Structure and photoluminescence of di-amidosil nanohybrids incorporating europium triflate

S.C. Nunes^a, V. de Zea Bermudez^{a,1}, J. Cybinska^{b,c}, R.A. Sá Ferreira^b, L.D. Carlos^{b,*},
J. Legendziewicz^c, M.M. Silva^d, M.J. Smith^d, D. Ostrovskii^e

^a Departamento de Química and CQ-VR, Universidade de Trás-os-Montes e Alto Douro, 5001-801 Vila Real, Portugal

^b Departamento de Física and CICECO, Universidade de Aveiro, 3810-193 Aveiro, Portugal

^c Faculty of Chemistry, University of Wrocław, 14 F. Joliot-Curie, 50-383 Wrocław, Poland

^d Departamento de Química, Universidade do Minho, Campus de Gualtar, 4710-057 Braga, Portugal

^e Department of Applied Physics, Chalmers University of Technology, 41296 Göteborg, Sweden

Abstract

The sol-gel process was used to prepare amorphous di-amide cross-linked alkyl/siloxane hybrid materials (di-amidosils) incorporating europium triflate ($\text{Eu}(\text{CF}_3\text{SO}_3)_3$). Samples with $200 \leq n \leq 8$ (where n is the molar ratio of carbonyl oxygen atoms per Eu^{3+} ion) were studied. The conformations of the alkyl chains of the host matrix in the doped di-amidosils (essentially *gauche*) are not affected by the presence of the salt. The Eu^{3+} ions bond to the $\text{C}=\text{O}$ groups of the amide cross-links in the whole range of salt concentration examined. "Free" and weakly coordinated triflate ions were detected in all the samples analyzed. At $n = 8$ an ionic aggregate of unknown nature is formed. The hybrids introduced are room temperature white light emitters due to the convolution of the hybrid host emitting centers (amide cross-linkages and siliceous nanodomains) and the Eu^{3+} intra- $4f^6$ $^3\text{D}_0 \rightarrow ^7\text{F}_{0-4}$ transitions. Photoluminescence data suggest that in the dilute di-amidosil with $n = 100$ the Eu^{3+} ions occupy the same type of chemical local environment.

1. Introduction

The sol-gel process [1] is a synthetic route well adopted for the production of multifunctional hybrid organic/inorganic materials [2] with potential technological application in a series of domains, including optics. The combination of appropriate experimental conditions (in particular, water content, solvent, catalyst, pH) of the sol-gel route with the adequate choice of the organic and inorganic components influence the morphology, molecular structure and properties of the hybrids.

Based on this strategy, several stable and efficient white-light photoluminescent amine-functionalized hybrids lacking metal activator ions were studied [3–9]. The highest external photoluminescence (PL) quantum yield reported is that of the aminopropyltriethoxysilane-formic acid hybrid ($35 \pm 1\%$) [5]. Values of 20% were estimated for the di-urea and di-urethane cross-linked poly(oxyethylene) (POE)/siloxane hybrid frameworks (di-ureasils and di-urethanesils, respectively) [7,8]. The di-amide cross-linked alkyl/siloxane hybrid networks (di-amidosils) yield considerably lower quantum yields (5.4%) [10].

In the present work we will dope with Eu^{3+} ions a di-amidosil hybrid structure incorporating alkylene chains with eight methylene groups. The structure, thermal behaviour and photoluminescence features of di-amidosil samples with a wide range of Eu^{3+} concentration will be examined. Another goal of this study is the elucidation of the coordination process of the trivalent lanthanide ions in the di-amidosil medium. We must emphasize that, in contrast with the situation found in the di-ureasil and di-urethanesil systems, in which the host hybrid matrix provides two coordinating sites for the guest cations (the oxygen atoms of the POE chains and the carbonyl oxygen atoms of the urea ($-\text{NHC}(=\text{O})\text{NH}-$) and urethane ($-\text{NHC}(=\text{O})\text{O}-$) cross-links, respectively), in the di-amidosils the only available coordinating sites are the carbonyl oxygen atoms of the amide ($-\text{NHC}(=\text{O})-$) cross-links.

2. Experimental

2.1. Materials

Ethanol ($\text{CH}_3\text{CH}_2\text{OH}$, Merck), pyridine (py, Aldrich) and tetrahydrofuran (THF, Merck) were stored over molecular sieves. Amberlyst A-21 Ion-Exchange resin (Amberlyst resin, 4.7 meq/g, Aldrich) was washed with THF and stored in an oven at 80°C . Sebacyl chloride ($\text{ClC}(=\text{O})-(\text{CH}_2)_8\text{C}(=\text{O})\text{Cl}$, SC, Aldrich) and 3-aminopropyltriethoxysilane ($(\text{CH}_3\text{CH}_2\text{O})_3\text{Si}(\text{CH}_2)_3\text{NH}_2$, APTES, Fluka), europium trifluoromethanesulfonate (or europium triflate, $\text{Eu}(\text{CF}_3\text{SO}_3)_3 \cdot x\text{H}_2\text{O}$, Aldrich) were used as received. High purity distilled water was used in all experiments.

2.2. Synthesis

The first stage of the synthesis of the Eu^{3+} -doped xerogel samples, which involves the formation of the di-amidopropyltriethoxysilane precursor (d-ADPTES(8)), was reported in detail elsewhere [10]. In the second stage of the synthetic procedure, a solution of $\text{Eu}(\text{CF}_3\text{SO}_3)_3$ in $\text{CH}_3\text{CH}_2\text{OH}$ and water was added to the THF solution of d-ADPTES(8) (molar ratio APTES: $\text{CH}_3\text{CH}_2\text{OH}:\text{H}_2\text{O} = 1:4:2$) prepared in the first stage. The resulting mixture was stirred in a sealed flask for 30 min and then cast to a Teflon mould, which was covered with Parafilm and left in a fume cupboard for 24 h. The mould was then transferred to an oven at 50°C and the sample was aged for a period of 2 weeks. The samples were obtained as transparent and rigid monoliths.

The doped materials have been identified by the notation d-A(8)_n $\text{Eu}(\text{CF}_3\text{SO}_3)_3$, where 8 is the number of methylene groups of the alkyl chain and n (composition) represents the molar ratio of carbonyl oxygen atoms per cation.

Details of the preparation of the Eu^{3+} -doped di-amidosil hybrids are given in Table 1.

2.3. Experimental techniques

The X-ray diffraction (XRD) patterns were recorded at room temperature with a Rigaku Geigerflex D/max-c diffractometer system using monochromated $\text{Cu K}\alpha$ radiation ($\lambda = 1.541 \text{ \AA}$) over the 2θ range of between 4 and 70° at a resolution of 0.05° . The samples were analyzed as films and not were submitted to any thermal pre-treatment.

Differential scanning calorimetry (DSC) measurements were obtained with a DSC131 Setaram DSC. Disk sections with a mass of approximately 10–20 mg were removed from the ormolite samples, placed in 40 μl aluminium cans and stored in a desiccator over phosphorous pentoxide for 1 week at room temperature under vacuum. After the drying treatment the cans were hermetically sealed and the thermograms were recorded. Each sample was heated from 20 to 250°C at $10^\circ\text{C min}^{-1}$. The purge gas used in all experiments was high purity nitrogen (N_2) supplied at a constant $35 \text{ cm}^3 \text{ min}^{-1}$ flow rate.

Samples for thermogravimetric analysis (TGA) were transferred to open platinum crucibles and analyzed using a Rheometric Scientific TG 1000 thermobalance at a heating rate of $10^\circ\text{C min}^{-1}$ using high purity N_2 as purging gas ($20 \text{ cm}^3 \text{ min}^{-1}$). Prior to measurement, the xerogels were vacuum-dried at 80°C for about 48 h and stored in an argon-filled glove box.

The Fourier-transform infrared (FT-IR) spectra were acquired at room temperature using a Bruker 22 (Vektor) spectrometer placed inside a glove-box with a dry argon atmosphere. The spectra were collected over the $4000\text{--}400 \text{ cm}^{-1}$ range by averaging 150 scans at a spectral resolution of 2 cm^{-1} . Solid samples (2 mg) were finely ground, mixed with approximately 175 mg of dried potassium bromide (Merck, spectroscopic grade) and pressed into pellets. Prior to recording the spectra, the pellets were first vacuum dried at $80\text{--}90^\circ\text{C}$ for about 60 h, in order to reduce the levels of adsorbed water and solvent, and then transferred into a glove-box.

The Fourier-transform Raman (FT-Raman) spectra were recorded at room temperature with a Bruker IFS-66 spectrometer equipped with a FRA-106 Raman module and a near-infrared YAG laser with wavelength of 1064 nm . The spectra were collected over the $3200\text{--}300 \text{ cm}^{-1}$ range at a resolution of 2 cm^{-1} . The accumulation time for each spectrum was 4 h.

To evaluate complex band FT-IR and FT-Raman envelopes and to identify underlying spectral components, the iterative least-squares curve-fitting procedure in PeakFit [11] software was used extensively throughout this study. The best fit of the experimental data was sought by varying the frequency, bandwidth and intensity of the bands. As the samples analyzed are disordered, the spectral peaks were fitted using a Gaussian shape. The standard errors of the curve-fitting procedure were less than 0.002. A linear baseline with a tolerance of 0.3% was employed.

The photoluminescence spectra were recorded at room temperature with a modular double grating excitation spectrofluorimeter with a TRIAX 320 emission monochromator (Fluorolog-3, Jobin Yvon-Spex) coupled to a R928 Hamamatsu photomultiplier, using the front face acquisition mode. The excitation source was a 450 W Xe arc lamp. The emission spectra were corrected for detection and optical spectral response of the spectrofluorimeter and the excitation spectra were corrected for the spectral distribution of the lamp intensity using a photodiode reference detector.

3. Results and discussion

3.1. Structure and thermal properties

The XRD patterns of the d-A(8)_nEu(CF₃SO₃)₃ di-amidosils with $n=200$ and 8, reproduced in Fig. 1a, exhibit a broad, Gaussian band centred around 20.8°, associated with ordering within the siloxane domains [12]. The broad weak hump that appears around 42° in the diffractogram of d-A(8)₈Eu(CF₃SO₃)₃ is attributed to the second-order of the peak at 20.8° (Fig. 1a). Structural unit distances of 4.3 Å were calculated for these hybrids, using the Bragg law. The coherent length L over which the structural unit survives in the samples with $n=200$ and 8 was estimated using the modified Scherrer equation, $L = \lambda / (\Delta \cos \theta)$, where I and A , in radians, are the maximum intensity and integrated area of the peaks, respectively, and λ is the wavelength of the incident radiation. The L values derived for both compounds (17 and 14 Å, respectively) are considerably higher than those reported for d-A(8) [10].

The DSC measurements corroborate the conclusion drawn from XRD data that the d-A(8)_nEu(CF₃SO₃)₃ xerogels with $200 \geq n \geq 8$ are entirely amorphous (Fig. 1b).

The TGA curves of the samples studied (not shown) resemble closely that of the d-A(8) host framework [10]. In the doped di-amidosils a progressive mass loss is detected in the curves, with an onset of about 240 °C. From approximately 350 °C the rate of mass loss increases abruptly. Although the degradation of the d-A(8)₈Eu(CF₃SO₃)₃ xerogel is also initiated at about the same temperature, it takes place in three steps.

3.2. Cation coordination

To gather phase-state and structural information of the Eu³⁺-doped d-A(8)-based hybrids we will examine the FT-Raman CH₂ symmetric and asymmetric stretching (ν_s CH₂ and ν_a CH₂, respectively) modes. To evaluate the strength of the hydrogen bonds established in the d-A(8)_nEu(CF₃SO₃)₃ xerogels we will inspect their FT-IR spectra in the amide I and amide II regions [13]. At last, to probe the surrounding experienced by the triflate ions in the same set of samples at increasing salt content we will analyze the coordination-sensitive SO₃ symmetric stretching (ν_s SO₃) mode.

3.2.1. Polymer chain conformations and state of disorder

The room-temperature FT-Raman spectra of selected d-A(8)_nEu(CF₃SO₃)₃ compounds in the ν_s CH₂ and ν_a CH₂ regions (3000–2800 cm⁻¹) are represented in Fig. 2.

The FT-Raman ν CH₂ region of the Eu³⁺-doped di-amidosil hybrids with $200 \geq n \geq 8$ exhibits two prominent bands centered at 2925 and 2890 cm⁻¹ and a shoulder at 2857 cm⁻¹ (Fig. 2). The features at 2925 and 2857 cm⁻¹ are ascribed to the ν_s CH₂ fundamental and to the Fermi resonance between the ν_s CH₂ fundamental with the many overtones of the CH₂ bending vibrations, respectively, and are characteristic of disordered alkyl

chains [14–16]. The intense 2890 cm⁻¹ event is associated with the ν_a CH₂ stretching mode of alkyl chains in the amorphous state [14–16].

We may infer from these results that the alkyl chains of the di-amidosil materials are fully disordered, as suggested by the XRD and DSC data discussed above, and adopt, as expected, essentially *gauche* conformations. Another conclusion retrieved from the analysis of the FT-Raman ν_s CH₂ and ν_a CH₂ regions is that the conformations of the polymer chains of d-A(8) are not affected by the presence of the lanthanide salt.

3.2.2. Eu³⁺/amide interaction and hydrogen bonding

The amide I (essentially C=O stretching) and amide II (essentially N–H in-plane bending) regions [17–19] of the d-A(8)_nEu(CF₃SO₃)₃ materials are depicted in Fig. 3a. The results of the curve-fitting performed in the 1800–1500 cm⁻¹ interval are displayed in Fig. 3b.

3.2.3. Amide I region

Comparison of the amide I band profile (1800–1600 cm⁻¹) of the non-doped d-A(8) hybrid [10] with those of the doped samples (Fig. 3b) demonstrates that the addition of increasing amounts of Eu(CF₃SO₃)₃ to d-A(8) gives rise to several spectral changes within the whole range of salt concentration examined, a finding that indicates that in all the di-amidosils analyzed the Eu³⁺ ions bond to the C=O groups of the amide cross-links. The significant band redistribution observed in the amide I envelope upon doping results from the coordination of the Eu³⁺ ions to free carbonyl groups of the amide linkages and to carbonyl groups belonging to the hydrogen-bonded amide–amide aggregates characteristic of the non-doped d-A(8) hybrid.

The broad amide I envelope of the di-amidosil sample with $n=200$ was resolved into the six components at approximately 1758, 1736, 1715, 1672, 1650 and 1626 cm⁻¹ (Fig. 3b), already detected in the d-A(8) material [10]. The 1758 cm⁻¹ feature is assigned to amide linkages whose N–H and C=O groups are non-bonded [10]. The 1736 and 1713 cm⁻¹ components are ascribed to disordered amide–amide aggregates of increasing strength [10]. The 1679, 1652 and 1623 cm⁻¹ features are attributed to the absorption of C=O groups in considerably more ordered hydrogen-bonded amide–amide aggregates of increasing strength [10]. The significant number of components (and thus amide–amide aggregates) found may be correlated with a high degree of structural disorder of the d-A(8)₂₀₀Eu(CF₃SO₃)₃ xerogel.

At $n=80$ the growth of a new feature at 1609 cm⁻¹ (Fig. 3b) is indicative of the formation of a new ordered amide–amide aggregate, possessing considerably stronger hydrogen bonds than those established in the more diluted samples. Fig. 3b proves that the proportion of the latter aggregates in the samples grows rapidly with salt doping at the expense of the breakdown of other less ordered aggregates.

The disappearance of the feature due to free amide linkages (1758 cm⁻¹) at $n=40$ (Fig. 3b) allows us to infer that the saturation of the amide cross-links occurs at this composition.

3.2.4. Amide II region

The amide II mode (1600–1500 cm⁻¹) of the xerogel with $n=200$ was decomposed into two peaks at 1563 and 1534 cm⁻¹ (Fig. 3b), suggesting that hydrogen-bonded aggregates with two hydrogen bond strengths exist. The new component that emerges at 1588 cm⁻¹ (Fig. 3b) in the sample with $n=80$ and increases with salt addition is tentatively correlated with the development of the band at 1609 cm⁻¹. We note that in the doped samples the low-frequency amide I components are partly superimposed with amide II components: the amide I component at 1626 cm⁻¹ receives some contribution from the amide II component at 1588 cm⁻¹, whereas the amide I component at 1609 cm⁻¹ receives contribution from the amide II 1588 and

in the FT-Raman $\nu_3\text{SO}_3$ band profiles of representative xerogels are depicted in the inset of Fig. 4.

The $\nu_3\text{SO}_3$ band of the FT-Raman spectra of the di-amidosils studied was decomposed into two components: a band at 1032 cm^{-1} , a weak shoulder around 1026 cm^{-1} (inset of Fig. 4). A very weak feature centred at 1009 cm^{-1} is also discerned in the case of the samples with $n=8$ (inset of Fig. 4).

The presence of the 1032 cm^{-1} band in the FT-Raman spectra of di-amidosils with $n \geq 8$ confirms the occurrence of "free" anions [21]. We cannot, however, discard the contribution to the 1032 cm^{-1} band of the "cross-link separated ion pairs", as observed in analogue materials [24]. The shoulder found at 1025 cm^{-1} is tentatively associated with weakly coordinated triflate ions [24]. The 1009 cm^{-1} event is attributed to the formation of an ionic aggregate of unknown nature.

3.3. Photoluminescence features

Fig. 5 shows the emission spectra of the d-A(8)₁₀₀Eu(CF₃SO₃)₃ di-amidosil acquired at different excitation wavelengths. All the spectra are composed of a large broad band between 380 and 620 nm and a series of straight lines ascribed to Eu³⁺ intra-4f⁶ transitions between the ⁵D₀ excited state and the ⁷F₀₋₄ levels of the ground multiplet. The large broad band, already observed in the non-doped d-A(8) matrix [10], results from the overlap of two distinct emissions mediated by donor-acceptor pair transitions that occur within the amide cross-linkage [7,9] and within the siliceous skeleton, due to the presence of oxygen related defects, *O—O—Si≡(CO₂), a conclusion retrieved from electron paramagnetic resonance studies of the di-ureasils [9]. Upon increasing the excitation wavelength, the hybrid host emission deviates to the red, as already reported for d-A(8) [10] and for the non-doped di-ureasils [7–9,12] and di-urethanesils [7,9]. This effect was recently interpreted as radiative recombinations involving thermal relaxation within localized states, in the framework of the extended multiple trapping approach [25,26]. The Eu³⁺ ⁵D₀ → ⁷F₀₋₄ transitions, in particular, their energy, full width at half maximum and number of observed lines, are independent of the excitation wavelength, suggesting that at low salt concentration, all the Eu³⁺ ions occupy the same average local environment, a finding that corroborates the results derived from the above spectroscopic analysis (Section 3.2).

The inset in Fig. 5 depicts the excitation spectrum of d-A(8)₁₀₀Eu(CF₃SO₃)₃ monitored within the Eu³⁺ ⁵D₀ → ⁷F₂ transition. The spectrum exhibits a large broad band peaking at $\approx 335\text{ nm}$ and a series of straight lines ascribed to Eu³⁺ intra-4f⁶ transitions. On the basis of the assignment proposed for Eu(CF₃SO₃)₃-doped di-ureasil hybrids this broad band may be ascribed to intraconfigurational ligands-to-Eu³⁺ ligand-to-metal charge transfer (LMCT) [27,28].

4. Conclusions

The structure, thermal properties and photoluminescence features of a series of alkyl/siloxane hybrids incorporating Eu(CF₃SO₃)₃ were investigated. The hybrids are multi-wavelength emitters due to the convolution of the hybrid host emitting centers (amide cross-linkages and siliceous nanodomains) and the typical Eu³⁺ intra-4f⁶ ⁵D₀ → ⁷F₀₋₄ transitions. Photoluminescence data suggest that in the dilute di-amidosil ($n=100$) the Eu³⁺ ions occupy the same average chemical local environment, corroborating the results derived from the structural analysis.

Acknowledgements

This work was supported by Fundação para a Ciência e para a Tecnologia (FCT) (POCTI/P/CTM/46780/03). S.C. Nunes acknowledges FCT for a grant (SFRH/BD/13559/03) and J. Cybinska thanks the European Union Marie Curie Training Site Fellowship for funding the stay in the University of Aveiro and the Polish Committee for Scientific Research (Grant No. 3 T09A 024 26) for partial financial support.

References

- [1] C.J. Brinker, G.W. Scherer, *Sol-Gel Science, The Physics and Chemistry of Sol-Gel Processing*, Academic Press, San Diego, CA, 1990.
- [2] P. Gomez-Romero, C. Sanchez (Eds.), *Functional Hybrid Materials*, Wiley/Interscience, New York, 2003.
- [3] V. Bekiar, P. Lianos, *Chem. Mater.* 10 (1998) 3777.
- [4] Y. Uchida, Y.-I. Nobu, I. Momiji, K. Matsui, *J. Sol-Gel Sci. Technol.* 19 (2000) 705.
- [5] W.H. Green, K.P. Le, J. Grey, T.T. Au, M.J. Sailor, *Science* 276 (1997) 1826.
- [6] Y. Han, J. Lin, *J. Solid State Chem.* 171 (2003) 396.
- [7] L.D. Carlos, R.A. Sá Ferreira, V. de Zea Bermudez, S.J.L. Ribeiro, *Adv. Funct. Mater.* 11 (2) (2001) 111.
- [8] L. Fu, R.A. Sá Ferreira, N.J.O. Silva, L.D. Carlos, V. de Zea Bermudez, J. Rocha, *Chem. Mater.* 16 (2004) 1507.
- [9] L.D. Carlos, R.A. Sá Ferreira, R.N. Pereira, M. Assunção, V. de Zea Bermudez, *J. Phys. Chem. B* 108 (2004) 14924.

Table 1
Details of the synthesis of the d-A(8)_nEu(CF₃SO₃)₃ xrogels

d-A(8) _n Eu(CF ₃ SO ₃) ₃		
First step		
SC	1.000 mL	4.7 mmol
APTES	1.101 mL	4.7 mmol
Amberlyst resin	1.197 g	5.6 mmol
Py	0.0758 mL	0.94 mmol
THF	40 mL	
Second step		
CH ₃ COOH	1.093 mL	19.7
H ₂ O	0.169 mL, 10 mL	9.4
<i>n</i>	<i>m</i> (Eu(CF ₃ SO ₃) ₃)	
200	0.0197	
100	0.0395	
80	0.0494	
40	0.0987	
8	0.4937

Fig. 1. XRD diffractograms (a), DSC thermograms (b) of selected d-A(8)_nEu(CF₃SO₃)₃ di-amidosils.

Fig. 2. FT-Raman spectra of the d-A(8)_nEu(CF₃SO₃)₃ di-amidosils in the $\nu_s\text{CH}_2$ and $\nu_a\text{CH}_2$ regions.

Fig. 3. FT-IR spectra of the d-A(8)_nEu(CF₃SO₃)₃ di-amidosils in the amide I and amide II regions (a) and curve-fitting results (b).

Fig. 4. FT-Raman spectra of the d-A(8)_nEu(CF₃SO₃)₃ di-amidosils in the ν_s SO₃ region. The inset shows the curve-fitting results of representative samples.

Fig. 5. Emission spectra of the d-A(8)₁₀₀Eu(CF₃SO₃)₃ di-amidosil obtained under different excitation wavelengths: (1) 350 nm, (2) 395 nm and (3) 420 nm. The inset shows the excitation spectrum monitored around 617.5 nm.