials to have potential applications in medicine, industry, luminescent fibres and various biomaterials fields.

1. Introduction

There has been extensive arousing of interest in core–shell structure nanomaterials because of the interesting properties that can be employed in optical, electrical, magnetic and biological applications [1–7]. It can be found that a nanometre material was covered with another nanometre material by chemical bond or another affinity. The functionality of their properties is a critical factor that promotes the development of nanocomposites materials [8–11]. In particular, luminescence applications of rare earth core–shell nanomaterials are very attractive because of their superior luminescence intensity. Nowadays, they are used or are being tested for use in such fields as medicine, industry, luminescent fibres and various biomaterials [12–17]. Now, such rare earth core–shell nanomaterials have attracted considerable attention due to possessing high photostability and thermal stability that they have potential applications in luminescent areas [18–20]. Rare earth core–shell nanometre composite was a research subject that would be a good choice for improving the luminescence intensity and lifetime.

In the rare earth core–shell nanomaterials field, SiO₂ as the core was popular in recent years. SiO₂ microspheres are regarded as ideal core materials with several advantages [21]. First, SiO₂ possesses strong physical stability, which can fix the organic functional groups. Furthermore, SiO₂ can be obtained at room temperature because of convenient reaction conditions. SiO₂ is considered an ideal low-cost material that has previously been used for various core microsphere. SiO₂ core–shell nanomaterials can be obtained by covalent bonds. Good results have been obtained with functionalized siloxanes, because they form strong covalent bonds with most SiO₂ surfaces due to the presence of hydroxyl groups. The large number of commercially available trialkoxysilanes with various functional groups offers unique possibilities for the task-specific surface modification of SiO₂ microsphere. For example, MABA-Si can act as a ‘bridge molecule’ that connects with rare earth and SiO₂ to enhance physical stability and decrease the energy loss. In this way, core–shell structure materials connected by covalent bond are stable so that the covalent bond is difficult to break. As a result, these kinds of core-shell structure nanometre composites have high luminescence intensity. Therefore, these materials have become an active field of research due to their physical and chemical properties, as well as their potential application. So far, silica has been investigated in the field of DNA, fluorescent probes and sensing [22,23].

In our work, the synthesis and structure as well as luminescence properties of the SiO₂(600)@Tb(MABA-Si)·L composites that have SiO₂ as the core and ternary terbium complex as the shell was studied. Functionalized organosilane (denoted as MABA-Si) not only graft onto the SiO₂ surface by covalently bonding but also coordinates with rare earth ions (Tb³⁺). To improve the luminescent performance of rare earth ions (Tb³⁺), another kind of small-molecule ligand with a conjugate system (phenanthroline (phen) or dipyridine (dipy)) was introduced, not only meeting the rare earth ions (Tb³⁺) coordination number but also having more efficient energy absorption and energy transfer. Terbium core–shell composites possess high luminescence intensity and long lifetime. The study of core–shell structure terbium luminescent nanomaterial is more meaningful to dispose of the potential application.

2. Material and methods

2.1. Chemicals

The starting materials for the preparation of SiO₂ were tetraethoxysilane (TEOS), ammonium hydroxide, water and anhydrous ethanol. Tb₄O₇ (99.999%) was dissolved in perchloric acid to prepare Tb(ClO₄)₃·nH₂O. 3-(triethoxysilyl)-propyl isocyanate (TEPIC, 96%, Aldrich), pure phen, dipy, m-aminobenzoic acid were also used. All other chemical reagents were analytical grade.

2.2. Physical measurements

Elemental analysis was taken with a HANAU analyser. Infrared spectra (IR, ν = 4000–400 cm⁻¹) was obtained by a Nicolet NEXUS-670 FT-IR spectrophotometer, which was determined by the KBr pellet technique. Luminescence excitation and emission spectra were performed on FLS980 spectrophotometer.
at room temperature (slit width was 0.5 nm). Luminescence lifetime measurements were recorded by FLS980 Combined Steady State and Lifetime Spectrometer (slit width was 0.5 nm). Scanning electron microscope (SEM) images were recorded with a Hitachi S-4800. Transmission electron microscopy (TEM) and energy dispersive X-ray spectroscopy were performed on a FEI Tecnai F20 operated at 200 kV. Conductivity measurement was made by using $1 \times 10^{-3}$ mol l$^{-1}$ solution in dimethylformamide (DMF) on a DDS-11D conductivity metre at room temperature. The terbium content of the complex was measured by EDTA titration using xylenol-orange as an indicator.

### 2.3. Synthesis of the ternary terbium complexes

#### 2.3.1. Synthesis of silylated $m$-aminobenzoic acid (MABA-Si)

The synthesis scheme of MABA-Si is shown in [Figure 1](#). $m$-Aminobenzoic acid (2 mmol) dissolved in 40 ml chloroform, 4 mmol 3-(triethoxysilyl)-propyl isocyanate was added dropwise into above solution with stirring at 60°C for 12 h. The obtained white precipitate was isolated by centrifugation, washed with water and ethanol and dried in an oven overnight at 60°C [24,25]. Yield: 40%. The resultant sample was characterized by $^1$HNMR and elemental analysis. $^1$HNMR: $\delta$ 0.56 ppm (4H), $\delta$ 1.04–1.51 ppm (18H), $\delta$ 2.93 ppm (4H), $\delta$ 3.33–3.47 ppm (12H), $\delta$ 3.73 ppm (4H), $\delta$ 7.43–7.57 ppm (2H) and $\delta$ 12.4 ppm (1H). Anal. Calcd. of C$_{28}$H$_{49}$N$_3$O$_{10}$Si$_2$ ($M$ = 631 g mol$^{-1}$): C, 51.35%; H, 7.76%; N, 6.66%; found: C, 50.80%; H, 7.82%; N, 6.55%. m.p.: 46–48°C.

#### 2.3.2. Synthesis of ternary terbium complexes of Tb(MABA-Si)$\cdot$L$_2$$\cdot$(ClO$_4$)$_3$$\cdot$2H$_2$O

MABA-Si (1 mmol) and 2 mmol phen (or dipy) were dissolved in 10 ml anhydrous ethanol, and then 1 mmol Tb(ClO$_4$)$_3$$\cdot$nH$_2$O was added in the above solution with stirring at 60°C for 2 h, the Tb$^{3+}$: MABA-Si: L molar ratio of 1:1:2. The white precipitate was isolated by centrifugation and washed with anhydrous ethanol. The elemental analysis and molar conductivities of the products were measured (Table 1). Anal. Calcd. of Tb(MABA-Si)$\cdot$dipy$_2$$\cdot$(ClO$_4$)$_3$$\cdot$2H$_2$O ($M$ = 1509.26 g mol$^{-1}$): C, 38.33; H, 6.44; N, 4.79; Tb, 10.21; found: C, 37.40; H, 6.49; N, 4.57; Tb, 10.53; and Anal. Calcd. of Tb(MABA-Si)$\cdot$phen$_2$$\cdot$(ClO$_4$)$_3$$\cdot$H$_2$O ($M$ = 1557.7 g mol$^{-1}$): C, 40.02; H, 6.37; N, 4.28; Tb, 9.85; found: C, 39.90; H, 6.29; N, 4.43; Tb, 10.02. The corresponding molar conductivities were 148 S cm$^2$ mol$^{-1}$ and 160 S cm$^2$ mol$^{-1}$.

### 2.4. Preparations of core–shell structure ternary terbium composites SiO$_2$(600)@Tb(MABA-Si)$\cdot$L

#### 2.4.1. Synthesis of SiO$_2$ monodisperse

Spherical SiO$_2$(600) was prepared by outstanding Stober method [27]. A total of 50 ml anhydrous ethanol, 2.6 ml ammonium hydroxide, 5 ml tetraethyl orthosilicate and 15 ml water were mixed with stirring for 6 h at room temperature (Table 2). A white silica colloidal suspension was formed. The solid product was washed thoroughly with water and anhydrous ethanol [28].
Table 2. The volume of materials to prepare silica and reaction time.

| EtOH (ml) | H₂O (ml) | TEOS | NH₃H₂O (ml) | time (h) | size (nm) |
|-----------|----------|------|-------------|---------|-----------|
| 50        | 15       | 5.0  | 2.6         | 5       | 600       |

2.4.2. Synthesis of SiO₂(600)@MABA-Si

To make MABA-Si graft onto SiO₂ microspheres by the Si–O–Si bond, the SiO₂ microspheres were activated with ammonium hydroxide. SiO₂ (0.1 g) was dissolved in 10 ml water and 10 ml ethanol mixture solution. A certain amount of ammonium hydroxide was added into the above solution to adjust the pH to 9.2 with stirring for 12 h. The precipitate was washed with water and anhydrous ethanol three times. The obtained activated SiO₂ microspheres and 0.2 g ligand MABA-Si were redissolved in 20 ml ethanol solution. The mixture solution was dispersed for 10 min by ultrasonication, then 10 ml water was added drop by drop. The above mixture solution was stirred for 10 h. The obtained precipitate was separated by centrifugation, washed with water and ethanol and dried in an oven at 60°C. As a result, MABA-Si was grafted onto SiO₂ core by formation of Si–O–Si bond, SiO₂(600)@MABA-Si was obtained.

2.4.3. Synthesis SiO₂(600)@Tb(MABA-Si)·L

Core–shell structure ternary terbium composite SiO₂(600)@Tb(MABA-Si)·dipy was prepared as follows: 0.1 g SiO₂(600)@MABA-Si and 0.2 g dipy were dissolved in 10 ml anhydrous ethanol, then the 5 ml anhydrous ethanol solution of 0.1 g Tb(ClO₄)₃·nH₂O was added into the above mixture solution. The mixture solution was stirred at room temperature for 12 h, then the white precipitate was obtained. The obtained precipitate was separated by centrifugation, washed with distilled water and ethanol and dried in an oven at 60°C. The core–shell structure ternary terbium composite of SiO₂(600)@Tb(MABA-Si)·dipy was synthesized successfully. The synthesis procedure for SiO₂(600)@Tb(MABA-Si)·phen was similar to that of SiO₂(600)@Tb(MABA-Si)·dipy except dipy was replaced by phen.

3. Results and discussion

3.1. IR spectra

3.1.1. IR spectra of ternary terbium complexes

Figure 2a–c shows the IR spectra of MABA-Si, dipy and Tb(MABA-Si)·dipy₂·(ClO₄)₃·2H₂O. In the spectrum of MABA-Si, the characteristic peaks located at 1639 cm⁻¹ (νC=O) and 1558 cm⁻¹ (δNH) were attributed to stretching vibration and bending vibration of –CONH– (figure 2a). The characteristic absorption of amide group (–CONH–) suggested that MABA-Si has been successfully synthesized by the amidation reaction with MABA and 3-(triethoxysilyl)-propyl isocyanate. The characteristic peaks located at 1700 and 1417 cm⁻¹ belonged to stretching vibration and bending vibration of –COOH.

Figure 2b shows IR spectrum of dipy. The stretching vibration of C= N appeared at 1578 and 1455 cm⁻¹. Furthermore, in the IR spectrum of ternary terbium complex Tb(MABA-Si)·dipy₂·(ClO₄)₃·2H₂O (figure 2c), the stretching vibration and bending vibration of –CONH– (figure 2a) were attributed to the amidation reaction with MABA and 3-(triethoxysilyl)-propyl isocyanate. The characteristic peaks located at 1700 and 1417 cm⁻¹ belonged to stretching vibration and bending vibration of –COOH.

The IR spectra of MABA-Si, phen, Tb(MABA-Si)·phen₂·(ClO₄)₃·2H₂O are shown in figure 3a–c. Comparing the spectrum of Tb(MABA-Si)·phen₂·(ClO₄)₃·2H₂O with MABA-Si, the characteristic absorption peaks of carboxylic group appeared at 1689 cm⁻¹, indicating that the carbonyl group of MABA-Si was coordinated with Tb³⁺ ions by carboxylic group and amide groups [29–33]. The stretching vibration of C= N red-shifted low wavenumber, which appeared at 1557 and 1439 cm⁻¹ in the ternary terbium complex Tb(MABA-Si)·dipy₂·(ClO₄)₃·2H₂O. The stretching vibration of C= N had obvious red shift, which showed that Tb³⁺ ions coordinated with two nitrogen atoms of dipy [34].
to 1521 cm$^{-1}$, $\delta_{\text{C-H}}$ red-shifted to 717 cm$^{-1}$ and 847 cm$^{-1}$, respectively. It displayed that the Tb$^{3+}$ ions coordinated with double nitrogen atoms of phen [35].

In addition, the characteristic absorption peaks of perchlorate group can be found in the ternary terbium complex (figure 3c). The characteristic absorption peaks of perchlorate groups appeared around at 1148 cm$^{-1}$, 1119 cm$^{-1}$, 1085 cm$^{-1}$, 622 cm$^{-1}$, which indicated that perchlorate was involved in the coordination. One perchlorate group bonded with the Tb$^{3+}$ ion, which corresponded with the results of the molar conductivity. Based on the literature, the vibration of perchlorate group just appeared at 1090 and 623 cm$^{-1}$, which demonstrated that perchlorate group is responsible for Td symmetry, and perchlorate group did not coordinate with Tb$^{3+}$ ions. When perchlorate coordinated with Tb$^{3+}$ ions, the perchlorate appeared at approximately 1145 cm$^{-1}$, 1115 cm$^{-1}$, 1079 cm$^{-1}$, 925 cm$^{-1}$ and 627 cm$^{-1}$; it was assigned to the C$_{2v}$ symmetry [36,37]. It showed that three perchlorates of ternary terbium complexes were not completely Td symmetry. Some of them were C$_{2v}$ symmetry which indicated that perchlorate was involved in the coordination.

3.1.2. IR spectra of core–shell structure ternary terbium composites SiO$_2$(600)@Tb(MABA-Si)$\cdot$L

Figure 4a–d gives IR spectra of SiO$_2$, SiO$_2$(600)@MABA-Si, SiO$_2$(600)@Tb(MABA-Si)$\cdot$phen and SiO$_2$(600)@Tb(MABSi)$\cdot$dipy. In the spectrum of SiO$_2$, the characteristic absorption peaks of Si–O–Si located
Figure 4. IR spectra of SiO$_2$ (a), SiO$_2(600)$@MABA-Si (b), SiO$_2(600)$@Tb(MABA-Si)-phen (c) and SiO$_2(600)$@Tb(MABA-Si)-dipy (d).

at 1102 cm$^{-1}$, and Si–OH was identified at 955 cm$^{-1}$ (figure 4a). Thus, the Si–OH groups were predominantly adsorbed on the surfaces of SiO$_2$. Figure 4b shows the IR spectrum of SiO$_2(600)$@MABA-Si. The absorption peak located at 1695 cm$^{-1}$ was attributed to stretching vibration of –COOH. The characteristic peaks located at 1656 cm$^{-1}$ and 1560 cm$^{-1}$ belonged to stretching vibration of –CONH– group of SiO$_2(600)$@MABA-Si. The broad bands located at approximately 1100 cm$^{-1}$ and 801 cm$^{-1}$ were assigned to the asymmetric stretching vibration and symmetric stretching vibration of Si–O–Si band, respectively. Furthermore, the peak of Si–O–Si intensity is greatly enhanced, which should result from the MABA-Si grafting onto the SiO$_2$. It displays that the first ligand MABA-Si generates the Si–OH, and the Si–OH condensate with the Si–OH on the surface of SiO$_2$ microspheres. In the IR spectrum of SiO$_2(600)$@Tb(MABA-Si)-phen (figure 4c), the characteristic absorption peak of carboxylic group –COOH appeared at 1656 cm$^{-1}$. Furthermore, the –CONH– characteristic bands appeared at 1556 cm$^{-1}$, indicating that carbonyl group and amide group were coordinated with Tb$^{3+}$ ions. The peak that appeared at 1522 cm$^{-1}$ was ascribed to stretching vibration of nitrogen atoms of phen in SiO$_2(600)$@Tb(MABA-Si)–phen. It showed an obvious red shift compared with free phen (figure 3a), which proved that phen successfully coordinated with the Tb$^{3+}$ ions. The IR spectrum of MABA-Si in SiO$_2(600)$@Tb(MABA-Si)-dipy (figure 4d) is similar to that in SiO$_2(600)$@Tb(MABA-Si)-phen. The characteristic peaks of dipy that appeared at 1522 cm$^{-1}$ and 1453 cm$^{-1}$ showed that dipy successfully coordinated with the Tb$^{3+}$ ions. IR spectra showed that the ternary terbium complexes formed on the surface of SiO$_2$ microspheres. The core–shell ternary terbium composites SiO$_2(600)$@Tb(MABA-Si)-L were synthesized.

3.2. The TEM and SEM of core–shell structure ternary terbium composites

Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) were used to monitor the fabrication of the as-synthesized products. Figure 5 shows the SEM (a), TEM of the SiO$_2$ (b) and TEM of the SiO$_2(600)$@MABA-Si (c, d). From figure 5a and b, we can observe that the as-formed SiO$_2$ core has a smooth surface, and the diameter is approximately 600 nm. The typical TEM images of SiO$_2(600)$@MABA-Si are shown in figure 5c,d, which reveals that SiO$_2(600)$@MABA-Si has a core–shell structure and presents a uniform spherical morphology with thin layer. The images (figure 6a–d) of SiO$_2(600)$@Tb(MABA-Si)-phen and SiO$_2(600)$@Tb(MABA-Si)-dipy show that the surface of SiO$_2(600)$@Tb(MABA-Si)-L becomes much rougher and has an obvious layer, which might be caused by the ternary terbium complexes grafted onto the surface of SiO$_2$ core. Figure 6b indicates that the Tb(MABA-Si)-dipy and Tb(MABA-Si)-phen surface layer has a diameter of approximately 5 nm. EDX analysis of SiO$_2(600)$@Tb(MABA-Si)-L (figure 7) confirms the existence of Cl, Tb, N, O and Si, which gives experimental evidence for the existence of the core–shell structure ternary terbium composites. The formation mechanism of core–shell structure composite is inferred (figure 8). In this process, Si–O–Si chemical bond can be formed by hydrolysis-polycondensation method from ethoxy of MABA-Si and hydroxyl groups of the SiO$_2$ surface. Then the carboxyl oxygen atoms of MABA-Si groups can be
Figure 5. The SEM of SiO$_2$ (a), TEM of SiO$_2$ (b) and SiO$_2$(600)@MABA-Si (c,d).

coordinated with Tb$^{3+}$ ions. It is quite possible that the ternary terbium complex grafted onto the surface of the SiO$_2$ at the early stage of the reactions, due to the synthesized Si–O–Si band.

3.3. Luminescence properties

The luminescence properties of ternary terbium complexes and core–shell structure ternary terbium composites SiO$_2$(600)@Tb(MABA-Si)-L have been investigated. The excitation spectra of Tb(MABA-Si)-dipy$_2$·(ClO$_4$)$_3$·2H$_2$O and SiO$_2$(600)@Tb(MABA-Si)-dipy were measured by monitoring the emission of Tb$^{3+}$ at 543 nm. As shown in figure 9, a broad excitation band extending from 200 to 400 nm presented the main peak centred at 298 nm. The corresponding emission spectra of the products are shown in figure 10. The emission peaks of the core–shell structure ternary terbium composite SiO$_2$(600)@Tb(MABA-Si) dipy and corresponding complex were located at 489, 543, 583 and 621 nm, which correspond to the $^5$D$_4$→$^7$F$_j$ transitions of Tb$^{3+}$ ions. The strongest emission peak located at 543 nm was attributed to $^5$D$_4$→$^7$F$_5$ transitions of Tb$^{3+}$ ions. The strongest emission intensity of SiO$_2$(600)@Tb(MABA-Si)-dipy and Tb(MABA-Si)-dipy$_2$·(ClO$_4$)$_3$·2H$_2$O is 10 894 848 and 4 370 973 arb. units, respectively. It suggests that the very effective energy transfer from the ligand to Tb$^{3+}$ ion in the complexes and core–shell structure ternary terbium composites and corresponding ternary terbium complexes. Two kinds of materials exhibit excellent characteristic green luminescence. It is worth noting that the core–shell structure ternary terbium composite SiO$_2$(600)@Tb(MABA-Si)-dipy shows approximately 2.49 times stronger emission than the corresponding ternary terbium complex (table 3). Figure 11 presents typical excitation spectra of ternary terbium complex Tb(MABA-Si)-phen$_2$·(ClO$_4$)$_3$·2H$_2$O and core–shell structure ternary terbium composite SiO$_2$(600)@Tb(MABA-Si)-phen. The obtained products possessed broad excitation bands with maxima at 306 nm and were recorded by monitoring the emission of Tb$^{3+}$ ions at 543 nm. The emission spectra of SiO$_2$(600)@Tb(MABA-Si)-phen and corresponding complex are shown in figure 12. SiO$_2$(600)@Tb(MABA-Si)-phen and corresponding complex exhibited characteristic emission peaks of Tb$^{3+}$ $^5$D$_4$→$^7$F$_j$ (j = 6, 5, 4, 3) transition at 489 nm ($^5$D$_4$→$^7$F$_6$), 543 nm ($^5$D$_4$→$^7$F$_5$), 583 nm ($^5$D$_4$→$^7$F$_4$), 621 nm ($^5$D$_4$→$^7$F$_3$). The strongest emission peak located at 543 nm was attributed to $^5$D$_4$→$^7$F$_5$ transitions
Figure 6. The TEM images of core–shell structures SiO$_2$(600)@Tb(MABA-Si)·phen (a,b), SiO$_2$(600)@Tb(MABA-Si)·dipy (c,d).

Figure 7. The EDX spectrum of core–shell structure ternary terbium composites.

of Tb$^{3+}$ ions. The strongest emission intensity of Tb(MABA-Si)·dipy$_2$(ClO$_4$)$_3$·2H$_2$O is 12 029 100 arb. units. It is more remarkable that strongest emission intensity of core–shell structure ternary terbium composite SiO$_2$(600)Tb(MABA-Si)·phen is 40 339 128 arb. units, which is 3.35 times higher than that of the corresponding complex (table 3). The emission intensity of the obtained core–shell structure composites was increased, compared with the corresponding ternary complexes. We contribute this enhancement to the unique core–shell structure, in which the SiO$_2$ cores greatly enhance the physical stability of ternary
Figure 8. The formation mechanism of core–shell structures SiO$_2$(600)@Tb(MABA-Si)·L.

Figure 9. Excitation spectra of SiO$_2$(600)@Tb(MABA-Si)·dipy (a) and Tb(MABA-Si)·dipy$_2$·(ClO$_4$)$_3$·2H$_2$O (b).

Figure 10. Emission spectra of SiO$_2$(600)@Tb(MABA-Si)·dipy (a) and Tb(MABA-Si)·dipy$_2$·(ClO$_4$)$_3$·2H$_2$O (b).

terbium complexes and decrease the energy loss of ternary terbium complexes molecular vibration. The luminescence emission intensity was increased. SiO$_2$ core and organic ligands played a mutually synergistic part in the energy transfer process of the ligands to Tb$^{3+}$ ions.

To further discuss the luminescence properties of the resulting core–shell structure ternary terbium composites and corresponding complexes, the typical decay curves were measured. The resulting lifetime data of core–shell structure ternary terbium composites are given in table 4. The lifetime of the
Figure 11. Excitation spectra of SiO$_2$(600)@Tb(MABA-Si)-phen (a) and Tb(MABA-Si)-phen$_2$·(ClO$_4$)$_3$·2H$_2$O (b).

Figure 12. Emission spectra of SiO$_2$(600)@Tb(MABA-Si)-phen (a), Tb(MABA-Si)-phen$_2$·(ClO$_4$)$_3$·2H$_2$O (b).

Table 3. Emission spectra data of the complexes and core–shell structure composites.

| complexes                        | slit width (nm) | $\lambda_{EX}$ (nm) | $\lambda_{EM}$ (nm) | $I$ (arb. units) | energy transition | intensity changes |
|----------------------------------|-----------------|----------------------|----------------------|------------------|-------------------|------------------|
| Tb(MABA-Si)-phen$_2$·(ClO$_4$)$_3$·2H$_2$O | 0.5             | 298                  | 543                  | 12 029 100       | $^5$D$_4$$\rightarrow$$^7$F$_5$ | —                |
| SiO$_2$(600)@Tb(MABA-Si)-phen    | 0.5             | 298                  | 543                  | 40 339 128       | $^5$D$_4$$\rightarrow$$^7$F$_5$ | 3.35             |
| Tb(MABA-Si)-dipy$_2$·(ClO$_4$)$_3$·2H$_2$O | 0.5             | 306                  | 543                  | 4 370 973        | $^5$D$_4$$\rightarrow$$^7$F$_5$ | —                |
| SiO$_2$(600)@Tb(MABA-Si)-dipy    | 0.5             | 306                  | 543                  | 10 894 848       | $^5$D$_4$$\rightarrow$$^7$F$_5$ | 2.49             |

$\text{Tb}^{3+}$ ions can be expressed by

$$I(t) = I_0 + A_1\exp\left(\frac{-t}{\tau_1}\right) + A_2\exp\left(\frac{-t}{\tau_2}\right)$$

(3.1)

and

$$\langle \tau \rangle = \frac{(A_1\tau_1^2 + A_2\tau_2^2)}{(A_1\tau_1 + A_2\tau_2)}$$

(3.2)

where $I(t)$ is the luminescence intensity varying with time $t$, and $\tau_1$ and $\tau_2$ are lifetime. The lifetimes of ternary terbium complex Tb(MABA-Si)-phen$_2$·(ClO$_4$)$_3$·2H$_2$O and corresponding composite are 0.57714 and 1.08274 ms, respectively. The lifetimes of ternary terbium complex Tb(MABA-Si)-dipy$_2$·(ClO$_4$)$_3$·2H$_2$O and corresponding composite are 1.03614 and 1.26420 ms, respectively. It is found that the core–shell structure ternary terbium composites present longer luminescent lifetimes than
corresponding complex. It suggested that the rare earth complexes and core materials were connected by covalent bonds enhanced the luminescent stability.

4. Conclusion

In this paper, two novel core–shell structure ternary terbium composites luminescent materials SiO$_2$(600)@Tb(MABA-Si)-L were prepared by grafting the Tb(MABA-Si)-L$_2$-(ClO$_4$)$_2$-2H$_2$O complexes onto the surfaces of SiO$_2$ core. In the reaction system, MABA-Si of Tb(MABA-Si)-L$_2$-(ClO$_4$)$_2$-2H$_2$O and SiO$_2$ core formed Si–O–Si band by means of a molecule bridge that derived from the silylated hydrolysis and condensation. The luminescence properties indicate that core–shell structure ternary terbium composites SiO$_2$(600)@Tb(MABA-Si)-L have stronger emission intensity than the corresponding complexes. And the core–shell structure ternary terbium composites have longer lifetimes. The formation of core–shell structure can increase the luminescence properties and reduce the amount of rare earth. This study provided new guidance in the design and fabrication of innovative rare earth materials. The synthesized novel core–shell structure ternium ternary composites have new opportunities to develop the application of rare earth element terbium.

Table 4. The lifetime of ternary terbium complexes and corresponding core–shell composites.

| terbium complexes and core–shell composites | excited state | lifetime (ms) | $\chi^2$ |
|---------------------------------------------|---------------|--------------|---------|
| Tb(MABA-Si)-phen$_2$-(ClO$_4$)$_2$-2H$_2$O  | $^5$D$_4$      | 0.57714      | 0.9993  |
| SiO$_2$(600)@Tb(MABA-Si)-phen              | $^5$D$_4$      | 1.08274      | 0.9987  |
| Tb(MABA-Si)-dip$_2$-(ClO$_4$)$_2$-2H$_2$O  | $^5$D$_4$      | 1.03614      | 0.9989  |
| SiO$_2$(600)@Tb(MABA-Si)-dip              | $^5$D$_4$      | 1.26420      | 0.9972  |

Data accessibility. The datasets supporting this article are available at the Dryad Digital Repository (http://dx.doi.org/10.5061/dryad.ht529) [38].

Authors’ contributions. Y.-Y.M. carried out the molecular laboratory work, participated in data analysis, carried out sequence alignments, participated in the design of the study and drafted the manuscript; W.-X.L. and Y.-S.Z. carried out the statistical analyses; J.-R.B., Y.-L.L. and L.-N.F. collected field data; K.-S.Y, Y.Q. and A.-P.W. conceived of the study, designed the study and helped draft the manuscript. All the authors gave their final approval for publication.

Competing interests. We declare we have no competing interests.

Funding. This work is supported by the Major Projects of Natural Science Foundations of Inner Mongolia Science Foundation (2015ZD01) and the Natural Science Foundations of Inner Mongolia Science Foundation (2015MS00502).

Acknowledgements. All the people who contributed to the study are listed as co-authors.

References

1. Runowski M, Gryzb T, Zep A, Krzyzkowska P, Gorecka E, Giersig M, Li S. 2014 Eu$^{3+}$ and Tb$^{3+}$-doped LaPO$_4$, nanorods, modified with a luminescent organic compound, exhibiting tunable multicolour emission. RSC Adv. 4, 46305–46312. (doi:10.1039/c4ra0668c)
2. Runowski M, Gryzb T, Li S. 2012 Magnetic and luminescent hybrid nanomaterial based on Fe$_3$O$_4$ nanocrystals and GdPO$_4$Eu$^{3+}$-nanoneedles. J. Nanomater. Res. 14, 1188. (doi:10.1007/s11051-012-1188-7)
3. Dutta Choudhury S, Badurow R, Ray K, Lakowicz JR. 2014 Surface-plasmon induced polarized emission from Eu(III) – a class of luminescent lanthanide ions. Chem. Commun. 50, 9010. (doi:10.1039/c4cc03633f)
4. Yang Z, Kang S, Zhou R. 2014 Nanomedicine: de novo design of nanodrugs. Nanoscale 6, 663–677. (doi:10.1039/c4nr04535h)
5. Chan CF et al. 2014 Bifunctional up-converting lanthanide nanoparticles for selective in vitro imaging and inhibition of cyclin D as anti-cancer agents. J. Mater. Chem. B 2, 84–91. (doi:10.1039/c3tb2034k)
6. Liang Y, Li Y, Wang H, Zhou J, Wang J, Regier T, Dai H. 2011 Co$_3$O$_4$ nanocrystals on graphene as a synergistic catalyst for oxygen reduction reaction. Nat. Mater. 10, 780–786. (doi:10.1038/nmat3087)
7. Khan LU, Brito HF, Hosa J, Protia KR, Muraca D, Felinto MFCF, Teotonio EES, Malta OL. 2014 Red-green emitting and superparamagnetic nanomarkers containing Fe$_3$O$_4$ functionalized with calixarene and rare earth complexes. Inorg. Chem. 53, 12 902–12 910. (doi:10.1021/ic5018856)
8. Pleaca CT, Dumitrache F, Morjan I, Niculescu AM, Sandu I, Ilie A. 2016 Synthesis and characterization of polyaniline–Fe$_3$O$_4$ magnetic nanocomposite powder. Apl. Surf. Sci. 374, 213–221. (doi:10.1016/j.apsusc.2015.11.043)
9. Qiu P, Zhou N, Chen H, Zhang C, Guo G, Cui D. 2013 Recent advances in lanthanide-doped upconversion nanomaterials: synthesis, nanostructures and surface modification. Nanoscale 5, 11 552–11 525. (doi:10.1039/c3nr03642a)
10. Nagabhushana H, Sunitha DV, Sharma SC, Prashanth SC, Nagabhushana BM, Chakradhar RPS. 2014 CeS$_2$O$_4$:Eu$^{3+}$, red nanophosphors prepared by low temperature solution combustion technique, its structural and luminescent properties. J. Alloy. Compd. 616, 284–292. (doi:10.1016/j.jallcom.2014.05.228)
11. Ishi H, Kawa S, Nagao D, Konno M. 2015 Synthesis of phosphor-free luminescent, monodisperse, mesoporous silica nanoparticles in the co-presence of double- and single-chain cationic surfactants. Adv. Powder Technol. 27, 448–453. (doi:10.1016/j.apt.2016.01.010)
12. Li H, Kang J, Yang J, Wu B. 2016 Distance dependence of fluorescence enhancement in Au nanoparticle@mesoporous silica@europium complex. J. Phys. Chem. C 120, 16 907–16 912. (doi:10.1021/acs.jpcc.6b01312)
13. Wei W, Zhao Y, Peng S, Zhang H, Bian Y, Li H, Li H. 2014 Yolk-shell nanomaterials as a Ru-containing core and a radially oriented mesoporous silica shell: facile synthesis and application for one-pot biomass conversion by combining with enzyme. ACS Appl. Mater. Interfaces 6, 20 851–20 859. (doi:10.1021/am5052608)

14. Chowdhury S, Wu Z, Jaquinsgerstl A, Liu S, Dembska A, Armitage BA, Rongchao J, Linda AP. 2011 Wavelength dependence of the fluorescence quenching efficiency of nearby dyes by gold nanoclusters and nanoparticles: the roles of spectral overlap and particle size. J. Phys. Chem C 115, 20 105–20 112. (doi:10.1021/jp204836w)

15. Singh LP, Srivastava SK, Mishra R, Ningthoujam RS. 2014 Multifunctional hybrid nanomaterials from water dispersible CaF2:Eu3+ and Fe3O4 for luminescence and hyperthermia application. J. Phys. Chem. C 118, 18 087–18 096. (doi:10.1021/jp502825p)

16. Shi D, Sadat ME, Dunn AW, Mast DB. 2015 Optical heater-thermometer nanoplatform Liz-Marzán LM, Rocha J, Carlos LD. 2013 All-in-one multifunctional hybrid nanoparticles. Nanoscale 5, 4474–4487. (doi:10.1039/c4nr0533k)

17. Li MJ, Chen Z, Yam YW, Zuo Y. 2008 Multifunctional ruthenium(II) poly(pyridine complex-based core-shell magnetic silica nanocomposites: magnetism, luminescence, and electrochemistry. J. Lumin. 128, 1328–1335. (doi:10.1016/j.jlumin.2006.06.019)

18. Debasu ML, Ananias D, Pastoriza-Santos I, Liz-Marzán LM, Rocha J, Carlos LD. 2013 All-in-one optical heater-thermometer nanoplatfrom operative from 300 to 2000 K based on Er3+ emission and blackbody radiation. Adv. Mater. 25, 4868–4874. (doi:10.1002/adma.201300492)

19. Wei S, Wang Q, Zhu J, Sun L, Lin H, Guo Z. 2011 Multifunctional composite core-shell nanoparticles. Nanoscale 3, 4474–4502. (doi:10.1039/c1nm00748b)

20. Li WX, Zheng YS, Cao XF, Bai J, Fu ZF, Bao JR, Li YL. 2016 Preparation, characterization, and luminescence properties of dysprosium perchlorate with MBA-Si and phen or dipy complexes as well as SiO2@Oy(MABA-Si)L core-shell structure nanometerter luminescent composites. J. Lumin. 178, 470–478. (doi:10.1016/j.jlumin.2016.06.019)

21. Gosh Chaudhuri R, Paria S. 2012 Core/shell nanomaterials: classes, properties, synthesis mechanisms, characterization, and applications. Chem. Rev. 112, 2373–2433. (doi:10.1021/cr100449n)

22. Ansari AA, Hasan TN, Syed NA, Labin JP, Parchur AK, Shafi G, Ahsitaw AH. 2011 In-vitro cytotoxicity, genotoxicity, and bio-imaging evaluation of one-pot synthesized luminescent functionalized mesoporous SiO2@Eu(OH)3 core-shell microspheres. Nanomedicine 9, 1328–1335. (doi:10.1016/j.nano.2013.05.016)

23. Liu C, Yan B. 2015 Highly effective chemosensor of a luminescent silica/lanthanide complex@MOF heterostructured composite for metal ion sensing. Rsc Adv. 5, 101 982–101 988. (doi:10.1039/c5ra19973e)

24. Liu M, Gan L, Chen L, Xu Z, Zhu D, Hao Z, Chen L. 2012 Supramolecular core-shell nano silica@liposome nanocapsules for drug delivery. Langmuir 28, 10 725–10 732. (doi:10.1021/la3021645)

25. Wang QM, Yan B. 2004 Novel luminescent terbium molecular-based hybrids with modified m-amino benzoic acid covalently bonded with silica. J. Mater. Chem. 14, 2450–2454. (doi:10.1039/b402667e)

26. Li HR, Lin J, Zhang HJ, Fu LS, Meng QG, Wang SB. 2002 Preparation and luminescence properties of hybrid materials containing europium(III) complexes covalently bonded to a silica matrix. Chem. Mater. 14, 3651–3655. (doi:10.1021/cm020830)

27. Davies GL, Barry A, Gunko YK. 2009 Preparation and size optimisation of silica nanoparticles using statistical analyses. Chem. Phys. Lett. 468, 239–244. (doi:10.1016/j.cplett.2008.12.031)

28. Fielding LA, Tonnar J, Armes SP. 2011 All-acrylic film-forming colloidal polymer/silica nanocomposite particles prepared by aqueous emulsion polymerization. Langmuir 27, 11 129–11 144. (doi:10.1021/la202066n)

29. Geary GW. 1971 α-Haloalkyl and related reagents. Their preparation and synthetic utility. J. Coord. Chem. Rev. 7, 81–94. (doi:10.1016/0010-8545(00)80009-0)

30. Qin C, Wang XL, Wang AE, Su ZM. 2005 A series of three-dimensional lanthanide coordination polymers with lutidine and unprecedented lutidine-related topologies. Inorg. Chem. 44, 7122–7129. (doi:10.1021/ic050906b)

31. Petrov VA, Marshall WJ, Grushin VV. 2002 The first perfluoroacetylacetone metal complexes: as unexpectedly robust as tricky to make. Chem. Commun. 5, 520–521. (doi:10.1039/b112149j)

32. Cho J, Lough AJ, Ju CK. 2003 Monomeric and polymeric copper(II) hexaaza macrocyclic complexes with bta anions (bta = 1,2,4,5-tetramethylenetetra carboxylic acid). Inorg. Chem. Acta 332, 305–310. (doi:10.1016/j.ica.2002.10.009)

33. Crutchley RJ, Lever ABP. 1982 Comparative chemistry of bipyrazyl and bipyridyl metal complexes: spectroscopy, electrochemistry and photochemistry. Inorg. Chem. 21, 2267–2282. (doi:10.1016/0020-1693(83)80114-0)

34. Qian GD, Wang MQ, le SZ, Chin. 1998 Synthesis characterization and fluorescence of Eu3+, Tb3+ complexes with heterocyclic ligands containing nitrogen. Chinese J. Lumin 19, 60–65. (http://kns.cnki.net/KCMS/detail/detail)

35. Xu CJ, Chin J. 2006 Synthesis and photoluminescence properties of Eu(Gd) complexes with salicylic acid and α-phenanthroline. Rare Earth Soc. 24, 361. (http://kns.cnki.net/KCMS/detail/detail)

36. Rosenthal MR. 1973 Myth of the noncoordinating nitrogen. J. Chem. Educ. 50, 331–335. (doi:10.1021/ic0503331)

37. Hathaway BJ, Underhill AE. 1961 The infrared spectra of some transition-metal perchlorates. J. Chem. Soc. 65, 3091–3096. (doi:10.1039/p10000003091)

38. Ma Y-Y, Li W-X, Zheng Y-S, Bao J-R, Li Y-L, Feng L-N, Yang K-S, Qiao Y, Wu A-P. 2018 Data from: Preparation, characterization and luminescence properties of core-shell ternary terbium composites SiO2@Eu(Tb)(MABA-Si)L. Dryad Digital Repository. (http://kns.cnki.net/KCMS/detail/detail)