

## ENERGY TRANSFER AND EMISSION PROCESSES IN SPIN-COATED EUROPIUM (III) ORGANIC LIGHT EMITTING DEVICES

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### INTRODUCTION

Thin films organic light emitting devices (OLEDs) are currently the focus of substantial research effort due to potential application in the flat panel display industry [1]. Organic light devices consist of one or several vacuum deposit and/or spin-coating layers sandwiched between anode and cathode. Transparent anode is done from an indium - tin oxide (ITO) on a glass substrate. The cathode is made-up from a low work function metal. During measurement a bias voltage is applied between the two electrodes, electrons and holes are injected into the organic layers. Full color displays require pure red, green and blue emission. The recombination of these holes and electrons generates excited states of the fluorescent polymers or organic fluorescent dyes or organometallic compounds. The obtained energy during recombination is enough for excitation of molecules to singlet ( $S_1$ ) and triplet ( $T_1$ ) states. Population of these levels is determinate by statistic spin factors (1:3). It is the reason why the internal quantum efficiency of OLEDs is limited to 25% [2]. Nevertheless, pure emission colors from conjugated polymers or organic dyes are difficult to obtain because their luminescence half-bandwidths is about 80 - 150 nm.

In contrast to organic chromophores, lanthanide chelates have very sharp emission spectra. Fluorescence of lanthanide complex with organic ligands is based on intermolecular energy transfer from the triplet state of the ligand to the 4f energy states of the metal ion. The theoretical internal quantum efficiency is principally not limited. Emission bands are extremely sharp and the quantum efficiency of photoluminescence is high.

### EXPERIMENT

Molecular structure of the organic compounds used in devices is shown in Fig. 1. The poly(N-vinylcarbazole) (PVK) (trade name Luvican, provided by Basf) was purified by dissolving in chloroform and re-precipitating it in methanol six times. The powder was then re-dissolved in solution of tris-(tiophenyltrifluoromethylacetyl-acetonate)(phenanthroline) - europium(III) ( $\text{Eu}(\text{TTA})_3(\text{phen})$ ) in chlorobenzene. Concentration of  $\text{Eu}(\text{TTA})_3(\text{phen})$  was 2% and 5% ( $\text{PVK}2\text{Eu}(\text{TTA})_3$  and  $\text{PVK}5\text{Eu}(\text{TTA})_3$  respectively). Layers from 0.05  $\mu\text{m}$  to 1  $\mu\text{m}$  thick were cast onto glass (for absorption investigations), mica

disk with diameter 20 mm (for photoluminescence measurements (PL)) or ITO (for electroluminescent investigations (EL)).

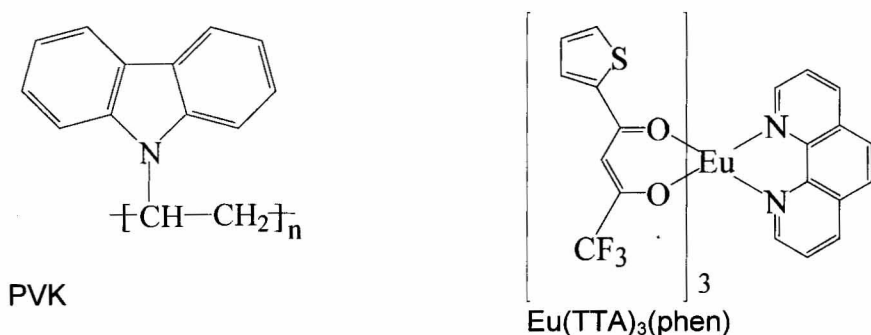


Figure 1. Molecular structure of organic materials used in the devices

The samples were dried in room temperature for 1 hour in vacuum of  $7 \times 10^{-4}$  Pa. The low work function electrodes (Ca, Al) were thermally evaporated through shadow mask at a pressure of  $5 \times 10^{-3}$  Pa. Light - emitting devices diagram is shown in Fig. 2.

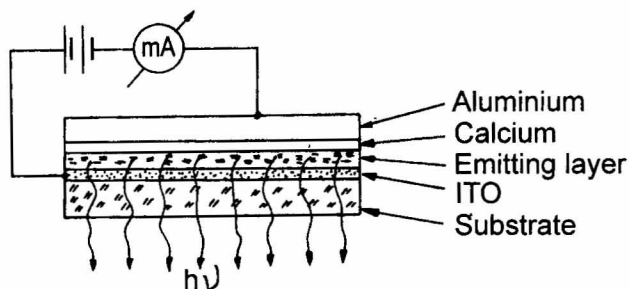


Figure 2. Light - emitting devices diagram

Photoluminescence (PL) measurements were carried out in an air. Sample temperature was 292 K. The sample was excited by 75 watt Xenon arc lamp installed in a high intensity illumination system with a monochromator. The photoluminescence and electroluminescence intensity was monitored using the spectrograph connected to the LN/CCD-1024E camera (chip format 1024 x 256, spectral range: 190 nm-1080 nm). The CCD camera is also liquid nitrogen cooled. It is connected to temperature controller, which is necessary to stabilise work temperature of the camera (from 143 K to 203 K). The resolution of the system depends on variety of factors including grating type, binning operation and slit widths. For these measurements it was set to give resolution of 4 nm. The spectra were numerically calibrated with respect to wavelength and intensity. Absorption spectra were measured

using Spectrophotometer UV-2401PC (Shimadzu Scientific Instruments). The resolution was 1 nm.

## RESULTS

The absorption spectra of thin films of PVK and PVK2Eu(TTA)<sub>3</sub> and PVK5Eu(TTA)<sub>3</sub> are almost identical (see Fig. 3). The absorption spectrum of Eu(TTA)<sub>3</sub>(phen) has maximum associated with transition from S<sub>0</sub> to S<sub>1</sub> at c.a. 350 nm. It is in the same region like absorption of S<sub>0</sub> to S<sub>1</sub> in PVK.

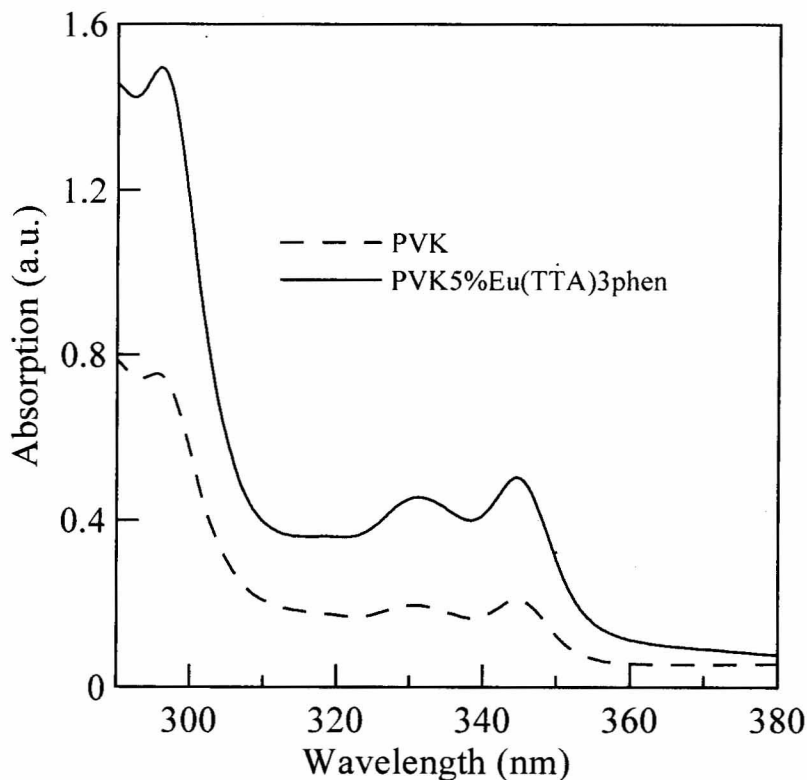


Figure 3. Absorption spectra of PVK and PVK5Eu(TTA)<sub>3</sub>phen thin films measured in room temperature.

Photoluminescence (PL) spectra of PVK, PVK2Eu(TTA)<sub>3</sub> and PVK5Eu(TTA)<sub>3</sub> are shown in Fig. 4. In PL spectra it was observed weak blue fluorescence of the PVK and strong red fluorescence of the Eu(TTA)<sub>3</sub>(phen).

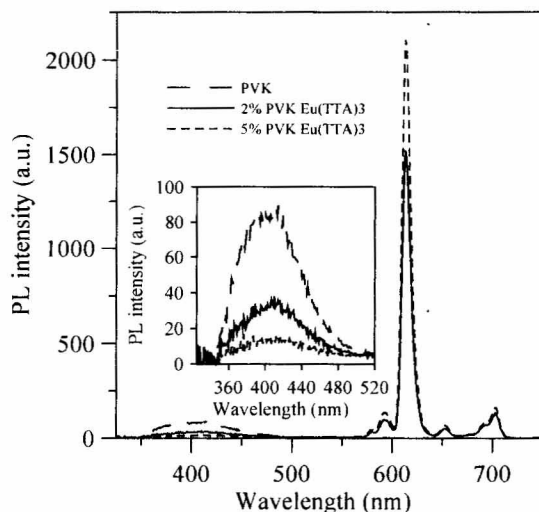


Figure 4. PL in PVK, PVK2Eu(TTA)<sub>3</sub> and PVK2Eu(TTA)<sub>3</sub> thin films after excitation by Xe 75W lamp (286nm), at room temperature.

The PL spectra are almost independent of the wavelength of excitation. In this spectrum one can see a broad maximum at c.a. 410 nm associated with excimer fluorescence of PVK. The sharp and more intensive red fluorescence maximum at c.a. 614 nm is connected with transition from  $5D_0$  to  $7F_2$  levels  $\text{Eu}^{3+}$ . Fluorescence of  $\text{Eu}^{3+}$  is independent of excitation wavelength. The reason is that excited states of  $\text{Eu}^{3+}$  are formed by energy transfer from PVK. Energy transfer from PVK to  $\text{Eu}^{3+}$  is shown in Fig 4. When the concentration of  $\text{Eu}(\text{TTA})_3$  increases, the intensity of PVK fluorescence decreases while the intensity of  $\text{Eu}(\text{TTA})_3$ phen fluorescence increases.

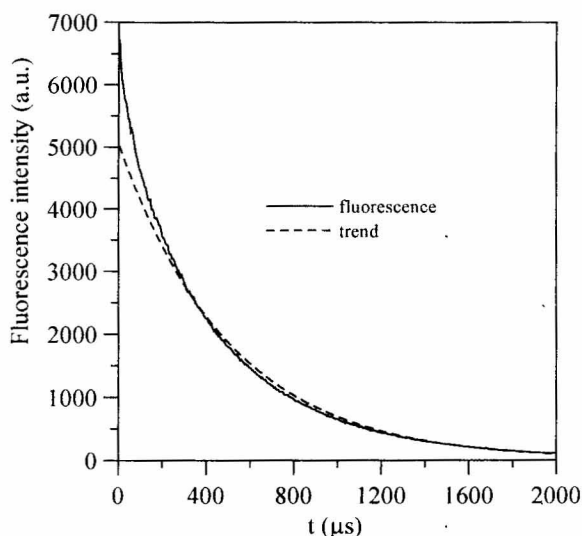


Figure 5. Kinetics decay of fluorescence of PVK5Eu(TTA)<sub>3</sub>phen after excitation 340 nm. The decay time is equal to c.a. 502  $\mu\text{s}$ .

The kinetics of red fluorescence of PVK5Eu(TTA)<sub>3</sub>phen after excitation at 340 nm is shown in Fig. 5. The decay time ( $\tau_{PL}$ ) is equal to c.a. 500  $\mu$ s. This  $\tau_{PL}$  is similar to  $\tau_{PL}$  of Eu(TTA)<sub>3</sub>(phen) in another polymers (particularly in polymethylmethacrylate (PMMA)) [3]. The Fig. 5 shows that immediately after pulse excitation fluorescence kinetics rate decay is faster then at the end of the process. It may be connected with the concentration quenching.

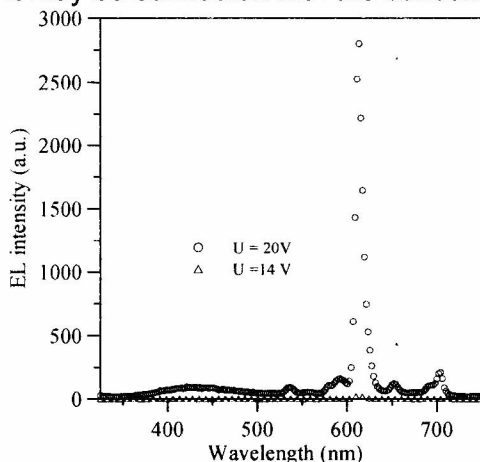


Figure 6. Electroluminescence of PVK 5Eu(TTA)<sub>3</sub>phen thin film at room temperature.

Electroluminescence (EL) spectrum of PVK5Eu(TTA)<sub>3</sub>phen is shown in Fig. 6. EL spectrum is composed of weak fluorescence of PVK and strong, red fluorescence of Eu(TTA)<sub>3</sub>phen. The ratio of Eu(TTA)<sub>3</sub>phen to PVK for EL intensities is greater then the same ratio for PL intensities. It is probably related with different mechanisms of PL and EL. Current density-voltage and EL intensity-voltage characteristics of ITO/PVK5EU(TTA)<sub>3</sub>phen/Ca/Al are shown in Fig. 7. From 13V it was observed fast increase of EL intensity and current.

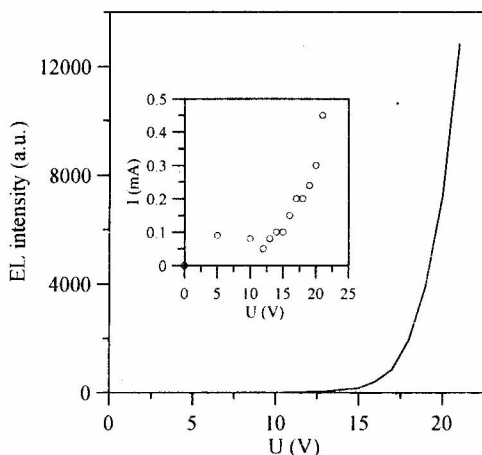


Figure 7. Current and EL intensity-voltage of PVK 5Eu(TTA)<sub>3</sub>phen thin film measured at room temperature.

## DISCUSSION

Fluorescence of the PVK decreases with increasing concentration of  $\text{Eu}(\text{TTA})_3(\text{phen})$ . It is probably associated with Forster energy transfer of electronic excitation from  $S_1$  state of PVK to Eu complex. In the EL spectra only narrow red emission of  $\text{Eu}(\text{III})$  was observed. The overlap integrals of donor fluorescence and absorption of acceptor in the investigated system are similar to these integrals in the system: poly(2-(6'-cyano-6'-methylheptyloxy)-1,4-phenylene) (CN-PPP) + 5% tris(dibenzoylmethane)(monophenanthroline) $\text{Eu}(\text{III})$  ( $\text{Eu}(\text{dbm})_3(\text{phen})$ ). The quenching intensity fluorescence of polymers in these systems is similar [4]. Probably also the quenching mechanism (Forster energy transfer) is the same.

The reason of different mechanisms of excited states formation in PL and EL is that in carriers recombination processes it is involved not only PVK but also  $\text{Eu}(\text{TTA})_3(\text{phen})$ . Excited states  $S_1$  and  $T_1$  of  $\text{Eu}(\text{TTA})_3(\text{phen})$  are direct as a result of recombination processes. Intersystem crossing  $S_1 \rightarrow T_1$  and intermolecular energy transfer  $T_1 \rightarrow D_1$  with quantum yield equal 1 produced excited states  $5D_0$  of  $\text{Eu}^{3+}$ . The quantum yield of  $5D_0 \rightarrow 7F_6$   $\text{Eu}(\text{TTA})_3(\text{phen})$  in polymer films is equal 0.7 [3,5]. It is the reason of high red electroluminescence intensity in the investigated system. The optimization of the thickness of film and concentration of luminophore could further increase electroluminescence properties of the device.

## REFERENCE

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