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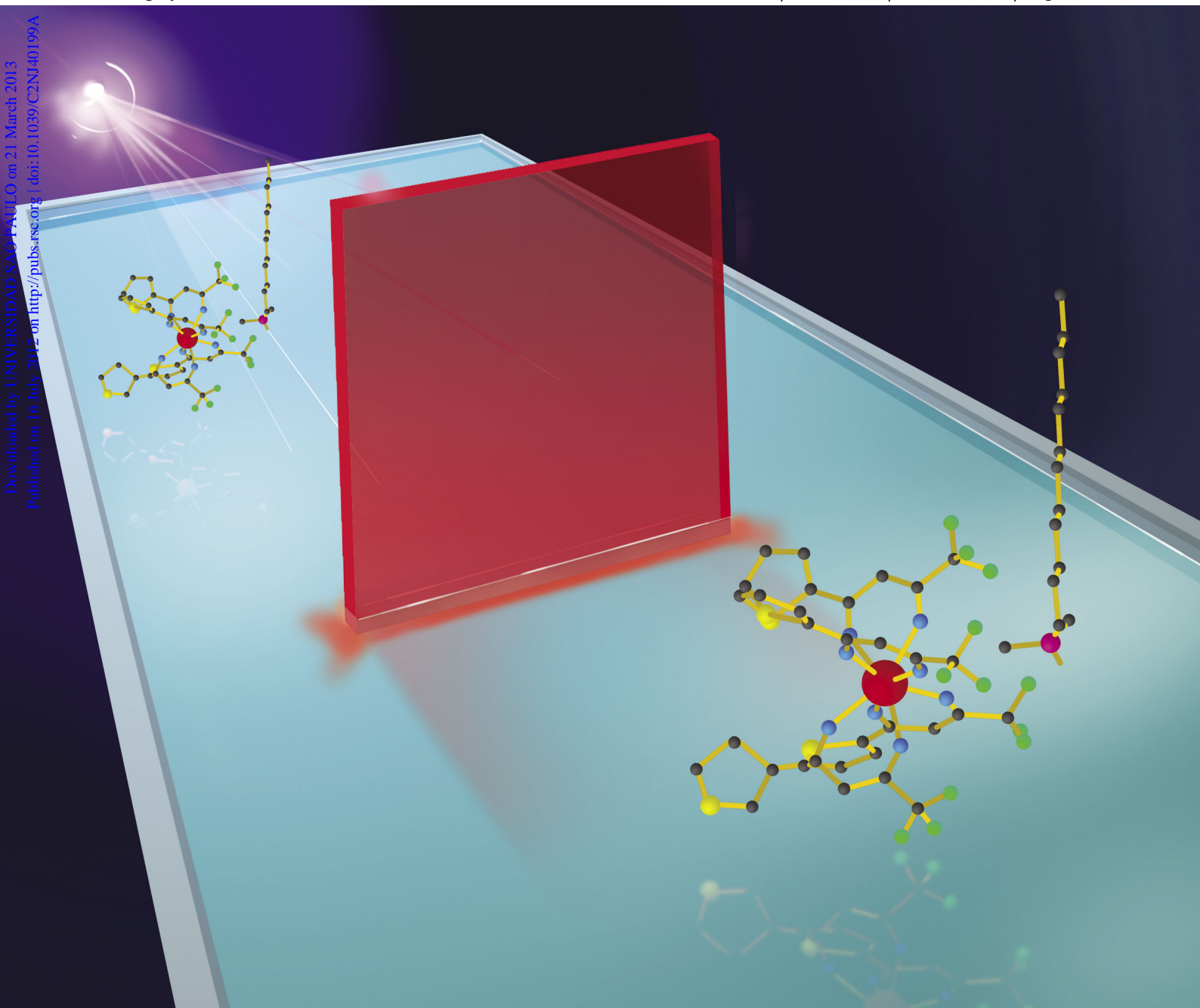
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PAPER

Synthesis of a functionalized europium complex and deposition of luminescent Langmuir–Blodgett (LB) films

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The synthesis, characterization and formation of Langmuir–Blodgett (LB) films for the luminescent $[(C_{12}H_{25})_2(CH_3)_2N][Eu(tta)_4]$ complex, where $[(C_{12}H_{25})_2(CH_3)_2N]^+$ is didodecyltrimethylammonium and the tta ligand is thenoyltrifluoroacetone, are reported. The coordination of tta ligands to the Eu^{3+} ion was confirmed by FTIR spectroscopy and the emission spectrum comprised bands corresponding to ${}^5D_0 \rightarrow {}^7F_{0-4}$ transitions. The lifetime (τ) from the emission state (5D_0) was 0.41 ms, measured by monitoring the hypersensitive ${}^5D_0 \rightarrow {}^7F_2$ transition, with the curve being fitted with a first-order exponential function. The surface pressure–area isotherm indicated that the anionic complex may form condensed structures at the air–water interface due to the amphiphilic properties of the counter ion and the β -diketone ligand. Y-type LB films of $[(C_{12}H_{25})_2(CH_3)_2N][Eu(tta)_4]$ were deposited on quartz substrates, with preserved luminescence and a band assigned to the ${}^5D_0 \rightarrow {}^7F_2$ transition. The molecular arrangement at the air/water interface and the preserved luminescence in LB films are consistent with theoretical predictions using a semi-empirical Sparkle/AM1 calculation method for the molecule in vacuum. These tools were used for the first time to predict the behavior of organized films.

Introduction

The luminescence of rare earth β -diketone complexes has special features, including sharp lines owing to the intra-configurational f–f transitions and lifetimes as long as several milliseconds.^{1–3} These complexes are known to yield bright emission under UV irradiation because of the effective energy transfer from the ligands to the central ions, by the so-called “antenna effect”. The latter depends on the triplet energy of the β -diketone ligand being in resonance with the emitting state of the europium ion. In order to exploit these emission properties in luminescent devices, it is necessary to assemble the rare earth complexes in solid films, where the main challenge is the preservation of the luminescence since quenching may occur owing to a close molecular packing. Therefore, the control of molecular architecture in the films is highly desired, particularly for optimizing the luminescence efficiency.

One of the methods suitable for achieving this molecular control is the Langmuir–Blodgett (LB) technique. LB films are

used to address challenges inherent to organic devices, mainly to light emitting diodes (OLEDs and PLEDs),⁴ since the film properties can be tuned at the molecular level. Major developments have been made with rare earth compounds that are highly luminescent but do not have good film-forming properties. Europium complexes have been used to produce LB films whose photoluminescence properties differed from those in solution or of non-ordered, solid films.^{5,6} Furthermore, it has been possible to correlate the film-forming characteristics and the photoluminescence properties of europium complexes.^{7–9} The transfer of LB films is facilitated when amphiphilic molecules are mixed with europium(III) complexes in Langmuir films, and two families of compounds are commonly used for this purpose. In the first, the Lewis base adducts of tris(β -diketonate) are used in mixed films containing long-chain amphiphilic molecules. In these cases, other absorbing ligands such as phen (phenanthroline), tppo (triphenylphosphine oxide) or bipy (bipyridine) acted as substituents to enhance luminescence.^{10,11} The other family includes an anionic complex with a general formula of $Q[Eu(tta)_4]$, referred to as tetrakis complexes of rare earth beta-diketonates, used with amphiphilic quaternary ammonium ions or *N*-alkylpyridinium (Q^+) as counter ions.^{12–14} For instance, a tetrakis complex with a 4:1 ligand-to-metal ratio, where a single positively charged counter ion ensured the electrical neutrality of the complex, was used to obtain LB films. Two amphiphilic europium–dibenzoylmethane

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complexes containing hexadecyltrimethyl ammonium and octadecyltriethyl ammonium were studied by Zhou *et al.*, both of which could form stable luminescent Langmuir films.¹⁵ Stability could also be obtained by saturation of the aqueous phase with the complex $[\text{Eu}(\text{tta})_4]^-$ ions, and by making mixed monolayers with octadecylamine.^{16,17}

In the functionalization of highly luminescent complexes, selecting an appropriate ligand and counter ion is necessary to study the molecular arrangement. Huang *et al.* found that the europium(III) complex anions not only optimize the formation of multilayers but also enhance the optical efficiency of organic molecules.¹⁴ Qian *et al.* studied stable monolayers and multilayers of $[(\text{C}_{18}\text{H}_{37})_2(\text{CH}_3)_2\text{N}][\text{Eu}(\beta\text{-diketonate})_4]$, where the double aliphatic chain was efficient because of stronger intermolecular interactions through London forces, thus leading to a structured film on the air/water interface.¹⁷ The use of counter ions containing double aliphatic chains, such as cationic quaternary ammonium surfactants, is not mentioned in the literature, in spite of being among the most widely used commercially in the field of bactericides, as DNA carrier systems for gene transfection and as vehicles for drug delivery.^{18,19} The importance of these surfactants arises from the possible mimicking of cell membranes, as is the case for the synthetic double-chained cationic surfactant didodecyltrimethylammonium bromide $[(\text{C}_{12}\text{H}_{25})_2(\text{CH}_3)_2\text{N}]^+$ (DODAB). DODAB tends to aggregate spontaneously in aqueous solutions with formation of bilayer structures.²⁰

In this study, we have a two-fold purpose for the synthesis of the $[(\text{C}_{12}\text{H}_{25})_2(\text{CH}_3)_2\text{N}][\text{Eu}(\text{tta})_4]$ complex, namely to introduce functional groups to impart spreading ability at the air/water interface and provide organized, stable monolayers where the molecular arrangement helps preserve the luminescence properties of the europium ions. A further contribution here is associated with the use of a theoretical model to explain the geometrical arrangement of specific groups of ligands and counter ions before film spreading. The model includes geometric parameters that characterize the structure of the molecule and the distances between its components and energy parameters, primarily the energy required to disrupt the weak bonds. The results from this modeling will be explored in determining the interaction of molecules of the $[(\text{C}_{12}\text{H}_{25})_2(\text{CH}_3)_2\text{N}][\text{Eu}(\text{tta})_4]$ complex at the air–water interface, thus representing an important feature in the field of LB films from functionalized complexes, whose choice of molecular architecture has been made only empirically so far.^{12–17} In addition, with experiments such as the ones reported here procedures can be established to use europium complexes as structural probes for studying monolayers from surfactants, such as DODAB, that mimic cell membranes.

Materials and methods

Synthesis and characterization of $[(\text{C}_{12}\text{H}_{25})_2(\text{CH}_3)_2\text{N}][\text{Eu}(\text{tta})_4]$

The $[(\text{C}_{12}\text{H}_{25})_2(\text{CH}_3)_2\text{N}][\text{Eu}(\text{tta})_4]$ complex, shown in Fig. 1, was synthesized as follows: the thenoyltrifluoroacetone ligand (4.2 mmol) and the salt didodecyltrimethylammonium bromide (4.2 mmol) were dissolved in ethanol under stirring. $\text{EuCl}_3 \cdot 6\text{H}_2\text{O}$ (1.0 mmol) in ethanol solution was slowly added drop-by-drop to the first solution, and the pH of the final mixture was

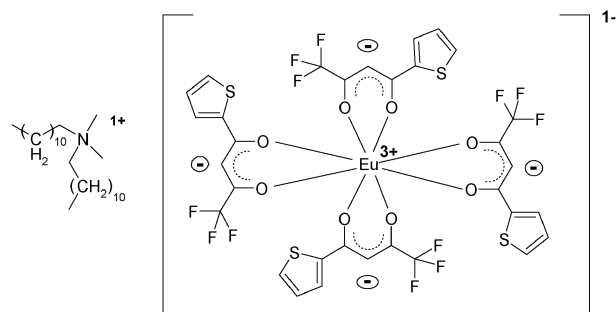


Fig. 1 $[(\text{C}_{12}\text{H}_{25})_2(\text{CH}_3)_2\text{N}][\text{Eu}(\text{tta})_4]$ complex structure.

adjusted to 5.0 by slowly adding aqueous NH_4OH (1 mol L^{-1}). The solution was kept under heating at $40\text{--}50^\circ\text{C}$ and stirring for 2 to 3 h. The solid formed was filtered out and dried in a vacuum oven at room temperature. To determine the triplet energy levels the analogous gadolinium complex was synthesized using the procedure described above. The chemical formula was obtained using complexometric titration with EDTA, C and H microanalysis (Perkin Elmer 2400) and thermogravimetric analysis (TA Instruments SDT 2960). Infrared spectra were recorded for KBr pellets on a FT-IR Perkin Elmer 2000 instrument working in the $4000\text{--}400 \text{ cm}^{-1}$ range. The ground state geometry for the europium complex was obtained using Mopac2009™ using the keywords: *AMI, SPARKLE, XYZ, BFGS, PRECISE, GNORM = 0, CHARGE = 0*.

Langmuir–Blodgett films

Surface pressure–area (π – A) isotherms and Langmuir–Blodgett (LB) films were studied on a KSV3000 (KSV Instruments) Langmuir balance. A Milli-Q system was used to produce ultrapure water with a resistivity of $18.2 \text{ M}\Omega \text{ cm}$. The monolayers were formed by spreading *ca.* 200 μL of a chloroform solution of the complex on the water surface. The solvent was allowed to evaporate for 10 min prior to sweeping the surface with the movable barriers; then π – A isotherms were recorded. LB films were transferred onto hydrophilic quartz plates at a surface pressure of 19 mN m^{-1} , using downstroke and upstroke speeds of $7.5\text{--}10 \text{ mm min}^{-1}$. All experiments were carried out at room temperature ($25 \pm 1^\circ\text{C}$).

The photoluminescence spectra of the complex in the powder form or as LB films were obtained with a Fluorolog Horiba Jobin Yvon spectrophotometer model FL3–222 FLUOROLOG SPEX 212L, with a 450W xenon continuous lamp, not ozone free. The lifetime was obtained on a Jobin Yvon phosphorimeter model FL–1040 with a pulsed lamp.

Results and discussion

Ground state geometry for the europium complex

Theoretical methods have been used to determine the geometry around the central ion in coordination complexes,²¹ spectroscopic parameters of lanthanides complexes,²² atom polarizabilities²³ and molecular orientation in Langmuir–Blodgett films.^{24,25} The ground state geometry and the coordination polyhedron of lanthanide complexes,²⁶ especially europium(III) complexes, could be determined using semi-empirical methods that are

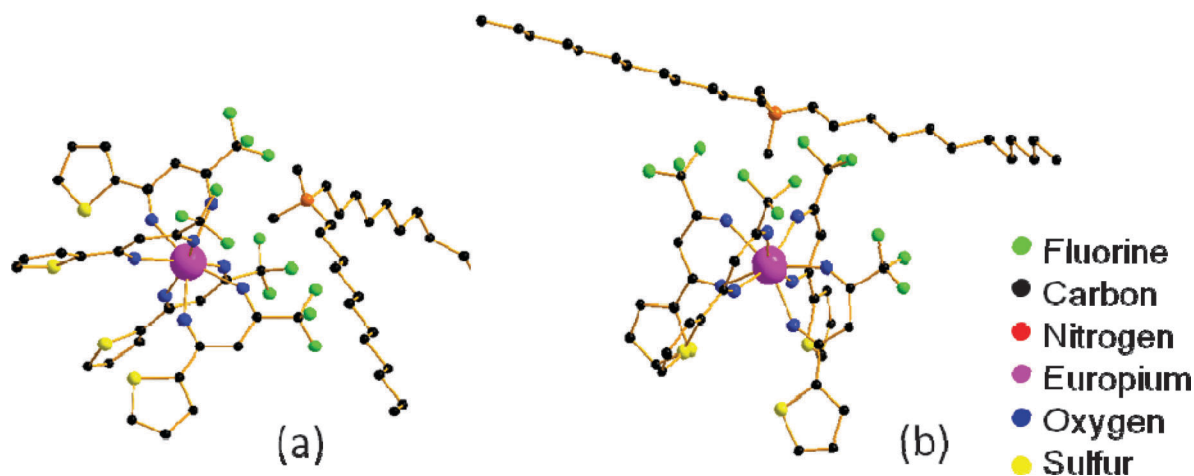


Fig. 2 Structure of $[(C_{12}H_{25})_2(CH_3)_2N][Eu(tta)_4]$ provided by Sparkle/AM1 in two different views in (a) and (b).

advantageous for their high precision in predicting bond lengths and bond angles, in addition to requiring low computational power. Recent results have shown good prediction for the ground state geometry, when compared to monocystal data.^{21,27–29} Here the ground state geometry shown in Fig. 2 was calculated using Sparkle/AM1³⁰ implemented in the Mopac2009™ package.³¹ The Sparkle model replaces the lanthanide ion by a core with +3e charge, so that only the electrostatic interaction between the ion and the ligand is considered. The structural parameters of the coordination polyhedron, shown in Table 1, are given by the distance between the europium ion and ligand (R), the angle between the z axis and the ligand atom (θ) and the angle of the

projection of vector r in the xy plane and the x axis (Φ). The average distance Eu–O (tta) of 2.3926 Å is close to the distance estimated using X-ray diffraction data for the $[Eu(tta)_3(H_2O)_2]$ monocystal.³²

According to the structure obtained with Sparkle/AM1, all CF_3 groups lie in a direction pointing toward the nitrogen atom of the cation, with the coordination polyhedron being close to a square antiprism. This orientation is driven by the attraction between the positive charge in the nitrogen atom and the negative partial charge in the CF_3 groups. The distance of 3.5 Å between the nitrogen and fluorine atoms confirms the ion–dipole interaction. The distances between N^+ and CF_3 groups are shown in Fig. 3.

Fig. 4 shows the charge distribution along the tta molecule. In the complex structure a separation between CF_3 groups and diketone groups is noted. The differences in charge density give rise to a dipole in the complex, with CF_3 groups being the negative part, represented in pink, while the positive density is shown in green. The density of the sulfur atom is not shown due to the poor interaction with europium ions to obtain β -diketonate complexes. Obtaining the charge distribution may help understand the molecular arrangement in the film, in addition to predicting further properties of the complex. For example, the charge separation may be important to

Table 1 Polar coordinates for $[(C_{12}H_{25})_2(CH_3)_2N][Eu(tta)_4]$ provided by Sparkle/AM1

Bond	$d/\text{Å}$	$\theta/^\circ$	$\Phi/^\circ$
Eu–O	2.3900	52.4067	12.7520
Eu–O	2.3985	110.1695	38.9062
Eu–O	2.3894	38.8837	129.9425
Eu–O	2.3992	100.7131	117.2390
Eu–O	2.3904	105.1817	197.3511
Eu–O	2.3865	59.2270	241.3851
Eu–O	2.3981	162.7340	286.9074
Eu–O	2.3884	101.2022	307.3688

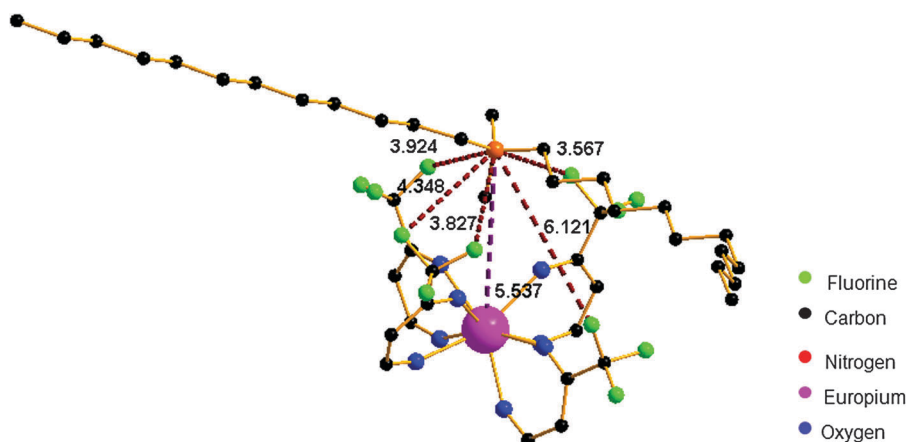


Fig. 3 Distances (Å) between N^+ and CF_3 groups, and between N^+ and Eu^{3+} (thiophene rings were omitted for the sake of a better visualization).

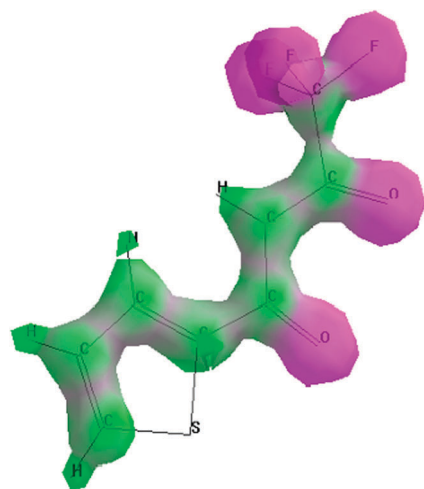


Fig. 4 Charge distribution along the tta molecule. The pink color depicts the negative charge density, while the green color depicts the positive charge density.

understand the high quantum efficiency of 53.8% of the complex in the powdered form, which could in turn explain why the films to be reported exhibit luminescence properties.

Characterization of the complex

Complexometric titration and elemental analysis results in percentage experimental (calculated) were $\text{Eu}^{3+} = 10.43$ (10.70), $\text{C} = 49.38$ (49.08) and $\text{H} = 5.02$ (5.11). These percentages suggest the stoichiometry of the anionic complex $[(\text{C}_{12}\text{H}_{25})_2(\text{CH}_3)_2\text{N}][\text{Eu}(\text{tta})_4]$, as expected. The FTIR spectra in Fig. 5 feature two C=O stretching vibrations for the tta

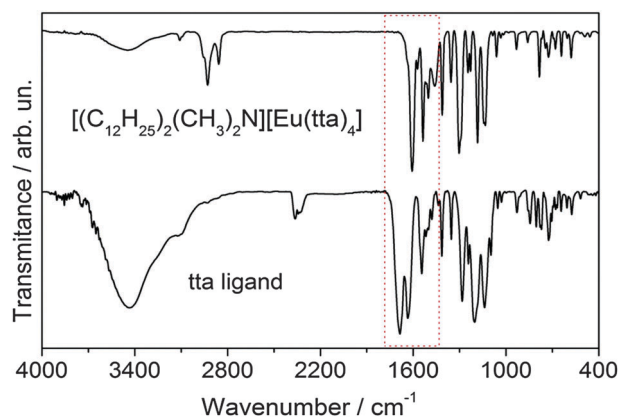


Fig. 5 Infrared spectra for the $[(\text{C}_{12}\text{H}_{25})_2(\text{CH}_3)_2\text{N}][\text{Eu}(\text{tta})_4]$ complex and free tta ligand, in KBr pellets.

ligand, assigned to asymmetric and symmetric forms. The IR spectrum of the europium complex exhibits only the $\nu_s(\text{C}=\text{O})$ absorption band due to a strong interaction between oxygen atoms from β -diketone and europium (stabilized by the resonance system from the chelate ring), which also causes a shift of 16 cm^{-1} . The shift in the C=O stretching from $\sim 1632\text{ cm}^{-1}$ in the free tta ligand to $\sim 1616\text{ cm}^{-1}$ in the complex form is taken as evidence that the europium ion is coordinated through the β -diketone oxygen atoms. A large band at 3400 cm^{-1} in the free tta spectrum arises from water absorbed by the KBr pellet during the measurement. All other ligand vibration frequencies are listed in Table 2, being in agreement with the literature.³³

Photoluminescence characterization

The radiative properties depend on the triplet of the tta ligand and the energy levels of the europium ions. Here we have determined the triplet level as $1.91 \times 10^4\text{ cm}^{-1}$ from the emission spectra of gadolinium complexes. Because the energy of the triplet of tta is higher than the ${}^5\text{D}_0$ energy level for europium, energy transfer between the ligand and europium(III) can occur. The photoluminescence study of the anionic complex was carried out through excitation and emission spectra and a luminescence decay curve at 298 K. The excitation spectrum of $[(\text{C}_{12}\text{H}_{25})_2(\text{CH}_3)_2\text{N}][\text{Eu}(\text{tta})_4]$ in the powdered form exhibits bands corresponding to intraligand ($\pi-\pi^*$, $n-\pi^*$), intraconfiguration f-f (${}^7\text{F}_0 \rightarrow {}^5\text{D}_2$ at 464 nm) and charge transfer (O–Eu) transitions, shown in Fig. 6(a). The emission spectrum obtained with $\lambda_{\text{exc}} = 409\text{ nm}$ is shown in Fig. 6(b), featuring the same profile when excitation was performed in resonance with the Eu^{3+} energy levels. (The choice of the 409 nm wavelength for excitation was based on a systematic monitoring of the emission spectra for various excitation energies within the absorption region of the intraconfigurational transitions of the europium ion and ligand.) These results confirm an efficient antenna mechanism with the tta ligands. The f-f intraconfigurational transition lines were assigned to ${}^5\text{D}_0 \rightarrow {}^7\text{F}_{0-4}$ dominated by the hypersensitive ${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$ transition. The splitting in the emission spectrum for the powder is explained by the point symmetry around the europium ion.

Fig. 7 shows the luminescence decay from the emission state (${}^5\text{D}_0$) measured upon monitoring the hypersensitive ${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$ transition. The lifetime (τ) was 0.41 ms, which is smaller than that for other tetrakis beta-diketonate europium complexes owing to the non-radiative multiphonon mechanisms of the didodecyl chain.^{1,2} The linear fitting in Fig. 7(b) for the $[(\text{C}_{12}\text{H}_{25})_2(\text{CH}_3)_2\text{N}][\text{Eu}(\text{tta})_4]$ complex confirms that the decay may be explained with a first-order exponential function.

Table 2 Infrared frequencies (wavenumber in cm^{-1}) at room temperature for the tta free ligand and $[(\text{C}_{12}\text{H}_{25})_2(\text{CH}_3)_2\text{N}][\text{Eu}(\text{tta})_4]$ complex

Compound	Wavenumber/ cm^{-1}				
	$\nu_s(\text{CH}_2)$	$\nu_{\text{ass}}(\text{C}=\text{O})$	$\nu_s(\text{C}=\text{O})$	$\nu(\text{C}=\text{C})$	$\nu\text{C}-\text{CF}_3$ $\delta\text{C}-\text{F}$
tta ligand	2972	1691	1632	1541	1138 1295
$[(\text{C}_{12}\text{H}_{25})_2(\text{CH}_3)_2\text{N}][\text{Eu}(\text{tta})_4]$	2956	—	1616	1540	1139 1308

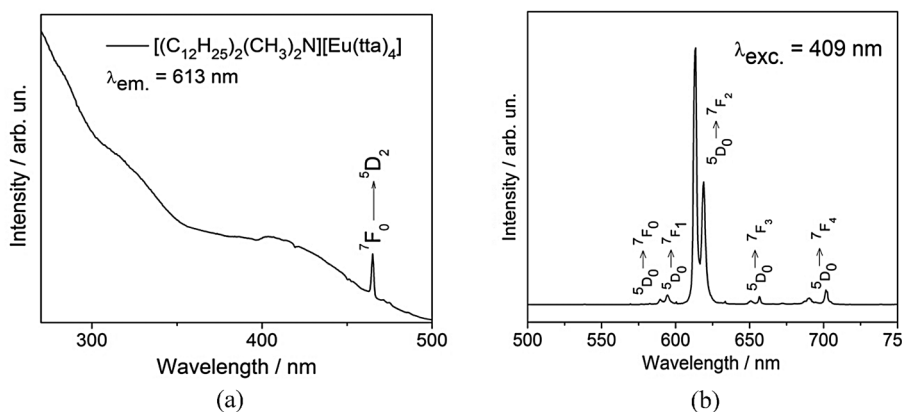


Fig. 6 (a) Excitation spectrum with emission at $\lambda_{em} = 613$ nm for $[(C_{12}H_{25})_2(CH_3)_2N][Eu(tta)_4]$ at 298 K. (b) Emission spectrum with excitation at $\lambda_{exc} = 409$ nm for $[(C_{12}H_{25})_2(CH_3)_2N][Eu(tta)_4]$ at 298 K.

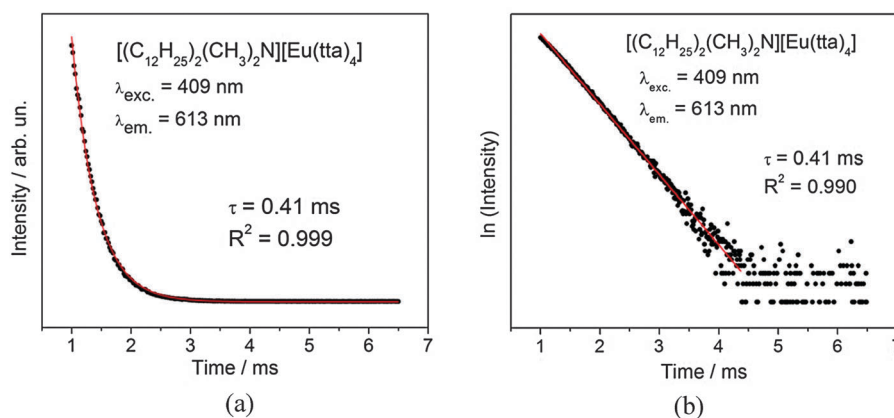


Fig. 7 (a) Decay of the luminescence for the 5D_0 state of europium(III), yielding a lifetime of 0.41 ms. (b) Linear fitting of $\ln(\text{intensity})$ with time using an exponential function.

Langmuir and Langmuir–Blodgett films

Taking advantage of the amphiphilic nature of the counter ion of the complex synthesized here, we produced Langmuir monolayers and LB films. Langmuir monolayers of other europium complexes with short chains or amphiphilic counter-ions have already been reported.^{6,9,13,34} Using amphiphilic counter-ions is an alternative to the use of subphases saturated with the ligand, a common practice used to increase monolayer stability.^{35,36} The four main types of forces acting are: van der Waals, electrostatic, solvation (hydration) and steric forces. The intermolecular forces between diketone and counter-ion can be classified into three categories: (i) purely electrostatic, (ii) polarization forces that arise from the dipole moments induced in atoms and molecules by the electric fields of nearby charges and permanent dipoles and (iii) repulsive steric forces that balance the attractive forces at very short distances.

The surface pressure–area (π -A) isotherm for $[(C_{12}H_{25})_2(CH_3)_2N][Eu(tta)_4]$ spread on the surface of a pure water subphase is shown in Fig. 8. It can be inferred from the high pressure attained that stable films were formed, with no loss of materials to the subphase. The increase in surface pressure yields an in-plane elasticity (reflection of film rigidity) of *ca.* 40–50 $mN\ m^{-1}$, the upper limit of the liquid-condensed phase. In subsidiary experiments we noted that collapse only occurs above 40 $mN\ m^{-1}$, again indicating that the films are

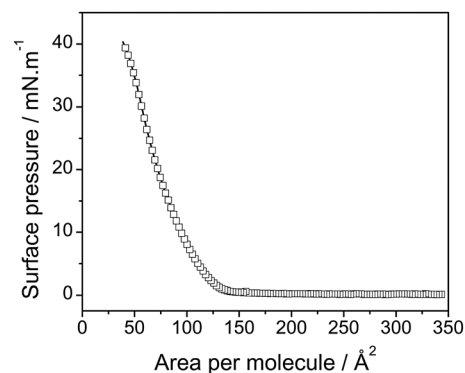


Fig. 8 Surface pressure–area isotherm for the $[(C_{12}H_{25})_2(CH_3)_2N][Eu(tta)_4]$ monolayer.

stable and amenable to transfer in the form of Langmuir–Blodgett (LB) films, as will be shown below.

From the chemical structure of the complex, we infer that the long didodecyl chains of the ligand should point to the air, being organized parallel to each other. Moreover, the more hydrophilic portions of the complex, such as the europium core complexed with the carbonyl groups and the ammonium salt, should be anchored to the water surface, even being immersed. As the calculations showed that the CF_3 groups

from tta point towards the nitrogen atoms when the molecule is in vacuum, we can speculate that such groups are located in the hydrophilic portion of the film, mainly because hydrogen bonds can stabilize the aqueous subphase and CF_3 groups. On the other hand, since tta molecules are polar, the thiophene groups should be preferentially together with the europium atoms and carbonyl groups. Actually, the assembly of the complex at the air–water interface is rather complicated, and the arrangement depicted here must be confirmed using other techniques.

The area extrapolated from the steeper part of the curve was 125 \AA^2 , which is consistent with the area for similar complexes.^{13,35} In the studies of ref. 13 and 35, the complexes did not have long amphiphilic chains, and the area occupied by the molecules was attributed to the complex itself, supposed to lie parallel to the water surface. This hypothesis was supported by theoretical data.¹³ Because the area measured for the amphiphilic complex used here is almost the same as that in the other complexes, and much larger than the cross sectional area of the aliphatic chains, we may assume that the polar core of the complex (comprising the europium complex anion, dimethylammonium cation, carboxyl and thiophene groups) is responsible for the area occupied at the air/water interface and the packing state of the monolayer.

The spreading of mixed films with film-forming materials (such as typical amphiphiles) is sometimes a requirement for good deposition of europium complexes as LB films.^{7,15} However, for $[(\text{C}_{12}\text{H}_{25})_2(\text{CH}_3)_2\text{N}][\text{Eu}(\text{tta})_4]$ this was not the case, which is advantageous since mixing with other materials could interfere with the optical properties of the compounds. Y-type LB films could be transferred from the pure $[(\text{C}_{12}\text{H}_{25})_2(\text{CH}_3)_2\text{N}][\text{Eu}(\text{tta})_4]$ monolayer at 19 mN m^{-1} , with a transfer ratio close to unity. The excitation spectra of LB films on quartz substrates are similar to those obtained for the material in the powdered form. The excitation peak centered at 307 nm, assigned to the π – π^* transition in the tta ligand, was used to obtain the emission spectra of $[(\text{C}_{12}\text{H}_{25})_2(\text{CH}_3)_2\text{N}][\text{Eu}(\text{tta})_4]$. The emission spectra for LB films with different numbers of layers are shown in Fig. 9.

The ${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$ transitions in LB films centered at 618 nm are different from those in the most hypersensitive one in the powdered form, and it is not possible to speculate about the

local symmetry for two reasons: (i) the emission intensity was considerably smaller owing to the low number of emission centers, and (ii) the spectra were obtained with a different acquisition mode, including a larger slit window, which decreases the spectrum resolution. Though films of only three thicknesses were used, we noted a linear trend in the emission intensity area for the ${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$ transition with the number of layers (result not shown). This indicates that the mass transferred in each layer is approximately the same, and that the packing of further layers does not cause quenching of the luminescence.

Conclusions

The synthesis and characterization of the amphiphilic europium complex $[(\text{C}_{12}\text{H}_{25})_2(\text{CH}_3)_2\text{N}][\text{Eu}(\text{tta})_4]$ are reported, along with the formation of stable Langmuir monolayers at the air/water interface. The extrapolated area for the Langmuir monolayer indicated that the packing state of the complex is primarily controlled by the hydrophilic groups, *viz.* the europium atom, the dimethylammonium cation and the thiophene groups, which face the water subphase. Luminescent Y-type LB films with tens of monolayers were deposited from the pure $[(\text{C}_{12}\text{H}_{25})_2(\text{CH}_3)_2\text{N}][\text{Eu}(\text{tta})_4]$ Langmuir monolayer. The use of an anionic counter ion eliminated the need of co-spreading a non-luminescent surfactant or of inserting aliphatic chains in the structure, which normally causes quenching of luminescence intensity.^{9,10,16–18} This preserved luminescence of LB films may be explained firstly by the high quantum efficiency of the complex (as obtained from theoretical calculations). Furthermore, its suitability for higher degrees of molecular packing without loss of optical performance should be highlighted. This is a result of the chemical design directed by theoretical calculations, used as a tool to predict and interpret film properties, which is another important contribution of this study. Although the calculations were used to estimate the ground state geometry of molecules under vacuum, they provided us with some insight into the behavior of specific groups (CF_3 and NH_4^+) in their possible interactions in Langmuir films.^{11–16} For instance, we were able to explain interactions between cations and anions, and the molecular arrangement of $[(\text{C}_{12}\text{H}_{25})_2(\text{CH}_3)_2\text{N}][\text{Eu}(\text{tta})_4]$ using Sparkle/AM1.

Our results indicate that the $[(\text{C}_{12}\text{H}_{25})_2(\text{CH}_3)_2\text{N}][\text{Eu}(\text{tta})_4]$ complex may be used in electronic devices owing to the preserved luminescence. Moreover, this luminescent, amphiphilic complex can now be used as a probe when incorporated in Langmuir monolayers of phospholipids or other surfactants that mimic cell membranes. The complex is particularly suitable to investigate local phenomena dominated by the specificity of the headgroup/anion and electronegativity in chemical interactions.

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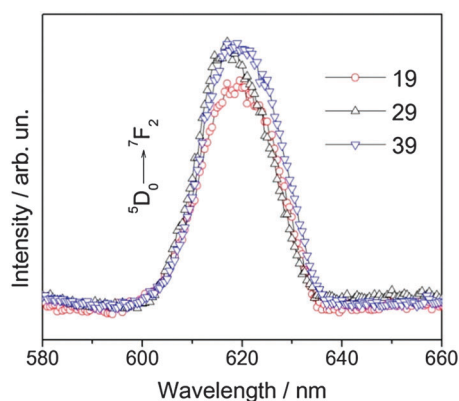


Fig. 9 Emission spectra with excitation at $\lambda_{\text{ex}} = 307.0 \text{ nm}$ of LB $[(\text{C}_{12}\text{H}_{25})_2(\text{CH}_3)_2\text{N}][\text{Eu}(\text{tta})_4]$ films with different numbers of layers (indicated in the inset).

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