

Luminescence Properties of SiO₂@Eu(phen-Si) (sulphoxide) Core-Shell Nanometer Composite

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Abstract. A novel ternary europium complex Eu(Phen-Si)·(H₂L)₂·(ClO₄)₃·6H₂O was prepared using (phen)-N-(CONH(CH₂)₃Si(OCH₂CH₃)₃)₂ (Phen-Si) as the first ligand and 2-carboxyphenyl carboxymethyl sulphoxide (H₂L) as the second ligand. The corresponding different thickness core-shell structure SiO₂@Eu(phen-Si)·L nano composites were synthesized, with silica spheres as core, ternary europium complex (Eu(Phen-Si)·(H₂L)₂·(ClO₄)₃) as shell. The ternary europium complex has been characterized by element analysis, molar conductivity, and IR spectra. The SiO₂@Eu(phen-Si)·L core-shell structure composite was characterized by TEM and IR spectra. Core-shell structure composites exhibited stronger fluorescence properties than that of the ternary europium complex. The emission intensity of the two core-shell composites was 1.79, 3.99 times stronger than the ternary europium complex, respectively. The fluorescence lifetime of the core-shell structure composites were longer than the ternary europium complex.

1 Introduction

The core-shell nano composite is a nanoparticle of novel structure. It is an orderly assembly structure, which can be constituted of a nanomaterial coated with another nanomaterial by chemical bonds or physical adsorption. Therefore, it is a higher level nano composite structure. Because of its unique property, differing from any of its unary substance, many core-shell nano composites are intensely studied in the past decades [1-3].

Coating with other materials, the surface of nanoparticle changes the structure of the layer, size, or composition. It has the advantages that unary material does not have and open up a new approach for the new material design. Because of its easily controlling particle size, low cost, security, and low toxicity, SiO₂ is the most widely used core-shell structure nanoparticles. As a hotspot in the field of nanometer materials, the study of SiO₂ as core materials was reported more and more, with the rare earth inorganic materials used most as the coating layer [4-7]. Instead, research of rare earth organic complexes as cladding layer was reported few.

Silane coupling agent is a kind of bi-functional organic matter, generally formulated as Y(CH₂)_nSiX₃. Y represents the organic functional groups, such as amino, carboxyl and double nitrogen, etc. X represents the alkoxy. Y group can combine with rare earth ions. X

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group can form Si-O-Si chemical bonds with hydroxyl groups of the SiO₂ through hydrolysis. As a result, rare earth ions and SiO₂ are connected together by silane coupling agent, as a "molecular bridge". Yan Bing and Zhang HongJie teams did a lot work in this area [8-9].

In this article, the phenanthroline of amino silane functionalization phen-Si, was used as a silane coupling agent. A novel ternary europium organic complex Eu(Phen-Si)·(H₂L)₂·(ClO₄)₃·6H₂O has been synthesized for the first time, using Phen-Si as the first ligand, 2-carboxyphenyl carboxymethyl sulphoxide(H₂L) as the second ligand. The SiO₂@Eu(phen-Si)·L core-shell structure nano composites have been prepared, using silica spheres as the core, the ternary europium organic complex Eu(Phen-Si)·(H₂L)₂·(ClO₄)₃·6H₂O as the shell, denoted as SiO₂@Eu(phen-Si)·L. Analytical and characterization tests were applied to the prepared complex and nano-particle composite.

2 The experiment

2.1 Materials

All chemicals were analytical grade and were used as received without further purification. Eu₂O₃ (purity > 99.99%) were all supplied by Beijing Chemical Reagent Company. The Eu(III) perchlorate was prepared from dissolving in 2 mol·L⁻¹ HClO₄, and then evaporated and dried in vacuum. 2-carboxyphenyl carboxymethyl sulphoxide (H₂L), phen, Tetraethoxysilane (TEOS, Aldrich), 3-(triethoxysilyl)-propyl isocyanate (96%, TEPIC, Aldrich).

2.2 Physical measurements

Elemental analysis was carried out on a HANAU analyzer. Conductivity measurement was carried out on a DDS-11D conductivity meter. The europium content of the complex was determined by EDTA titration. The infrared spectra was determined on a Nicolet NEXUS-670 FT-IR spectrophotometer. Fluorescence properties were determined on a FLS920 fluorescence spectrometer. Microstructures were recorded by Scanning electronic microscope (Hitachi S-4800), and transmission electron microscope (FEI Tecnai F20).

2.3 Synthesis of the ligand phen-Si and the ternary rare earth complex

Phen-Si was synthesized according to the method of the literature [10-12]. Yield: 40%.Mp: 46~48°C. Anal. calcd. For C₃₂H₅₁N₅O₈Si₂(M=689g/mol): C, 56.23%; H, 7.31%; N, 10.21%, found: C, 55.73%; H, 7.43%; N, 10.16%. Then 1 mmol Phen-Si and 2 mmol H₂L were dissolved in ethanol. The solution of 1 mmol Eu(ClO₄)₃·nH₂O ethanol was added into the above mixed solution under stirring at 80°C for 0.5 h. Finally, white precipitate was obtained by washing for several times with ethanol and water. (yield>90%).

2.4 Synthesis of the SiO₂@Eu(phen-Si)·L core-shell structure nano composites

Mono-disperse spherical SiO₂ was synthesized by Stöber method. The average diameter of SiO₂ was 250nm. Phen-Si was dissolved in 5 ml ethanol, adding to the solution which was a mixture contained SiO₂, 5 ml alcohol and 5 ml water, and the pH was set to 9 by an appropriate amount of ammonia. Then the mixture was stirred 2h at room temperature.

Finally, the core-shell structure nano composites were successfully synthesized. 1 ml $\text{SiO}_2@(\text{phen-Si})$ was dispersed in 20 ml ethanol. The molar ratio of $\text{SiO}_2@(\text{phen-Si})$: sulfoxide: Eu^{3+} was 1:2:1. The H_2L and Eu(III) perchlorate were added into the silica solution sequentially. The mixture was stirred 0.5 h at 80°C . Then a white precipitate was obtained.

3 Results and discussions

3.1 The composition the complex

Analytical data for the complex, presented in Table 1. The result of molar conductivity value of the complex in DMF was accordingly formulated as 1:2 electrolytes [13]. EDTA titration result showed that the content of the europium ion was 9.22%. According to the elemental analysis and EDTA titration data, the composition of the ternary complex was suggested as $\text{Eu}(\text{Phen-Si})\cdot(\text{H}_2\text{L})_2\cdot(\text{ClO}_4)_3\cdot 6\text{H}_2\text{O}$.

Table 1. Composition (%) and Molar Conductivities ($\text{S}\cdot\text{cm}^2\cdot\text{mol}^{-1}$) of Rare earth Complex (25°C)

Complex	C	N	H	RE	λ_m
$\text{Eu}(\text{Phen-Si})\cdot(\text{H}_2\text{L})_2\cdot(\text{ClO}_4)_3\cdot 6\text{H}_2\text{O}$	35.29(35.22)	4.17(4.11)	3.73(3.93)	9.22(8.92)	148.5

3.2 SEM and TEM

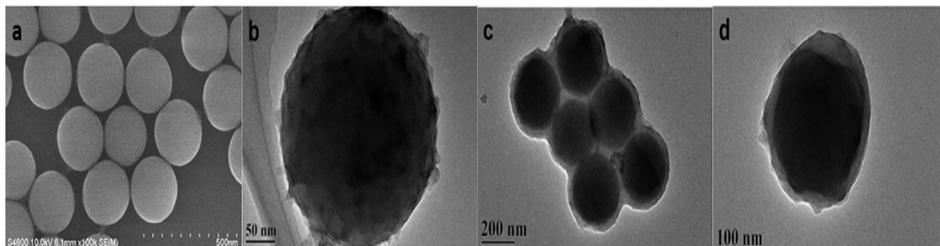


Fig 1. The SEM & TEM images of SiO_2 and $\text{SiO}_2@Eu(\text{phen-Si})\cdot\text{L}$, (a) $\text{SiO}_2(250\text{nm})$, (b) $\text{SiO}_2@Eu(\text{phen-Si})\cdot\text{L}(20)$, (c,d) $\text{SiO}_2@Eu(\text{phen-Si})\cdot\text{L}(30)$

According to the SEM (Fig.1a), it could be seen that the SiO_2 had regular micro-structure with an average size of 250nm, smooth surface and good dispersity. Fig.1b-d showed the morphologies of core-shell structure $\text{SiO}_2@Eu(\text{phen-Si})\cdot\text{L}$ with different thickness. It showed that the size of SiO_2 kernel was 250nm, the thickness of the coating layer was 20 and 30nm, which can be expressed as $\text{SiO}_2@Eu(\text{phen-Si})\cdot\text{L}(20)$, $\text{SiO}_2@Eu(\text{phen-Si})\cdot\text{L}(30)$. The ternary europium complex had been coated on SiO_2 cores, the $\text{SiO}_2@Eu(\text{phen-Si})\cdot\text{L}$ core-shell structure had been formed successfully.

3.4 Infrared spectra

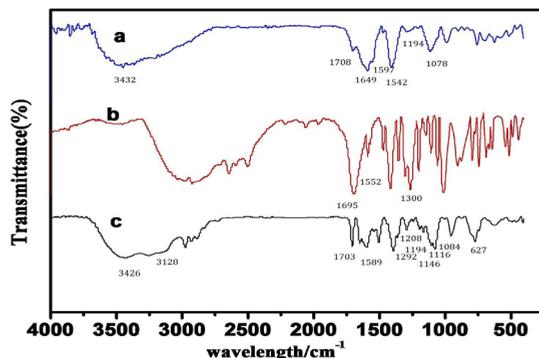


Fig 2. The IR spectra of (a) Phen-Si, (b) $(\text{COOH})\text{C}_6\text{H}_4\text{SOCH}_2\text{COOH}$, (c) $\text{Eu}(\text{H}_2\text{L})_2 \cdot (\text{phen-Si}) \cdot (\text{ClO}_4)_3 \cdot 6\text{H}_2\text{O}$

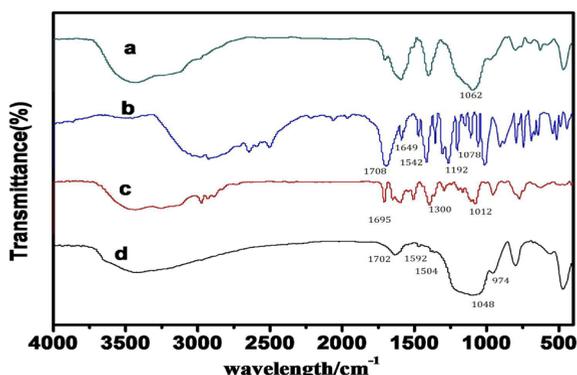


Fig 3. The IR spectra of (a) SiO_2 , (b) phen-Si (c) H_2L , (d) $\text{SiO}_2 @ \text{Eu}(\text{Phen-Si}) \cdot \text{L}_{(20)}$

The IR of the two ligands and the $\text{Eu}(\text{Phen-Si}) \cdot (\text{H}_2\text{L})_2 \cdot (\text{ClO}_4)_3 \cdot 6\text{H}_2\text{O}$ ternary complex could be seen in Fig.2a-c. In the phen-Si IR spectrum (Fig.2a), the $\nu\text{C}=\text{O}$ and $\nu\text{-CONH-}$ appeared at 1708cm^{-1} , 1694cm^{-1} and 1542cm^{-1} respectively. After coordinating with Eu^{3+} , they shifted to lower wave number which appeared at 1703cm^{-1} , 1589cm^{-1} and 1552cm^{-1} (Fig.2c). It suggested that europium ion was bonded with phen-Si through the double nitrogen atoms of phen. Similarly, in the sulfoxide IR spectrum (Fig.2b), the $\nu\text{S}=\text{O}$, $\nu\text{C}=\text{O}(\text{COOH})$ and $\nu\text{C-OH}(\text{COOH})$ shifted from 1012cm^{-1} , 1695cm^{-1} and 1300cm^{-1} to 989cm^{-1} , 1589cm^{-1} and 1292cm^{-1} respectively. Which suggested that rare earth ion bonded with H_2L through the COOH group [14]. When the perchlorate group wasn't coordinated, it was T_d symmetry. There were two absorptions bands of $1084\text{--}1092\text{cm}^{-1}$ and $621\text{--}629\text{cm}^{-1}$. When ClO_4^- was coordinated, it showed C_{2v} symmetry and there were five absorptions [15]. In the IR spectra of the complexes, five absorptions could be seen clearly at 1145 , 1116 , 1080 , 920 and 627cm^{-1} . Combined with the molar conductivity, it could be induced that the one perchlorate group in the complex was bonded with the $\text{Eu}(\text{III})$ ion by the oxygen atoms, and the coordination was bidentate.

Fig.3a-d was the IR of the SiO_2 , phen-Si, H_2L and the $\text{SiO}_2 @ \text{Eu}(\text{phen-Si}) \cdot \text{L}_{(20)}$. The $\nu\text{C}=\text{O}$, $\nu\text{-CONH-}$ shifted from 1708cm^{-1} , 1694cm^{-1} and 1542cm^{-1} to 1702cm^{-1} , 1592cm^{-1} and 1504cm^{-1} respectively. It indicated that europium ion was bonded with phen-Si through the double nitrogen atoms of phen.

Similarly, in Fig.3c-d, the $\nu\text{S=O}$ shifted from 1013 cm^{-1} to 974 cm^{-1} , which suggested that europium ion bonded with oxygen atom in sulfinyl group. These results suggest that the complex were formed in the shell layer of core-shell composite.

3.5 Luminescence properties

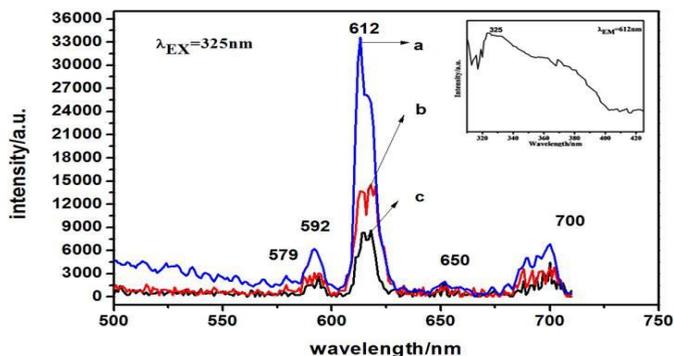


Fig 4. Fluorescent emission spectrum of (a) $\text{SiO}_2@\text{Eu}(\text{Phen-Si})\cdot\text{L}_{(30)}$, (b) $\text{SiO}_2@\text{Eu}(\text{phen-Si})\cdot\text{L}_{(20)}$, (c) $\text{Eu}(\text{phen-Si})\cdot(\text{H}_2\text{L})_2\cdot(\text{ClO}_4)_3\cdot 6\text{H}_2\text{O}$ Inset: Fluorescent excitation spectrum of $\text{Eu}(\text{phen-Si})\cdot(\text{H}_2\text{L})_2\cdot(\text{ClO}_4)_3\cdot 6\text{H}_2\text{O}$

The excitation and emission spectrum of the europium complex and the core-shell structure composites were measured in solid state at room temperature (Fig.4). The excitation spectrum of the products was obtained by monitoring their emissions at 612nm. The maximum peak was at 325nm (Fig.4 Inset). There were five emission peaks in the emission spectrum(Fig.4a-c), which were attributed to the characteristic ${}^5\text{D}_0-{}^7\text{F}_J$ ($J = 0, 1, 2, 3, 4$) transitions of $\text{Eu}(\text{III})$ at 579, 592, 612, 650 and 700nm, and the ${}^5\text{D}_0-{}^7\text{F}_2$ transition of $\text{Eu}(\text{III})$ was the strongest at 612nm. The emission intensity of the $\text{Eu}(\text{III})$ ion was 8220 a.u. in europium complex (Fig.4c). However, under the same condition, the emission intensity of $\text{SiO}_2@\text{Eu}(\text{Phen-Si})\cdot\text{L}_{(20)}$ and $\text{SiO}_2@\text{Eu}(\text{Phen-Si})\cdot\text{L}_{(30)}$ core-shell structure composites were 14341 and 32803 a.u. respectively. It was 1.79, 3.99 times greater of the ternary europium complex, respectively. The fluorescence of the core-shell composite was more enhanced than ternary europium complex. On the other hand, according to the Fig.4, the thickness of the coating layer could affect the emission intensity of composites. It meant that when the size of SiO_2 core was fixed, with the increase of the emission intensity was increased with the increase of the thickness of the coating layer.

3.6 The fluorescence decay curve

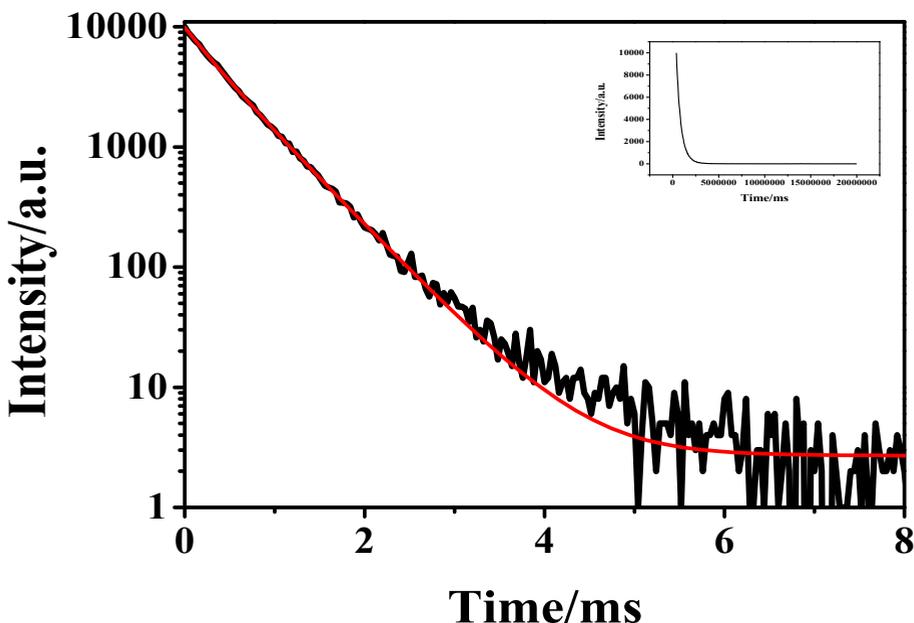


Fig 5. Fit Curves of $\text{Eu}(\text{phen-Si})\cdot(\text{H}_2\text{L})_2\cdot(\text{ClO}_4)_3\cdot 6\text{H}_2\text{O}$ Insert: Decay Curves of $\text{Eu}(\text{phen-Si})\cdot(\text{H}_2\text{L})_2\cdot(\text{ClO}_4)_3\cdot 6\text{H}_2\text{O}$

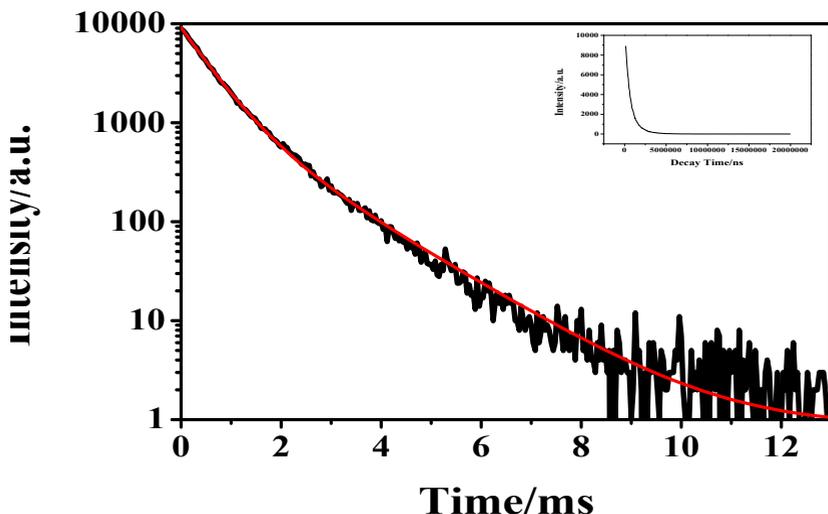


Fig 6. Fit Curves of $\text{SiO}_2@\text{Eu}(\text{Phen-Si})\text{L}_{(30)}$ Insert: Decay Curves of $\text{SiO}_2@\text{Eu}(\text{Phen-Si})\text{L}_{(30)}$

The fluorescence decay curve and double exponential fit curve of the europium ternary complex and $\text{SiO}_2@\text{Eu}(\text{Phen-Si})\text{L}_{(30)}$ core-shell composites was shown in the Fig.5,6. The fluorescence lifetime value of the europium ternary complex and $\text{SiO}_2@\text{Eu}(\text{Phen-Si})\text{L}_{(30)}$ core-shell composites were calculated by the double exponential mode. The lifetime of the Eu(III) ion could be obtained from the Eq. (1),

$$I_{(t)} = I_0 + A_1 \exp\left(-\frac{t_1}{\tau_1}\right) + A_2 \exp\left(-\frac{t_2}{\tau_2}\right) \quad (1)$$

$$\langle \tau \rangle = (A_1\tau_1^2 + A_2\tau_2^2) / (A_1\tau_1 + A_2\tau_2) \quad (2)$$

Where I_t was the fluorescence intensity varying with time t , and τ_1 and τ_2 were lifetime. The corresponding data were calculated. As the result, the lifetime of the europium ternary complex was 527.70 μs , but the lifetime of $\text{SiO}_2@\text{Eu}(\text{Phen-Si})\text{L}_{(30)}$ core-shell composites was 680.00 μs . The results were consistent with corresponding variation tendency of emission intensity.

4 The Conclusion

The novel complex of ternary europium complex $\text{Eu}(\text{Phen-Si})\cdot(\text{H}_2\text{L})_2\cdot(\text{ClO}_4)_3\cdot 6\text{H}_2\text{O}$, two core-shell structure composites $\text{SiO}_2@\text{Eu}(\text{phen-Si})\cdot\text{L}_{(20)}$ and $\text{SiO}_2@\text{Eu}(\text{phen-Si})\cdot\text{L}_{(30)}$ were prepared. Core-shell structure composites exhibited superior fluorescence properties than that of the ternary europium complex. The emission intensity of the two core-shell composites was 1.79, 3.99 times than the ternary europium complex, respectively. The fluorescence lifetime of the core-shell structure composites was longer than the ternary europium complex. Because rare earth organic complexes were used as coating layer, thickness is nanometer order of magnitude, so the dosage of rare earth organic complexes can be decreased. As a result, the cost of materials will be greatly reduced. The complex and the core-shell structure composite had excellent luminescent properties.

The $\text{SiO}_2@\text{Eu}(\text{phen-Si})\cdot\text{L}$ core-shell structure nano composites had application potential as red luminescent materials and derived application. So this prepared approach provides an applicable new choice for future novel luminescent materials.

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References

1. H.J. Feng, Y. Che, F.Q. Tang, J. Ren. *Mater. Lett.* **60**, 737–740 (2006).
2. S.C. Ho, D.W. Lee. *J. Colloid Interface Sci.* **355**, 70-75 (2011).
3. S.X Li, D.M Tang, Z.F Tian, X.J Liu. *J. Mater. Chem. C*, **5**, 1042–1051 (2017).
4. B.E. William, P.M. Cinta. *Opti. Mater.* **34**, 355-359 (2011).
5. G.X. Liu, G.Y. Hong. *J. Solid State Chem.* **178**, 1647-1651 (2005).
6. V. Yu, T.I. Yermolayeva. *Radiat. Meas.* **46**, 551-554 (2011).
7. D. Sofia, M. Moritz. *Langmuir.* **27**, 14025–140 (2011) 32.
8. Z.Y Yan, B. Yan. *Inorg Chem. Commun.* **47**, 96-98 (2014).
9. B. Yan, C. Wang. *Inorg Chem. Commun.* **14**, 1494-1497 (2011).
10. E. Koft, F.H. Case. *J. Org Chem.* **27**, 865-866 (1962).
11. E. Meggers, D. Kusch, B. Giese. *Helv. Chim. Acta.* **80**, 640 (1997).
12. G.M. Kloster, S.P. Watton. *Inorg Chim. Acta.* **297**, 156 (2000).
13. W. Geary. *Coordin. Chem. Rev.* **7**, 81-121 (1971).
14. A.Balam, M.L.P. Reddy, M. Jayakanna. *J. Phys. Chem. B.* **113**, 14128 (2009).
15. M.R. Rosenthal. *J. Chem. Educ.* **50**, 331-335 (1973).