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Preparation of luminescent sol–gel films from europium and terbium 3-(3′-triethoxysilylpropyl)pentane-2,4-dione complexes

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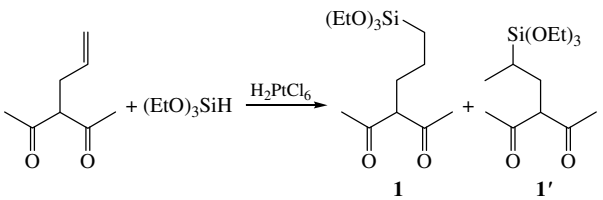
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Transparent luminescent sol–gel films have been prepared from the complexes of Eu^{III} and Tb^{III} with the new ligand 3-(3′-triethoxysilylpropyl)pentane-2,4-dione synthesised by the reaction of 3-allylpentane-2,4-dione with triethoxysilane in the presence of Speier catalyst.

The sol–gel technique allows the preparation of hybrid organo-inorganic materials for practical applications such as heterogeneous catalysis,[1,2] photonics,[3,4] medicine, and rare metal separation technologies.[6]

The well-known sol–gel technique is based on the carbofunctional trialkoxysilanes $(RO)_3Si(CH_2)_n$-Z.[7] The latter can be prepared by the silylation of functional organic compounds containing C=C bonds by trialkoxysilanes $(RO)_3SiH$, or by the replacement of Cl atoms by alkoxy groups in $Cl_3Si(CH_2)_n$-Z.

β-Diketones are used as analytical reagents in photometry. Stable volatile transition and rare earth metal complexes have been prepared from silicon-containing derivatives for the use in chemical vapour deposition (CVD) processes.[8,9] Here, the preparation of europium and terbium complexes with a new functional ligand containing a β-diketone fragment and a triethoxysilyl group is reported. Such compounds open up the possibility of forming novel sol–gel materials (hybrid films, fibres and porous glasses) for many practical applications.



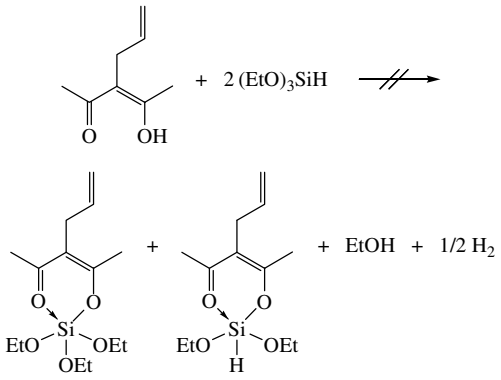
Scheme 1

3-(3′-Triethoxysilylpropyl)pentane-2,4-dione **1** was synthesised by the silylation of 3-allylpentane-2,4-dione by triethoxysilane in the presence of Speier catalyst (Scheme 1).† Note that the replacement of an ethoxy group and a hydrogen atom in triethoxysilane by a hydroxy group of the ketone in the enol form, is possible in principle (Scheme 2).

However, we found that, without the addition of H_2PtCl_6, 3-allylpentane-2,4-dione did not interact with triethoxysilane even at 80–100 °C. No reaction was also observed in the case of tetraethoxysilane or hexamethyldisilazane.

Pentane-2,4-dione silylated at the allyl group exists mainly in the ketone form. The very low intensity of the C–OH band in the region 3500–3400 cm^{-1} shows that the proportion of the

† *3-(3′-Triethoxysilylpropyl)pentane-2,4-dione* **1**. To 49.3 g (0.30 mol) of $(EtO)_3SiH$, 15.0 g (0.107 mol) of 3-allylpentane-2,4-dione and 10 drops of a 0.02 M $H_2PtCl_6 \cdot 6H_2O$ solution in THF were added. After slight heating an intense reaction took place accompanied by a darkening of the reaction mixture. Further heating at 150 °C for 10 h followed by distillation afforded 14.3 g of transparent yellow liquid boiling at 80–98 °C (3 Torr). Redistillation gave 8.7 g (27%) of **1**, bp 89–92 °C (3 Torr), n_D^{20} 1.4364. IR (ν/cm^{-1}): 3420 (w, CO–H), 2975 (vs, C–H), 2940 (vs, C–H), 2895 (vs, C–H), 1730 (sh), 1700 (vs, C=O), 1670 (w, C=O), 1625 (w, C=C), 1480 (w), 1445 (m), 1385 (s), 1355 (s), 1300 (m), 1250 (m), 1165 (vs, SiOEt), 1100 (vs, SiOEt), 960 (vs, SiOEt), 795 (vs, SiOEt), 680 (vw), 630 (vw), 475 (m), 450 (m). ^{1}H NMR (200 MHz, $CDCl_3$) δ: 0.55–0.66 (m, 2H, CH_2Si), 0.77, 0.80, 0.84, 0.88 (q, 1H, CHSi), 1.13, 1.14, 1.16, 1.20, 1.18, 1.21 (s, 9H, *Me*CH_2O), 1.32–1.46 (m, 2H, CH_2), 1.77, 1.81, 1.85, 1.89 (q, 2H, CH_2), 2.06, 2.09, 2.12 [t, 3H, MeC(O)], 2.23, 2.28, 2.32 (t, 3H, MeCOO), 3.54, 3.58, 3.61, 3.65 [q, 1H, C*H*$(COMe)_2$], 3.70, 3.74, 3.77, 3.79, 3.81, 3.82 (s, 6H, MeCH_2O). ^{29}Si NMR (200 MHz, $CDCl_3$) δ: 41.2, 45.5, 45.7, 46.1. UV (film on quartz, λ/nm): 227, 290. Found (%): C, 54,93; H, 9.30; Si, 10.06. Calc. for $C_{14}H_{28}O_5Si$ (%): C, 55.23; H, 9.27; Si, 9.23.



Scheme 2

enol form is very small. Silylation causes the complete disappearance of the band at 3080 cm^{-1} (ν_{C-H} in H–C=C) and the appearance of very intense bands of the triethoxysilyl group at 1165, 1110, 960 and 795 cm^{-1}. 3-Allylpentane-2,4-dione shows four bands in the region 1800–1500 cm^{-1}; two bands at 1745 and 1700 cm^{-1} can be related to the C=O bond vibration and the other two (1645, 1615 cm^{-1}) correspond to the C=C bond vibrations in the allyl and enol groups. The introduction of the triethoxysilyl fragment greatly simplifies the spectrum in the region 1800–1500 cm^{-1} because of the very low concentration of the enol form and the *Z*- and *E*-isomers. Compound **1** contains a very strong band at 1700 cm^{-1} and two very weak bands at 1670 and 1625 cm^{-1}. The first absorbance corresponds to the vibration of the ketone form C=O bond and the other two characterise the enol components [1670 (C=O) and 1625 cm^{-1} (C=C)].

In the UV spectrum, two bands at 227 and 290 nm are present (intensity ratio of 1.6:1) corresponding to the $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions, respectively.

The ^{1}H NMR spectrum of **1** shows two intense multiplets (at 1.10–1.30 and 3.70–3.90 ppm) for the Si ethoxy groups. Resonances for the methyl protons (2.10–2.40 ppm) in the MeC(O)– and MeC(=C)O– fragments and three multiplets (0.60–0.70, 1.35–1.50 and 1.80–1.93 ppm) corresponding to methylene substituents in the triethoxysilylpropyl group $(EtO)_3SiCH_2CH_2CH_2$ are also observed. Two signals of much lower intensity at 0.3–0.4 and 3.65 ppm are assigned to the hydrogen atom of the allyl group silylated at the β-position MeC*H*[Si(OEt)$_3$]CH$_2$ and to the hydrogen atom of the β-diketone fragment MeC(O)C*H*C(O)Me. The splitting of the signal can be explained by the presence of isomers **1**,**1′** and traces of the enol form in the *Z* and *E* positions. The ^{29}Si NMR spectrum showed four close signals of different intensities in the region –45 to –47 ppm, which confirm the presence of four isomers (out of six possible) of **1**, as confirmed by GL chromatography.

Lanthanoid alkoxides are the most convenient reagents for β-diketonate lanthanoid complex preparation since they allow the performance of the reaction in water-free media. The reaction products contain no water but only alcohol, which can be easily removed from the reaction mixture.

The reaction of europium(III) or terbium(III) isopropylate gives rise to tris(β-diketonate)s **2**, **3**, which are coloured viscous liquids easily hydrolysed with moist air.‡

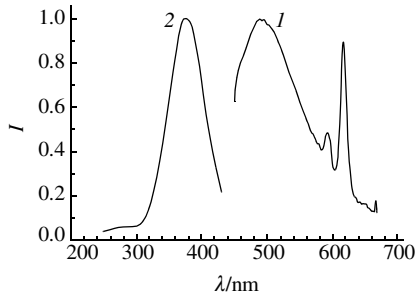


Figure 1 Fluorescence (*1*, λ_{exc} = 398 nm) and fluorescence excitation (*2*, λ_{rec} = 460 nm) spectra of a film prepared from **2** (14 wt% Eu).

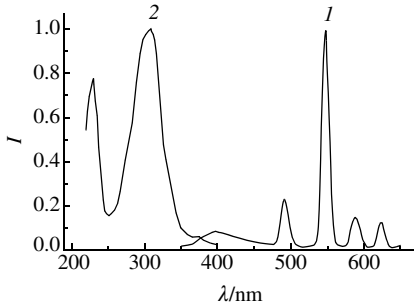
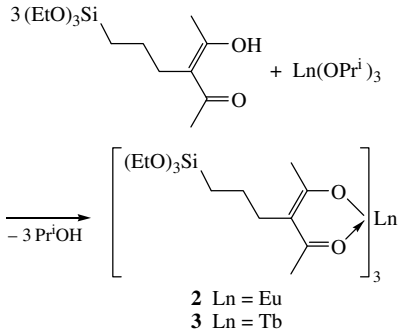


Figure 2 Fluorescence (*1*, λ_{exc} = 305 nm) and fluorescence excitation (*2*, λ_{rec} = 547 nm) spectra of a film prepared from **3** (70 wt%) and APTES (30 wt%) (10 wt% Tb).

The formation of the lanthanoid complex causes significant changes in the IR spectrum in the β-dicarbonyl fragment vibration region. The ν(C=O) absorption band of the starting diketone (1700 cm^{-1}) is shifted to the lower frequency region (1590–1570 cm^{-1}). The position and intensities of the triethoxysilyl group bands in the silylated β-diketoketone ligand remain almost unchanged on formation of complexes **2** and **3** confirming that the inner coordination sphere of the lanthanoid cation does not include *n*-donor EtO substituents. The absorption in the region corresponding to the hydroxyl group vibration (3420 cm^{-1}) is of very low intensity.



Scheme 3

The incorporation of triethoxysilyl groups into compounds **1**–**3** gives the possibility of forming transparent films and gels.§ Silylated β-diketone **1** can be hydrolysed with air moisture giving viscous oligomers after 24 h. Further heating up to 100 °C causes the evaporation of more than half of the product with the formation of a solid film. In order to improve the optical and mechanical quality of the films, the addition of 3-aminopropyltriethoxysilane (APTES, 20–30 wt%) is used affording solid films,

‡ *Tris[3-(3′-triethoxysilylpropyl)pentane-2,4-dionate]europium* **2**. To the solution of 1.0 g (3.04×10^{-3} mol) of europium isopropylate in 10 ml of diethyl ether, 3.1 g (1.02×10^{-2} mol) of **1** in 5 ml of diethyl ether were added. The tube was sealed and heated at 60–70 °C for 3 h. The solvent was removed *in vacuo*. The viscous orange residue was dissolved in 7 ml of hexane, and 15 ml of acetonitrile were added. The precipitate was washed with acetonitrile and dried *in vacuo* affording 2.2 g (67%) of **2** (fine orange powder). IR (ν/cm^{-1}): 1714, 1674, 1588 (O=C–C=C–O–Eu), 1345, 1285, 1254 (CH), 1168, 1107, 1082, 966, 789 (SiOEt), 885, 678, 546, 480, 455, 410. Found (%): C, 46.31; H, 7.37; Eu, 14.96; Si, 7.75. Calc. for $C_{42}H_{81}EuO_{15}Si_3$ (%): C, 47.48; H, 7.68; Eu 14.86; Si, 7.88.

Tris[3-(3′-triethoxysilylpropyl)pentane-2,4-dionate]terbium **3**. To a solution of 1.35 g (0.004 mol) of terbium isopropylate in 10 ml of diethyl ether 3.65 g (0.012 mol) of **1** in 5 ml of diethyl ether were added. After 7 h, the mixture was centrifuged and the solvent and isopropyl alcohol were removed from the supernatant transparent yellow solution. The resulting residue was taken up in 5 ml of toluene and then 10 ml of acetonitrile were added giving a precipitate, which was separated, washed with toluene and then dried for 1 h at 50–60 °C *in vacuo*. 3.22 g (0.03 mol, 75%) of light yellow powder **3** were obtained. IR (ν/cm^{-1}): 1714, 1664, 1573 (O=C–C=C–O–Tb), 1345, 1300, 1259 (CH), 1168, 1102, 1082, 961, 799 (SiOEt), 895, 673, 481. Found (%): C, 46.90; H, 7.56; Si, 8.01; Tb, 15.05. Calc. for $C_{42}H_{81}O_{15}Si_3Tb$ (%): C, 47.18; H, 7.63; Si, 7.88; Tb, 14.86.

which remain transparent after heating up to 150 °C demonstrating the high hydrolytic stability of **1**. Complexes **2** and **3** rapidly form solid films in air. For example, the europium derivative cast from ether solution gives a transparent yellow film in 20–30 min. However, to form films from the terbium complex, it is necessary to add 50 wt% APTES.

The fluorescence excitation spectrum of a film produced from **1** and APTES shows an intense band at 379 nm (λ_{rec} = 460 nm). The emission spectrum consists of a wide band at 440 nm (λ_{exc} = = 370 nm) typical of organosilsesquioxane matrices containing N–H bonds.[10] The fluorescence and fluorescence excitaton spectra of a film of europium complex **2** on quartz are shown in Figure 1. The fluorescence excitation spectrum shows a single band at 377 nm (the recording wavelength is 460 nm). The change of λ_{rec} to 617 nm results in two bands at 259 and 333 nm. The fluorescence spectrum with excitation at 398 nm showed three narrow lines at 593, 618 and 667 nm corresponding to the $^5D_0 \rightarrow {}^7F_1$, $^5D_0 \rightarrow {}^7F_2$ and $^5D_0 \rightarrow {}^7F_3$ transitions of the europium cation and a wide intense band for the matrix emisson at 491 nm. Reduction of the excitation wavelength to 370 nm significantly decreases the intensity of the Eu^{3+} luminescence and shifts the maximum of the emission band to 468 nm.

The fluorescence and fluorescence excitation spectra of a film formed from terbium complex **3** on addition of APTES are presented in Figure 2. The fluorescence excitation spectrum (recording wavelength of 547 nm) consists of two bands in the UV region at 230 and 308 nm. Excitation at 305 nm gives an emission spectrum with four narrow peaks at 491, 547, 585 and 623 nm corresponding to the $^5D_4 \rightarrow {}^7F_6$, $^5D_4 \rightarrow {}^7F_5$, $^5D_4 \rightarrow {}^7F_4$ and $^5D_4 \rightarrow {}^7F_3$ *f*–*f* transitions of Tb^{3+} and a weak matrix emission at 393 nm. The $^5D_4 \rightarrow {}^7F_5$ transition has the greatest intensity. Reduction of the exciting frequency (λ_{ex} = 370 nm) changes the spectrum dramatically. A strong decrease in the cation luminescence takes place and the matrix emission at 416 nm becomes predominant.

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§ *Film preparation.* (*a*) Complex **2** was dissolved in diethyl ether (ratio of 1:3). The solution was put on a quartz surface with a capillary tube. In 20 min, a transparent hard yellow film 28 μm in thickness was obtained. (*b*) To a solution of 0.128 g of **3** in 0.3 ml of diethyl ether, 0.067 g of APTES were added. The resulting liquid was put on a quartz surface with a capillary tube. After 3 h, a light yellow transparent hard film 37 μm in thickness was obtained.