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Electroluminescence of self-assembled films of poly (*p*-phenylene vinylene) and J-Aggregates

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Abstract

The preparation of thin films of poly (*p*-phenylene vinylene) (PPV) and J-aggregates of a cyanine dye (TDBC) is described. The films are prepared from aqueous solutions by the layer-by-layer self-assembly method using water soluble precursor of PPV and thermal conversion by heating of the whole film structure. The aggregates in solution are characterized by a narrow (FWHW 10 nm) absorption and fluorescence band at 590 nm. In PPV/J-aggregate films only the J-band emission of the aggregates is observed. The emission spectra are identical in photoluminescence and in electroluminescence. No spectral changes are observed between aggregates in solution and in the film.

Keywords: Poly (*p*-phenylene vinylene), Organic semiconductors based on conjugated molecules, Self-assembly using surface chemistry, Electroluminescence, Photoluminescence.

Introduction

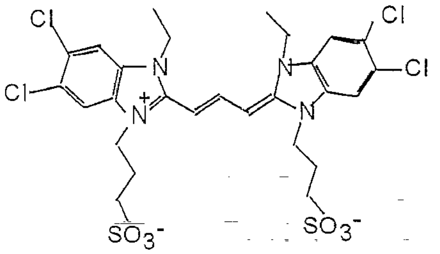
The interaction of light with aggregates or crystallites of dye molecules leads to the formation of Frenkel excitons [1] which are delocalized over several molecules even at room temperature. The energy of these extended exciton states with respect to the S_0-S_1 transition energy of the monomers is determined by the detailed molecular packing within the aggregates. If the molecules are strongly tilted with respect to the packing direction, the allowed excitonic transition is located at lower energies and the structures are called J-aggregates [2]. The dye TDBC (see Fig. 1 for molecular structure) is known to form such aggregates with a strong red shifted and narrow absorption band accompanied by a nearly resonant fluorescent emission [3]. Although the quantum yield of fluorescence emission is only about 10% at room temperature these aggregates may be promising as emitter materials in organic LEDs. The reason is the high mobility of excited states within the aggregates which makes them favorable as extended traps for charge carriers and efficient recombination centers.

Aggregates of cyanine dyes can be formed either in aqueous or other polar solutions by increasing the dye concentration [4] or by adsorption of the dye from solution at solid surfaces [5]. However, the low stability of the aggregates makes it difficult to combine or blend them with other optically or electronically active organic materials in order to fabricate devices.

Here, for the first time, the successfull combination of J-aggregates of TDBC molecules with PPV for the fabrication of LEDs is reported.

Experimental

The molecular structure of the cyanine dye TDBC is shown in Fig. 1. Aqueous solution with concentrations of 10^{-5} M was prepared with a small amount of NaOH to adjust pH above 7. J-aggregates are formed at this concentration. Films were built by the self-assembly method invented by Decher [6]. Pre-PPV and dye aggregates serve as polycations and -anions, respectively. At each dipping cycle the sample was immersed 20 min into the solution and afterwards rinsed with clean water and dried by blowing with nitrogen. The successive adsorption of dye and pre-PPV leads to the formation of one (pre-PPV/J-TDBC) double layer. The precursor of PPV was converted to the conjugated form by heating the complete sample to 130 °C at 10^{-4} bar for 12 h. For the fabrication of light emitting devices the film was prepared on ITO glass with aluminum electrodes evaporated on top.



TDBC

Fig. 1. Structure of TDBC (5,5'- 6,6'- tetrachloro- 1,1'- diethyl- 3,3'- di(4- sulfobuthyl) benzimidocarbocyanine).

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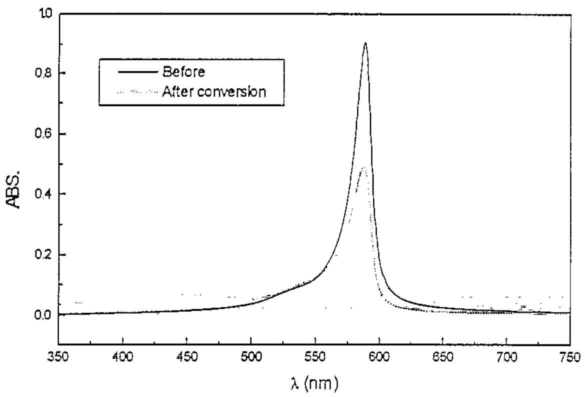

Fig. 2. Absorption spectra of 40 double layers of PPV/J-TDBC before and after thermal conversion of the PPV.

Photoluminescence (PL) and electroluminescence (EL) spectra were recorded with a home-built setup using a sensitve CCD-spectrometer (S&I) with an optical fiber in front of the sample. For PL excitation a 50 W mercury lamp and a 1/8 m monochromator were used.

Results and Discussion

In Fig.2 the absorption spectra of a film with 40 double layers of PPV and J-aggregates of TDBC $(PPV/J\text{-}TDBC)_{40}$ are shown. The spectra are recorded before and after the thermal conversion of the precursor of PPV to its conjugated form. Before the heat treatment only the typical J-band absorption at 590 nm and a small shoulder at 540 nm are visible. The J-band has the same maximum position and bandwidth as measured for the aggregates in solution. The small shoulder is attributed to dye monomers which have a maximum in absorption at 540 nm. The absorbance of the J-band is increasing nearly linearly during the layer-by-layer deposition process. Since the absorption coefficient of the aggregates is not known it is impossible to estimate the surface coverage of aggregates from the optical spectra. However, microscopical investigations show a nearly complete coverage of the surface with aggregates after one aggregate/polymer dipping cycle [7].

After thermal conversion of the PPV the absorbance of the J-aggregates is decreased by approx. 40%. At the same time the typical absorption of the PPV appears with a maximum at 430 nm. The monomer absorption at 540 nm remains nearly constant. The position and width of the J-band remains unaltered. Therefore, one can conclude that thermal conversion leads partially to the destruction of aggregates which increases monomer concentration within the film. Part of the monomer molecules is evaporated from the film.

In Fig. 3 the fluorescence emission of the PPV/J-TDBC film is shown excited at 400 nm. Only the narrow emission of the J-aggregates can be detected, although the excitation falls within the absorption of the PPV and zero absorption of TDBC.

In Fig. 3b the EL emission of the same sample is shown. The emission spectrum observed in EL is identical to the PL spectrum. The applied voltage was 7 V and the current density approx. 10 mA/cm^2. Under these conditions the light could be seen with naked eyes in a dark room.

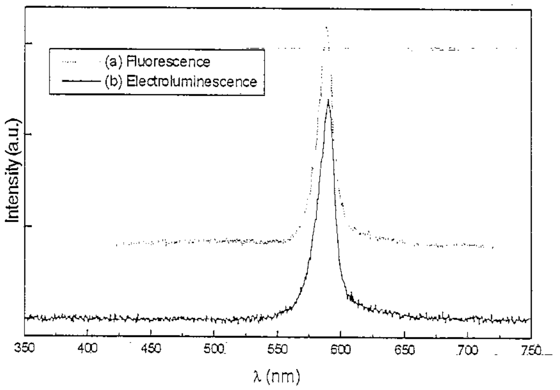

Fig. 3. Fluorescence (a) and electroluminescence (b) emission of 40 double layers of PPV/J-TDBC. The emission is normalized and the EL spectrum is shifted by a constant offset. PL was excited at 400 nm.

The lifetime of the device was only a few minutes in ambient air, but it could be improved remarkably by adding an additional layer of spin coated PPV on top of the PPV/J-TDBC system. Those devices show emission of both, the PPV and the aggregates, and they can be operated for at least one hour in ambient air [7].

Conclusions

The layer-by-layer self-assembly method is applicable to build thin films of the conjugated polymer PPV and aggregates of a cyanine dye. The excitation energy is completely transferred from the PPV to the aggregates. This was also confirmed by fluorescence excitation spectroscopy. No spectral shift between photo- and electroluminescence emission was observed. Since J-aggregates are formed from a large amount of different dye molecules with emission wavelengths covering the whole visible spectrum [8] light emitting devices of various colors may be accessible by this combination of PPV and J-aggregates by the self-assembly method.

Acknowledgements

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