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Hybrid Luminescent Films Obtained by Covalent Anchoring Terbium Complex to Silica-based Network

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Abstract: New monomer N-(4-carboxyphenyl)-NL-(propyltriethoxysilyl)urea (**1**) which acts as both a ligand for Tb^{3+} ion and a sol-gel precursor has been synthesized and characterized by ^1H NMR, and MS. Hybrid luminescent thin films consisting of organoterbium covalently bonded to a silica-based network have been obtained *in situ via* a sol-gel approach. Strong line emission of Tb^{3+} ion was observed from the hybrid luminescent films under UV excitation.

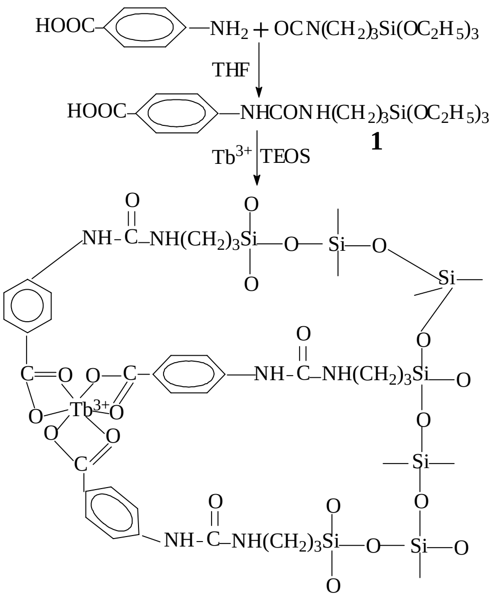
Keywords: Hybrid thin film, luminescence, sol-gel.

The sol-gel technique has been proven to be a suitable method for the design of organic-inorganic hybrid materials. Advantages of this approach include low processing temperature, the very large choice for the components[1]. However, there are significant drawbacks in using these systems, which include inhomogeneous distributions of both components, leaching of dopants and limitations on the concentrations of dopants used. Covalent anchoring of ligands onto the backbones of the silica network *via* Si-C bonds has been used as an alternative to overcome the above-mentioned shortcomings[2-3].

In this work, we present a new monomer N-(4-carboxyphenyl)-NL-(propyltriethoxysilyl)-urea (**1**) which acts as a ligand for Tb^{3+} and a sol-gel precursor. The hybrid luminescent materials were prepared by reacting monomer **1** with tetraethoxysilane (TEOS) in the presence of Tb^{3+} ion. (see **Scheme 1**).

The synthesized monomer **1** was characterized by ^1H NMR, IR, as well as MS spectra[4]. The Tb^{3+} solution of N, N'-dimethylformide (DMF) and deionized H_2O were added to the monomer solution of DMF and hydrolyzed with tetraethoxysilane by acidic catalysis. The solution was dip-coated onto quartz substrate to get hybrid thin films. UV-Vis spectra for both monomer and hybrid thin films showed a broad absorption band in the near UV range. This absorption band corresponds to the transition from the ground state of the ligand to the first excited state (S_0-S_1). A strong green emission was observed in the emission spectrum, which indicated that the surrounding aromatic ligand absorbed energy and transferred energy to the chelated Tb^{3+} ion. The line-emissions of the hybrid thin films of Tb^{3+} were assigned to the transitions from the $^5D_4$ level to the ^7F_j (J= 6, 5, 4, 3) levels at 485, 545, 584, 621 nm, respectively, with $^5D_4 \rightarrow {}^7F_5$ emission as the most prominent band. The decay curve of hybrid thin film was singly exponential, showing that the Tb^{3+} ion lies in the same average chemical environment. The resulting lifetime is 1.2 ms which is slightly lower than that of pure complex due to a possible quenching by silanol groups.

Scheme 1



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References and Notes

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4. Spectral data of monomer **1:** IR: KBr (cm^{-1}) 1689 ν(C=O), 1193 ν(Si-C), 1080 ν(Si-OEt). MS (ES) *m/z* 407.4(M+Na$^+$). ^{1}H NMR (DMSO, 400 MHz) δ(ppm) 12.45 (bs, 1H, COOH), 8.79 (s, 1H, NH), 7.78 (d, 2H, J=8.8 Hz, ArH), 7.47 (d, 2H, J=8.8 Hz, ArH), 6..31 (t, 1H, J=5.6 Hz, NH), 3.75 (q, 6H, J=6.8 Hz, OCH_2), 3.07 (q, 2H, J=6.4 Hz , NCH_2), 1.48 (quint, 2H, J=8.0 Hz, CH_2), 1.15 (t, 9H, J=6.8 Hz, CH_3(OEt)), 0.56 (t, 2H, J=6.8 Hz , $SiCH_2$).

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