Electroluminescence and optical properties of poly(phenylenevinylene)/J-aggregate composites

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Abstract

A composite material of poly(phenylenevinylene) (PPV) doped by dye aggregates was prepared. A very efficient and temperature activated energy transfer (ET) from the PPV to the dye aggregates was attributed to Förster ET accompanied by exciton diffusion. A clear complementary relation between the photoluminescence (PL) and electroluminscence (EL) images was observed for thin (15 nm) PPV-based OLEDs. So-called "black spots" in EL become bright ones when the photoluminescence of the same area was excited. This effect was attributed to the presence of an insulating layer between the polymer and aluminium. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

Doping of conjugated polymers by fluorescent dyes is mainly used to tune the colour and increase the emission efficiency of organic light emitting diodes (OLEDs) [1]. In the current contribution we present a study of photoluminescence (PL) and electroluminescence (EL) of thin light emitting diodes made of poly(phenylenevinylene) (PPV) and of PPV doped by 3,3′-bis-[3-sulfopropyl]-5,5′-dichloro-9-ethylthiacarbocyanine (THIATS) and its J-aggregates [2]. Dye aggregates being dispersed in an electroactive polymer act as extended traps for excitons and as very effective fluorescent recombination centres [3,4]. The choice of THIATS allowed us to prepare a stable solution of J-aggregates and the PPV precursor in water while this was not possible for another dye [4] due

to incompatibility of the pH-sensitivity of the mixed compounds. The formation of the so-called "black spots" on the active area of an operating OLED is a well-known phenomenon [5] responsible for EL degradation. "Black spots" (BS) are usually circular areas with very low EL efficiency as compared to the surrounding. In distinction to the majority of studies on OLEDs, we used a very thin active layer of about 15 nm (instead of 100 nm in common OLEDs) which allowed us to demonstrate a complementary relation between electroluminescent (EL) and photoluminescent (PL) properties of OLED areas subjected to BS degradation.

2. Experimental

The positively charged water-soluble tetrahydrothiophenium PPV precursor (pre-PPV) was

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synthesized as described elsewhere [6,7]. Mixing an aqueous solution (ca. 10^{-4} M) of the negatively charged THIATS dye with an aqueous solution of the positively charged pre-PPV (ca. 10^{-2} M) was found to cause extensive aggregation. The absorption spectrum maximum shifted from 550 nm, corresponding to dye monomers in water, to 625 nm (Fig. 1(a)), which is a typical absorption band of J-aggregates [2], while the width of the band was reduced to 15 nm (400 cm^{-1}). In this solution, J-aggregates revealed a high fluorescence quantum yield of ca. 40%, and a narrow fluorescence band around 630 nm. Films were prepared by spincoating from a pure pre-PPV solution with a concentration of monomer of 2×10^{-2} M and PPV/THIATS composite

solutions where the PPV/THIATS monomer concentration ratio was varied from 40/1 to 6000/1. Thermal conversion of pre-PPV into the conjugated polymer was carried out by heating in 10^{-3} Torr at 150°C for 11 h. The thickness of the films was estimated from topographic profiles of "scratched" samples measured on an atomic force microscope (Topometrics Explorer) and was found as small as 15 nm. OLEDs of the following arrangement were fabricated: ITO/PVK(20 nm)/PPV(15 nm)/Al; ITO/PPV(15 nm)/Al and ITO/PVK(20 nm)/[PPV + THIATS composite (10–15 nm)]/PPV(15 nm)/Al. The layer of poly(N-vinylcarbazole) (PVK) layer was used in order to reduce the hole injection from ITO resulting in a more balanced charge injection into the device. Photo-images of OLEDs excited by 430 nm light (PL-image) and by electrical current (EL-image) were obtained by the use of an optical microscope with episcopic fluorescence attachment coupled to a photo-camera. Temperature dependent fluorescence spectra exited by a CW He–Cd laser ($\lambda_{ex} = 442$ nm) were measured in a liquid helium cryostat. In these experiments polymer films deposited on glass substrates were always covered by a 100–200 nm aluminium layer to prevent fast photodegradation of the material when exposed to air [7].
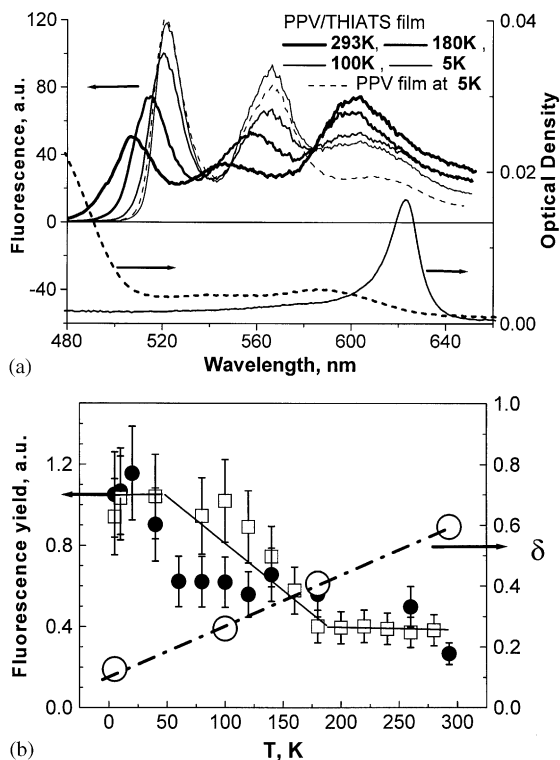

Fig. 1. (a) Absorption spectrum (bottom) of the composite film before (thin line) and after thermal conversion (thick dashed line). PL spectra of the PPV/THIATS and PPV films at different temperatures (top); (b) temperature dependence of the total fluorescence yield (open squares and solid circles) and of the parameter δ for the same film (large open circles). The lines are eye guides.

3. Results and discussion

The absorption spectrum of the PPV/THIATS composite film changed drastically after the heat treatment (Fig. 1(a)). A wide band at 400–450 nm, corresponding to the PPV absorption [6], with optical density of about 0.2 appeared. The band of the J-aggregates became much broader and less red shifted (585 nm) compared to the data obtained before heating. We attribute it to short aggregates where only a few dye molecules are coherently coupled. Moreover, a monomer band was observed at about 550 nm. That disintegration of aggregates we attribute to substantial changes happening in the film morphology and dielectric properties as well by the disappearance of the charge during the conversion of the precursor to the conjugated polymer.

The fluorescence spectra of the PPV/THIATS (1300/1) composite film, excited at 442 nm via the PPV band, are shown in Fig. 1(a) for different temperatures. The spectrum exhibits both the PPV-related vibrational progression with bands at 510 and 550 nm and a wide red band in the range of 600–650 nm. We attribute this long-wavelength fluorescence to aggregated dye species. The excitation spectrum of the 610 nm band almost coincides with the absorption band of PPV. The total fluorescence quantum yield of the PPV/THIATS films on glass substrates was estimated to be 6–10%. One can, therefore, conclude that very efficient energy transfer (ET) occurs from the initially excited polymer to the dye species. An example of the temperature dependence of the fluorescence spectra of a PPV/THIATS composite film (1300/1) is shown in Fig. 1(a). It is clearly seen that the contribution of the dye aggregates to the total fluorescence increases with temperature. The total fluorescence yield of the films was found to decrease with increasing temperature (Fig. 1(b)). The efficiency of the ET can be characterized by ratio δ of the fluorescence spectrum integrated over the band of aggregates to the integral of the total fluorescence spectrum. According to the definition $\delta = 1$ corresponds to 100% energy transfer to the aggregates while $\delta = 0$ shows that no ET occurs. As it is shown in Fig. 1(b) at room temperature 60% of light originated from the aggregates, while at $T = 5$ K the contribution of the aggregates is $<15\%$. One could expect the Förster ET to be quite important due to the substantial overlap of the PPV fluorescence spectrum and the absorption band of dye aggregates. However, it is quite hard to obtain the observed temperature activated acceptor fluorescence in the framework of the Förster model. We suggest that exciton diffusion in PPV [8] toward the dye species is the main mechanism of ET responsible for observed temperature dependence. This process is temperature activated as far as it is an intrinsic feature of the exciton diffusion in disordered solids [9].

PL and EL of PPV/THIATS composite OLEDs were found to be very similar. This suggests that the ET process does not depend on the way (by light or by electric field) the film is excited.

Due to the very small thickness of the polymer layer the degradation of OLEDs, fabricated as described in the experimental section, occurred within tens of minutes. A typical current density ranged from 5 to 100 mA/cm² at a biased voltage from 2 to 8 V for fresh and aged samples, respectively. PL and EL images of a PPV-only OLED are presented in Fig. 2. The EL-image reveals the classical black spot picture [5]. Comparing the EL and PL images of the same samples clearly shows that these images are complementary. In other words, the EL image is a negative of the PL image. The occurrence of this phenomenon did not depend on the size of dark areas in the EL image and it was observed for PPV/THIATS composite OLEDs as well as for OLEDs without THIATS. In contrast to thicker samples usually studied, for thin layers the bulk fluorescence does no longer hide the phenomena affecting the fluorescence originating at the interfacial region. Moreover the low optical density (less than 0.25) makes it possible to carry out photoexcitation of the region near the interface between the polymer and the metal. There are practically no indications of such an effect in the literature. To our knowledge, only McElvain et al. [5] noticed a slight increase of the BS brightness in the PL image of Alq₃-based OLEDs. However, no further attention was paid to and no explanation was suggested for that interesting phenomenon. The anticorrelation between PL and EL images can be rationalized in terms of the contact-assisted quenching of singlet excitations. More specifically, we attribute this effect to the formation of an insulating intermediate layer between the polymer and the aluminium electrode. For more details we refer the reader to Ref. [7]. Such a modification of the interface, on the one hand, leads to a reduction of the electron
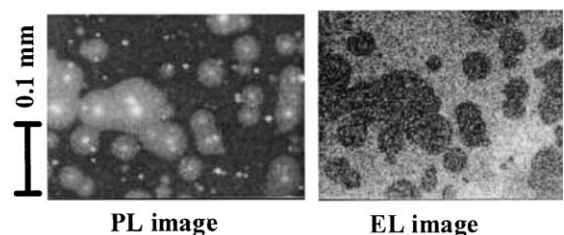

Fig. 2. PL and EL images of the thin ITO/PPV/AL OLED.

injection and to a concomitant decrease of the EL intensity and, on the other hand, it suppresses the PL quenching via exciton dissociation at the metal surface [10] and enhances PL.

4. Conclusions

An efficient and temperature activated energy transfer from the conjugated polymer to the dye aggregates was attributed to exciton diffusion. A clear complementary relation between PL and EL images was observed in thin PPV-based OLEDs. Black spots on the OLED's active area, observed during the operation, become bright ones when the photoluminescence of the same area was excited. This phenomenon was explained by formation of a thin insulating layer between the polymer and the aluminium contact reducing the electron injection, and PL quenching due to exciton dissociation at the metal–polymer interface.

Acknowledgements

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