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# Electroluminescence of Polymer Nanocomposites

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The electroluminescence of J-aggregates was detected in polymer systems doped with cyanine dye molecules. J-aggregate/polymer composites exhibiting intense absorption band with a maximum in the red range were developed on the base of polyimides and a copolymer formed from phenylacetylene and 4-methylcoumarin-4-pentynoate. Efficient electrolumunescence was revealed in these systems. It was found out that J-aggregates play an active role in charge carrier transport in the composite materials.

*Keywords:* electroactive polymers; J-aggregates; nanocrystals; electron-hole transport; polymer LEDs

## INTRODUCTION

Electroactive polymers exhibiting intense electroluminescence (EL) have been considered promising candidates for large-area applications due to their good mechanical properties and easy processing. Polymer/nanoparticle composites are of particular interest. We have found that electroluminescent cyanine dye associates, known as J-aggregates, may be formed at certain conditions in electron-hole conducting polymers. J-Aggregates are considered as organic nanocrystals with high nonlinear optical coefficients referring to intermediates in molecular composition between structurally ordered crystalline materials and single molecules[1-3]. They attracted great attention recently due to their potential application in high technology field, for instance, in modern optical communication systems [4].

## EXPERIMENTAL

Thiacarbocyanine dye used for the formation of crystalline phase was 3,3'-di(γ-sulfopropyl)-9-ethyl-5,5'-dimethoxythiacarbocyanine pyridinium (CD) (Fig. 1, (d)). This has well-determined polarographic half-wave redox potentials relative to a saturated calomel electrode: $E_{1/2}^{red}$ = - 1.32 V, $E_{1/2}^{ox}$ = +0.68 V [5].

Aromatic polyimide (API) prepared from 9,10-bis(m-aminophenylthio)-anthracene (BPTA) and 1,3-bis(3,4-dicarboxyphenoxy)benzene dianhydride [6] and copolymer (CP) formed from phenylacetylene and 4-methylcoumarin-4-pentynoate (5 wt.%) were used as electroactive binders. These polymers are soluble and form transparent films of excellent quality [7-10]. The experimental details on the manufacture of polymer/J-aggregates light-emitting diodes (LEDs) described elsewhere [7].

## RESULTS AND DISCUSSION

The absorption spectra of the CD in chloroform solution ($\lambda_{max}$ = 590 nm) and the polymer/J-aggregate composites ($\lambda_{max}$ = 660 nm) are shown in Fig. 1(a). Selective exposure to light of 550 nm wavelength the API film doped with CD brought about the appearance of CD PL band with $\lambda_{max}$ = 617 nm (Fig. 1(b) (doted line)). At the excitation of the API/J-aggregate specimen with the radiation of $\lambda$ = 610 nm, i.e. in the range of J-aggregate absorption, an intense narrow emission band with $\lambda_{max}$ = 665 nm belonging to this nanocrystalline phase (Fig. 1(b), (solid line)) was observed. Fig. 1(c) shows the EL spectra observed in three different LEDs. The intrinsic EL of the pure API (dashed line) had a maximum at 495 nm. Devices with the CD doped API layers exhibited an emission band with a maximum at 617 nm (doted line). The API/J-aggregate layer had an intense and narrow emission band with $\lambda_{max}$ position at 675 nm (solid line). In the latter case, no emission of free (non-aggregated) dye molecules was observed despite their residual presence in low concentration. The major problem in explaining the J-aggregate EL was the limited information available to use in assessing the redox potentials of these nanocrystalline particles in the polymer binder. The only published data concern photoinduced oxidation of a mixture consisting of the CD molecules and their J-aggregates adsorbed on the surface of a semiconductor [11]. It was demonstrated that the J-aggregates act as a component which reduces the photooxidation of free dye molecules in the mixture, i.e. oxidation potential level for cyanine dye aggregates $E^{ox}_{1/2}$ (J-aggregate) should lie higher than $E^{ox}_{1/2}$(CD). It was also inferred that the oxidation potential levels ( $E^{ox}_{1/2}$ ) for CD dye aggregates and cyanine dye molecules are

closely positioned. One would presume that the relative location of these levels for a polymeric matrix containing CD molecules and J-aggregates would also be close. The energy gap ($\Delta E_g$) between the HOMO and LUMO of the J-aggregates may be approximated from the low-energy edge of their absorption band in the API layer (Fig. 1a, solid line). This value was found to be $\Delta E_g \cong 1.49$ eV. Therefore, the $E^{red}_{1/2}$ for J-aggregates is located below that of the dye molecules ($E^{red}_{1/2}$ (CD) = 3.3 eV).

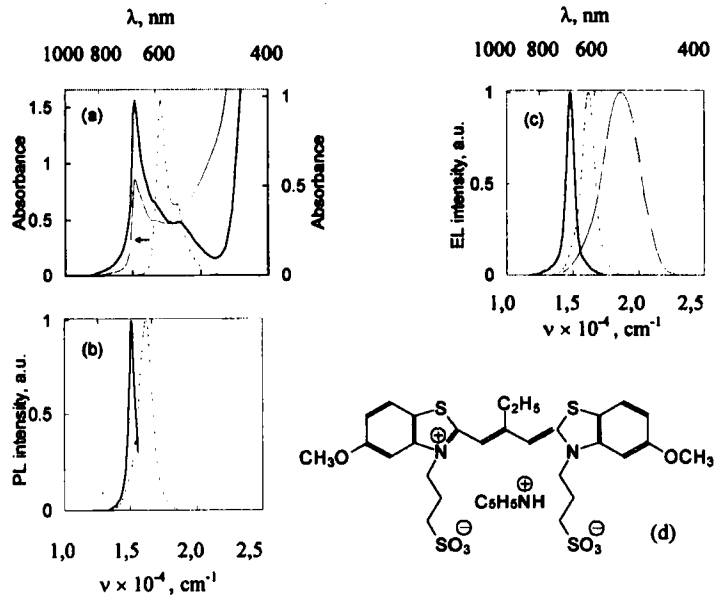


FIGURE 1. Absorption and emission spectra of CD and API/J-aggregate. (a) Absorption spectra of CD in chloroform ($10^{-4}$M) (doted line) and J-aggregates in API (solid line) and CO (dashed line) layers. (b) PL of CD (15 wt %) in API layer at 550 nm excitation and J-aggregates in API at 610 nm excitation (solid line). (c) EL of pure API (dashed line), CD (15 wt %) in API (doted line) and J-aggregates in API (solid line). (d) Chemical structure of CD.

The inference drawn is that the J-aggregates should behave as exciton energy absorbers in the composite, in accord with our experimental results.

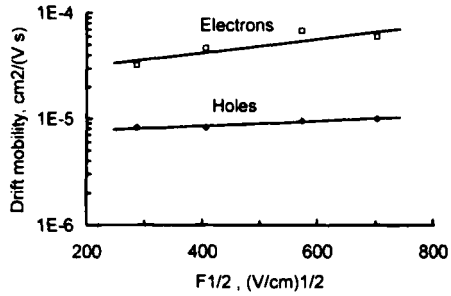


FIGURE 2. Time-of-flight measurements of electron and hole mobilities vs. the square root of the electric field in API/J-aggregate composites.

Response time characteristics were obtained by measuring the EL light waveforms. Rectangular voltage pulses of 100 μs duration were used. The API layer (d = 100 nm) had a lag time, $t_d \cong 7$ μs. The transport properties changed drastically in the presence of J-aggregates. No lag time was observed in API/J-aggregate films. At ambient temperature and electric field of $3 \times 10^5$ V $cm^{-1}$, the direct time-of-flight measurements of charge-carrier mobility (μ) (Fig. 2) gave high values for electrons and holes: $\mu_e = 6.7 \times 10^{-5}$ and $\mu_h = 10^{-5}$ $cm^2$ $V^{-1}s^{-1}$. These are ten times as much as for the pure API. It should also be noted that the electron mobility is higher than the hole mobility in API/J-aggregate layers.

In conclusion, the obtained results indicate an active role of J-aggregates in the charge-carrier transport for API/J-aggregate composites. Relative values of energy levels of the J-aggregates makes them effective exciton energy acceptors.

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