Low-density polyethylene films doped with Eu(III) complex,
their properties and applications

Pogreb Roman\textsuperscript{a}, Finkelshtein Binyamin\textsuperscript{b}, Shmukler Yuri\textsuperscript{b}, Musina Albina\textsuperscript{a}, Popov Oleg\textsuperscript{c}, Stanevsky Oleg\textsuperscript{d}, Yitzchaik Shlomo\textsuperscript{c}, Gladkikh Alexander\textsuperscript{d}, Shulzinger Alexander\textsuperscript{d}, Streltsov Vladimir\textsuperscript{d}, Davidov Dan\textsuperscript{e}, Bormashenko Edward\textsuperscript{a}\textsuperscript{*}

\textsuperscript{a}The College of Judea and Samaria, The Research Institute, Ariel, 44837, Israel
\textsuperscript{b}Actipol LTD, Katzrin, 12900, Israel
\textsuperscript{c}Department of Inorganic Chemistry, The Hebrew University of Jerusalem, Jerusalem 91904, Israel
\textsuperscript{d}Tel Aviv University, Ramat Aviv, Tel Aviv, 69978, Israel
\textsuperscript{e}Racach Institute of Physics, The Hebrew University of Jerusalem, Jerusalem 91904, Israel

ABSTRACT

Light-converting polyethylene film containing Eu(III) complex with phenanthroline was manufactured under an extrusion process. The film was characterized first by means of time-of-flight secondary-ion-mass spectrometry (TOF-SIMS), ultraviolet-visible-infrared (UV-Vis-IR) spectroscopy, study of excitation and luminescence spectra, quantum yield and lifetime of luminescence. The quantum yield of luminescence was measured as 5±2\%, and the lifetime of luminescence was determined about 470 \textmu s. TOF-SIMS surface mapping showed the uniform distribution of Eu(III) over the film. Visualization of strong picosecond UV laser beams through the use of the developed film has been demonstrated.

Keywords: Polyethylene; Europium; Luminescence; Extrusion; Spectrum Visualization.

Corresponding author. Phone +972 3 9066134. E-mail address Edward@YCARIEL.YOSH.AC.IL
1. INTRODUCTION

In the last years, increased research activities have been carried out in the field of trivalent lanthanide complexes, which are light-emissive compounds with potential applications in different fields, including light-converting optical devices, amplifying waveguides, emitters in liquid lasers, electroluminescence devices (including light-emitting diodes), information storage devices, and agricultural sheets\textsuperscript{1–4}.

In this work, we report on a new light-converting material, implementing the host-guest concept. It is polyethylene film doped with [Eu(Phen\textsubscript{2})(NO\textsubscript{3})\textsubscript{3}] complex. The film absorbs UV light in the wide range of 320–370 nm and emits at $\lambda = 611$ nm. This film possesses the mechanical and optical properties of matrix polymer and is highly processable using traditional extrusion equipment. Eu(III) is uniformly distributed over the film.

Phenanthroline is known to form stable complexes with metals, being a donor of the absorbed energy\textsuperscript{5,6}. The structure and properties of this complex were thoroughly described\textsuperscript{7}. The central Eu atom coordinates five ligands (two phenanthroline molecules and three nitrate groups) so that effective energy transfer from a ligand to a Eu\textsuperscript{3+} ion can lead to the so-called “antenna” effect, increasing the intensity of Eu-emission\textsuperscript{8}.

It is clear that uniform distribution of the dopant in the polymer matrix is essential for the effective light conversion, but at the same time a study of such distribution is not a trivial task. The first time, we applied secondary-ion-mass spectrometry time-of-flight (TOF-SIMS) for such an investigation. Before that, TOF-SIMS was applied for the study of a distribution of the additives in thermoplastic and thermosetting polymers\textsuperscript{9–11}.
2. EXPERIMENTAL

2.1. Materials
Low-density polyethylene (LDPE) Ipethene 100, supplied by Carmel-Olefinim (melt flow index 0.3 g/10 min, ISO 1183, $t = 190^\circ$C), was chosen as a polymer matrix material. The dopant [Eu(Phen)$_2$(NO$_3$)$_3$] was formed via a reaction of europium nitrate with 1,10-phenanthroline. For better dispersion of the dopant in the polymer matrix, it was thoroughly mixed with polyethylene wax and parabene oil.

2.2. Processing
The process of preparing the Eu(III)-doped film included the following main steps (see Fig. 1): 1) preliminary mixing of components, using a single-screw extruder (diameter of the screw 32 mm, $L/D = 25$); 2) pelleting; 3) drying; 4) extrusion of the film using a Plast Engineering Knauf extruder (diameter of the screw 30 mm, $L/D = 26$) equipped with mixing zone, blown film die and drawing unit. Temperature regime was maintained from 160 to 180$^\circ$C during the extrusion process according to heating zones. Europium content in the film was 0.1–0.2 wt.%, film thickness was 60 ±0.5 µm.

2.3. Procedures
Transmission UV-Vis spectra were recorded using a Varian Carry 500 Scan spectrometer, and transmission IR spectra – using a Bruker Vector 22 FTIR spectrometer. Excitation and photoluminescence spectra were measured on a Shimadzu RF-5301PC spectrofluorimeter. Quantum yield for a sample was determined according to a known procedure, providing absolute yields while avoiding absolute measurements by comparison of absorption, emission, and excitation spectra to those of standard quinine sulfate solution$^{12,13}$. The procedure included the following steps: 1) excitation wavelength was chosen to give the maximum photoluminescence intensity; 2)
absorption was measured at this wavelength; 3) absorption and emission were compared to those values for a standard solution of fluorescein (Aldrich); 4) quantum yield was calculated as a ratio between the number of photons emitted by the Eu$^{3+}$ ion and the number of photons absorbed by the film.

Distribution of Eu(III) over the film was evaluated by a Physical Electronics TRIFT II TOF-SIMS instrument using a 15 kV $^{69}$Ga$^+$ primary ion gun. Bombardment of the film surface with primary ions leads to ion ejection from film components due to atomic collision cascades or electronic excitation processes. Mass spectra of secondary ions supply information on the chemical structure and composition of the film$^{9,11}$.

All measurements were performed at ambient temperatures.

3. RESULTS AND DISCUSSION

3.1. TOF-SIMS study of the Eu distribution in the polymer matrix

Distribution of Eu(III) in the polymer matrix was established using a TOF-SIMS study. Figure 2 presents the results of the TOF-SIMS measurements performed on the samples, obtained under the processing technology given above. The characteristic positive ions for Eu(III)-doped LDPE film are identified in Table 1.

The presence of characteristic positive ions CH$_2^+$, CH$_3^+$, C$_2$H$_3^+$, C$_2$H$_5^+$ etc. in the TOF-SIMS spectral data was discussed previously by Feng et al.$^{11}$. However, C$_1^+$ ions only are present in the spectrum, and C$_2^+$, C$_3^+$, C$_4^+$ ions as reported by Feng et al.$^{11}$ are absent. Two isotopes of Europium ($^{151}$Eu and $^{153}$Eu) could be recognized distinctly from our data. The mass-spectrum presented in Fig. 2 indicates one more intriguing fact: strong peaks corresponding to $m/z$ = 151.92 and $m/z$ = 153.91. This is interpreted as evidence of EuH$^+$ fragments in the mass-spectrum of the doped film. This fact could be variously attributed to interaction of Eu(III) with a polyethylene matrix, and to a
formation of EuH complexes under bombardment of a film surface with primary ions. Ions $^{153}\text{Eu}^+$, $^{151}\text{Eu}^+$, $^{153}\text{Eu}^+$ are inherent for $[\text{Eu(Phen)}_2(\text{NO}_3)_3]$ complex.$^7,14$. From the practical point of view, it was important to study the dopant distribution in the polymer matrix. The intensity of the Eu mass spectrum measured over the surface is proportional to the concentration of Eu atoms on that surface. Surface mapping of the film sample revealed rather uniform distribution of Eu(III) over the film. Relative root-mean-square deviation in the average surface content of Eu(III) atoms was estimated to be less than 0.15.

3.2. Photoluminescence spectra

Figure 3 presents the excitation and emission spectra of the LDPE film doped with Eu(III) complex. The emission spectrum of europium with the maximum at about 611 nm can be recognized, with ($^5\text{D}_0\rightarrow^7\text{F}_2$) transition being responsible for more than 90% of the emitted energy.$^2,7$ The line of emission $\lambda = 615$ nm was determined earlier$^7$ for $[\text{Eu(Phen)}_2(\text{NO}_3)_3]$ complex due to ($^5\text{D}_0\rightarrow^7\text{F}_2$) transition. This shift of the emission maximum is caused by the effect of the surrounding polyethylene matrix. The excitation spectrum exhibits an intense broad ligand-centered band in the region around 350 nm, confirming energy transfer from phenanthroline molecules to Eu(III) energy levels. Characteristic of 1,10-phenanthroline are long-wavelength absorption bands (allowed transitions) at 326 and at 339 nm ($\pi-\pi^*$ transitions)$^{14}$. A more detailed definition of the spectral features of the emission spectrum was performed with a set-up, depicted in Fig. 4a. Sample film was irradiated by 10 ns pulses from a Surelite Nd:YAG Laser at 3rd harmonic (355 nm). Light emitted from the film was collected by a lens system and passed through a CVI 1/2m monochromator. Afterwards, the light signal was detected with a photomultiplier tube (Hamamatsu
R928) and counted by Stanford Research Systems Photon Counter (SR400). The emission spectrum of the film, taken with an accuracy to within 0.5 nm, is shown in Fig. 4b. The emission maximum was observed at 611.5 nm. Half-width of the peak was about 1.5 nm.

The quantum yield of photoluminescence in the film, defined as the ratio between the number of photons emitted by the Eu(III) ion and the number of photons absorbed by the film, was evaluated as 5±2%. Rather strong light scattering of the film has not been taken into account; thus more correct absorption measurements could lead to a larger quantum yield.

3.3. Transmission spectra

Figure 5 presents UV-Vis-IR spectra of the films: spectrum 1 – Eu(III)-doped film, spectrum 2 – pure polyethylene film. Two broad absorption bands are observed in spectrum 1 in the UV region: around 270 and 350 nm. The absorption band at 350 nm is attributed to ligand-to-Eu(III) charge transfer bands. It can be seen from Fig. 5 that Eu(III)-doped film gives the same transmission as a virgin PE film in the broad visible-near-IR band: 450–1000 nm. This fact is of great importance for various applications of the film. Significant increase of absorption in the far-IR, caused by additives, should present no special problems for applications.

3.4. Lifetime of luminescence and optical applications of the Eu(III)-doped films

Time dependence of luminescence intensity was measured according to the next scheme (Fig. 6a). The sample was illuminated with a Leopard D-10 High-Energy Picosecond Nd:YAG laser at the wavelength $\lambda = 355$ nm, pulse duration 20 ps, frequency 10 Hz. UV light beyond the sample was cut with a UV filter and the spectral region 600±40 nm was selected with a broadband interference filter E 46-152. Intensity of luminescence
originated upon radiating the sample was collected with a PIN detector (model 818-BB-21) and displayed by an Agilent 54642A oscilloscope. Time dependence of emission intensity is shown in Fig. 6b: \( \ln(I_0/I) \) v. \( (t-t_0) \) was plotted and approximated with a linear dependence. The long-lived component of the lifetime of luminescence was calculated to be about 470 µs. This value is according to data reported by other authors for Eu(III) complexes dissolved\(^3,14\) or associated with some polymer matrix\(^1,15\). Due to this high value of the lifetime, our film is suitable for various optical applications such as visualization of UV laser beams. We have performed such visualization of a UV picosecond laser (\( \tau = 20 \) ps) beam at the wavelength of 355 nm. It has to be emphasized that polyethylene demonstrates an extremely high laser irradiation damage threshold, so the above-mentioned films are attractive for visualization of strong short-pulsed laser beams. We have determined that Eu(III)-doped LDPE films allow visualization of UV laser beams with a power density as high as \( 10^4 \) MW/cm\(^2\).

4. CONCLUSIONS

Light-converting, UV absorbing LDPE film doped with Eu(III) complex with phenanthroline was manufactured. Time-of-flight secondary-ion-mass spectrometry of the film was carried out first. The TOF-SIMS study indicated the homogenous distribution of the dopant in the polymer matrix. Absorption, excitation and luminescence spectra were studied in detail. The maximum emission was at 611.5 nm, half-width of an emission peak being equal to 1.5 nm. The shift of emission maximum caused by surrounding polymer matrix is reported. Quantum yield was appreciated to be at about 5%. The long-lived component of luminescence lifetime about 470 µs was obtained. Suitability of the developed films for the visualization of strong short-pulsed UV laser beams with a power density as high as \( 10^3 \) MW/cm\(^2\) was demonstrated.
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REFERENCES


**SYMBOLS AND ABBREVIATIONS**

TOF-SIMS – time-of-flight secondary-ion-mass spectrometry

UV-Vis-IR – ultraviolet-visible-infrared

Phen – phenanthroline

LDPE – low-density polyethylene
Fig. 1. Technological process of preparing LDPE film containing Eu(III) complex.
**Fig. 2.** Results of TOF-SIMS measurements. Left: relative intensity of Eu(III) mass peak, measured over the surface, spacing between points about 1 mm. Right: mass spectrum. The lower graph is enlarged image of the mass spectrum part with Eu(III) peaks.
Fig. 3. Excitation and emission spectra of the film.
Fig. 4. a Experimental set-up: 1 – Surelite Nd:YAG Laser in 3rd harmonic at 355nm, 2 – sample, 3 – focusing lens, 4 – CVI 1/2m monochromator, 5 – photomultiplier tube Hamamatsu PMT; b detailed emission spectrum of the film in the region 600–640 nm.
Fig. 5. UV-Vis-IR spectra of the films: 1 – Eu(III)-doped film, 2 – pure polyethylene film.
**Fig. 6.**

a Scheme of the experiment on determining lifetime of a luminescence.  

b Time dependence of a luminescence intensity.
Table 1. Characteristic positive ions of Eu(III)-doped film

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