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Optically hybrid lanthanide ions (Eu^{3+}, Tb^{3+})-centered materials with novel functional di-urea linkages

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The synthesis of 3-(triethoxysilyl)-propyl isocyanate (TEPIC) modified by (3-aminopropyl)triethoxysilane (APS) and the preparation of the corresponding organic–inorganic molecular-based hybrid material with the two components equipped with covalent bonds is described. The coupling agent moiety is a convolution of TEPIC and APS through –NHC(=O)NH–groups, which is applied to coordinate to RE^{3+} and further formed Si–O backbones after hydrolysis and polycondensation processes. For comparison and luminescence efficiency purposes, we added 2,2-bipyridyl to the above hybrids in order to increase the conjugating effects and sensitize rare earth ions emissions. Luminescence spectra were utilized to characterize the photophysical properties of the hybrid material obtained, and the above spectroscopic data reveal that the triplet energy of 2,2-dipyridyl in this favorable hybrid system matches with the emissive energy level of RE^{3+}. In this way, the intramolecular energy transfer process took place within these molecular-based hybrids and strong green and red emissions of RE^{3+} have been achieved. Copyright © 2005 John Wiley & Sons, Ltd.

KEYWORDS: molecular-based hybrid materials; luminescence; rare earth ions

INTRODUCTION

The synthesis of 'hybrid organic–inorganic materials' has appeared over the past decade with the expansion of soft inorganic chemistry processes, and this has provided a wealth of opportunities for both organic and inorganic networks to exhibit their extraordinary properties, such as luminescent materials in lighting and displays, optical amplifiers, and lasers.[1,2] Generally speaking, inorganic matrices doped with a metal complex, especially lanthanide organic complexes introduced in silica gel, have already been found to show superior emission intensities, and organic components are considered to be efficient sensitizers for the luminescence of rare earth ions; in short, the antenna effect. Our research group is presently concentrated on the lanthanide ions (europium, terbium, samarium, dysprosium) complexes with aromatic carboxylic acid, bipyridyl or their derivatives.[3–11] In addition, anchored lanthanide complexes with various ligands in a sol–gel-derived matrix have been investigated in many of the latest studies.[12–14] Indeed, the mild synthetic methods provided by the sol–gel approach, which is based on hydrolysis/polycondensation reactions of metal alkoxides, allow the composites to exhibit high versatility, offering a wide range of chances for preparation of tailor-made materials in terms of their unique features. In particular, the microstructure, the external shape or the degree of combination between the two phases can be controlled by changing the sol–gel reaction conditions. In recent years, good control of the coupling between the hosts and the guest molecules has been quite useful for the design of hybrid materials for definite applications. For instance, with conventional doping methods, the problem of the quenching effect of luminescent centers is difficult to solve because of the high-energy vibration by the surrounding hydroxy groups, and only weak functional interactions (such as hydrogen bonding, van der Waals force or weak static effect) between organic and inorganic parts.[15] Furthermore, the inhomogeneous dispersion of the two phases and leaching of the photoactive molecules frequently occur in these sorts of hybrid material, for which the concentration

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of the complex is also largely limited. Naturally, another attractive possibility concerns the complexation of the rare earth ions using ligands that are covalently fixed to the hybrid networks. Up to now, a few studies in terms of the covalently bonded hybrids have appeared, and the as-derived molecular-based materials exhibit a monophasic appearance even at a high concentration of rare earth complexes.[16–28] Some previous research has been done on complexes of rare earth–pyridine–dicarboxylic acid or their derivatives, and the feasibility of the dicarboxylic acid system has been firmly proved.[22] Zhang and co-workers started to modify 1,10-phenanthroline and di-pyridine in order to prepare the determined molecular-level hybrid materials.[17,18] Our research team recently put more emphasis on rare earth coordination behavior and we have now developed modified *ortho*, *meta*-aminobenzoic acid as 'molecular bridge' which not only can develop chelating effects that can bind to rare earth ions, but also anchor a silica matrix with an aminoalkoxysilane group.[26–28] According to the latest research by Carlos and co-workers,[29–31] amino-functional hybrids lacking metal ions could be classified into two major groups (di-ureasils and di-urethanesils) and the Eu^{3+} coordination shell involves the carbonyl-type oxygen atoms of the urea bridges. In order to restrict phase separation between the organic molecules and the rigid inorganic network, and to increase the concentration of dopant, we first use 3-(triethylsilyl)-propyl isocyanate (TEPIC) modified by (3-aminopropyl)triethoxysilane (APS) carrying a tri-alkoxysilyl group as a functionalized organic ligand (T-A), then we designed a covalently bonded hybrid inorganic–organic system that incorporated rare earth (Eu, Tb) nitrate to T-A and a second ligand, 2,2-bipyridyl, was inserted into the hybrids. The reaction processes for the hybridization formula T-A may be described as follows: step I involves the individual hydrolysis of T-A; step II, however, is related to the polycondensation reactions between hydroxyl groups of T-A. Hence, condensation of the tri-alkoxysilyl chromophores in the presence of lanthanides salts leads to the formation of novel structured hybrid materials consisting of efficiently sequestered lanthanide species linked to powerful modified T-A grafted to the inorganic hosts. Furthermore, the first results on luminescence are promising, and the molecular-based hybrids bearing the RE–O coordination bond and Si–O covalent bond can exhibit the strong green and red luminescence of RE^{3+}.

EXPERIMENTAL

Chemicals and procedures

TESIC and APS were provided by Lancaster Synthesis Ltd. The solvents used were purified by common methods. Other starting reagents were used as received. A typical procedure for the preparation of T-A was as follows: 2 mmol TESIC was first dissolved in dehydrated tetrahydrofuran by stirring and 2 mmol APS was then added to the solution by drops. The whole mixture was refluxed at 65 °C under argon for 12 h. After isolation, a pale-yellow oil of T-A was furnished. ^1H NMR ($CDCl_3$), $C_{19}H_{44}N_2O_7Si_2$(T-A): δ5.83 (2H, d), 4.26 (1H, t), 3.72 (6H, m), 3.6 (2H, t), 3.47 (8H, d), 3.4 (1H, t), 3.37 (1H, s), 3.3 (1H, s), 2.71 (1H, s), 2.53 (1H, d), 2.51 (1H, d), 1.76 (4H, s), 1.16 (2H, s), 1.12 (10H, m), 0.59 (3H, t); ^{13}C NMR ($CDCl_3$), $C_{19}H_{44}O_7N_2Si_2$: δ97.1 (C_1), 65.6–72.4 (CH_2(OEt)), 49.9–57.6 (C_2–C_3), 38.6–40.3 (C_4, C_5, C_6, C_7), 23.5 (CH_3(OEt)). The sol–gel-derived hybrid containing rare earth ions was prepared as follows: T-A was dissolved in dimethylformamide (DMF) with stirring, A stoichiometric amount of $RE(NO_3)_3{\cdot}6H_2O$ was added to the final stirring mixture. After 1 h, 2,2-bipyridyl was added to the solution. Then, one drop of diluted hydrochloric acid was added to promote hydrolysis. The mole ratio of $RE(NO_3)_3{\cdot}6H_2O$/T-A/bipy/H_2O was 1 : 3 : 1 : 9. The mixture was agitated magnetically to achieve a single phase, and thermal treatment was performed at 50 °C until the sample solidified (see Fig. 1). For the purpose of comparison, we also prepared hybrid material directly by rare earth nitrate and T-A ligands.

Measurements

All measurements were completed at room temperature. ^1H NMR spectra was recorded in $CDCl_3$ on a Bruker AVANCE-500 spectrometer with tetramethylsilane (TMS) as internal reference. Fluorescence excitation and emission spectra were obtained on a Perkin–Elmer LS-55 spectrophotometer, with excitation slit width of 10 nm and emission slit width of 5 nm.

RESULTS AND DISCUSSION

The excitation and emission spectra of the resulting hybrid materials are shown in Figs 2–6. The excitation spectra of Eu,Tb–T-A–bipy were obtained by monitoring the emission of Eu^{3+} (A) and Tb^{3+} (B) ions at 614 nm, or 545 nm and dominated by a broad band centered at 246 or 248 nm. As for the hybrids composed of the lanthanide and T-A binary system, we could observe very weak characteristic emission lines with quite high baselines which were caused by the emissions of silica hosts (Fig. 3). In Fig. 4, $^5D_4 \rightarrow {}^7F_4$ and $^5D_4 \rightarrow {}^7F_3$ transitions were heavily affected by a broad $^5D_4 \rightarrow {}^7F_5$ peak, which suggested that an inefficient energy transfer process occurred between the matrices and terbium ions. After the introduction of the second ligand, bipyridyl, the emission lines of the molecular-based hybrid materials, which were assigned to the transitions from the $^5D_0 \rightarrow {}^7F_1$, $^5D_0 \rightarrow {}^7F_2$, $^5D_0 \rightarrow {}^7F_3$, $^5D_0 \rightarrow {}^7F_4$, were at 590 nm, 614 nm, 650 nm and 700 nm respectively for Eu^{3+}, and $^5D_4 \rightarrow {}^7F_j$ ($j = 6, 5, 4, 3$) transitions at 490, 544, 587 and 622 nm were obtained for terbium (Figs 5 and 6). Among these emission peaks, the most striking green luminescence ($^5D_4 \rightarrow {}^7F_5$) and red emissions ($^5D_0 \rightarrow {}^7F_2$) were exhibited in their emission spectra, which indicated that effective energy transfer took place from bipyridyl to the chelated RE ions. Therefore, we

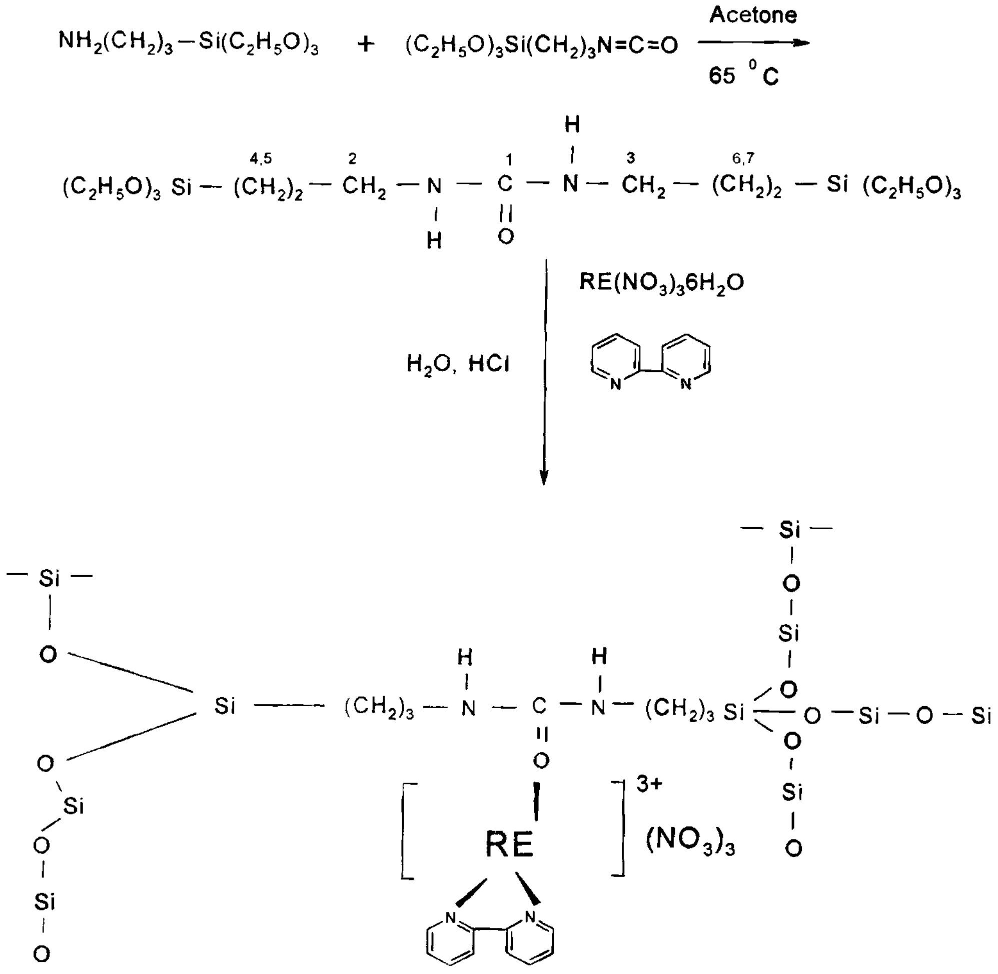

Figure 1. Scheme of the synthesis process of T-A ligand and predicted structure of resulting hybrid materials.

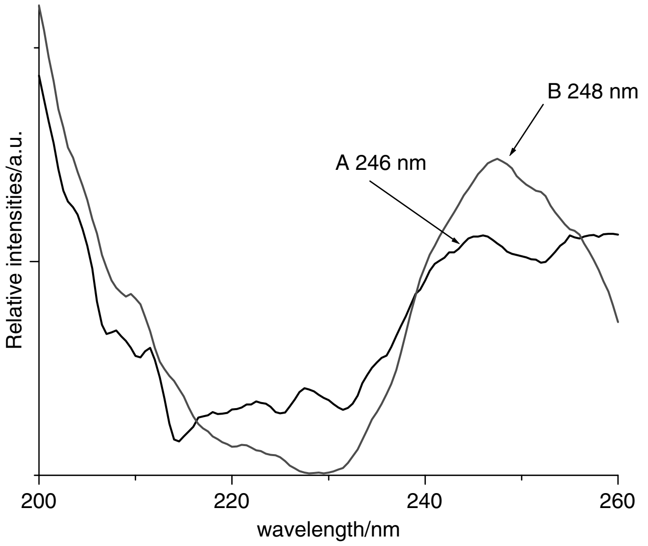

Figure 2. Excitation spectra of (A) Eu–T-A–bipy molecular-based hybrids and (B) Tb–T-A–bipy molecular-based hybrids.

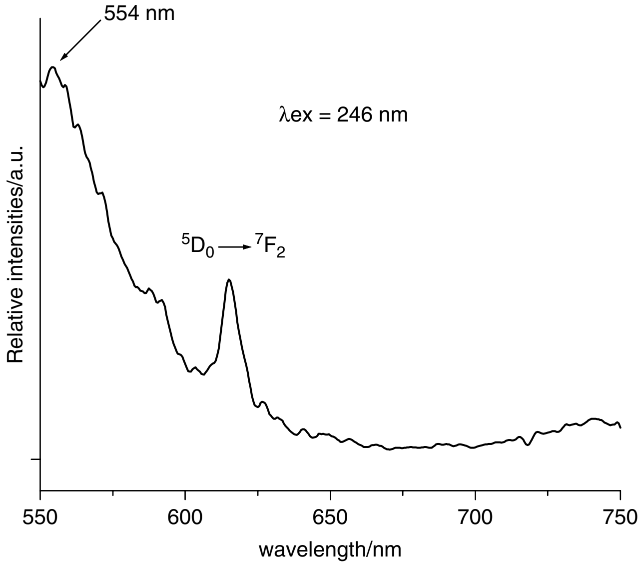

Figure 3. Emission spectra of Eu–T-A binary hybrids.

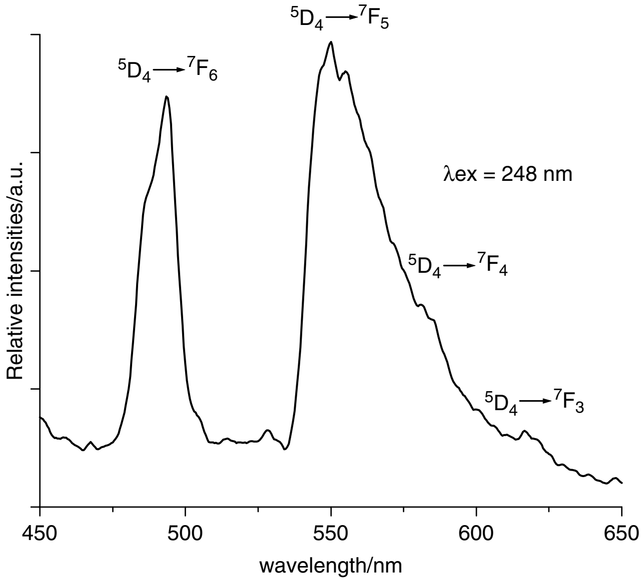

Figure 4. Emission spectra of Tb–T-A binary hybrids.

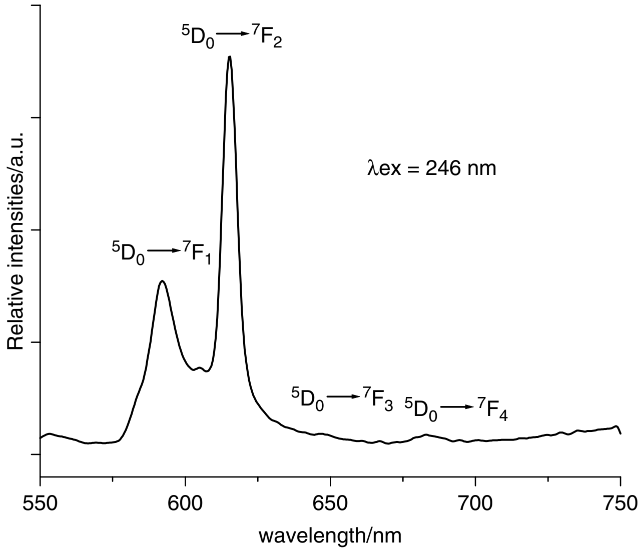

Figure 5. Emission spectra of Eu–T-A–bipy molecular-based hybrids.

may expect that, through this efficient method, leaching of the photoactive molecules can be avoided, a higher concentration of metal ions can be obtained and clustering of the emitting centers can be prevented because the hybrids belong to the molecular level.

The scanning electron micrographs (Fig. 7) for this hybrid material show that a homogeneous molecular-based material was attained and no phase separation was observed; this is because of the strong covalent bonds bridging between the inorganic and organic phases, and they are composed rather uniformly so that the two phases can exhibit their distinct

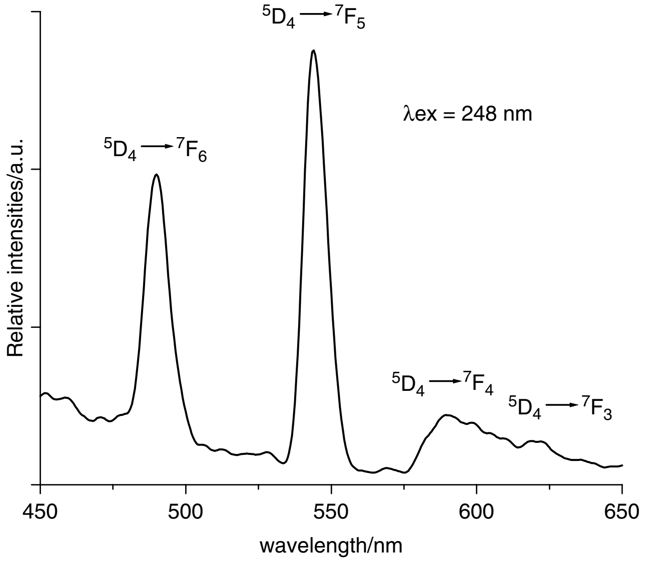

Figure 6. Emission spectra of Tb–T-A–bipy molecular-based hybrids.

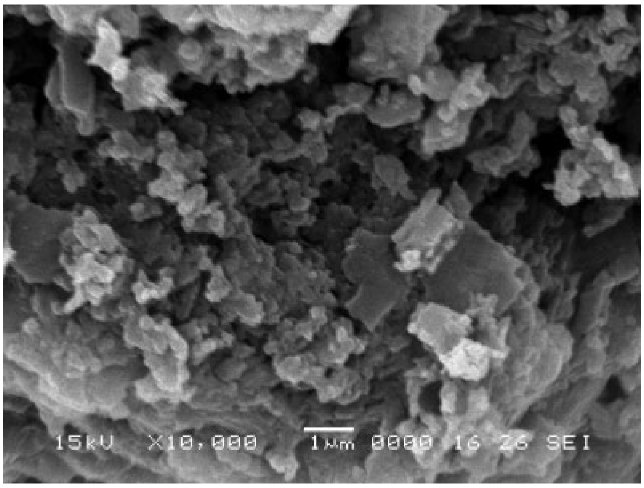

Figure 7. SEM graph of Eu–T-A–bipy molecular-based hybrids.

properties together. In addition, it is interesting to notice that many large pores dispersed in the surface of materials mainly through the formation of backbone of Si–O–Si and its polycondensation. It is estimated that this high porosity and large pore size may facilitate the future application of optical properties.

CONCLUSIONS

To investigate the coordination behavior between ureasils and rare earth ions, we designed a novel molecular-based hybrid material, i.e. TEPIC has been modified with functional

APS as a crosslinking intermediate, which plays a double role. On the one hand, it can coordinate to lanthanide ions through carbonyl groups; on the other hand, the hydrolysis and polycondensation reactions of the triethoxysilyl of T-A are ascribed to the formation of Si–O–Si network structures with this ethoxy group. Meantime, strong red or green luminescent systems were obtained. In addition, the resulting hybrids could be shaped as monoliths or as transparent films with the desired luminescence efficiency. Variations of the organic ligand structure lead to diverse coordinating properties and to various absorption capabilities. As a consequence, the energy absorption and transfer from ligands to the central ions, or the emission efficiency, could be increased by this potential method. Further advantages include enhancing long-term chemical stability, use as a source of monochromatic emission in photonic crystals, and designing large scope of photoactive materials based on molecular level.

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