

Electroluminescence in Polymer/J-Aggregate Nanocomposites

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Abstract

Efficient electroluminescence (EL) was observed in a new type of electroactive organic-polymer composites based on cyanine dye J-aggregates. Such systems exhibit very narrow EL emission spectra, the position of which may be varied within the green-red range, by modifying the molecular structure of the dyes.

Introduction

In recent years, nano-size-component heterostructures have been the subject of widespread investigations. The interdisciplinary field of nano-scale materials command the attention of the scientists involved in basic research as well as in high tech development. These types of compounds and composites often exhibit exotic physical and chemical properties different from those observed in bulk materials. One of the main trends in this area is an advent of new functional nanocomposites leading to the use of the novel principles of device functioning.

Newly developed polymer composites based on nano-sized organic crystals - J-aggregates - is illustrative of some potential application of the nano-scale systems in plastic electroluminescent devices. Above all mention should be made of the most promising next-generation ultra-thin, flat, lightweight and low-power displays. The J-aggregates of cyanine dyes originally described more than sixty years ago¹, may be considered to be nanocrystalline compounds intermediate in molecular scale between structurally ordered crystalline materials and single molecules^{2,3}. Due to the variety of possible applications that these species have as crystalline organic components, they have become the subject of intense investigations. These molecular assemblies have coherently coupled transition dipole moments which give rise to high third order susceptibility, and are suitable for third harmonic generation. The saturable absorption of the J-aggregates allows passive Q-

switching and hence the design of sophisticated optical operating devices for modern optical communication systems⁴. These nanocrystalline species exhibit intense absorption and photoluminescence bands which are present in the visible or the near IR depending on the particular dye's used molecular structure. The distinguishing features of J-aggregates as opposed to non-aggregated dye molecules, are narrowing and red shift of both their long-wave absorption and luminescence bands. These properties are particularly useful for semiconductor diode laser techniques and information storage applications.

Results and Discussion

The ability of cyanine dye molecules (CDs) to form J-aggregates is determined by the chemical structure of the dyes. This factor also dictates the position of absorption and luminescence spectra as well as thermal stability of the nanospecies. CDs very readily form J-aggregates in water. Under specific conditions, some types of CDs give J-aggregates in certain macromolecular media including electroactive electron-hole conducting polymers⁵. Due to the small size of the nanocrystalline particles which are much smaller than the wavelength of visible light, no light scattering is observed in such polymer/J-aggregate composite layers. These composites combine the optical characteristics typical for organic crystals and the electronic properties of semiconductor polymers. In this report, it will be shown that polymer nanocomposites based on J-aggregates may be looked upon as alternative to novel light-emitting materials for flat plastic displays and various electroluminescent devices

The technique of polymer/J-aggregate composite formation is simple. It does not need to use any chemical components to initiate nanophase formation as opposed to some other nanocomposite manufacturing procedures.

Carbocyanine dyes used for the formation of crystalline phase were 3,3'-di(γ -sulfo-propyl)-9-ethyl-5,5'-dimethoxy-

thiacarbocyanine pyridinium (CD-1) and 3,3'-di(γ -sulfopropyl)-9-ethyl-5,5'-diphenyloxcarbocyanine pyridinium (CD-2) (Fig. 1). These have well-determined polarographic half wave redox potentials relative to a saturated calomel electrode: $E_{1/2}^{\text{red}} = -1.32$ V, $E_{1/2}^{\text{ox}} = +0.68$ V and $E_{1/2}^{\text{red}} = -1.4$ V, $E_{1/2}^{\text{ox}} = +0.94$ V, respectively. Aromatic polyimides (APIs) and specially synthesized copolymer (CO) were used as electroactive polymer binders. API prepared from 9,10-bis(m-aminophenylthio)anthracene (BPTA) and 1,3-bis(3,4-dicarboxyphenoxy)benzene dianhydride⁶ and copolymer⁷ (CP) coformed from phenylacetylene and 4-methylcoumarin-4-pentynoate (5 wt.%) were used as electroactive binders.

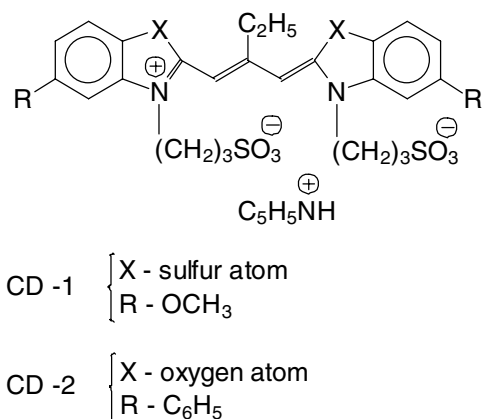


Figure 1. Chemical structures of cyanine dyes.

These polymers have been shown to be efficient electron and hole conductors⁵ and when spun from chloroform solutions form transparent films of high quality. For CD crystals (0.1 mg) and API or CO powder (1.0 mg) were dissolved in chloroform (150 μ l) at 60°C. The solution was left for 20 min at the temperature. Then cooled to 19°C and held at that temperature for 25 min. After warming to 60°C again, the procedure was repeated several times until the majority of dye molecules became associated into the nanocrystalline phase of J-aggregates. LEDs were then fabricated by conventional spin coating under ambient conditions, of the chloroform solutions containing the API and J-aggregates. It is worth noting that nanocrystalline phase formation continued some time in the dry layers. The nanocrystalline phases of CD J-aggregates exhibited higher stability in the binders. The LEDs consisted of a 100 nm thick API/J-aggregate composite layers sandwiched between transparent indium-tin oxide and Mg:Ag electrodes. The Mg:Ag electrodes were prepared by vacuum vapor deposition at pressures below 5×10^{-6} Torr. Intense EL belonging to J-aggregate nanocrystalline phase was observed from these samples, with quantum efficiency about 0.2 % and brightnesses over 100 cd/m² being measured at 7V. All measurements were carried at room temperature in air.

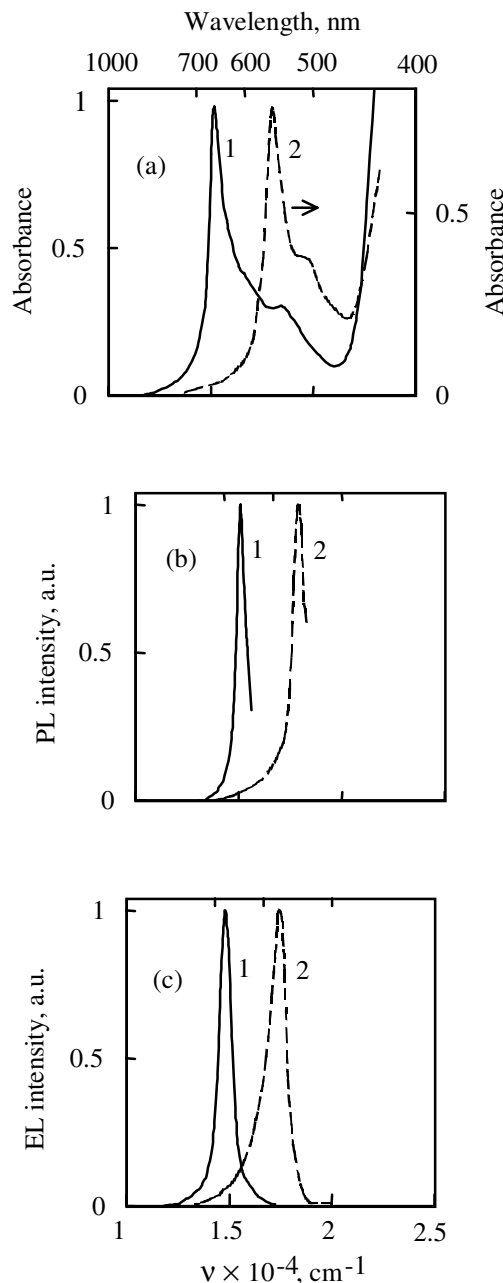


Figure 2 Absorption and emission spectra of CDs and API/J-aggregate (a) Absorption spectra of API/J-aggregate composites based on CD-1 (solid line) and CD-2 (dashed line). (b) PL of J-aggregates in API: for CD-1 - at 610 nm excitation (solid line), and for CD-2 - at 510 nm excitation (dashed line). (c) EL of API/J-aggregates based on CD-1 (solid line) and CD-2 (dashed line).

The absorption spectra of the polymer/J-aggregate composites based on the CD-1 and CD-2 had λ_{max} at 590 nm and 660 nm, respectively [Figure 2 (a)]. It is evident from the presence of shoulders on the high energy side of the J-aggregate peaks that low concentrations of other

components are present in the composites. The majority of these are dye molecules which remained free during the growth of J-aggregates. Excitation of the API/J-aggregate specimen with light of $\lambda = 610$ nm, i.e. within the J-aggregate absorption band of CD-1, brought about an intense narrow emission band with $\lambda_{\max} = 665$ nm, belonging to this nanocrystalline phase¹⁸ (Fig.2b, (solid line)). Very similar photoluminescent (PL) behavior exhibited API/J-aggregate composites based on the CD-2 when excited with light of $\lambda = 510$ nm, i.e. within the J-aggregate absorption band.

Figure 2c shows the EL spectra observed in the LEDs containing API/J-aggregate emission layers. Intense and very narrow emission bands were observed in composite layers containing CD-1 ($\lambda_{\max} = 675$ nm) and CD-2 ($\lambda_{\max} = 575$ nm) nanophases. It should be stressed that neither API, nor free (non-aggregated) dye molecule intrinsic spectra of EL were therewith observed for both systems. Figure 3 shows the trace of color coordinates in the CIE chromaticity diagram. The LEDs with API/J-aggregate layers based on CD-1 and CD-2 emitted almost saturated light of the red and green-yellow colors. We observed no change of the colors as the voltage increase.

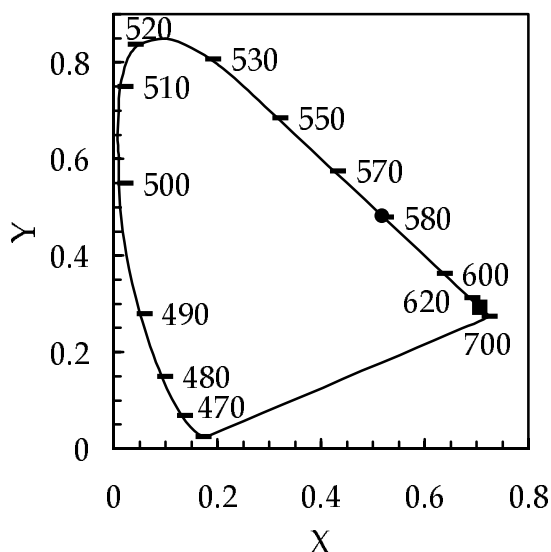


Figure 3. CIE chromaticity diagram with coordinates corresponding to emission of LEDs with API/J-aggregate layers based on CD-1 (filled square) and CD-2 (filled circle).

It was demonstrated that the J-aggregate particles act as a component which reduces the photooxidized free dye molecules in the mixture of CD/J-aggregates adsorbed on the surface of a semiconductor⁸, i.e. $E_{1/2}^{\text{ox}}$ (J-aggregate) lies higher than $E_{1/2}^{\text{ox}}$ (CD). It was also inferred that the oxidation potential levels ($E_{1/2}^{\text{ox}}$) of the both components 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 (ΔE_g) between the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) of the J-aggregates may be roughly approximated, from the λ_{\max} position of their absorption band in the API layer (Fig.1, solid line). This value was found to be $\Delta E_g \cong 1.88$ eV. Therefore, the $E_{1/2}^{\text{red}}$ for J-aggregates is located slightly below that of the dye molecules ($E_{1/2}^{\text{red}}$ (CD-1) = 3.3 eV). The inference drawn is that the J-aggregates should behave as exciton energy absorbers in the composite, in accord with our experimental results.

In the composites based on CD-1 J-aggregates, at ambient temperature and electric field of 3×10^7 V cm⁻¹, the direct time-of-flight measurements of charge-carrier mobility (μ) gave high values for electrons and holes: $\mu_e = 6.7 \times 10^{-5}$ and $\mu_h = 10^{-5}$ cm² V⁻¹s⁻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 layers⁷. The obtained results indicate an active role of J-aggregate nanophase in the charge-carrier transport for API/J-aggregate composites. These data support the experimental results¹⁰ obtained by measuring the EL light waveforms registered while using rectangular voltage pulses.

Conclusion

We have studied efficient EL in a new type of electron-hole conducting polymer composites, based on cyanine dye J-aggregates. These materials exhibit very narrow EL emission spectra, the position of which may be varied within the visible range, by modifying the molecular structure of the dyes. The relative value of the energy levels of the J-aggregates make them effective exciton energy acceptors. The nanocrystalline phase also appears to improve the charge transport characteristics of the composite layers.

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Biography

Eugene Mal'tsev received the M.S. degree in physical chemistry from Moscow State University, Russia, in 1968, and the Ph.D. degree from the A.N. Frumkin Institute of Electrochemistry, Russian Academy of Sciences (FIERAS), in 1974. He received the Doctor of Sciences degree in physical chemistry from the FIERAS, 1992, and currently, he is a group manager at the FIERAS. His current research interests are optical and electronic properties of organic materials for potential application in polymer optoelectronic devices.