



JOHANNES KEPLER  
UNIVERSITÄT LINZ

Netzwerk für Forschung, Lehre und Praxis



*Light Emitting Diodes (LED's) based on Rare Earth Emitters*

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Betreuung:

*Prof. Dr. Serdar Niyazi Sariciftci*

Von:

*Markus Koppe*

Mitbetreuung:

*Dr. Helmut Neugebauer*

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Linz, Oktober 2002

Markus Koppe

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## **Abstract**

Rare earth emitters are of great interest in optical telecommunication for converting electrical pulses into optical pulses and for amplification of light at certain wavelengths in the visible and near infrared region. The raising need for optical telecommunication systems entails the demand for cheap and easy processable materials. Organic systems would fulfil these requirements better than inorganic systems, which are mainly used till now.

In this thesis the principle and the synthesis of such organic systems are described. The characterisation of different systems was performed by absorption spectroscopy and photoluminescence spectroscopy.

The use of synthesised organic rare earth systems in organic light emitting diodes (OLED's) is described and OLED – devices are characterised by electroluminescence studies and current – voltage – characteristics.

## **Zusammenfassung**

Seltenerdmetall enthaltende Emitter sind in der optischen Telekommunikation von großem Interesse um elektrische Impulse in optische Impulse umzuwandeln und um Licht mit gewissen Wellenlängen im sichtbaren und nahen infraroten Bereich zu verstärken. Die steigende Nachfrage an optischen Telekommunikationssystemen zieht den Bedarf an billigen und leicht verarbeitbaren Materialien nach sich. Organische Systeme würden diesen Anforderungen besser gerecht werden als anorganische Materialien, die bis jetzt hauptsächlich verwendet werden.

In dieser Diplomarbeit sind das Prinzip und die Synthesen solcher organischen Systeme beschrieben. Die Charakterisierung verschiedener Systeme wurde mit Hilfe von Absorptionsspektroskopie und Photolumineszenzspektroskopie durchgeführt.

Die Verwendung der synthetisierten organischen Seltenerdmetallsysteme in organischen Leuchtdioden (OLED's) wird beschrieben und die Charakterisierung der OLED's wird mit Hilfe von Elektrolumineszenzmessungen und Strom – Spannungs – Kurven durchgeführt.

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# 1 Introduction

## 1.1 Motivation

The field of optical telecommunication has drawn great attention since the first demonstration of low-loss optical fibres in the 1970`s. After the first introduction of long-distance optical-fibre transmission systems in the late 1980`s and the emergence of the erbium doped fibre amplifier in 1987 there is a growing demand for cheap and easily processable materials for the production of optical data transmission systems [1][2].

The accessibility of the Internet for more and more people (“global wiring”) entailed an enormous growth in data traffic and so there is the growing need for a large bandwidth (information – carrying capacity). But Internet bandwidth is only a small part of total bandwidth in use [3]. Ostensible other broadband services (HDTV – High Definition Television, Video-On-Demand, interactive television, voice traffic etcetera) and applications which process a huge amount of data (multimedia applications, video conferencing etcetera) will be available to more and more people (FTTH – concept “Fibre To The Home”).

Copper wires cannot satisfy the need for high volume data transfer because of low transmission speed and small signal bandwidth. Information transmission by using optical cables, which transport pulses of light instead of electricity, increases bandwidth tremendously [4].

Since their first introduction in the late 1980`s, high capacity long distance optical fibre transmission systems have advanced from transmission speeds of  $140 \text{ Mbit s}^{-1}$  for the first transatlantic system to exceed  $1 \text{ Tbit s}^{-1}$  ( $1 \text{ Tbit s}^{-1} = 10^{12} \text{ bit s}^{-1}$ ) in just 10 years. Laboratory demonstrations of optical transmission at  $100 \text{ Gbit s}^{-1}$  per channel and the use of over 100 channels in one single fibre are in progress.

The telecommunication systems installed now are working at  $40 \text{ Gbit s}^{-1}$ . At these speeds the electronics is becoming difficult to work with, and very elaborate design is necessary. Could one stay in the optical domain when amplifying, reshaping, routing etcetera the electronics will no longer be a issue. The speed limit working with all optical components has been

foreseen to be up to  $1 \text{ Tbit s}^{-1}$ . This new technology requires new materials for generation, guiding, switching, multiplexing and amplification of light.

Beside of that there are several economical and technical disadvantages of glass fibres. High costs and inconvenient processibility (especially flexibility) opens the field for polymer optical fibres (POF's) [5] [6].

Polymer optical fibres are nowadays of great commercial interest because they can maintain flexibility at thicker fibre sizes making them more easy to handle and to install. For creation of an optical transmission system totally made of organic compounds new materials are needed, which are transparent at certain wavelengths and can be optically and electrically illuminated.



## 1.2 Applications in Optical Telecommunication

### 1.2.1 Silica and Polymer Optical Fibres

The principal of optical fibres is the transmission through transparent media on the basis of total internal reflection, which is possible in core-cladding configuration. It consists of a circular core of uniform refractive index surrounded by a cladding of slightly lower refractive index.. In the case of step-index optical fibres [7] the high refractive index is constant along the fibre core cross-section and changes at once to the low refractive index of the cladding. The second technological important type is the graded index fibre, for which the refractive index gradually changes from a high value in the centre of the core to a lower value at the perimeter of the core. Different refractive indexes can be attained by using two different materials or by surface treatment of the optical fibre.

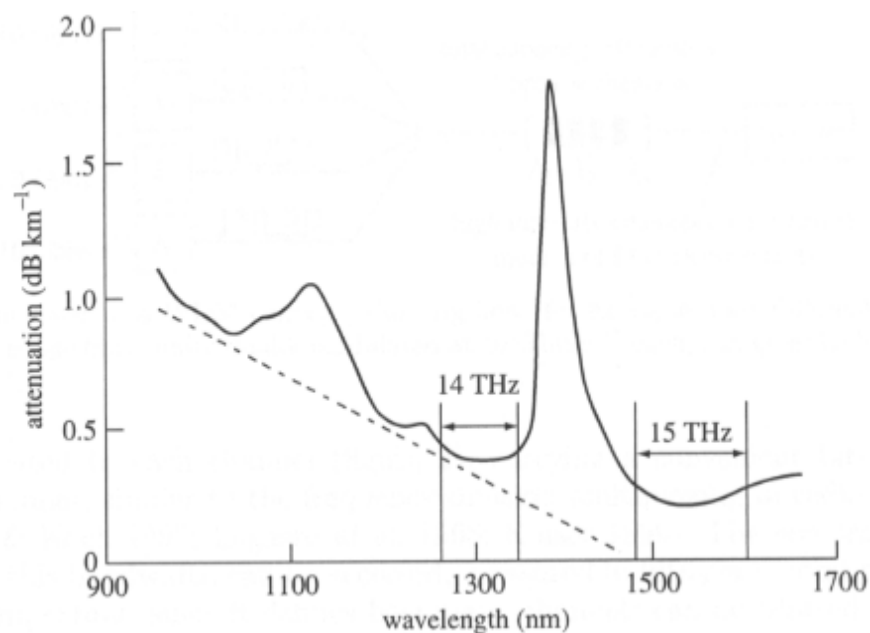


Figure 1 The regions of great bandwidth where optical fibres work well are defined by the regions of low attenuation. The dotted line shows the fundamental Rayleigh scattering limit. (Figure taken from [8])

The primary limit on the amount of transferable data is the available transmission bandwidth of the medium itself. The transmission bandwidth of single-mode optical silica fibres

(operation at a certain wavelength) can provide over 100 nm optical bandwidth, which is defined by the low spectral attenuation region of 1500 nm – 1620 nm called third telecommunication window (100 nm represents over 15 THz of potential frequency space for the transmission data). Between 1250 nm and 1360 nm there is an other low attenuation region that can provide additional 14 THz (see Figure 1).

The recent research on optical fibres resulted in an minimal attenuation of about 0.1 dB km<sup>-1</sup>. Removal of especially the hydroxyl ion (OH<sup>-</sup>) impurities in the silica fibre lowers losses due to the absorption around 1.4 μm almost down to the fundamental limit defined by the Rayleigh scattering (see Figure 1). The basic vibration of hydroxyl ions at 2.37 μm is responsible for that high absorption around 1.4 μm because it is the region of the first overtone of the O-H vibration. The development of the new low loss optical fibres was very important for the success of optical telecommunication.

Recently there has been increasing interest in the development of polymer optical fibres (POF's). The ductility of polymers is an important advantage that entails properties like easy processing, easy handling, low cost and large core diameters. The large core diameter of up to more than 1 mm enables high efficiencies of fibre coupling [9], which is much more difficult to design for glass cores. Glass optical fibres have smaller core diameters ranging from just a few micrometers for single mode up to 125 μm for multi-mode fibres. Therefore glass fibres are not often used for local area networks (LAN's) because a lot of connections have to be realized. Another advantages of polymer optical fibres are the low density (light-weight-properties) and good flexibility.

Besides of that is the low loss window remarkable which is in the visible region with its absolute minimum of about 70 dB km<sup>-1</sup> at 580 nm (for polymethylmethacrylate, PMMA, see Figure 2). Nowadays the minimum of about 130 dB km<sup>-1</sup> at 650 nm is used exclusively because there are no high-performance light emitting diodes at the wavelength of 580 nm, which are necessary for converting electrical pulses into optical ones.

A serious problem is the low thermal resistance of polymer optical fibres. Recent investigations on exchanging H-atoms with halogen atoms or deuterium atoms resulted in a better heat resistance up to 160 °C and attenuations of 20 dB km<sup>-1</sup> at 650 nm [10]. Because of

the high costs fully deuterated or halogenated compounds are more of academic interest until now. However DuPont's Teflon AF<sup>®</sup> and Asahi's Cytop<sup>®</sup> are two commercially available amorphous perfluoropolymers for which reduction of price in the future can be expected due to development of line production for low loss infrared optics [13].

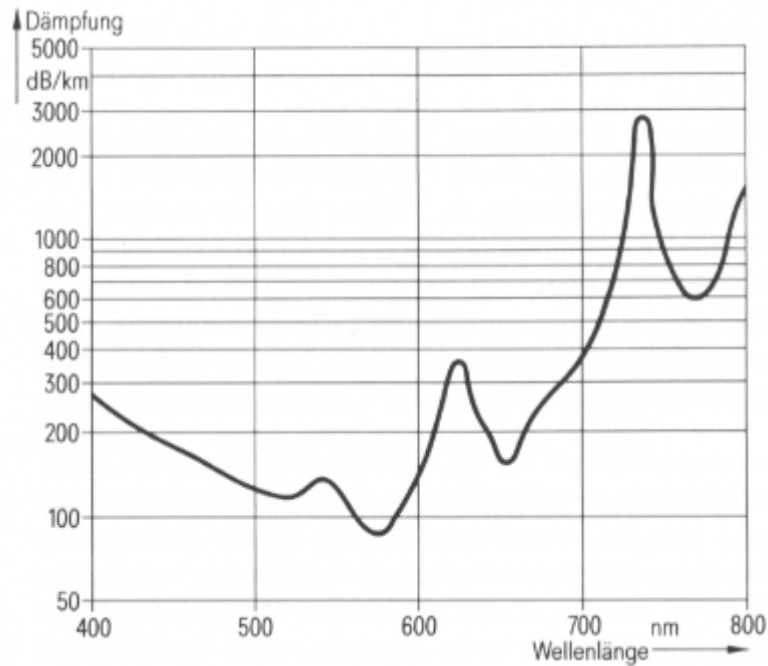


Figure 2 Spectral attenuation of polymethylmethacrylate fibre. (Figure taken from [7])

In the near infrared region (1000 nm – 1600 nm) the problem of vibrational absorptions due to C-H and O-H bonds is more serious than in the visible range. Pure PMMA has an attenuation of about  $10^4$  dB km<sup>-1</sup> at 1.55  $\mu$ m. For using polymer optical fibres in the same spectral region like glass fibres, elimination of O-H bonds and substitution of C-H bonds with fluorine compounds (C-F) or deuterium compounds (C-D) is essential [11] [12].

Examples for such modified polymers are the group of PFCB-type polymers (perfluorinated cyclobutene type polymer), Teflon AF<sup>®</sup> and Asahi's Cytop<sup>®</sup> which have their theoretical attenuation minima below 1 dB km<sup>-1</sup> (see Figure 3) in the near infra-red region around 1.3  $\mu$ m. Even for the third telecommunication wavelength at 1.55  $\mu$ m the attainable attenuation would be lower than 10 dB km<sup>-1</sup>. A theoretical loss spectrum of such polymers is shown in Figure 3.

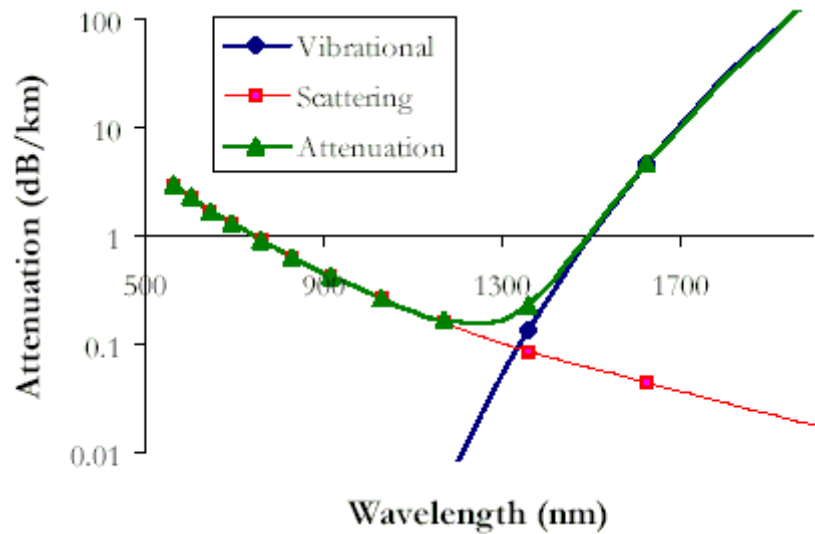


Figure 3 Theoretical loss spectrum of PFCB-type polymers (Figure taken from [13])

## 1.2.2 Optical Amplifiers

For long distance communication it is necessary to compensate the losses in the fibre by regenerating the signal typically every 50 –150 km (depending on the data rate). This is currently done by optical amplifiers. An amplifying medium contains a material capable of luminescence at the signal beam wavelength. The luminescent material needs to be pumped with a laser, which excites the molecules to a higher energy level, thus generating a population inversion between the first excited state and the ground state. A signal beam travelling through the amplifying medium will stimulate the emission of light, which is of the same wavelength and phase [14]. For amplification of an 1.55  $\mu\text{m}$  - signal erbium doped fibre amplifiers (EDFA's) are used due to the  ${}^4I_{13/2} \rightarrow {}^4I_{15/2}$  transition (see 1.3.1). In 1987 the still increasing effort of research and development of the erbium doped fibre amplifier started, which was an important invention for today's importance of optical telecommunication technologies.

The core of the fibre is doped with erbium ions during fibre fabrication. The amplifier is pumped at either 1.48  $\mu\text{m}$  or 0.98  $\mu\text{m}$  with a commercially available semiconductor diode laser coupled into the amplifier with a wavelength multiplexer.

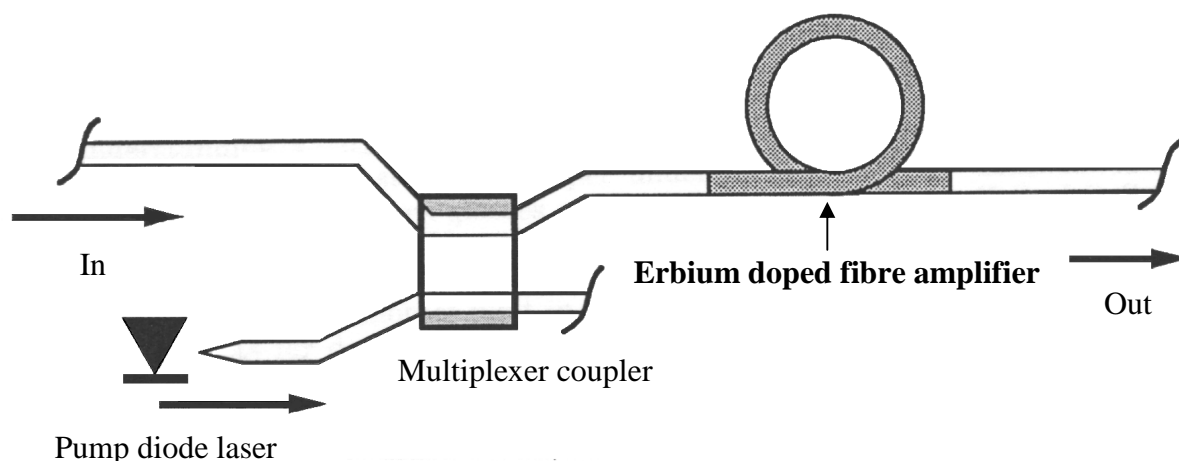


Figure 4 Erbium doped fibre amplifier (EDFA). Used for amplification of light around  $1.55 \mu\text{m}$  by pumping with a diode laser.

### 1.3 The Lanthanoids

The rare earths form a group of chemically similar elements, which have in common an open 4f shell. The valence shell of the atoms is made up of the 4f, 5d and 6s electrons. The 4f orbitals in the lanthanoid elements are located relatively close to the nucleus and so these electrons are shielded very effectively by outer electrons ( $5s^2 5p^6 6s^2$ ). The fact that the 4f electrons do not behave as valence electrons illustrates the chemical similarity of the rare earth elements.

For luminescence processes the properties of the mainly trivalent ions are much more important than those of the neutral atoms. (Cerium (Ce), Praseodymium (Pr) and Terbium (Tb) may also be tetravalent; Samarium (Sm), Europium (Eu) and Ytterbium (Yb) are often divalent; the rest of the group is always trivalent). All trivalent ions have xenon like rare gas shell and in addition N 4f electrons ( $N = 0-14$ ). This means for erbium  $[\text{Xe}]4f^{12}6s^2$  and for the trivalent ion  $[\text{Xe}]4f^{11}$ .

#### 1.3.1 Photophysical properties of trivalent lanthanoid ions

**Absorption:** Lanthanoid ions absorb radiation in very sharply defined bands (f-f 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 [15]. When the symmetry of the ion is removed with an asymmetrical external crystal field, the transitions become allowed. The shielding of the 4f electrons also accounts for the observation that the absorption spectra of the lanthanoid ions are only weakly perturbed upon complexation with a ligand. The effect is limited to slight displacements of the bands to higher wavelengths.

**Luminescence:** The emission of a complexed trivalent rare earth ion arises from radiative transitions among the energy levels in the  $4f_n$  electronic configuration of these ions. In the absence of any interaction between these  $n$  electrons, the levels would be degenerate. Because of interelectronic Coulombic repulsion, however, the degeneracy is removed and the levels are split over a range of about  $20000 \text{ cm}^{-1}$ . A further splitting in the order of  $1000 \text{ cm}^{-1}$  occurs due to spin-orbit interactions but is neglected for subsequent discussions.

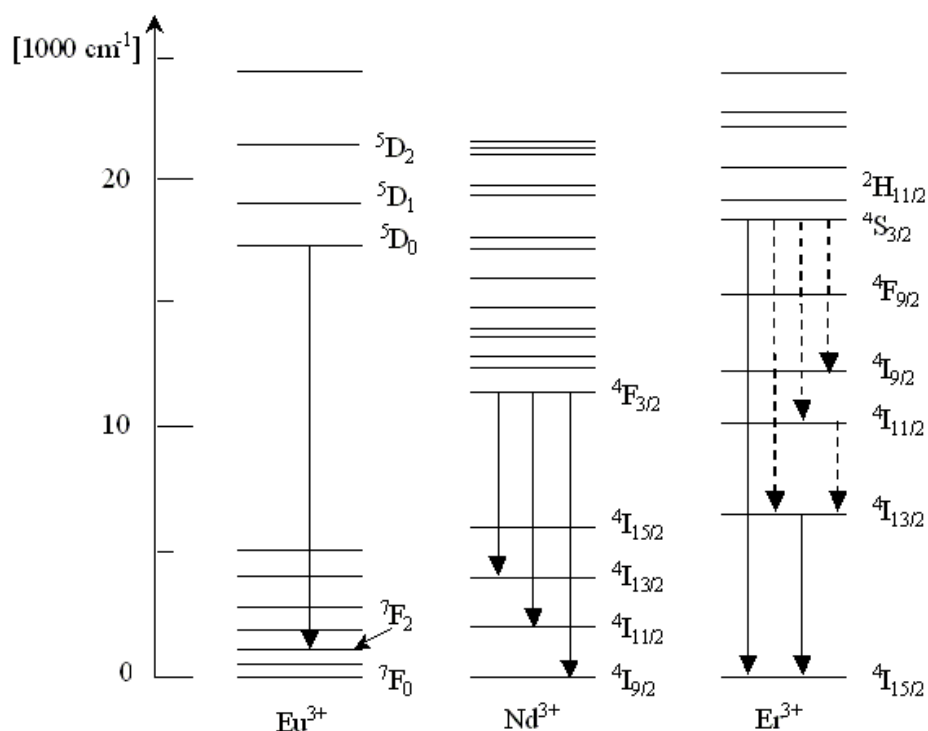


Figure 5 A cutout of important energy levels of three rare earth ions. Full line indicates radiative decays. The dashed lines indicate non-radiative decays. (Data taken from [16][17])

In Figure 5 the main energy levels of three lanthanoid ions, which will be discussed in more detail in the experimental part, are shown. The important levels are identified with their Russell-Saunders symbols.

The Europium ion ( $\text{Eu}^{3+}$ ) is a strong emitter in the visible region. After excitation with energy of at least 2.18 eV the energy state  $^5\text{D}_0$  is populated and, by recombination to the  $^7\text{F}_2$  state, light with 614 nm is emitted. For the Neodymium-ion ( $\text{Nd}^{3+}$ ) a minimum excitation energy of 1.07 eV is required to get an emission of three different wavelengths according to the  $^4\text{F}_{3/2} \rightarrow ^4\text{I}_{13/2}$  (890 nm),  $^4\text{F}_{3/2} \rightarrow ^4\text{I}_{11/2}$  (1050 nm) and  $^4\text{F}_{3/2} \rightarrow ^4\text{I}_{9/2}$  (1350 nm) transitions. For the Erbium-ion a minimum excitation energy of 1.28 eV is required to get an emission in the near infrared region around 1.55  $\mu\text{m}$  ( $^4\text{I}_{13/2} \rightarrow ^4\text{I}_{15/2}$  transition). If the excitation energy is greater than 2.34 eV also green emission according to the  $^4\text{S}_{3/2} \rightarrow ^4\text{I}_{15/2}$  transition around 540 nm can be observed.

The group of rare earth elements contains also other emissive ions in the visible and near infrared region. In principle the rare earth ions can be classified in three groups [18] according to their strength of luminescence.

1.  $\text{Tb}^{3+}$ ,  $\text{Dy}^{3+}$ ,  $\text{Eu}^{3+}$  and  $\text{Sm}^{3+}$  are the strongest emitters, which all have a fluorescence in the visible region. ( $\text{Tb}^{3+}$ : 545 nm,  $^5\text{D}_4 \rightarrow ^7\text{F}_4$ ;  $\text{Dy}^{3+}$ : 573 nm,  $^4\text{F}_{9/2} \rightarrow ^6\text{H}_{13/2}$ ;  $\text{Eu}^{3+}$ : 614 nm,  $^5\text{D}_0 \rightarrow ^7\text{F}_2$ ;  $\text{Sm}^{3+}$ : 643 nm,  $^4\text{G}_{5/2} \rightarrow ^6\text{H}_{11/2}$ ).
2.  $\text{Er}^{3+}$ ,  $\text{Pr}^{3+}$ ,  $\text{Nd}^{3+}$ ,  $\text{Ho}^{3+}$ ,  $\text{Tm}^{3+}$  and  $\text{Yb}^{3+}$  are weak emitters in the near infrared region. The weakness of their luminescence is based on the fact that these ions have closely spaced energy levels, making the non radiative transition easy. For the erbium ion there are, besides some other very weak spin forbidden lines (e.g.  $4f^{n-1}5d \rightarrow 4f^n$ ), two characteristic transitions: one in the visible region at about 550 nm ( $^4\text{S}_{3/2} \rightarrow ^4\text{I}_{15/2}$ ) and the other, the most important one for commercial use as described before, at 1.55  $\mu\text{m}$  ( $^4\text{I}_{13/2} \rightarrow ^4\text{I}_{15/2}$ ).
3.  $\text{La}^{3+}$ ,  $\text{Gd}^{3+}$  and  $\text{Lu}^{3+}$  exhibit no ion fluorescence because the lowest-lying resonance level lies far above the triplet level of any of the commonly used ligands.

## 1.4 The Concept

### 1.4.1 Rare Earth Complex Systems

To manage the problem with low absorption coefficients of the free lanthanoid ions, the trivalent ions can be complexed with high absorbing ligand systems, which transfer energy to the central ion (antenna effect [19]). Different types of chelating ligands like  $\beta$ -diketones [20,21,22], pyridines [23], bipyridines [24], cryptands [25], calixarenes [26], cyclodextrins [27], crown ethers [28] and some others are known. Such complexed systems have great attributes of solubility in a lot of common organic solvents like chloroform, benzene, toluene, etc.. Therefore they are also good soluble in polymer matrices in contrast to pure salts of lanthanoids.

#### 1.4.1.1 Structure of Rare Earth Complex System

All complex systems studied in this thesis are mixed, octacoordinated rare earth chelate systems [29] containing 3 molecules of a  $\beta$ -diketo-system and 1 molecule of a nitrogen containing heteroaromatic system as bidentate ligand and a trivalent rare earth ion as central ion.

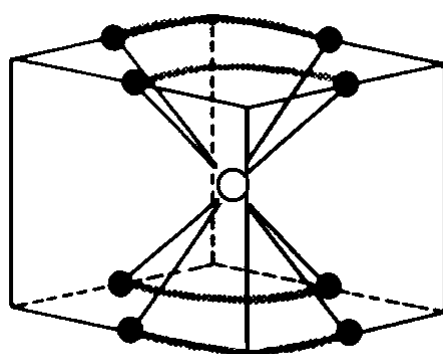


Figure 6 Simplified octacoordinated structure of rare earth complex system. [O] Indicates the central atom (rare earth ion), [●] indicates oxygen or nitrogen atoms of the ligand system.



The  $\beta$ -diketo-system is the unit, which is responsible for absorbing the excitation energy and transferring this energy to the central ion. The nitrogen containing heteroaromatic system that is the same one in every studied complex system, does normally not contribute to the absorption. The role of this ligand is to get the octacoordination and to ban water out of the complex, which is very important because of disturbing OH-vibrations (see 1.2.1).

### 1.4.2 Polymer Host-Matrices

For the design of totally organic luminescing rare earth solid-state devices appropriate polymers are used. The polymers may act both as simple host materials and as systems, which transfer energy after any excitation (optical and electrical) to the embedded complex that gives the characteristic luminescence of the central ion.

### 1.4.3 Energy Transfer Mechanism

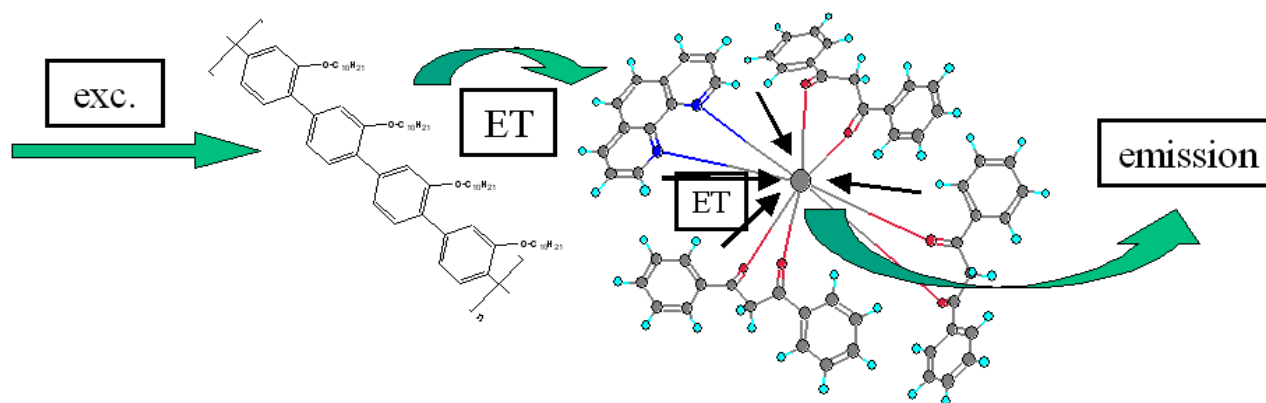


Figure 7 Illustration of the concept of polymer / lanthanoide-complex system. (exc.= excitation, ET = energy transfer)

The energy level diagram in Figure 8 shows the schematic positions of energy levels for polymer / lanthanoide-complex systems illustrated in Figure 7. The path indicated by a full line shows the ideal way of successive energy transfers to achieve lanthanoide luminescence originating from exciting the polymer.

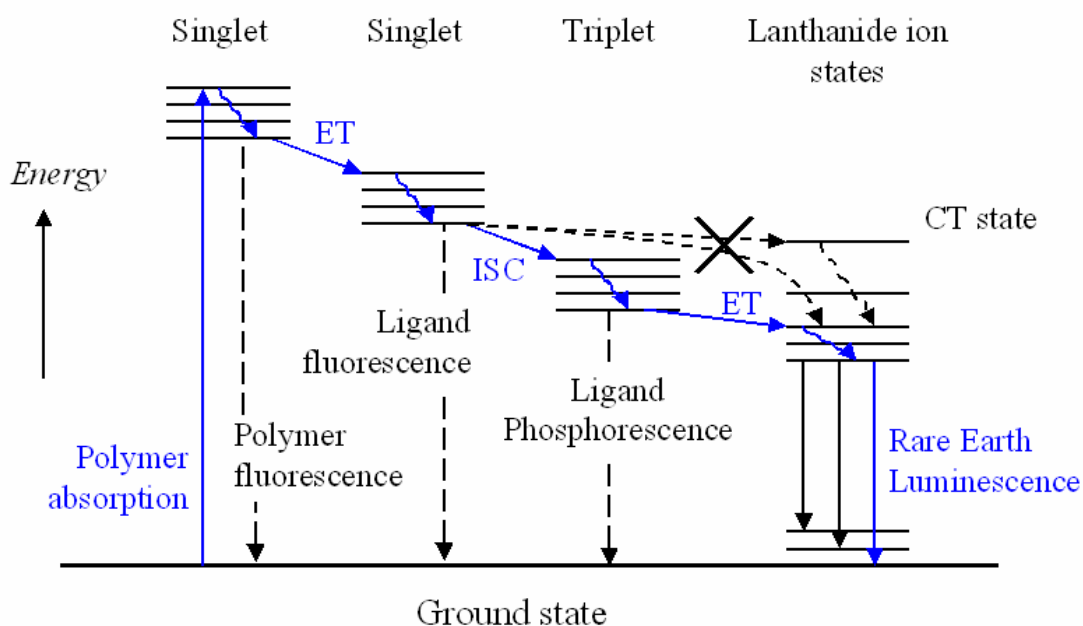


Figure 8 Schematic positions of energy levels in polymer / lanthanide-complex systems. The full lines show the desired way energy should go. The dashed lines show possible radiative decays. (ET = energy transfer, ISC = inter system crossing, CT = charge transfer)

As a first step the polymer is excited and energy is transferred from excited polymer singlet state to an excited state of the ligand system. This transfer mechanism can be described as a Förster transfer, so the best yield of energy transfer is obtained when the energy difference of excited and accepting level is small. If the energy gaps of the polymer and the ligand system do not fit, no energy transfer takes place which results in simple polymer luminescence. After a successful transfer of energy to the excited singlet states of the ligands five different possibilities besides radiationless recombination for further transfers and transitions are conceivable:

1. Ligand fluorescence ( $S_1 \rightarrow S_0$ ) if no or low inter system crossing (ISC) takes place.
2. Direct energy transfer from the  $S_1$ -level to a rare earth ion state (not allowed as it is spin forbidden).
3. Another possibility involves electron transfer to a CT state of the complex. [30].

→ after an intersystem crossing, there are two other possibilities

4. Ligand phosphorescence is possible if there is no appropriate lanthanoid level.
5. If there is a suitable level of a lanthanoid ion, energy can be transferred to this level.

As can be seen, the energy of the triplet level in the complex system is of great importance. The position of the triplet state and the resonant (emitting) energy levels of the ions is responsible for the luminescence efficiency of the system. The lowest triplet state energy level of the complex must be nearly equal to or must lie above the resonance energy level of the rare earth ion [31] [32] [33].

## 1.5 This Thesis

This work will deal with the synthesis and characterisation of organic systems, which emit light in the visible (614nm) and near infrared (890 nm, 1.05  $\mu\text{m}$ , 1.35 $\mu\text{m}$ , 1.55  $\mu\text{m}$ ) region. All these wavelengths are standard wavelengths for optical telecommunications.

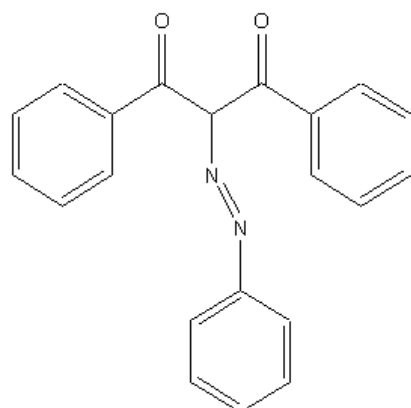
Different conjugated and non-conjugated polymer host matrices for various appropriate rare earth complex systems are studied.

The fabrication and characteristics of organic photoluminescent and electroluminescent devices containing the rare earth ions  $\text{Eu}^{3+}$ ,  $\text{Nd}^{3+}$  and  $\text{Er}^{3+}$  are presented.

## 2 Experimental

### 2.1 Synthesis of Ligand Systems

#### 2.1.1 2-Phenylazo-1,3-diphenyl-propane-1,3-dione



2-Phenylazo-1,3-diphenyl-propane-1,3-dione (azoDBM)

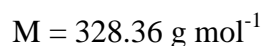
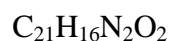


Figure 9 Structure of 2-Phenylazo-1,3-diphenyl-propane-1,3-dione

The 2-phenyldiazo-1,3-diphenyl-propane-1,3-dione (phenylazodibenzoylmethane, azoDBM) ligand was synthesised by an azo-coupling reaction [34] with dibenzoylmethane (DBM) and a diazonium salt.

#### *Diazotisation* [35]:

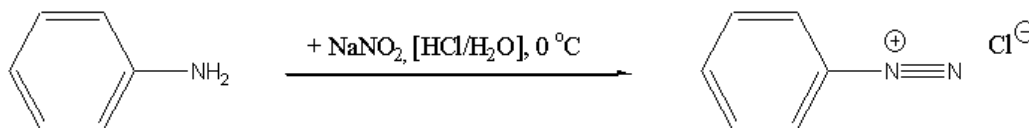


Figure 10 Formation of aryl-diazonium chloride (diazotisation).

4.54 ml (50 mmol) aniline were dissolved in a mixture of 15 ml of concentrated hydrochloric acid and 15 ml of water contained in a 250 ml flask. After cooling down to 0 °C to 5 °C with a mixture of ice and water; 3.45 g of powdered sodium nitrite in 20 ml of water were added in portions of about 2 - 3 ml to the cold, well-stirred solution of phenylamine hydrochloride. The

temperature was always between 0 °C and 5 °C. After complete addition some urea was admixed and stirred again for 20 minutes.

***Azo-coupling:***

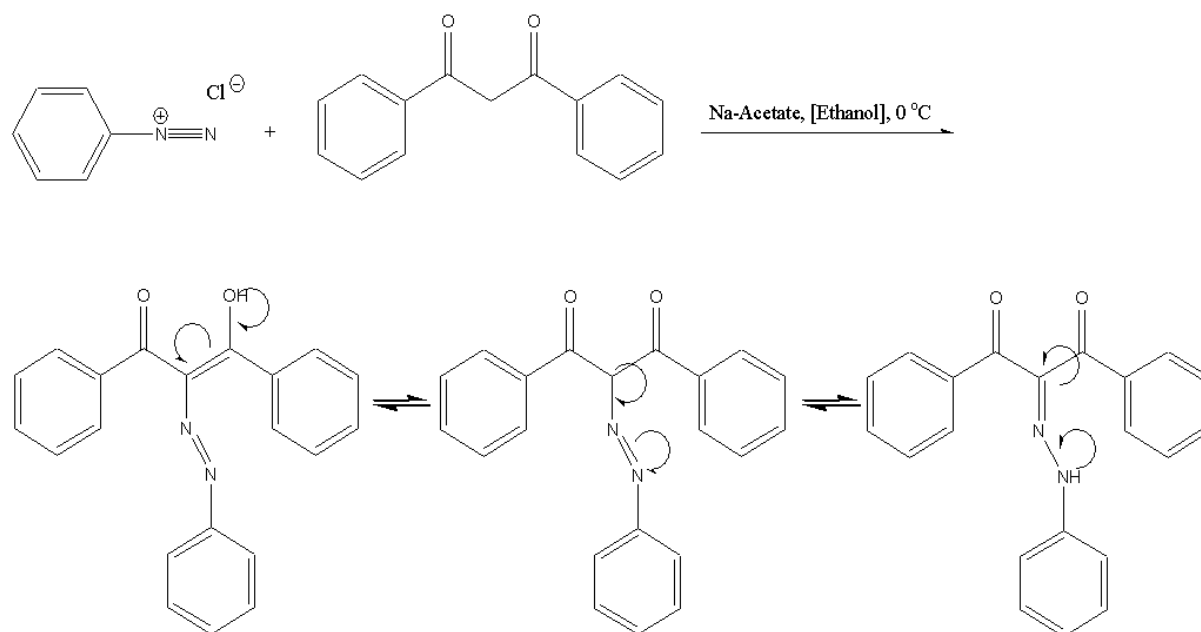


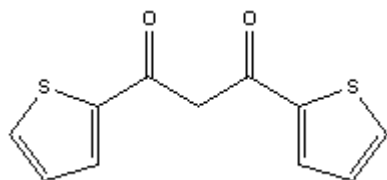
Figure 11 Azo-coupling reaction with aryl-diazonium chloride and dibenzoylmethane.

To a mixture of 5 mmol (1.12 g) dibenzoylmethane in 10 ml ethanol and 7.5 mmol sodium acetate in 6 ml ethanol, 5 mmol of aryl-diazonium chloride was added under stirring and cooling between 0 °C and 5 °C. A strong yellowish precipitate formed immediately, which was washed with water after complete addition and recrystallised from a water-alcohol mixture.

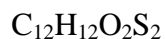
(m.p.: 85-87 °C; <sup>1</sup>H-NMR (200 MHz, δ, CDCl<sub>3</sub>): 7.95-8.05 (m, 6H), 7.48-7.60 (m, 9H), 6.88 (s, 1H) ppm). Also the spectroscopic data shown in Figure 19 point the validity of the structure (see Figure 11) out [45].

All <sup>1</sup>H-NMR characterisations were carried out on a Bruker DRX 200. All mass spectra were taken on a Fisons MD 800 (solids probe; Cl<sup>+</sup> / methane 3.5; source temperature 180 °C)

### 2.1.2 1,3-Dithienylpropane-1,3-dione



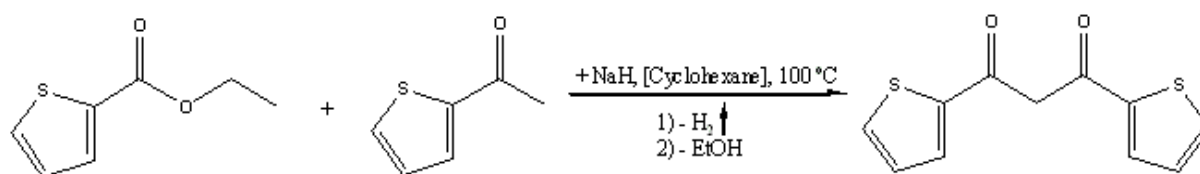
1,3-Dithienylpropane-1,3-dione  
(DTPD)



$$M = 252,35 \text{ g mol}^{-1}$$

The synthesis of 1,3-dithienylpropane-1,3-dione follows the classical way of a so called Claisen-condensation [36].

#### *Claisen-Condensation:*



A solution of 5 mmol (630 mg) acetylthiophene and 10 mmol (1.56 g) thiophene-2-carboxylic acid ethyl ester in waterfree cyclohexane was put drop wise to a boiling suspension of sodium hydride in water free cyclohexane. The solution was refluxed till the gas processing was finished. After cooling down to room temperature a mixture of 4 ml glacial acetic acid and 20 ml of water was added carefully. Past the addition of extra 20 ml of water the organic phase was separated and the aqueous phase was extracted two times with 50 ml ether. The collected organic phases were washed with some water and dried over  $\text{Na}_2\text{SO}_4$ .

After evaporation of the dried organic phase the orange coloured oily substance was cooled with ice and after addition of few drops of n-pentane a yellowish precipitate formed and was recrystallised from methanol.

(m.p.: 94-96 °C;  $^1\text{H-NMR}$  (200 MHz,  $\delta$ ,  $\text{CDCl}_3$ ): 7.79 (d,  $J = 3.3$  Hz, 2H), 7.63 (d,  $J = 4.4$  Hz, 2H), 7.18 (dd,  $J = 4.4$  Hz and  $J = 3.3$  Hz, 2H), 6.56 (s, 2H) ppm; CI-MS:  $m/z = 237$   $[\text{M-H}]^+$ ) [37] [38].

## 2.2 Synthesis of Complex Systems

### 2.2.1 Overview on Used Ligand Systems

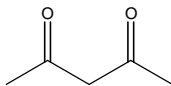
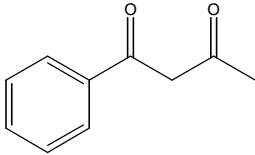
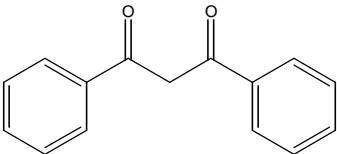
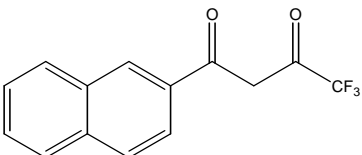
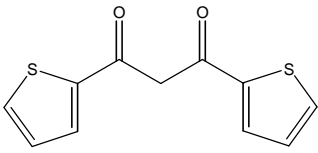
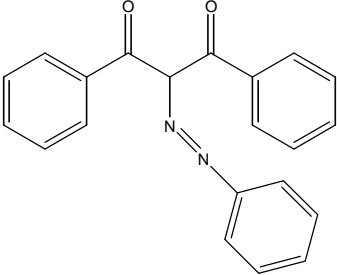
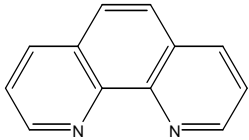
Ligand	(Trivial-)Name / IUPAC-Name / Shortcut
	Acetylacetone <sup>1</sup> Pentane-2,4-dione AcAc
	Benzoylacetone <sup>1</sup> 1-Phenyl-butane-1,3-dione Bac
	Dibenzoylmethane <sup>1</sup> 1,3-Diphenyl-propane-1,3-dione DBM
	Trifluoroacetylacetyl naphthalene <sup>1</sup> 4,4,4-Trifluor-1-(2-naphthyl)-1,3-butanedione TFAcAcN
	Dithienylpropanedione 1,3-Dithienyl-1,3-propanedione DTPD
	Phenylazodibenzoylmethane 1,3-Diphenyl-2-phenylazo-propane-1,3-dione azoDBM
	[1,10] Phenanthroline <sup>1</sup> Phen

Figure 12 Overview on used ligand systems.

<sup>1</sup> Purchased from Sigma-Aldrich GmbH

### 2.2.2 Formation of Complex System

All complexes were prepared with the following slightly modified method according to the literature [40].

To a solution of 3 ml of 2 M sodium hydroxide in 50 ml ethanol p.a. were added under stirring 6 mmol of the  $\beta$ -diketonate system and 2 mmol of 1,10 phenantroline (phen) (see 1.4.1.1). After complete dissolving an ethanolic solution of 2 mmol of rare earth(III) chloride was added drop wise to the well 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 mass spectrometry.

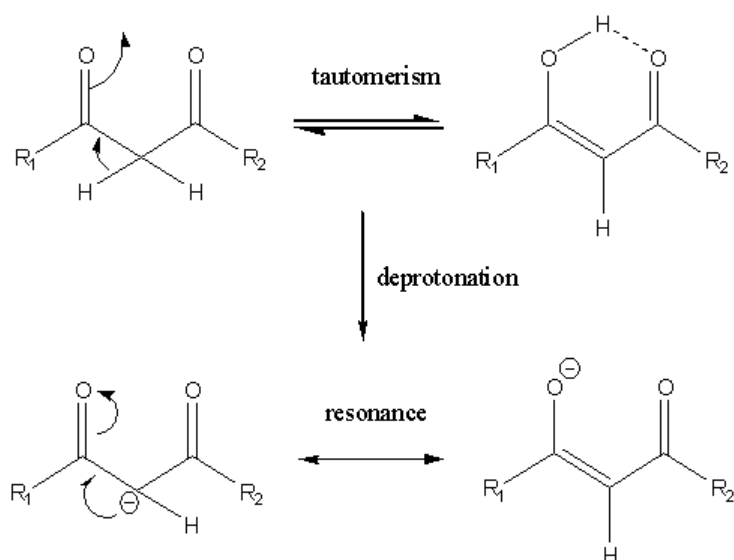


Figure 13 Complexation mechanism of  $\beta$ -diketonate systems initiated by deprotonation.

Three mol of this negative charged unit and 1 mol of a trivalent (rare earth-) ion are used to form 1 mol of the hexacoordinated neutral complex. One additional mole of 1,10-phenantroline is used to get the stable and waterfree octacoordinated form (see 1.4.1.1).

Characterisation by <sup>1</sup>H NMR spectroscopy was not possible because of shifting properties of rare earth complex materials [39] and a strong broadening of the signals.



Characterisations were done by absorption spectroscopy (see Figure 20 and Figure 21). In these spectra it is clearly observable that each complex (Eu-, Nd-, and Er-complexes) consist of 1,10-phenanthroline and the particular  $\beta$ -diketonate system.

The melting points of synthesised complexes gives additional information for characterisation. Melting points of rare earth complexes, which contain more than one molecule of 1,10-phenanthroline are higher compared to the melting point of the favoured composition [40]. Melting points of rare earth complexes, which contain only  $\beta$ -diketonate ligands are lower compared to the melting point of the favoured composition [29] [40] [41] [42]. The central atom of the studied rare earth complexes does not have much influence on the melting point of the complex. Melting points for characterisation were taken from [29] [37] [40] [43] [44]. All measured melting points (see Figure 14) agree with the literature values.

<b>Complex</b>	<b>Melting Point [°C]</b>
Eu(AcAc) <sub>3</sub> phen	> 230
Eu(Bac) <sub>3</sub> phen	195-197
Eu(DBM) <sub>3</sub> phen	185-187
Eu(azoDBM) <sub>3</sub> phen	181-183
Eu(DTPD) <sub>3</sub> phen	173-175
Eu(TFACAcN) <sub>3</sub> phen	193-195
Er(AcAc) <sub>3</sub> phen	> 230
Er(Bac) <sub>3</sub> phen	198-200
Er(DBM) <sub>3</sub> phen	181-183
Er(azoDBM) <sub>3</sub> phen	180-182
Er(DTPD) <sub>3</sub> phen	178-180
Er(TFACAcN) <sub>3</sub> phen	198-200
Nd(DBM) <sub>3</sub> phen	180-182
Nd(DTPD) <sub>3</sub> phen	170-172

Figure 14 Melting points of synthesised rare earth complexes.

### 2.3 Polymer Host Materials

Different conjugated and non-conjugated polymers were used for embedding various rare earth complexes for photoluminescence and electroluminescence studies. The preparation of the complex polymer mixtures is described in 2.4. The photophysical properties of the materials are described in 3.1.

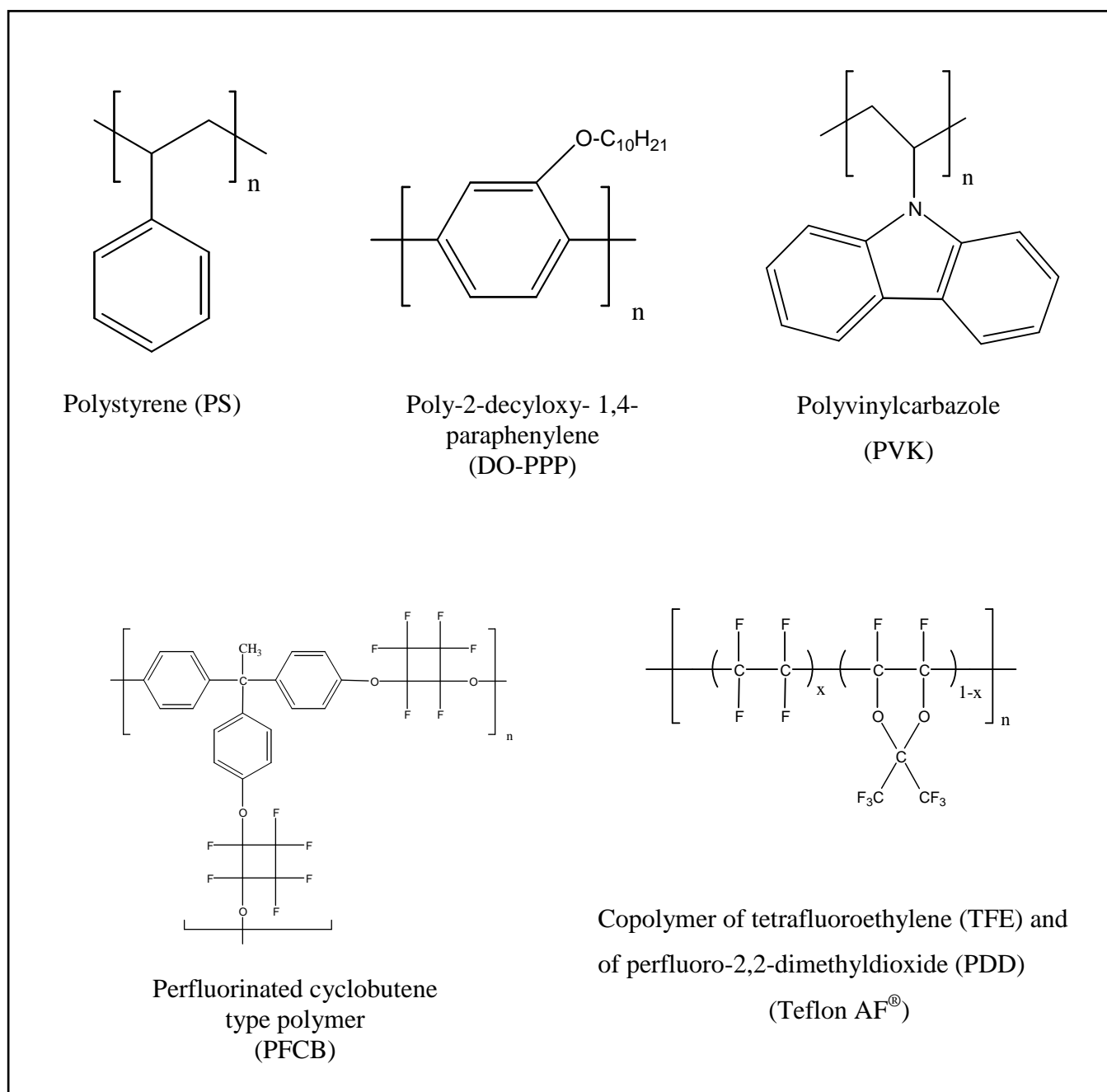


Figure 15 Structures of different polymers used for embedding rare earth complexes for photoluminescence and electroluminescence studies.

## 2.4 Polymer – Complex Mixture Preparation and Film Fabrication

Polymers were dissolved in different solvents with a concentration of  $1 \text{ mg ml}^{-1}$ . The solutions were used for film fabrication by spin coating (1500 rpm) and dropcasting ( $70 \text{ }\mu\text{l}$ ). To remove almost all the solvent films were dried over night in vacuum at about  $40 \text{ }^\circ\text{C}$ .

For dropcast films polymers were dissolved in chloroform. For spincoat films polymers were dissolved in toluene because of better film qualities.

The proper amount of rare earth complex was dissolved in different polymer solutions ( $1 \text{ mg ml}^{-1}$ ) and stirred over night to provide good homogeneity. The  $\text{Eu}(\text{AcAc})_3\text{phen}$  : polymer ratio was 1:5 (based on mass).  $0.2 \text{ mg ml}^{-1}$   $\text{Eu}(\text{AcAc})_3\text{phen}$  is equal to  $0.32 \text{ mmol ml}^{-1}$ , which is the concentration for all complexes in 1 m-% polymer solutions.

## 2.5 Absorption Measurements

All absorption measurements were carried out on a HP 8453 UV-Vis spectrophotometer. For all measurements polymer or complex / polymer films on a glass substrate were used.

## 2.6 Photoluminescence Measurements

### 2.6.1 Setup for Photoluminescence Measurements

For all the photoluminescence measurements discussed in 3.1.2 the setup shown in Figure 16 was used. Excitation was done with an Innova  $\text{Ar}^+$ -laser or with a xenon lamp. Luminescence was detected with a combination of an ARC Acton Research Corporation Spectro Pro - 300i grating monochromator (slit: 1 mm) and silicon (visible region up to  $1 \text{ }\mu\text{m}$ ) / InGaAsSb (near infrared region) detector. To avoid oxygen quenching effects measurements were carried out in vacuum ( $10^{-5}$  -  $10^{-6}$  mbar). Recording of the data was done by a self-written Test-Point<sup>®</sup>-program.

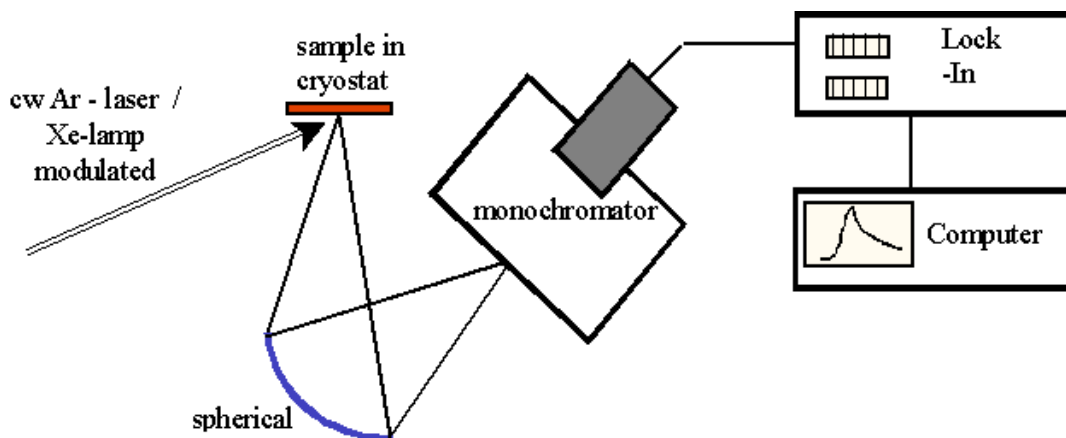


Figure 16 Setup for photoluminescence measurements.

## 2.7 Electroluminescence Measurements

### 2.7.1 Device Preparation of Organic Light Emitting Diodes (OLED's)

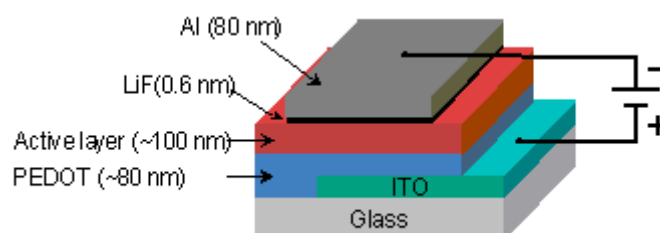


Figure 17 Design of organic light emitting diodes (OLED's)

ITO (indium tin oxide) coated glass (1.5 cm x 1.5 cm) was used as substrate material for device fabrication of organic light emitting diodes (OLED's). The advantage of ITO which makes it interesting for OLED's applications is that conductive and optically transparent films can be fabricated. So the ITO is an electrode (anode) in this system. On the ITO layer a PEDOT (poly-3,4-ethylenedioxythiophene) layer of about 100 nm was spincoated as hole injection layer. After the PEDOT layer was dried at least over night the active layer which was a mixture of a conductive polymer solution and a dissolved rare earth complex (preparation see 2.4) was spincoated. The thickness of the active layer was controlled by the rotational speed (1500 rpm) and the concentration of the polymer solution (1 m-%). The

thickness of the active layer was measured with an AFM (Atomic Force Microscope; tapping mode AFM Dimension 3100, Digital Instruments).

After deposition of the active layer the substrates were dried again over night in vacuum atmosphere to remove all of the solvent. The last step of the OLED-device fabrication was the evaporation of the top-electrode (cathode), which consists of 6 Å LiF and 80 nm Al.

### 2.7.2 Setup for Electroluminescence Measurements

All measurements were carried out inside a glove-box to avoid influences of oxygen or water. For recording current-voltage characteristics (I-V curves) a certain voltage was applied and the resulting current was measured by a Keithley 2400 Source Meter. Recording of data was performed with a self-written Test-Point<sup>®</sup>-program. To study the occurring electroluminescence during recording the I-V-characteristics the setup shown in Figure 18 was used.

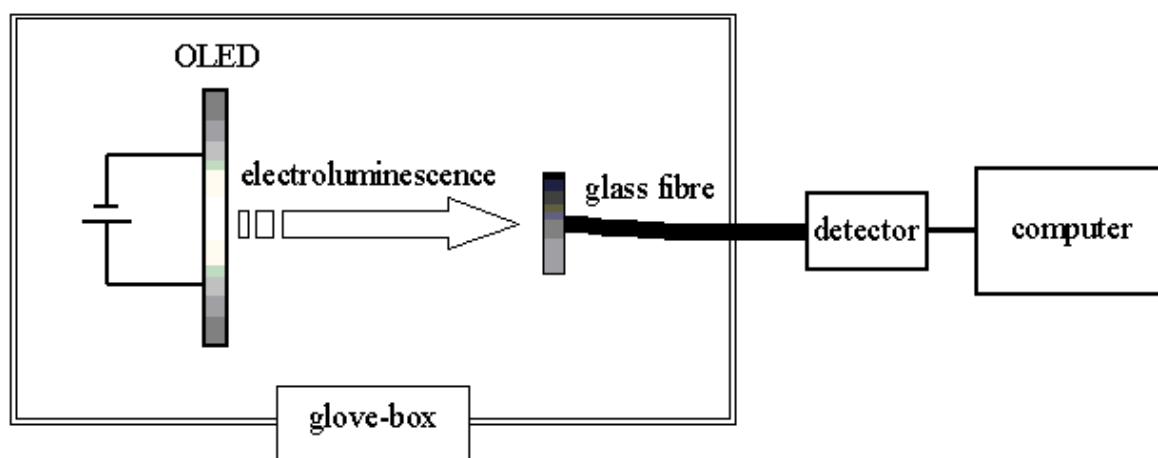


Figure 18 Setup for electroluminescence measurements inside the glove-box.

The detector was an AVS-S2000 (Avantes Spectrometer) with the corresponding software SpectraWin 5.0 for recording the luminescence spectra.

### 3 Results and Discussion

#### 3.1 Optical Studies

##### 3.1.1 Absorption

###### 3.1.1.1 Absorption Spectra of Ligand Systems

In Figure 19 absorption spectra of 1,10-phenanthroline (phen) and six  $\beta$ -diketonate ligand systems are shown (shortcuts are explained in 2.2.1). Each ligand (except acetylacetone which is liquid) was embedded in polystyrene, which does not absorb any light in the shown region.

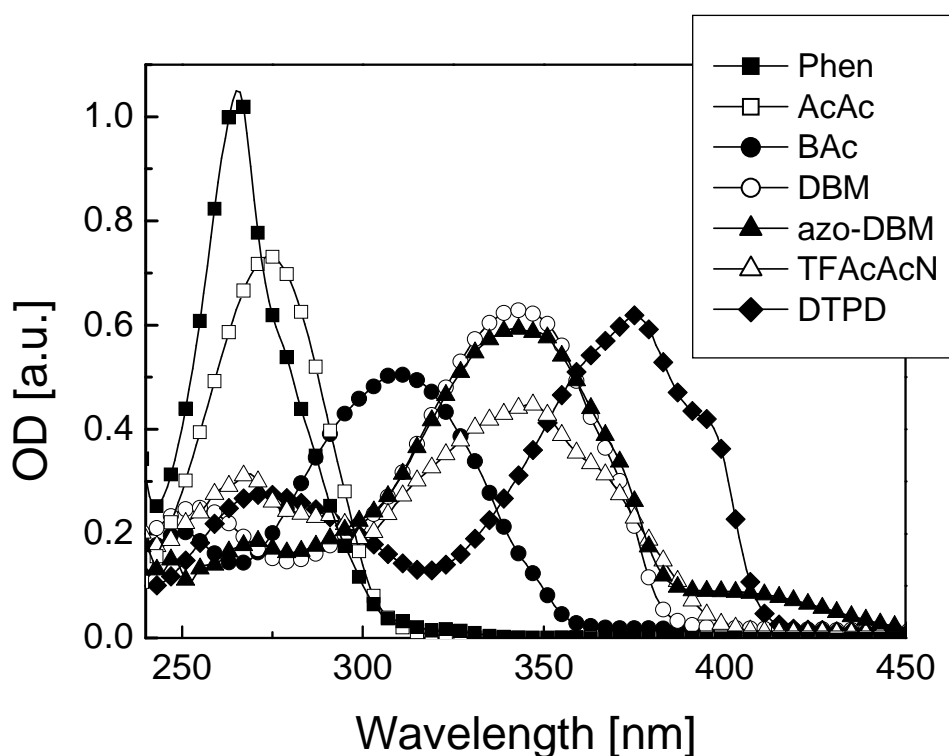


Figure 19 Absorption spectra of different ligand systems used for complexation of rare earth ions. AcAc was measured in liquid form. All other ligands were embedded in polystyrene films.

It can be clearly observed that additional aromatic groups shift the absorption maximum towards lower energies. The absorption maxima range from 275 nm up to 380 nm.

The spectrum of phenylazodibenzoylmethane (azoDBM) shows, compared to the spectrum of dibenzoylmethane (DBM), a shoulder that ranges from 400 nm to 450 nm. This absorption band originates from the phenylazo group [45]. The low intensity of this band compared to the band from 300 nm to 400 nm indicates a trans configuration of the phenylazo group. If the conformation of the phenylazo group would be cis the band between 400 nm and 450 nm would be much more intense than the peak between 300 nm and 400 nm [45].

The absorption peak of the dithienylpropanedione (DTPD) ligand, which consists of two heteroaromatic thienyl-units, is the most red shifted one.

### 3.1.1.2 Absorption Spectra of Complex Systems

#### *Eu-Complexes:*

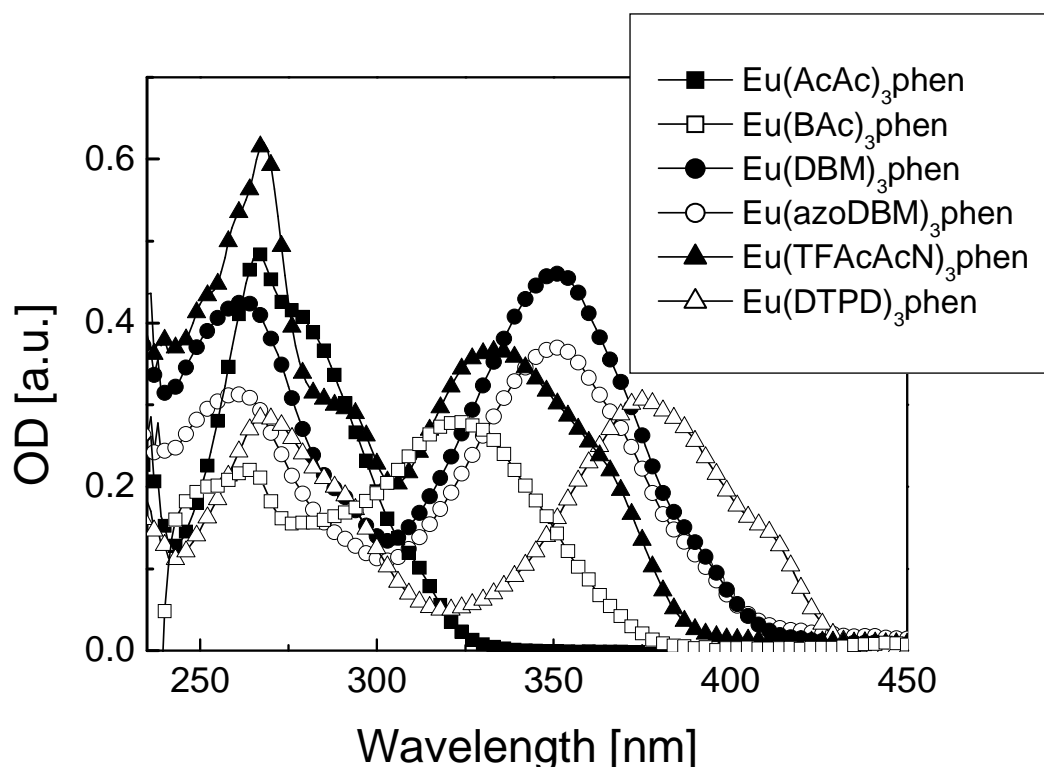


Figure 20 Absorption spectra of europium complex systems embedded in polystyrene films.

Compared to the absorption spectra shown in Figure 19 the position of the maxima of the absorption peaks do not change very much. Only the shapes of the peaks change slightly. Every complex shows a clearly observable band around 270 nm, which is an indication of the presence of phenantroline in every complex system.

The only remarkable difference shows the absorption spectrum of the  $\text{Eu}(\text{azoDBM})_3\text{phen}$  complex compared to the ligands spectrum. The intensity of the shoulder from 400 nm to 450 nm got weaker. The cause for that may be a conjugation hindrance of the azo dye because of complexation.

#### *Comparison of rare earth complexes:*

In Figure 21 complexes with DTPD - ligands with the central atoms  $\text{Eu}^{3+}$ ,  $\text{Er}^{3+}$  and  $\text{Nd}^{3+}$  are compared (all of the same concentration). For each system no significant differences can be seen. This is also true for the other synthesised complexes but because of better clearness only one example is demonstrated below.

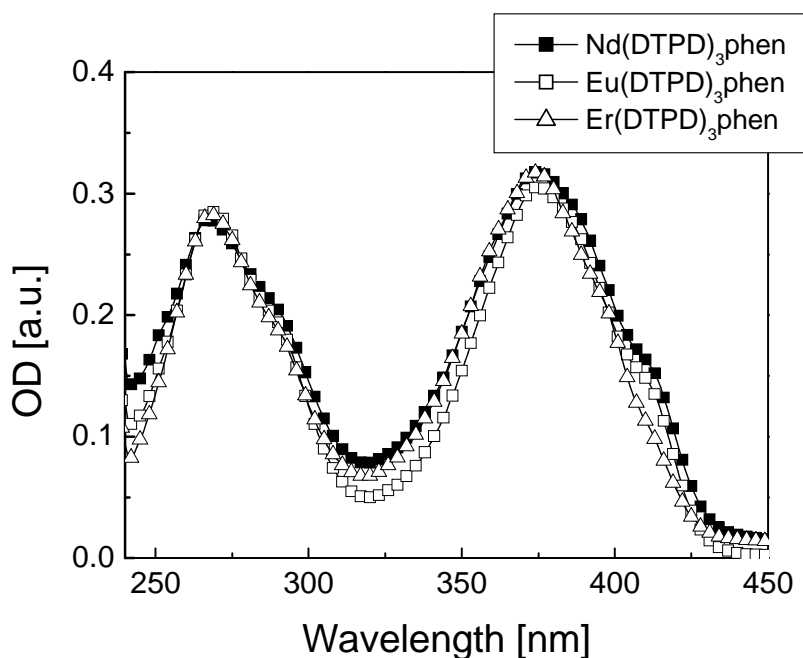


Figure 21 Comparison of rare earth dithienylpropanedione complexes in polystyrene films with different central atoms.



In all spectra the phenantroline absorption peak at about 260 nm and the absorption peak of the particular  $\beta$ -diketonate ligand system is clearly observable what indicates reproducible and similar formation of the complex systems with different central atoms.

### 3.1.1.3 Absorption Spectra of Polymers

In Figure 22 the absorption spectra of three different polymers (perfluorocyclobutene (PFCB) type polymer, Teflon AF and polystyrene see Figure 15) are shown. The polymers were measured as films on glass substrate. Glass absorption prevents spectral results at wavelengths lower than 270 nm. In the region where usually  $\beta$ -diketonate systems absorb (300 nm - 400 nm), no absorption is observable.

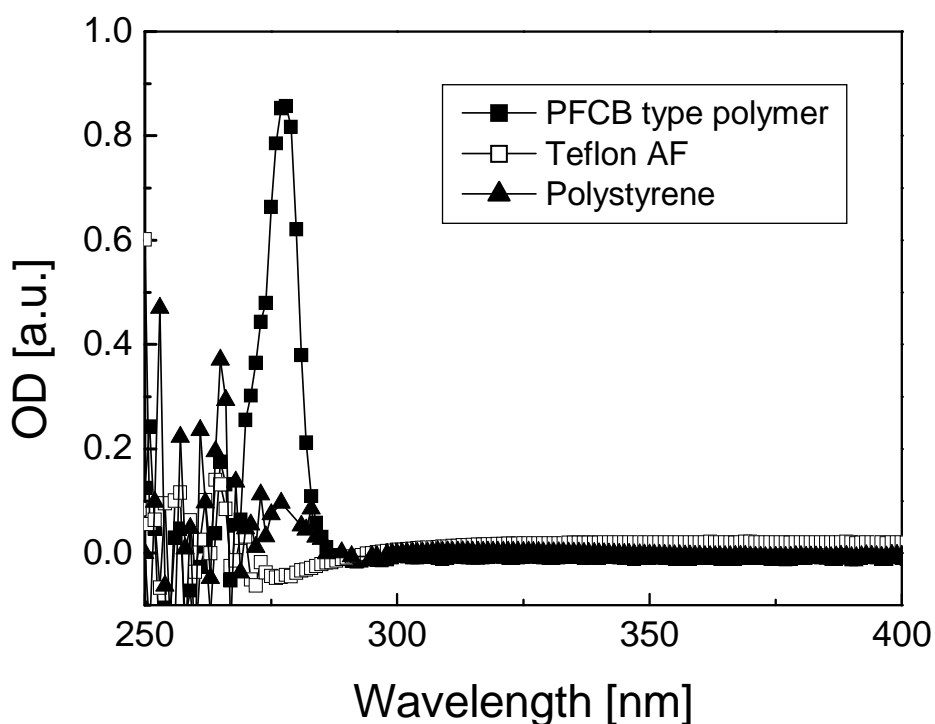


Figure 22 Absorption spectra of three different polymers.

The absorption spectra of the two polymers poly-2-decyloxy-1,4-paraphenylene (DO-PPP) and poly-vinylcarbazole (PVK) (see Figure 15) are shown in Figure 23. Each polymer has broad absorption features from 300 nm to 380 nm.

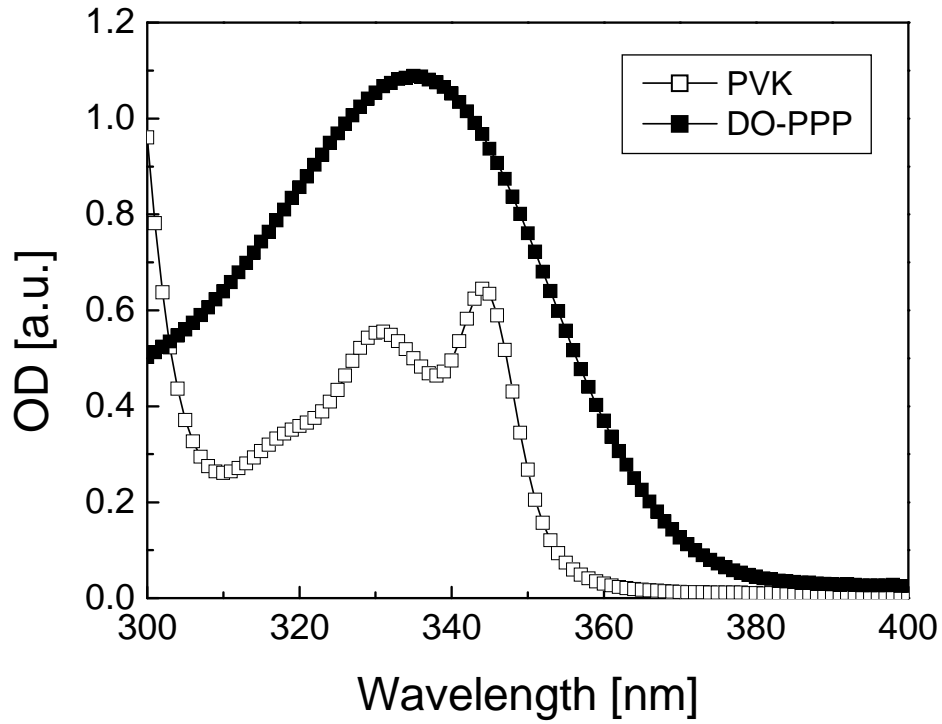


Figure 23 Absorption spectra of two different polymers.

### 3.1.2 Photoluminescence

#### 3.1.2.1 Ligand Systems

In Figure 24 the photoluminescence of  $\beta$ -diketonate systems is shown. Emission resulted from excitation at the absorption maximum of each complex. For acetylacetonate (AcAc) no emission was observable. The intensity of the photoluminescence of dithienylpropanedione and trifluoroacetylacetonate are three to four times higher than the intensity of the other ligands but anyhow quite weak compared to europium luminescence (see 3.1.2.2) or polymer luminescence (see 3.1.2.5).

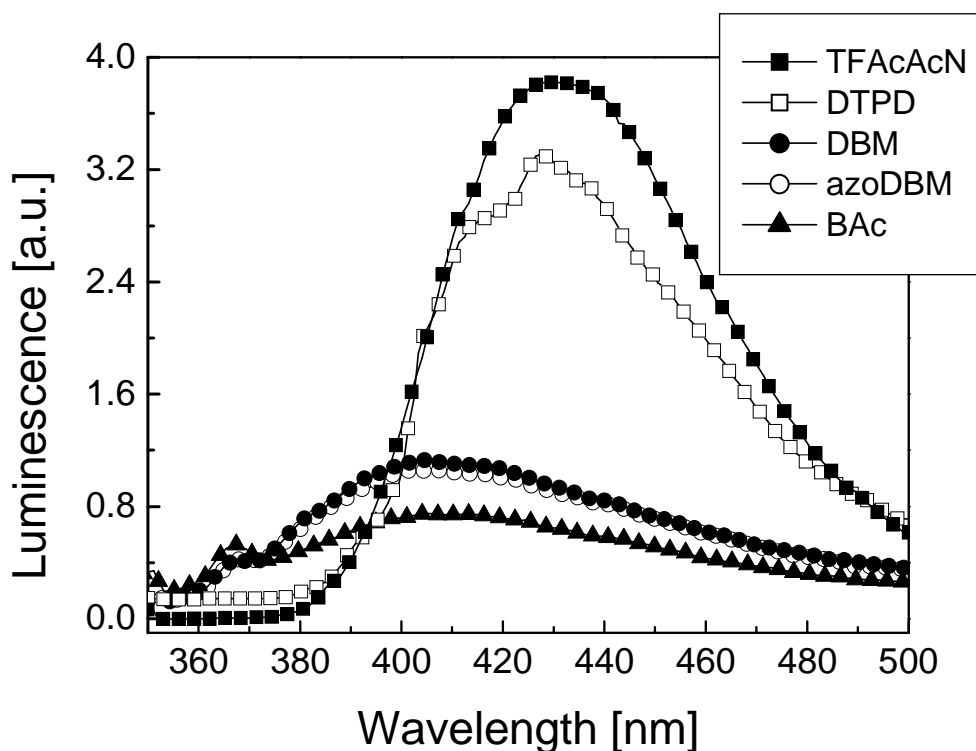


Figure 24 Photoluminescence spectra of  $\beta$ -diketonate ligand systems embedded in polystyrene films. Excitation for each complex at its absorption maximum.

### 3.1.2.2 Europium – Complexes

In Figure 25 and Figure 26 the photoluminescence of all synthesised europium complexes is shown. Each complex was excited at its absorption maximum. It is clearly observable that the dithienylpropanedione (DTPD) containing and trifluoroacetylnaphthalene (TFAcAcN) containing europium complexes show the most intense photoluminescence.

No significant luminescence except the europium emission bands is detectable in the range from 370 nm to 800 nm, which indicates a high energy transfer rate from the ligand ( $\beta$ -diketonate ligand) to one of the excited europium energy states.

The main red emission peak at 614 nm originates from the  $^5D_0 \rightarrow ^7F_2$  transition. The two other much weaker europium-peaks at 580 nm and 590 nm originate from the  $^5D_0 \rightarrow ^7F_0$  resp.  $^5D_0 \rightarrow ^7F_1$  transition (see 1.3.1)

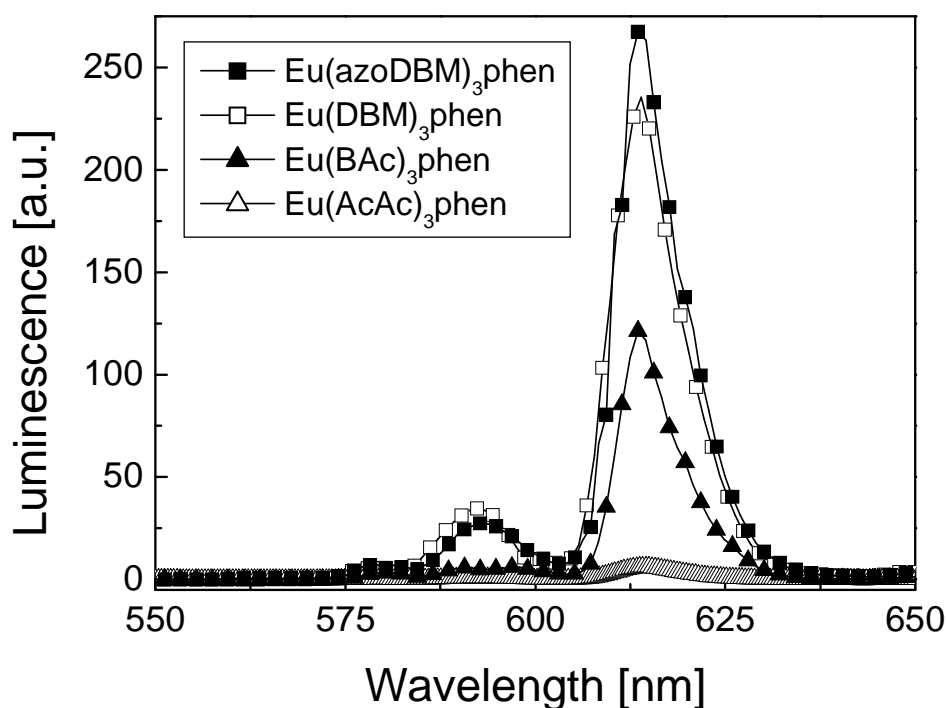


Figure 25 Photoluminescence of europium complexes excited at the absorption maximum of each complex.

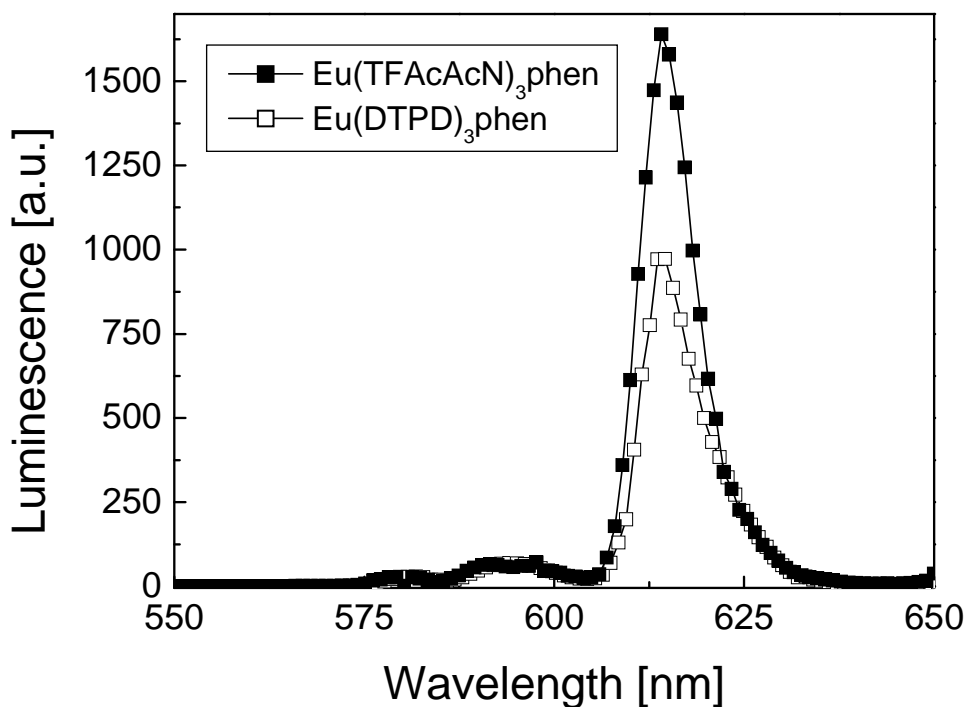


Figure 26 Photoluminescence of europium complexes excited at the absorption maximum of each complex.

### 3.1.2.3 Erbium – Complexes

The typical erbium emission occurs around  $1.54\ \mu\text{m}$  and is usually much weaker than europium emissions because of a lot of non radiative decay possibilities after the excitation via a  $\beta$ -diketonate complex system. All erbium complexes embedded in polystyrene films were excited with a cw- $\text{Ar}^+$  laser at 350 nm with a power of 60 mW in average (30 mW on the substrate surface, due to chopper wheel and mirror losses).

In Figure 27 the photoluminescence of different erbium complexes is shown. Excitation of the erbium complexes with acetylacetonate (AcAc) and dibenzoylmethane (DBM) resulted in a weak erbium emission around  $1.54\ \mu\text{m}$  after cooling down with liquid nitrogen to 77 K. At room temperature there was no erbium emission detectable.

The same behaviour was observed for  $\text{Er}(\text{BAC})_3\text{phen}$  and  $\text{Er}(\text{azoDBM})_3\text{phen}$  complexes. For the erbium ion these four ligand systems are not appropriate to achieve acceptable emission.

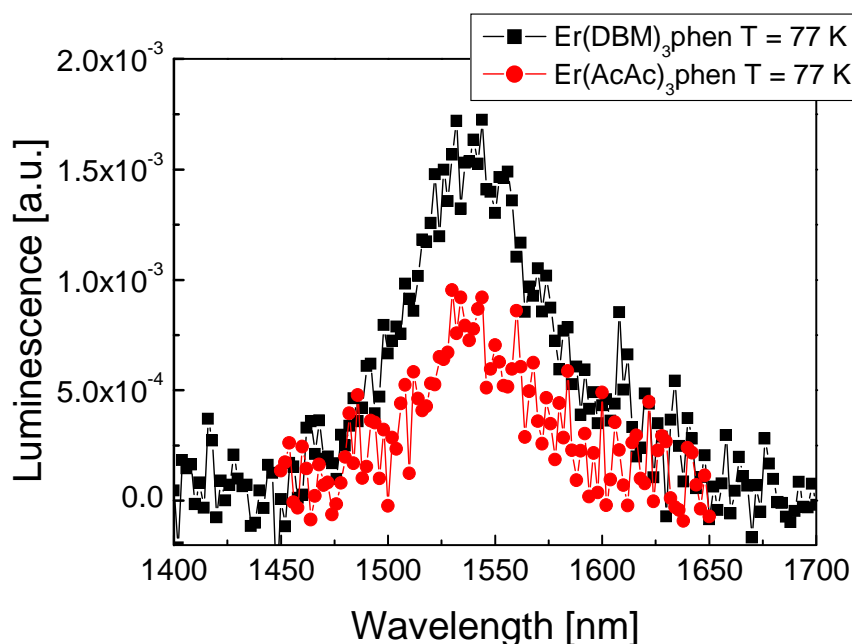


Figure 27 Erbium photoluminescence of different  $\beta$ -diketonate complexes.

Figure 28 shows that exciting the erbium complex with dithienylpropanedione as  $\beta$ -diketonate ligand system gives a more intense photoluminescence at liquid nitrogen temperature. Even the intensity of the photoluminescence at room temperature is comparable with the intensities of the erbium complexes shown in Figure 27.

Similar intensities of the erbium emission compared to  $\text{Er}(\text{DTPD})_3\text{phen}$  were observed by exciting the erbium trifluoroacetylaphthalene complex (see Figure 29). The signal to noise ratio is better for this substance (see 1.2.1).

An explanation for the better properties of dithienylpropanedione and trifluoroacetylaphthalene as ligands for emissive erbium complexes could be that the triplet levels of the ligands which are always involved in energy transfer mechanisms (see 1.4.3) are more suitable to transfer energy to the  $^4\text{F}_{9/2}$  energy level of the erbium ion instead of transferring energy to the  $^4\text{S}_{3/2}$  level. So there are less possibilities for radiationless decays.

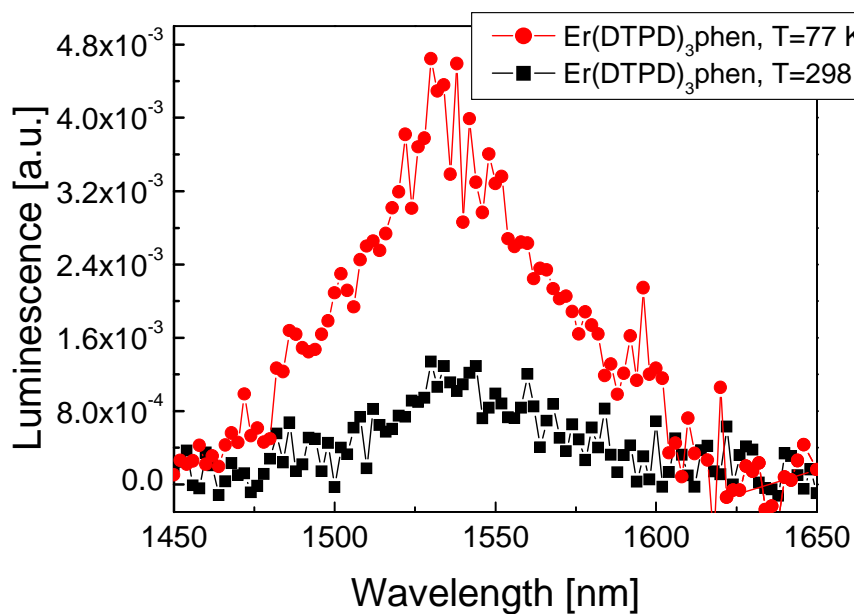


Figure 28 Erbium photoluminescence of dithienylpropanedione containing complex

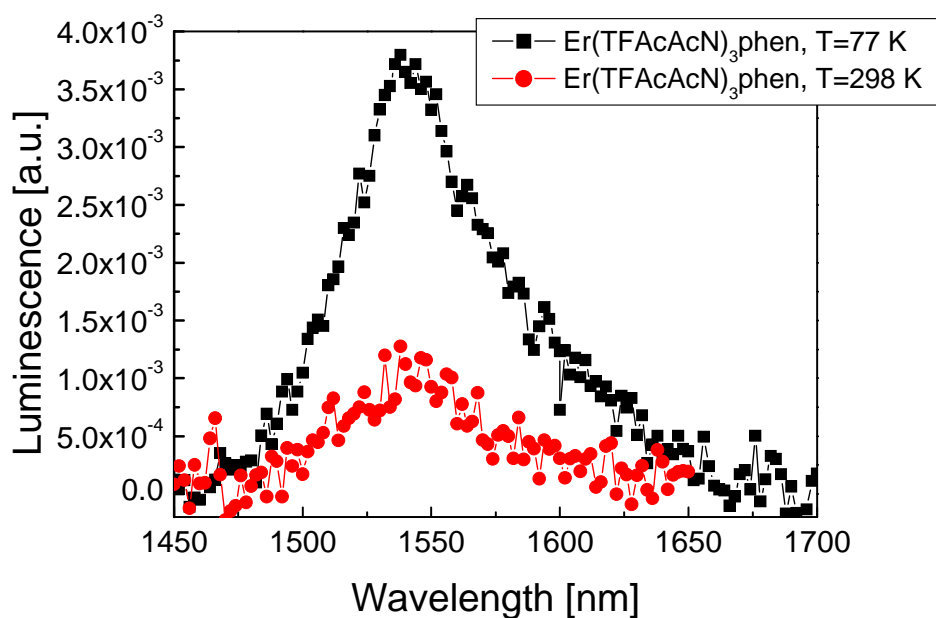


Figure 29 Erbium photoluminescence of trifluoroacetylaphthalene containing complex.

### 3.1.2.4 Neodymium – Complexes

Neodymium is known to have three different emission lines in the near infrared region. The three emission lines appear at 890 nm ( ${}^4F_{3/2} \rightarrow {}^4I_{13/2}$ ), 1050 nm ( ${}^4F_{3/2} \rightarrow {}^4I_{11/2}$ ) and 1.35  $\mu\text{m}$  ( ${}^4F_{3/2} \rightarrow {}^4I_{9/2}$ ) (see 1.3.1).

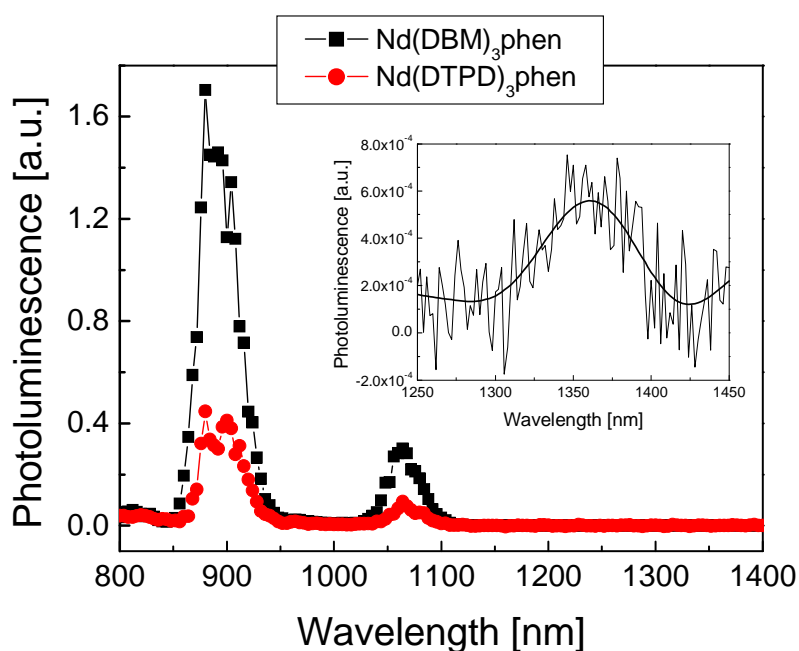


Figure 30 Photoluminescence of two different neodymium complexes. The inset shows the enlarged region around 1.35  $\mu\text{m}$ .

In Figure 30 the photoluminescence spectra of two different neodymium complexes embedded in polystyrene are shown. A very intense peak around 890 nm and the emission peak around 1050 nm were observed. The third occurring 4f transition is, compared to the other two neodymium emissions lines, very weak, which is corresponding to strong emission quenching properties of polymers in this near infrared region.



### 3.1.2.5 Polymers

The blue photoluminescence spectra of the two polymers poly-2-decyloxy-1,4-paraphenylene (DO-PPP) and poly-vinylcarbazole (PVK) (see Figure 15) which are absorbing light around 350 nm are shown and compared to the absorption spectra in Figure 31 and Figure 32.

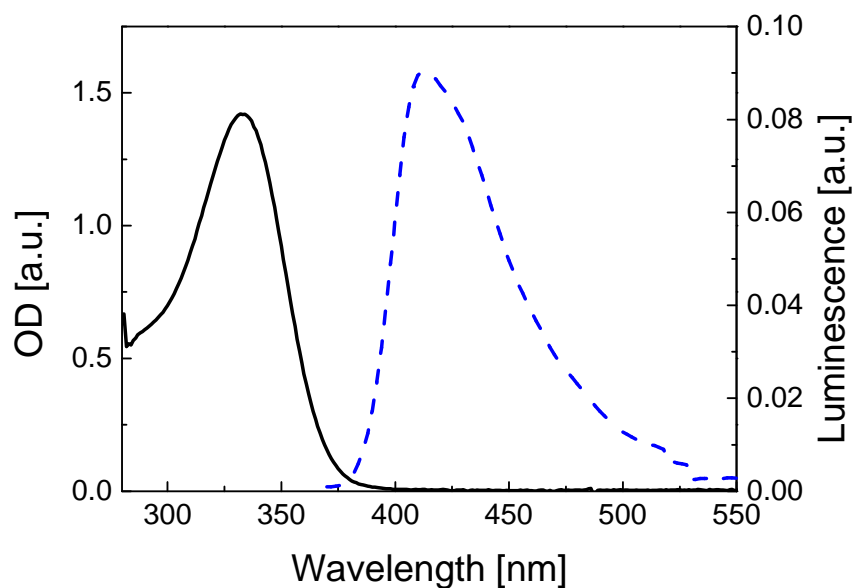


Figure 31 Blue photoluminescence (dashed line) of poly-2-decyloxy-1,4-paraphenylene (DO-PPP).

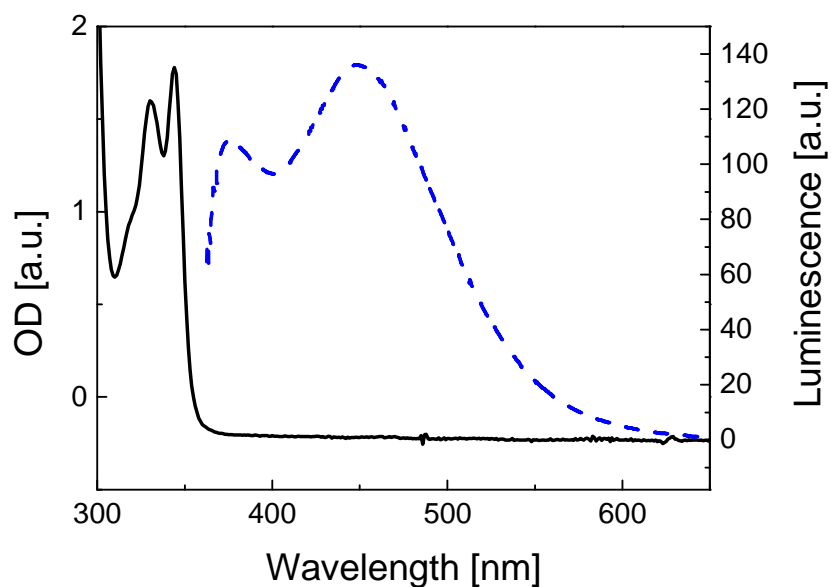


Figure 32 Blue photoluminescence (dashed line) of poly-vinylcarbazole (PVK)

### 3.1.3 Photoluminescence in Different Host Matrices

In the following chapters the various influences of different host matrices on the luminescence properties of rare earth complexes are described.

#### 3.1.3.1 Eu – Complexes

To realise the concept described in 1.4.3 polymer host matrices, which provide a good overlap of their luminescence spectra and the absorption spectra of the embedded complex are needed.

In Figure 33 the overlap of the absorption spectrum of  $\text{Eu}(\text{DTPD})_3\text{phen}$  complex and the photoluminescence spectra of the two polymers poly-2-decyloxy-1,4-paraphenylene (DO-PPP) and poly-vinylcarbazole (PVK) are shown. This europium complex overlaps best of all studied complexes (see Figure 20).

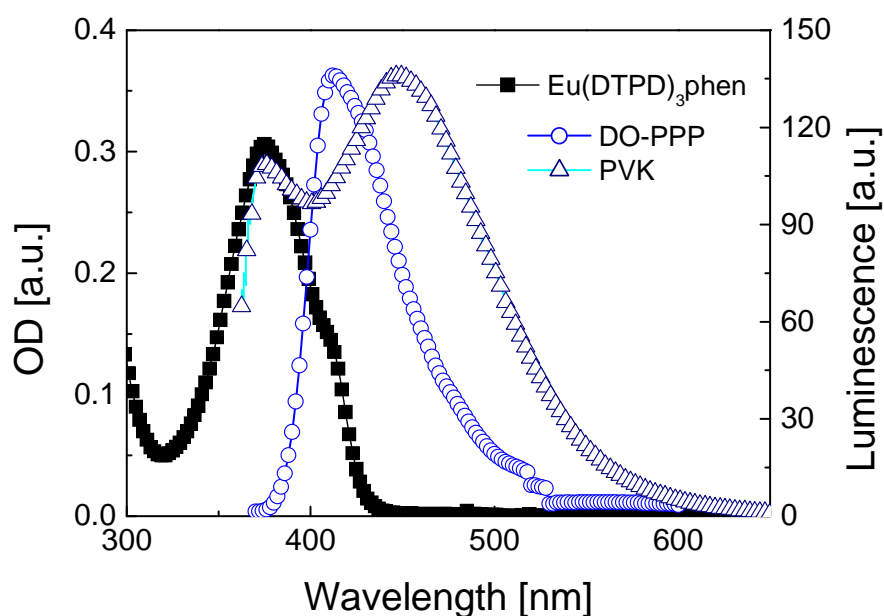


Figure 33 Overlap of  $\text{Eu}(\text{DTPD})_3\text{phen}$  complex absorption with different polymer luminescence. Closed symbols indicate absorption spectrum; open symbols indicate luminescence spectra.

The photoluminescence spectra of different europium complexes that were embedded in polyvinylcarbazole films (see 2.4) are shown in Figure 34.

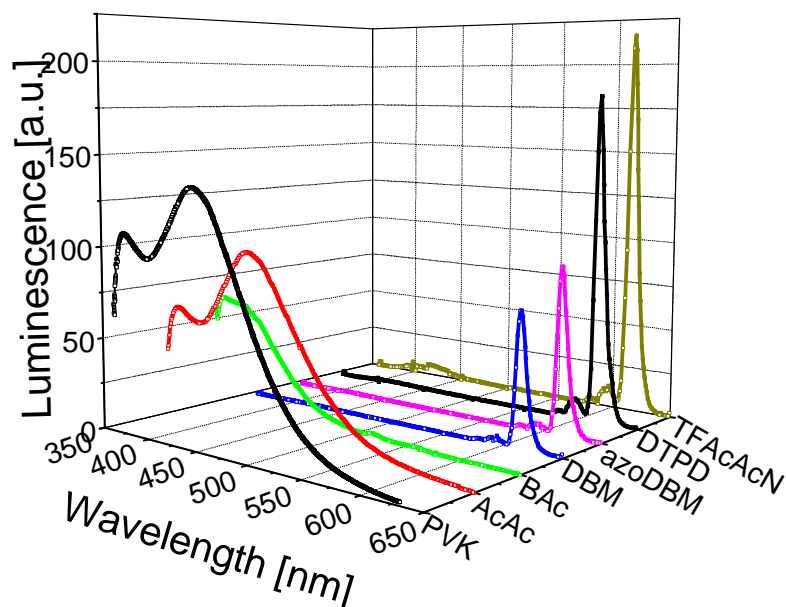


Figure 34 Photoluminescence spectra of different europium complexes embedded in PVK films.

By comparison of the absorption spectra of the different europium complexes and the luminescence spectrum of PVK (see Figure 32) the effect of the increasing overlap of the absorption spectra of  $\text{Eu}(\text{AcAc})_3\text{phen}$  to  $\text{Eu}(\text{TFACACN})_3\text{phen}$  with the luminescence spectrum of PVK is noticeable. The diagram shown in Figure 34 proves the assumption of the theory. The absorption spectrum of  $\text{Eu}(\text{AcAc})_3\text{phen}$  does not overlap with the polymer luminescence spectrum and so there is no europium emission observable and the luminescence of the polymer well detectable. The two complexes  $\text{Eu}(\text{DTPD})_3\text{phen}$  and  $\text{Eu}(\text{TFACACN})_3\text{phen}$  with the most red shifted absorption spectra in the studied group of complexes show the best overlap and according to 3.1.2.2 the most intense europium luminescence accompanied by a complete quenching of the polymer luminescence. In the case of  $\text{Eu}(\text{DBM})_3\text{phen}$  and  $\text{Eu}(\text{azoDBM})_3\text{phen}$  the polymer luminescence is also completely quenched and again the intensity of the europium luminescence corresponds with the results shown in 3.1.2.2.

This is also an indication for a working energy transfer cascade from the polymers excited singlet state to the excited europium state for the europium complexes with the ligands DBM, azoDBM, DTPD and TFACACN.

Another indication for energy transfer is the quenching of the polymer luminescence for some polymer-complex mixtures.

As demonstrated in Figure 33 the overlap of the europium complex absorption band and the photoluminescence of DO-PPP are lower than for PVK. The consequences of this result are shown in Figure 35.

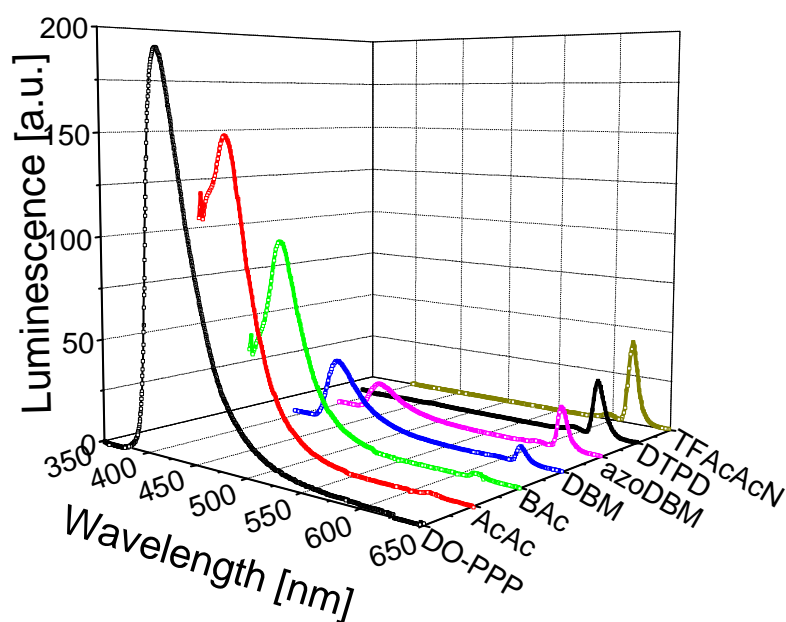


Figure 35 Photoluminescence spectra of different europium complexes embedded in DO-PPP films.

$\text{Eu}(\text{DBM})_3\text{phen}$  and  $\text{Eu}(\text{azoDBM})_3\text{phen}$  are not able to quench all the polymer luminescence of DO-PPP. Because of a low energy transfer rate from the polymer to the europium complex the intensities of the europium luminescence are correspondingly weaker. These are additional proofs for neglecting direct excitation of the complex system because of less capability of polymer luminescence quenching and lower intensity of europium luminescence although the concentration of the complex embedded in the polymer film is the same.

Eu(DTPD)<sub>3</sub>phen and Eu(TFACACN)<sub>3</sub>phen are able to quench all the polymer luminescence but the intensity of the europium emission compared to the europium complex – PVK system is very low. This is an indication of a very low energy transfer rate and because of the absence of the polymer luminescence a lot radiationless decays occur.

Compared to the intensities of the europium emissions of complexes embedded in polystyrene films which originate from direct excitation (see 3.1.2.2) the luminescence intensities of europium complexes excited by energy transfer from PVK or DO-PPP are lower. However since the energy transfer cascade shown in Figure 8 has been proved to work, increased rare earth luminescence can be expected by usage of polymers with better matching energy levels.

### 3.1.3.2 Er – Complexes

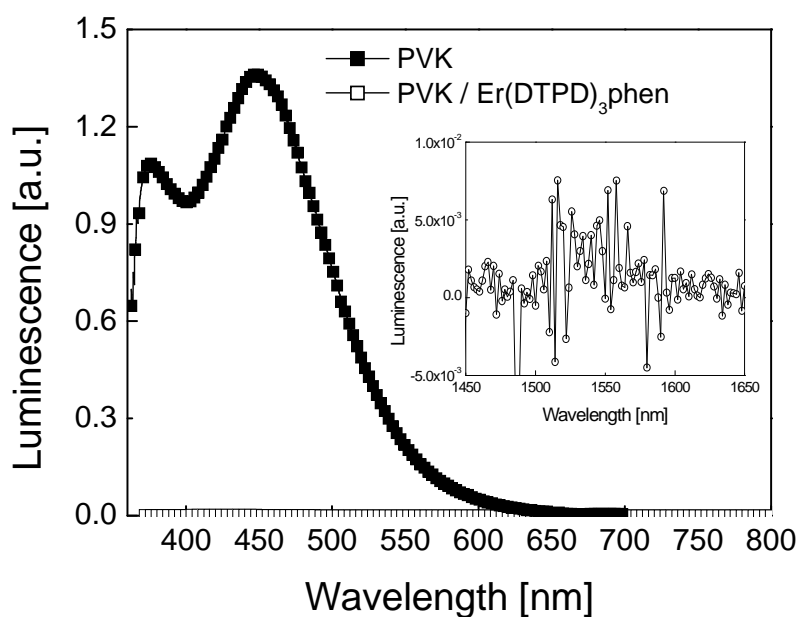


Figure 36 Total quenching of PVK photoluminescence. Inset shows the region around 1.54  $\mu\text{m}$ .

As described in 3.1.2.3 the erbium emission at 1.54  $\mu\text{m}$  is much weaker than the europium luminescence. Embedding different erbium complexes in DO-PPP or PVK matrices did not show any positive effect. The erbium luminescence was almost absent although the polymer

luminescence was completely quenched. This is unclear, because we should expect an energy transfer upon quenching of the host luminescence to the guest lanthanoid.

As described in 1.2.1 polymer host matrices like polystyrene, DO-PPP, PVK and some more are responsible for lowering the emissions in the near infrared, the region of the erbium luminescence. Reducing the content of C-H bonds by replacing this polymer host with fluorinated polymer matrices should lower the attenuation of erbium luminescence.

The effect on the erbium luminescence by using a partially fluorinated polymer called perfluorinated cyclobutene type polymer (PFCB, see Figure 15) is shown in Figure 37. The erbium luminescence at liquid nitrogen temperature is more intense compared to excited erbium complexes in polystyrene matrix (see Figure 28). The intensity at room temperature does not change significantly. But at both temperatures the much better signal to noise ratio is remarkable.

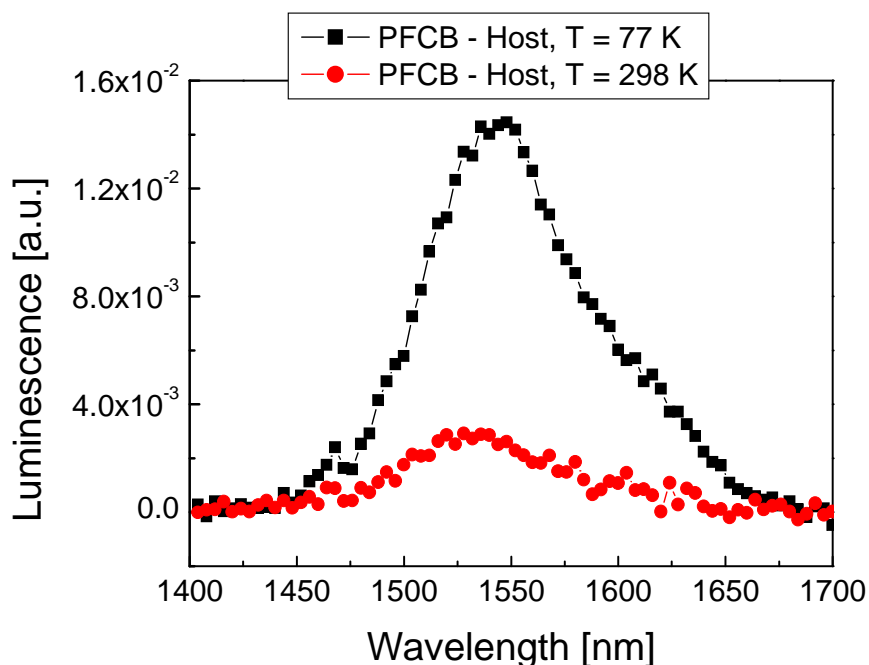


Figure 37 Photoluminescence of Er(DTPD)<sub>3</sub>phen embedded in PFCB type polymer films.

By using a totally fluorinated polymer like Teflon AF<sup>®</sup> (see Figure 15) the intensity difference of the erbium luminescence at room temperature and liquid nitrogen temperature is much lower compared to the intensity difference in non fluorinated or partially fluorinated host matrices.

The cause for the lower intensity of the erbium emission in the system Er(DTPD)<sub>3</sub>phen / Teflon AF<sup>®</sup> compared to Figure 37 might be the bad dissolution of the complex in the solvent of Teflon AF<sup>®</sup>. The solvent of commercially available Teflon AF<sup>®</sup> - solutions is a perfluorinated alkane. These polymer solutions are not able to dissolve an erbium complex completely. By stirring over night only a suspension is achievable. However, the quality of the films, which were fabricated of the polymer – complex suspensions by spincoating were acceptable.

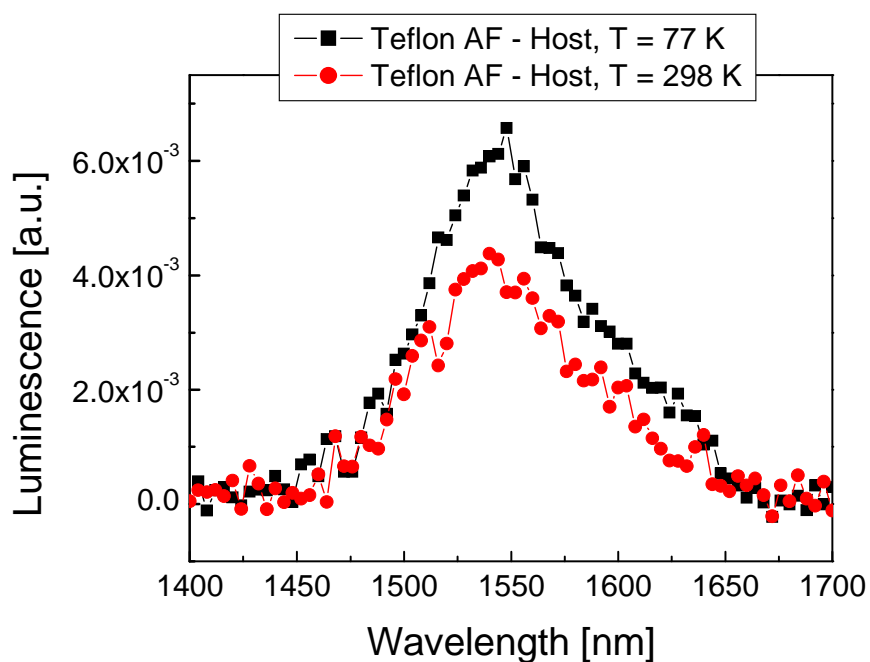


Figure 38 Photoluminescence of Er(DTPD)<sub>3</sub>phen embedded in Teflon AF<sup>®</sup> polymer films

### 3.1.3.3 Nd – Complexes

The exchange of the polymer host matrices for the neodymium complex  $\text{Nd}(\text{DTPD})_3\text{phen}$  to fluorinated polymers is also promising as demonstrated in Figure 39. The intensities of the three luminescence peaks in the near infrared region at 890 nm, 1050 nm and 1.35  $\mu\text{m}$  are greatly enhanced (see 3.1.2.4, Figure 30).

Especially the peak at 1.35  $\mu\text{m}$  which is an important wavelength in optical telecommunication has beside the higher intensity a much better signal to noise ratio.

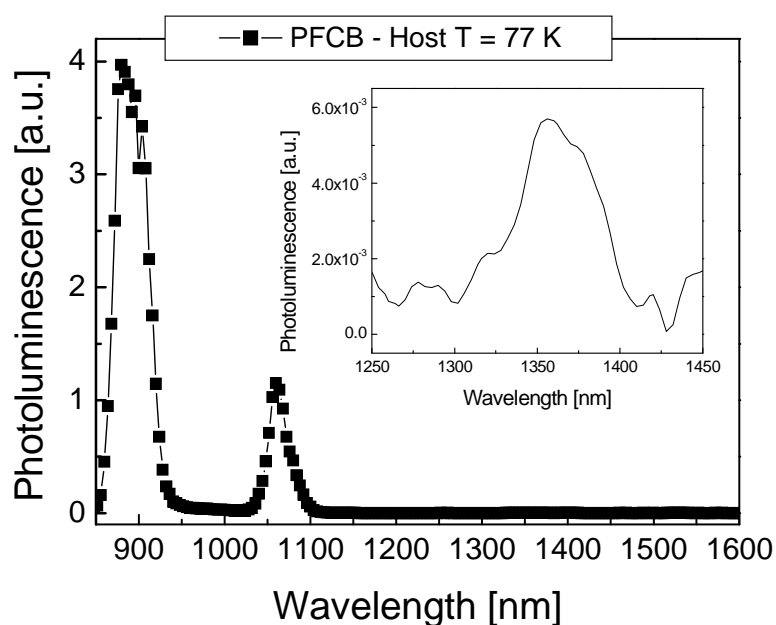


Figure 39 Photoluminescence of  $\text{Nd}(\text{DTPD})_3\text{phen}$  embedded in PFCB type polymer films.



## 3.2 Organic Light Emitting Diodes (OLED's)

### 3.2.1 Polymer Electroluminescence

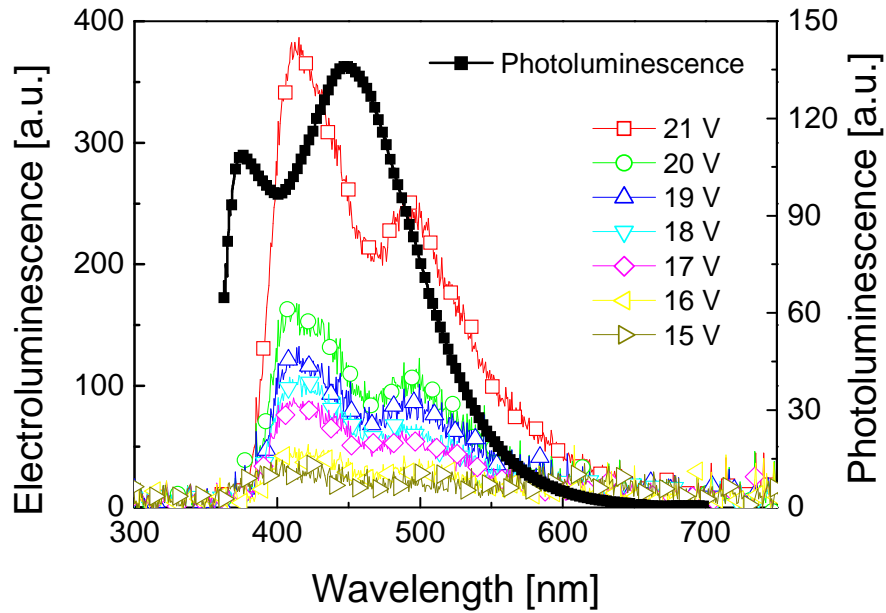


Figure 40 Electroluminescence of PVK – OLED's at different voltages indicated by open symbols. Corresponding photoluminescence is indicated by closed symbols.

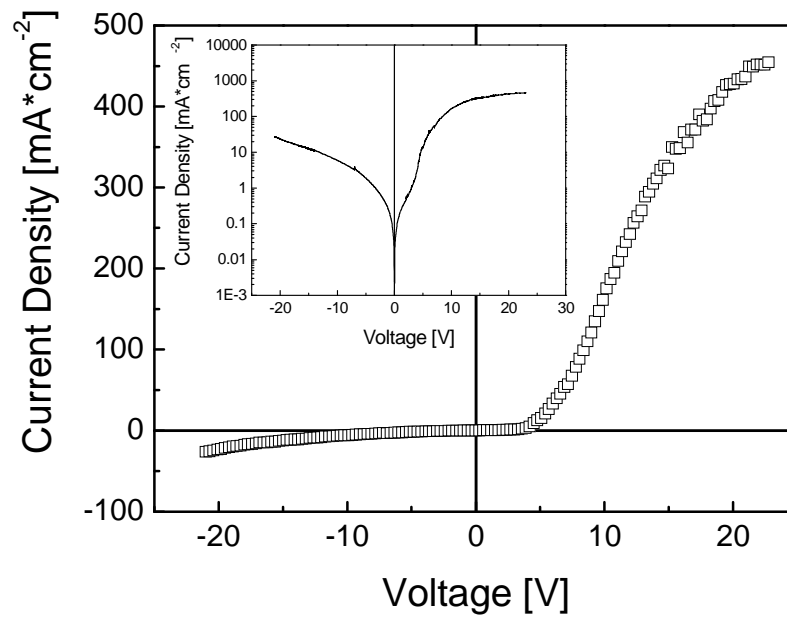


Figure 41 Current-voltage characteristics of PVK – OLED. (Inset shows the logarithmic scale)

In Figure 40 the voltage dependent electroluminescence of polyvinylcarbazole (PVK) is demonstrated. The current-voltage characteristics shown in Figure 41 indicate a good diode behaviour. In backward direction there is a  $1.6 \cdot 10^1$  lower current running through the cell. At both polarities the cell was stable at least a higher voltages.

The electroluminescence of DO-PPP shown in Figure 42 is red shifted compared to the photoluminescence. Organic light emitting diodes made of this polymer are not so stable than made of PVK. As shown in Figure 43 the LED blocks the current in backward direction quite good and opens at about 1.5 V. The DO-PPP – LED is not able to accept more than about 7 V but the polymer luminescence intensity is even at that voltage comparable with the PVK electroluminescence at 21 V.

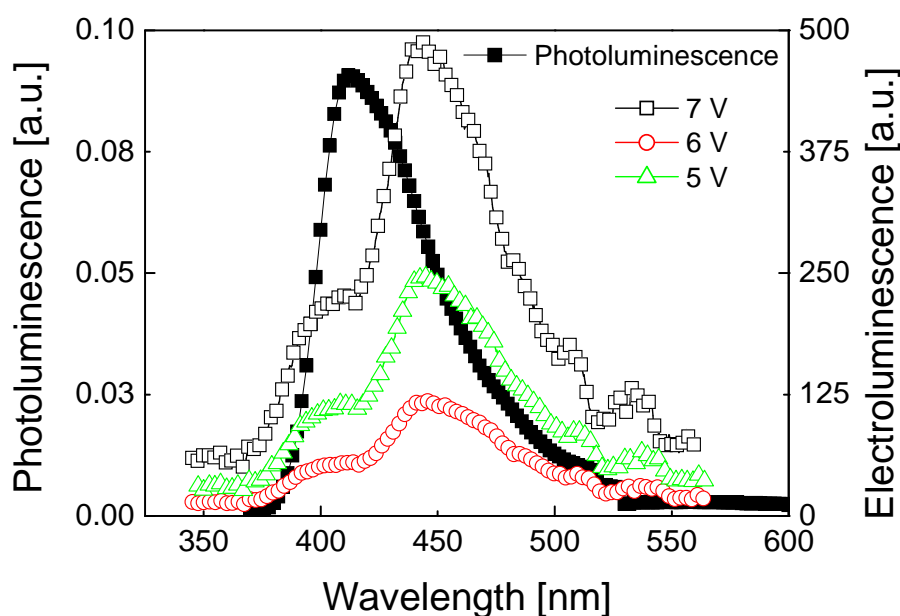


Figure 42 Electroluminescence at different voltages vs. photoluminescence of DO-PPP. Closed symbols indicate photoluminescence; open symbols indicate electroluminescence.

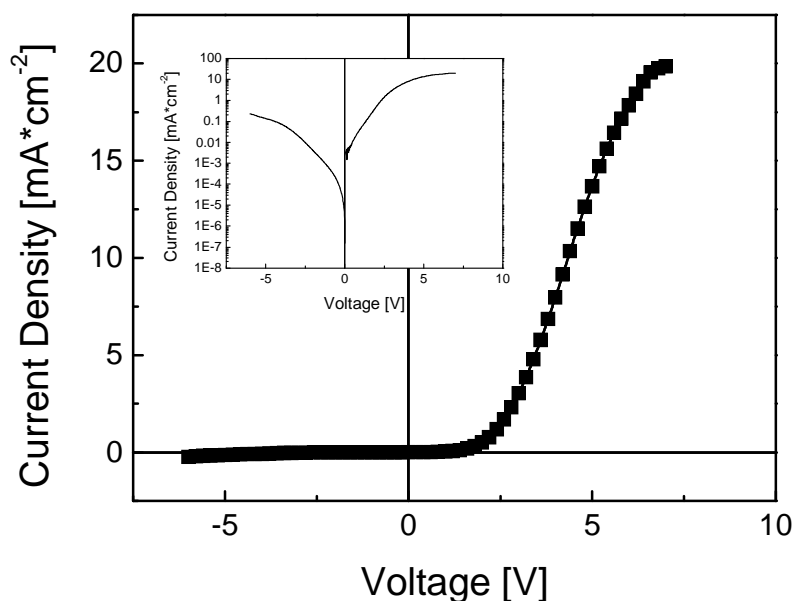


Figure 43 Current-voltage characteristics of DO-PPP – OLED. (Inset shows the logarithmic scale)

### 3.2.2 Europium Electroluminescence

The usage of polymer – europium complex mixtures (fabrication described in 2.4) as active layers in organic light emitting diodes in order to get the red europium electroluminescence at 614 nm is described in the following chapter.

In Figure 44 the electroluminescence of the  $\text{Eu}(\text{DTPD})_3\text{phen}$  complex in PVK is shown. The characteristic europium emission can be observed (compare with the results of 3.1.2.2).

The current-voltage characteristics of the  $\text{Eu}(\text{DTPD})_3\text{phen}$  / PVK – OLED shown in Figure 44 illustrate a lower operational voltage to get luminescence compared to the pure PVK – OLED.

According to the photoluminescence measurements in 3.1.3.1 the polymer electroluminescence is again completely quenched (see Figure 46)

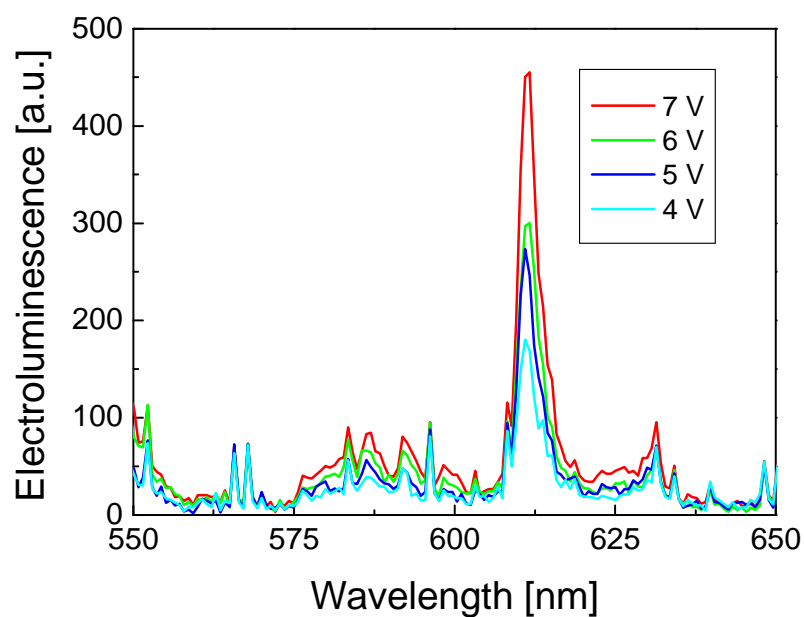


Figure 44 Electroluminescence at different voltages of  $\text{Eu}(\text{DTPD})_3\text{phen} / \text{PVK}$  - OLED

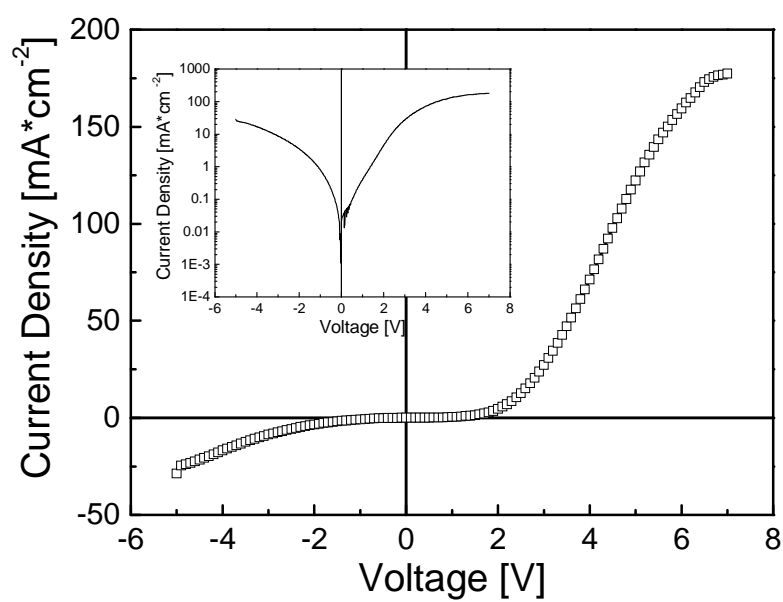


Figure 45 Current-voltage characteristics of  $\text{Eu}(\text{DTPD})_3\text{phen} / \text{PVK}$  - OLED. (Inset shows the logarithmic scale).

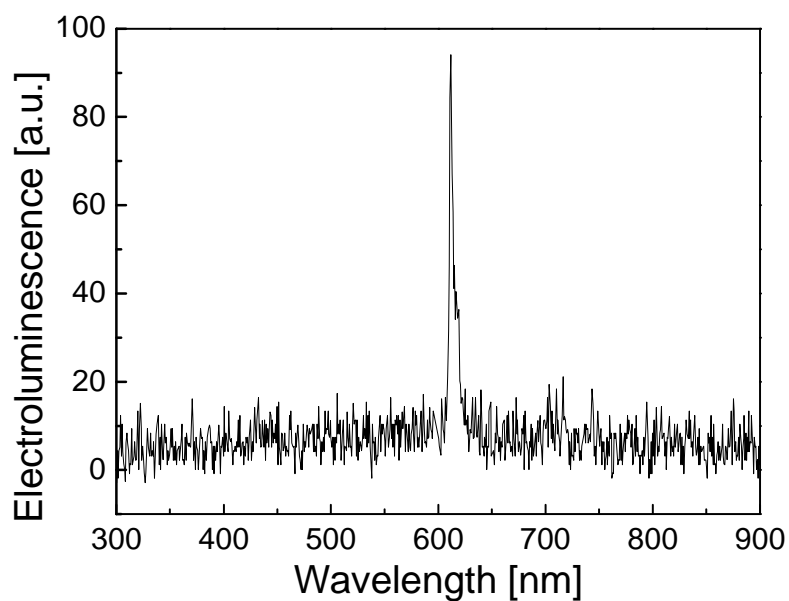


Figure 46 Full spectrum of  $\text{Eu}(\text{DTPD})_3\text{phen} / \text{PVK} - \text{OLED}$

The europium electroluminescence intensity of the  $\text{Eu}(\text{TFACACN})_3\text{phen} / \text{PVK}$  mixture is according to 3.1.3.1 larger than of the  $\text{Eu}(\text{DTPD})_3\text{phen} / \text{PVK}$  mixture. Figure 47 shows the characteristic europium electroluminescence at 614 nm.

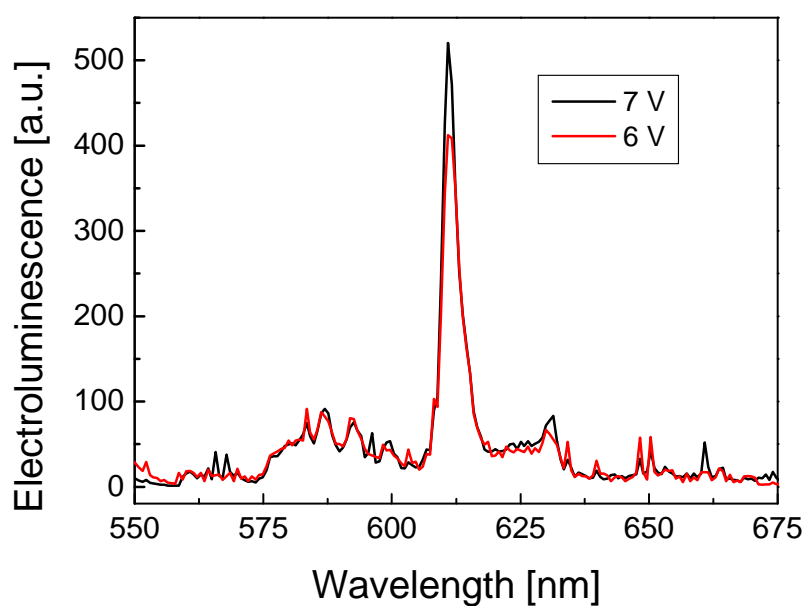


Figure 47 Electroluminescence of a  $\text{Eu}(\text{TFACACN})_3\text{phen} / \text{PVK} - \text{OLED}$

The current-voltage characteristics shown in Figure 48 are equal to the characteristics of  $\text{Eu}(\text{DTPD})_3\text{phen}$  what means that with the same voltage a more intense europium electroluminescence is achievable.

The polymer electroluminescence is again completely quenched in this system.

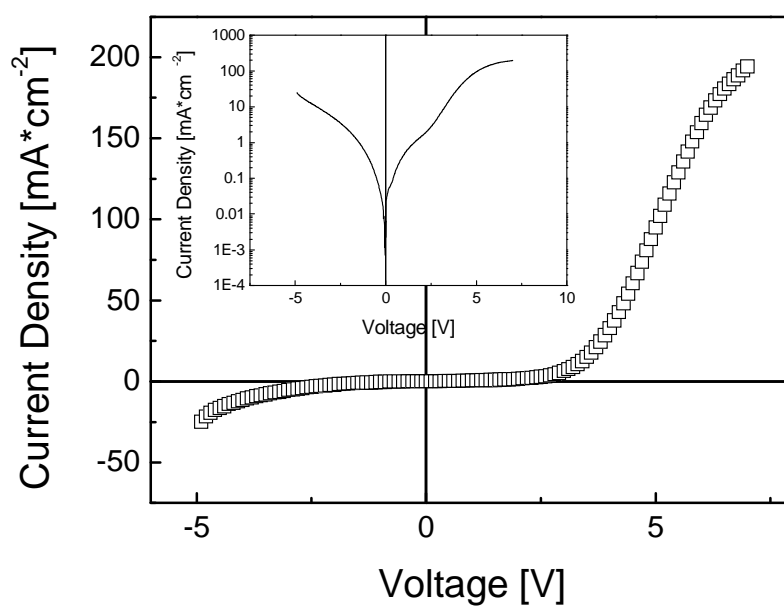


Figure 48 Current voltage characteristics of  $\text{Eu}(\text{TFACACN})_3\text{phen} / \text{PVK} - \text{OLED}$ . (Inset shows the logarithmic scale).

## 4 Summary

To get the luminescence of rare earth elements which are important for the optical telecommunication an external crystal field of the rare earth ions is required. Because when the symmetry of the ion is removed with an asymmetrical external crystal field, the intra 4f transitions, which are involved in absorption and luminescence processes become allowed. Embedding this rare earth complexes in appropriate luminescent polymer hosts makes an energy transfer from the excited polymer to the rare earth complex system possible.

In this work the synthesis of some  $\beta$ -diketonate ligand systems and some corresponding complexes of the rare earth elements Eu, Er and Nd is shown. Photoluminescence at 614 nm, 890 nm, 1.05  $\mu\text{m}$ , 1.35  $\mu\text{m}$  and 1.55  $\mu\text{m}$  of various rare earth complexes is demonstrated (see Figure 48).

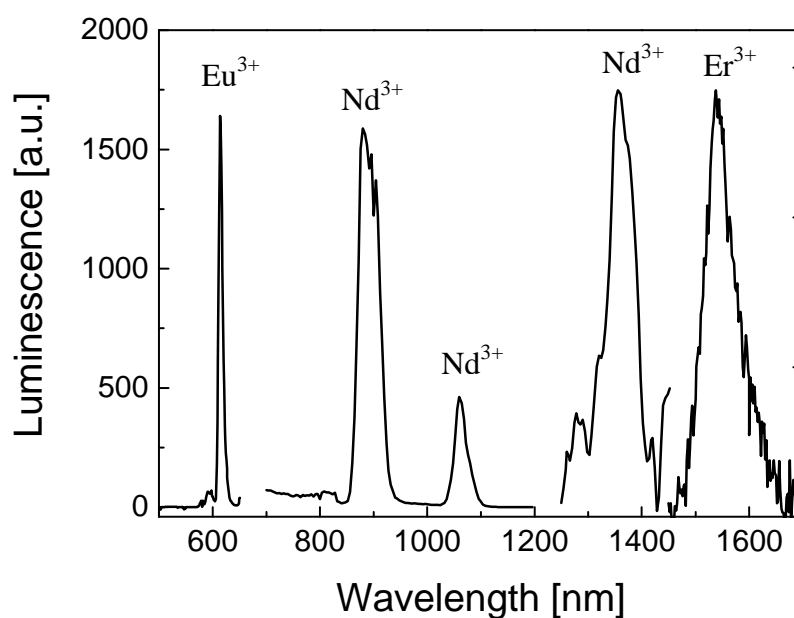


Figure 48 Photoluminescence of  $\text{Eu}^{3+}$ ,  $\text{Nd}^{3+}$  and  $\text{Er}^{3+}$ . (Intensities are not comparable)

For achieving the characteristic emission of each rare earth element the ligand systems dithienylpropanedione (DTPD) and trifluoroacetyl naphthalene (TFAcAcN) are demonstrated as the best matching ligands, which are investigated (see Figure 12).

DTPD and TFAcAcN are also best applicable for the energy cascade mechanism to get rare earth luminescence by exciting the polymer host, which is successfully demonstrated with europium systems. The excitation of the erbium complex - PVK system shows a complete quenching of the polymer luminescence and a weak erbium signal.

A better overlap of the complex absorption and the polymer luminescence would transfer more energy to the complex energy states and so the intensity of rare earth luminescence could be increased. This will be possible with additional aromatic groups in the ligand system or the synthesis of polymers, which have emission bands at higher energies.

For infrared emitting devices there are strong quenching effects in commonly used transparent polymers like polystyrene (PS) or polymethylmethacrylate (PMMA). This is a main problem for the applications in optical telecommunications.

The usage of fluorinated polymer host matrices (Teflon AF<sup>®</sup> and PFCB type polymer) for embedding rare earth complexes shows for infrared emitting devices an increase of the emission intensity. Excitation of Er(DTPD)<sub>3</sub>phen and Er(TFAcAcN)<sub>3</sub>phen embedded in Teflon AF<sup>®</sup> shows characteristic erbium emission even at room temperature.

The synthesis of luminescent fluorinated polymers, which emit at about 400 nm would be very interesting for the application of the energy cascade mechanism for infrared emitting systems.

Polyvinylcarbazole (PVK) and poly-2-decyloxy-1,4-paraphenylene (DO-PPP) were successfully used as active layers in organic light emitting diodes (OLED's) to achieve blue electroluminescence at about 450 nm. The current-voltage characteristics of fabricated devices indicates good diode behaviour.



Embedding of  $\text{Eu}(\text{DTPD})_3\text{phen}$  and  $\text{Eu}(\text{TFAcAcN})_3\text{phen}$  complexes in the active layer of PVK – OLED's changed the diode behaviour. Turn on voltages are reduced from about 15 V to about 4-7 V. By applying a certain voltage the characteristic europium luminescence is observable. No polymer electroluminescence occurs so the energy cascade mechanism is also working in organic light emitting diodes.

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## Curriculum Vitae

Linz, Oktober 2002

### Angaben zu meiner Person:

- Geboren am 11.06.1976 in Linz
- Familienstand: ledig

### Schulbildung:

- 1982-1986 VS Leonding
- 1986-1994 Bundesrealgymnasium Khevenhüller BRG 2
- 1994-2002 Studium an der Johannes Kepler Universität Linz:  
Wirtschaftsing.wesen Technische Chemie (WITECH)

### Sprachkenntnisse:

- Englisch: fließend und verhandlungssicher

### Bisherige Arbeitgeber:

- Sommer 1990-1994: Stadtgemeinde Leonding
- Sommer 1994: Post und Telekom Österreich
- Sommer 1995: Krankenhaus der Barmherzigen Schwestern Linz
- Sommer 1996: PGV Pressegroßvertrieb Salzburg
- Sommer 1997: VOEST Alpine Stahl Linz
- 1997-1999: Fa. Tuscher
- 1999-2001: Österreichischer Wachtdienst

## Curriculum Vitae

Linz, October 2002

### Personal:

- Born on the 11<sup>th</sup> of June 1976 in Linz, Austria
- Martial status: unwed

### Education:

- 1982-1986 Primary school Leonding
- 1986-1994 Grammar school Khevenhüller BRG 2 (Linz)
- 1994-2002 Studies at the Johannes Kepler University of Linz:  
technical chemistry and management

### Foreign Languages:

- English: business fluent

### Further Employers:

- Summer 1990-1994: Stadtgemeinde Leonding
- Summer 1994: Post und Telekom Österreich
- Summer 1995: Krankenhaus der Barmherzigen Schwestern Linz
- Summer 1996: PGV Pressegroßvertrieb Salzburg
- Summer 1997: VOEST Alpine Stahl Linz
- 1997-1999: Fa. Tuscher
- 1999-2001: Österreichischer Wachtdienst

## List of Publications

- Er<sup>3+</sup> - Emission From Organic Complexes Embedded In Thin Polymer Films  
M. Koppe, C. J. Brabec, N. S. Sariciftci, Y. Eichen, G. Nakhmanovich, E. Ehrenfreund, O. Epstein, W. Heiss  
*Synthetic Metals* **121** (2001) 1511-1512
- Organic Rare Earth Complexes in Polymer Matrices and Light Emitting Diodes  
M. Koppe, H. Neugebauer, N.S. Sariciftci  
submitted to *Molecular Crystal*
- Modified Organic ER- $\beta$ -Diketo – Complexes  
M. Koppe<sup>1</sup>, H. Neugebauer, N.S. Sariciftci  
submitted to *Synthetic Metals*

## Contribution to Conferences

- Er<sup>3+</sup> - Emission From Organic Complexes Embedded In Thin Polymer Films  
M. Koppe, C. J. Brabec, N. S. Sariciftci, Y. Eichen, G. Nakhmanovich, E. Ehrenfreund, O. Epstein, W. Heiss, ICSM 2000 Gastein (Austria)
- Organic Rare Earth Complexes in Polymer Matrices and Light Emitting Diodes  
M. Koppe, H. Neugebauer, N.S. Sariciftci, ICEPOM-4 Lviv (Ukraine)

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