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Electroluminscence in Ether-substituted Poly(phenylenevinylenes)

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The electroluminescent devices presented in this paper were fabricated using poly[1,4-phenylene-1,2-di(4-phenoxyphenyl) vinylene] as a light-emitting layer; green emission was observed with maximum wavelength at 530 nm and emission energy 3.8×10^{-4} J cm^{-2}, achieved at current density 41.6 mA cm^{-2}.

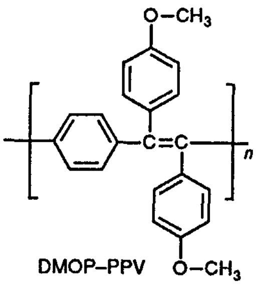
Electroluminescent (EL) devices based on organic thin layers arouse great interest because of their possible application as large area light-emitting displays.[1–4] Scientists are interested in making semiconductor devices out of soluble organic polymers because these materials offer important advantages over conventional inorganic semiconductors. Polymers are easier to process and fabricate into different shapes and they form flexible layers. The advantage of organic EL devices is also their cheapness.

The organic EL device has a 'sandwich-type' structure, in which a thin (*ca.* 1000 Å) organic emitting layer is located between two electrodes (one, hole-injecting and the other, electron-injecting). In polymer layers usually only the holes are mobile, so light generation occurs near the electron-injecting electrode surface when a DC voltage is applied, owing to the recombination of electrons and cation-radicals. A transparent layer of indium/tin oxide (ITO) is usually used as a hole-injecting electrode, and metals (Al, Mg, Ca) as electron-injecting electrodes. Different organic materials were used as a light-emitting layer.

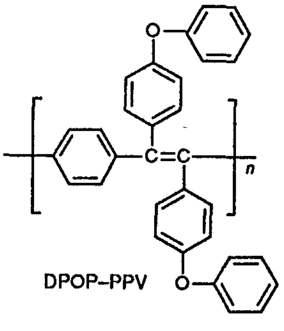
Recent publications on EL phenomena in organic materials display great interest in the use of conjugated polymers, such as substituted poly(phenylenevinylenes) (PPV) as light-emitting layers.[2–4] The important advantage of these polymer systems is the possibility of emission-wavelength tuning during synthesis. Burn and coworkers[3] showed the possibility of chemical tuning of emission wavelength in substituted PPV from 591–508 nm. The conversion efficiency β (photons emitted *versus* electrons injected) of their device with configuration ITO/PPV/Al is equal to $2\times10^{-2}\%$. β grows to *ca.* 1% at drive voltage *ca.* 3 V when polyaniline (PANI) is employed as a hole-injecting electrode and Ca as an electron-injecting electrode.

Kido and coworkers[5] used a double-layer structure with a luminescent metal complex, 8-hydroxyquinoline aluminium (Alq_3), and a hole transporting layer, poly(methylphenylsilane) (PMPS). The use of the hole transporting layer for hole injection from the electrode into the emitting layer significantly lowers the drive voltage to a value of a few volts.[6] When DC voltage is applied to the device described EL is observed with emission maximum at 510 nm. Green emission with a luminance of over 1000 cd m^{-2} was achieved at a current density 100 mA cm^{-2}.[5] This value of luminance corresponds to an emission energy of 8.7×10^{-4} J cm^{-2} and in this case $\beta = 0.32\%$ (photon $electron^{-1}$). The value of energy conversion efficiency is equal to 0.28%. The EL spectrum of the cell is identical to the photoluminescence (PL) spectrum of Alq_3, indicating that the EL originates from Alq_3. Luminescence was negligible for the cell without PMPS. This indicates that the PMPS layer enables hole transport and blocks electron injection, thus controlling the recombination process.

In this paper we present the results of investigation of PL and EL in substituted PPVs, namely poly[1,4-phenylene-1,2-di(4-phenoxyphenyl)vinylene] (DPOP-PPV) and poly[1,4-phenylene-1,2-di(4-methoxyphenyl)vinylene] (DMOP-PPV). Electron transport characteristics of these polymers were published earlier.[8,9]



DMOP–PPV



DPOP–PPV

Thin films for measurements were prepared by casting PPV solutions in $CHCl_3$ on a glass substrate previously coated with an ITO layer or on the film of electrochemically-generated PANI. The second electrode of aluminium was deposited on the surface of the PPV film by vacuum thermal evaporation. EL and PL spectra were measured on a 'Hitachi M850' fluorimeter.

EL with emission maximum located at 530 nm and $\beta = 0.13\%$ in the device with configuration ITO/DPOP-PPV/Al was observed as DC voltage (20–40 V) was applied. The drive voltage in this case is more than published values, because of the greater value of the PPV-film thickness (*ca.* 3000 Å). Efficiency is strongly dependent on the electrodes employed. So, in our device with configuration PANI/DPOP-PPV/Al, the value of β equals 0.38% (photon $electron^{-1}$) and the value of energy conversion efficiency is equal to 0.32%. The EL spectra of the cell with configuration PANI/DPOP/PPV/Al is shown in Fig. 1. The intensity of EL is given in arbitrary units, but the emission maximum corresponds to energy 3.8×10^{-4} J cm^{-2} at current density 41.6 mA cm^{-2}. In DPOP/PPV films with addition of polar *o*-dinitrobenzene (*o*-DNB) the EL intensity decreases (Fig. 1, curve 2). It is known that molecules with high dipole moments quench luminescence; the dipole moment of *o*-DNB is 6 D. In the cell PANI/DMOP-PPV/Al, EL was absent. In Fig. 2 the PL spectra of DMOP-PPV and DPOP-PPV with and without addition of *o*-DNB are shown. The intensity of PL in DPOP-PPV with addition of *o*-DNB is lower than in pure DPOP-PPV. PL in DMOP-PPV is negligible. Thus, the efficiency of EL is directly connected with PL efficiency. This is one reason why no EL is observed in DMOP-PPV films. Another reason is connected with the peculiarity of the electronic transport in DPOP-PPV.

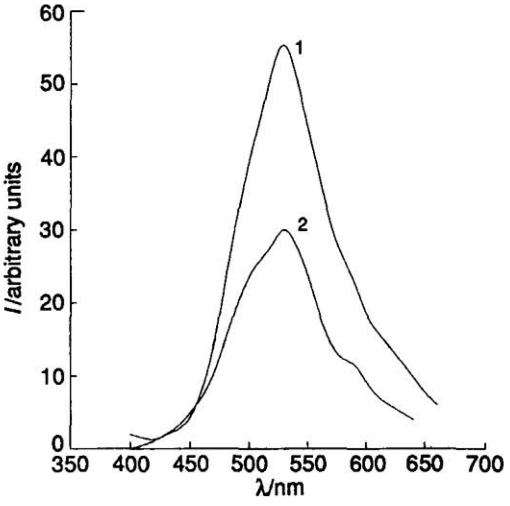
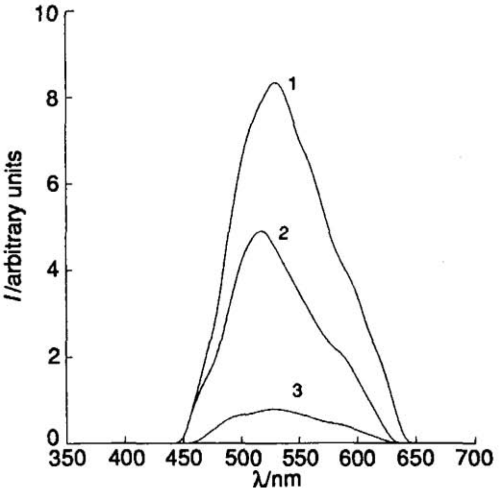


Fig. 1 EL spectra in DPOP-PPV films with (2) and without (1) addition of *o*-DNB



The higher EL efficiency in DPOP-PPV, in comparison with published values of efficiency in other EL layers entering the PANI/PPV/Al structure, is determined by the fact that in DPOP/PPV both holes and electrons are mobile.[8,9] In this case, the recombination of charge carriers occurs in the bulk of polymer with high luminescence yield. In other PPVs only the holes are mobile, and recombination occurs near the electron-injecting contact, the excited states of PPV being quenched on the metal surface. Efficiency in this case is low. It is interesting to note that the use of calcium as an electron-injecting electrode in comparison with an indium electrode increases the intensity of EL 200 fold.[2] We believe that the use of Ca as an electron-injecting electrode will also increase the emission intensity and conversion efficiency in the electroluminescent system using DPOP-PPV.

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