

Synthesis and Spectral Properties of Novel Fluorescent Poly(oxyethylene Phosphate) Tris(β -diketonate) Europium (III) Complexes

S. Stanimirov · A. Vasilev · E. Haupt · I. Petkov ·
T. Deligeorgiev

Received: 17 March 2008 / Accepted: 8 May 2008 / Published online: 4 June 2008
© Springer Science + Business Media, LLC 2008

Abstract Novel poly(oxyethylene phosphate) tris(β -diketonate) europium (III) complexes have been synthesized by an improved procedure using the Atherton–Todd reaction conditions. N-ethyl-diisopropylamine has been used as a mild base and propylene oxide as an acid scavenger in order to obtain poly(oxyethylene phosphate) in yield and purity higher than those achieved by conventional methods. The compounds have been characterized by ^1H , ^{13}C , and ^{31}P NMR and FTIR techniques. Their absorption, fluorescent excitation and emission spectra of chloroform and absolute ethanol solutions have been recorded and studied. The luminescent quantum yields and decay times have been determined and a dependence on the length of the oxyethylene spacer between phosphate groups has been established. The new polymer complexes are water soluble and have increased luminescence decay time in comparison with corresponding ternary complexes.

Keywords Poly(oxyethylene phosphate) · Atherton–Todd · Eu(III) complexes

Introduction

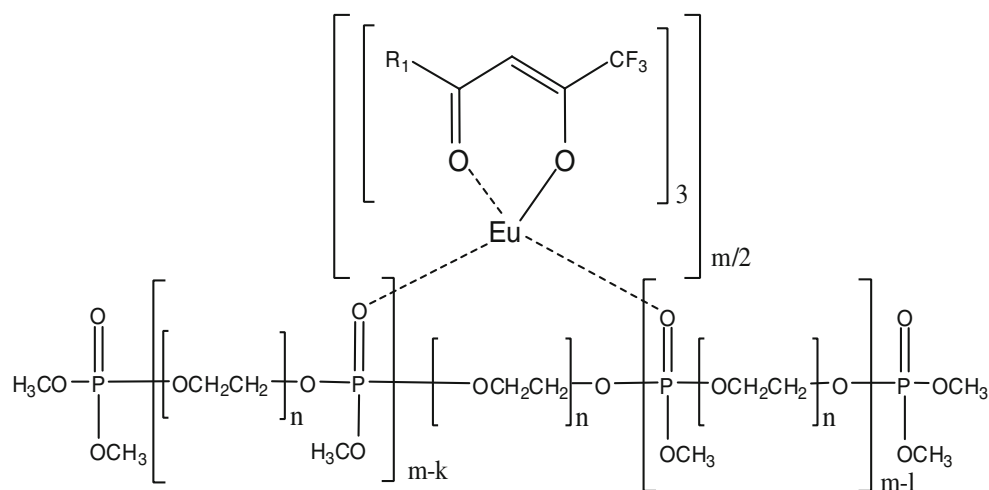
Since 1942, when Weissman observed for the first time their luminescence upon UV irradiation [1], europium (III) β -diketonates have been studied intensively. That is why these compounds have been investigated for various applications—as laser materials [2, 3], for fluorometric determination of lanthanide elements [4, 5], as highly sensitive fluorometric probes for biological molecules [6–8], as paramagnetic probes for biological molecules [9], and as an emissive material in organic light emitting devices (OLEDs) [10–12]. OLEDs are of great interest due to their efficient emission in the visible region and their possible application in new types of flat-panel full-color displays. The materials, used for OLED preparation have to meet a wide range of criteria including product quality, marketing, and manufacture cost. OLEDs are injection type devices, showing low driving voltages of less than 10 V [13, 14]. Rare earth metal complexes could be used as emissive materials in OLEDs as their photoluminescence gives a sharp spectral band. Europium complexes are candidates for sharp red emissive materials in OLEDs [15] due to their light emission at 612 nm assigned to the Eu(III) ion. An intramolecular energy transfer takes place from the triplet of the organic ligand to the $^5\text{D}_1$ and $^5\text{D}_0$ [16] energy levels of the Eu(III) ion. The theoretical internal quantum efficiency of this transfer is very high and depends on the kind of organic ligand used. Having this in mind, the application of novel Eu complexes could improve the quantum efficiency of the red light OLEDs [17].

S. Stanimirov (✉) · I. Petkov
Laboratory of Organic Photochemistry, Faculty of Chemistry,
University of Sofia,
1 James Bourchier Blvd.,
1164 Sofia, Bulgaria
e-mail: sstanimirov@chem.uni-sofia.bg

A. Vasilev · T. Deligeorgiev
Department of Applied Organic Chemistry, Faculty of Chemistry,
University of Sofia,
1164 Sofia, Bulgaria

E. Haupt
Department of Chemistry, Institute of Inorganic and Applied
Chemistry, University of Hamburg,
20146 Hamburg, Germany

Scheme 1 Structure of the complexes. (k and l can vary from 1 to m , and $k+l=m+1$)



The high cytotoxic activity (in vitro) in a panel of human tumor cell lines described recently [18] is another promising application of europium (III) complexes. Poly(oxyethylene phosphonate)s are known as polymers exhibiting extremely low own toxicity [19] and have been used as carriers for biologically active substances [20, 21, 24, 27].

Here we report on the synthesis of a new type of luminescent polymers using europium complexes as starting materials. Poly(oxyethylene phosphonate)s were used as a fourth ligand in Eu β -diketonate complexes. The outstanding spectral properties of the polymer complexes prepared (luminescence efficiency, sharp emissive band, color purity) are determined by the starting Eu(III) complexes. Using such kind of macromolecules the preparation of thin solid films should become easier. In this case the production of emissive layers by costly vacuum decomposition techniques could be replaced by simple spin coating. Bonding Eu(III) complexes to such kind of polymers increases the water solubility of the latter—an advantage for various bio applications [22].

Scheme 1 presents the structures of the compounds synthesized—Eu(III) complexes of different β -diketonates: benzoyltrifluoroacetate (BTA), naphyltrifluoroacetate (NTA), thenoyltrifluoroacetate (TTA) and two kinds of poly(oxyethylene phosphonate)s applied as a fourth neutral ligand. The starting poly(oxyethylene phosphonate)s (POE-

PAT200 and POEPAT400) have the different length of the oxyethylene spacer between two adjacent phosphate groups (Table 1).

Experimental

Materials and synthesis

All initial β -diketonate compounds, $\text{EuCl}_3 \cdot 6\text{H}_2\text{O}$, dimethyl phosphonate, *N*-ethyl-diisopropylamine, carbon tetrachloride, propylene oxide are commercial products (Aldrich) and were used as obtained. Poly(ethylene glycol)s (PEG) 200 and 400—commercial products from Aldrich—were dried before use for 8 h at 100–110 °C by bubbling a stream of dry argon through the liquid and simultaneously application of dynamic vacuum (<1 mmHg) [23, 24].

Synthesis of poly(oxyethylene phosphonate)s (POEPNAT 200 and 400)

POEPNAT200: The transesterification was carried out according to [24–27]. PEG 200 (53.04 g [0.265 mol]) and dimethyl phosphonate (58.37 g [0.530 mol]) were placed into a three-necked flask equipped with a magnetic stirrer,

Table 1 Description of the complexes structures with respect to Scheme 1

Polymer complexes	R1	Numbers	Meters	molEu/g ^a	Synthetic yield (%)
Eu1POEPAT200	–C ₆ H ₅	4	13	7.1×10^{-4}	47
Eu2POEPAT200	–C ₁₀ H ₇	4	13	4.5×10^{-4}	45
Eu3POEPAT200	–C ₄ H ₃ S	4	13	6.2×10^{-4}	41
Eu1POEPAT400	–C ₆ H ₅	8	13	4.8×10^{-4}	48
Eu2POEPAT400	–C ₁₀ H ₇	8	13	5.9×10^{-4}	39
Eu3POEPAT400	–C ₄ H ₃ S	8	13	4.3×10^{-4}	43

^a Mole Eu(III) per gram polymer

thermometer, and a reflux condenser. The process was performed under continuous stirring at 165 °C. The progress of the reaction was monitored by the amount of methanol removed. When 90% of the theoretical amount of methanol was removed a vacuum pump (1 mmHg) was switched on. The polytransesterification was completed in 6 h. POEPNAT200 was obtained as a dense colorless liquid. ^1H NMR (CDCl_3): δ (ppm) 3.64–3.67 (m, $-\text{OCH}_2\text{CH}_2-$), 3.70–3.73 (m, $-\text{POCH}_2\text{CH}_2-$), 3.78 (days, $^3J_{(\text{P}, \text{H})}=12$ Hz, $-\text{POCH}_3$), 4.16–4.30 (m, $-\text{POCH}_2\text{CH}_2-$), 6.88 (days, $^1J_{(\text{P}, \text{H})}=709.1$ Hz, PH end group), 6.96 (days, $^1J_{(\text{P}, \text{H})}=716.4$ Hz, PH repeating units); $^{13}\text{C}\{\text{H}\}$ NMR (CDCl_3): δ (ppm) 64.73 (days, $^2J_{(\text{P}, \text{C})}=5.87$ Hz, $-\text{POCH}_2-$), 70.13–70.23 (m, $-\text{POCH}_2\text{CH}_2-$), 70.53–70.58 (m, $-\text{OCH}_2\text{CH}_2-$); ^{31}P NMR (CDCl_3): δ (ppm) 9.5 (s, P repeating units), 10.18 (s, P end group).

POEPNAT400 was prepared using the same procedure, starting from 58.63 g (0.146 mol) of PEG 400 and 32.24 g (0.293 mol) of dimethyl phosphonate. ^1H NMR (CDCl_3): δ (ppm) 3.65–3.69 (m, $-\text{OCH}_2\text{CH}_2-$), 3.70–3.73 (m, $-\text{POCH}_2\text{CH}_2-$), 3.78 (days, $^3J_{(\text{P}, \text{H})}=12$ Hz, $-\text{POCH}_3$), 4.18–4.27 (m, $-\text{POCH}_2\text{CH}_2-$), 6.88 (days, $^1J_{(\text{P}, \text{H})}=709.1$ Hz, PH end group), 6.95 (days, $^1J_{(\text{P}, \text{H})}=716.5$ Hz, PH repeating units); $^{13}\text{C}\{\text{H}\}$ NMR (CDCl_3): δ (ppm) 64.70 (days, $^2J_{(\text{P}, \text{C})}=6.16$ Hz, $-\text{POCH}_2-$), 70.15 (days, $^5J_{(\text{P}, \text{C})}=5.23$ Hz, $-\text{POCH}_2\text{CH}_2-$), 70.53–70.58 (m, $-\text{OCH}_2\text{CH}_2-$); ^{31}P NMR (CDCl_3): δ (ppm) 9.52 (s, P repeating units), 10.21 (s, P end group).

Synthesis of poly(oxyethylene phosphates) (POEPAT 200 and 400)

POEPAT200: Thirty milliliters of dichloromethane, 14.7 ml of carbon tetrachloride and 8.91 g (0.0386 mol repeating phosphonate units) of POEPNAT400 were placed into a three-necked flask equipped with a magnetic stirrer, thermometer, reflux condenser and a dropping funnel. After that POEPNAT400 was fully dissolved and 4.62 ml of methanol added. Then 6.5 ml of *N*-ethyl-diisopropylamine in 25 ml of dichloromethane were added dropwise under stirring at RT for 30 min. After 3 h 2.4 ml of propylene oxide were added and the reaction mixture was stirred for another hour. POEPAT400 was precipitate by addition of diethyl ether. The product was purified by precipitating its dichloromethane solution in diethyl ether and dried at 30–40 °C under reduced pressure. ^1H NMR (CDCl_3): δ (ppm) 1.30–1.48 (m, $-\text{OCH}_2\text{CH}_3$), 3.54–3.66 (m, $-\text{OCH}_2\text{CH}_3$), 3.59 (days, $J^3=12$ Hz, $\text{CH}_3\text{OP}(\text{O})\text{O}-$), 3.58–3.70 (m, $-\text{CH}_2\text{CH}_2\text{OCH}_2\text{CH}_2-$), 3.65–3.70 (m, $(-\text{CH}_2\text{CH}_2\text{O})_3\text{P}(\text{O})$), 3.68–3.73 (m, $-\text{CH}_2\text{CH}_2\text{OP}(\text{O})(\text{OCH}_3)_2$), 3.78 (days, $J^3=11.2$ Hz, $-\text{CH}_2\text{CH}_2\text{OP}(\text{O})(\text{OCH}_3)_2$), 3.99–4.08 (m, $-\text{CH}_2\text{OP}(\text{O})-$), 4.14–4.23 (m, $-\text{CH}_2\text{OP}(\text{O})(\text{OCH}_3)_2$); $^{13}\text{C}\{\text{H}\}$ NMR (CDCl_3): δ (ppm) 52.9 (s, $-\text{POCH}_3$), 64.5 (s, P

($\text{O})(\text{CH}_2\text{CH}_2-$), 66.4 (s, $-\text{CH}_2\text{OP}(\text{O})(\text{OCH}_3)_2$), 70.2 (s, $-\text{OCH}_2\text{CH}_2-$, $-\text{CH}_2\text{CH}_2\text{OP}(\text{O})(\text{OCH}_3)_2$); ^{31}P NMR (CDCl_3): δ (ppm) 0.00 (s, $(-\text{CH}_2\text{CH}_2\text{O})_3\text{P}(\text{O})$), 1.26 (s, $\text{CH}_3\text{OP}(\text{O})\text{O}-$), 1.87 (s, $-\text{CH}_2\text{OP}(\text{O})(\text{OCH}_3)_2$).

POEPNAT400: Synthesis of the polymer POEPAT400 was carried out at the same procedure starting from mixture of 30 ml of dichloromethane, 10.33 ml of carbon tetrachloride, 10.52 g (0.0267 mol repeating phosphonate units) of POEPNAT400 and adding of 3.25 ml of methanol, and 4.57 ml of *N*-ethyl-diisopropylamine in 25 ml dichloromethane. ^1H NMR (CDCl_3): δ (ppm) 1.29–1.52 (m, $-\text{OCH}_2\text{CH}_3$), 3.56–3.65 (m, $-\text{OCH}_2\text{CH}_3$), 3.57–3.72 (m, $-\text{CH}_2\text{CH}_2\text{OCH}_2\text{CH}_2-$), 3.62–3.72 (m, $\text{CH}_3\text{OP}(\text{O})\text{O}-$), $(-\text{CH}_2\text{CH}_2\text{O})_3\text{P}(\text{O})$), 3.69–3.71 (m, $-\text{CH}_2\text{CH}_2\text{OP}(\text{O})(\text{OCH}_3)_2$), 3.78 (days, $J^3=11.2$ Hz, $-\text{CH}_2\text{CH}_2\text{OP}(\text{O})(\text{OCH}_3)_2$), 3.99–4.09 (m, $-\text{CH}_2\text{OP}(\text{O})-$), 4.13–4.22 (m, $-\text{CH}_2\text{OP}(\text{O})(\text{OCH}_3)_2$); $^{13}\text{C}\{\text{H}\}$ NMR (CDCl_3): δ (ppm) 53.2 (s, $-\text{POCH}_3$), 64.8 (s, $\text{P}(\text{O})(\text{CH}_2\text{CH}_2-$), 66.5 (s, $-\text{CH}_2\text{OP}(\text{O})(\text{OCH}_3)_2$), 70.55 (s, $-\text{OCH}_2\text{CH}_2-$, $-\text{CH}_2\text{CH}_2\text{OP}(\text{O})(\text{OCH}_3)_2$); ^{31}P NMR (CDCl_3): δ (ppm) 0.00 (s, $(-\text{CH}_2\text{CH}_2\text{O})_3\text{P}(\text{O})$), 1.13 (s, $\text{CH}_3\text{OP}(\text{O})$), 1.84 (s, $-\text{CH}_2\text{OP}(\text{O})(\text{OCH}_3)_2$).

Synthesis of tris (β -diketonate) europium (III) complexes

40 ml of an aqueous solution of 0.366 g (1 mmol) $\text{EuCl}_3 \cdot 6\text{H}_2\text{O}$ were added drop wise to a stirred suspension of 3 mmol β -diketonate in 40 ml ethanol and ammonium hydroxide (pH 8–9). The mixture was stirred at RT for 30 min. A pale-yellow precipitate formed immediately and a strong red luminescence could be seen upon UV-illumination. The mixture was stirred for about 1 h. Eighty milliliters of water were added upon cooling for completion of the precipitation and the mixture was stirred for another hour. Most of the ethanol was removed on a rotary evaporator, and the mixture was kept overnight at 4 °C. The precipitate was filtered off, dried overnight in vacuo over sodium hydroxide and recrystallized from hot acetone/ethanol (1:2) mixture to give a pale-yellow powder. **Eu1** (tris[benzoyltrifluoroacetate]europium) ^1H NMR (CDCl_3), δ (ppm): 2.71 (s H_2O), 3.12 (s 3 β -H), 7.26–7.47 (m 9 Ar), 7.89 (s 6 Ar); **Eu2** (tris[naphtyltrifluoroacetate]europium) ^1H NMR (CDCl_3), δ (ppm): 3.06 (s 3 β -H), 7.54–7.66 (m 6 Ar), 7.89–8.03 (m 6 Ar), 8.34 (days 3 Ar, $J^3=8.61$ Hz), 8.71 (s 3 Ar); **Eu3** (tris[thenoyltrifluoroacetate]europium) ^1H NMR (CDCl_3), δ (ppm): 3.258 (s 3 β -H), 6.206 (s 3H Ar), 6.491 (s 3H Ar), 6.98 (s 3H Ar).

Synthesis of POEPAT200 and POEPAT400 tris (β -diketonate) europium (III) complexes

The synthesis was carried out in a three-necked flask equipped with a stirrer, thermometer and a condenser. A

solution of 0.4 mmol of ternary Eu(III) complex in 10 ml of dichloromethane was added under continuous stirring to 0.8 mmol (0.19 g, 4.3×10^{-3} mol/g repeating units) of POEPAT200 or to 0.8 mmol (0.32 g, 2.5×10^{-3} mol/g repeating units) of POEPAT400 dissolved in 10 ml (20 ml for complexes with POEPAT400) of dichloromethane. After removing a half of the dichloromethane by heating the reaction mixture, the flask was cooled and the product precipitated from diethyl ether.

Eu1POEPAT200 ^1H NMR (CDCl_3): δ (ppm) 1.5–1.8 (m, $-\text{OCH}_2\text{CH}_3$), 3.32–4.18 (m, $-\text{OCH}_2\text{CH}_2-$; s, β -H BTA), 7.00–7.13 (m, Ar), 7.4 (s, Ar), 7.91 (s, Ar); ^{13}C {H} NMR (CDCl_3): δ (ppm) 70.3–71.4 (m, $-\text{OCH}_2\text{CH}_2\text{O}-$, $-\text{P}(\text{O})\text{CH}_2$), 125 (s, Ar).

Eu2POEPAT200 ^1H NMR (CDCl_3): δ (ppm) 1.82–2.25 (m, $-\text{OCH}_2\text{CH}_3$), 2.75 (s, β -H NTA), 3.69–4.56 (m, $-\text{OCH}_2\text{CH}_2-$), 7.44–8.05 (m, Ar); ^{13}C {H} NMR (CDCl_3): δ (ppm) 71 (m, $-\text{OCH}_2\text{CH}_2\text{O}-$, $-\text{P}(\text{O})\text{CH}_2$), 125.6 (s, Ar), 126.8 (s, Ar), 128 (s, Ar) 129 (s, Ar).

Eu3POEPAT200 ^1H NMR (CDCl_3): δ (ppm) 1.86 (s, $-\text{OCH}_2\text{CH}_3$), 3.33–4.8 (m, $-\text{OCH}_2\text{CH}_2-$; s, β -H TTA), 6.77 (s, Ar), 6.9 (s, Ar), 7.02 (s, Ar); ^{13}C {H} NMR (CDCl_3): δ (ppm) 18 (s, $-\text{OCH}_2\text{CH}_3$), 67–73.7 (m, $-\text{OCH}_2\text{CH}_2\text{O}-$, $-\text{P}(\text{O})\text{CH}_2$), 123.5 (s, Ar), 126.8 (s, Ar), 133 (s, Ar).

Eu1POEPAT400 ^1H NMR (CDCl_3): δ (ppm) 1.9 (s, $-\text{OCH}_2\text{CH}_3$), 3.41 (s, β -H BTA), 3.55–4.38 (m, $-\text{OCH}_2\text{CH}_2-$), 7.00–8.04 (m, Ar); ^{13}C {H} NMR (CDCl_3): δ (ppm) 70.3–71.4 (m, $-\text{OCH}_2\text{CH}_2\text{O}-$, $-\text{P}(\text{O})\text{CH}_2$), 125 (s, Ar).

Eu2POEPAT400 ^1H NMR (CDCl_3): δ (ppm) 1.94–2.2 (m, $-\text{OCH}_2\text{CH}_3$), 2.74 (s, β -H NTA), 3.63–4.43 (m, $-\text{OCH}_2\text{CH}_2-$), 7.41–8.13 (m, Ar); ^{13}C {H} NMR (CDCl_3): δ (ppm) 71 (m, $-\text{OCH}_2\text{CH}_2\text{O}-$, $-\text{P}(\text{O})\text{CH}_2$), 125.6 (s, Ar), 126.8 (s, Ar), 128 (s, Ar) 129 (s, Ar).

Eu3POEPAT400 ^1H NMR (CDCl_3): δ (ppm) 2.0–2.17 (m, $-\text{OCH}_2\text{CH}_3$), 3.43 (s, β -H TTA), 3.70–4.82 (m, $-\text{OCH}_2\text{CH}_2-$), 6.75 (s, Ar), 6.88 (s, Ar), 7.16 (s, Ar); ^{13}C {H} NMR (CDCl_3): δ (ppm) 18 (s, $-\text{OCH}_2\text{CH}_3$), 67–73.7 (m, $-\text{OCH}_2\text{CH}_2\text{O}-$, $-\text{P}(\text{O})\text{CH}_2$), 123.5 (s, Ar), 126.8 (s, Ar), 133 (s, Ar).

A shift of the P = O stretching vibration [coordination with Eu(III)] could not be observed in the IR spectra due to its overlapping by the broad band for C–O–C stretching ($1,300$ – $1,000\text{ cm}^{-1}$) from the polymer chain.

The concentration of Eu(III) in the polymers was determinate by ICP atomic emission spectroscopy. The polymers were dissolved in aqua regia. These results were compared with the data from the titration of the polymer solutions with hydrochloric acid in the sample compartment of Cary Eclipse spectrophotometer until the luminescence disappeared. The results obtained by both methods were very close (Table 1).

Instruments and measurements

^1H , ^{13}C , and ^{31}P NMR (400 MHz) spectra were recorded on a Bruker Avance-400 at RT. The ^1H NMR spectra were referenced to internal TMS, ^{13}C NMR spectra—relative to the solvent signals ($\text{CDCl}_3=77.0\text{ ppm}$) and ^{31}P NMR spectra—electronically to external 85% aq. H_3PO_4 . The ^{13}C multiplicities were determined via DEPTQ spectra. The ICP analyses were performed on a Spectroflame D504 ICP–AES. The FTIR spectra in solid state were recorded on a Shimadzu FTIR-8400s spectrometer. The UV and luminescence spectra of the complexes (10^{-5} M solutions in chloroform) were recorded on a Thermo Spectronic Unicam 500 spectrophotometer and on a Varian Cary Eclipse luminescence spectrophotometer, respectively.

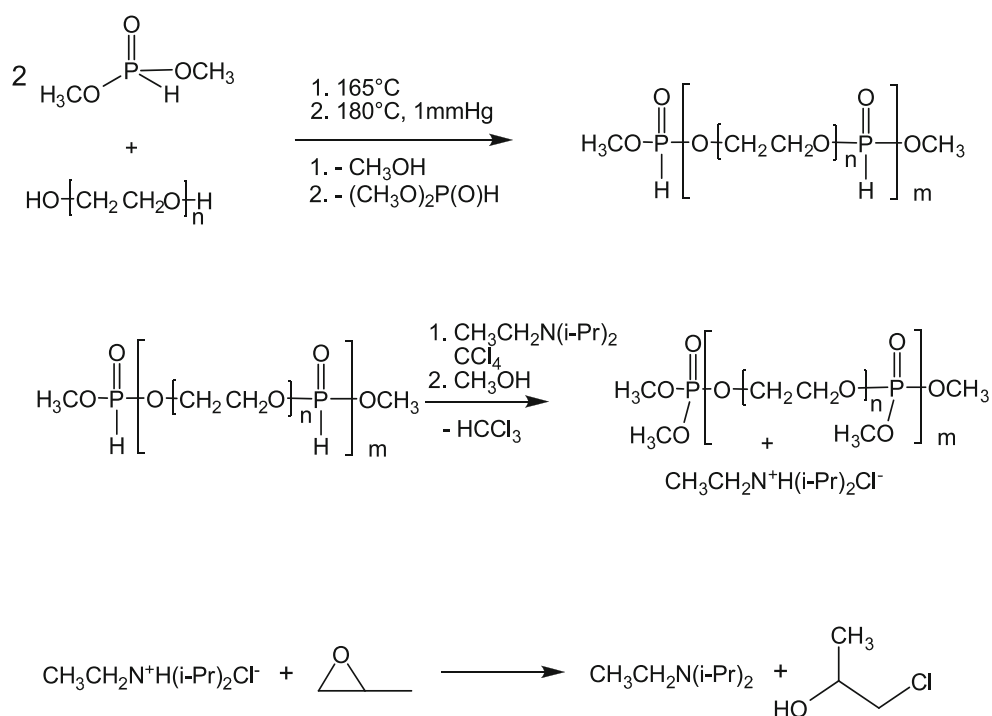
For determination of the relative quantum yields (QY) of the complexes we used five abs. ethanol solutions for each compound at different concentration (optical density 0.1–0.01) according to the procedure described by Williams et al. [28], QY was calculated from the gradients, obtained from the plots of the wavenumber-integrated emission intensity vs. absorbance, of the sample with two standards, rhodamine 101 with QY 1 in abs. Ethanol [29] and cresyl violet with QY 0.54 in Methanol [30, 31].

Results and discussion

Synthesis

The poly(oxyethylene phosphonate)s (POEPNAT, Scheme 2) were synthesized by transesterification of dimethyl phosphonate with poly(oxyethylene glycol)s (PEG) according to a procedure, described by Troev and co-workers [24]. In order to prevent the formation of a high molecular weight polymer, two fold excess of dimethyl phosphonate (with respect to PEG) was used. Two polyethylene glycols of different molecular weight were used as starting materials for the preparation of two types of luminescent poly(oxyethylene phosphonate) polymers with different contents of luminescent units per mass unit (Scheme 2).

The synthesis of poly(oxyethylene phosphate)s POEPAT200 and POEPAT400 (Scheme 2) was carried out applying improved Atherton–Todd reaction conditions [25]. The reaction between poly(oxyethylene phosphonate), carbon tetrachloride and methanol was carried out in dichloromethane. To avoid undesired cleavage of the polymer chain during the Atherton–Todd reaction sterically hindered Hünig's base (*N*-ethyl-diisopropylamine) was used. In this compound the nitrogen atom is shielded by two isopropyl and an ethyl groups, so only a proton is small enough to

Scheme 2 Synthetic route of the poly(oxyethylene phosphate)s

reach the free electron pair. This compound can be regarded as a base but not as a nucleophile [32]—a fact making it an appropriate reagent for this reaction. It is well known that it can abstract only unhindered protons and cannot break the PO–R bond. Thus the length of the macromolecular chain of the starting phosphonates can be preserved and side-reactions avoided during the Atherton–Todd stage of the reaction. This is why we applied *N*-ethyl-diisopropylamine instead of the widely used triethylamine [25]. This first improvement of the synthetic procedure resulted in transformation of poly(oxyethylene phosphonate) into poly(oxyethylene phosphate) in almost theoretical yields.

Products with increased molecular weight can be obtained during the Atherton–Todd reaction. Probably this can be attributed to bonding of the free –CH₂OH end groups of the polymer to the activated phosphonate groups. To avoid such bonding and the resulting net effect, the methanol excess in the reaction mixture has to be rather high (up to threefold the theoretical). Accordingly the synthesis was performed in diluted reaction mixtures under intensive stirring.

The addition of propylene oxide to the crude reaction mixture facilitates the elimination of *N*-ethyl-diisopropylammonium hydrochloride formed. That could be regarded as another improvement of the synthetic procedure. Quaternary ammonium salts have always been a problem in the preparation of pure polymers, as they exhibit restricted solubility in non-polar solvents (e.g. diethyl ether) and can precipitate along with the target polymer. On the other hand,

the products of the decomposition of the *N*-ethyl-diisopropylammonium hydrochloride (see Scheme 2) are soluble and remain in the solution after the polymer precipitation. In this way the target polymers can be obtained in a very pure form after up to three precipitations.

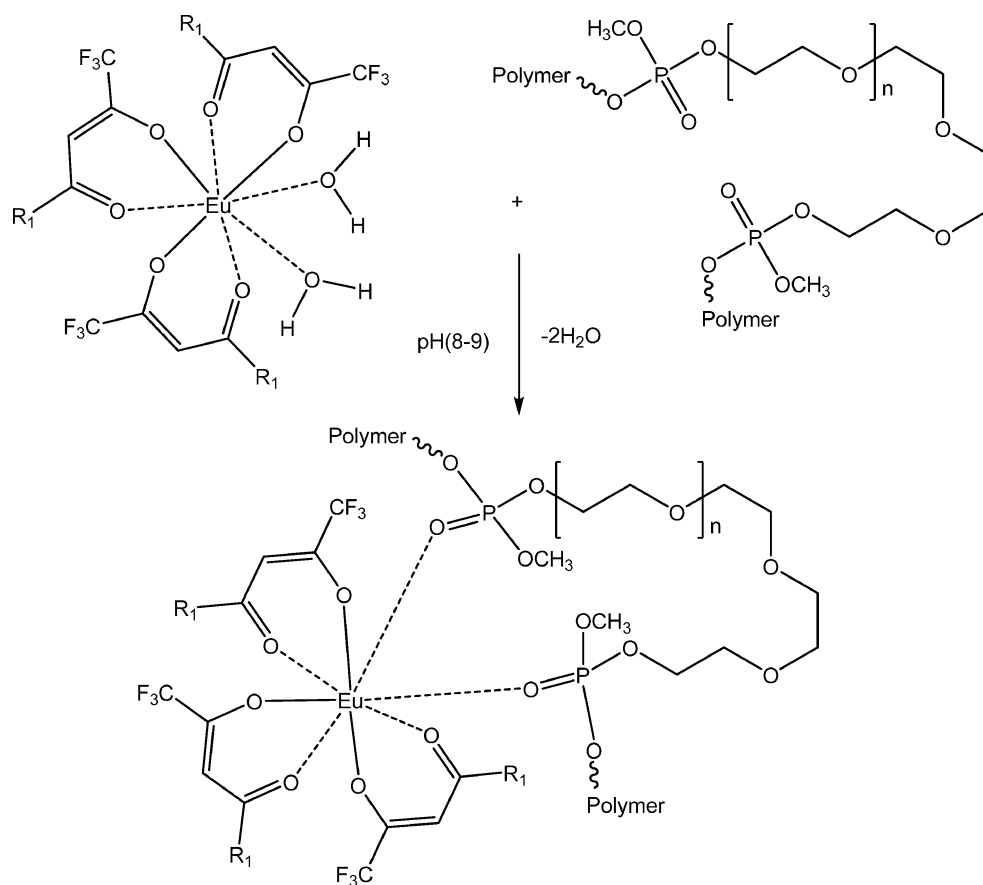
All tris (β-diketonate) europium (III) complexes were prepared by a modified method [33, 34]. An aqueous solution of EuCl₃·6H₂O was added to a suspension the β-diketonate in ethanol and the reaction mixture was alkalized with ammonium hydroxide.

The interaction of the dichloromethane solutions of the ternary Eu(III) complex and the polymer (POEPAT200 or POEPAT400) yielded the final products—poly(oxyethylene phosphate) tris (β-diketonate) europium (III) complexes (Scheme 3).

NMR spectra

¹H, ¹³C DEPTQ (distorsionless enhancement by polarization transfer including the detection of quaternary nuclei), ³¹P NMR and two-dimensional techniques such as ¹H COSY (correlation spectroscopy), ¹H–¹³C HSQC (heteronuclear single quantum correlation), and ¹H–³¹P HMBC (heteronuclear multiple bond correlation) NMR spectroscopy techniques have been used to characterize the obtained products. All NMR spectra confirm the structure and purity of the target polymers. The NMR data have been used for the determination of the number-average molecular weight of the poly(oxyethylene phosphonate)s. The number of

Scheme 3 Synthetic route of the poly(oxyethylene phosphate) tris(β -diketonate) europium (III) complexes



repeating units in the polymer chain has been calculated ($m=13$) using the ratio (6:1) of the integral intensities of the P–H protons of the repeating units towards that of the end phosphonate groups as each chain has two phosphonate end groups, (Figs. 1, 2). This corresponds to an average molecular weight of 3,230 g/mol for POEPNAT200 and 5,518 g/mol for POEPNAT400, respectively [19]. The ratios between the intensities of the signals for repeating units and end groups are the same in both 1H and ^{31}P NMR spectra of the polymers.

No signals for P–H doublets could be detected for both repeating units and end groups in the 1H NMR spectra of the POEPATs prepared. This shows that the Atherton-Todd reaction proceeds under the reaction conditions applied in a higher yield compared to known results [24, 26]. Noteworthy are the new signals at about 3.62 ppm (3.63 ppm for POEPAT400, respectively) assigned to $CH_3OP(O)-$ group from the chain. The multiplets for $-CH_2OP(O)-$ groups are shifted from 4.2 ppm to 4.02 ppm, which could be considered as an additional proof for the transformation of

Fig. 1 1H NMR spectrum of POEPNAT200 in $CDCl_3$

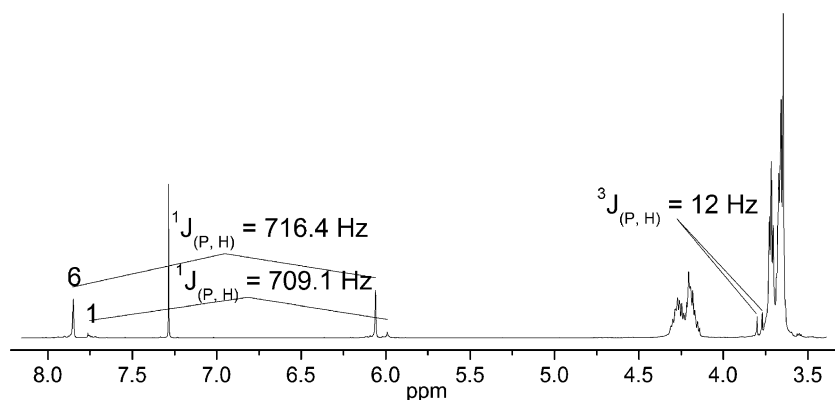
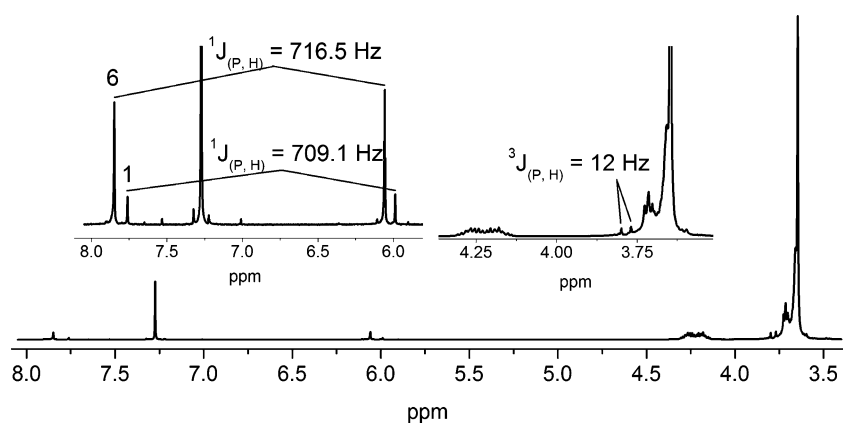


Fig. 2 ^1H NMR spectrum of POEPNAT400 in CDCl_3



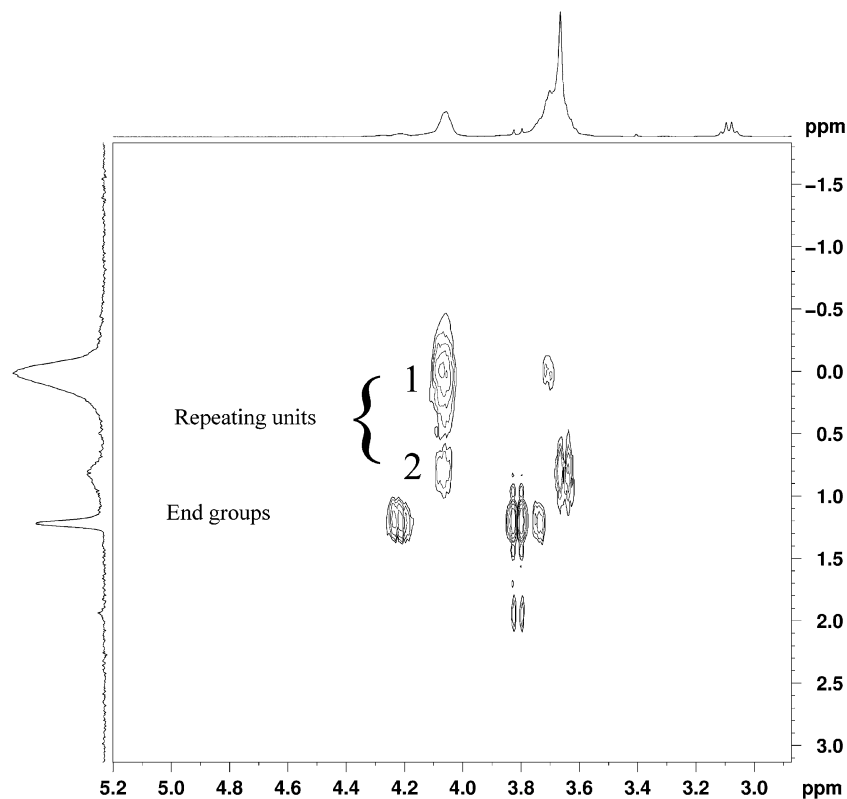
the starting polymer. The ^{31}P NMR spectra have two or three peaks. There are two kinds of signals for phosphorous from the repeating units and one signal for end groups ($-\text{CH}_2\text{OP}(\text{O})(\text{OCH}_3)_2$). The signal for the end group appears at a lower field. When the reaction is performed in more concentrated reaction mixture or at a stoichiometrical quantity of methanol (with respect to phosphonate groups), two kinds of signals are observed for phosphorus from the repeating units. The first signal is related to $(-\text{CH}_2\text{CH}_2\text{O})_3\text{P}(\text{O})$ and the second one to $\text{CH}_3\text{OP}(\text{O})(\text{OCH}_2\text{CH}_2)_2$ (Fig. 3). The low methanol content in the reaction mixture and its restricted mobility results in a bonding of the free $-\text{OCH}_2\text{CH}_2\text{OH}$ groups from a polymer

to the activated phosphonate groups (net effect). This undesired reaction could be avoided using the synthetic procedure already described. The spectral data obtained confirms the high rate of POEPNAT conversion into POEPAT when applying the proposed by us improved Atherton–Todd synthetic procedure.

As in the ^1H NMR spectra the signals overlap, forming a broad multiplet, the exact positions of the ^1H NMR signals in the range 3.6–3.7 ppm have been determined by the two dimensional spectra ($^1\text{H}-^{13}\text{C}$, $^1\text{H}-^{31}\text{P}$; Fig. 4).

The peaks for the polymer complexes are shifted to a lower field, if compared to the same peaks in the spectra of the starting polymer. That is due to the strong paramagnetic

Fig. 3 $^1\text{H}-^{31}\text{P}$ HMBC NMR spectrum of POEPAT200 in CDCl_3 . (1) $(-\text{CH}_2\text{CH}_2\text{O})_3\text{P}(\text{O})$, (2) $\text{CH}_3\text{OP}(\text{O})(\text{OCH}_2\text{CH}_2)_2$



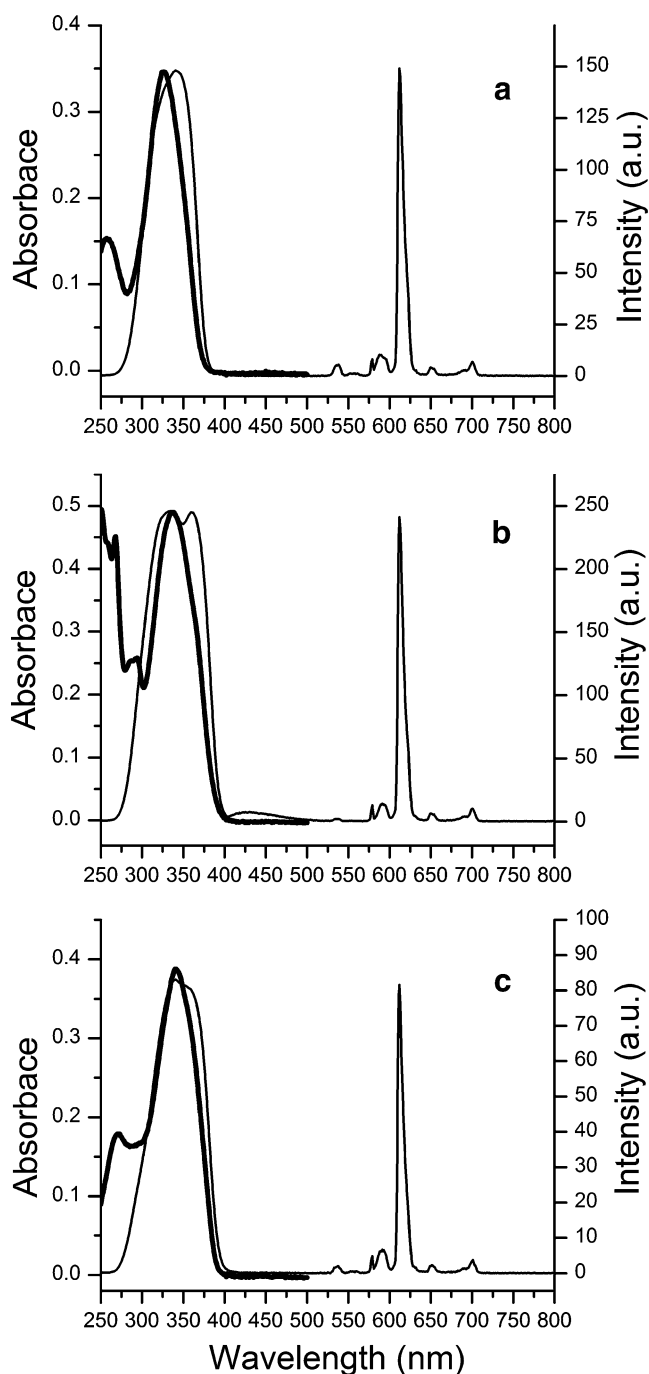


Fig. 4 Absorption spectra—**bold line**, excitation spectra ($\lambda_{em.} = 612$ nm) and emission spectra ($\lambda_{ex.} = 343$ nm)—**thin line**, of 10^{-5} M solutions in chloroform of **a** Eu1POEPAT200, **b** Eu2POEPAT200, **c** Eu3POEPAT400

properties of the Eu(III) ions which deshield the adjacent nuclei. In fact such kind of β -diketonate complexes of Eu(III) are lanthanide shift reagents and can be used for transforming second order NMR spectra into first order [35]. Because of these strong paramagnetic properties of europium there are no signals in ^{31}P NMR spectra. The absence of the ^{31}P signal and the shift of the peaks for CH_2 groups could be regarded as an evidence for bonding

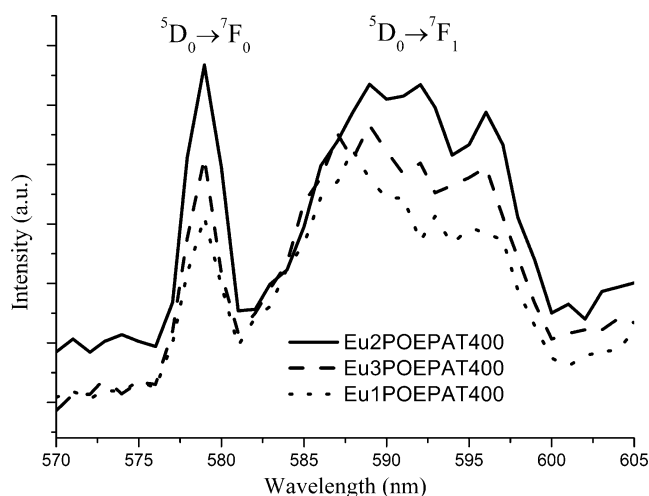


Fig. 5 Emission spectra representing, caused by Stark's effect, fine structure of the $^5\text{D}_0 \rightarrow ^7\text{F}_1$ transition, normalized at 612 nm

between europium and phosphorus through an oxygen bridge.

UV absorption and luminescent spectra

All polymer complexes prepared are highly luminescent (for such kind of compounds). Their spectral properties are presented in Fig. 5. The absorption maxima appear at 328, 337, and 341 nm for Eu1, Eu2, and Eu3, respectively, and all of them emit at 612 nm. The peak positions in the luminescent spectra for all polymer complexes are the same. The fact should be attributed to the mechanism by which europium complexes absorb and emit light (Fig. 7). They absorb a quantum with the β -diketonate part of the molecule and then this excited part transfers energy through T_1 energy level of the ligands to the $^5\text{D}_1$ level of the Eu(III) [36]. Then the system relaxes and emits mainly from $^5\text{D}_0$ to $^7\text{F}_J$ ($J=0, 1, 2, 3,$ and 4) levels. For all complexes the

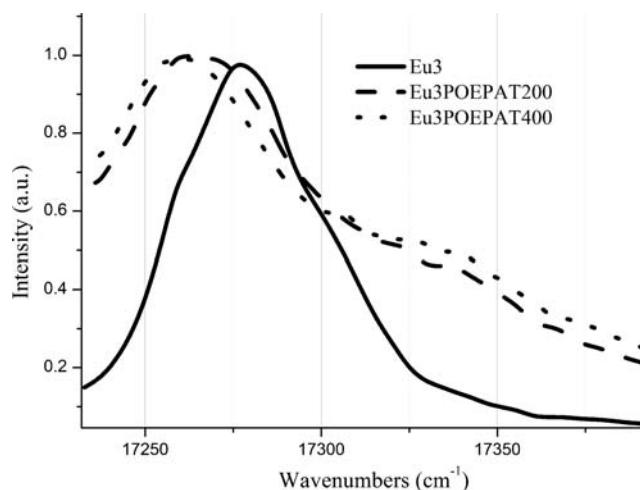
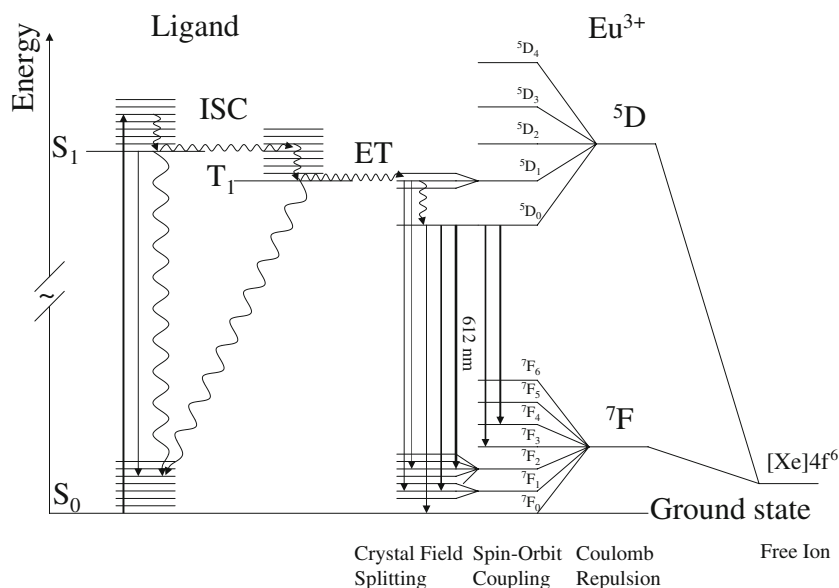


Fig. 6 $^5\text{D}_0 \rightarrow ^7\text{F}_0$ emission band position for ternary (*Eu3*) and polymer (*Eu3POEPAT200* and *Eu3POEPAT400*) complexes in acetone. Luminescent intensity is normalized at peak maximum

Fig. 7 Proposed energy transfer mechanism for Eu(III) complexes



energy difference between the excited and the ground levels is almost the same. Compared to spin-orbit coupling (Fig. 7) the Stark splitting will be small due to effective shielding of the 4f-electrons. However, it is large enough to produce a fine structure of the spectrum pattern related to the Eu(III) ion transitions, especially for ${}^5D_0 \rightarrow {}^7F_1$ one [37] (Fig. 5).

Bonding to a polymer causes a shift (13–18 cm^{-1}) of the ${}^5D_0 \rightarrow {}^7F_0$ band in Eu(III) complexes spectra toward lower energies (Fig. 6). That reveals a change in the total charge of europium [38], or in the ligand coordination number [39] after the ternary complexes have been transformed into polymer ones (Fig. 7).

The luminescent spectra differ from each other by the integrated intensity ratio of the bands they consist of. The difference between the ratios of the ${}^5D_0 \rightarrow {}^7F_2$ to ${}^5D_0 \rightarrow {}^7F_1$

transition is due to the different symmetry of the complexes resulting from the different ligands [40]. Considering the results shown in Table 2, one can see the change in symmetry of the ternary complexes upon bonding to a polymer ligand. The higher this ratio, the lower symmetry of the complex there is. Since the intensity of the ${}^5D_0 \rightarrow {}^7F_1$ transition (which has only magnetic dipolar distribution) does not depend on the ion surrounding, the increase in the ratio depends on the intensity of the electric dipolar transition ${}^5D_0 \rightarrow {}^7F_2$. This intensity (${}^5D_0 \rightarrow {}^7F_2$) enhances when the site symmetry of the complexes is increased and the Eu(III) center is moved apart from the inversion center. Hence, Laporte rule and forbiddance for f-f transitions relax leading to an increase in electric dipolar transitions intensity. The intensity of the bands for each of the compounds is also different on account of ligand ability

Table 2 Photophysical properties of the complexes

Complexes	λ_{max} (nm)	ϵ^{a} ($\text{M}^{-1} \text{cm}^{-1}$)	$I_{5D_0 \rightarrow 7F_2} / I_{5D_0 \rightarrow 7F_1}^{\text{b}}$	η^{c} (%)	τ_1^{d} (μs)		
					Solid state	Ethanol	Chloroform
Eu1	326	40,200	5.3	31	489	434	243
Eu1POEPAT200	326	36,200	4.7	26	568	387	295
Eu1POEPAT400	328	33,500	4.97	21	554	349	262
Eu2	337	50,000	11.59	36	334	340	175
Eu2POEPAT200	335	55,800	12.33	35	406	336	221
Eu2POEPAT400	338	67,800	13.76	35	417	345	237
Eu3	343	70,000	8.28	34	238	382	206
Eu3POEPAT200	342	66,200	6.73	26	464	392	228
Eu3POEPAT400	341	59,000	7.86	25	470	364	274

^a Molar absorptivity of the complexes in chloroform solutions

^b Ratio between integrated peak areas for ${}^5D_0 \rightarrow {}^7F_2$ and ${}^5D_0 \rightarrow {}^7F_1$ transitions

^c Relative quantum yields

to absorb and transfer energy toward the metal ion and of a probability for an emission from excited 5D_0 energy level as well. The quantitative expression of this phenomenon is the quantum yield discussed below (Table 2).

The absorbance and excitation spectra of the corresponding ternary and polymer complexes have the similar shape and peak positions, but they have different molar absorptivities (Table 2). Obviously the molar absorptivities of the β -diketonate moiety are affected in a different manner by the starting polymers. These differences in the photochemical properties of the complexes are most probably due to the specific structural changes in the complexes and their interaction with the polymer as a matrix. The length of the oxyethylene spacer between two phosphate groups has a certain role in these interactions as well. The different spacer length could cause the different “crown” effect and twisting of the polymer chain. That results into a better bonding of the P = O groups to the europium center and into a better interaction with the ligands. The ligands interact with the polymer directly when the poly(oxyethylene) chain is involved and this leads to a change in the ligands properties as light absorbers.

Luminescent quantum yields and decay times

The quantum yields and decay times of the polymer complexes in the solid state and solutions are presented in Table 2. One can see that the QYs of the polymer complexes are lower than those of the ternary complexes. The decrease of the QYs is most probably due to the increase in the radiationless rate constants with respect to emission rates that is caused by vibronic coupling with the vibrations of the P = O groups and with polymer chain. These vibrations are more in solution than in the solid state. The polymer chains in solution are free and the higher degrees of freedom facilitate radiationless deactivation path ways. Therefore the observed decay times (Table 2) in the solid state are higher than those in solution. Furthermore the decay times for the polymer complexes in the solid state are higher than those for the ternary complexes. Hence, in the solid state we can expect quantum efficiency for polymer complexes higher than that for the ternary ones [41]. The data for the polymer complexes (Table 2) also point at a relation between the fluorescent QY decrease and the length of the polymer spacer between two P = O groups. The differences are too small and could be in range of the experimental error (which in this case is smaller than 10%) but deserve mentioning.

Conclusions

Two types of poly (oxyethylene phosphate)s have been prepared using an improved synthetic procedure of Atherton–

Todd reaction, i.e. applying sterically hindered Hünig’s base as a mild reagent with reduced nucleophilic properties and propylene oxide. The products are of average molecular weights and purity higher than those of the compounds synthesized by the conventional method. The synthesized polymers can coordinate with ternary europium complexes. The obtained final compounds possess spectral properties very close to those of the starting small molecules [Eu(III) complexes]. The polymer complexes exhibit increased water solubility and decay time, if compared to the corresponding ternary complexes. These properties make them promising candidates for organic bio markers. More detailed investigations of their properties related to the structure and future applications are under way.

Acknowledgements This study was funded by the Bulgarian Ministry of Education and Science, National Science Fund, Project “University research center on nanotechnologies and new materials” and also supported by the Official Cooperation Programs between the Universities of Sofia (Bulgaria) and Hamburg (FRG).

References

- Weissman SI (1942) Intramolecular energy transfer. The fluorescence of complexes of europium. *J Chem Phys* 10:214–217
- Reisfeld R, Jorgenson CK (1977) *Lasers and excited states of rare earths*. Springer, Berlin
- Nakamura K, Hasegawa Y, Wada Y, Yanagida S (2004) Novel luminescent Eu(III) complex with remarkably narrow emission band. *Chem Phys Lett* 398:500–504
- US 5124268 (1992)
- Jia Z, Yang J, Wu X, Wang F, Liu S, Sun C (2006) Study on a fluorometric method for the determination of protein in serum using quercetin–lanthanum (III)–sodium dodecyl benzene sulfonate–protein system. *Anal Lett* 39:67–81
- Beddard GS (1981) In: West MA (eds) *Fluorescent probes*. Academic, London.
- Richardson FS (1982) Terbium(III) and europium(III) ions as luminescent probes and stains for biomolecular systems. *Chem Rev* 82:541–552
- Bünzli JCG, Piguet C (2005) Taking advantage of luminescent lanthanide ions. *Chem Soc Rev* 34:1048–1077
- Horrocks WD Jr, Albin M (1984) Lanthanide ion luminescence in coordination chemistry and biochemistry. *Prog Inorg Chem* 31:1–104
- Kuz'mina NP, Eliseeva SV (2006) Photo and electroluminescence of lanthanide(III) complexes. *Russ J Inorg Chem* 51:73–88
- Evans RC, Douglas P, Winscom CJ (2006) Coordination complexes exhibiting room-temperature phosphorescence: evaluation of their suitability as triplet emitters in organic light emitting diodes. *Coord Chem Rev* 250:2093–2126
- Holder E, Langeveld BMW, Schubert US (2005) New trends in the use of transition metal-ligand complexes for applications in electroluminescent devices. *Adv Mater* 17:1109–1121
- Tang CW, Vanslyke SA (1987) Organic electroluminescent diodes. *Appl Phys Lett* 51:913–915
- Kido J, Okamoto Y (2002) Organo lanthanide metal complexes for electroluminescent materials. *Chem Rev* 102(6):2357–2368

15. Tsutsui T, Takada N, Saito S, Ogino E (1994) Sharply directed emission in organic electroluminescent diodes with an optical-microcavity structure. *Appl Phys Lett* 65:1868–1870
16. Silva FRG, Menezes JFS, Rocha GB, Alves S, Brito HF, Longo RL, Malta OL (2000) Emission quantum yield of europium (III) mixed complexes with thenoyltrifluoroacetate and some aromatic ligands. *J Alloys Comp* 303–304:364–370
17. Okada K, Wang YF, Nakaya T (1998) A novel red organic electroluminescent device using Eu complex as an emitting layer. *Synthetic Metals* 97:113–116
18. Momekov G, Deligeorgiev T, Vasilev A, Peneva K, Konstantinov S, Karaivanova M (2006) Evaluation of the cytotoxic and pro-apoptotic activities of Eu(III) complexes with appended DNA intercalators in a panel of human malignant cell lines. *Med Chem* 2:439–445
19. Kossev K, Vassilev A, Popova Y, Ivanov I, Troev K (2003) Functionalization of poly(oxyethylene phosphonate) under phase-transfer catalyst conditions. *Polymer* 44(2):1987–1993
20. Brosse J, Fontaine L, Derouet D, Charatanathvom S (1989) Fixation d'amines pharmacologiquement actives sur les polyphosphonates, 1. Etude sur molécule modèle. *Makromol Chem* 190:2329–2338
21. Brosse J, Derouet D, Fontaine L, Charatanathvom S (1989) Fixation of pharmacologically active amines on polyphosphonates, 2. Application to benzocaïne and phenethylamine. *Makromol Chem* 190:2339–2345
22. Gunnlaugsson T, Leonard JP, Senechal K, Harte AJ (2003) pH responsive Eu(III)–phenanthroline supramolecular conjugate: novel “Off-On-Off” Luminescent Signaling in the Physiological pH Range. *J Am Chem Soc* 125:12062–12063
23. Barnes J, Holt P (1975) Potential antiradiation polymers, 1. Isothiuronium salts, thiosulphates and dithiocarbamates. *Makromol Chem* 176:275–283
24. Tsevi R, Novakov P, Troev K, Roundhill DM (1997) Synthesis of poly(oxyethylene phosphonate)s bearing oxirane groups in the side chain. *J Polym Sci A, Polym Chem* 35:625–630
25. Pretula J, Penzek S (1990) High-molecular-weight poly(alkylene phosphonate)s by condensation of dialkylphosphonates with diols. *Makromol Chem* 191:671–680
26. Tsevi R, Todorova G, Kossev K, Troev K, Roundhill DM (1993) Immobilization of bioactive substances on poly(alkylene phosphate)s, 1. Immobilization of 2-phenylethylamine. *Makromol Chem* 194:3261–3269
27. Georgieva R, Tsevi R, Kossev K, Kusheva R, Balgijiska M, Petrova R, Tenchova V, Gitsov I, Troev K (2002) Immobilization of amino thiols on poly(oxyalkylene phosphates). Formation of poly(oxyethylene phosphates)/cysteamine complexes and their radioprotective efficiency. *J Med Chem* 45:5797–5801
28. Williams ATR, Winfield SA, Miller JN (1983) Relative fluorescence quantum yields using a computer-controlled luminescence spectrometer. *Analyst* 108:1067–1071
29. Karstens T, Kobs K (1980) Rhodamine B and rhodamine 101 as reference substances for fluorescence quantum yield measurements. *J Phys Chem* 84:1871–1872
30. Magde D, Brannon JH, Cremers TL, Olmsted J (1979) Absolute luminescence yield of cresyl violet. A standard for the red. *J Phys Chem* 83(6):696–699
31. Eaton DF (1988) Reference materials for fluorescence measurement. *Pure Appl Chem* 60:1107–1114
32. Moore L, Taylor SM, Soloshonok VA (2005) An efficient and operationally convenient general synthesis of tertiary amines by direct alkylation of secondary amines with alkyl halides in the presence of Hunig's base. *Arkivoc* (EJ-1549C):287–292
33. Melby LR, Rose NJ, Abramson E, Caris JC (1964) Synthesis and fluorescence of some trivalent lanthanide complexes. *J Am Chem Soc* 86:5117–5125
34. De Sá GF, Malta OML, De C, Donegá M, Simas AM, Longo RL (2000) Spectroscopic properties and design of highly luminescent lanthanide coordination complexes. *Coord Chem Rev* 196:165–195
35. Hinckley CC (1969) Paramagnetic shifts in solutions of cholesterol and the dipyrindine adduct of trisdipivalomethanatoeuropium (III). A shift reagent. *J Am Chem Soc* 91:5160–5162
36. Malta OL (1997) Ligand–rare-earth ion energy transfer in coordination compounds. A theoretical approach. *J Lumin* 71:229–236
37. Forest H, Ban G (1969) Evidence for Eu^{+3} emission from two symmetry sites in $\text{Y}_2\text{O}_3:\text{Eu}^{+3}$. *J Electrochem Soc* 116:474–478
38. Albin M, Horrocks WDeW (1985) Europium(III) luminescence excitation spectroscopy. Quantitative correlation between the total charge on the ligands and the ${}^7\text{F}_0$ - ${}^5\text{D}_0$ transition frequency in europium(III) complexes. *Inorg Chem* 24:895–900
39. Choppin GR, Wang ZM (1997) Correlation between ligand coordination number and the shift of the ${}^7\text{F}_0$ - ${}^5\text{D}_0$ transition frequency in europium(III) complexes. *Inorg Chem* 36:249–252
40. Stanimirov SS, Hadjichristov GB, Petkov IK (2007) Emission efficiency of diamine derivatives of tris[4,4,4-trifluoro-1-(2-thienyl)-1,3-butanedion]europium. *Spectrochim Acta A: Mol Biomol Spectrosc* 67:1326–1332
41. Werts MHV, Jukes RTF, Verhoeven JW (2002) The emission spectrum and radiative lifetime of Eu^{3+} in luminescent lanthanide complexes. *Phys Chem Chem Phys* 4:1542–1548