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Communications to the Editor

Novel Erbium-Substituted Oligothiophene Chelates for Infrared Emission

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In the field of organic light-emitting diodes, stable rare earth ion complexes bearing conjugated ligands are receiving increasing attention since they combine the advantages of the organic ligand (high absorption cross section, high conductivity) with those of the inorganic component (sharp emission bands, long lifetimes). In these systems the excited state levels of the emitting ion are populated by an efficient intramolecular energy transfer—probably involving triplet states—from the optically (or electrically) excited ligand, which acts as an efficient light-harvesting antenna. As both the absorption of the organic ligand and the emission of the lanthanide ion can be tuned, a variety of materials exhibiting a wide range of optical properties can be envisaged. By means of this approach, it is possible to have access to all the three infrared (IR) transparency spectral windows of interest for telecommunication based on silica optical fibers (800−900, 1300, and 1500 nm).[1−3] In particular, Er^{3+} complexes give access to the emission in the IR region not reached by all-organic dyes. Thus, a lanthanide containing OLED, which can be grown onto any suitable substrate,[4] when coupled to a fast modulator could provide a new and low-cost approach to developing silicon-based optoelectronic technology.

One of the major problems of many lanthanides complexes is their relatively low solubility. To overcome this drawback and increase the metal concentration in the matrix, organic polymers such as polystyrene, poly(methyl methacrylate),[5] and poly(*N*-vinylcarbazole)[6] were used in blend preparation. Organic ligands have also been directly attached onto polymeric chains as shown by Okamoto and more recently by Do and Ma[7] by using two different approaches. In the former case polyelectrolytes have been synthesized by usual methods, and then they have reacted with lanthanide salts to form Ln ionomers. In the latter a Ln complex properly functionalized has been inserted in Eu−polymer complexes through copolymerization with styrene or methyl methacrylate. Recently, the former approach has been used by Liu et al. employing a triblock copolymer Na-styrenesulfonate−ethylene glycol−Na-styrenesulfonate.[8]

In this paper we address the preparation and characterization of new infrared luminescent materials based on Er^{3+} which can be excited in the visible region thanks to oligothiophene ligands (OT) featuring the carboxylate functionality. The choice of the this type of ligand is motivated by the following considerations: (i) good solubility (device fabrication by spin-coating and incorporation in polymeric optical fibers); (ii) good transport properties (electrically excited devices); (iii) possibility to polymerize the complexes to obtain Er^{3+}-containing conjugated polymers (lower excitation threshold, high stability, reduced crystallization capabilities); (iv) efficient intersystem crossing into the triplet state and match between Er^{3+} and ligand electronic levels (high efficiency of the resonant transfer).

Herein, the preparation of trivalent erbium-3,4-bis(carboxylatemethyl)-α-terthiophene (T3-Er) and the corresponding α-pentathiophene (T5-Er) complexes will be reported together with their emission in the IR region following excitation in the ligand absorption band (see Figure 1). Our findings demonstrate the formation of

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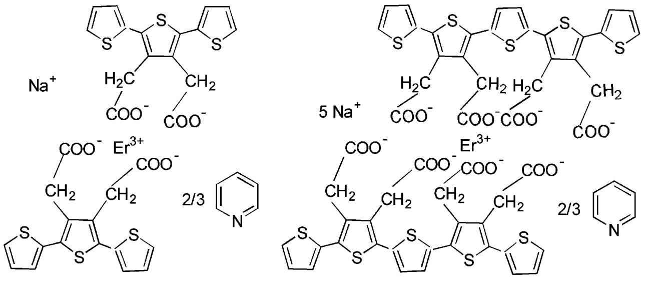

Figure 1. Chemical structures of T$_3$Er and T$_5$Er complexes (left and right, respectively).

stable complexes and the occurrence of an efficient intramolecular energy transfer from the organic ligand to Er^{3+}. These complexes will be used as models for the preparation of future thiophene-based polyelectrolytes in order to establish the number of thiophene rings to be inserted between the carboxylated thiophenes—acting as clamps for the lanthanide ion—to avoid quenching due to clustering.

The properly substituted OT were synthesized following the procedure reported in the literature,[9] and then their sodium salts have been prepared through the corresponding acid.

To a solution of NaOH (73.5 mg, 1.83 mmol) in water (8 mL) was added methyl {4′-(methoxycarbonyl)methyl-[2,2′; 5′,2″]terthiophen-3′-yl}acetate (100 mg, 0.255 mmol), and the resulting mixture was refluxed until the complete dissolution of the substrate (typically, 3 h). After cooling, the mixture was washed with ether (to remove unreacted starting material) and acidified with 1 M H_2SO_4 (pH ~ 5) with cooling. The resulting precipitate was collected by suction filtration and then recrystallized from methanol to give pure {4′-(hydroxycarbonyl)methyl-[2,2′;5′,2″]terthiophen-3′-yl}acetic acid (74.26.mg, 80% yield), which was characterized by ^{1}H NMR (broad singlet at 12.6 ppm in DMSO). A mixture of the diacid (51.8 mg, 0.14 mmol) and NaOMe (15.2 mg, 0.28 mmol) in MeOH (15 mL) was refluxed under nitrogen for 2 h. After cooling, the Na dicarboxylate was obtained by precipitation with hexane (2 mL) and dried. All the procedures for complex preparation were carried out under nitrogen and using dry reagents, also to avoid the presence of water, oxygen, and alcohol residues which can quench metal photoluminescence. The Na salt was dissolved in pyridine (5 mL) and added to a refluxing solution of $ErCl_3$ (9 mg, 0.033 mmol) in pyridine (2 mL). After refluxing for 10 h, the mixture was cooled, filtered (to remove NaCl), and slowly concentrated to afford pale pink-yellow crystals of the T3-Er complex. The related T5-Er was obtained as a yellow-orange solid following an analogous procedure.

The paramagnetic properties of Er complexes do not permit NMR characterization of the compounds which were characterized by FTIR and UV–vis spectroscopies. Comparison between IR spectra of T3COOH (C=O stretching 1695 cm^{-1}) and T5COOH (C=O stretching 1700 cm^{-1}) and the corresponding Er^{3+} complexes showed a shift toward higher energy of 45 and 28 cm^{-1}, respectively. This behavior is unusual for Ln carboxylate; in fact, other authors observed a shift toward lower energy for both aliphatic and aromatic Eu carboxylate,[7,10] and a red shift was also observed by complexing sulfonate Na salt with Eu, Tr,[8] and Er.[11] A reasonable explanation of this fact can be related to the presence onto the same thiophenic ring of the two acetoxylate clamps reciprocally influencing to force the C=O residue of the groups away from Er atom, thus reducing the contribution of the mesomeric structure. However, this shift clearly indicates the OT can complex rare earth ions via the carbonyl oxygen of carboxylate groups. In the T5-Er complex spectrum very broad bands are observed in the 1450–1560 cm^{-1} region attributable to the presence of Na carboxylate, indicating that the T5 derivative uses two clamps only for the complexation (see Figure 1).

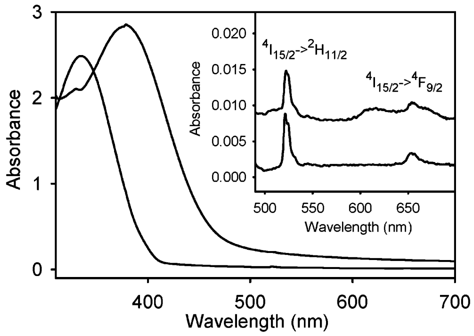

Figure 2. Absorption spectra of the T3-Er (left trace) and T5-Er (right trace) complexes in DMSO solution. In the inset the enlarged 500–700 nm spectral region is also shown. For clarity, the spectra in the inset are shifted 0.007 absorbance from each other and have been corrected for the background due to the low-energy tail of the main UV absorption bands.

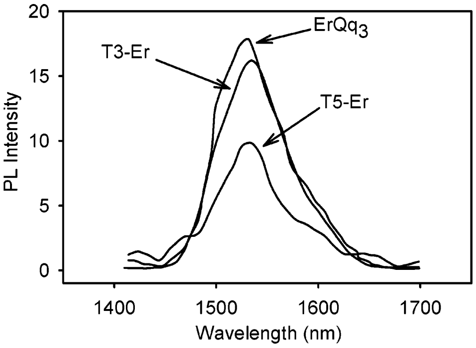

Figure 3. Infrared PL spectra of the T5-Er and T3-Er complexes in pyridine anhydrous solution collected at room temperature by exciting the organic ligand with the 353 line of an Ar$^+$ laser. For comparison, also the PL spectrum of the ErQ_3 obtained in the same experimental conditions is reported. All spectra are corrected for the number of absorbed photons.

In Figure 2 the absorption spectra of the T3-Er and T5-Er complexes in DMSO solutions are shown. The main features of both spectra are the intense and broad UV absorption bands of the ligands centered at about 335 and 380 nm for T3-Er and T5-Er, respectively. The presence of weak peaks at 523 and 654 nm (see inset of Figure 2) due to the Er^{3+} transitions $^4I_{15/2} \rightarrow {}^2H_{11/2}$ and $^4I_{15/2} \rightarrow {}^4F_{9/2}$ proves that the complexation occurred. The PL spectra in the NIR spectral region of T3-Er and T5-Er (Figure 3), obtained by exciting the organic ligand with the 353 nm line of and Ar$^+$ laser, exhibit an intense emission around 1.54 μm corresponding to the $^4I_{13/2} \rightarrow {}^4I_{15/2}$ Er transition. For comparison in Figure 3 the PL spectrum of the ErQ_3, collected exactly in the same conditions, is also reported. The spectral shape of the spectra is almost identical, indicating that the energy of this transition is substantially independent of the ligand because the 4f Er shell is shielded by the outer $^5s_2$ and $^5p_6$ orbitals. However, the overall PL efficiency is strongly affected by the rate of the organic–inorganic energy transfer process, and although the absolute PL

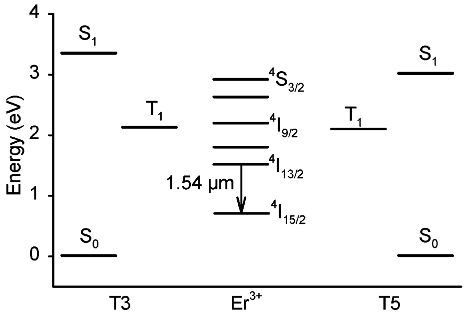

Figure 4. Sketch of the relevant energy levels involved in the Nir emission in T3-Er and T5-Er complexes. Absorption takes place between the S_0 and S_1 single state of T3 and T5 and then relaxes toward the corresponding T_1 triplet states. From the latter the energy transfer to the Er^{3+} excited states (probably mainly to the $^4I_{9/2}$) occurs. After thermalization, the radiative transition $^4I_{13/2} \rightarrow {}^4I_{15/2}$ produces light emission at 1.54 μm.

efficiency remains unknown, it is noteworthy to notice that T5-Er and especially T3-Er complexes show PL efficiencies as high as ErQ_3, which is, up to now, one of the best IR rare earth complex emitters.

The photophysical pathway leading to the 1.54 μm emission can be summarized as follows. The strong absorption bands of the ligand allows for the initial excitation (optical or electrical) of its singlet excited state, followed by intersystem crossing to the lower lying triplet states. This process is enhanced by the presence of heavy atoms in the complex. Energy transfer from the triplet state of the ligand to the upper resonance levels of the metal ion may then occur by exchange interaction. The efficiency of this latter process is affected by the coordination geometry and the degree of matching between the ligand triplet level and the Er upper states. In Figure 4 a sketch of the electronic levels involved in the T5-Er and T3-Er complexes is reported. From cyclovoltammetric measurements (in acetonitrile + 0.1 M Bu_4NClO_4, reference electrode a silver/0.1 M silver perchlorate in acetonitrile 0.34 V vs SCE), both the HOMO and the LUMO energy values were estimated (5.22 and 1.9 eV for T3 and 5.2 and 2.2 eV for T5 ligands, respectively). The positions of the singlet levels of the ligands were obtained from LUMO and those of the triplet levels from the ref 12, while that of Er^{3+} ions is given in ref 13. It is evident the close correspondence of the T_1 triplet level of both T5 and T3 and the $^4I_{9/2}$ excited state of the Er^{3+}, which is at the base of the good transfer efficiency of these complexes. Moreover, the higher efficiency of the T3-Er complex with respect to the T5-Er can be explained by considering the higher triplet production in short OTs than in long ones.[14] In summary, the syntheses of two new $Er^{3+}-OT$ complexes which are promising candidates, together with future related polymers, as IR emitters were reported. Their PL efficiency at 1.54 μm is comparable to that of the best emitters in this class of materials.

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