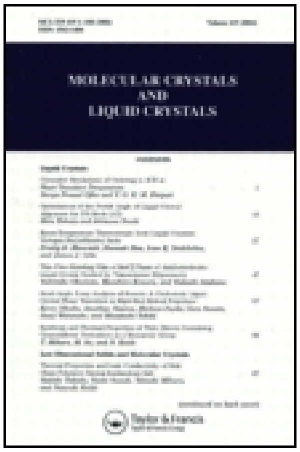

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Photo- and Electroluminescence of Doped Polymers in Langmuir-Blodgett Structures

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Light emitting diodes consisting of molecular-doped polymeric LB films with alternating electron-transport and hole-transport emitting layers are first described. Electroluminescent cells were prepared using standard ITO and Mg/Ag electrodes. PMMA/PBD (1:3) composition was used to form the electron-transport layers (I). The hole-transport one (II) was formed from PVK/TPB (3% mol.). Three cell types have been studied. Two of them had the same structure ITO/II(50 nm)/I(50 nm)/Mg/Ag but were prepared using different methods: spin-coating and LB technique. The third cell type had a multilayer LB structure: ITO/I(10 nm)/II(4 nm)/I(10 nm)/II(4 nm)/I(4 nm)/II(10 nm)/Mg/Ag. Considerable distinctions were observed in electroluminescence spectra of spin-coated and LB structures. Possible reasons for those distinctions are discussed. The multilayer LB structure was one decimal order more stable in air than the bilayer one.

Keywords: organic luminophors; polymers; photoluminescence; electroluminescence; light emitting diodes

INTRODUCTION

Organic light emitting diodes (LEDs) based on thin-film functionalized polymeric materials(1) attract recently the ever-encreasing attention due to they are materials of promise for application in flat colour displays. One prospective ways of LEDs parameters improvement is to develop multilayer structures consisting of doped polymers(2,3) and to use the Langmuir-Blodgett (LB) technique for preparation of blocking, emitting, transport and transport-emetting layers(4-11). Successful attempts to prepare organic LEDs with alternating transport and emitting layers have been described in(11,12). In this work, LEDs containing multilayer structures consisting of molecular-doped polymers LB films with alternating electron-transport and hole-transport layers are first described.

Experimental and discussion

Electroluminescent cells were prepared using a transparent In_2O_3/SnO_2 (ITO) electrode having the surface resistance 18 Ω/□ and a metallic Mg/Ag one. Poly(methylmethacrylate) (PMMA) doped by 2-(4-biphenylyl)-5-(4-amylphenyl)-1,2,4-oxadiazole (PBD) at a ratio of 1:3 (in what follows, the composition I) was used to form electron-transport layers (ETL), while hole-transport ones (HTL) were formed of poly(9-vynilcarbazole) (PVK) doped by 3% mol. of tetraphenyl-butadiene (TPB) (composition II).

Three cell types were studied. In the first case, the polymeric layer consisted of an about 50 nm thick PVK+TPB film applied onto ITO from a toluenic solution (C=1% by mass.) by the spin-coating method and a PMMA+PBD film applied onto heat-treated first film from a chloroformic solution (C=0.5 % by mass.) using the same method. The total film thickness of cell 1 was about 100 nm. The cell 2 was similar to the cell 1 in the composition but was constructed from monomolecular films using the LB technique. In the third cell type, the polymeric functional layers included alternating films of **I** and **II** compositions formed from LB monolayers. The electroluminescent cell structure consisted of ITO(150 nm)/**I**(10 nm)/**II**(4 nm)/**I**(10 nm)/**II**(4 nm)/**I**(4 nm)/**II**(10 nm)/Mg/Ag (200 nm) (cell 3) (Fig.1).

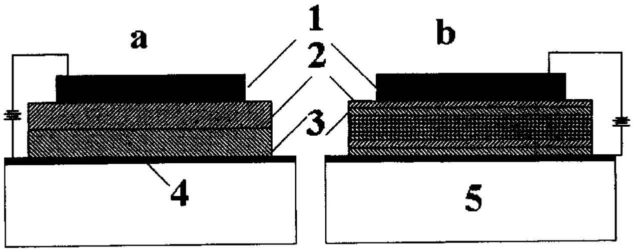

FIGURE 1 Structure of the bilayer (a) and multilayer (b) cells: 1 - Mg/Ag, 2 - ETL, 3 - HTL, 4 - ITO, 5 - glass substrate.

Photoluminescence (PL) spectra of all cells taken under excitation by λ = 350 nm have a maximum at 440 nm corresponding to TPB fluorescence spectrum. It is seen from Fig.2 that PL and electroluminescence (EL) spectra are essentially coincident for the cell 1 while EL spectra of LB structures (cells 2, 3) differ considerably and are shaped as a wide spectrum in 350 - 700 nm range. The computerized deconvolution of EL spectra for the multilayer LB structure (cell 3) using Gaussian lineshapes allowed to discriminate five overlapping luminescence bands with maxima at 400, 440, 488, 560 and 648 nm. The EL spectrum of bilayer LB structure has the same parameters but the relative integral intensity of the 560 nm band is 1.3 times lower.

Analysis of literature data as well as of TPB and PBD PL spectra measured by use in diluted solutions, in polycrystalline state and in LB films, and of excitation spectra with luminescence recording on main EL bands wavelengths allowed to identify them partially. The 440 nm maximum is

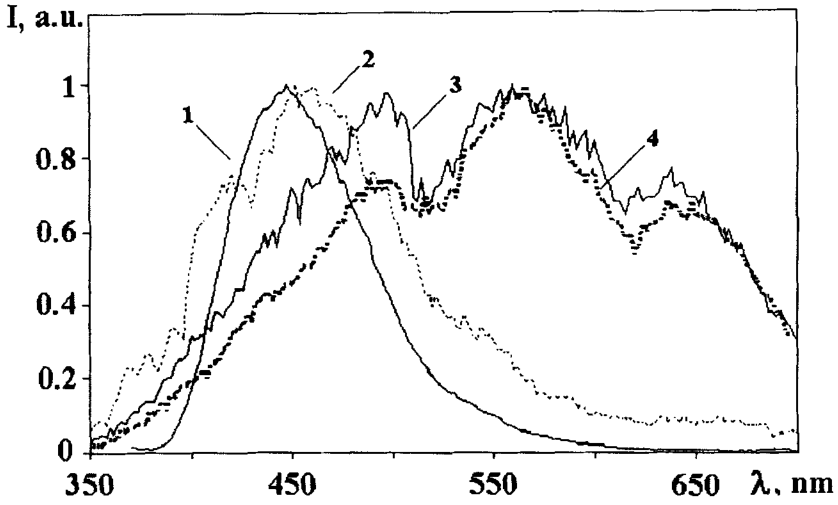

FIGURE 2 PL - (1) and EL (2) spectra of a spin-coated film; EL spectra of bilayer (3) and multilayer (4) LB structures.

related to $S_1 \rightarrow S_0$ transition in TPB molecule. The spectrum with a maximum at 488 nm can be explained by exiplexes formation between carbazole groups of PVK and chromophoric fragments of PBD. The excitation spectrum of 640 nm luminescence (Fig.3) coincides with that of PBD absorption in diluted toluenic solution, thus allowing to ascribe the 648 nm EL band to molecular or mixed PBD aggregates formed on interlayer boundaries. This is confirmed by the appearance of the band with λ_{max} = 640 nm in PL spectra and its gradual intensity growth as the interlayer boundaries number increases. A band with a maximum at 560 nm is observed in EL spectra of LB structures. That band has been revealed neither in all PL spectra under investigation nor in EL spectra of spin-coated structures. We have associated the emission with a maximum at 560 nm with a triplet PBD state(14) that is not occupies at the photoexcitation, perhaps due to a low inter-system crossing rate, but may be occupied easily in the course of electron-hole recombination(15). The

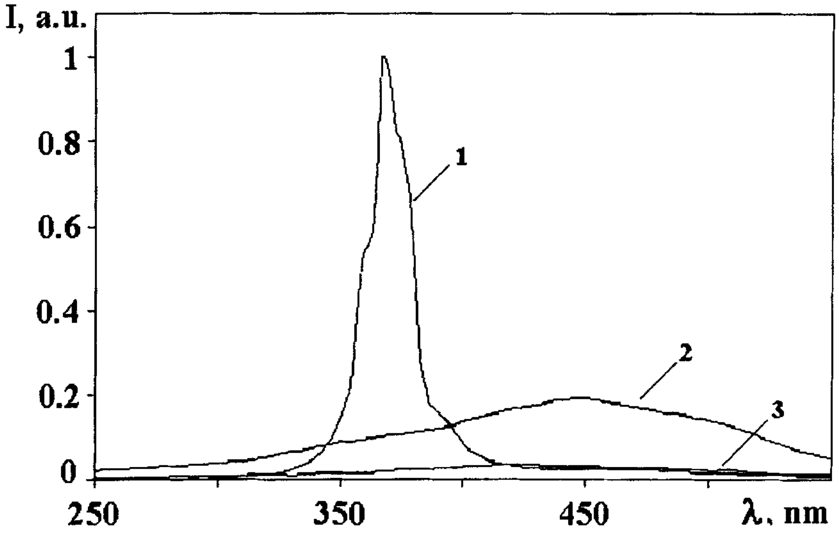

FIGURE 3 Photoluminescence-excitation spectra of a multilayer LB structure with detection wavelength at: 1 - 640 nm; 2 - 470 nm; 3 - 560 nm.

formation of triplet exciplexes on LB layer interfaces is among possible mechanisms responsible for that emission. This assumption requires of course a further investigation.

All obtained LEDs exhibit electroluminescence under applied voltage of 10 - 14 V at the current density about 100 mA/cm^2. The multilayer LB structure is found to be a decimal order more stable (over 60 h in air at room temperature) than the bilayer one. This fact can be explained by the presence of several interlayer boundaries acting as barriers for charge transport and favour the elimination of disbalance between holes and electrons. Moreover, a substantial number of alternating electron-transport and hole-transport layers enhances the probability of local tunneling channels formation between layers and hinders the direct breakthrough of the dielectric organic layer.

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