Structure and photoluminescence of di-amidosil nanohybrids incorporating europium triflate


Abstract

The sol-gel process was used to prepare amorphous di-amide cross-linked alkylsiloxane hybrid materials (di-amidosil) incorporating europium triflate (Eu(Cl3)(SO4)3). Samples with 200 ≤ x ≤ 8 (where x is the molar ratio of carbonoyl oxygen atoms per Eu3+ ion) were studied. The conformations of the alkyl chains of the host matrix in the doped-di-amidosil (essentially glassy) are not affected by the presence of the salt. The Eu3+ ions bound to the ClO4− 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 x ≈ 8 an ionic aggregate of unknown nature is formed. The hybrids introduced are room temperature white light emitters due to the convolution of the host emitting centers (amide cross-links and silicon nanodots) and the Eu3+ 5D0 → 7F2 transitions. Photoluminescence data suggest that in the diluted di-amidosil with x = 100 the Eu3+ 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 aminepropylphosphonyloxycarbonyl-functional hybrid (35 ± 1%) [5]. Values of 20% of the intensity of the di-urea and di-urethane cross-linked poly(oxyethylene) (POE) silicate hybrid framework (di-ureasils and di-urethaneils, respectively) [7,8]. The di-amide cross-linked alkylsiloxane hybrid networks (di-amidosils) yield considerably lower quantum yields (5-10%) [10].

In the present work we will dope with Eu3+ 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 Eu3+ 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-urea and di-urethane systems, in which the host hybrid matrix provides two coordinating sites for the guest cations (the oxygen atoms of the POE chains and the carbonate oxygen atoms of the urea (NH=)(O)(N)=) and urethane (NH=)(O)(O)= cross-links, respectively), in the di-amidosil the only available coordinating sites are the carbonyl oxygen atoms of the amide (NH=)(O)=) cross-links.

2. Experimental

2.1. Materials

Etanol (CH3-OH, Merck), pyridine (95%, Aldrich) and tetrahydrofuran (THF, Merck) were stored over molecular sieves. Amberlite A-21 ion-exchange resin (Amberlite, 47 mg/ml, Aldrich) was washed with THF and stored in a mason jar at 60°C. Solvents of reagent grade (C6H5OH, CH3OH, C6H5NO2, C6H5Br, CH3Cl, CH3CN, CH3COOH, HCl, NaOH, NaHCO3, Na2SO3, K2CO3, H2SO4, HClO4, HNO3, H2O) were used.

2.2. Synthesis

The first step of the synthesis of the Eu3+-doped target samples, which involves the formation of the amidomethylhydroxysilane precursor (MAHPS), was performed as described [10]. In the second stage of the synthetic procedure, a solution of [Eu(THF)3Cl] in CH3Cl/CH3OH and water was added to the TBP solution of MAHPS (molar ratio [APEG]/[CH3Cl]/[CH3OH]/[H2O] = 0.4) to prepare the free ion. The resulting mixture was stirred in a sealed flask for 30 min and then cast to a Teflon mould, which was removed with paraffin 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 absorption d(λ, cm, Eu(III))= λ cm, λ cm, where λ is the number of methylene groups of the alkyl chain and cm) represent the initial ratio of carbonoyl oxygen atoms per cation.

Details of the preparation of the Eu3+-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 diffractometer using monochromated Cu Kα radiation (λ = 1.541 Å) over the 2θ range of between 4 and 70° at a resolution of 0.05°. The samples were studied as films and were not submitted to any thermal pre-treatment.

Differential scanning calorimetry (DSC) measurements were obtained with a DSC-1313 Shimadzu DSC. DSC sections were measured at approximately 10-20 K/min. The samples (2-3 mg) were scanned in an aluminium pan and a reference pan that was not loaded. The temperature was increased to 100°C at a heating rate of 10°C/min. The purge gas used in all experiments was high purity nitrogen (99.99%) at a rate of 30 cm3 min⁻¹.

Samples for thermogravimetric analysis (TGA) were transferred to open platinum crucibles and analyzed using a Stanton-Scintag TG/1000 thermobalance at a heating rate of 10°C/min using high purity N2 (99.99% purity) at a rate of 30 cm3 min⁻¹. The purge gas used in all experiments was high purity nitrogen (99.99%) at a rate of 30 cm3 min⁻¹.

Samples for photoluminescence analysis (PLA) were transferred to open platinum crucibles and analyzed using a Fluorolog 3 (F3) spectrophotometer. The samples were excited at room temperature with a 440-nm LED at a power of 1 W. The samples were placed in a vacuum chamber and measured at a resolution of 1 cm⁻¹. The fluorescence was detected using a People-2 (A2) spectrometer. The samples were excited at 405-nm LED at a power of 1 W. The samples were placed in a vacuum chamber and measured at a resolution of 1 cm⁻¹.

The samples were excited using a Tenor-Trans Raman (785-nm) laser, which was operated at a power of 1 W and a resolution of 1 cm⁻¹. The samples were placed in a vacuum chamber and measured at a resolution of 1 cm⁻¹.
To evaluate complex band FT-IR and FT-Raman envelopes and to identify individual spectral components, the reverse 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. All the successful deconvolutions were performed using a Gaussian shape. The standard errors of the curve-fitting procedure were less than 0.002. A linear baseline with a tolerance of 0.01% was employed.

The photoluminescence spectra were recorded at room temperature with a modulated double-grating excitation spectrophotometer with a TGRAS 300 emission monochromator (Horiba Jobin Yvon-Spex) coupled to a R2020A illuminator photomultiplier, using the front face acquisition mode. The excitation source was a 450 W Xe arc lamp. The emission spectra were corrected for detector and optical spectral response of the spectrophotometer and the excitation spectra were corrected for the spectral distribution of the lamp intensity using a photometric reference detector.

3. Results and discussion

3.1. Structure and thermal properties

The XRD patterns of the d-A(8)bEn(CF3)2SO2)2 di-amidosiloxane with n = 200 and 8, reproduced in Fig. 1a, exhibit a broad, Gaussian band centred at 20 = 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)bEn(CF3)2SO2)2 is attributed to the second-order of the peak at 20.8° (Fig. 1a). Structural unit distances of 4.3A 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 = d(20) / (A cos(θ)), where d and A, in radians, are the maximum intensity and integrated area of the peaks, respectively, and θ 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)bEn(CF3)2SO2)2 xerogels with n ≥ 20 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-amidosiloxane 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)bEn(CF3)2SO2)2 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 Eu2+ doped d-A(8)b hybrids we will examine the FT-Raman CH3 symmetric and asymmetric stretching (νCH3 and νsCH3, respectively) modes. To evaluate the strength of the hydrogen bonds established in the d-A(8)bEn(CF3)2SO2)2 xerogels we will inspect their FT-IR spectra in the amide I and amide II regions [15]. At last, to probe the surrounding experienced by the tritiate ions in the same set of samples at increasing salt content we will analyse the coordination-sensitive SO3 symmetric stretching (νSO3) mode.

3.2.1. Polymer chain conformations and state of disorder

The room-temperature FT-Raman spectra of selected d-A(8)bEn(CF3)2SO2)2 compounds in the νsCH3 and νasCH3 regions (3000-2800 cm⁻1) are represented in Fig. 2.

The FT-Raman νsCH3 region of the Eu2+ doped di-amidosiloxide hybrids with 200 ≥ n ≥ 8 exhibits two prominent bands centered at 2925 and 2890 cm⁻1 and a shoulder at 2875 cm⁻¹ (Fig. 2). The features at 2925 and 2857 cm⁻¹ are ascribed to the νsCH3 fundamental and to the Fermi resonance between the νsCH3 fundamental with the overtones of the CH3 bending vibrations, respectively, and are characteristic of discarded alky chains [14–16]. The intense 2890 cm⁻¹ event is associated with the νsCH3 stretching mode of alkyl chains in the amorphous state [14–16].

We may infer from these results that the alkyl chains of the di-amidosiloxide materials are fully disordered, as suggested by the XRD and DSC data discussed above, and adapt, as expected, essentially gauche conformations. Another conclusion retrieved from the analysis of the FT-Raman νsCH3 and νasCH3 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. Eu2+–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)bEn(CF3)2SO2)2 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

Comparisons 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 En(CF3)2SO2)2 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-amidosiloxane the Eu2+ 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 Eu2+ 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-amidosiloxide sample with n = 200 was resolved into six components at approximately 1758, 1756, 1715, 1672, 1650 and 1626 cm⁻¹ (Fig. 3b), already detected in the d-A(8)b material [10]. The 1758 cm⁻¹ feature is assigned to amide linkages whose N–H and C=O groups are non-bonded [10]. The 1756 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)bEn(CF3)2SO2)2 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 that those established in the more disordered 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 1584 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 II 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 νSO\(_3\) band profiles of representative zirconias are depicted in the inset of Fig. 4.

The νSO\(_3\) band of the FT-Raman spectra of the di-amidostilz studied was decomposed into two components: a band at 1032 cm\(^{-1}\), a weak shoulder around 1025 cm\(^{-1}\) (inset of Fig. 4). A very weak feature centered 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-amidostils with n≥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)\(_{30}\)Eu(CF\(_3\)SO\(_3\))\(_3\) di-amidostilz 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 Eu\(^{3+}\) intra-4f\(^0\) transitions between the 5D\(_0\) excited state and the 7F\(_{2}\) 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 siloxane skeleton, due to the presence of oxygen related defects, *O=O-Si=O(CO)\(_2\)*, a conclusion retrieved from electron paramagnetic resonance studies of the di-ureasils [7]. Upon increasing the excitation wavelength, the hybrid host emission deviates to the red, as already reported for d-A(6) [10] and for the non-doped di-ureasils [7,9,12] and d-urotsansilis [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 Eu\(^{3+}\) D\(_{0}\) → 7F\(_{4}\) 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 Eu\(^{3+}\) 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)\(_{30}\)Eu(CF\(_3\)SO\(_3\))\(_3\) monitored within the Eu\(^{3+}\) D\(_{0}\) → 7F\(_{2}\) transition. The spectrum exhibits a large broad band peaking at 335 nm and a series of straight lines ascribed to Eu\(^{3+}\) intra-4f\(^0\) transitions. On the basis of the assignment proposed for Eu(CF\(_3\)SO\(_3\))\(_3\)-doped di-ureasils hybrids this broad band may be ascribed to intracational ligands-to-Eu\(^{3+}\) ligand-to-metal charge transfer (LMCT) [27,28].

### 4. Conclusions

The structure, thermal properties and photoluminescence features of a series of alkyl/alkoxane hybrids containing Eu(CF\(_3\)SO\(_3\))\(_3\) were investigated. The hybrids are multi-wavelength emitters due to the convolution of the hybrid host emitting centers (amide cross-linkages and siloxane nanodomains) and the typical Eu\(^{3+}\) intra-4f\(^0\) transitions. Photoluminescence data suggest that in the di-amidostilz (n=100) the Eu\(^{3+}\) ions occupy the same average chemical local environment, corroborating the results derived from the structural analysis.

Acknowledgements

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References

Table 1
Details of the synthesis of the d-Ad(3,13,23,53,85,98)-i-pentadecafluorofuran xerogels

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<td></td>
<td></td>
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<td>4.7 mmol</td>
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<tr>
<td>SC</td>
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<tr>
<td>APTES</td>
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<td>1.197 g</td>
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<td>Amberlyst resin</td>
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<td>0.54 mmol</td>
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<td>THF</td>
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\( \text{ml} \text{[1H(135SO₃)]} \)

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<th>n</th>
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Fig. 1: XRD diffractograms (a), DSC thermograms (b) of selected d-Ad(3,13,23,53,85,98)-i-pentadecafluorofuran xerogels.

Fig. 2: FT-Raman spectra of the d-Ad(3,13,23,53,85,98)-i-pentadecafluorofuran xerogels in the \( \nu_1\text{CH}_2 \) and \( \nu_2\text{CH}_2 \) regions.
Fig. 3. FT-IR spectra of the d-A(d)Ba(C55)2O2: di-amidostil in the amide I and amide II regions (a) and curve-fitting results (b).

Fig. 4. FT-Raman spectra of the d-A(d)Ba(C55)2O2: di-amidostil in the \( \gamma _{SCy} \) region. The inset shows the curve-fitting results of representative samples.

Fig. 5. Emission spectra of the d-A(d)Ba(C55)2O2: di-amidostil obtained under different excitation wavelengths: (1) 390 nm, (2) 395 nm and (3) 400 nm. The inset shows the excitation spectrum monitored around 417.5 nm.