Layer-by-Layer Deposition of J-Aggregates and Polyelectrolytes for Electroluminescence Applications: A Spectroscopic Study

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Abstract. The self-assembly method of layer-by-layer deposition of oppositely charged polyelectrolytes is used to insert J-aggregates of the dye tetrachloro-diethyl-disulfobutyl-benzimido-carbocyanine (TDBC) into thin polymeric films. The J-aggregates are characterized by a narrow absorption- and fluorescence band with its maximum at 590 nm, which is red-shifted with respect to the monomeric transition at 515 nm. The dyes are either coadsorbed with the polyelectrolytes poly(allylamine hydrochloride (PAH) and poly(styrene sulfonate) (PSS), or alternately deposited with the precursor of poly(phenylene vinylene) (pre-PPV). The optical properties of the aggregates are not changed significantly by the deposition process. The pre-PPV/TDBC films are heated under vacuum to convert the PPV to its conjugated form. The resulting films can be used for the fabrication of light-emitting devices. The optical properties such as fluorescence and electroluminescence are dominated by the J-aggregates. The excitation energy of PPV is transferred to the dye aggregates with an efficiency of 100%. The electroluminescence is not very stable and shows a very slow turn-on time. However, the combination of self-assembled PPV/TDBC layers with a spin-coated film of PPV results in stable electroluminescence emission under ambient conditions. In this case, light is emitted from both species, the PPV and the J-aggregates, whereas the ratio of the two intensities strongly depends on temperature.

I. INTRODUCTION

Since the first demonstration of thin film organic LEDs,[1–3] remarkable progress has been made with respect to efficiency and photochemical stability. Commercial products based on organic materials are expected to be available very soon. However, an important problem which has to be considered in solid films of any conjugated material is the appearance of excimers and luminescence quenching due to close packing of the aromatic π-electron systems. The typical signature of excimers is weak and delayed fluorescence emission that appears as a broad and essentially structureless band which is red-shifted with respect to the excitonic emission of the amorphous material. This behavior was explicitly found in thin films of a modified type of poly(phenylene vinylene) (PPV), namely the MEH-PPV.[4,5] Later, the existence of non-radiating crystalline domains of sub-micron size was proven for thin PPV films by the use of scanning near-field optical microscopy.[6]

For any electroluminescent material the appearance of aggregation, or crystallization, or even domains of high orientational order, are completely undesirable because they act as traps for optical excitations. However, there are special types of molecular aggregates that show strong fluorescence emission instead of luminescence quenching, namely, the so called J- or Scheibe-aggregates. These aggregates show bright and narrow

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emission and would be highly desirable as emitting traps in thin films. However, there may be problems in building up the films because of different pH and temperature requirements affecting adsorption and stability of the aggregates. To our knowledge, only two articles have been published about the attempt to utilize J-aggregates for electroluminiscence. In one article, the Langmuir–Blodgett technique is used to build up the films,[7] and in the second one the aggregates are blended with a conjugated polymer.[8] In this article, we show a method to incorporate aggregates into polymer matrices and will investigate the electroluminiscence properties of thin films of conjugated PPV with a high content of J-aggregated material, as prepared by the layer-by-layer deposition technique of oppositly charged polyelectrolytes.[9]

A. Excitons and Excimers in Dye Aggregates

The optical properties of dye aggregates are reasonably well described by the theory of Frenkel excitons, which was originally developed for molecular crystals,[10–13] and is also applicable to small aggregates, even under conditions of strong disorder.[11] It is based on the electrostatic interaction between transition dipoles of neighboring chromophores. Therefore, the interaction with photons leads to a collective excitation of several molecules forming an extended exciton state. The excitation energy of these states strongly depends on the geometry of the molecular packing in the aggregates. To give a short explanation, let us consider two molecules forming dimers as depicted in Fig. 1. Due to the dipole–dipole interaction between the transition dipoles (indicated by the double arrows in the figure), two new excitonic states are formed. If the molecules are aligned parallel, the new state that is associated with in-phase oscillation of the transition dipoles carries the whole oscillator strength, while the other state is dipole forbidden. In the configuration labeled as "H", where the molecules are stacked side by side, the transition with the higher energy becomes allowed and hence the absorption is hypsochromically shifted. However, the excitation is able to relax into the forbidden state, from which radiative decay into the ground state is only possible if the electronic states interact with vibronic states. This leads to weak and delayed emission with a broad and mainly structureless spectrum that is red-shifted with respect to the monomeric transition energy. Dye aggregates showing such a behavior usually are named "H-aggregates".

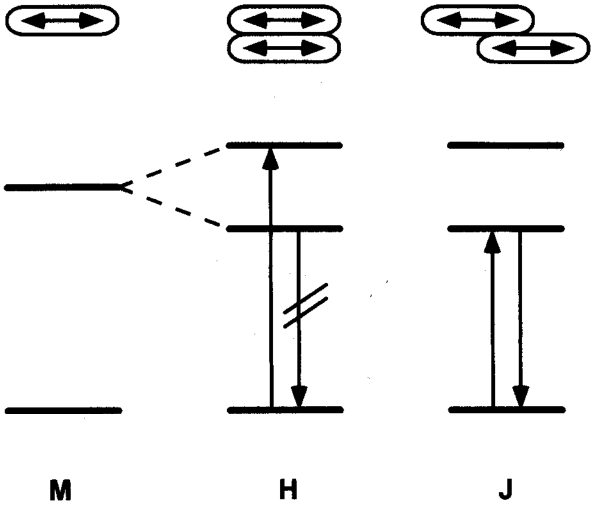

Fig. 1. Schematic representation of the exciton energy levels of a dimer depending on the geometrical arrangement. The transition dipole of the molecules is marked by the double arrow. *Left:* the S_0 and S_1 energy of a monomer. *Middle:* parallel packing with head-to-head arrangement. The dipole allowed transition is located at higher energies ("H-aggregate"). *Right:* head-to-tail arrangement. The allowed transition is at the lower energy state ("J-aggregate").

The appearence of excimers is caused by a very similar effect: in this case, the molecules in the excited state interact with the ground state of neighboring molecules. This results in a combined state which is also forbidden, similar to the "H"-exciton state of the dimer above. In contrast to the "H" excitons which are also observable in large aggregates, excimers are restricted to dimeric interactions.

If the molecules are combined in a head-to-tail configuration, as indicated in Fig. 1 by "J", the lower energy level becomes dipole allowed. In this case, a narrow absorption band is observed which is red-shifted with respect to the monomeric absorption. Additionally, strong fluorescence emission appears from the same state with very small Stokes shift. Aggregates that show these features are called "Scheibe-" or "J-aggregates", named by Scheibe and Jelley, who were the first to discover this behavior in solutions of a cyanine dye.[14,15]

The scheme of Fig. 1 is easily extendable from the dimers to larger aggregates. In this case, the two energy levels have to be replaced by a band of energies; however, only the top and bottom levels carry significant oscillator strength for H- and J-aggregates, respectively. The delocalization of the exciton causes significant narrowing of the spectra.[16,17] Structural disorder, on the one hand, reduces the coupling strength and hence the splitting energy of the two states and, on the other hand, broadens the distribution of oscillator strength within the energy band.[11]

In the case of conjugated polymers, their rigid backbone favors a parallel alignment of segments of the conjugated chains.[5] Therefore, it is quite reasonable to assume that crystalline domains exhibit a spectroscopic behavior similar to H-aggregates or, if no features are visible in the absorption spectra, excimers. In both cases, the transition from the state with lowest excitation energy to the ground state is dipole forbidden and thus the aggregates act as fluorescence quenchers. In contrast, the lowest exciton energy of J-aggregates carries the whole oscillator strength. Thus, they are able to collect the excitation energy like usual trap states but the relaxation within the J-aggregates always leads to radiative states. It is this circumstance which makes the J-aggregates very attractive for applications as luminescent pigments in a matrix of another conjugated material.

J-aggregates are formed by many types of cyanine dyes upon increasing their concentration in a polar solvent.[18] The detailed aggregate structure varies with the chemical structure of the dye molecule.[18–20] Here, we are utilizing J-aggregates of tetrachloro-diethyl-disulfobutyl-benzimido-carbocyanine (TDBC), whose optical properties have been extensively studied in the literature.[21] In Fig. 2 the absorption spectra of the TDBC monomers as well as the J-aggregates are shown, together with the chemical structure of the molecule. The aggregation/is obtained in basic solutions at concentrations above ~10^{-5} M. From the temperature dependence of the fluorescence lifetime it was suggested that TDBC forms two-dimensional aggregates in aqueous solution.[22] Very recent light-scattering experiments confirmed these assumptions [23] and led us to the conclusion that these dyes form monomolecular sheets, where the chromophores are attached to each other by the planar backbone, and the charged sulfobutyl groups are pointing outside of the aggregate plane.

B. Adsorption of Dyes and Polyelectrolytes

It was the aim of the work described here to incorporate J-aggregates into thin films of conjugated polymers for electroluminescence studies. Since the packing of the molecules within the aggregates is essential for their optical properties, it is important that the structure is preserved within the polymeric film. All attempts to mix the aggregate solution with the water-soluble precursor of PPV failed. The main reason was incompatibility of the pH values required for the dye and the PPV. Additionally, most of the dye was destroyed and presumably evaporated during the thermal treatment of the PPV.

Therefore, we selected another method, namely the alternate adsorption of oppositely charged polyelectrolytes, also referred to as layer-by-layer deposition or self-assembly. This technique makes use of the electrostatic adsorption of charged species from aqueous solutions. It was introduced by G. Decher several years ago[9] and was applied to the fabrication of well-defined multilayer structures composed of various materials, such as conjugated polymers,[24–27] inorganic particles,[28,29] and biological species.[30,31]

However, difficulties arise when small dye molecules are used for alternate adsorption with polyelectrolytes. In this case, the high mobility of the dyes within the polyelectrolyte film[32] and the good solubility in the water solution lead to significant extraction of the adsorbed dye layer when the sample is immersed into the subsequent polyelectrolyte solution.[33] The relative amount of dyes extracted at each step depends not only on the size and valence of the molecules, but also on the ionic strength of the polymeric solution.[34] Fortunately, the dye extraction can be reduced by mixing the dyes with a poyelectrolyte of same or opposite sign of the

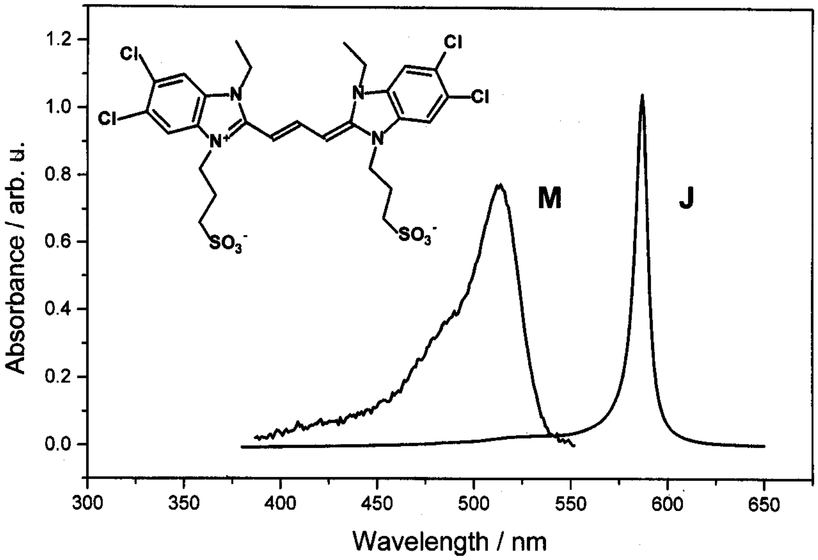

Fig. 2. Absorption spectra of the dye tetrachloro-diethyl-disulfobutyl-benzimido-carbocyanine (TDBC) in aqueous solution. M: monomer spectrum, recorded at low concentration ($c < 10^{-6}$ M); J: aggregate spectrum, recorded at high concentration ($c \approx 2 \cdot 10^{-5}$ M). The chemical structure of TDBC is shown in the insert.

charges.[35] To our knowledge, the adsorption of J-aggregates at polyelectrolyte multilayers has not been investigated so far. It is, therefore, not obvious which of the methods is more suitable to obtain film formation with reasonable quality and large content of dye aggregates.

In this article, we will describe both methods, the coadsorption as well as the direct alternate adsorption of J-aggregates with polyelectrolytes in section III A. In section III B, electroluminescence measurements of the system are presented, and in section III C, these films are combined with spin-coated films of PPV, and their electroluminescence properties are investigated.

II. EXPERIMENTAL SECTION

A. Materials

The dye tetrachloro-diethyl-disulfobutyl-benzimidocarbocyanine (TDBC) (see Fig. 2) was purchased from FEW chemicals (Wolfen, Germany) and the polyelectrolytes poly(ethylene imine) (PEI) and poly(styrene sulfonate) (PSS) were purchased from Aldrich. All commercial substances were used without further purification. The precursor of poly(phenylene vinylene) (pre-PPV) was synthesized following the route of Wessling and Zimmermann[36] and Hörhold et al.[37] The thermal conversion was performed after film preparation under vacuum ($p = 10^{-3}$ mbar) at a temperature of 130 °C for 11 h.

B. Multilayer Preparation

For the film preparation polyelectrolyte concentrations of 10^{-2} mol/L were used without any additional salt, if not specified otherwise. The deposition was performed automatically using a home-built apparatus according to the following procedure: first, the substrates were covered with a single layer of PEI by immersion into the solution for 30 min. For each other layer deposition, the samples were dipped for 20 min into the corresponding polyelectrolyte solution and afterwards rinsed with water three times. This procedure was repeated $2n$ times in order to obtain n polyanion/polycation double layers. We call each deposited pair of polyanions and polycations a "double layer", although the internal structure of the film may not consist of separated multilayers (see the discusion below). The complete film was dried with argon after the last layer was deposited. The pre-PPV solution was held at 6 °C during the whole deposition procedure.

C. Electroluminescence and Spectroscopy

For the fabrication of electroluminescence devices the films were prepared on indium tin oxide (ITO)- covered glass substrates (Balzers, Liechtenstein; sheet resistance 60 Ω / □) and a second electrode of aluminum was evaporated on top. The samples were mounted in a cryostat (CryoVac, closed cycle cooling system) for temperature dependent measurements under inert gas (helium). The light emission was detected using a thermoelectrically cooled CCD camera (S&I, Erwitte, Germany) attached to a monochromator (Acton SP 275). The light was focused into an optical fiber which was connected to the monochromator. The spectra were not corrected for the sensitivity of the detector. Fluorescence spectra were recorded with the same apparatus with a mercury lamp (50 W) and a small monochromator (HR 10, Jobin-Yvon) as an excitation source.

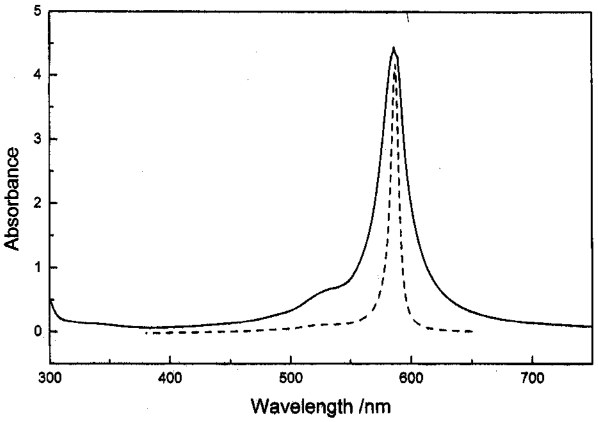

Fig. 3. Absorption spectrum of a mixed solution of PAH (45 mM) and TDBC (0.58 mM). The maximum of the J-aggregate band is located at 587 nm. The shoulder at 525 nm is caused by monomers which are additionally present in the solution. The dashed line represents the spectrum of the J-band of a pure TDBC solution as a reference.

III. RESULTS AND DISCUSSION

A. Polymer/Dye Film Deposition

We have investigated two basic concepts to incorporate the J-aggregates into self-assembled polyelectrolyte films. In the first case, the dye was mixed with a polycation and alternately deposited with a polyanion; in the second case, the dye aggregates were directly alternated with polyanions. First, we will consider the case of dye/polycation coadsorption. However, we did not succeed to prepare multilayer films when the dye was mixed with polyelectrolytes carrying the same charges, like poly(styrene sulfonate) (PSS), as was reported for other systems.[35] Instead, good multilayer growth was observed for mixtures between the anionic dye and the polycations.

1. Coadsorption of polymer and dye. TDBC is soluble at basic pH values, and aggregates form at concentrations higher than ~10^{-5} mol/L. Solutions of poly(allylamine hydrochloride) (PAH) have pH values close to 9; therefore, the two solutions could be mixed without any precipitation for small molar concentrations of the dye. In Fig. 3 the absorption spectrum of a TDBC/PAH solution is shown which contained ~1% of TDBC with respect to the monomers of PAH. The J-aggregate absorption band is located at 587 nm, which corresponds to the same transition energy as observed for

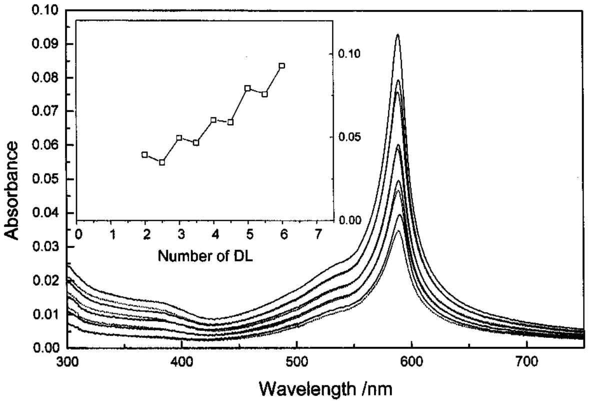

Fig. 4. Absorption spectra of $n = 2,...,6$ double layers of the TDBC/PAH mixture alternated with PSS. The solid line spectra are recorded after dipping into the TDBC/PAH solution, the dotted line spectra after the adsorption of PSS. Insert: Peak absorption vs. number of layers.

aggregates of pure TDBC solution.[21,38] Only the width of the J-band is slightly increased and the lineshape has changed (especially at the low energy side) from a Gaussian to a Lorentzian curve. The shoulder close to 540 nm is due to monomers that are additionally present in the solution.

According to the different charges of TDBC (one negative charge in excess per molecule) and the PAH (one positive charge per monomer unit), it is reasonable to assume that complexes are formed between the aggregates and the polycation. From the peak position of the J-band, which is very sensitive to the details of the molecular packing,[19] we conclude that the aggregate structure of TDBC is not changed significantly by the complexation. However, the Lorentzian lineshape of the J-band indicates distortion and defects within the aggregates. This connection of lattice distortions with the changes of the lineshape of the excitonic absorption bands was described theoretically by Knoester et al.[11]

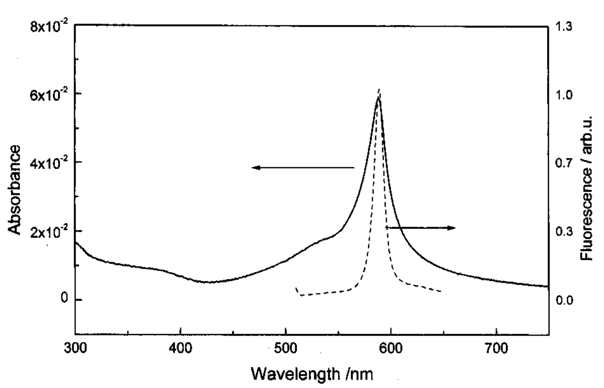

Fig. 5. Absorption and fluorescence spectrum of four double layers of PSS/(TDBC/PAH); excitation wavelength for the fluorescence was 500 nm.

In Fig. 4, the growth of a multilayer film by alternate adsorption of PAH/TDBC and PSS is monitored by the absorption spectra, measured after dipping into the dye and polymer solution, respectively. No changes of the aggregate spectrum are observed during the film deposition. In the insert of Fig. 4, the peak absorption of the J-band is plotted vs. the number of layers. It is clearly visible that the amount of adsorbed dye decreases by less than 10% after the adsorption of a succeeding layer of PSS. This low extraction of dye molecules during the adsorption step of the polymer could only be achieved if no additional salt was used in the PSS solution and with the pH adjusted to the alkaline range (≈8.5).

In Fig. 5, the absorption and fluorescence spectrum of a film of 4 double layers of PSS alternated with PAH/TDBC is shown. The typical narrow emission band (FWHM less than 20 nm) of the J-aggregates is seen with a small Stokes shift of less than 2 nm. These findings are identical to those for aqueous solutions of pure TDBC and support the assumption that the aggregate structure is conserved during the film-building process.

2. Alternate adsorption. TDBC was not miscible with the precursor polyelectrolyte of poly(phenylene vinylene) (PPV) to concentrations where a significant amount of dye is in the aggregated state. The problem arises from the different requirements for the pH value. The dye is soluble only in the alkaline range, but addition of NaOH to the solution of pre-PPV initiates the conversion reaction of the PPV and thus leads to flocculation. Only for pH values in the range of 8 to 9 we suceeded to prepare a metastable solution of pre-PPV and TDBC which precipitates after several hours. On the other hand, if TDBC is added to the solution of pre-PPV at its native pH (6.5), the dyes immediately form crystallites and precipitate. Addition of HCl could stabilize the pre-PPV solution, on the one hand, but on the other hand, it completely bleaches the dye.

However, the precipitation of the TDBC/pre-PPV complex could be utilized for the alternate adsorption of the two species. Therefore, a glass substrate was covered first by a layer of PEI and PSS in order to initiate the adsorption of pre-PPV. In the following, the film is built up by repeating *n* times the alternate adsorption of pre-PPV and TDBC, as described in section II. As in the case of the TDBC/PAH mixture, the adsorbed material during one deposition cycle including one-time dipping into the dye solution and one-time dipping into the pre-PPV solution is referred to as one *double layer*, without the intention to describe the internal structure of the resulting film as a multilayer system.

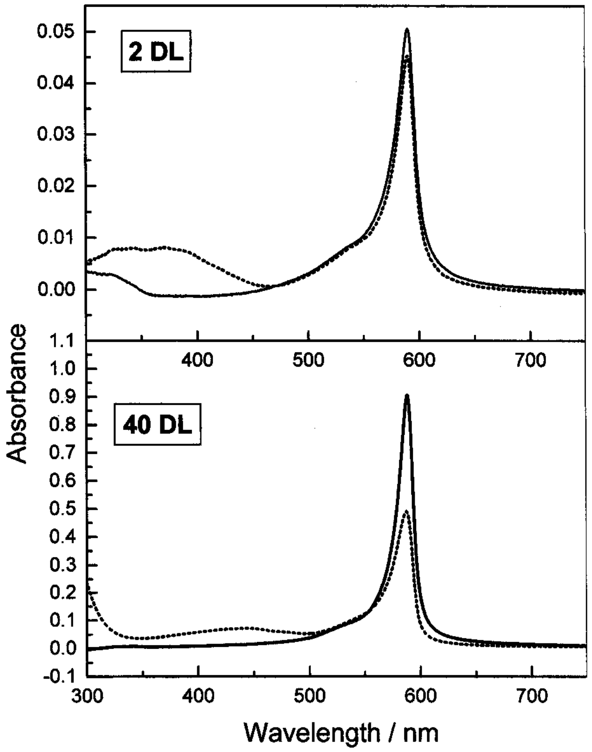

Fig. 6. Absorption spectra of 2 and 40 double layers of PPV/TDBC before (dashed line) and after (solid line) thermal treatment of the PPV.

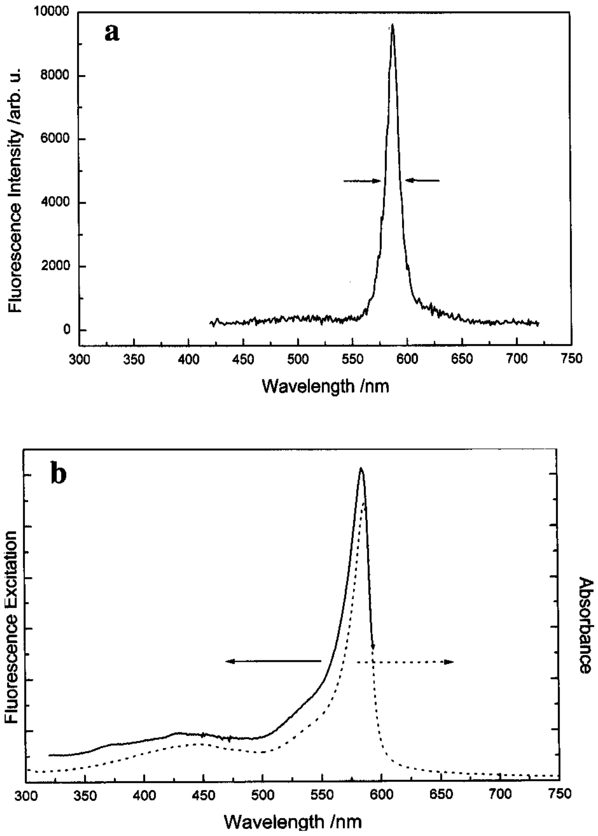

Fig. 7. (a) Fluorescence spectrum of a sample of 20 double layers of PPV/TDBC after thermal conversion of the PPV, excited at 400 nm. (b) Comparison between absorption spectrum (dotted line) and fluorescence excitation spectrum (solid line) of the same sample as in (a). The excitation spectrum was recorded at 600 nm emission.

In Fig. 6, the absorption spectra of 2 and 40 double layers of PPV/TDBC are shown before and after thermal treatment, respectively. From the maximum absorbance it can be concluded that the amount of TDBC aggregates in the film is growing linearly with the number of layers. Only the relative amount of monomers within the film decreases, as can be seen from the shoulder of the absorption spectra at 540 nm.

After the thermal elimination of the PPV, again a decrease of TDBC absorption is observed. While the loss of TDBC is less than 10% in the case ot two double layers, it approaches 50% for the case of thick samples. The transformation of the PPV to its conjugated form can be noticed from the emerging absorption bands below 450 nm. This absorption is red-shifted by ~50 nm in the 40 double layer sample compared to the thin one.

The ratio of the absorbance of TDBC to PPV indicates that the major part of the film material consists of dye aggregates and/or non-conjugated pre-PPV. The red-shift of the PPV absorption with increasing film thickness may be explained by increase of conjugation length. This indicates higher flexibility of the polymeric chains in thicker films since the chains have to reorganize during the heating process in order to stretch and thus to obtain long conjugated segments. This higher flexibility may be a consequence of less dense packing of material within the film with increasing thickness. From the decreasing density one also can understand the higher loss of TDBC material during the elimination process. With increasing number of double layers, the dye aggregates are less fixed within the PPV matrix. Therefore, they are more easily destroyed and evaporated during the thermal treatment. Additionally, X-ray reflectivity measurements of samples with 20 and more double layers show very large roughness of the film/air surface (of the order of 50 Å).

The fluorescence properties of alternately adsorbed PPV/TDBC films are summarized in Fig. 7. The fluorescence spectrum shows only J-aggregate emission and no fluorescence of the PPV, although excitation was performed at 400 nm, where TDBC has no absorption bands and only PPV is absorbing. Therefore, it is assumed that the excitation energy is transferred from PPV to the TDBC with an efficiency of 100%. This is confirmed by the fluorescence excitation spectra shown in Fig. 7b. The absorption spectrum is plotted together with the excitation spectrum, recorded at the aggregate emission of 600 nm. Both spectra are nearly identical and the PPV bands clearly show up in the excitation spectrum.

B. Electroluminescence Properties

The films of alternately adsorbed PPV and TDBC were used as emitter materials for electroluminescence (EL) measurements. Therefore, the films were prepared on ITO-covered glass, and an aluminum electrode was evaporated on top. Although the roughnesses of the films was very high, we succeeded in preparing samples with a thickness of less than 100 nm and area of 0.5 cm^2 without shortages from the electrodes.

Application of more than 7 V with the positive pole connected to the ITO electrode yields current densities of ~10 mA/cm^2. At this current density, the emission from the J-aggregates could be recorded. If the device was operated in reverse bias, the sample was destroyed and no electroluminescence could be observed.

The electroluminescence spectrum of a sample of 20 double layers is shown in Fig. 8. The spectrum is identical to the fluorescence emission, and no additional red shift is observed as is the case for many other organic materials. Again, no light emission from PPV appears. It is not clear if this is due to charge carrier recombination solely at the aggregates or a Förster energy transfer mechanism.

A very slow turn-on behavior of the light emission was characteristic for these devices. In the insert of Fig. 8, the light intensity is plotted against the time after application of a voltage of 10 V. The current turned on immediately and was held constant over the whole time interval. At the falling edge of the voltage, the light intensity as well as the current were switched off within the time resolution of the measurement of ~1 s.

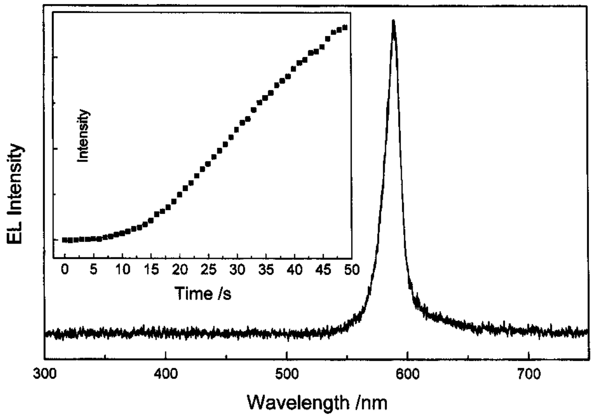

Fig. 8. Electroluminescence spectrum of a sample of 40 double layers of PPV/TDBC sandwiched between ITO and aluminum electrodes. The applied voltage was 10 V. Insert: time dependence of the electroluminescence intensity after turn-on of the voltage. Operation was under ambient conditions at room temperature.

Two different mechanisms may be considered as the possible reason for the long time delay of the light emission after application of the electric field: first, the charge carriers may be deeply trapped by the aggregates. In this case, the initial current only serves to fill the traps and recombination of charge carriers increases when the traps become filled throughout the whole film. Second, ions (probably dye molecules) are moving in the film due to the electric field and enrich at one of the electrodes. As a result, the field drops mainly across this thin ion concentration layer which dramatically increases the field strength and thus enhances carrier injection. This effect is well known from light-emitting electrochemical cells.[39]

C. Combination with Spin-Coated Films

To improve the electroluminescence properties, we added a separate layer of pure PPV on top of the TDBC/PPV assembly by spin coating. Throughout this article, we will call such a film a *two-layer* system. The typical thickness of the spin-coated film was in the range of 50–100 nm. The spin-coated layer has several advantages: first, the large surface roughness of the self-assembled layers is smoothened, which allows the evaporation of better defined electrodes; second, the J-aggregate emission is separated from the aluminum electrode, which avoids quenching by the metal; third, it provides information about the charge transport within the TDBC/PPV system compared to the pure PPV. If the carrier mobilities are higher in the simple PPV layer than in the composite material, the emission should again solely appear from the J-aggregates and the PPV should play

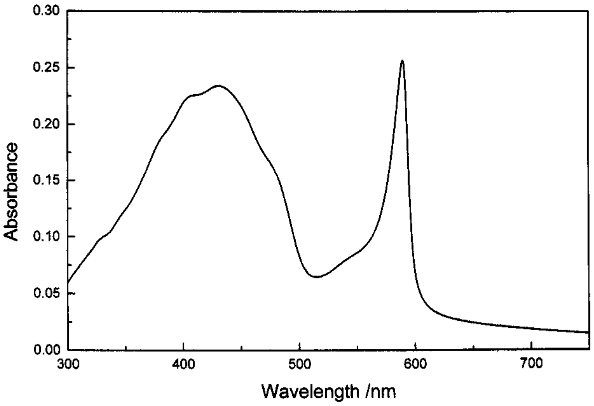

Fig. 9. Absorption spectrum of a two-layer sample consisting of 20 double layers of PPV/TDBC and a spin-coated layer of PPV after thermal conversion of the PPV.

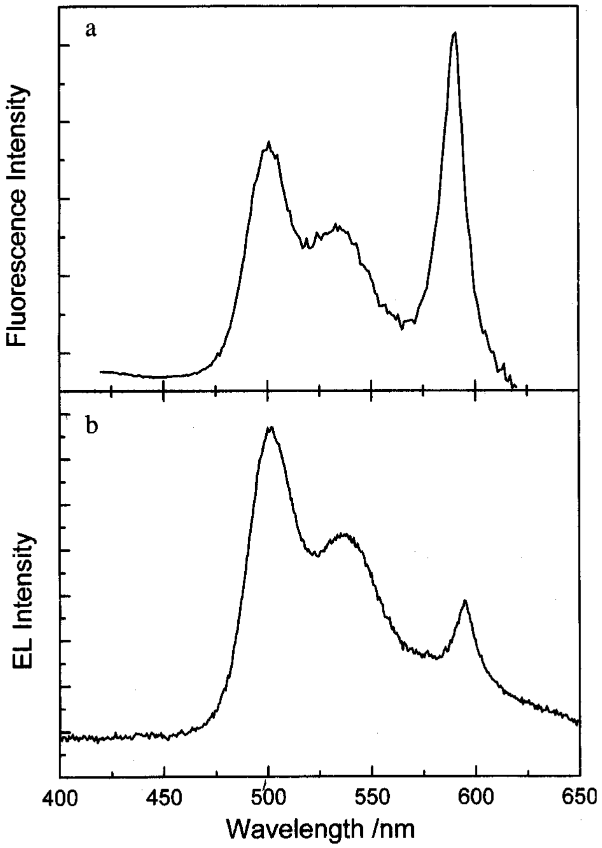

Fig. 10. Fluorescence (PL) and electroluminescence (EL) spectrum of the sample of Fig. 9, recorded at room temperature. PL was excited at 400 nm, EL was excited by applying 8 V positively biased at the ITO electrode.

the role of a charge transport layer.

In Fig. 9, the absorption spectrum of a two-layer device after the heating process is shown. A film of PPV with a thickness of ~50 nm was spin-coated on top of 20 double layers of TDBC/PPV. It is remarkable that no significant amount of the previously self-assembled layers is removed or washed away by the spin coating process. The separation into two distinct layers, one that contains pure PPV and another that consists of TDBC/PPV, is also evident from the fluorescence spectra shown in in Fig. 10a. The fluorescence was excited at 400 nm, which is close to the maximum of the PPV absorption and where almost no absorbance of the TDBC can be found. The J-band emission again is excited via energy transfer from the PPV. The strong fluorescence of PPV results from the spin-coated layer; this is a strong indication that the dye molecules do not dissolve into the spin-coated PPV layer.

The fluorescence intensities of PPV and the TDBC J-aggregates are of the same order of magnitude, which is explained by the similar absorbance and the fact that both substances have similar quantum yields. The values reported in the literature are in the range of 5–10%.[40,21]

However, in electroluminescence, such a two-layer structure favors the emission of the PPV layer. In Fig. 10b the EL spectra are shown for the same layer system as measured in Fig. 10a, but sandwiched between ITO and aluminum electrodes. The device was operated in the standard configuration with a positive voltage applied to the ITO electrode. Typically, the light emission was observed with the naked eye at current densities of more than 3 mA/cm^2, which was achieved at voltages above 8 V. In this forward bias, the devices turned out to be quite stable and could be operated for minutes in ambient air and for hours under vacuum. No light emission was observed under reversal of the applied voltage, although the current–voltage curve was symetrical with respect to the origin.

The EL spectrum is dominated by the PPV emission with the J-aggregate emission as a small shoulder; the resulting color appears greenish to the eye. Since the fluorescence quantum yield is very similar for both systems, the outstanding emission of the PPV must be caused by recombination of charge carriers within the spin-coated PPV layer. Two factors determine the location of the recombination zone: first, the PPV layer is located next to the aluminum electrode and thus injection of electrons is less efficient than hole injection from the ITO substrate into the PPV/TDBC layer. Hence, electrons are the minority carriers and they are responsible for the location of the recombination zone. Second, the electron mobility of PPV is known to be very low.[41] From the observation that recombination takes place mostly in the PPV layer, one can conclude that the hole mobility within the PPV/TDBC zone must be higher than the electron mobility within the spin-coated PPV.

To investigate the electron mobility of the PPV/TDBC, in principle one needs the inverse symmetry of the two layers, i.e., the PPV layer must be located next to the ITO side and the self-assembled film next to the aluminum electrode. Therefore, we tried to assemble the pre-PPV and TDBC layers on top of a spin-coated layer of pre-PPV. Surprisingly, the spin-coated layer was not washed away by the subsequent dipping process, and we were able to continue the self-assembly of the J-aggregates and the pre-PPV. However, a considerable amount of dye aggregates was penetrating into the spin-coated pre-PPV film, as could be seen from an increase of the dye absorption by a factor of 5 compared to the films shown in Fig. 9. As a result, fluorescence as well as electroluminescence emission was observed solely from the aggregates due to energy transfer processes. So far,

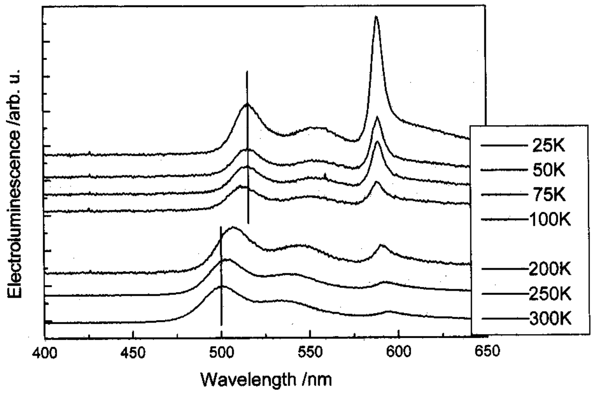

Fig. 11. Temperature dependent electroluminescence spectra of the two-layer sample of Fig. 9.

we have not found a method to build up the desired film structure with acceptable quality.

An interesting behavior is observed on cooling the sample. In Fig. 11, electroluminescence spectra recorded at different temperatures from 300 K down to 25 K are shown. In all cases, 7 V was applied positively biased at the ITO side with a current density of ~10 mA/cm^2. The PPV emision is shifted with its maximum from 500 nm at room temperature to 525 nm at 25 K, accompanied with a slight decrease of the inhomogenous broadening of the band. This behavior is well known for PPV and previously described in the literature.[42] It is explained by freezing out the torsional modes of the polymer chain. In contrast, the J-aggregate band remains at a fixed position while its intensity increases by more than a factor of ten with cooling. At 25 K, an additional long tail of emission is observed at the red side of the J-band. This broad emission is probably caused by trap states which do not appear at higher temperatures because of thermal deactivation. It is not surprising that the wavelength of the maximum of the aggregate band is independent of temperature since it is solely defined by electronic processes, without interactions with vibronic transitions.

The relatively high intensity of the J-aggregates at low temperature can be explained by the well-known increase of the fluorescence quantum yield from about 5% at room temperature to 100% at 4 K.[21] However, at present, we cannot exclude that there is also a contribution from the charge carrier dynamics which might be different at low temperature. Further investigations are necessary to separate these two contributions.

IV. SUMMARY AND CONCLUSIONS

The possibility to create organic films with a high amount of J-aggregates opens the route for the fabrication of novel materials with outstanding optical properties due to the peculiar features of the aggregates. The most prominent advantage of J-aggregates among other conjugated organic materials is the efficient narrow-band emission from an excitonic state that is bathochromic-shifted with respect to the monomeric transition energy. This property results from the specific molecular packing within the aggregate and the corresponding exciton band structure which concentrates all oscillator strength at the low energy edge of the band. For that reason, J-aggregates are an attractive system for highly luminescent traps within a matrix of conjugated material. Another well-known property of J-aggregates is their ability to sensitize silver halides via an electron transfer process.[18] Therefore, they should also be suitable as a charge transporting material. Comprising these properties, films of J-aggregated material are expected to be an excellent substance for electroluminescence applications.

In this article, we have made use of the alternating adsorption of oppositely charged polyelectrolytes to build incorporate J-aggregates of the dye TDBC into thin films of an isolating polyelectrolyte (PAH) or the conjugated polymer PPV. The driving force for the film formation is the complexation of the dye aggregates with the polyelectrolytes, where the complexes are held together by electrostatic interactions. This was demonstrated by mixing the negatively-charged dye aggregates with the positively-charged polyelectrolyte PAH. These materials stick together without destroying the aggregate structure; the resulting complex still preserves enough positive excess charges to be alternately adsorbed with the negatively charged PSS. If the pure aggregates are alternately deposited with pre-PPV, the complexation occurs instantaneously during the adsorption of the aggregate at the polymer interface and vice versa. Obviously, the intermolecular forces responsible for the aggregation of the dyes are still higher than the electrostatic forces between the dyes and the polyelectrolytes. Therefore, the aggregates are not destroyed during the film formation, as can be seen from the spectra.

First attempts to fabricate electroluminescent devices from the PPV and TDBC aggregates were quite successful, although the stability and efficiency were not satisfactory. The experiments performed with the layer-by-layer deposited PPV/TDBC films clearly show that the aggregates serve as efficient acceptors for energy transfer processes. The excitation energy of the PPV was completely transferred to the aggregates in photo- as well as in electroluminescence. The combination of the self-assembled system with a spin-coated layer of pure PPV shows a new way to fabricate complex multilayer structures utilizing the different techniques. Those two-layer samples can not only help to improve the electroluminescence properties, but also allow an estimate of the relative mobilities of the charge carriers within the different materials. Therefore, multilayer structures made of different materials are of great interest for their potential technological applications, but furthermore they are helpful for basic research on the fundamental electronic properties of the materials itself.

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REFERENCES AND NOTES

(1) Burroughs, J.; Bradly, D.D.C.; Brown, A.R.; Marks, R.N.; Mackay, K.; Friend, R.H.; Burns, P.L.; Holmes, A.B. *Nature* **1990**, *347*, 539.
(2) Braun, D.; Heeger, A. *Appl. Phys. Lett.* **1991**, *58*, 1982.
(3) Tang, C.; VanSlyke, S. *Appl. Phys. Lett.* **1987**, *51*, 913.
(4) Yan, M., Rothberg, L.J.; Papadimitracopoulos, F.; Galvin, M.E.; Miller, T.M.; *Phys. Rev. Lett.* **1994**, *73*, 744.
(5) Conwell, E.; Perlstein, J.; Shaik, S. *Phys. Rev. B* **1996**, *54*, R2308.
(6) Dearo, J.; Weston, K.; Buratto, S.; Lemmer, U. *Chem. Phys. Lett.* **1997**, *277*, 532.
(7) Era, M.; Hayashi, S.; Tsutsui, T.; Saito, S. *J. Chem. Soc., Chem. Commun.* 1985, 537.
(8) Mal'tsev, E.; Shapiro, B.I.; Brusentseva, M.A.; Berendyaev, V.I.; Kotov, B.V.; Vannikov, A.V.; *Appl. Phys. Lett.* **1998**, *73*, 3641.
(9) Decher, G. *Science* **1997**, *277*, 1232.
(10) Davydov, A.S. *Theory of Molecular Excitons*, Plenum Press, New York, 1971.
(11) Knoester, J. *J. Chem. Phys.* **1993**, *99*, 8466.
(12) Kirstein, S.; Möhwald, H. *J. Chem. Phys.* **1995**, *103*, 826.
(13) Kirstein, S.; Möhwald, H. *Adv. Mater.* **1995**, *7*, 460.
(14) Jelley, E.E. *Nature* **1936**, *138*, 1009.
(15) Scheibe, G.; Mareis, A.; Ecker, H. *Naturwissenschaften* **1937**, *29*, 474.
(16) Scherer, P.O.J.; Fischer, S.F. *Chem. Phys.* **1984**, *86*, 269.
(17) Kobayashi, T. *J-Aggregates*, World Scientific, Singapore, 1996.
(18) Mees, T.H.J., Ed. *The Theory of the Photographic Process*, 4th ed.; Macmillan: New York, 1977.
(19) Pawlik, A.; Rossi, U.D.; Kirstein, S.; Dähne, S. *J. Phys. Chem. B* **1997**, *101*, 5646.
(20) Kirstein, S.; Steitz, R.; Garbella, R.; Möhwald, H. *J. Chem. Phys.* **1995**, *103*, 815.
(21) Moll, J.; Dähne, S.; Durrant, J.; Wiersma, D. *J. Chem. Phys.* **1995**, *102*, 6362.
(22) Potma, E.O.; Wiersma, D.A. *J. Chem. Phys.* **1998**, *108*, 4894.
(23) Berlepsch, H.V.; Böttcher, C.; Ouart, A.; Burger, C.; Dähne, S.; Kirstein, J.; *Phys. Chem.*, in press.
(24) Fou, A.; Rubner, M. *Macromolecules* **1995**, *28*, 7115.
(25) Tarabia, M.; Hong, H.; Davidov, D.; Kirstein, S.; Steitz, R.; Neumann, R.; Avny, Y.; *J. Appl. Phys.* **1998**, *83*, 725.
(26) Hong, H.; Steitz, R.; Kirstein, S.; Davidov, D. *Adv. Mater.* **1998**, *10*, 1104.
(27) Lehr, B.; Seufert, M.; Wenz, G.; Decher, G. *Supramol. Sci.* **1996**, *2*, 199.
(28) Schmitt, J.; Decher, G.; Dressik, W.J.; Brandow, S.L.; Geer, R.E.; Shashidbar, R.; Calvert, J.M.; *Adv. Mater.* **1997**, *9*, 61.
(29) Gao, M.; Richter, B.; Kirstein, S.; Möhwald, H. *J. Phys. Chem. B* **1998**, *102*, 4096.
(30) Lvov, Y.; Ariga, K.; Ichinose, I.; Kunitake, T. *J. Am. Chem. Soc.* **1995**, *117*, 6117.
(31) Lvov, Y.; Haas, H.; Decher, G.; Möhlwald, H.; Michailov, A.; Mtchedlishvily, B.; Margunova, B.; Vainshtain, B.; *Langmuir* **1994**, *10*, 4232.
(32) Klitzing, R.V.; Möhwald, H. *Macromolecules* **1996**, *29*, 6901.
(33) Ariga, K.; Lvov, Y.; Kunitake, T. *J. Am. Chem. Soc.* **1997**, *119*, 2224.
(34) Linford, M.; Auch, M.; Möhwald, H. *J. Am. Chem. Soc.* **1998**, *120*, 178.
(35) Ariga, K.; Onda, M.; Lvov, Y.; Kunitake, T. *Chem. Lett.* 1997, 25.
(36) Wessling, R.; Zimmermann, R. US Patent, 3 401 152, 1968.
(37) Hörhold, H.-H.; Helbig, M.; Raabe, D.; Opfermann, J.; Scherf, U.; Stockmann, R.; Weis, D.; *Z. Chem.* **1987**, *4*, 126.
(38) Przhonska, O.; Slominsky, Y.; Stahl, U.; Daehne, S. *J. Fluorescence* **1996**, *69*, 105.
(39) Li, Y.F.; Caoand, J.; Gao, J.; Wang, D.L.; Yu, G.; Heeger, A.J.; *Synth. Met.* **1999**, *99*, 243.
(40) Köpping-Grem, G. Leising, G.; Schimetta, M.; Stelzer, F.; Huber, A.; *Synth. Met.* **1996**, *76*, 53.
(41) Meyer, H.; Haarer, D.; Naarmann, H.; Hörhold, H. *Phys. Rev. B* **1995**, *52*, 2587.
(42) Pichler, K.; Halliday. D.A.; Bradley, D.D.C.; Burn, P.L.; Friend, R.H.; Holmes, A.B.; *J. Phys.: Condens. Matter* **1993**, *5*, 7155.