Design, synthesis and properties of new materials based on densely crosslinked polymers for polymer optical fiber and amplifier applications
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Development of a Polymer Optical Fiber Amplifier by using terpositive europium – an applicable concept

ABSTRACT
Lanthanide (III) ions are badly soluble in polymers. To overcome that problem, the ions are encapsulated in organic chelates or complexing ligands and which solubilize these complexes in polymers. Such complexes have been prepared with crown-ethers, \( \beta \)-diketonates and bipyridines. These complexes have been evaluated for their usefulness as active component in Polymer Optical Fiber Amplifiers (POFAs), regarding their absorption and fluorescence efficiency and their solubility into polymer systems. The most suitable of these systems show efficient intramolecular energy transfer from ligand to terpositive europium ion and, subsequently, emission of 613 nm light with high intensity and quantum yield.

Bipyridine cryptates are found to be less efficient fluorophores than diketonate chelates and are laborious to prepare. Crown ether complexes suffer from high hygroscopicity and are non-sensitizing ligands. Sensitizing activity of ligands is of extreme importance for the intensity of photoluminescence of europium (III).

Incorporation in crosslinking polymer systems, viz. hexamethyleneisocyanate-based poly(isocyanurate) and poly(phenylmethylvinylhydrosiloxane)s, revealed an irreversible instability of hexafluorodiketonate-complexes, accompanied by a loss of luminescence activity. This was attributed to temperature effects and the presence of other complexing species (e.g. catalysts).
Diketonates functionalized with 2-(t-butylphenyl)-5-(4-biphenyl)-1,3,4-oxadiazole (PBD) showed much better complex stability and an Active Polymer Optical Fiber (APOF) based on polytrimerized hexamethylenediisocyanate and 1 wt. % of Eu(PBD)₃(TOPO)₂ has been fabricated, successfully. TOPO stands for trioctylphosphine oxide and acts as a synergic shielding ligand. TOPO strongly enhances the fluorescence intensity of the complex and its solubility in organic solvents and polymers. Substituting diketonates with a PBD moiety led to strong red luminescence when chelated to europium (III), due to a high absorption capacity and efficient intramolecular energy transfer. The addition of synergic ligands other than trioctylphosphine oxide, such as phenanthroline and bathophenanthroline, demonstrated a further improvement of the fluorescence intensity.

The Eu(PBD)₃(TOPO)₂ complex in polytrimerized HDI showed a high lifetime of fluorescence of 0.66 ms. Furthermore, a high value for the emission cross section has been found of 3.2 x 10⁻²¹ cm², which is equal to values found for rare-earth doped silica glasses that have been used, successfully, for Glass Optical Fiber Amplifiers (GOFAs).

A further increase of the absorption capacity using sensitized europium chelates and non-bonded sensitizers as dopants has been demonstrated by a cascade energy transfer experiment in the solid state.

The (cascade) energy transfer concept for lanthanide fluorophores is found to be very promising for amplification of light in polymer optical fibers and planar waveguides.

**INTRODUCTION**

The use of polymers in optical telecommunication applications has resulted in an increasing demand for optical signal amplifying systems. As polymers interfere with an optical signal by absorbing part of its energy, transmission distance in, for instance, polymer optical fibers is limited.¹ To enlarge the transmission distance of optical signals in polymer optical fibers one must compensate for the loss of energy. By coupling the fibers to an optical amplifying device, a weakened optical signal is boosted and thus regenerated in strength. Such a boosting medium contains a material
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capable of having stimulated emission at the signal beam wavelength. The active material, which is luminescent, is pumped by a laser beam that excites the molecules to a higher energy level. A signal beam traveling through the medium stimulates the emission of light of the same wavelength and phase from the excited molecules, and thus the signal intensity is increased.²⁻⁴

For the incorporation of luminescent molecules (fluorophores) one can choose between organic or inorganic fluorophores, the latter represented by bivalent and trivalent lanthanide ions. Our research has been focused on employing those lanthanides as the active species in polymer optical fiber amplifier materials. The reasons for this choice are a high optical damage threshold, photophysical properties independent upon local environment, sharp well-defined fluorescent bands, large shifts between absorption and fluorescence wavelengths and a tunability of the fluorescence wavelength.¹ An important property to focus on when designing a system for amplification purposes based on lanthanides is the observed lifetime of the metastable-state, which should be maximized for efficient lasing and amplifying properties.⁵

Recently increasing research activities have been carried out in the field of developing polymer systems with lanthanide ions or ion complexes incorporated. Most of these are aimed at making polymer optical amplifiers or lasers.⁵⁻¹¹ Koeppen and coworkers⁵ made a theoretical consideration of the feasibility of rare earth (RE)-doped polymers for amplification purposes. They showed that gains up to 20 or 30 dB are realizable when using europium chelates doped in poly(methyl methacrylate).

This chapter describes the research conducted to design and synthesize europium complexes suitable for amplification of light in polymer optical fibers. The europium complexes were developed in relation to the following:
The solubility of RE-ions in organic polymer media should be strongly improved.

The fluorescence of RE-ions is quite weak due to a forbidden electronic transition (4f-4f). Surrounding the RE-ion with organic ligands, in particular a mixed assembly, improves the absorption cross-section of the fundamental absorption, significantly.

Steric hindrance from the ligands and the saturation of the coordination sphere prevent non-radiative decay of the excited state (cross-coupling interactions between RE-ions; energy transfer to quenching species, in particular water).

If the ligand system acts as a chromophore, it can possibly transfer the absorbed energy to the RE-ion in a non-radiative way and, in that case, increasing the overall absorption coefficient and the fluorescence intensity. The energy states of the excited ligand (triplet states) should be just above well-isolated energy states of the RE-ion for efficient intramolecular energy transfer (resonance energy exchange).

We propose densely crosslinked polymers to be the most suitable host matrix for fluorescent lanthanide complexes. Through the high degree of crosslinking, the mobility of the network chains is severely restricted and the quenching of fluorescence is reduced by minimizing collisions of the chains with the rare earth complex. It has been mentioned that a good protecting sheath around the rare earth-ion would make the influence of polymer chain collisions less important\(^1\). However, enveloping the complex itself in a tight polymer network structure may be highly favorable for its stability, in particular at higher temperatures. The importance of this has recently been recognized by others, as well\(^{12,13}\).

Strong quenching of luminescence in the near-infrared through high-energy vibrations of mainly O-H and C-H bonds (overtones) is difficult to avoid. Research has been focused on luminescence phenomena in the visible wavelength region as here the vibrational C-H overtone absorptions are strongly attenuated. Moreover, for the same
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reason, polymers have their low-loss windows in that spectral region (around 600 nm). Europium, luminescing at 613 nm, is therefore the most interesting lanthanide for this moment.

EXPERIMENTAL

Materials
All reactions were carried out under a nitrogen atmosphere. Starting materials were used as received from their suppliers, unless stated otherwise. The lanthanide salts, supplied by Aldrich, were thoroughly dried under vacuum before use and stored dry. Special care was taken with respect to purity in the complexation reactions of drying reagents, solvents and glassware. The solvents were dried by distillation under a nitrogen atmosphere. Diethyl ether was distilled firstly from P2O5 and secondly from LiAlH4, tetrahydrofuran was distilled from potassium, dichloromethane from CaH2 and pentane from P2O5. Acetonitrile was distilled before use, methanol, ethanol and chloroform were used as received.

Synthesis
Eu(NO3)3·18-crown-6 (1)
To a vigorously stirred solution of 4.0 g (9 mmol) of Eu(NO3)3.5H2O in 25 mL methanol in a 500 mL 3-necked flask was slowly added a solution of 2.37 g (9 mmol) of 18-crown-6-ether (Acros Chimica) in 25 mL methanol. A white crystalline precipitate formed almost immediately. After dissolving the precipitate in 150 mL methanol, pentane was added dropwise to the mixture with stirring until the first traces of permanent turbidity resulted. After stirring overnight the precipitate was filtered, washed with hexane and dried overnight at 60°C under reduced pressure.
Anal. calcd. for C12H24O15N3Eu (602.29): Eu 25.23, C 23.93, H 4.02, N 6.98; found: Eu 24.96, C 24.05, H 4.14, N 7.01.

6-hydroxy-2-picoline14 (3)
To a magnetically stirred mixture of 135 g (1.25 mol) 6-amino-2-picoline (Aldrich), 135 mL conc. H2SO4 and 1 L H2O, a solution of 155 g (2.25 mol) NaNO2 in 300 mL H2O was added dropwise in ca. 3.5 h. The temperature was not allowed to rise above 50°C. After cooling, the mixture was made alkaline by adding Na2CO3, followed by removal of the solvent by rotary evaporation. The residue was extracted with boiling CHCl3, which after evaporation gave the product, 122.9 g (1.13 mol, 90%) orange crystals m.p. 153-154°C.
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\(^{1}\)H-NMR (CDCl\(_3\)); \(\delta\) (ppm): 2.35 (s, CH\(_3\), 3H), 6.06 (d, C(5)-H, J = 7.6 Hz, 1H), 6.42 (d, C(3)-H, J = 10.2 Hz, 1H), 7.38 (t, C(4)-H, J = 7.2, 7.9 Hz, 1H), 13.29 (br s, OH, 1H).

6-bromo-2-picoline\(^{14}\) (4)
A mixture of 77.7 g (0.59 mol) 6-hydroxy-2-picoline and 64.0 g (0.23 mol) phosphorxybromide was refluxed at 160°C for 30 min. After cooling to room temperature, the solidified reaction mixture was quenched with 125 mL H\(_2\)O and made alkaline with Na\(_2\)CO\(_3\) and extracted in portions with ether. The ethereal layers were dried and concentrated by rotary evaporation. The product was distilled under reduced pressure (Kugelrohr, 145°C / 31 mbar), resulting in a colorless liquid, yield 58.7 g (0.34 mol, 57%).

\(^{1}\)H-NMR (CDCl\(_3\)); \(\delta\) (ppm): 2.39 (s, CH\(_3\), 3H), 6.97 (d, C(3)-H, J = 7.6 Hz, 1H), 7.14 (d, C(5)-H, J = 8.2 Hz, 1H), 7.31 (t, C(4)-H, J = 7.6, 7.8 Hz, 1H).

6,6´-dimethyl-2,2´-bipyridine\(^{15}\) (5)
A stirred mixture of 48.3 g (0.28 mol) 6-bromo-2-picoline, 28.6 g (0.42 mol) NaCHO\(_2\), 1.7 g 5% Pd/C, 15 g powdered iron, 11.2 g (42 mmol) benzyltriethylammonium chloride (BTAC), 30 ml 32% w/w NaOH and 75 mL H\(_2\)O were refluxed for about a week during which portions (5-10% of the starting amounts) of NaCHO\(_2\), Pd/C, BTAC and iron were added every 12 h. The reaction was followed by TLC (silica gel, cyclohexane/ethyl acetate (2:1)) by monitoring the disappearance of the starting material, 6-bromo-2-picoline. The reaction mixture was filtered and the reaction vessel thoroughly washed with H\(_2\)O and CH\(_2\)Cl\(_2\). After separating the layers, the aqueous layer was further extracted with 3 x 200 mL CH\(_2\)Cl\(_2\). The combined organic layers were evaporated and the resulting dark brown liquid was distilled under reduced pressure (kugelrohr, 143°C/0.05 mbar) to give the product as white crystals, yield 16.6 g (0.09 mol, 64%).

\(^{1}\)H-NMR (CDCl\(_3\)); \(\delta\) (ppm): 2.60 (s, CH\(_3\), 6H), 7.12 (d, C(5)-H, C(5´)-H, J = 7.6 Hz, 2H), 7.65 (t, C(4)-H, C(4´)-H, J = 7.6, 7.8 Hz, 2H), 8.14 (d, C(3)-H, C(3´)-H, J = 8.2 Hz, 2H).

6,6´-bis(bromomethyl)-2,2´-bipyridine\(^{16}\) (6)
In a three-necked flask fitted with a reflux condenser, a mixture of 2.80 g (15 mmol) 6,6´-dimethyl-2,2´-bipyridine and 5.10 g (28.6 mmol) N-bromosuccinimide (NBS) in 150 mL CCl\(_4\) was refluxed for 30 min. Then, 50 mg benzoyl peroxide (BPO) was added and the mixture was refluxed for an additional 4 h. After cooling to room temperature the succinimide was filtered off, and the mixture was cooled to 0°C. This gave a first portion of the product as white crystals, yielding 1.85 g (5.4 mmol, 36%). Concentrating the mother liquor and recrystallizing the residue resulted in a second
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portion, slightly contaminated with other brominated compounds like 6-methyl-6’-bromomethyl-2,2’-bipyridine, 6-bromomethyl-6’-dibromomethyl-2,2’-bipyridine and 6,6’-bis(dibromomethyl)-2,2’-bipyridine. The first, clean portion was used further.

\[ ^1 \text{H-NMR (CDCl}_3\); \delta (ppm): 4.63 (s, CH\textsubscript{2}, 4H), 7.47 (dd, C(5)-H, C(5’)-H, J = 7.8, 1.0 Hz, 2H), 7.83 (t, C(4)-H, C(4’)-H, J = 7.8 Hz, 2H), 8.39 (dd, C(3)-H, C(3’)-H, J = 7.8, 1.0 Hz, 2H). \]

Analyt. calcd. for C\textsubscript{12}H\textsubscript{10}Br\textsubscript{2}N\textsubscript{2} (342.0): C 42.11, H 2.92, N 8.19, Br 46.72; found: C 42.13, H 3.08, N 8.14, Br 46.76.

p-toluenesulfonamide monosodium salt

In a oven-dried three-necked flask fitted with a large stirring magnet, reflux condenser, nitrogen inlet and septum, 7.5 g 55-65% NaH suspension in oil (4.4 g NaH; 186 mmol) was placed and washed with 3 x 50 mL dry pentane, using a syringe. The residual pentane was removed by applying vacuum. Then, 80 mL dry THF was added to form a suspension, to which a solution of 31.9 g (186 mmol) p-toluenesulfonamide in 200 mL dry THF was added dropwise in 3.5 h. The resulting slurry was dried by rotary evaporation under nitrogen atmosphere. The product was stored under nitrogen.

\[ ^1 \text{H-NMR (DMSO); \delta (ppm): 2.25 (s, CH}_3\text{, 3H), 3.30 (s, NH, 1H), 7.07 (d, C(3)-H, C(5)-H, J = 7.2 Hz, 2H), 7.53 (d, C(2)-H, C(6)-H, J = 7.2 Hz, 2H). \]

8,21-ditosyl-8,21,27,28,29,30-hexa-azapentacyclo[21.3.1.1\textsuperscript{2,6}.1\textsuperscript{10,14}.1\textsuperscript{15,19}]triaconta-1(27),2,4,6(30),10,12,14(29),15,17,19(28),23,25-dodecaene\textsuperscript{17} (7)

A mixture of 1.60 g (4.7 mmol) 6,6’-bis(bromomethyl)-2,2’-bipyridine and 1.81 g (9.35 mmol) p-toluenesulfonamide monosodium salt in dry ethanol\textsuperscript{16} was refluxed under nitrogen atmosphere for 24 h in a three-necked flask with reflux condenser and N\textsubscript{2}-inlet. After cooling to below 0°C the mixture was filtered, producing a slightly yellow solid, which was washed with cold water. Unlike the results reported by Newkome and co-workers, the product was found to be slightly soluble in CHCl\textsubscript{3}, and therefore it was purified by recrystallisation from this solvent, yielding 0.79 g (1.5 mmol; 66%) white crystals, m.p. > 260 °C.

\[ ^1 \text{H-NMR (CDCl}_3\); \delta (ppm): 2.51 (s, Ts-CH\textsubscript{3}, 6H), 7.1-7.5 (m, C(5)-H, C(5’)-H, TsC(2)-H, TsC(3)-H, TsC(5)-H, TsC(6)-H), 7.63 (dd, C(4)-H, C(4’)-H, J = 7.8, 1.2 Hz, 4H), 7.84 (d, C(3)-H, C(3’)-H, J = 8.2 Hz, 4H). \]

8,21,27,28,29,30-hexa-azapentacyclo[21.3.1.1\textsuperscript{2,6}.1\textsuperscript{10,14}.1\textsuperscript{15,19}]triaconta-1(27),2,4,6(30),10,12,14(29),15,17,19(28),23,25-dodecaene\textsuperscript{17} (8)

0.113 g Macrocycle 7 (0.16 mmol) was dissolved in 1 mL conc. H\textsubscript{2}SO\textsubscript{4} and the mixture was heated to 110°C for 2 h. After cooling to room temperature, 2 mL H\textsubscript{2}O was added and the mixture was poured

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with caution into a solution of 2 g NaOH in 15 mL H2O. However, the resulting mixture proved to be still acid, so a concentrated aqueous solution of NaOH was added in portions until pH 8 was reached. The product, which precipitated as a white solid was extracted with 3 x 30 mL CHCl3. This eventually yielded the product as slightly yellowed white crystals, 0.046 g (0.12 mmol; 75%). The product proved to be not totally pure, but recrystallization from CHCl3 and other common solvents failed due to the small amount of product isolated.

\[ ^1H-NMR \ (CDCl_3); \delta \ (ppm): \ 1.76 \ (br \ s, N-H, 2H), \ 4.08 \ (s, CH_2, 8H), \ 6.96 \ (dd \ C(5)-H, C(5´)-H, J = 7.0, 1.0 Hz, 4H), \ 7.26 \ (t, C(4)-H, C(4´)-H, J = 7.4 Hz, 4H), \ 7.71 \ (dd, C(3)-H, C(3´)-H, J = 7.8, 1.5 Hz, 4H). \]

6, 6´, 6´´, 6´´´, 6´´´´, 6´´´´´, bis[nitrilotri(methylene)]tris(2,2´-bipyridine) (9), NaBr complex thereof

A magnetically stirred mixture of 0.040 g (0.101 mmol) macrocycle 8 and 0.107 g (0.99 mmol) Na2CO3 in 55 mL distilled acetonitrile was heated to reflux. A solution of 0.032 g (0.093 mmol) 6,6´-bis(bromomethyl)-2,2´-bipyridine in 30 mL distilled acetonitrile was added dropwise, and the resulting mixture was refluxed for another 24 h. After cooling the mixture to room temperature, the insoluble salts were filtered off and the filtrate was dried by rotary evaporation. The resulting yellowish-white crystals were washed by subsequently adding and removing small amounts of cold methanol by a pipette. The product yield amounted to 0.0095 g (0.014 mmol; 14%).

\[ ^1H-NMR \ (CDCl_3); \delta \ (ppm): \ 3.83 \ (s, CH_2, 12H), \ 7.31 \ (d (lit: dd), C(5)-H, C(5´)-H, J = 7.2 Hz, 6H), \ 7.83 \ (d (lit: t), C(4)-H, C(4´)-H, J = 7.4 Hz, 6H), \ 7.90 \ (d (lit: dd), C(3)-H, C(3´)-H, J = 7.2 Hz, 6H). \]

Eu(NO3)3 complex of 6, 6´, 6´´, 6´´´, 6´´´´, 6´´´´´, bis[nitrilotri(methylene)]tris(2,2´-bipyridine)

9.5 mg Sodium bromide cryptate 9 (0.014 mmol) was dissolved in 1 mL CHCl3 and the resulting solution was added in one portion to a stirred solution of 6.0 mg (0.014 mmol) Eu(NO3)3 in 3 mL freshly distilled acetonitrile. The resulting mixture was refluxed for 48 h. The cooled mixture was filtered to remove insoluble components like NaNO3 and the filtrate was concentrated under reduced pressure until it became slightly opaque. The product which crystallized from the solution was dried after removing the solvent carefully with a pipette. The white crystals were washed with small portions of CH2Cl2/MeOH (98:2) and freshly distilled diethylether.

EuCl3 complex of macrocycle 8 (8,21,27,28,29,30-hexa-azapentacyclo[21.3.1.12,6.110,14.115,19]triaconto-1(27),2,4,6(30),10,12,14(29),15,17,19(28),23,25-dodecaene)

To a stirred solution of 33 mg (0.0837 mmol) macrocycle 8 in 2 mL CH2Cl2, a solution of 31 mg (0.0837 mmol) EuCl3 in 3 mL methanol was added in one portion and the resulting mixture was
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heated to 60°C for 3 h. Slow evaporation of the solvent yielded the product, which was recrystallized by slow diffusion of ether into an ethanol solution (ca 10 mL) of the product.

tris(1,5-hexafluoro-2,4-pentanedionate) europium (III)

\([\text{tris(hexafluoroacetyl acetonate) europium (III): Eu(hfa)₃}]^6\) (10)

To a stirred solution of 2.00 g (9.61 mmol) hexafluoroacetyl acetonate [H(hfa)], supplied by Aldrich, in 25 mL ether, a solution of 1.046 g (2.45 mmol) Eu(NO₃)₃ in 25 mL water was added dropwise and the mixture was stirred for another 60 min. The phases were separated and the ethereal layer was washed with 3 x 15 mL water, after which the solvent was removed by rotary evaporation. The product (1.63 g; 2.11 mmol; 86%) was isolated as white crystals and stored in a dry environment.


tris(1,5-hexafluoro-2,4-pentanedionate) bis(trioctylphosphine oxide) europium (III)

\([\text{Eu(hfa)₃(TOPO)₂}]^6\) (11)

A solution of 4.01 g (9.36 mmol) Eu(NO₃)₃ in 100 mL water was added dropwise to a magnetically stirred solution of 5.85 g (28.12 mmol) H(hfa) and 7.30 g (18.89 mmol) trioctylphosphine oxide (Aldrich) in 100 mL distilled ether. The mixture was stirred for 30 min. and separated, after which the ethereal layer was washed with 2 x 75 mL water. The solvent was removed by rotary evaporation and the product, a slightly yellow, strongly fluorescent oil was dried under vacuum and stored in a dry environment.


tris(1,4-hexafluoro-1,3-butanedionate) bis(tripiperidinophosphine oxide) europium (III)

\([\text{Eu(hfa)₃(PIPO)₂}]\) (12)

The tripiperidinophosphine oxide (PIPO), supplied by Aldrich, was distilled under reduced pressure (Kugelrohr, 205°C / 0.1 mbar) before use, yielding white, extremely hygroscopic crystals. To a stirred solution of 1.46 g (7.01 mmol) hexafluoroacetyl acetonate and 1.34 g (4.67 mmol) PIPO in 30 mL distilled ether, a solution of 1.00 g (2.34 mmol) Eu(NO₃)₃ in 30 mL water was added dropwise. The mixture was stirred for 15 min., separated and the ethereal layer washed with 3 x 25 mL water. After removal of the solvent, the product (2.40 g; 1.75 mmol; 75%) was dried under vacuum. The white crystals have a strong tendency to become yellow upon standing, a process which can be slowed by storing them under N₂. During this process, much of the fluorescence activity of the compound is lost.

2-((t-butylphenyl)-5-(4-biphenylacetyl)-1,3,4-oxadiazole [Acetyl-PBD]\textsuperscript{20,21}

To a suspension of 70 g (524.6 mmol) aluminum chloride in 150 mL dry dichloromethane, under nitrogen atmosphere, was added 22 mL (309.4 mmol) freshly distilled acetyl chloride. The mixture was then stirred and heated to reflux. A solution of 21.0 g (59.25 mmol) t-butyl-PBD (2-((t-butylphenyl)-5-(4-biphenyl)-1,3,4-oxadiazole, hereafter referred to as PBD), purchased from Aldrich, in 220 mL dry dichloromethane was added dropwise (over ~2 h). The mixture was refluxed for another 2 h, subsequently allowed to cool down to room temperature and stirred overnight. The cooled reaction mixture was slowly poured to 500 mL ice, vigorously stirred until all the ice melted, and then extracted. The organic layer was washed twice with water and dried on sodium sulfate. After evaporation of the solvent, the crude mixture was recrystallized from acetone to give 13.8 g (0.028 mol; 47%) of a pale yellow powder.

\textsuperscript{1}H-NMR (CDCl\textsubscript{3}); \textbf{\textit{δ}} (ppm): 1.39 (s, 9H), 2.67 (s, 3H), 7.58 (d, J = 8.4 Hz, 2H), 7.64 (d, J = 8.4 Hz, 2H), 7.81 (d, J= 8.4 Hz, 2H), 8.09 (d, J = 8.4 Hz, 2H), 8.10 (d, J = 8.4 Hz, 2H), 8.25 (d, J = 8.4 Hz, 2H).

1,1,1-trifluoro-4-PBD-2,4-butanedione [PBD-trifluorobutanedione]\textsuperscript{22-24}

To a stirred suspension of 550 mg (10.18 mmol) sodium methoxide in dry ether, was slowly added 1 mL (8.40 mmol) ethyltrifluoroacetate (Aldrich) with a syringe, followed by 3.06 g (6.21 mmol) acetyl-PBD under a nitrogen flow. A pale-ochre precipitate appeared. The mixture was stirred overnight at room temperature. The precipitate was filtered on a Büchner filter, subsequently dissolved in 100 mL chloroform and stirred for 2 h with 20 mL 10%-aqueous sulfuric acid. The organic layer was extracted, washed twice with 50 mL water and dried on sodium sulfate. After evaporation of the solvent, the product was recrystallized from ether to give 3.04 g (6.2 mmol; 99.8%) of a pale-yellow powder.

\textsuperscript{1}H-NMR (CDCl\textsubscript{3}); \textbf{\textit{δ}} (ppm): 1.39 (s, 9H), 6.65 (s, 1H), 7.58 (d, J = 8.4 Hz, 2H), 7.64 (d, J = 8.4 Hz, 2H), 7.81 (d, J= 8.4 Hz, 2H), 8.09 (d, J = 8.4 Hz, 2H), 8.10 (d, J = 8.4 Hz, 2H), 8.27 (d, J = 8.4 Hz, 2H).

tris(1,1,1-trifluoro-4-PBD-2,4-butanedionate) europium (III) [Eu(PBD)\textsubscript{3}] (13)

To a stirred suspension of 5.00 g (10.15 mmol) PBD-trifluorobutanedione in 250 mL ethanol was added 585 mg (10.83 mmol) sodium methoxide; the mixture was stirred at room temperature for a few
hours without complete dissolution. To this suspension was added a solution of 1.24 g (3.39 mmol) EuCl$_3$ . 6H$_2$O in 20 mL ethanol. A pale-yellow precipitate immediately appeared and a strong red fluorescence could be seen on UV-illumination. The mixture was stirred for 3-4 h, subsequently 400 mL water was added upon cooling to complete the precipitation and the mixture was stirred again for 1 h. Most of the ethanol was removed on a rotary evaporator and the mixture was allowed to stand overnight at 4°C. The precipitate was collected by filtration over a Büchner filter and dried overnight in vacuo over sodium hydroxide, to give 5.45 g (3.28 mmol; 32%) of a pale-yellow powder.

Anal. calcd. for Eu(C$_{28}$H$_{22}$F$_3$N$_2$O$_3$)$_3$(H$_2$O)$_2$ (1662.46): Eu 9.14, C 60.69, H 4.24, N 5.06; found: Eu 9.01, C 60.35, H 4.21, N 5.06.

tetrakis(1,1,1-trifluoro-4-PBD-2,4-butanedionate) europium (III) monopiperidinium [Eu(PBD)$_4$] (16)

To a stirred suspension of 1.03 g (2.09 mmol) PBD-trifluorobutanedione in 100 mL ethanol was added 0.21 mL (2.12 mmol) piperidine; the salt dissolved at room temperature. To this solution was added a solution of 192 mg (0.524 mmol) EuCl$_3$ . 6H$_2$O in 10 mL ethanol. A pale-yellow precipitate immediately appeared and a strong red fluorescence could be seen on UV-illumination. The mixture was stirred for 1 h, 150 mL water was added to complete the precipitation, and the mixture was stirred again for 1 h. Most of the ethanol was removed on a rotary evaporator, and the mixture was allowed to stand overnight at 4°C. The precipitate was collected by filtration through a Büchner filter and dried overnight in vacuo over sodium hydroxide, to give 1.04 g (0.61 mmol; 29%) of a pale-yellow powder.

Anal. calcd. for Eu(C$_{28}$H$_{22}$F$_3$N$_2$O$_3$)$_4$(C$_5$H$_{12}$N) (1712.59): Eu 9.14, C 63.76, H 4.57, N 5.72; found: Eu 7.12, C 62.80, H 4.66, N 5.48.

tris(1,1,1-trifluoro-4-PBD-2,4-butanedionate) bis(trioctylphosphine oxide) europium (III) [Eu(PBD)$_3$(TOPO)$_2$] (14)

A mixture of 100 mg (0.060 mmol) Eu-tris-PBD and 46.5 mg (0.120 mmol) trioctylphosphine oxide (TOPO) was dissolved in 20 mL dry THF and stirred at room temperature for 1 h. The solvent was evaporated and the product (a pale-yellow powder) was dried overnight in vacuo over sodium hydroxide.

Anal. calcd. for Eu(C$_{28}$H$_{22}$F$_3$N$_2$O$_3$)$_3$((C$_{8}$H$_{17}$)$_3$PO)$_2$ (2399.71): Eu 6.33, C 66.07, H 7.06, N 3.50; found: Eu 6.21, C 65.62, H 7.11, N 3.48.
**Chapter 8**

**tris(1,1,1-trifluoro-4-PBD-2,4-butanedioate) phenanthroline europium (III)**

\[\text{[Eu(PBD)₃(phen)] (15)}\]

A mixture of 100 mg (0.060 mmol) Eu-tris-PBD and 11.8 mg (0.060 mmol) phenanthroline monohydrate was dissolved in 20 mL dry THF and stirred at room temperature for 1 h. The solvent was evaporated and the product (a pale-yellow powder) was dried overnight \textit{in vacuo} over sodium hydroxide.

\textit{Anal. calcd. for Eu(C_{28}H_{22}F_{3}N_{2}O_{3})\cdot(C_{12}H_{8}N_{2}) (1806.64): Eu 8.41, C 63.82, H 4.13, N 6.20; found: Eu 8.29, C 63.44, H 4.20, N 6.03.}

**tris(1,1,1-trifluoro-4-PBD-2,4-butanedioate) bathophenanthroline europium (III)**

\[\text{[Eu(PBD)₃(bathophen)] (17)}\]

A mixture of 100 mg (0.060 mmol) Eu-tris-PBD and 21.2 mg (0.060 mmol) bathophenanthroline monohydrate was dissolved in 20 mL distilled THF and stirred at room temperature for 1 h. The solvent was evaporated and the product (a pale-yellow powder) was dried overnight \textit{in vacuo} over sodium hydroxide.

\textit{Anal. calcd. for Eu(C_{28}H_{22}F_{3}N_{2}O_{3})\cdot(C_{25}H_{16}N_{2}) (1934.81): Eu 7.85, C 65.80, H 4.27, N 5.79; found: Eu 7.86, C 65.67, H 4.30, N 5.53.}

**tris(1,1,1-trifluoro-4-thenoyl-2,4-butanedioate) europium (III)**

\[\text{[tris(thenoyltrifluoroacetone) europium (III): Eu(TTA)₃]}\]

To a stirred suspension of 500 mg (2.25 mmol) thenoyltrifluoroacetone (HTTA), purchased from Aldrich, in 30 mL ethanol was added 253 mg (2.25 mmol) potassium t-butoxide; the mixture was stirred at room temperature for 30 min. until complete dissolution. To this suspension was added a solution of 276 mg (0.75 mmol) EuCl₃ . 6H₂O in 10 mL ethanol. A pale-yellow precipitate immediately appeared and a strong red fluorescence could be seen on UV-illumination. The mixture was stirred for ca. 1 h, subsequently 80 mL water was added upon cooling to complete the precipitation and the mixture was stirred again for 1 h. Most of the ethanol was removed on a rotary evaporator, and the mixture was allowed to stand overnight at 4ºC. The precipitate was collected by filtration through a Büchner filter, dried overnight \textit{in vacuo} over sodium hydroxide, then recrystallized from a hot toluene/hexane mixture to give a pale-yellow powder.

\textit{Anal. calcd. for Eu(C_{9}H_{4}F_{3}O_{2}S)\cdot(H_{2}O)\cdot2 (851.51): Eu 18.63, C 35.35, H 1.48, S 11.79; found: Eu 18.48, C 35.25, H 1.63, S 12.06.}
Preparation of a rare earth-doped polymer optical fiber

1 Wt. % of Eu(PBD)$_3$(TOPO)$_2$ has been dissolved in hexamethylene diisocyanate (HDI), supplied by Acros Chimica. Reaction occurred slowly at room temperature, after adding 2 wt. % of catalyst ($N,N',N''$-tris(dimethylaminopropyl)hexahydrotetrazine – Polycat, Air Products). Just prior to gelling (after 6 - 8 h) the mixture was injected in a FEP-tubing (Fluoroethylene-co-fluoropropylene, Polyfluor Holland). The reaction was allowed to proceed in the tubing at 30°C for 48 h.

Characterization

$^1$H-NMR spectra were recorded on a 200 MHz or 300 MHz Varian Gemini spectrometer. All chemical shifts are referenced to TMS (0 ppm), denoting the splitting patterns in the following manner: s (singlet), d (doublet), dd (double doublet), t (triplet), q (quartet) and m (multiplet). UV-Visible spectra were recorded on a SLM-Aminco 3000 Array spectrometer in spectral grade solvents. Solid-state measurements have been performed on a thin film. Fluorescence spectra were taken on a Perkin-Elmer LS50B spectrometer in spectral grade solvents. Solid state measurements have been performed on a thin film or slice. The same apparatus has been used for measuring lifetimes of excited state and quantum yields. Quantum yields have been determined by using 1-thionyl-4-trifluoro-1,3-butanedioate europium (III) (preparation see above) as the standard ($\Phi_\text{Fl} = 0.22$ in toluene).$^{25}$ All solutions were made in benzene. The following formula has been used:

$$\Phi_\text{Fl} = \frac{A_\text{Fl}}{A_\text{st}} \cdot \frac{c_\text{st}}{A_\text{st}} \cdot \frac{\Phi_\text{st}}{\varepsilon} \cdot c$$

$\Phi_\text{Fl}$ = quantum yield of fluorescence  
$A_\text{Fl}$ = area of fluorescence peak at 613 nm  
$\varepsilon$ = extinction coefficient  
$c$ = concentration

Subscript st means: standard

Note: Before performing the absorption and fluorescence measurements, the Eu(hfa)$_3$(TOPO)$_2$ complex was freshly isolated from a diethyl ether solution in which it is stable for longer times of storage.
RESULTS AND DISCUSSION

1) Europium (III) crown ether complexes

Initial developments were focused on making crown ether complexes of rare earth ions in order to enhance the solubility of lanthanides in polymer matrices. Many complexes have been prepared including those with a polymerizable functionality. Important to note is that only by using lanthanide nitrates, complexes could be successfully prepared. Attempts to make lanthanide complexes with various functional *silacrown ethers* yielded interesting compounds of which some acted as a catalyst for the trimerization of diisocyanates. These materials, so called poly(isocyanurates), were of our interest for the production of thermally stable polymer optical fibers.\(^26, 27\) Crown ether complexes indeed showed some improved solubility in organic media but they still suffered from a high hygroscopicity. The main drawback of utilizing crown ether ligands is that they do not improve the absorption coefficient of the compounds as they are not capable of absorbing optical energy.

Hereafter, research has been focused on diketonate chelates and bipyridine complexes. For the latter we were inspired by the work of J.-M. Lehn and coworkers. They demonstrated that a bipyridine cryptate enveloping tervalent europium shows intense red fluorescence even in a water solution.\(^16, 18\) Motivation for working on diketonate chelates has come from published work mainly from the 1960s, as has been amply described in chapter 1, the introduction of this thesis.
2) Diketonate chelates vs multidentate bipyridine complexes of Eu³⁺-ions

2.1 Remarks on the synthesis of the polypyridine macro(bi)cyclic complexes

Most of the reactions involved in the seven-step synthesis of the cryptand ligand 9 (Figure 2.1) introduce no crucial problems. However, the synthetic procedure is laborious and by no means simple, especially the several coupling and cyclization steps. It needs to be noted that this seven-step synthesis in itself is far from ideal producing large amounts of the end products. Most of the reaction steps proceed with yields well below 100% (usually 50-70%). Assuming yields of 50% each step means after seven steps an overall yield of only < 1%. This is a large drawback of using these bipyridine cryptates. The complexation reactions usually proceeded readily.
Figure 2.1  Synthesis of the bipyridine macrocycles
2.2 Remarks on the synthesis of the $\beta$-diketonate complexes

$\beta$-Diketonates form complexes with lanthanides readily and initially no major difficulties in producing $\text{Eu(hfa)}_3$ and $\text{Eu(hfa)}_3(\text{TOPO})_2$ (Figure 2.2) were encountered. The former can be easily obtained by equilibrating a solution of the ligand in ether with a solution of the europium salt (either the nitrate or the chloride) in water.

\[
\text{Eu(hfa)}_3, 2\, \text{H}_2\text{O} \quad (10)
\]

\[
\text{Eu(hfa)}_3(\text{TOPO})_2 \quad (11)
\]

\[
\text{Eu(hfa)}_3(\text{PIPO})_2 \quad (12)
\]

**Figure 2.2** Complexes of tris(1,5-hexafluoro-2,4-butanedionate) europium (III) [$\text{Eu(hfa)}_3$], tris(1,5-hexafluoro-2,4-butanedionate) bis(trioctylphosphine oxide) europium (III) [$\text{Eu(hfa)}_3(\text{TOPO})_2$] and tris(1,5-hexafluoro-2,4-butanedionate) bis(tripiperidinophosphine oxide) europium (III) [$\text{Eu(hfa)}_3(\text{PIPO})_2$].

$\text{Eu(hfa)}_3(\text{TOPO})_2$ was produced as described by Halverson: again an equilibration of an ethereal solution containing the ligands and an aqueous solution containing the salt. Some of our observations led us to believe that $\text{Eu(hfa)}_3(\text{TOPO})_2$ may not be stable for extended periods of time due to elimination of hfa. Elemental analysis of a sample which took place several months after synthesis indicated that the hfa content of the...
product was well below the expected. The results best fitted a ratio of Eu:hfa:TOPO = 1:1:3 (NMR showed a hfa : TOPO ratio of 1 : 2.5). It is not clear to us by what mechanism hfa elimination can take place in the absence of free protons so we have to assume that some source of protons (probably moisture in the air) plays a role. Provided that this process takes place, the removal can be explained by the low boiling point (57°C) of Hhfa under atmospheric pressure. Thus, the ligand can easily be ‘distilled’ from the mixture at normal drying conditions. This is an unexpected drawback as chelating ligands usually bind very strongly. However, lanthanides are notorious for their poor binding capabilities caused by their weak interaction with their environment, as has been previously described. The presence of a base like TOPO near the metal center, enhancing its electron density and thus reducing its binding capacity will only make this problem more severe. Eu(hfa)$_3$(TOPO)$_2$ seemed to be stable for longer periods when stored as a solution in ether. The PIPO-based complex appeared to be not stable at all; strong yellowing of initially white crystals and loss of red fluorescence was observed over time.

2.3 UV-Vis absorption spectra of bipyridine Eu-complexes and $\beta$-diketonate Eu-chelates

The resulting complexes were analyzed for their absorption and fluorescence characteristics. Examination of the UV-Vis absorption spectra provides important information. Firstly, it is clearly shown for both the polypyridine and the $\beta$-diketonate complexes that the metal is indeed bound by the ligand because complexation causes a large shift in the ligand absorption peaks. In the polypyridine complexes, for example, the bipyridine absorption (288 nm in the free ligand) undergoes an appreciable red shift when the cation is bound through the bipyridine nitrogen atoms. The extent of this red shift may well be related to the extent of interaction between the bipyridine units and the cation and hence to the ease of energy transfer form ligand to cation. The bipyridine absorption is shifted to 303 nm for the cryptate (9) and to 302 nm in the case of the macrocycle (8) complex.
From the UV/Vis absorption spectra, we can measure directly the absorption capability of the complexes as expressed in the molar extinction coefficient $\varepsilon$. All complexes exhibit greatly enhanced absorption capacity when compared to the absorption of the free europium ion. As is shown in Table 2.1, the intensity of the ligand-centered absorption bands exceeds that of the strongest Eu$^{3+}$ f-f band at 395 nm by a factor $10^4$ – $10^5$. The cryptate Eu⊂9 was the most strongly absorbing complex of the ones tested. As expected, the absorption of the macrocycle complex Eu⊂8 is markedly lower because the ligand contains only two bipyridine arms (chromophores) instead of three. Indeed, the molar extinction coefficient is about 70% of the one found for the cryptate. The $\beta$-diketonate complexes absorb UV-radiation less strongly. The molar extinction coefficients of the hfa-based compounds are still quite high and still much higher than those of the free europium ion. The observation that Eu(hfa)$_3$(TOPO)$_2$ has a higher molar extinction coefficient than Eu(hfa)$_3$ can be attributed to the fact that apparently, trioctylphosphine oxide also absorbs radiation in this region. However, as TOPO is not capable of energy transfer to the cation$^{19}$, the absorption by this synergic ligand will not lead to europium fluorescence emission at 613 nm and is thus in essence a waste of pump energy. Therefore, the effective absorption efficiency of both compounds can be thought of as almost the same because both contain three hfa-chelate units that are responsible for energy transfer fluorescence.

### 2.4 Fluorescence excitation and emission spectra

The bipyridine-based compounds exhibit strong fluorescence even when simply irradiated in the solid state by a normal UV-lamp. The same holds for Eu(hfa)$_3$(TOPO)$_2$, which is an oil that even luminesces slightly in daylight, of which the UV radiation intensity is much lower than that of a UV-lamp. This reflects that there is sufficient shielding and furthermore the high bulkiness of the sheath prevents ion-ion interactions. Eu(hfa)$_3$, on the
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Table 2.1  
Absorption data of several europium complexes [a].

<table>
<thead>
<tr>
<th>Compound</th>
<th>$\lambda_{\text{max}}$ [b] (nm)</th>
<th>$\varepsilon (\lambda_{\text{max}})$ (M$^{-1}$cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Eu(NO$_3$)$_3$·5H$_2$O</td>
<td>395 (f-f)</td>
<td>1.3</td>
</tr>
<tr>
<td>EuCl$_3$·6H$_2$O</td>
<td>395 (f-f)</td>
<td>1.4</td>
</tr>
<tr>
<td>Eu(hfa)$_3$·2H$_2$O[c]</td>
<td>305 (LC)</td>
<td>7.02 x 10$^3$</td>
</tr>
<tr>
<td>Eu(hfa)$_3$(TOPO)$_2$</td>
<td>303 (LC)</td>
<td>1.91 x 10$^4$</td>
</tr>
<tr>
<td>Eu⊂9(NO$_3$)$_3$</td>
<td>303 (LC)</td>
<td>2.87 x 10$^5$</td>
</tr>
<tr>
<td>Eu⊂8.Cl$_3$</td>
<td>302 (LC)</td>
<td>2.00 x 10$^5$</td>
</tr>
</tbody>
</table>

[a] in methanol at 300 K. [b] f-f: metal-centered absorption band, LC: ligand-centered absorption band. [c] hydrated form is expected to form quickly in this solvent.

Other hand, only luminesces in the dehydrated form which can be obtained by drying the compound under vacuum.

Inspection and comparison of the excitation spectra indicate that energy transfer from the excited ligand to the metal ion does take place as expected. The emitting metal ion state is populated through irradiation in the ligand absorption band. The excitation spectra show that this is a much more efficient way of populating the europium excited state than by direct excitation at 395 nm.

Further examination of the excitation spectra, however, yields an unexpected feature in the fact that for all complexes the maxima in the excitation spectra are considerably displaced relative to those of the UV-absorption spectra, as is illustrated for Eu(hfa)$_3$(TOPO)$_2$ in Figure 2.3. As is shown, the absorbance is very small in the wavelength range for which fluorescence is maximal. The unexpected characteristic can be explained to be a solvent effect, because in benzene solution the wavelength of maximum excitation coincided nicely with the absorption maximum (Figure 2.3).
Figure 2.3  Solvent effect on the absorption and excitation ($\lambda_{em} = 613$ nm) spectra of the Eu(hfa)$_3$(TOPO)$_2$ complex. A: spectra from solutions in methanol; B: spectra from solutions in benzene.
An evident feature, which occurs for all the complexes, is the absence of overlap between the absorption and fluorescence peaks, indicating that self-absorption of the complex is of no consequence at a signal beam wavelength of 613 nm (Figure 2.4). This property will contribute to the efficiency of the light amplifying process.

**Figure 2.4**  *Fluorescence emission (solid line) and excitation (dotted line) spectra of the cryptate complex Eu⊂9 in methanol at 300 K.*

To compare the fluorescence intensity of the different complexes under identical conditions, the area under the emission peak at 613 nm, has been integrated. The concentrations were the same throughout the series. The integrated peak area (i.p.a.) is used as a (rough) measure (saturation effects are not taken into account) for the efficiency of the total fluorescence process, which is a sum of the different steps: absorption, energy transfer and emission. The integrated peak areas of the fluorescence emission at 613 nm for the different complexes are given in Table 2.2.
Table 2.2  Integrated peak areas (i.p.a.) of the 613 nm fluorescence peaks.

<table>
<thead>
<tr>
<th>Compound [a]</th>
<th>λ&lt;sub&gt;ex&lt;/sub&gt; (f-f) [b] (nm)</th>
<th>i.p.a. [c]</th>
<th>λ&lt;sub&gt;ex&lt;/sub&gt; (ET) [b] (nm)</th>
<th>i.p.a. [c]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Eu(NO&lt;sub&gt;3&lt;/sub&gt;)&lt;sub&gt;3&lt;/sub&gt; . 5H&lt;sub&gt;2&lt;/sub&gt;O</td>
<td>395</td>
<td>3.8</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>EuCl&lt;sub&gt;3&lt;/sub&gt; . 6H&lt;sub&gt;2&lt;/sub&gt;O</td>
<td>395</td>
<td>4.6</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Eu(hfa)&lt;sub&gt;3&lt;/sub&gt; . 2H&lt;sub&gt;2&lt;/sub&gt;O (10)</td>
<td>395</td>
<td>9.0</td>
<td>337</td>
<td>1095.6</td>
</tr>
<tr>
<td>Eu(hfa)&lt;sub&gt;3&lt;/sub&gt;(TOPO)&lt;sub&gt;2&lt;/sub&gt; (11)</td>
<td>395</td>
<td>35.8</td>
<td>345</td>
<td>1091.3</td>
</tr>
<tr>
<td>Eu ⊂ 9 . (NO&lt;sub&gt;3&lt;/sub&gt;)&lt;sub&gt;3&lt;/sub&gt;</td>
<td>395</td>
<td>21.6</td>
<td>342</td>
<td>352.6</td>
</tr>
<tr>
<td>Eu ⊂ 8 . Cl&lt;sub&gt;3&lt;/sub&gt;</td>
<td>395</td>
<td>5.1</td>
<td>338</td>
<td>324.4</td>
</tr>
</tbody>
</table>

[a]  in methanol at 300 K, c = 1 mM. [b]  f-f: europium absorption band, ET: energy transfer through absorption in the ligand band (max. λ<sub>ex</sub>) [c]  integration of 613 nm fluorescence peak

2.5  Shielding efficiency

When irradiating the complex directly in the europium f-f band at 395 nm, neither ligand absorption nor energy transfer are of importance to the fluorescence efficiency. The molar extinction coefficient of the europium band is expected to be more or less the same for all complexes since energy transfer does not play a role (small crystal field effects excluded). Thus, only the shielding capacity of the ligand will influence the i.p.a. of the different complexes. The results, which can be found in the third column of Table 2.2, show that all complexes do more or less shield the cation as their i.p.a.’s are all larger than those of the free salts. Especially the cryptate complex and Eu(hfa)<sub>3</sub>(TOPO)<sub>2</sub> are good shielders. The shielding capability of the cryptate 9 is undoubtedly much higher than that of the macrocycle 8. The latter will probably present an incomplete coordination sphere to the cation, leaving a number of sites available for a quenching agent to approach the cation. Indeed, the performance of the macrocycle is only marginally better than that of the unshielded salts.
2.6 Effects of energy transfer on the fluorescence intensity

When the complexes are irradiated in the ligand absorption band, the outcome of the peak integration is quite different. Comparison of the i.p.a.’s of Eu(hfa)$_3$ and Eu(hfa)$_3$(TOPO)$_2$, for example, shows that these are now more or less the same. As argued above, the shielding in the latter complex is by far the best while both compounds exhibit about the same hfa-based absorption capability. The only explanation for these results is, therefore, a dramatic difference in the ease of energy transfer between the two complexes in favor of Eu(hfa)$_3$. The presence of TOPO in the complex does not only have the consequence of increasing the shielding, but also a second, negative, effect. The P=O-Eu bond has an electron-donating character toward the europium ion. This lessens the ion’s capacity of accommodating extra electron density and it hence also decreases the Eu-hfa chelate bond strength. This may very well result in a greater Eu-hfa distance and a loss of energy transfer efficacy. Apparently, this loss is so dramatic that it completely counteracts the favorable effect of extra shielding. The same, but less dramatic observation can be made when comparing the i.p.a.’s of the cryptate complex and the macrocyclic complex while irradiating in the ligand absorption band. Again, the performance of the cryptate is not as good as could be expected from the shielding and the higher absorption alone. Apparently, these favorable properties of the cryptate are not enough to counteract fully the negative effect on the i.p.a., which is again ascribed to a poorer energy transfer.

It is too soon to say whether this effect will always occur when the number of ligands is increased. However, it may well be the case, as the presence of additional ligands will always weaken the interaction of the cation with any one of these ligands. In that case, it will be quite necessary to look for very strongly binding ligands, in which the Eu-L bond remains sufficiently strong for reasonable energy transfer.

When comparing the fluorescence i.p.a.’s of the hfa-based and the bipyridine-based complexes, the main difference is found in the fluorescence intensity when irradiating in the ligand absorption band. The fluorescence of the hfa-based complexes is almost
three times as strong as that of the bipyridine complexes. The differences in the absorption characteristics and the shielding capabilities totally fail to account for this. Again, the energy transfer-step is very crucial. The $\beta$-diketonate-Eu chelate bond is known to be strong and appears here to be stronger than the Eu-bipyridine bond, giving much better energy transfer. Such an influence of the metal ion-ligand bond distance on energy transfer efficiency has also been observed by Balzani and coworkers. They have studied, extensively, many polybipyridine complexes with europium and terbium. Their and our observations are consistent with the theory of Förster and Dexter. This theory predicts that the probability of energy transfer scales to $1/R^6$, with $R$ being the distance between the sensitizer and the acceptor (the metal ion in this case). Because a forbidden electronic transition in the lanthanide metal ion is involved, the dipole-dipole interaction between the metal ion and the ligand is weak. And thus, the energy transfer efficiency is sensitive to bond length in lanthanide-sensitizer complexes.

Generally, energy transfer takes place from the lowest triplet excited state of the sensitizer to the nearest energy level of the rare earth metal ion. For europium this is the $5D_1$ level. The lowest triplet state energy of the hfa-ligand is 22.000 cm$^{-1}$ and that of bipyridine-ligands about 23.000 cm$^{-1}$. The $5D_1$ energy level of Eu$^{3+}$ is found at around 18.000 cm$^{-1}$. Therefore, the excitation energy transfer between the lowest triplet state energy level of the hfa-ligand and the $5D_1$ level of Eu$^{3+}$ is expected to be more efficient due to the smaller energy gap.

### 2.7 Solubility of the complexes in organic solvents

The solubility of the complexes in organic solvents roughly increases in the order: Eu(NO$_3$)$_3$ / EuCl$_3$ < Eu-cryptate complex < Eu-macrocyclic complex < Eu(hfa)$_3$ << Eu(hfa)$_3$(TOPO)$_2$. It is therefore not surprising that the cryptate Eu⊂9 was in the past found to be of use especially in aqueous environment in which it dissolves well, where the shielding of the complex is very important. Lehn and co-workers found excellent absorption characteristics in conjunction with reasonable energy transfer and efficient shielding and argued that this complex was able to convert about 1 % of the incident
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UV-photons into emitted visible photons, even in diluted aqueous solution. For our purpose, this compound has one major drawback: it is only soluble in polar solvents such as water, methanol and, to a lesser extent, chloroform. The solubility in polymers will be too low for our purpose. In a way, complexes based on the macrocyclic polypyridine 8 are much more versatile. The open coordination sites on the cation can be used to introduce ligands with a higher solubility. Moreover, the ligand has two easily functionalizable N-H bonds, which can be used for introducing organic groups or even for covalent bonding of the ligand into a polymer backbone. This will improve solubility greatly. The macrocycle is a less efficient shielder than the cryptand, but this will be of much less consequence in an organic environment where water is much less abundant.

The effect of the presence of TOPO in a complex on the solubility is dramatic. The three large alkyl tails on the synergic ligand completely alter the character of the complex, making it very soluble in organic solvents and polymers.

2.8 Eu(hfa)$_3$(TOPO)$_2$ in a densely crosslinked polymer matrix

The final step in making an optical fiber amplifier involves dissolving the complexes in a polymer matrix. A hexamethylenediisocyanate-based polyisocyanurate network polymer turned out to be unsuitable for the Eu(hfa)$_3$(TOPO)$_2$ complex. The reason for that lies in the fact that the thermoset polymer needs to be crosslinked after the complex has been added. The catalyst used in the crosslinking reaction interacts with the complex, destroying both. This problem was encountered for both catalysts: $N,N',N''$-tris(dimethylaminopropyl)hexahydrotriazone and stannous (II) bis(2-ethylhexanoate). The amine groups on the former probably displace some or all of the ligands on the europium complex, the latter perhaps induces some kind of ligand exchange. The effect was the same in both cases; fluorescence was lost, the mixture turned brightly yellow very quickly and it failed to solidify.

The behaviour of the complex in hydrosilylation-curable poly(phenylmethylvinylhydro- siloxane)$^{34,35}$ has also been tested. Fluorescence measurements showed that the complex is completely stable in the siloxane
Development of a Polymer Optical Fiber Amplifier

prepolymer, the same species being responsible for the luminescence in polymer and organic solvent. However, the prepolymer have to be cured at high temperature (150°C) at which the complex is not stable. When curing a fiber doped with the complex, we found that the material yellowed over time while almost all luminescent activity was lost.

A serious side effect of the above-mentioned polymers being little transparent for UV-radiation is the fact that the pump radiation intended to excite the europium complexes is also absorbed by the matrix. This will also be the case for polymers such as PMMA, PS and PC. This is a hazard, resulting in both a loss of pump energy and the danger of destroying the polymer matrix with the pump laser. It may therefore be well understood that complexes that absorb at higher wavelengths, well above 400 nm, are preferable. This may be achieved by extending the conjugation length of the ligand, thus increasing its absorption wavelength and using fundamental transitions of europium located at higher wavelengths (e.g. 416 nm or 562 nm). If this is possible without lowering the complexating power of the ligand too far for complexation (due to a strong delocalisation of electrons) and an efficient energy transfer to take place, remains to be seen.

Another approach is based on increasing the energy harvesting capacity of the ligand system, so as to lower the threshold pump power necessary for stimulated emission. This approach seems much better realizable and examples will be given below.

3) Progress in developing efficient luminescent Eu³⁺-complexes based on β-diketonate chelates with high absorption and emission cross-sections.

The β-diketonate-lanthanide chelates showing an efficient energy transfer are relatively simple to prepare and can be well soluble in organic media. A further optimization has been put through by synthesizing new β-diketonates, modified with a side group possessing a large π-conjugated system. After complexation with terpositive lanthanide ions, such diketonate-lanthanide chelates have a higher extinction coefficient, a larger fluorescence intensity and higher wavelengths of excitation. As the large π-conjugated system, 2-(t-butylphenyl)-5-(4-biphenylyl)-1,3,4-oxadiazole (PBD) has been chosen.
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PBD is a strongly fluorescent and well-known laser dye. Moreover, PBD is an electron transporter,\textsuperscript{37} which makes PBD-lanthanide complexes interesting compounds for light-emitting devices. The PBD-moiety enlarges the absorption capacity of the diketonate-lanthanide complex, significantly, with respect to the hexafluoro-substituted diketonates. Much more optical energy can be harvested from the pump source. Furthermore, the stability of the diketonate complex increases as ligand evaporation, observed for Eu(hfa)\textsubscript{3}(TOPO)\textsubscript{2} complexes, will not occur. Based on PBD, five complex systems have been prepared (Figure 3.1). The synthesis route is depicted in Figure 3.2.

Starting from commercially available \textit{t}-butyl-PBD, a Friedel-Crafts acylation was applied to obtain the acetylated PBD moiety. By using the Claisen condensation of the acetylated PBD and ethyl trifluoroacetate the diketone is formed. The europium complexes have been made by first making the sodium salt of the diketonate and thereafter a substitution of the sodium by europium, usually with a EuCl\textsubscript{3}-salt in ethanol.\textsuperscript{38}
Figure 3.1  Europium chelates based on PBD-functionalized diketonate.
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The diketonate has been functionalized with one PBD substituent and a trifluoromethyl group. The latter substituent has been chosen to minimize C-H quenching effects, for its hydrophobic nature and for electron-withdrawing effects.\textsuperscript{19, 22}

![Chemical structure](image)

**Figure 3.2** *Synthesis route for PBD-functionalized β-diketones.*

3.1 Photophysical properties of PBD-based complexes

The photophysical properties of the complexes are given in Tables 3.1 and 3.2. Figure 3.4 shows typical absorption, excitation and photoluminescence spectra.

Upon complexation, the PBD-functionalized diketonate does not show a red shift in the absorption spectrum (Figure 3.3). The absorption characteristics are fully determined by the large PBD unit. Any electronic influences due to complexation with europium are not reflected in differences of the ligands’ energy states.
### Table 3.1 Absorption properties of PBD-diketonate europium (III) complexes [a].

<table>
<thead>
<tr>
<th>Compound</th>
<th>c</th>
<th>$\lambda_{\text{max}}$</th>
<th>$\varepsilon(\lambda_{\text{max}})$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Eu(PBD)$_3$</td>
<td>1.53</td>
<td>353</td>
<td>$8.2 \times 10^4$</td>
</tr>
<tr>
<td>Eu(PBD)$_4$</td>
<td>1.52</td>
<td>351</td>
<td>$9.1 \times 10^4$</td>
</tr>
<tr>
<td>Eu(PBD)$_3$(TOPO)$_2$</td>
<td>0.68</td>
<td>351</td>
<td>$1.0 \times 10^5$</td>
</tr>
<tr>
<td>Eu(PBD)$_3$(phen)</td>
<td>1.53</td>
<td>348</td>
<td>$1.1 \times 10^5$</td>
</tr>
<tr>
<td>Eu(PBD)$_3$(bathophen)</td>
<td>0.76</td>
<td>347</td>
<td>$1.2 \times 10^5$</td>
</tr>
<tr>
<td>Eu(hfa)$_3$(TOPO)$_2$</td>
<td>9.61</td>
<td>312</td>
<td>$1.0 \times 10^4$</td>
</tr>
<tr>
<td>Eu(TTA)$_3$ [b]</td>
<td>3.58</td>
<td>339</td>
<td>$4.6 \times 10^4$</td>
</tr>
</tbody>
</table>

[a] in benzene at 300 K. [b] Eu(TTA)$_3$ has been measured for reference.

**Figure 3.3** Absorption spectra of free and Eu-bound PBD-ligand.
All PBD-based complexes possess high molar extinction coefficients. The absorption coefficient increases upon increasing number of absorbing aromatic groups. Eu(PBD)$_4$ has a higher $\varepsilon$ than Eu(PBD)$_3$ due to an extra PBD-ligand. The higher $\varepsilon$ of the Eu(PBD)$_3$(TOPO)$_2$ complex in relation to the Eu(PBD)$_3$ without the synergic ligands can be attributed to the absorption of the synergic phosphine oxide group. As already explained in section 2.3 this will not contribute to the energy transfer. Addition of phenanthroline and bathophenanthroline, which both contribute to energy transfer, significantly increase the absorption coefficient of the europium complexes. As the latter possesses a more extended $\pi$-system, the $\varepsilon$ is higher.

One more comment can be made about the absorption characteristics. The absorption maximum shifts slightly to the blue starting from Eu(PBD)$_3$ going to Eu(PBD)$_3$(bathophen). The more electrons are available for complexation, the weaker each individual ligand-Eu interaction becomes.

### Table 3.2 Integrated peak areas (i.p.a.) of the 613 nm fluorescence peaks of PBD-diketonate europium complexes [a].

<table>
<thead>
<tr>
<th>Compound</th>
<th>$\lambda_{ex}$ (f-f) (nm)</th>
<th>i.p.a.</th>
<th>$\lambda_{ex}$ (ET) (nm)</th>
<th>i.p.a.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Eu(PBD)$_3$</td>
<td>(13) 395</td>
<td>17.5</td>
<td>350</td>
<td>1074</td>
</tr>
<tr>
<td>Eu(PBD)$_4$</td>
<td>(16) 395</td>
<td>25</td>
<td>340</td>
<td>3425</td>
</tr>
<tr>
<td>Eu(PBD)$_3$(TOPO)$_2$</td>
<td>(14) 395</td>
<td>97</td>
<td>350</td>
<td>14985</td>
</tr>
<tr>
<td>Eu(PBD)$_3$(phen)</td>
<td>(15) 395</td>
<td>387</td>
<td>346.5</td>
<td>44366</td>
</tr>
<tr>
<td>Eu(PBD)$_3$(bathophen)</td>
<td>(17) 395</td>
<td>224</td>
<td>346.5</td>
<td>46000</td>
</tr>
<tr>
<td>Eu(hfa)$_3$(TOPO)$_2$</td>
<td>(11) 395</td>
<td>1.7</td>
<td>312</td>
<td>2648</td>
</tr>
<tr>
<td>Eu(TTA)$_3$ [b]</td>
<td>395</td>
<td>12.8</td>
<td>340</td>
<td>3469</td>
</tr>
</tbody>
</table>

[a] in benzene at 300 K and the concentration normalized to 1 $\mu$M. [b] Eu(TTA)$_3$ has been measured for reference.

The integrated peak area of the fluorescence at 613 nm of the PBD-diketonate complexes are given in Table 3.2. For reference, the i.p.a.’s of Eu(hfa)$_3$(TOPO)$_2$ and Eu(TTA)$_3$ are given as well. Two notes have to be made here. Firstly, an i.p.a.-value
for the Eu(hfa)$_3$(TOPO)$_2$ chelate has been given in Table 2.2 of section 2.4, as well, however for a concentration of 1 mM and in methanol as the solvent, both accounting for the difference. Secondly, as the PBD-derivatized $\beta$-diketonates absorb significantly at 395 nm the comparison to the complexes from Table 2.2 and 2.3 as also with the complex Eu(TTA)$_3$ is not valid, if the i.p.a-values obtained by excitation at 395 nm are considered. Only a relative comparison between de PBD-complexes is allowed to be made.

It cannot be concluded from the i.p.a. values, obtained by directly exciting the europium in its fundamental absorption band (395 nm), that an extra PBD-diketonate ligand (4 instead of 3) improves the shielding, because the ligands absorb at 395 nm as well. And, as a matter of fact, four absorbing ligands would increase the fluorescence intensity anyhow, as we already have seen for the bipyridine complexes. Introducing two TOPO groups as synergic ligands does improve the shielding, dramatically. By using phenanthroline and bathophenanthroline, the effectiveness of the shielding increases spectacularly relative to the other complexes. The i.p.a. of the chelate with phenanthroline supersedes that of the one with bathophenanthroline due to a slightly weaker interaction with europium of the latter.

Using PBD-diketonate ligands alone does not increase the i.p.a. of the fluorescence excited at the LC-band (excitation maximum) relative to Eu(hfa)$_3$(TOPO)$_2$ and Eu(TTA)$_3$. The synergic ligands enormously improve the fluorescence intensity. For TOPO this is due to the shielding effect. For phenanthroline and bathophenanthroline this is due to both the shielding effect and the contribution to energy transfer. As the absorption coefficient of the complex with bathophenanthroline as synergic ligand is higher, the i.p.a. is higher as well. The complexes all show an efficient intramolecular energy transfer.
Table 3.3 *The fluorescence properties of PBD-diketonate europium complexes [a].*

<table>
<thead>
<tr>
<th>Compound</th>
<th>$c$ [µmol/L]</th>
<th>$\lambda_{\text{max, ex}}$ [nm]</th>
<th>$\tau$ [ms]</th>
<th>$\Phi_{\text{Fl}}$ [c]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Eu(PBD)$_3$</td>
<td>1.53</td>
<td>350</td>
<td>0.19</td>
<td>0.04</td>
</tr>
<tr>
<td>Eu(PBD)$_4$</td>
<td>1.52</td>
<td>340</td>
<td>0.31</td>
<td>0.11</td>
</tr>
<tr>
<td>Eu(PBD)$_3$(TOPO)$_2$</td>
<td>0.68</td>
<td>350</td>
<td>0.34</td>
<td>0.44</td>
</tr>
<tr>
<td>Eu(PBD)$_3$(phen)</td>
<td>1.53</td>
<td>346.5</td>
<td>0.51</td>
<td>0.53</td>
</tr>
<tr>
<td>Eu(PBD)$_3$(bathophen)</td>
<td>0.76</td>
<td>346.5</td>
<td>0.51</td>
<td>0.49</td>
</tr>
<tr>
<td>Eu(hfa)$_3$(TOPO)$_2$</td>
<td>9.61</td>
<td>312</td>
<td>0.71</td>
<td>0.77</td>
</tr>
<tr>
<td>Eu(TTA)$_3$ [d]</td>
<td>3.58</td>
<td>340</td>
<td>0.29</td>
<td>0.22</td>
</tr>
</tbody>
</table>

[a] in benzene (degassed) at 300 K. [b] $\tau$ is the decay time of fluorescence at 613 nm. [c] $\Phi_{\text{Fl}}$ is the fluorescence quantum efficiency. [d] Eu(TTA)$_3$ has been measured for reference.

Table 3.3 shows the quantum efficiency and the decay times of the PBD-diketonate chelates in degassed benzene. The quantum efficiency increases in the same line as the i.p.a.’s (LC) throughout the series, being highest for the phenanthroline and bathophenanthroline chelates. Using a synergic agent is very important as the Eu(PBD)$_3$(TOPO)$_2$ complex shows a high quantum yield, as well. The very high quantum yield of Eu(hfa)$_3$(TOPO)$_2$ could not be explained. Certainly not, if effects such as ligand evaporation is taken into account. Generally, improving the shielding results in longer decay times of fluorescence. Decay times of 0.5 ms are in such a range that amplification phenomena in rare earth-doped polymer optical fibers may occur.\textsuperscript{5}
3.2 Cascade energy transfer

By spin-coating, thin films (~ 350 nm) of PBD, Eu(PBD)$_4$ and a 90/10 blend of PBD and Eu(PBD)$_4$, have been prepared. Figure 3.6 shows the photophysical properties of the three systems. The blend demonstrates a cascade energy transfer mechanism in which intermolecular energy transfer coincides with intramolecular energy transfer. Upon chemical modification of PBD, the UV-absorption has shifted to higher wavelength. The fluorescence spectrum of PBD overlaps the absorption spectrum of the PBD-Eu$^{3+}$ chelate. This allows for an efficient intermolecular energy transfer. The PBD-matrix functions as an energy harvesting source. The large amount of absorbed energy is transferred to the PBD-chelate, which itself transfers the energy intramolecularly to the chelated europium ion. Subsequently, europium emits light of 613 nm ($^5D_0 \rightarrow ^7F_2$).

Co-doping with an absorbing species capable of intermolecular energy transfer to the ligand system of the lanthanide complex contributes to the total absorption capability.
and subsequently helps to enlarge the number of excited europium ions. A higher density of excited europium ions will result in a higher gain coefficient. Furthermore, the high energy harvesting capacity results in a low pump power threshold for laser generation. A similar observation has been made for an organic dye system, for which PBD was also the host material.\textsuperscript{39} Upon doping with dyes, for which the absorption overlaps with the emission band of another dye, resonance energy transfer results. In that way cascade energy transfer was demonstrated for a system with 4 dye molecules. The system showed spectral narrowing and laser generation with low pump power thresholds.

This concept of cascade energy transfer is highly promising for developing polymer optical fiber amplifiers and deserves further exploration.

\textbf{Figure 3.6} Demonstration of cascade energy transfer in the solid state of Eu-PBD complex in a PBD-matrix.
3.3 The PBD-complexes in polymers

$\beta$-Diketonate complexes are not very stable against high temperatures, which is a problem when processing thermoplastic polymers or when curing thermosets. The complexes $\text{Eu(PBD)}_3(\text{phen})$ and $\text{Eu(PBD)}_3(\text{bathophen})$ were found to be incompatible with both a siloxane rubber-like polymer (Nusil, MED6820: a poly(phenylmethylsiloxane) system) and poly(lauryl methacrylate) (PLMA). The complexes needed to be modified with solubility-enhancing alkyl tails. The $\text{Eu(PBD)}_3(\text{TOPO})_2$ complex was incompatible with the silicon polymer, as well. However, in PLMA it did give a homogeneous mixture (~ 2 wt. %). As the quantum yield and absorption coefficient are high, this complex would be a very promising candidate for POFAs. PLMA is a viscous liquid at room temperature, which makes it difficult to fabricate an optical fiber from it. Also high temperatures are necessary for processing, interfering with complex stability.

An active POF has been prepared, successfully, by dissolving 1 wt. % of $\text{Eu(PBD)}_3(\text{TOPO})_2$ in HDI. The HDI polytrimerized into a densely crosslinked poly(isocyanurate) at ambient temperature ($30^\circ\text{C}$). The crosslinking process took place in a FEP-tubing. The resulting optical fiber showed strong red luminescence. A very bright pulse of red light was generated by side pumping using 364 nm UV-light. Unfortunately, it was not possible to dissolve more than 1 wt. % without facing phase separation phenomena. The complexes $\text{Eu(PBD)}_3$, $\text{Eu(PBD)}_3(\text{phen})$ and $\text{Eu(PBD)}_3(\text{bathophen})$ did not dissolve to a significant extent (less than 1 wt. %). Clearly the molecular structure of PBD should be modified with alkyl chains to enlarge solubility in organic media. Due to its long alkyl chains, TOPO already significantly improved the solubility of the PBD-complex.
3.4 Photophysical properties of Eu(PBD)$_3$(TOPO)$_2$ in solid state (densely crosslinked polyisocyanurate)

Figure 3.7 presents the excitation and emission spectrum of Eu(PBD)$_3$(TOPO)$_2$ in HDI-based polyisocyanurate. The spectra are entirely similar to spectra obtained from solution (benzene). The complex has a long living meta-stable energy state in the crosslinked polymer matrix (Figure 3.8). The lifetime (0.66 ms) is almost twice as large as that measured in solution (0.34 ms). This proves the validity of using densely crosslinked polymers as the host matrix. Through the high degree of crosslinking in such a polymer host, the mobility of the chains is severely restricted. This reduces the quenching fluorescence by minimizing the number of collisions of the polymer chains with the lanthanide complex. At the same time the complex is fully captured in the meshes of the network resulting in a stabilization of the complex geometry. Complex debonding at ambient and also at higher temperatures is less likely to occur in such a situation.

![Figure 3.7](image)

**Figure 3.7** Emission and excitation spectra of Eu(PBD)$_3$(TOPO)$_2$ in polytrimerized hexamethylenediisocyanate.
To fabricate a polymer optical fiber amplifier with rare earth ions as the active component, among others two fluorophore properties are very important. Firstly, the lifetime of fluorescence should be reasonably long. As shown above this is the case for the system under investigation. Secondly, the intensity of (stimulated) emission should be high. The latter is expressed as an emission cross section, which number should be known to estimate the gain characteristics.

The emission cross section can be determined from the spectral shape of the fluorescence, $I_e(\lambda)$ (Figure 3.7), and the spontaneous emission rate, $A_e = 1 / \tau$ (Figure 3.8). An approximate expression for the emission cross section, $\sigma_e(\lambda)$, is given by the Fuchtbauer-Ladenburg relation:

$$\sigma_e(\lambda) = A_e \lambda^4 / 8 \pi^2 n^2 c \Delta \lambda,$$

where $\Delta \lambda = \int_{\text{band}} I_e(\lambda) \, d\lambda / I_e^{\text{peak}}$. 

\[ \tau = 0.66 \text{ ms} \]
with $\lambda$ is the mean wavelength of the transition, $n$ is the refractive index of the polymer matrix and $c$ is the speed of light in vacuum. $I_{e}^{\text{peak}}$ is the peak fluorescence intensity of the band.

For the Eu(PBD)$_3$(TOPO)$_2$ complex in polytrimerized HDI, the emission cross section of the $^5D_0 \rightarrow ^7F_2$ transition of europium, was determined to be $3.2 \times 10^{-21}$ cm$^2$. The value is of the same order of magnitude as that found for erbium-doped and samarium-doped silica glasses that have been used to make fiber amplifiers and lasers.$^{3,40}$ To our knowledge, such an $\sigma_e$-value for fluorescent rare earth ions in a polymer matrix is found and reported for the first time. It demonstrates the feasibility of using polymers and fluorescent rare earth ions for optical fiber amplifiers. Comparative $\sigma_e$-values have been reported by Koeppen et al. for an organic samarium complex.$^5$ However, the reported values were determined in deuterated acetone. It is well known that the low-energy vibrations of C-D bonds result in a reduced quenching of the rare earth ions' fluorescence.

An evaluation of the single-pass gain characteristics led to the conclusion that the number density of molecules is such that about 20 meters of fiber would be required to measure any significant gain. The gain exponentially scales to $\sigma_e * N * L$, being the emission cross section, the ion number density and the fiber length, respectively.

Although all photophysical properties ($\tau$ and $\sigma_e$) are quite optimal for producing gain in the optical fiber, the number density of europium ions, $N$, was only $2 \times 10^{18}$ cm$^{-3}$. The complexes are very heavy and contain only a small percentage of europium. To enlarge the number density to preferably $10^{20}$ Eu$^{3+}$ cm$^{-3}$, the solubility should be increased. Functionalizing the PBD moiety with solubility-enhancing alkyl chains is a solution for this problem. The utilization of the cascade energy transfer principle is another.
CONCLUSIONS

Europium complexes have been prepared with sensitizing ligands. The complexes showed efficient intramolecular energy transfer and strong 613 nm luminescence. For the efficiency of the energy transfer process, the bond distance of the europium ion and sensitizing ligand appeared to be highly important. Higher absorption coefficients resulted in significantly higher fluorescence intensities. Crown ether and macrobipyridine complexes were found to be not very suitable, because of low solubility, high hygroscopicity and, in case of the bipyridine cryptates, the laborious preparation route. $\beta$-diketonates are relatively simple to prepare, are versatile in substituents, give good complexation with lanthanide ions and show highly efficient energy transfer. The fluorescence intensity of diketonate europium chelates strongly improved upon applying synergic ligands. Trioclylphosphine oxide, phenanthroline and bathophenanthroline are found to be useful synergic ligands. Trioclylphosphine oxide not only improved fluorescence intensity but strongly improved the solubility, as well. Phenanthroline and bathophenanthroline are very effective shielding ligands, and moreover, contribute significantly to the complex absorption capacity and show effective energy transfer to the europium ion. They do not contribute to the complex solubility in organic media, however.

Functionalization of the diketonate with 2-($t$-butylphenyl)-5-(4-biphenylyl)-1,3,4-oxadiazole (PBD), a large $\pi$-conjugated system, significantly increased the absorption coefficient.

The chelate Eu(PBD)$_3$(TOPO)$_2$ was soluble in hexamethylenediisocyanate up to 1 wt. %. Polytrimerization proceeded at ambient temperature without phase separation of the chelate. The polymer optical fiber, made thereof, generated bright fluorescent light of 613 nm, when side-pumped by 354 nm UV-light. The lifetime of the fluorescence in the densely crosslinked polymer matrix was almost twice as high as that found in a benzene solution (0.66 ms vs 0.34 ms). This result revealed the importance of having a polymer matrix, preferably densely crosslinked. In connection with that a high value for the emission cross section has been found, being $3.2 \times 10^{-21}$ cm$^2$. Such an value for an rare earth-doped polymer is found and reported for the first time.
Chapter 8

The absorption capacity and thereby the emission cross section and the gain coefficient may be raised further by using the cascade energy transfer concept. The concept of cascade energy transfer has been demonstrated in the solid state for a PBD / Eu(PBD)$_4$ 90/10 blend.

In conclusion, the energy transfer concept is very well applicable for developing *rare earth-doped polymer optical fiber amplifiers*. Main advantages are a strong and efficient luminescence of rare earth ions and a high energy absorption capability and thereby a low pump power threshold for *light amplification*. 
REFERENCES AND NOTES

1) Chapter 1 of this thesis and references therein.
Chapter 8

27) Chapter 6 of this thesis.
33) Chapter 2 of this thesis.
34) Chapter 3 of this thesis.