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Near-infrared photoluminescence of erbium tris(8-hydroxyquinoline) spin-coated thin films induced by low coherence light sources

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The authors present the characterization of spin-coated erbium tris(8-hydroxyquinoline) (ErQ_3) solution on glass substrates under high temperature conditions. Absorption and infrared photoluminescence, induced by laser and light emitting diode sources, were measured and compared to cast and evaporated ErQ_3 samples. A broad absorption band and $1.52 \mu\text{m}$ luminescence were observed, suggesting spin coating as a valid deposition technique for processing of organic infrared emitting diodes. © 2007 American Institute of Physics. [DOI: 10.1063/1.2755933]

In recent years, organolanthanide complexes have been widely used as emitting layers to obtain electroluminescence from organic light emitting diodes.¹⁻⁶ The main advantage of these compounds lies in the large absorption cross section of the allowed π - π^* optical transitions in the organic ligands, that acts as an efficient light harvesting antenna.⁷⁻⁹ This property enables optical excitation by means of low coherence and low-cost light sources, such as light emitting diodes (LEDs). Some organolanthanides have shown electroluminescence in the near-infrared range.¹⁰⁻¹⁶ Among the different erbium organic compounds analyzed in literature,^{7,17-19} erbium tris(8-hydroxyquinoline) (ErQ_3) is the most interesting organic infrared emitter because it has shown the highest photoluminescence²⁰⁻²² and electroluminescence²³⁻²⁵ intensities centered at 1525 nm; this corresponds to the low loss third window wavelength range used in standard optical communications. ErQ_3 is a small molecule; for this reason, organic light emitting diodes based on such a compound can be manufactured using vacuum processing techniques, such as thermal evaporation.²³⁻²⁵ It is known that these techniques need relatively expensive vacuum systems and long time to reach the right vacuum conditions (at least 10^{-6} mbar). It could be useful to manufacture an ErQ_3 -based organic LED (OLED) using an alternative deposition process that allows for cheaper and faster processing. To achieve these goals, we focused our study on the characterization of this compound in order to demonstrate that ErQ_3 OLED can be a solution processable device. Solution processing allows more flexibility for OLED implementation and design as with imprinting lithography, a promising lithographical technique that allows for an easy, cheap, and high resolution patterning of organic devices.^{26,27} In this letter, we report photoluminescence char-

acterization of ErQ_3 spin-coated sample demonstrating that the advantageous properties of this compound, i.e., wide absorption band and third window luminescence, are preserved by this deposition technique.

A solution was prepared by dissolving ErQ_3 powder in dimethyl sulfoxide (DMSO) (Sigma-Aldrich), that was experimented to be the most effective solvent for ErQ_3 . The solution concentration was set at 1% by weight. Glass substrates (Corning) were placed in an ultrasonic chamber in acetone solution (Sigma-Aldrich) for 15 min and then washed in isopropyl alcohol (Carlo Erba) for 10 min. Samples were then dried in nitrogen gas before coating processes. Due to the high boiling point of DMSO (189°C), the traditional spin-coating technique is unsuccessful, resulting in nonuniform coated thin films. Uniformity of the organic layers is the basic condition for the design of any organic semiconductor device based on thin film deposition. For this reason, a dedicated spin-coating method [high temperature spin coating (HTSC)] was developed using a heat source placed over the spin-coater holder. HTSC process was performed in two subsequent steps: step one at low spinning speed (500 rpm), to allow uniform spreading and adhesion of the solution over the whole substrate, and step two at higher speeds (from 1000 up to 2000 rpm) to define the thickness of the layer. Uniform thin films were obtained when both steps were performed with the substrate temperature at 110°C . ErQ_3 evaporated thin films were grown in a vacuum thermal evaporation chamber (Edwards) with a typical pressure of 0.2×10^{-6} mbar.

Absorption spectra were obtained by means of a Cary 50 UV-vis spectrophotometer (Varian). An InGaN laser (Photonic Technologies Instruments) and an ultraviolet (UV) emitting LED (Hktaiyuen), peaking, respectively, at 406 and 402 nm, were used as excitation sources. The LED light was focused by a system of lenses till to obtain a 1 mm^2 wide

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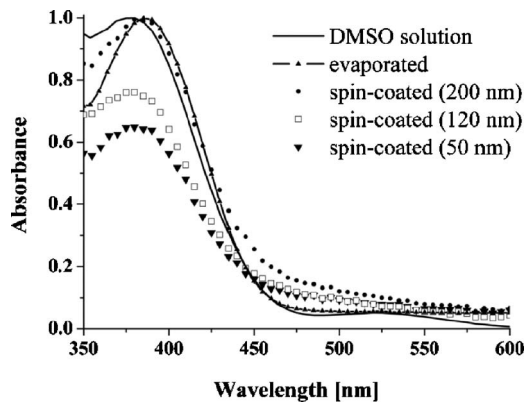


FIG. 1. Absorption spectra of ErQ_3 evaporated thin film, ErQ_3 solution, and ErQ_3 spin-coated thin films with different thicknesses. Spin-coated spectra are normalized to the thickest sample (200 nm).

spot on the tested samples, in order to have a meaningful comparison between laser-induced and LED-induced luminescence. Infrared photoluminescence was detected using a thermoelectrically cooled InGaAs photodiode (Newport) while the output signal was amplified by a coherent detection system involving a lock-in amplifier (EG&G). An Alpha Taly-Step (Tencor) was used to obtain the thickness values of spin-coated layers.

Absorption spectra of the spin-coated thin films in Fig. 1 show an absorption peak centered at 380 nm, corresponding to one of the $\pi \rightarrow \pi^*$ absorption transitions of the quinoline ligand.^{21,28,29} Comparing these spectra to the ones related to ErQ_3 evaporated thin films and ErQ_3 solution, a similar behavior can be observed, suggesting that the light sensitization scheme of the material is preserved by HTSC deposition. Laser-induced photoluminescence (PL) spectra of spin-coated thin films (see Fig. 2) show one peak at 1525 nm with an 80 nm full width at half maximum (FWHM). The inset shows the linear dependence of emission intensity on the thickness of spin-coated layers. Spin-coated PL spectra match PL spectra from ErQ_3 solution and ErQ_3 evaporated thin films^{20,22,29} (see Fig. 3). Although the excitation wavelength (406 nm) was far from the absorption peak of ErQ_3 (380 nm), we were able to obtain infrared luminescence just exploiting the high absorption cross section of the organic ligand. Comparing the laser-induced PL spectrum and a single UV-LED-induced PL spectrum (Fig. 4), we can ob-

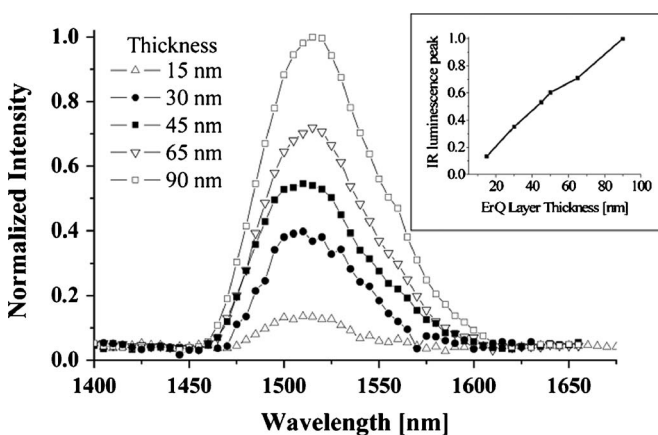


FIG. 2. Room-temperature PL spectra of ErQ_3 spin-coated thin films, following laser excitation at 406 nm. The inset shows the dependence of the IR emission peak on the thickness of ErQ_3 spin-coated thin films.

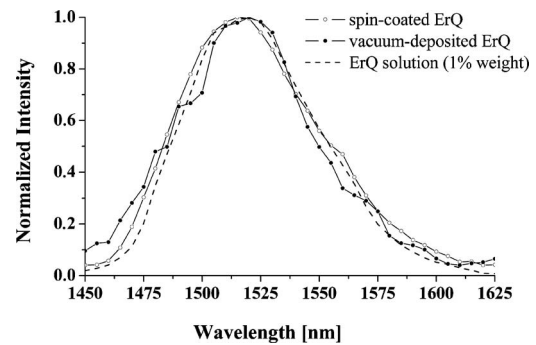


FIG. 3. Room-temperature PL spectra of ErQ_3 spin-coated thin film, ErQ_3 evaporated thin film, and ErQ_3 solution, following laser excitation at 406 nm.

serve that the two spectra have the same 1525 nm peak and similar FWHM (80 nm) and both present the characteristic shoulder at 1560 nm. We can also observe that the two spectra have similar normalized intensities if we consider that the excitation power density of the focused UV-LED is $340 \mu\text{W}/\text{mm}^2$ while that for the laser source is $38 \text{ mW}/\text{mm}^2$. In such a way, we demonstrate that pumping ErQ_3 by a low coherence source does not introduce efficiency loss. This is another practical demonstration of the easy and cheap optical excitation related to organolanthanides.

In summary, we have shown that it is possible to obtain uniform thin films by spin-coating deposition of ErQ_3 solution, demonstrating that the most interesting properties of this compound, which are a wide absorption band and infrared photoluminescence in the third window, do not change with respect to vacuum evaporated ErQ_3 thin films. This allows for the use of solution processing techniques to realize ErQ_3 -based infrared luminescent devices. These devices could be optically or electrically stimulated. In our opinion, ErQ_3 -based optically pumped devices, such as a waveguiding device, are very attractive considering that they could be pumped easily by low-cost light sources, as we demonstrated, exploiting the wide absorption spectrum of quinoline and the “antenna” sensitization scheme. In such a way, it could be possible to replace expensive high-power lasers requested for pumping erbium energy levels. ErQ_3 -based electrically stimulated devices, such as OLEDs, are a more com-

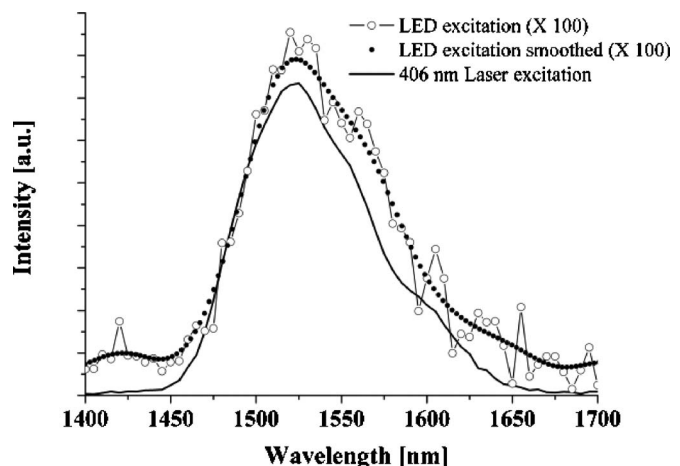


FIG. 4. Comparison between PL spectra of LED pumped spin-coated ErQ_3 and laser pumped spin-coated ErQ_3 .

plex target to achieve by solution processing. This is due to many causes, such as the need for full compatibility between the solvents used for dissolving materials, in order to avoid that the upper layer deposition damages the layers beneath. Another issue to consider is related to the high temperatures involved in the ErQ₃ solution processing, that preclude the use of most polymers whose electrical properties are modified at temperatures higher than 120 °C. Our preliminary experiments are focusing on OLED structures involving ErQ₃ as active layer and blue emitting small molecules, such as α -NPB (N,N'-Bis(naphthalen-1-yl)-N,N'-bis(phenyl)benzidine and oxadiazole-carbazole (6,4),³⁰ as charge transport layers. Blue emission from these compounds is studied for its possible energy coupling with quinoline, that strongly absorbs up to 430 nm. In such a way, the lost electrical excitation, due to the undesired charge recombination in the transport layers, can be partially recovered as optical excitation. We have indeed verified that low coherence sources with broad luminescence can be very efficient excitation sources for ErQ₃.

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