Coordination of Eu^{3+} Ions in Siliceous Nanohybrids Containing Short Polyether Chains and Bridging Urea Cross-links

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Infrared and photoluminescence spectroscopies have been used to investigate the local environment of the Eu^{3+} ions in luminescent sol−gel derived materials—*di-ureasils*—based on a hybrid framework represented by U(600). This host is composed of a siliceous backbone grafted, through urea cross-links, to both ends of polymer segments incorporating 8.5 oxyethylene repeat units. The active centers have been introduced as europium perchlorate, Eu(ClO$_4$)$_3$. Samples with compositions $n = 232, 62, 23, 12$, and 6 (where n denotes the ratio of (OCH$_2$CH$_2$) moieties per lanthanide ion) have been examined. The combination of the information retrieved from the analysis of characteristic bands of the FTIR spectra—the perchlorate and the Amide I/Amide II features—with that obtained from the photoluminescence data demonstrates that at compositions $n = 232$ and 62 the anions are free, whereas the Eu^{3+} ions are complexed by the heteroatoms of the polyether chains. At higher salt concentration, the cations are bonded, not only to the ClO$_4^-$ ions, but also to the ether oxygen atoms of the organic segments and to the carbonyl oxygen atoms of the urea linkages. The dual behavior of U(600) with respect to cation coordination has been attributed to the presence in this nanohybrid of strong hydrogen-bonded urea−urea structures, which, at low salt content, cannot be disrupted, thus inhibiting the formation of Eu$^{3+\cdots}$O=C(urea) contacts and promoting the interaction between the lanthanide ions and the (OCH$_2$CH$_2$) moieties. The present work substantiates the claim that the activation of the coordinating sites of the di-ureasil framework can be tuned by varying either the guest salt concentration at constant chain length or the length of the organic segments at constant salt concentration. This relevant property opens challenging new prospects in the fields of application of this class of hybrids.

Introduction

In recent years the combination of the rich silicon chemistry (in particular, the sol−gel route) with the host−guest concept, which is known to govern the formation of polymer electrolytes,[1−3] has successfully led to the production of a significant number of innovative organic/inorganic frameworks with tunable design and suitable characteristics.[4] The conjunction of the appropriate processing conditions with the adequate choice of the organic and inorganic components primarily determines the morphology, molecular structure, and properties of the xerogels. The major driving force behind the intense activity in this expanding area of research of materials science is undoubtedly the possibility of developing nanoscale systems with a variety of features that cannot be normally found in conventional macroscale composites or in traditional materials. The scope of application of nanohybrids is extraordinary, as they may find use in domains as diverse as electrochemistry, biology, mechanics, ceramics, electronics, and optics.[4]

The hybrid approach is particularly well adapted for the production of advanced materials for solid state lasers, phos-phors, displays, and optical amplifiers. The main strategy is to create a suitable organic/inorganic cage capable of encapsulating the luminescent centers, protecting them from deleterious quenching processes. In addition, an enhancement of light absorption through the so-called "antenna effects" brought about by the host structure itself is also desired. Among the various systems that have been proposed, mention must be made of the family of extremely versatile composite compounds that were first reported at the end of the past decade.[5−18] Their synthesis involves the introduction of Eu^{3+} [5−17] or Tb^{3+} [18] ions into a hybrid matrix initially employed for the preparation of basic proton conducting ormolytes (organically modified silicate electrolytes)[19] (see Scheme 1). The active lanthanide constituents have been incorporated as perchlorate,[5] triflate,[6−17] or nitrate[18] salts (Eu(ClO$_4$)$_3$, Eu(CF$_3$SO$_3$)$_3$, or Tb(NO$_3$)$_3$, respectively). The sol−gel derived host network, termed *di-ureasil*[19] and repre-sented by U(Y) (with Y = 2000, 900, and 600), where U represents the urea group and Y denotes the average molecular weight of the organic precursor used, comprises polyether-based chains of variable length covalently bonded on both ends to a siliceous backbone through urea functionalities

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($-$NHC($=$O)NH$-$). The di-ureasils display several remarkable properties. These xerogels may be easily produced as thin, elastomeric, and highly transparent monoliths, thermally stable up to 220 °C.[6,7,12,14] The use of the ormolyte structure is beneficial from the electrochemical standpoint. As the di-ureasils are essentially amorphous (a necessary condition for ion transport), the levels of conductivity observed[6,7,12,14] are very similar to those exhibited by the corresponding classical polyether-based electrolytes.[20] Unlike the latter systems, the di-ureasils offer the advantage of being able to accommodate considerably larger amounts of guest salt, thus preventing the "salting out" phenomenum to occur. However, it is unquestionably in the field of optics that these urea cross-linked silicates will presumably find application, since they display quite outstanding optical features. We have demonstrated that, apart from being white-light emitters,[6,7,13,15,17] the color emitted by the Eu^{3+}-doped di-ureasils may be readily tuned across the CIE (Commission Internationale d'Éclairage) chromaticity diagram by varying either the salt concentration or the excitation wavelength.[13,15,16]

A series of systematic anomalies detected in the infrared and photoluminescence spectra of the Eu(CF$_3$SO$_3$)$_3$-doped di-ureasils as salt concentration is increased provide strong evidence that the unique physicochemical behavior exhibited by these compounds is intimately associated with the cation coordinating ability of the hybrid matrix.[11-13,15] We have shown that in the U(2000))-based materials, which contain polymer segments with approximately 40.5 oxyethylene repeat units, the lanthanide cations prefer to bond to the oxygen atoms of the urea carbonyl groups rather than to the oxygen atoms of the polyether chains.[11-13,15] The picture just described remains valid as long as the saturation of the urea coordinating sites is not attained, a situation that only occurs when the composition n is 20 (where n is the ratio of (OCH$_2$CH$_2$) units per Eu^{3+} ion), meaning that at this salt concentration the number of available cross-links per lanthanide cation will be 1 (i.e, $n' = 1$, where n' is the ratio of Si atoms per Eu^{3+} ion).[12,15] At higher salt concentration, as no carbonyl groups are left free, the ether oxygen atoms of the polymer segments will ensure the complexation of the additional lanthanide ions. A high-melting stoichiometric crystalline complex is very likely formed at n around 5.[12]

The tunability of the coordination process in these long chain di-ureasils through the control of the guest salt concentration is extremely attractive, both from the fundamental and technological standpoints. The study of analogue materials possessing shorter polyether segments appears thus essential, since it is uncertain at this stage if the length of the organic moieties influences in any way the quite unusual cation complexation process detected in the U(2000)$_n$Eu(CF$_3$SO$_3$)$_3$ family. The major consequence that is expected to result from the inclusion of shorter polymer chains in the di-ureasil-type structure is the formation of a hybrid framework with a greater number of cross-links. In practice, this effect results primarily in a shift of the urea saturation composition to higher salt content.

In the present paper we will use infrared and photoluminescence spectroscopic techniques to determine the chemical species that belong to the Eu^{3+} coordination sphere in five U(600)-based xerogel compounds with compositions ranging from $n = \infty$ to 6. As this host contains polyether chains with about 8.5 (OCH$_2$CH$_2$) repeat units, the condition $n' = 1$ corresponds to a composition n around 4.

We have introduced the Eu^{3+} luminescent centers into U(600) as Eu(ClO$_4$)$_3$, because, although it is widely recognized as potentially dangerous and therefore commercially uninteresting,

ClO$_4^-$ is an excellent ion probe with characteristic internal vibrational modes that are easily detected in both the infrared and Raman spectra. A significant number of in-depth infrared and/or Raman spectroscopic works dealing with the investigation of the local environment around the cations in complexes of alkali metal salts and several host polymers using ClO$_4^-$ as counterion have been reported.[21-28]

In the FTIR analysis of the nearest-neighbor interactions of the cations in the U(600)-based xerogels, we will also examine the CO stretching, νCO, region of the doped di-ureasils, seeking spectral modifications indicative of changes undergone by the organic segments upon incorporation of Eu(ClO$_4$)$_3$. The solvation of the cations by the heteroatoms of the (OCH$_2$CH$_2$) repeat units of the polymer chains may be directly evaluated in this range of frequencies, since the prominent band ascribed to the CO stretching vibration of uncomplexed polyether moieties is known to undergo a shift to lower wavenumbers upon bonding of the ether oxygen atoms to the cations.[29-31]

We have recently reported that the amide I and amide II bands[32]—a pair of spectral events produced by the urea cross-links—yield extremely rich information, not only about the process of cation complexation in the di-ureasils,[11,12] but also about the extent and strength of hydrogen bonding throughout the materials.[8,11,12,33] We will therefore try to assess how the amide I and amide II regions of U(600) are modified as a result of the addition of increasing amounts of the guest perchlorate salt. The ultimate goal of such a study will be obviously to conclude if the urea linkages do play any active role in the coordination of the Eu^{3+} ions.

Experimental Section

Synthesis. All the chemicals used in the synthesis procedure described below were purchased from Fluka and Aldrich. The Eu^{3+}-doped di-ureasil xerogels studied are based on a hybrid host matrix containing short (CH$_2$CH$_2$O)-based polymer chains whose ends are grafted to a siliceous network by means of urea linkages. The cross-links between the organic and the inorganic components were formed by reacting the NH$_2$ groups of a diamine (chemically α,ω-diaminepoly(oxyethylene-*co*-oxypropylene) and commercially Jeffamine-ED600), the general formula of which is given in Scheme 1, with the $-$N$=$C$=$O group of 3-isocyanatepropyltriethoxysilane, ICPTES, in tetrahydrofuran, THF, under reflux at 80 °C for 6 h. The precursor of U(600) (termed ureapropyltriethoxysilane, UPTES) was isolated after evaporating the solvent (Scheme 1). Ammonium fluoride, NH$_4$F, dissolved in ethanol, was then added to UPTES to catalyze the hydrolysis reaction of the alkoxy groups. A volume of 0.2 mL of an aqueous solution of Eu(ClO$_4$)$_3$ was also added with stirring. A clear monolithic wet gel was produced within 4 h. Ethanol and water were slowly removed at 50 °C and a rubbery and transparent film was obtained. Samples with $n = $ 232, 62, 23, 12, and 6 were prepared. The doped ureasils have been identified by the designation U(600)$_n$Eu-(ClO$_4$)$_3$, where U originates from the word "urea", 600 indicates the average molecular weight of the diamine used, and $n = $ O/Eu represents the ratio of (OCH$_2$CH$_2$) monomer units per Eu^{3+} ion. An undoped sample ($n = \infty$) was also produced.

Infrared Spectroscopy. Mid-infrared spectra were acquired at room temperature with a FTIR Perkin-Elmer spectrometer Spectrum 2000 system. The spectra were collected over the range 4000$-$400 cm^{-1} by averaging 32 scans at a maximum resolution of 4 cm^{-1}. Solid samples (2 mg) were finely ground and analyzed by dispersing them in approximately 175 mg of dried spectroscopic grade potassium bromide (KBr, Merck) by
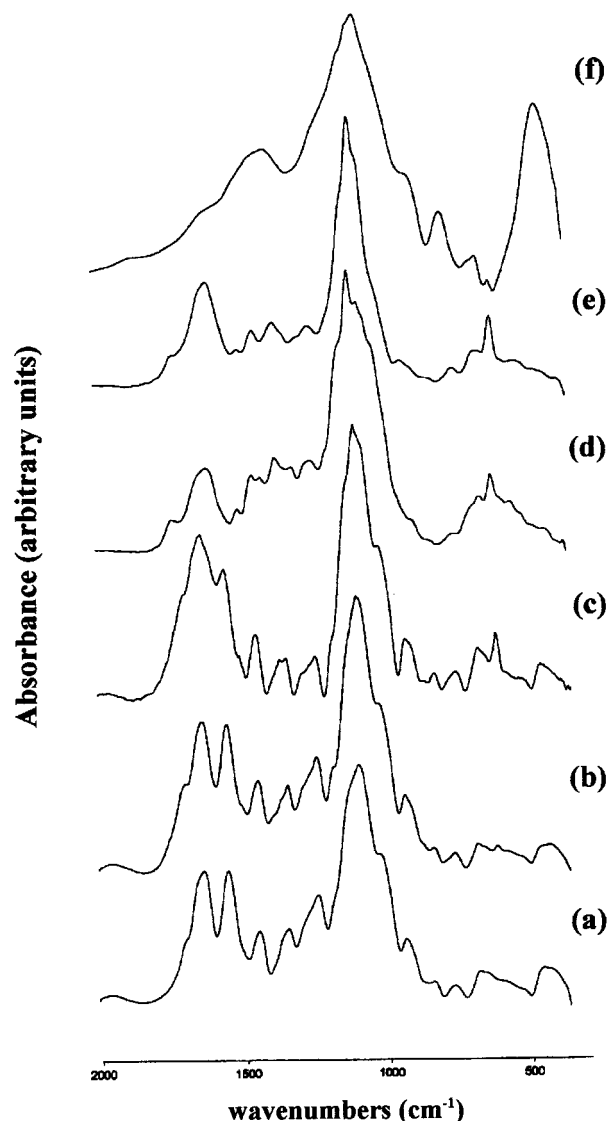
SCHEME 1: Synthesis of the Di-ureasil U(600)

the pressed-disk technique. A linear baseline was assumed in all cases in the frequency ranges where no significant absorptions were detected. To evaluate complex band envelopes and to identify underlying component bands of the spectra, the iterative least-squares curve-fitting procedure in the Peakfit[34] software was used extensively throughout this study. The best fit of the experimental data were obtained by varying the frequency, bandwidth, and intensity of the bands. Gaussian band shapes were employed. Prior to recording the spectra under ambient conditions, the disks were introduced in a desiccator over phosphorus pentoxide for at least 12 h at room temperature in order to reduce the levels of adsorbed water.

Photoluminescence Spectroscopy. The photoluminescence spectra were recorded at 14 K using a 0.25-m excitation KRATOS GM-252 monochromator and a 1-m 1704 SPEX Czerny-Turner spectrometer coupled to a Hamamatsu R928 photomultiplier. The luminescence was excited by a 300-W xenon arc lamp. The spectra were corrected for the detection spectral response.

Results and Discussion

Infrared Spectroscopy. *Bands Produced by the Perchlorate Ions.* An unperturbed ClO_4^- ion has tetrahedral (T_d) symmetry. The representation of the nine vibrational modes is $A_1 + E + 2T_2$. In dilute solutions four fundamental frequencies (ν_1, ν_2, ν_3, and ν_4) result, respectively, at about 935, 462, 1102, and 628 cm^{-1} in the Raman spectra.[35] While two of them—ν_1 (nondegenerate symmetric stretching vibration) and ν_2 (doubly degenerate deformation vibration)—are infrared inactive, the other two—ν_3 (triply degenerate asymmetric stretching vibration) and ν_4 (triply degenerate deformation vibration)—are both

infrared and Raman active. A free ClO_4^- ion has a very simple infrared spectrum with an intense ν_3 band located at approximately 1110 cm^{-1} and a much weaker ν_4 singlet near 620 cm^{-1}.[36]

Upon coordination to a metal cation, the symmetry environment of the ClO_4^- ion is significantly affected. As a consequence of the formation of associated species (solvent-separated ion pairs, contact ions pairs, or ion aggregates), the normally forbidden ν_1 and ν_2 bands appear in the infrared spectra.[37,38a,b,42] In addition, the infrared-allowed ν_3 and ν_4 events undergo a frequency shift and specially a splitting, which originates from the removal of the degeneracy from the E and T_2 modes.[37−42] The magnitude of the shift or separation depends on the strength of the interaction. Both spectral modifications are suitable tools to differenciate between unidentate and bidentate (or "bidentate-like") cation−anion association.[36,41−43]

The ν_3 and ν_4 bands of the infrared spectrum of a coordinated ClO_4^- ion usually display structure. In most solid perchlorates the ν_3 bands are separated by as much as 60 cm^{-1}.[35] The spacing between the most separated components of the ν_4 triplet is considerably less important (e.g., 44 cm^{-1} for anhydrous LiClO$_4$[42]). In general, the activated infrared-forbidden ν_1 and ν_2 modes of ClO_4^- give rise to weak features: a singlet near 950 cm^{-1} and a singlet or a structured band located at about 460 cm^{-1}, respectively.[36]

It may be readily inferred from the analysis of the spectra of the undoped and doped di-ureasils reproduced in Figure 1 that there is considerable overlapping of the perchlorate and polymer absorption bands: (1) the weak ν_1 band is expected at exactly the same wavenumber where the polyether chains of U(600) absorb weakly owing to the vibration of the CC stretching and CH$_2$ rocking modes;[8] (2) the weak ν_2 band(s) is (are) found in a region that comprises several weak and broad features attributed to the COC and CCO bending vibrations of the polymer backbone;[8] (3) the strong $\nu_3(ClO_4^-)$ band(s) is (are) situated between 1200 and 1000 cm^{-1},[36] the same range of frequencies where the most intense absorption band of the polymer chains of U(600) appears. This region includes a shoulder at 1151 cm^{-1}, originated from the coupling of the CO stretching and CH$_2$ rocking vibrations, a very strong feature near 1110 cm^{-1}, assigned to the CO stretching vibration, and a medium intensity peak at about 1037 cm^{-1}, associated with a mixture of CC and CO stretching and CH$_2$ rocking vibrations.[8] The spectral region characteristic of the deformation vibration of ClO_4^- (i.e., $\nu_4(T_2)$) is therefore the only one that allows us to inspect the chemical surrounding of the anion in the di-ureasil compounds.

Figure 2b and Table 1 show that in the range of wavenumbers between 800 and 500 cm^{-1} the most noticeable change that results from the addition of Eu(ClO$_4$)$_3$ to U(600) for a composition *n* of 232 is the presence of a single, weak band centered at 624 cm^{-1}. In the spectrum of the U(600)$_{62}$Eu(ClO$_4$)$_3$ xerogel, this event becomes stronger and is shifted to about 628 cm^{-1} (Figure 2c, Table 1). In the spectra of the more concentrated compounds, the 624 cm^{-1} band is no longer seen and a feature of medium intensity situated near 630 cm^{-1} appears instead (Figures 2d−f, Table 1). In the case of the U(600)-based di-ureasils with *n* = 23 and 12 the latter band emerges from a broad envelope composed by a series of less intense components (Figure 2d,e, Table 1).

Salomon et al.[26] have reported the existence of a pair of bands at 623 and 635 cm^{-1} in the $\nu_4(ClO_4^-)$ envelope of the infrared

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Figure 1. Room-temperature mid-infrared spectra of U(600)$_n$Eu(ClO$_4$)$_3$ di-ureasils in the 2000−400 cm^{-1} region: (a) $n = \infty$; (b) $n = 232$; (c) $n = 62$; (d) $n = 23$; (e) $n = 12$, and (f) $n = 6$.

spectra of the LiClO$_4$-poly(ethylene oxide) dimethyl ether (average molar mass 400) and LiClO$_4$-poly(ethylene oxide) diglycol (average molar mass 400) systems. These spectral events have been assigned to "spectroscopically free" ClO$_4$⁻ and to bound ClO$_4$⁻, respectively.[26] According to the same authors, the designation "spectroscopically free" ClO$_4$⁻ ion stands for solvent-separated ion-pairs Li⁺···ClO$_4$⁻ and solvent-separated dimers. Bound ClO$_4$⁻ ions will consist mainly of contact pairs, although the contribution of some contact dimers cannot be excluded.[26] Wieczorek et al.[28] have also observed two features in the ν_4 region of the infrared spectra of composite polymeric electrolytes made of polyether, poly(*N,N*-dimethyl-acrylamide), and LiClO$_4$: a band with a maximum at 620−623 cm^{-1} and a shoulder centered between 630 and 635 cm^{-1}. It should be finally referred that the infrared spectra of nine of the 11 solid perchlorates recorded by Ross[35] exhibit three split ν_4 bands at about 625−628, 628−637, and 637−641 cm^{-1}.

On the basis of the attribution proposed by Salomon et al.[26] and on the observations of Ross,[35] we ascribe the band seen at 624 and 628 cm^{-1} in the spectra of U(600)$_{232}$Eu(ClO$_4$)$_3$ and U(600)$_{62}$Eu(ClO$_4$)$_3$, respectively, to the presence of "spectroscopically free" ClO$_4$⁻ ions. Correspondingly, the absence of this feature and the growth of a group of new bands in the ν_4-
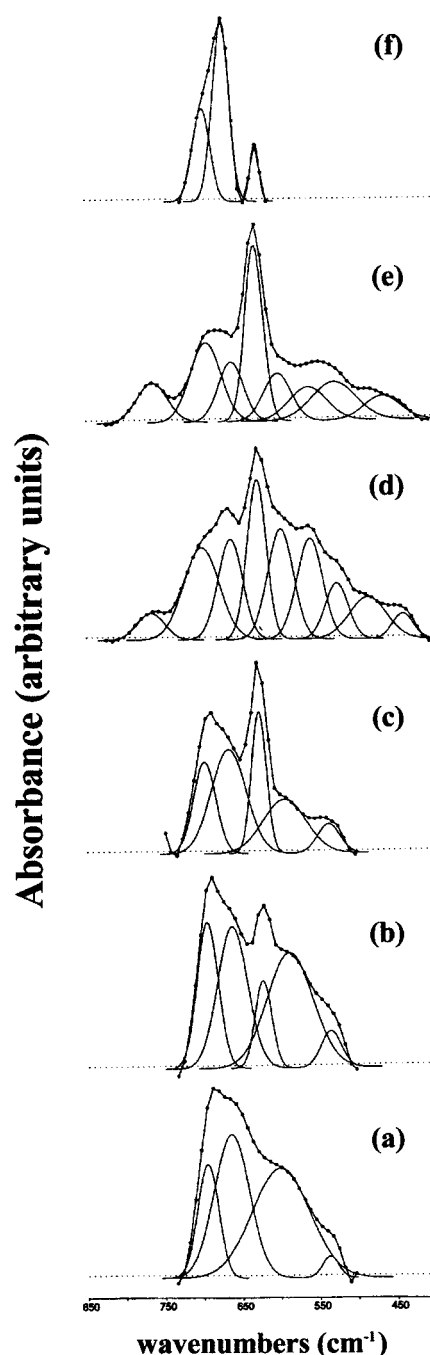
Figure 2. Curve-fitting results of the ν_4(ClO$_4$⁻) region of U(600)$_n$Eu-(ClO$_4$)$_3$ di-ureasils: (a) $n = \infty$; (b) $n = 232$; (c) $n = 62$; (d) $n = 23$; (e) $n = 12$, and (f) $n = 6$.

(T$_2$) spectral region of the samples with n lower than 62 unequivocally suggest that the anions are strongly perturbed via coordination to the cations, presumably forming contact ion pairs.

The complexity of the ν_4 region of the U(600)-based di-ureasils investigated in the present work renders the attribution of the various components determined through curve-fitting extremely difficult. Nevertheless, we feel tempted to draw some conclusions regarding the spectrum reproduced in Figure 2d. This spectrum illustrates very clearly that the most distinct events of the ν_4 band contour of U(600)$_{23}$Eu(ClO$_4$)$_3$ are situated near 664, 630, and 560 cm^{-1} (Table 1). Comparison of this result with that obtained by Leong et al.[42] for anhydrous solid LiClO$_4$ is useful. The remarkable coincidence found between the band frequencies of this perchlorate salt (664, 630, and 620

TABLE 1: Curve-Fitting Results of the $\nu_4(ClO_4^-)$ Region of the U(600)$_n$Eu(ClO$_4$)$_3$ Di-ureasils[a]

n	∞[8]	232	62	23	12	6	LiClO$_4$ [42]	attribution
				765w	764w			} b
			698 w	702 sh	694 sh	694 sh		
	696 sh	697 w						amide V[8]
			668 sh		672 sh			b
	666 wb	665 sh						c
				664 m	662 m		664	} $\nu_4(\mathbf{F_2})$
				630 m	631 m	630 m	630	
		624 w	628 m					
						620		
	602 sh	590 sh	595 sh	600 sh	601 sh			c
				560 m	562 m			$\nu_4(\mathbf{F_2})$
	538 sh	537 sh	538sh					COC/CCo bending[8]
				525 sh	528 sh			b

[a] Frequencies in cm^{-1}; m − medium, w − weak, sh − shoulder. [b] Nonassigned perchlorate bands. [c] Minor nonassigned polymer bands.

cm^{-1} [42]) and those of the hybrid sample with $n = 23$ induces us to propose that the three bands observed in the latter material result from the removal of degeneracy of the $\nu_4(T_2)$ mode. The extremely large spread of the triplet in this U(600)-based compound (about 104 cm^{-1}) versus that detected in LiClO$_4$ (44 cm^{-1} [42]) supports the argument that the cation−anion interactions are significantly stronger in this di-ureasil than in crystalline LiClO$_4$. This aspect derives very likely from the fact that the charge to ionic radius ratio of Eu^{3+} and Li$^+$ are equal to 3.16 and 1.11 Å^{-1},[44] respectively. Furthermore, the presence of the three components in the ν_4 region of the U(600)$_{23}$Eu(ClO$_4$)$_3$ nanohybrid may be tentatively interpreted as an indication that the perchlorate ion coordinates to the lanthanide ions along a bidentate or bidentate-like configuration.[36] The same arguments may obviously be extended to the sample with composition $n = 12$. However, these claims should be looked at with extreme care, since the origin of the other components observed in the spectral region under analysis remains unknown (Table 1).

Bands Produced by the Urea Cross-links. Valuable information regarding hydrogen bonding in the U(600)$_n$Eu(ClO$_4$)$_3$ samples may be gained from the analysis of the spectral signature of this family of nanohybrids in the amide I and amide II spectral regions. The coordination of the lanthanide ions to the carbonyl oxygen atoms of the urea linkages may be evidently also assessed in this range of frequencies.

In the di-ureasils the individual components found within the broad amide I envelope reflect the presence of hydrogen-bonded structures involving the interaction between the NH moieties of the urea linkages and the carbonyl oxygen atom of a neighbor urea group or the ether oxygen atoms of the polymer segments.[8] U(600) produces three isolated components at 1715, 1671, and 1641 cm^{-1} in the amide I region.[8] Owing to the extremely high number of urea moieties present in this hybrid, the formation of strong, ordered self-associated urea−urea associations dominates, producing the intense component observed at 1641 cm^{-1}.[8] The other two components of the Amide I band of U(600) have been assigned to the formation of a minor number of less ordered urea-polyether associations.[8] These results suggest that neither C=O nor N−H groups are left free in the material.[8] The amide II region of U(600) displays a single intense feature at 1565 cm^{-1}.[8]

The main objective of this section will be to get a better insight into the coordination processes that occur in the U(600)$_n$Eu(ClO$_4$)$_3$ xerogels within the range of salt composition examined. With this goal in mind, we will combine the relevant spectroscopic information gained from the study of the $\nu_4(T_2)$ region described above with the conclusions derived from the analysis of the amide I and amide II bands. In the discussion

that follows we will be particularly interested in evaluating the influence that the incorporation of increasing amounts of guest lanthanide salt has on the three hydrogen-bonded structures found in U(600). For the sake of clarity, we will complement the interpretation of the spectral data with a series of schematic drawings that tentatively represent the various associations formed in the materials.[33g,l] Previous studies[45] indicate that the urea−urea hydrogen-bonded structures of U(600) may be satisfactory represented by the aggregate shown in Scheme 2A. The exact nature of the two urea−polyether hydrogen-bonded associations which exist in the U(600) framework in a much lower proportion is, however, unknown. Based on the scheme association of urethane groups proposed by Zharkov et al.[33g] for polyether urethane elastomers, we will assume in the present work that the aggregates depicted in Scheme 2B,C correspond to the structures that produce the bands at 1671 and 1715 cm^{-1}, respectively.

Close inspection of the 1850−1450 cm^{-1} region of the spectra of the U(600)$_n$Eu(ClO$_4$)$_3$ compounds depicted in Figure 3 provides unambiguous evidence that in samples with n lower than 62 (Figure 3d,e, Table 2) the amide I and amide II bands of the undoped hybrid host (Figure 3a, Table 2) are greatly affected by the introduction of guest salt.

The examination of the spectrum of the most dilute hybrid reveals that the amide bands of U(600) remain completely unchanged in the presence of the lanthanide salt at this particular composition (Figure 3b, Table 2). This spectral finding of the utmost importance implies that the urea linkages of U(600)$_{232}$Eu-(ClO$_4$)$_3$ are definitely not involved in the coordination of the Eu^{3+} ions. This in turn unequivocally suggests that the ether oxygen atoms of the polymer chains of the organic segments must be solely responsible for the presence of the "spectroscopically free" ClO$_4^-$ ions. The new shoulder evident at approximately 1762 cm^{-1} in the spectrum of U(600)$_{232}$Eu(ClO$_4$)$_3$ (Figure 3b, Table 2) substantiates this explanation. Because of its extremely high frequency and low intensity, we ascribe this feature to the occurrence in the material of a minor number of non-hydrogen-bonded urea groups (Scheme 2D).[8] The existence of noninteracting cross-links in this poor-salt xerogel results very likely from the destruction of some urea−polyether hydrogen-bonded structures, such as those illustrated in Scheme 2B,C, meaning that the formation of each Eu^{3+}−ether oxygen atom coordinate bond leads to the disruption of the hydrogen bonds between that ether oxygen atom and the urea NH moieties.[33l] Normally one would immediately try to find further support to these claims in the νCO spectral region. Unfortunately, as already mentioned above, any conclusions regarding this range of frequencies are subject to much uncertainty due to extensive overlapping of the perchlorate and polymer bands.

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SCHEME 2: Tentative Representation of the Hydrogen-Bonded Associations Present in the U(600)ₙEu(ClO₄)₃ Di-ureasils, Where R and R′ Represent the Organic and Inorganic Components of the Hybrid Structure

(A)   (B)   (C)   (D)
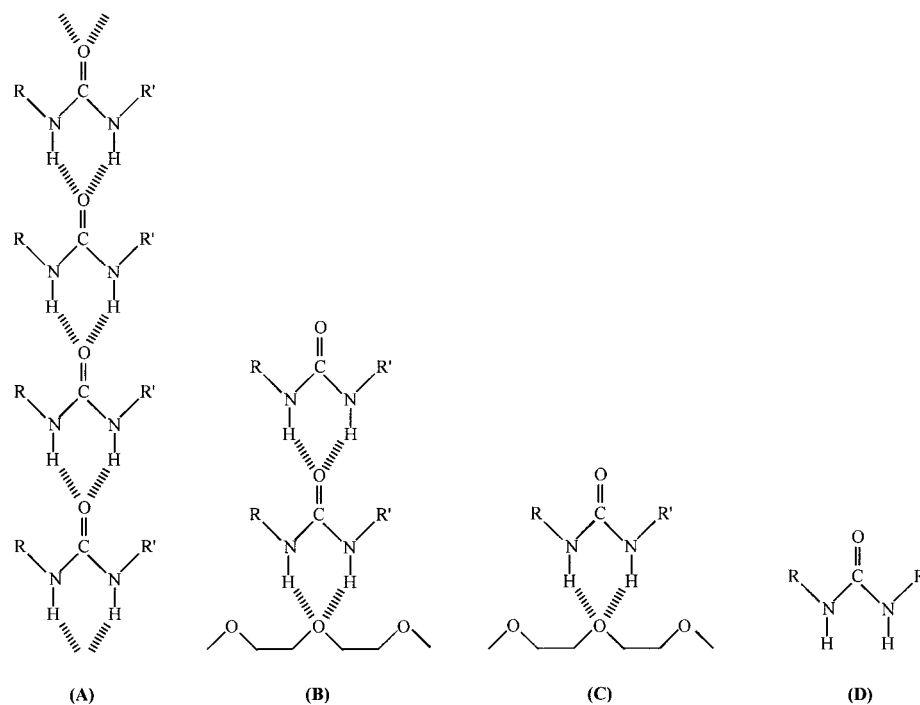
It is crucial to stress at this stage that the behavior of U(600)$_{232}$Eu(ClO$_4$)$_3$ is totally opposed to that of the corresponding U(2000)-based analogue. In the latter di-ureasil, at about the same concentration ($n = 200$), the cations are preferentially coordinated to the urea cross-links, rather than to the oxygen atoms of the oxyethylene moieties.[11,12] We propose that these facts must be intimately related to the type and strength of the associations formed via hydrogen bonding in each of the two hybrid frameworks. As the formation of strongly hydrogen-bonded urea−urea associations is favored in U(600) (Scheme 2A), whereas non-hydrogen-bonded urea groups dominate in U(2000) (Scheme 2D), it seems thus pertinent to expect that the disruption by the cations of the ordered urea−urea associations which exist in a majoritary proportion in the former xerogel must be rather difficult when $n = 232$. As a consequence, at this low salt concentration, a competition visibly arises between the lanthanide ions and the hydrogen bonds for interaction with the urea cross-links.

At $n = 62$ the main modifications detected within the same range of frequencies are the shift of the intense 1641 cm^{-1} feature to 1626 cm^{-1} and the presence of a new, weak band at 1515 cm^{-1} (Figure 3c, Table 2). Both findings mean that at this salt content, while most of the urea linkages keep on interacting with the polymer segments to form hydrogen-bonded structures presumably similar to B and C of Scheme 2, a few Eu^{3+} ions start already to be successful in breaking some hydrogen bonds of the urea−urea network of U(600) (Scheme 2A). Under such conditions, the free carbonyl oxygen atoms which originate from this process coordinate to the cations, forming structures probably involving short Eu$^{3+\cdots}$O=C(urea) contact distances. Thus Eu^{3+}−(urea)$_x$ associations (with x greater than 1) are thought to be responsible for the downshift of the 1641 cm^{-1} band. The appearance of the 1515 cm^{-1} feature in the amide II region of U(600)$_{62}$Eu(ClO$_4$)$_3$ is consistent with the presence of weaker hydrogen-bonded urea−urea structures in the material.[8] Free cross-links—produced by the breakdown of some urea−polyether aggregates—must again be responsible for the component discerned at 1759 cm^{-1}.

The contribution of the urea carbonyl oxygen atoms to the coordination shell of the lanthanide ions is unequivocally detected in the rich-salt samples (Figure 3d,e, Table 2). The interaction between the Eu^{3+} ions and the C=O moieties is accompanied by a dramatic downshift of the 1626 cm^{-1} band of U(600)$_{62}$Eu(ClO$_4$)$_3$ (Table 2) to 1602 and 1606 cm^{-1} respectively for U(600)$_{23}$Eu(ClO$_4$)$_3$ and U(600)$_{12}$Eu(ClO$_4$)$_3$ (Table 2). These spectral changes support the argument that at high doping levels a very significant number of strong Eu$^{3+\cdots}$O=C(urea) bonds are created. In the amide II region of the xerogels with $n = 23$ and 12 (Figures 3d,e, Table 2) the prominent amide II event situated near 1563 cm^{-1} in the spectra of the less concentrated materials (Figure 3b,c, Table 2) is no longer seen and a weak single band appears respectively at 1506 and 1511 cm^{-1} (Figure 3d,e, Table 2). As noted above, U(600)$_{62}$Eu(ClO$_4$)$_3$ also produces this feature (Figure 3c, Table 2). The latter results indicate not only that the hydrogen bonds associations of U(600)$_{23}$Eu(ClO$_4$)$_3$ and U(600)$_{12}$Eu(ClO$_4$)$_3$ are considerably weaker than those present in U(600)[8] but also that their concentration is much lower. Another important effect discerned in the spectra of the salt-rich U(600)-based materials is the disappearance of the pair of shoulders of the undoped host, ascribed to the presence of hydrogen-bonded urea−polyether associations, located at 1713 and 1673 cm^{-1} (Table 2). In the spectra of the xerogels with $n = 23$ and 12 the event at higher frequency is transformed into a weak band situated at approximately 1736 and 1733 cm^{-1}, respectively (Table 2), whereas the 1673 cm^{-1} feature undergoes a marked shift to 1651 and 1653 cm^{-1}, respectively (Table 2). These relevant data represent unmistakable proofs that agree with the claim that the hydrogen-bonded urea−polyether structures of the hybrid host are deeply disturbed at high salt content. The band around 1652 cm^{-1} very likely originates from the coordination of lanthanide ions to the carbonyl oxygen atoms of structures similar to B of Scheme 2. An aggregate loser than C (Scheme 2), presumably not involving bonding to the lanthanide ions, must yield the event located around 1735 cm^{-1}. This aspect is
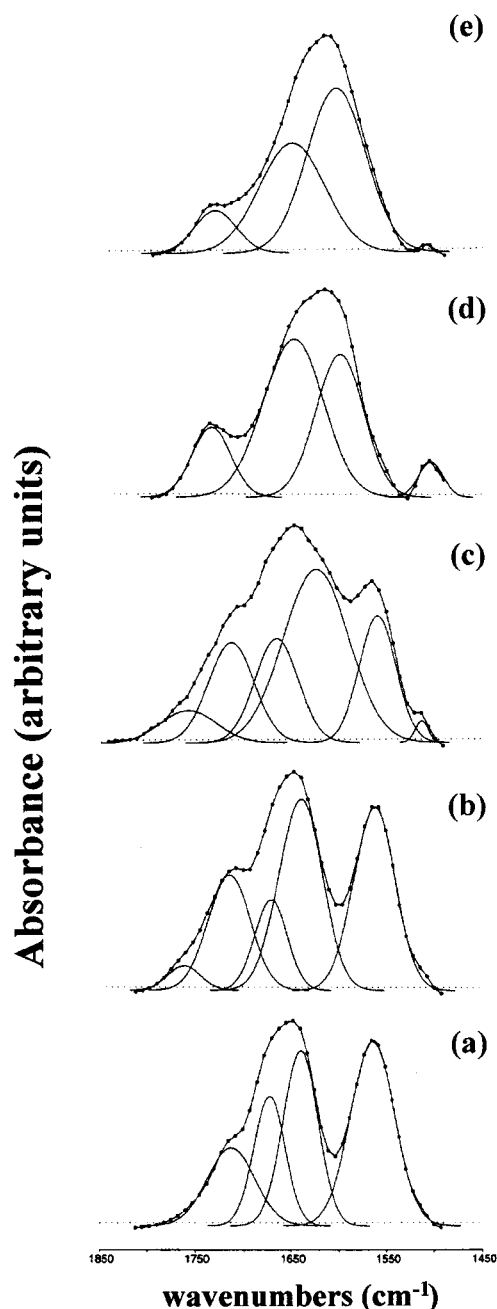
Figure 3. Curve-fitting results of the amide I and amide II regions of the U(600)$_n$Eu(ClO$_4$)$_3$ di-ureasils: (a) $n = \infty$; (b) $n = 232$; (c) $n = 62$; (d) $n = 23$, and (e) $n = 12$.

TABLE 2: Curve-Fitting Results of the Amide I and Amide II Regions of the U(600)$_n$Eu(ClO$_4$)$_3$ Di-ureasils[a]

n	∞	232	62	23	12	attribution[8]
		1762 sh	1759 sh			
				1736 w	1733 w	
	1713 sh	1715 sh	1715 sh			
	1673 sh	1672 sh	1667 sh			amide I
				1651 sh	1653 sh	
	1641 s	1641 s				
			1626 s			
				1602 m	1606 m	
	1565 s	1564 s	1561 s			amide II
			1515 w	1506 w	1511 w	

[a] Frequencies in cm^{-1}; s − strong, m − medium, w − weak, sh − shoulder.

fundamental, since it confirms that the saturation of the urea linkages is not attained, as predicted, at compositions above 4.
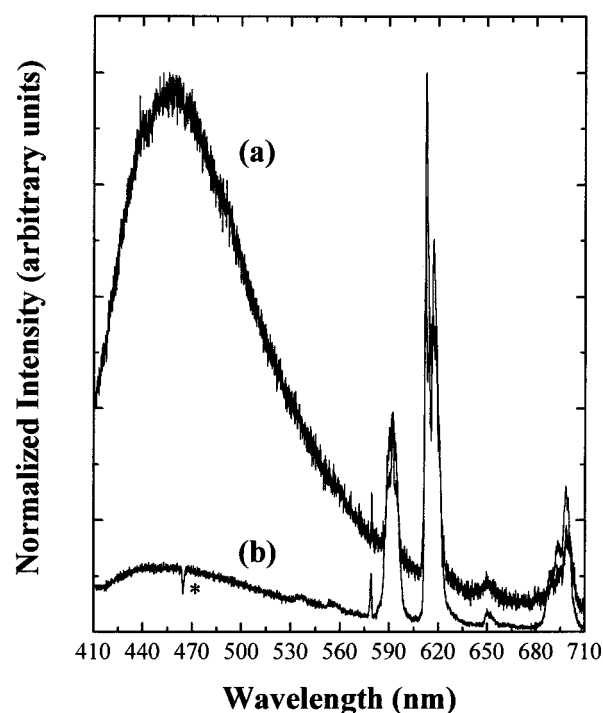
Figure 4. Emission spectra of selected U(600)$_n$Eu(ClO$_4$)$_3$ di-ureasils ($\lambda_{exc} = 395$ nm): (a) $n = 232$ and (b) $n = 6$.

Photoluminescence Spectroscopy. The emission spectra of the U(600)$_n$Eu(ClO$_4$)$_3$ compounds with $n = 232$ and 6, recorded at 14 K under 395-nm excitation, are represented in Figure 4a and b, respectively. The broad band seen in both spectra, already found in those of the undoped di-ureasils, has been interpreted as the result of the convolution of the emission from the NH groups of urea bridges and electron−hole recombinations occurring in the siliceous domains.[9] In addition, the U(600)$_{232}$-Eu(ClO$_4$)$_3$ and U(600)$_6$Eu(ClO$_4$)$_3$ xerogels produce a series of narrow lines (Figure 4a,b), which have been assigned to transitions between the first excited state, $^5D_0$, and the $^7F_{0-4}$ low-energy levels of the 4f^6 configuration. An intra-4f^6 self-absorption of the $^5D_2$ level (marked with an asterisk in Figure 4b) is observed in the spectrum of the most concentrated sample U(600)$_6$Eu(ClO$_4$)$_3$. It is noteworthy that the spectra reproduced in Figure 4a,b resemble closely those obtained at room temperature by Ribeiro et al.[5b]

The 14 K ion excitation spectra detected with the emission centered at 611 nm (not shown) are also very similar to those reported in Ribeiro et al.'s work.[5b] They display a broad band, with a maximum situated around 350 nm, which may be attributed to a charge transfer (CT) process between the hybrid host matrix and the Eu^{3+} ions.[13,46] This feature overlaps a group of Eu^{3+} sharp lines associated with the excitation of the $^5D_2$ and $^5L_6$ levels. The relative intensity between these lines and the broad band strongly depends on the composition of the sample. In the more dilute compounds, the large band dominates over the whole excitation spectra and only the excitation of the $^5L_6$ level can be discerned. This finding suggests that in the U(600)-based di-ureasils the incorporation of increasing amounts of guest salt leads to a decrease in the quantum efficiency of the energy-transfer process mentioned above. Several experimental data obtained very recently obtained fully corroborate this explanation.[46]

The $^5D_0 \rightarrow {}^7F_0$ transition region is presented in detail in Figure 5, at three different excitation wavelengths: 465 ($^5D_2$), 395 ($^5L_6$), and 345 nm (CT broad band). It must be noted that, as the $^5D_2$
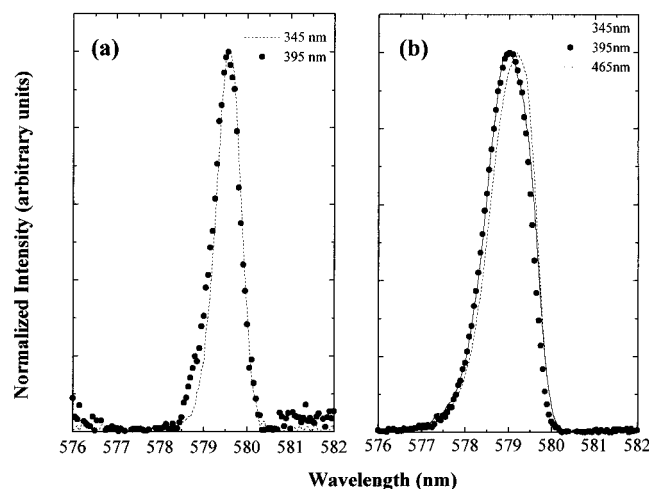
Coordination of Eu³⁺ Ions

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Figure 5. $^5D_0 \rightarrow {}^7F_0$ transition region of selected U(600)$_n$Eu(ClO$_4$)$_3$ di-ureasils: (a) $n = 232$ and (b) $n = 6$.

is not observed in the excitation spectrum of the $n = 232$ hybrid, the corresponding $^5D_{0-}{}^7F_0$ emission spectrum could not be recorded.

In the case of the most dilute di-ureasil examined (i.e., U(600)$_{232}$Eu(ClO$_4$)$_3$), no energetic position dependence is detected for the $^5D_0 \rightarrow {}^7F_0$ transition as the excitation wavelength ranges from the CT states to intra-$4f^6$ lines (Figure 5a). In contrast, when the salt-rich sample U(600)$_6$Eu(ClO$_4$)$_3$ is excited into the CT band a red shift in the $^5D_0 \rightarrow {}^7F_0$ energy, relative to the excitation into the $^5D_2 \rightarrow {}^5L_6$ levels, clearly results (Figure 5b).

The energy of the $^5D_0 \rightarrow {}^7F_0$ transition is usually related to the so-called "nephelauxetic effect",[46] which has been ascribed to the influence of covalence perturbations of the first ligand shell on the reduction of the Eu³⁺ attractive potential.[13,15,47,48] Since this line corresponds to a transition between two nondegenerate states, the red-shift detected in the xerogel with $n = 6$ as the excitation changes from the intra-$4f^6$ levels to the CT band is therefore certainly correlated with the presence of Eu³⁺ sites subject to distinct effective local fields. Moreover, the calculated effective full width at half-maximum of the $^5D_0 \rightarrow {}^7F_0$ line for U(600)$_6$Eu(ClO$_4$)$_3$ (36.1 cm⁻¹) (Figure 5b) is approximately twice the value measured for U(600)$_{232}$Eu(ClO$_4$)$_3$ (20.8 cm⁻¹) (Figure 5a). This result supports a structured profile for the $^5D_0 \rightarrow {}^7F_0$ transition in the former material, implying the existence of two different Eu³⁺ first coordination shells, including the carbonyl groups of the urea cross-linkages and the ether oxygen atoms of the polyether chains. On the basis of the presence of two different local environments, we may correlate the $^5D_0 \rightarrow {}^7F_0$ red shift (Figure 5b) with an increase in the number of excited Eu³⁺ local sites whose first coordination shell has a greater covalent character.[13,15,47] Taking into account the greater covalency involved in the interaction between the Eu³⁺ and the carbonyl groups versus that involving the ether-type oxygen atoms,[13,15,47] it seems reasonable to propose that bonding to the urea cross-links corresponds to the $^5D_0 \rightarrow {}^7F_0$ component with lower energy. This salt concentration dependence of the nature of the sites occupied by the Eu³⁺ ions in the U(600) medium is in perfect agreement with the FTIR observations discussed in detail above.

Conclusions

A family of europium perchlorate-doped nanohybrids, based on a sol–gel derived host framework named di-ureasil (simply designated as U(600)), composed of short polyether chains covalently bonded on both ends to a siliceous skeleton by means of urea linkages, is investigated by mid-infrared and photoluminescence spectroscopies with the goal of determining the nature of the species that surround the lanthanide ions.

The analysis of the perchlorate and amide I/amide II spectral regions and of the emission spectra of the U(600)-based compounds at increasing guest salt concentration has allowed us to conclude that in dilute samples (i.e., $n = 232$ and 62, where n stands for the molar ratio of (OCH$_2$CH$_2$) moieties per Eu³⁺ ion) salt dissociation is complete. Within this particular salt concentration range, the cations are complexed by the ether oxygen atoms of the polymer segments, because the urea cross-links are strongly self-associated via hydrogen bonding, forming a network all over U(600). Nevertheless, at higher salt content, the disruption of such hydrogen-bonded urea–urea structures becomes possible, allowing the carbonyl oxygen atoms of the urea groups to participate actively in the coordination of the Eu³⁺ ions. In the salt-rich xerogels the perchlorate anions apparently adopt a bidentate configuration to interact with the lanthanide ions.

The results obtained show that the coordination of the cations in the di-ureasils depends both on the guest salt concentration and on the length of the polymer chains incorporated. While in dilute short-chain di-ureasils the cations will prefer to bond to the ether oxygen atoms of the organic segments, a long-chain host will induce, in contrast, the interaction between the cations and the urea carbonyl oxygen atoms. In the latter type of hybrid, the complexation of the cations by the polyether chains will only occur at high salt content, beyond the composition for which the saturation of the cross-links is attained. Both coordinating environments (i.e., Eu³⁺···O═C(urea) and Eu³⁺···OCC(polymer)) are, however, present already in the low to medium salt concentration range when a host matrix containing low molecular weight polymer segments, such as U(600), is used.

The tunability of the cation coordination process detected in the di-ureasils transforms them into quite outstanding materials, enlarging substantially their fields of application.

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