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ORGANIC RARE EARTH COMPLEXES IN POLYMER MATRICES AND LIGHT EMITTING DIODES

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The synthesis of modified diketone ligands and the preparation of soluble Er^{3+} and Eu^{3+} tris-(β -diketone)phenantroline complexes are described. The complexes, embedded in thin films of different conjugated and non-conjugated polymeric host matrices were studied by luminescence spectroscopy and used as active layers in organic light emitting single layer diodes to observe their characteristic emissions. The study of the optoelectronic properties of β -diketo-complexes in a light emitting diode setup is presented.

Keywords: organic rare earth complexes; polymers; luminescence; light emitting diodes

1. INTRODUCTION

The rare earth metals lanthanoides form a group of chemically similar elements which have in common an open 4f shell. The fact that the 4f electrons do not behave as valence electrons illustrates the chemical similarity of the rare earth elements. Lanthanoides absorb radiation in very sharply defined bands (4f-4f transition). According to the selection rules for atomic spectra, f-f transitions of free lanthanoid ions are forbidden (LaPorte selection rule). This rule says that in a centrosymmetric molecule or ion, the only allowed transitions are those accompanied by a change of parity [1,2]. When the symmetry of the ion is removed by an asymmetrical external crystal field, the transitions become allowed. As one of the consequences, luminescence of complexed lanthanoides is enhanced. By

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complexing with appropriate ligands, the complex system has also the advantage to be more soluble in organic matrices than the pure salts. Different types of chelating ligands like β -diketones [3,4,5], pyridines [6], bipyridines [7], cryptands [8], calixarenes [9], cyclodextrins [10], crown ethers [11] and others are known.

The electrooptical properties of the complex system can be influenced by embedding these luminescent systems in organic polymeric host matrices. If the energy levels of the polymer and the complex are appropriate, the organic matrix can act as an energy transferring system for the complex. After exciting the polymer, energy can be transferred via a cascade to the central rare earth ion, which emits at its characteristic wavelength.

Especially the emission of the trivalent erbium ion at $1.55\mu\text{m}$ is important for telecommunication because it is in a wavelength range called "third telecommunication window". In that wavelength range classical glass fibres have a minimum in attenuation.

An important application, which uses erbium ions, is the erbium doped optical waveguide amplifier in inorganic matrices [12]. The problem in these systems is the relatively low concentration limit of doping with erbium due to concentration quenching effects [13]. Compared to inorganic systems this limit is higher in organic systems.

In the present work we studied mixed, octacoordinated rare earth chelate complex systems [14] containing 3 molecules of a β -diketo-system and 1 molecule of a nitrogen containing heteroaromatic system as

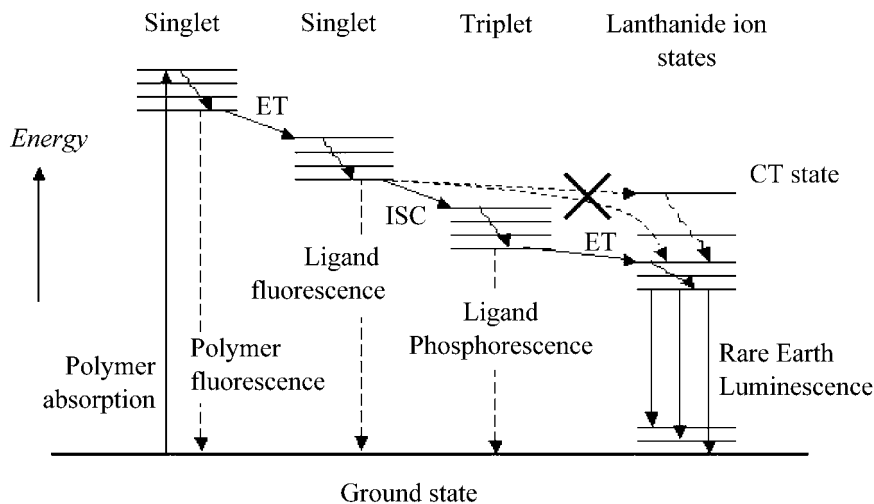


FIGURE 1 Energy cascade in polymer-complex system. Full line indicates the desired path of energy. Dotted line indicates possible loss mechanisms of energy.

bidentate ligands, which are embedded in polymer host matrices. The schematic positions of the energy levels in this system are demonstrated in Figure 1. The excited polymer transfers the energy via a Föster transfer to an appropriate complex system, which was selected also in respect to the energy of the ligands triplet state [15–16] in order to get energy transfer from the excited complex to the central ion. In this work we present europium luminescence achieved by optical and electrical excitation of a polymer, containing an europium complex and erbium luminescence after optical excitation of the erbium complex.

2. EXPERIMENTAL

2.1. Synthesis of β -Diketo Ligand

Two novel β -diketo ligands shown in Figure 2 (azoDBM and DTPD) were synthesized. The 1,3-dithienylpropane-1,3-dione ligand (DTPD) was synthesized by a standard Claisen reaction [17]. The 2-phenyldiazo-1,3-diphenyl-propan-1,3-dione (phenyldiazodibenzoylmethane, azoDBM) ligand was synthesized by an azo coupling reaction [18] with dibenzoylmethane (DBM) and a diazonium salt. The other ligands were purchased from Aldrich.

2.2. Synthesis of Complexes

All complexes were prepared with the following slightly modified method according to the literature. To a solution of 3 ml of 2 M sodium hydroxide in

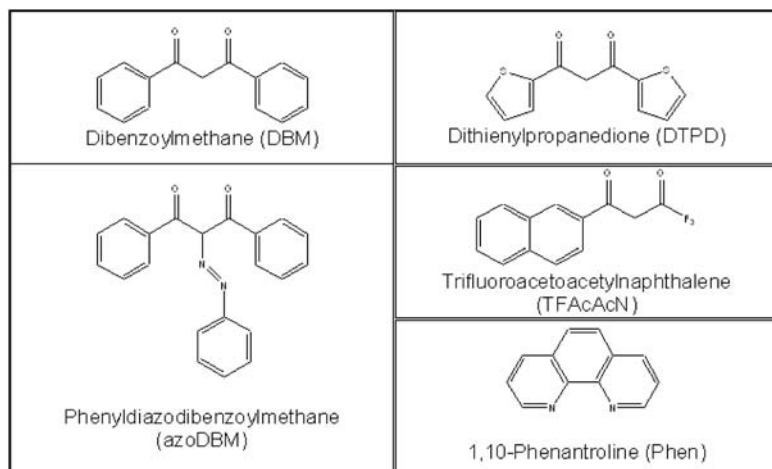


FIGURE 2 Overview of different ligand systems used in this work.

5 ml ethanol p.a. were added under stirring 6 mmol of the β -diketonate system and 2 mmol of 1,10 phenantroline (phen). After complete dissolving an ethanolic solution of 2 mmol of rare earth(III) chloride was added dropwise to the stirred solution. A precipitate formed immediately and after complete addition of the rare earth chloride, the mixture was stirred for an additional hour. The precipitate was filtered, washed with absolute ethanol and purified by recrystallisation from absolute ethanol or acetonitrile. The products were characterized by $^1\text{H-NMR}$ and mass spectrometry.

2.3. Fabrication of Polymer – Complex Mixtures

The rare earth complexes were dissolved in a polymer solution of polystyrene (PS) or polyvinylcarbazole (PVK) in toluene or benzene and stirred over night to provide good homogeneity. The complex : polymer ratio was 1 : 6. The solutions were used for film fabrication by spin coating and dropcasting.

The absorption measurements were carried out on a HP 8453 UV-Vis spectrophotometer, the luminescence measurements were carried out on a Hitachi F-4010 fluorescence spectrophotometer or on a laser setup. The organic light emitting diode devices were fabricated by spincoating the active layer (pure polymer solution or polymer + complex solution) on an ITO-glass substrate. The thickness of the active layer was about 100 nm. Al (80 nm) on LiF (0.6 nm) was evaporated on the substrate as top electrode. All electroluminescence studies were carried out inside a glove box.

3. RESULTS AND DISCUSSION

3.1. Ligand Systems

In Figure 3 the absorption spectra of the ligands are shown. The absorption maxima of all complexes, which originate from the β -diketo systems, are between 350 nm and 380 nm [19]. The wavelength region between 400 nm and 450 nm is quite important for our system because to get an energy transfer from the excited polymer to the complex there is the need for a good overlap of the luminescence spectrum of the polymer (see Fig. 4) and the absorption spectrum of the complex. As shown in Figure 3 DTPD fulfils this requirements better than the other ligands shown in the graph. In azoDBM the azo coupling causes a weak shoulder from 400 nm to 450 nm [20]. The phenantroline ligand which is in every complex system, does not contribute to the absorption in that range. The role of this ligand is to get the octacoordination and to ban water out of the complex.

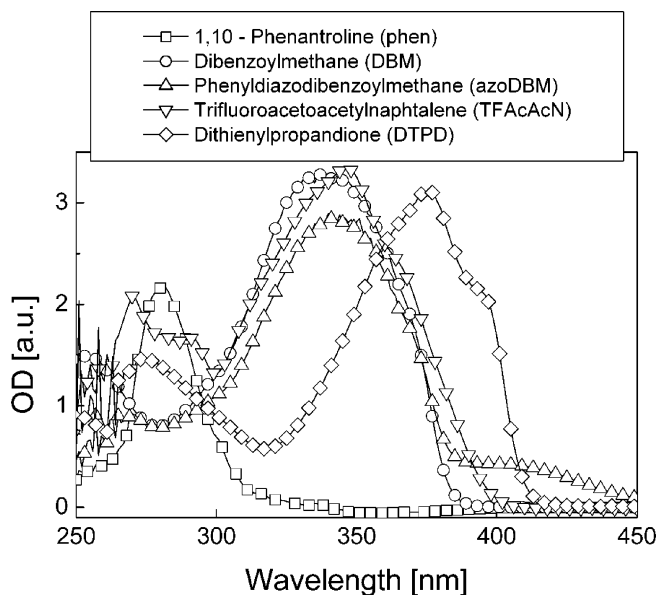


FIGURE 3 Absorption spectra of different ligand systems.

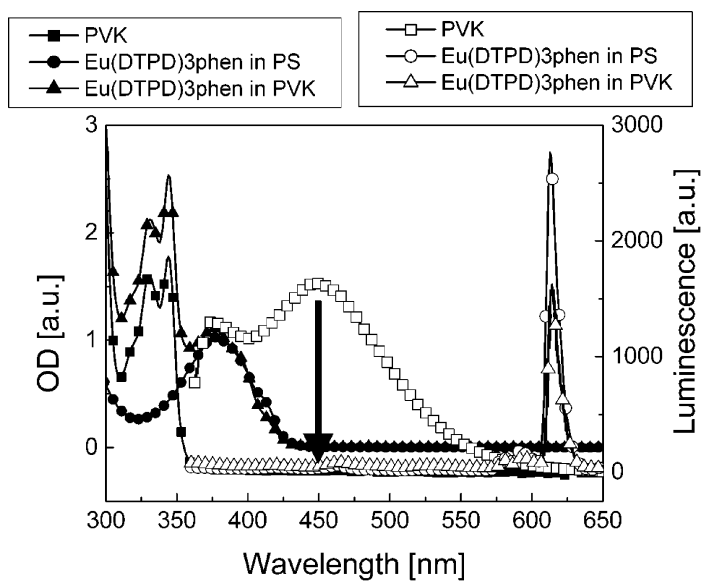


FIGURE 4 Closed symbols demonstrate absorption spectra. Open symbols demonstrate luminescence spectra.

3.2. Europium Complexes

Energy transfer from the polymer to the rare earth complexes was studied with europium complexes, which were synthesized as described in 2.2. Europium is one of the strongest emitters in the lanthanoid group. The main emission of the trivalent europium ion is at 618 nm according to the $^5D_0 \rightarrow ^7F_2$ transition [21]. As luminescent polymer polyvinylcarbazole (PVK) was used. As demonstrated in Figure 4 all polymer luminescence of PVK is quenched by adding a rare earth complex (here in the ratio 6:1 polymer:complex). Excitation at 350 nm with an Ar^+ -laser or with a xenon lamp provides the characteristic, clearly observable europium luminescence at 618 nm. The results show that the energy cascade works well but still there is a not neglectable amount of radiationless decays, which lowers the efficiency of the energy transfer. In Figure 5 the influence of azo coupling on energy transfer from the polymer to the complex is demonstrated. In contrast to our expectations it was observed that using the azo coupled ligand system the efficiency of energy transfer from PVK to the complex system is lower. We assume that the complexation of azoDBM lowers the conjugation in the system and therefore the effect of the azo coupling is lower than expected.

3.3. Erbium Complexes

The luminescence of the trivalent erbium ion is much weaker compared to europium [22]. The erbium complexes were studied embedded in a

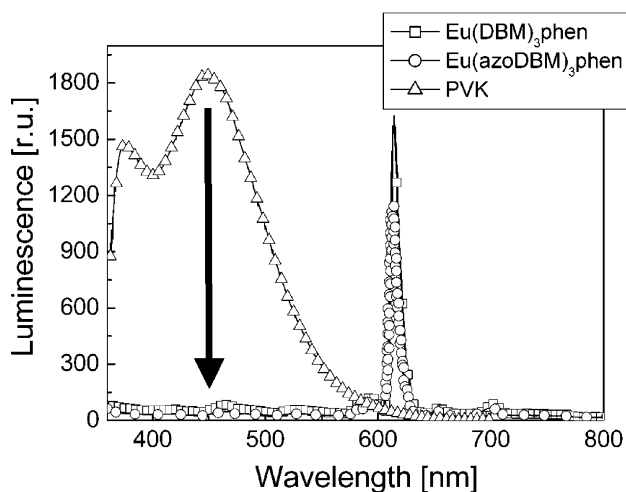


FIGURE 5 Luminescence spectrum of pure PVK polymer and luminescence spectra of two europium complexes excited at 350 nm.

polystyrene (PS) matrix, which provide processibility for film fabrication. Polystyrene was chosen as host matrix because direct excitation of a rare earth complex system is more effective than exciting via the energy transferring polymer PVK (shown in Fig. 4). The absorption spectra of the synthesized complexes are all similar to the europium complexes, so the excitation wavelength was again 350 nm to observe the erbium luminescence at 1.55 μm according to the $^4\text{I}_{13/2} \rightarrow ^4\text{I}_{15/2}$ transition. Erbium complexes with TFAcAcN and especially DTPD ligands showed significant luminescence.

In Figure 6 the photoluminescence of the erbium complex $\text{Er}(\text{DTPD})_3\text{phen}$ embedded in polystyrene is demonstrated. The excitation was done by an argon laser at 350 nm with a power of 60 mW. At liquid nitrogen temperature the erbium emission at 1.55 μm was clearly observed but at room temperature the signal was almost quenched. At room temperature there are more nonradiative decays of excited erbium states possible due to the internal vibrational absorption. Especially O-H and C-H bonds are responsible for this strong quenching of the erbium luminescence [16]. The quenching should be reduced by changing to a polymer host with no or less C-H bonds, e.g., the perfluorinated polymer Teflon AF[®], which also provides processibility in order to make transparent films of good quality. However, the solvent of the polymer, which is a perfluorinated alkane, does not dissolve the complex completely. Spincasting from a fine dispersion gave anyhow good films without noticeable phase separation.

By exciting the $\text{Er}(\text{DTPD})_3\text{phen}$ complex embedded in Teflon AF[®] at 350 nm with an argon laser (60 mW) again the erbium luminescence could be clearly observed (Fig. 7). Compared to the complex system in polystyrene a better signal to noise ratio and a much less erbium luminescence quenching at room temperature was obtained.

3.4. Light Emitting Diodes

The mixture of PVK and rare earth complex 1:6 as used for photoluminescence studies was also used as an active layer in an organic light emitting diode (OLED) setup to investigate the optoelectronic properties of the synthesized β -diketo complexes.

For comparison the properties of the host material PVK are shown in Figure 8. An electroluminescence signal of PVK, which can be tuned by the voltage, was clearly observed (Fig. 8a). The current/voltage characteristics (Fig. 8b) shows the good diode behavior of the device. With the europium complexes like $\text{Eu}(\text{DTPD})_3\text{phen}$ mixed to the polymer luminescence of Eu^{3+} (Fig. 9a) and the complete quenching of the polymer luminescence (insert in Fig. 9a) was observed, which indicates energy transfer from the polymer to the complex system. The current/voltage characteristics are shown in Figure 9b. The luminescence of the Eu^{3+} can be tuned with the voltage.

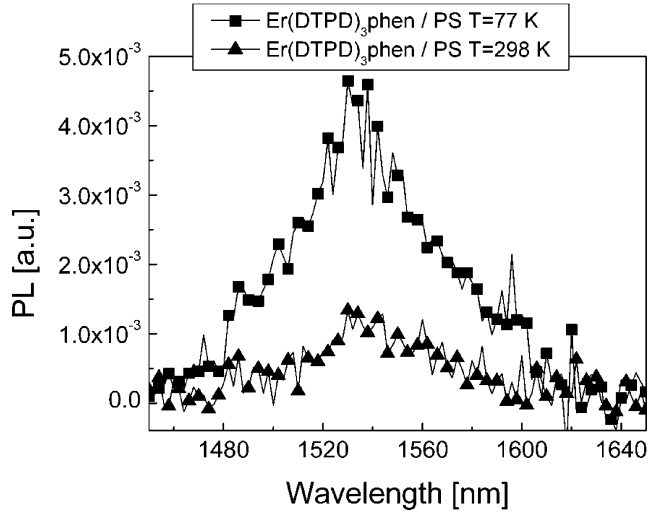


FIGURE 6 Erbium luminescence at liquid nitrogen temperature. Quenching of the erbium luminescence at room temperature.

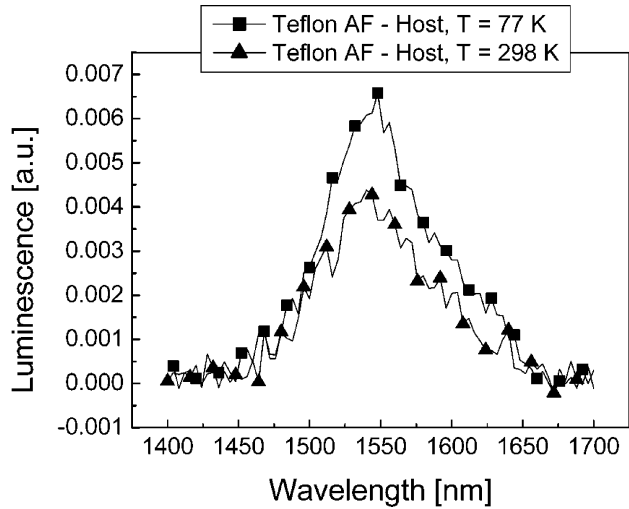


FIGURE 7 Erbium luminescence at liquid nitrogen temperature and at room temperature.

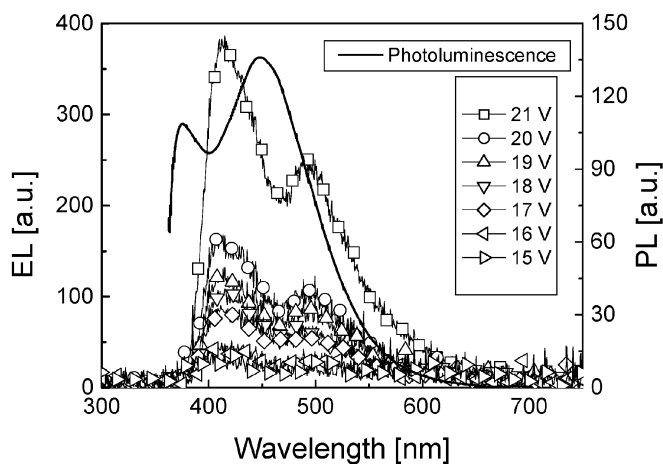


FIGURE 8a Photoluminescence (full line) and electroluminescence (open symbols) of PVK.

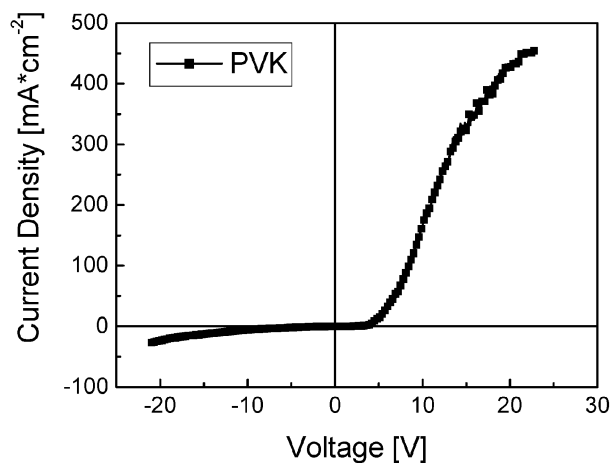


FIGURE 8b Current/voltage characteristics of PVK device.

4. CONCLUSION

We have shown the synthesis of novel β -diketo ligand and rare earth complex systems. The complexes were characterized after embedding in different polymer host matrices. Energy transfer from optically and

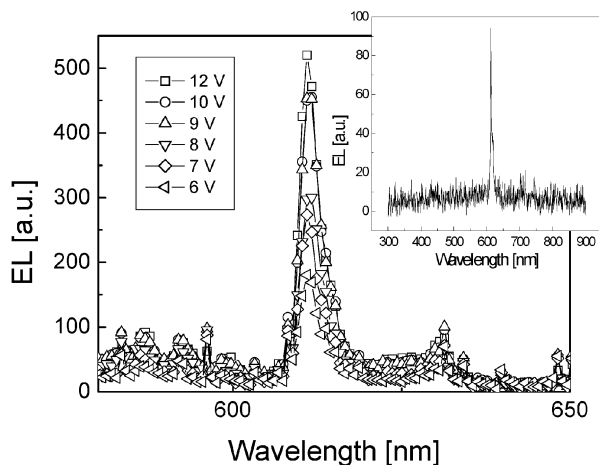


FIGURE 9a Electroluminescence of Europium originates from PVK + $\text{Eu}(\text{DTPD})_3\text{phen}$. The inset shows the quenching of the polymer electroluminescence between 400 nm and 600 nm.

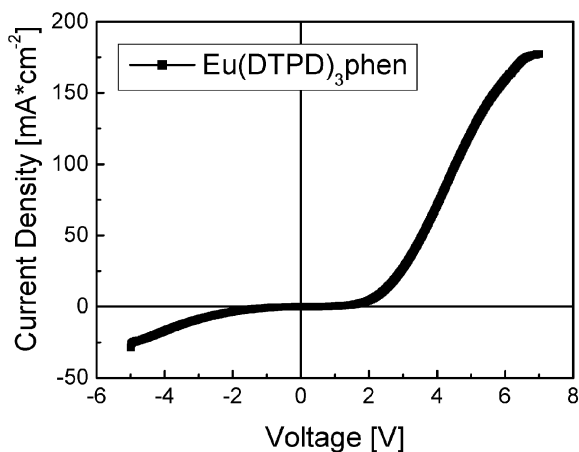


FIGURE 9b Current/voltage characteristics of PVK– $\text{Eu}(\text{DTPD})_3\text{phen}$ device.

electrically excited polymer hosts to the central ion of the complex system was studied.

For erbium as central ion, we demonstrated a suitable polymer and ligand system to obtain luminescence at $1.55\ \mu\text{m}$ even at room temperature, which is important for organic optical amplifier systems.

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