

Photo- and electroluminescence of new organic semiconductors

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ABSTRACT

The results of investigation of the luminescence under photo- and electroexcitation for four new compounds are presented. The spectral properties and photoluminescence are studied in ethanol, chloroform solutions and in films formed by thermovacuum deposition (TVD). The phosphorescence of compounds is investigated in ethanol at 77K temperature. The phosphorescence times of molecules are given.

The electroluminescence is obtained in multilayered structure ITO/PEDOT/NPD/L/Ca/Al. It is shown, that spectral region of the photoluminescence of TVD films and electroluminescence coincide. Relations of electroluminescence efficiency with molecule structure, photoluminescence quantum yield and possibility of thermally activated delayed fluorescence are discussed.

Organic semiconductors, spectral properties, photo- and electroluminescence, phosphorescence, OLED

INTRODUCTION

In organic LED based on small molecules emission of light occurs from singlet S_1 state usually. However in applied voltage field both singlet and triplet excitons are produced. Singlet excitons can undergo efficient fluorescent decay to the ground state, while triplet excitons decay to the singlet ground state nonradiatively as a rule. To increase the harvest of electroluminescence it is desirable to use both singlet and triplet excitons. It is possible owing to triplet to singlet up-conversion. This process is habited according to selection rules. But the prohibition is partially removed because of the spin-orbital interaction. In addition, this process is more likely the smaller S-T energy gap. As a result, both fluorescence and delayed fluorescence occur. The contribution of delay fluorescence into total luminescence of OLED has been observed many times¹⁻⁴.

In this paper we have investigated the spectral properties and luminescence for four new organic semiconductors in solutions and in film. To estimate the singlet - triplet gap the phosphorescence at 77K has been studied. The OLED structures have been fabricated and the results have been discussed within the framework of S_1 - T_1 energetic gap.

EXPERIMENTAL

The chemical structures of studied molecules are shown in fig.1. The absorption spectra investigated in chloroform solutions, fluorescence - in solutions and in films obtained by thermovacuum deposition (TVD). The absorption spectra have been recorded with spectrophotometer CM2203 (Solar, Belarus), fluorescence and phosphorescence spectra - with Varian Carry Eclipse. The quantum yield of fluorescence was determined by comparison with the standard, which was used as coumarin 102 with a quantum yield in ethanol of 0.955.

The electroluminescent (EL) properties were studied for simple sandwich structures ITO/PEDOT:PSS/NPD/L/Ca/Al. ITO – indium and tin oxides deposited on a glass substrate – served as the anode in these sandwich structures. PEDOT:PSS (2.8 wt.% aqueous solution of poly(3,4-ethyldioxythiophene: poly(styrenesulfonate) (Aldrich)) was deposited on ITO by the spin coating method with a speed of 4000 rpm for 30 s and dried at a temperature of 120°C. This substance was used not only to smooth the anode surface, but also to emit holes. NPD – N-4,N-4'-di(naphthalene-1-yl)-N-4,N-4'- diphenylmethane-4,4'-diamine – was deposited by the TVD method. This compound in sandwich structures transports holes. Ca, protected from oxidation by an Al layer, served as the cathode. Ca and Al were also deposited by the TVD method. Before the deposition of layers, the substrates with ITO were carefully washed in aqueous

ammonium solution with subsequent ultrasonic treatment in acetone and isopropyl alcohol. In the final stage, the substrates were treated with oxygen plasma using an ATTO system (Diener, Germany). Then all operations were carried out in a DELLIX glove box (China) in a dry nitrogen atmosphere with water and oxygen contents on the level of several ppm. The rate of deposition of organic layers was 0.2 Å/s, and that of the cathode was 2 Å/s in working volume vacuum of 10–5 mbar. The film thickness was controlled by a quartz sensor in the deposition process and was measured for reference substrates by a KLA-Tencor MicroXAM-100 profilometer. The electroluminescence characteristics were measured using the bench comprising a Keithley 237 high-voltage source measure unit and an AvaSpec 2048 fiber optic spectrometer. The current-voltage and voltage-brightness characteristics and the spectral composition of radiation were simultaneously measured. The electroluminescence brightness was calibrated against readings of a Konica Minolta LS-110 luminance meter.

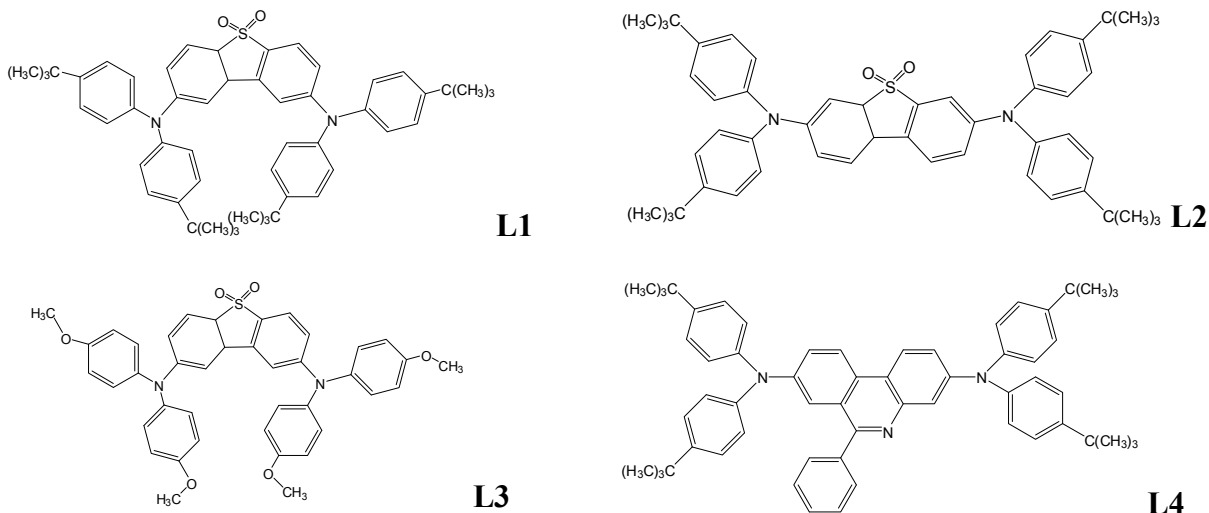


Fig.1 Chemical structure of the molecules

RESULTS AND DISCUSSION

The absorption and emission spectra of these compounds in chloroform solutions are shown in fig.2. It is seen that the emission of molecules having the same central fragment lies almost in the same spectral region 548 - 552 nm. The spectral characteristics of molecules in solutions of chloroform are given in Table.

Luminescence at low temperatures has been studied for L3 and L4. When the temperature is lowered from 297 K to 77 K, the fluorescence intensity increases manyfold, and the spectrum shifts to the blue region. At a temperature of 90-77 K the intense band of phosphorescence appears in the redder region. The phosphorescence decay time is 113 ms for L3 and 770 ms for L4. The mutual arrangement of the fluorescence and phosphorescence spectra at $T = 77$ K is shown in fig. 3. The energy gap between the maxima of the fluorescence and phosphorescence spectra at 77 K is 0.14 eV for L3 and 0.27 eV for L4. From these data it follows that the triplet–singlet conversion for L3 is more probable than for L4.

Electroluminescence of molecules is investigated in a sandwich structure ITO/PEDOT:PSS/NPD/L/Ca/Al. All compounds L1-L4 emit in the applied voltage field. Practically complete coincidence of the electroluminescence and photoluminescence spectra in films confirms that the radiation of the OLED structures belongs precisely to the molecules (fig.4). Despite the fact that the compounds have a similar structure and electroluminescence was studied under identical conditions, the electroluminescence characteristics differ markedly. Fig. 5 shows the brightness dependence of the electroluminescence on the voltage. Thus, at a voltage of 8 volts, the brightness of the OLED structure with L3 is 2500 cd/m² whereas for L4 only 60 cd/m². Of course, many factors effect on the electroluminescence efficiency, such as the energy balance of HOMO and LUMO levels of all components of OLED, and current conductivity, etc. But here we see the correspondence between the intensity of the electroluminescence and the energy gap between the S_1 and T_1 states. Thus, it can be assumed that the bright luminescence of L3 in the OLED structure is also due to the additional population of the singlet state via triplet-singlet thermal conversion.

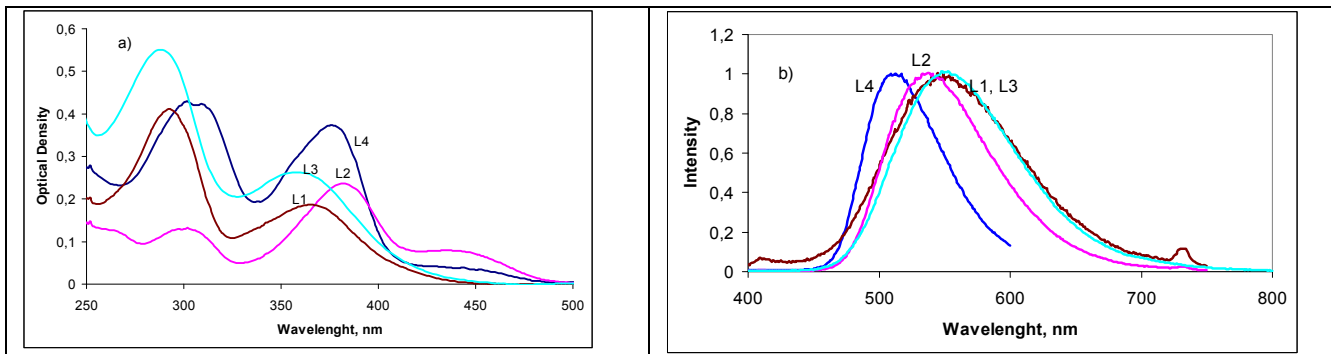


Fig.2. a -Absorption spectra of the compounds L1-L4 in chloroform. Concentration is 10^{-5} M, b - fluorescence spectra..

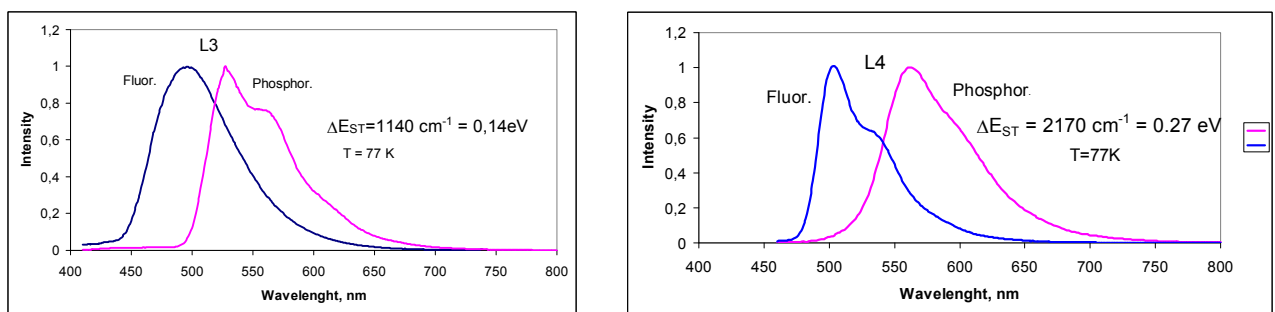


Fig.3. Spectra of fluorescence and phosphorescence of the compound L3 and L4

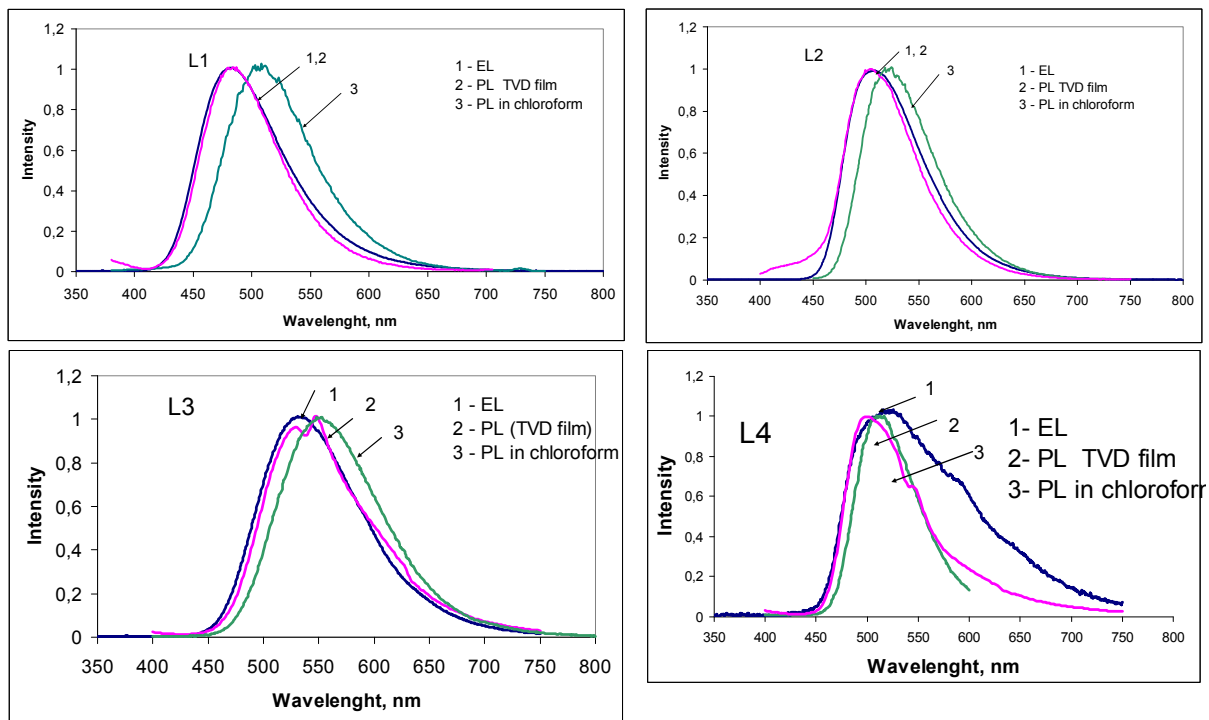


Fig.4. Electroluminescence (1) and photoluminescence spectra in TVD films (2) and in chloroform (3)

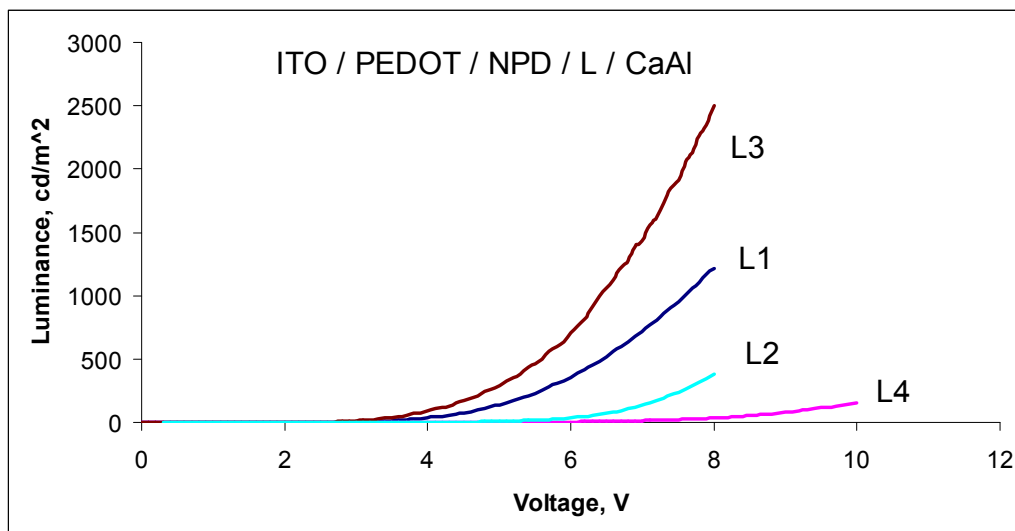


Fig.5. Brightness characteristics of the OLED structures.

Table 1. Spectral characteristics of the compounds in chloroform

Compound	λ_{abs} , nm	λ_{fl} , nm	Stokes shift, cm^{-1}	ϕ_{fl}
L1	366	548	9070	0.18
L2	382 + 440	540	4210	0.83
L3	358	552	9820	0.24
L4	377 + 440	512	3200	0.18

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