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A novel path to luminescent hybrid molecular materials: modifying the hydroxyl group of 6-hydroxynicotinic acid by grafting to a silica network

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In this paper, a novel path was put forward to modify the hydroxyl group of 6-hydroxynicotinic acid by 3-(triethoxysilyl)-propyl isocyanate and prepare the corresponding organic–inorganic molecular-based hybrid material with the two components connected by covalent bonds. The bridging unit is a derivative of 6-hydroxynicotinic acid that is utilized to coordinate to Tb^{3+} via hydrolysis and polycondensation processes with functional triethoxysilyl groups. Ultraviolet absorption, phosphorescence spectra and luminescence spectra were applied to characterize the photophysical properties of the hybrid material obtained and the spectroscopic data show that the triplet energy of modified 6-hydroxynicotinic acid efficiently initiates the antenna effect and matches the emissive energy level of the metal ions. As a result, the intramolecular energy transfer process is completed within these molecular-based hybrids. Copyright © 2005 John Wiley & Sons, Ltd.

KEYWORDS: terbium; luminescent hybrid molecular materials; 6-hydroxynicotinic acid

INTRODUCTION

Rare earth complexes have long been the subject of extensive research owing to their excellent luminescent characteristics from the electronic transitions between the 4f energy levels.[1–3] Weissman and co-workers first reported the light-emission characteristics of a lanthanide complex of β-diketone.[4] Since then, much work has been carried out to obtain various rare earth compounds with special structures and luminescence behaviour.[5–7] Also, it is well known that the luminescent mechanism is an intramolecular energy transfer from the ligands to the metal ions under excitation by near-ultraviolet light. However, the practical use of these complexes as luminescent devices or tunable solid-state lasers has not been realized because of their poor photo and thermal stability and mechanical properties. These weaknesses could be overcome by forming hybrid materials.

Inorganic–organic hybrid materials have attracted much attention in the last few years as potential hosts in diverse technological fields such as electronics, mechanics, dyestuffs, optics and biology. Following the classification by Sanchez *et al.*,[8] these hybrid materials can be divided into two major classes according to interaction among the different components or phases in hybrid systems. Class II hybrids exhibit a true interconnection, via covalent bonding, between the organic and inorganic components. Interpenetrated organic and inorganic networks may be present in hybrids of class I but, the two networks remain as two separated domains connected only via mechanical entanglements or secondary bonding (hydrogen bonding, van der Waals' forces or weak static effects).[9–13] In class II the organic groups are directly connected to the inorganic network and their role can be that of a network modifier, e.g. alkali ions in silica.

In nature, these hybrids belong to the molecular-based systems, which can realize the possibility of tailoring the complementary properties of novel multifunctional advanced materials through combination with chemical bonding within the different components in a single material.[14–17] Some previous research has concentrated on the modification of pyridine–dicarboxylic acid or their derivatives, and Zhang *et al.* focus on the modification of heterocyclic ligands such as 1,10-phenanthroline and bipyridyl.[18,19] Our research team have carried out extensive work in the preparation of molecular hybrids with a functional bridge connecting both the siliceous backbone

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and aromatic carboxylic acids by modification of amino or carboxyl groups of aromatic acids.[20–22] In this present work, we put forward another novel path to modify the hydroxyl group of 6-hydroxynicotinic acid and design a new covalently bonded hybrid inorganic–organic system based on hydrolysis and polycondensation reactions by triethoxysilyl groups of modified 6-hydroxynicotinic acid. The photophysical properties are discussed in detail.

EXPERIMENTAL

Chemicals and procedures

6-Hydroxynicotinic acid (6HNIC) and 3-(triethoxysilyl)-propyl isocyanate were provided by Lancaster Synthesis Ltd and the solvents used were purified by common methods. Other starting reagents were used as received. A typical procedure for the preparation of the bridging unit 6HNIC-Si was as follows: 2 mmol of 6HNIC was first dissolved in *N*,*N*-dimethyl formamide (DMF) by stirring and then 2 mmol of 3-(triethoxysilyl)-propyl isocyanate was added dropwise to the solution. The whole mixture was refluxed at 60 °C under argon for 12 h. After isolation, a pale yellow powder of 6HNIC-Si was obtained. ^{1}H NMR (DMSO) $C_{16}H_{26}O_7N_2Si$: δ 11.98 (1H, s), 7.98 (2H, m), 7.76 (1H, m), 6.34 (1H, t), 3.26 (2H, m), 2.88 (6H, m), 2.73 (9H, t), 1.47 (2H, m), 0.47 (2H, t). ^{13}C NMR (DMSO): δ 165.4 (C_6), 162.4 (C_1), 162.2 (C_1), 140.3–139.7 (C_2–C_4), 119.3 (C_7), 109.1 (C_3), 66.5 [CH_2(OEt)], 40.3 (C_8), 35.7 (C_9), 30.7 [CH_3(OEt)], 14.6 (C_{10}).

The sol–gel-derived hybrid containing metal ions was prepared as follows (see Fig. 1): 6HNIC-Si was dissolved in DMF by stirring, and minimal NaOH was used to adjust the pH to 6–7. A stoichiometric amount of $Tb(NO_3)_3 \cdot 6H_2O$ was added to the solution and then one drop of diluted hydrochloric acid was added to promote hydrolysis. The mole ratio of $Tb(NO_3) \cdot 6H_2O$–6HNIC-Si–H_2O was 1 : 3 : 9. The mixture was agitated magnetically to achieve a single phase in a covered Teflon beaker, and then it was aged at 50 °C until the onset of gelation, which occurred within 7 days. The gels were collected as monolithic bulks and ground to powder materials for photophysical studies.

Measurements

All measurements were completed at room temperature and NMR spectra were recorded in DMSO on a Bruker Avance-500 spectrometer with tetramethylsilane (TMS) as internal reference. Ultraviolet absorption spectra of these powder samples (5×10^{-4} mol l^{-1} acetone solution) were recorded

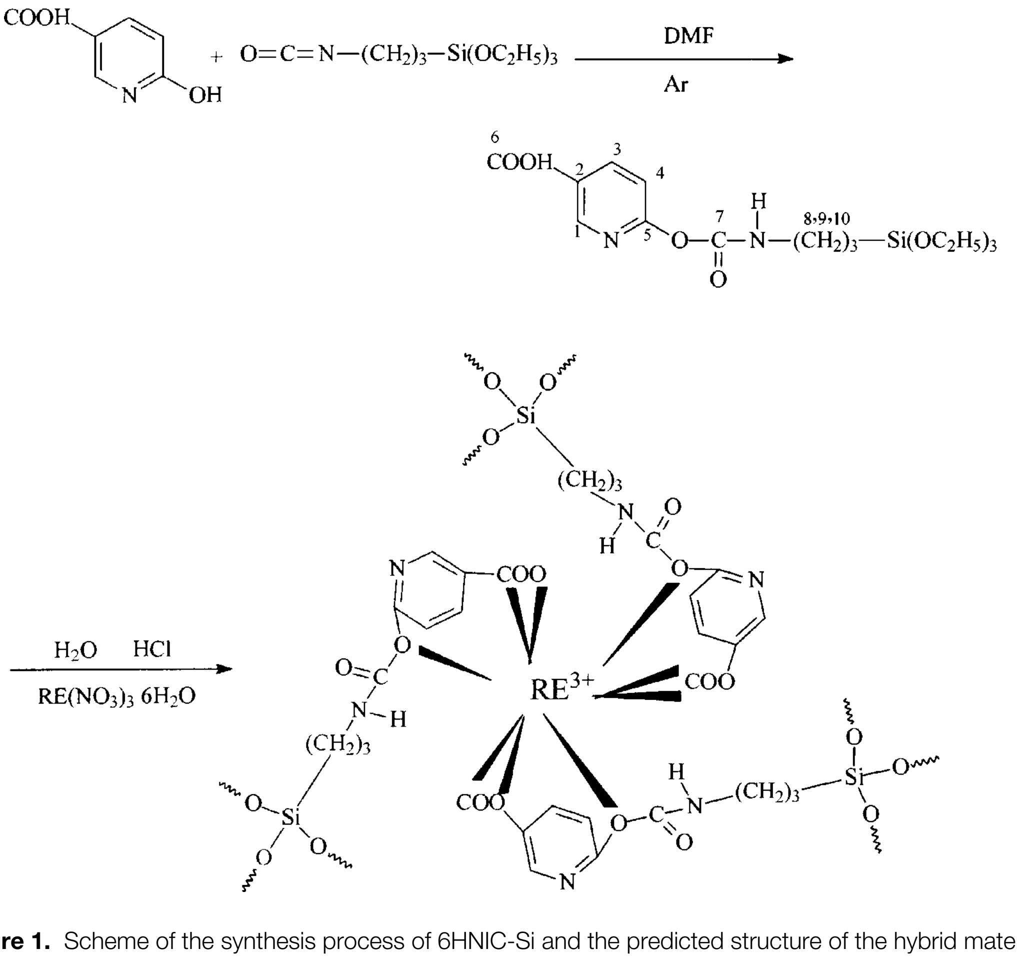

Figure 1. Scheme of the synthesis process of 6HNIC-Si and the predicted structure of the hybrid material.

with an Agilent 8453 spectrophotometer. Fluorescence excitation and emission spectra were obtained on a Perkin-Elmer LS-55 spectrophotometer (excitation slit width = 10 nm; emission slit width = 5 nm).

RESULTS AND DISCUSSION

The reaction model for the hybridization formula of this molecular-scale hybrid is shown in Fig. 2. At the beginning of the reaction (Step 1) hydrolysis of 6HNIC-Si is predominant but in Step 2 polycondensation reactions occur between the hydroxyl groups of 6HNIC-Si and tetraethyl orthosilicate (TEOS). After these treatments, the functional hybrids bearing the Tb–O coordination bond and the Si–O covalent bond can exhibit the strong characteristic luminescence of Tb^{3+}. The potential structure of the co-hybrid materials obtained by this means is illustrated in Fig. 3.

Fig. 4 exhibits the ultraviolet absorption spectra of 6-hydroxynicotinic acid (A), 6HNIC-Si (B) and 6HNIC-Si with excess Tb^{3+} ions (C). From these spectra, it is observed that a blue shift (A → B) of the major π–π^* electronic transitions (from 271 to 262 nm) occurs and it is estimated that during the grafting reaction of 6-hydroxynicotinic acid, the diverse ligand may limit the conjugating effect of double bonds and enlarge the energy difference levels among electron transitions. In terms of B and C, the complexation between rare earth ions and 66HNIC-Si decreases the energy levels of the corresponding transitions and exhibits an obvious red shift from 262 to 272 nm (B → C).

Fig. 5 shows the phosphorescence spectra of 6-hydroxynicotinic acid (A) and 6HNIC-Si (B). The phosphorescence spectrum indicates the character of the organic molecular ligands and a 6 nm red shift was observed between A and B (from 452 to 458 nm). The maximum phosphorescence band of B at 458 nm determined the triplet state energy of 6HNIC-Si to be 23 095 cm^{-1}. According to the energy transfer and intramolecular energy mechanism,[22–25] it can be predicted that the bridging unit 6HNIC-Si is suitable for the luminescence of terbium (20 500 cm^{-1}).

The excitation and emission spectra of the resulting hybrid materials are shown in Figs. 6 and 7. The excitation spectrum was obtained by monitoring the emission of Tb^{3+} (Fig. 6) at 545 nm and is dominated by a broad band with maximum peaks at 242, 258 and 293 nm. As a result, the emission lines of the hybrid material were assigned to the $^5D_4 \rightarrow {}^7F_J$ ($J = 6, 5, 4, 3$) transitions at 490, 544, 589 and 621 nm for terbium and a striking green luminescence was attained.

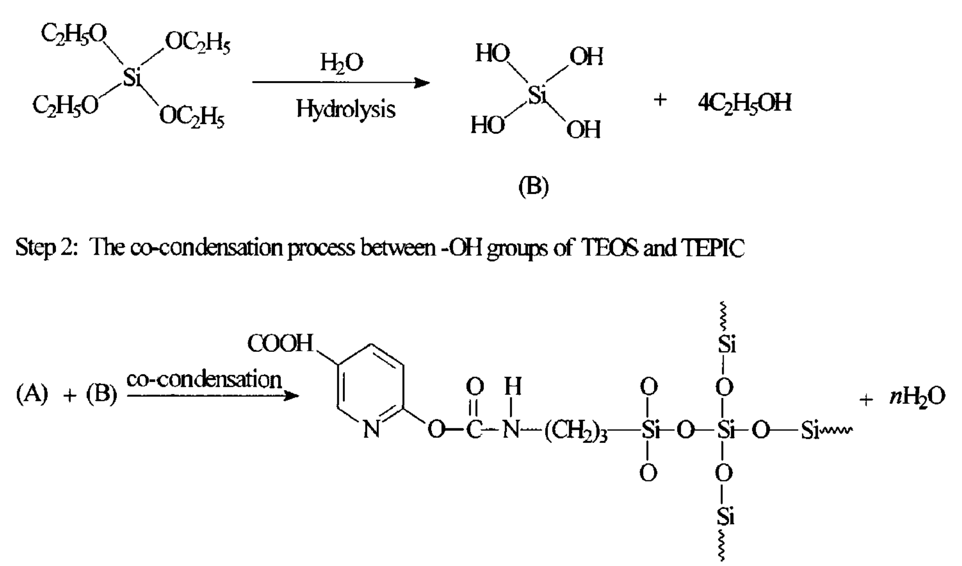

Figure 2. Scheme of the hydrolysis and polycondensation processes between 6HNIC-Si and tetraethyl orthosilicate (TEOS).

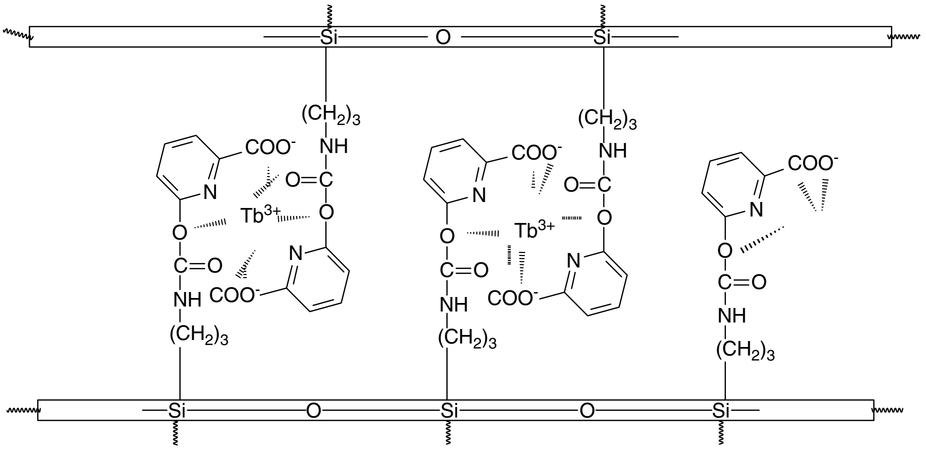

Figure 3. Schematic illustration of the hybrid materials.

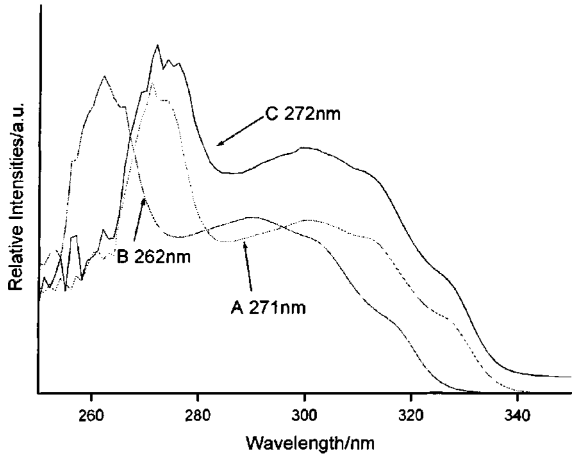

Figure 4. Ultraviolet absorption spectra of 6-hydroxynicotinic acid (A), 6HNIC-Si (B) and Tb-6HNIC-Si (C).

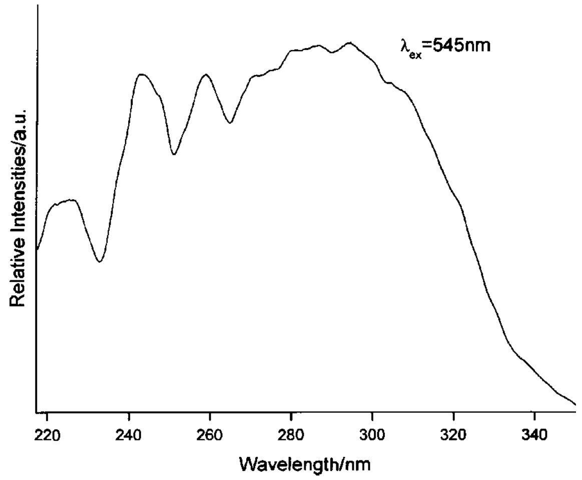

Figure 6. Excitation spectrum of the hybrid molecular materials.

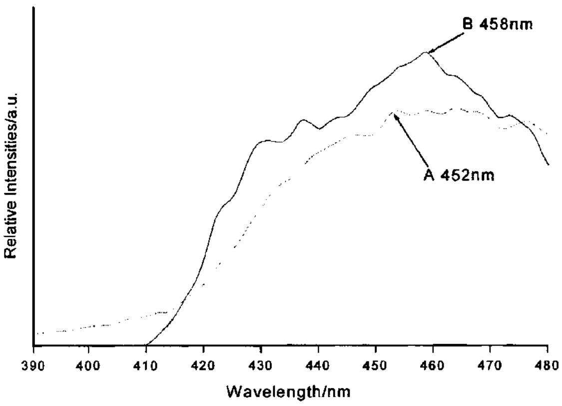

Figure 5. Phosphorescence spectra of 6-hydroxynicotinic acid (A), 6HNIC-Si (B) and Tb-6HNIC-Si (C).

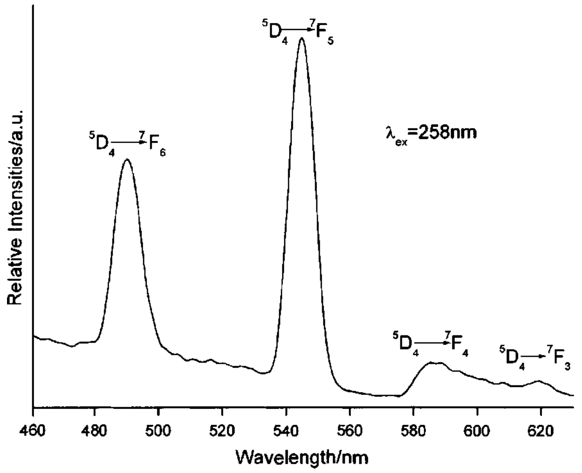

Figure 7. Emission spectrum of the hybrid molecular materials.

CONCLUSIONS

In summary, a novel modification path was used to functionalize the hydroxyl group of 6-hydroxynicotinic acid to achieve a reactive bridge molecule with a crosslinking 3-(triethoxysilyl)-propyl isocyanate molecule. Because the hydrolysis and polycondensation reactions between the triethoxysilyl of 3-(triethoxysilyl)-propyl isocyanate and TEOS lead to the formation of Si–O–Si network structures for their alkoxy groups, a new luminescent molecular-based hybrid material with a double chemical bond was constructed using 6-hydroxynicotinic acid coordinated to Tb^{3+}. In consequence, further detailed investigation of the above strong emission molecular-based hybrids will definitely contribute to the recognition of the paths needed for the fabrication of extending siloxane-based materials with interesting photo and electric luminescence features and high light emission efficiency.

Acknowledgement

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