

# A Model Oligomer Approach to Light-Emitting Semiconducting Polymers

PAUL F. VAN HUTTEN,  
VICTOR V. KRASNIKOV, AND  
GEORGES HADZIIOANNOU\*,†

*Department of Polymer Chemistry and Materials Science  
Centre, University of Groningen, Nijenborgh 4,  
9747 AG Groningen, The Netherlands*

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## Introduction

The current research on semiconducting polymers is focused on luminescent devices (light-emitting diodes, lasers) and strongly directed toward enhancing the efficiency of the quantum conversion. A lower turn-on voltage, a lower current, and a more balanced charge transport are key factors in meeting this objective. Such improvements will at the same time enhance the stability and durability of the devices. The desired characteristics are achieved by changing the device architecture and/or modifying the chemical structure of the polymer. The latter, chemical option usually involves changes in the nature, size, and arrangement of the substituents on the conjugated backbone.

Paul F. van Hutten was born in Leiden, The Netherlands, in 1953. He received his Ph.D. from the University of Groningen on studies of the morphology and mechanical properties of ultrastrong polyethylene fibers in 1981. From 1984 he worked on several polymer subjects at the Twente University of Technology. In 1990 he returned to Groningen to join the group of Georges Hadziioannou and started working on the optoelectronic properties of organic molecules.

Victor V. Krasnikov was born in Moscow, Russia, in 1956. After receiving his Ph.D. from Moscow University on studies of resonance nonlinear optical processes in atomic media in 1983, he continued working there in the area of nonlinear optics and laser spectroscopy, in the group of Professor S. A. Akhmanov. In 1993 he joined the group of Georges Hadziioannou in Groningen.

Georges Hadziioannou was born in Kavala, Greece, in 1953. He obtained his B.Sc. from the University of Thessaloniki and his D.Sc. (Docteur ès Sciences Physiques) from the University Louis-Pasteur in Strasbourg, France, in 1980. From 1980 to 1992 he was research associate at the University of Massachusetts, Department of Polymer Science and Engineering. From 1982 to 1986 he was a research staff member at IBM San Jose Research Laboratory in California and from 1986 group leader in the area of Surface and Interface Dynamics. In the period 1985–1989 he was Industrial Research Fellow at the National Bureau of Standards, Washington, DC, and consulting professor at the Chemical Engineering Department at Stanford University. In 1989 he was appointed full professor at the University of Groningen and since 1997 has also served as director of the Materials Science Centre. He is Chairman of the Board of the national research school Polymer Technology Netherlands (PTN). He was elected fellow of the American Physical Society in 1993, and received the Humboldt research award in 1998. His current research interests include synthesis of new functional homopolymers and block copolymers, polymer characterization with advanced techniques, solid-state properties of well-defined oligomers and polymers, photonic properties of semiconducting polymers, nanomechanical and nanorheological properties of polymers, and polymer surfaces and interfaces.

Poly(*p*-phenylenevinylene) (PPV) is one of the most extensively studied  $\pi$ -conjugated organic materials for the fabrication of polymeric light-emitting diodes (LEDs).<sup>1,2</sup> The introduction of alkyl or alkoxy side-chain substituents or the interruption of  $\pi$ -conjugation along the polymer backbone by means of copolymerization provides soluble and therefore processable materials and allows tuning of the emission properties.<sup>3–6</sup> Recently, the attachment of electron-withdrawing cyano groups onto the vinylene segments was found to result in red-light-emitting polymers with increased electron affinity, which drastically improved the quantum yields of luminescence in multi-layer LEDs.<sup>7,8</sup> Not only do the chemical approaches modify the characteristics of intrachain excitations and their migration behavior, but the interchain phenomena are affected as well.<sup>8,9</sup> The objective of much of the current scientific effort is to pinpoint and control the important factors in the competition between radiative and nonradiative decay.

Optical and electrical properties of conjugated materials are known to be strongly dependent on the coplanarity of the conjugated  $\pi$ -system and on the interchain distance of conjugated segments. Knowledge of the influence of substituents on these structural features is an essential part of the understanding of structure–property relationships in conjugated polymer materials. The aim of the study described in this paper is to explore such substituent effects, and to relate structural aspects of the solid state, such as molecular conformation and packing, with the physical properties of the solid, in particular its luminescence behavior.

Although the structural organization in solid PPV-based materials appears to be of fundamental interest, relatively little knowledge has been obtained. Unfortunately, polymers are quite inaccessible with regard to solid-state structure; this is particularly true for amorphous polymers, which are often preferred because of optical clarity. The study of well-defined conjugated oligomers therefore attracts increased attention since it has already proven to be valuable in the case of oligothiophenes, notably sexithiophene, where single crystals suitable for crystallographic analysis<sup>10,11</sup> and well-oriented thin films<sup>12,13</sup> can be obtained.

Particularly since PPV was found to have promising light-emission characteristics, efforts in the synthesis and study of related oligo(phenylenevinylene)s (OPVs) have intensified. Several of these model compounds have been obtained as single crystals, of which the structure has been determined by means of X-ray crystallography.<sup>14–16</sup> The availability of accurate information about the conformation and packing of model molecules in the single crystal allows one to put forward more detailed and less speculative explanations for optical and electrical behavior associated with the polymeric solid state. It will be instructive to see how the packing of molecules in the crystal depends on the substitution pattern of the molecule.

† E-mail: hadzii@chem.rug.nl.

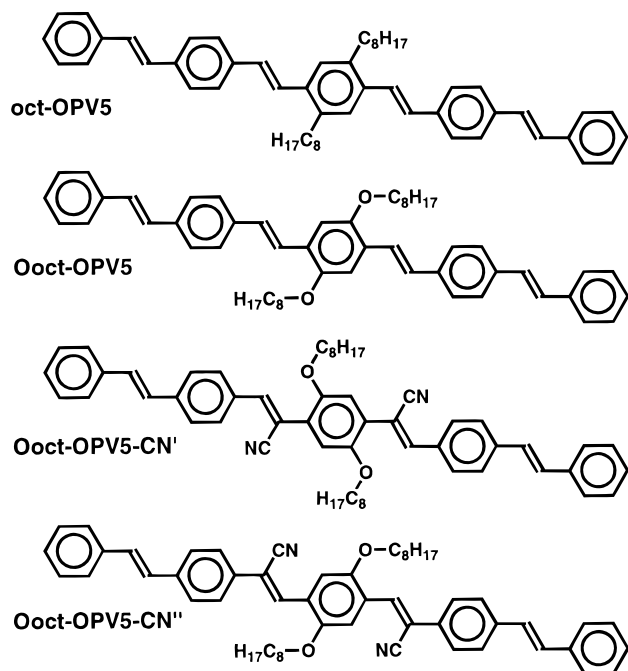


FIGURE 1. Chemical structure and nomenclature used for the oligo-(*p*-phenylenevinylene)s.

The structure of an oligomer crystal probably does not, by itself, have any predictive value for the structure of a related light-emitting polymer solid, but the insights obtained will be applicable to polymers and will help one select reasonable models for their solid state on the basis of optical properties. Furthermore, from a comparison of the molecular arrangement obtained from crystal data with predictions of the conformation of isolated molecules, as obtained from chemical modeling, one may gather insight into the origin of the differences between light-emission properties of solids and those of solutions.

The model compounds can also be used in device fabrication, since thin films of appropriate thickness can be obtained by sublimation and subsequent deposition onto a substrate in a vacuum. One of the foremost challenges is to find out how the morphology of the film bears on the device characteristics. Electrical as well as optical properties have turned out to be strongly dependent on both the molecular packing within the crystallites and the polycrystalline structure.

### Optical Properties of OPVs in Solution and Solid Matrix

The influence of substitution on the optical properties of OPV5s (Figure 1) in dilute solution is demonstrated in absorption (Figure 2, left) and photoluminescence (Figure 2, right) spectra. The absorption maximum of the alkoxy-substituted oligomer Ooct-OPV5 (422 nm) is red-shifted by 0.20 eV relative to the alkyl-substituted oligomer oct-OPV5 (395 nm), as a result of the electron-donating effect of the alkoxy substituents. In emission, the red shift is only slightly smaller, 0.16 eV. It has been demonstrated that cyano substitution onto the vinylene linkages of PPV results in a lowering of both the HOMO and LUMO levels.<sup>7</sup>

Since the LUMO level is stabilized more than the HOMO level, the absorption is red-shifted. Indeed, for the alkoxy-cyano-substituted oligomer Ooct-OPV5-CN'', a red shift in absorption (0.20 eV) and emission (0.25 eV) relative to Ooct-OPV5 is observed. However, the absorption of Ooct-OPV5-CN' is blue-shifted, because the spectrum has its maximum at 360 nm and there is only a shoulder around 400 nm. The excitation around 360 nm is also found for Ooct-OPV5 and Ooct-OPV5-CN'' and is assigned to a local excitation. These findings seem to support the results of our quantum-chemical modeling, which predicts a reduced planarity of the molecular  $\pi$ -system in Ooct-OPV5-CN' as a consequence of cyano substitution on the inner vinylene carbon. A larger twist angle at the central ring would favor a local excitation, and this may be further promoted by the conjugation of the cyano groups to the penultimate rings.

The luminescence of Ooct-OPV5-CN' is much less blue-shifted relative to Ooct-OPV5-CN'' than the absorption and is even slightly red-shifted relative to Ooct-OPV5. But, whereas the luminescence spectra of oct-OPV5, Ooct-OPV5, and Ooct-OPV5-CN'' are very similar in shape with a sharp maximum and clear vibronic details, the luminescence spectrum of Ooct-OPV5-CN' is featureless and also broader than those of the other oligomers. An explanation will be presented below.

There are also striking differences in the quantum yield of photoluminescence. High photoluminescence quantum yields, between 0.7 and 0.9, are found for oct-OPV5, Ooct-OPV5, and Ooct-OPV5-CN''. The PL decay curves are single-exponential and correspond to lifetimes around 1 ns. These values are similar to those reported for other substituted five-ring PPV oligomers.<sup>17</sup> However, in the case of Ooct-OPV5-CN', the photoluminescence quantum yield is extremely low, 0.04. PL lifetime measurements yield a fast double-exponential PL decay of 80 ps, indicative of an efficient nonradiative decay channel (Figure 3).

Starting from the assumption that the geometry relaxation after excitation is of primary importance with respect to the luminescence response, we decided to employ a solid polymer matrix to suppress conformational changes of the oligomers. For the measurements, dilute blends with polysulfone as the transparent host matrix were prepared. In Figure 3, the PL decay curves for the two cyano compounds in both chloroform and polysulfone are presented, as are the PL spectra of Ooct-OPV5-CN' in chloroform and polysulfone.

From the identical shape and position of the absorption spectra (not shown) in chloroform and polysulfone we conclude that the distribution of geometries of the Ooct-OPV5-CN' molecules is the same in both situations. In polysulfone, the nonradiative decay channel is effectively inhibited and a normal single-exponential decay with a time constant of 1.7 ns is observed. Clearly, the efficient nonradiative decay channel observed for Ooct-OPV5-CN' in chloroform is connected with the extent of conformational freedom it possesses in the surrounding medium. Restriction of the molecular motion severely reduces the efficiency of the nonradiative decay pathway. For Ooct-

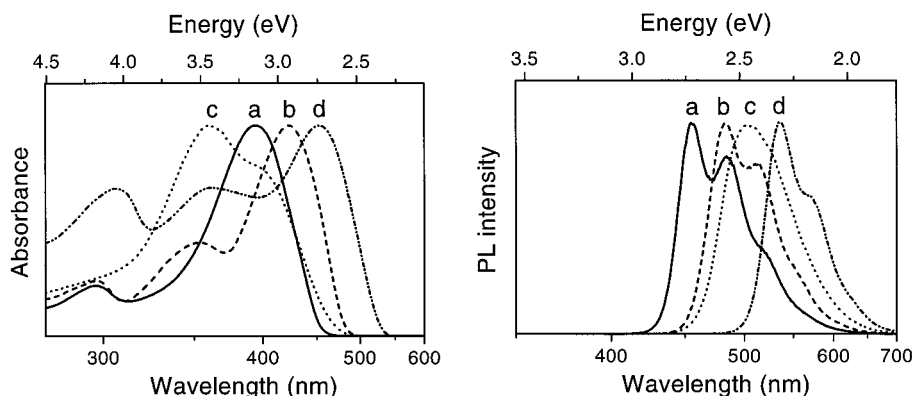


FIGURE 2. Normalized absorption (left) and photoluminescence (right) spectra of OPV5s in chloroform solution: (a) oct-OPV5, (b) Ooct-OPV5, (c) Ooct-OPV5-CN', (d) Ooct-OPV5-CN''.

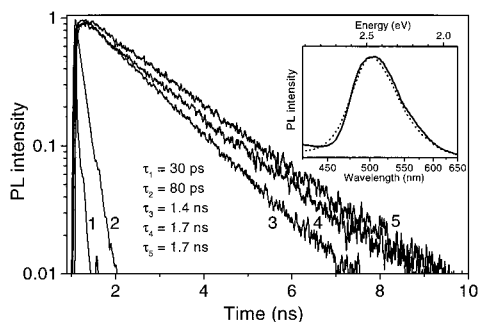


FIGURE 3. PL decay curves of cyano-substituted OPVs: (1) system response; (2) Ooct-OPV5-CN' in  $\text{CHCl}_3$ ; (3) Ooct-OPV5-CN'' in  $\text{CHCl}_3$ ; (4) Ooct-OPV5-CN'' in polysulfone; (5) Ooct-OPV5-CN'' in polysulfone. Inset: PL spectra of Ooct-OPV5-CN' in chloroform (solid line) and polysulfone (dotted line).

OPV5-CN'', the decay curves in solution and the solid polysulfone matrix do not differ much ( $\tau = 1.4$  and  $1.7$  ns, respectively). These results indicate that the conformational freedom is somehow associated with the position of the cyano substituents on the oligomer backbone. Nevertheless, the slight increase in the PL lifetime of Ooct-OPV5-CN'' may also be attributed to the same effect, which is probably general for all PPV-type compounds. It is not possible at this moment to specify the exact degree of freedom responsible for the fast nonradiative decay channel. It may be associated with a twisting or bending motion. Apparently, due to specific steric interactions in the case of Ooct-OPV5-CN', the excitation energy is lost to a large extent in such modes.

Although the PL lifetime has increased to usual values upon changing the matrix from chloroform to polysulfone, the emission spectrum (inset Figure 3) for Ooct-OPV5-CN' is unchanged; it is still broad and featureless. This points to inhomogeneous broadening, a result of the fact that emission comes from a distribution of rotamers with varying nonplanar geometries, highly constrained in the matrix.

It has been reported that the cyano group does not have a strong effect on the ground-state electronic structure of PPV-type molecules.<sup>18</sup> Apparently, however, the excited-state properties are strongly dependent on the position of this substituent. The results described above suggest that the compounds bearing the cyano group at

the inner vinylic carbon atoms rearrange strongly after excitation. The bond-length changes that occur upon excitation may lead to an increased steric interaction between the central ring and the cyano group on the inner position.

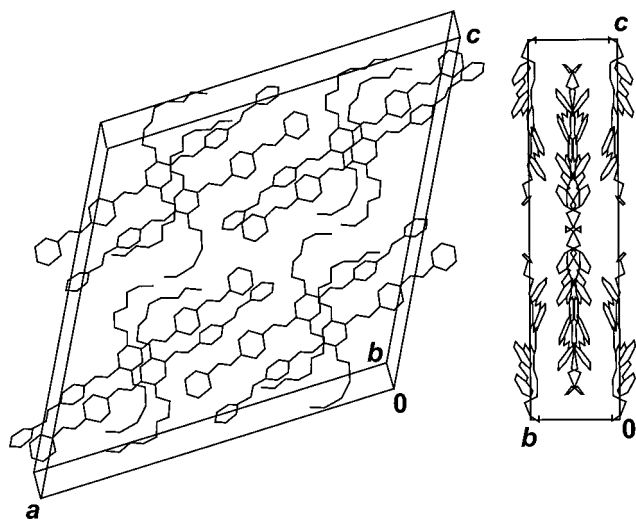
The influence of bond-order changes that result from excitation on the molecular conformation of PPV has not received attention so far. It is generally accepted that, in the case of polythiophene,  $\pi-\pi^*$  excitation will lead to increased planarity of the molecule.<sup>19,20</sup> In this respect, PPV and its derivatives and related molecules may differ considerably from polythiophene. In polythiophene there is only one bond between the rings; in PPV there are three (the vinylic linkage). Upon excitation, the bond order of the double bond decreases and one can expect significant rotational freedom around this bond, i.e., a much more flexible molecule (the mechanism underlying *cis-trans* isomerization.). We suggest that this "floppyness" plays a significant role in the competition between radiative and nonradiative decay. Hence, it would be worthwhile to investigate, at a sufficiently accurate level of theory or computation, differences in steric interaction and in bond order associated with a different position of the cyano group at the vinylic linkage.

The strikingly distinct behavior found for the two cyano-substituted model compounds indicates that the position of the cyano substituent on the vinylic linkage relative to the alkoxy-substituted ring is a crucial factor for the luminescence properties of cyano-substituted alkoxy-PPVs.

## Single Crystals of OPVs

Several OPVs have been synthesized and electrically and optically characterized, but only very few crystallographic studies have been carried out to date.<sup>21-23</sup> Our group recently reported the single-crystal X-ray data for Ooct-OPV5<sup>14</sup> as well as for Ooct-OPV5-CN'.<sup>15</sup> Although all OPV5s synthesized have been obtained as crystalline solids, only the octyloxy-substituted ones have been obtained, through crystallization from solution, as single crystals that were suitable for X-ray crystallographic analysis. Crystallographic data on the molecular geometry





**FIGURE 4.** Molecular packing of Ooct-OPV5 in the crystal lattice. Left: oblique view of the unit cell of Ooct-OPV5. Right: projection of the unit cell on a plane perpendicular to the *a*-axis.

should be the starting point for quantum-chemical computations on oligomers and polymers.<sup>24,25</sup>

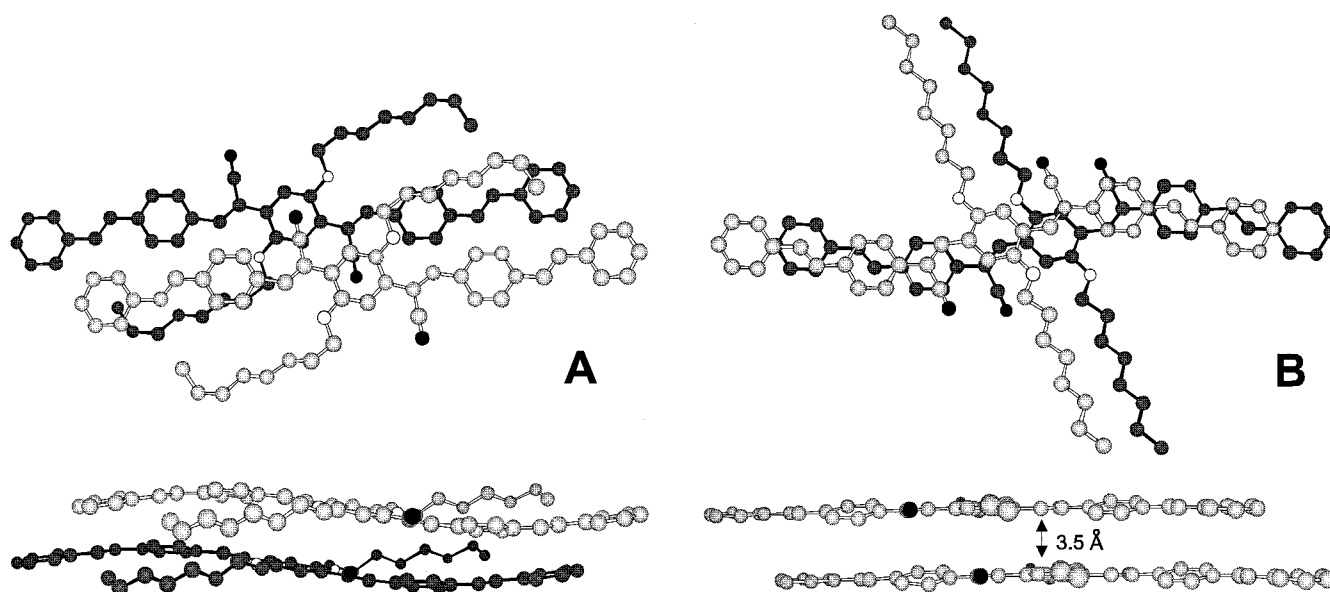
**Ooct-OPV5.** Ooct-OPV5 crystallizes into yellow needle-shaped crystals when crystallized from a THF/methanol mixture. The unit cell is monoclinic, space group  $I2/a$ , and contains eight discrete molecules separated by normal van der Waals distances.<sup>14</sup> The conjugated backbones lie parallel to each other and are lined up into strings along the *a*-axis and separated along the *c*-axis by a layer accommodating the aliphatic side chains (Figure 4). The molecules are contained in layers parallel to the (010) plane (interlayer distance  $b/2 = 3.77 \text{ \AA}$ ); the phenyl rings are not “ $\pi$ -stacked”. The side-chain carbons are not fully stretched in an all-trans configuration, but curved toward the periphery of the conjugated backbone. Strong disorder is found in one of the two octyloxy tails.

**Ooct-OPV5-CN’.** Orange plate-shaped crystals were obtained by crystallization from a chloroform/*n*-hexane solvent mixture. The unit cell is triclinic, space group  $P\bar{1}$ , containing one discrete molecule, which has a crystallographically imposed center of inversion.<sup>15</sup> The molecule has a remarkable, “wavelike” shape (Figure 5A). Such distortions indicate the presence of considerable packing forces. The dense packing (the crystal density of  $1.210 \text{ g cm}^{-3}$  is 10% higher than that of Ooct-OPV5) may be driven both by side-chain arrangement and by electrostatic interactions between the polar groups.

One does not expect  $\pi$ - $\pi$  interaction to occur for nearest (*a*-axis) neighbors, since the  $\pi$ -systems are both laterally and axially displaced, in a view perpendicular to the plane of the central ring (Figure 5A). The aromatic systems face the octyloxy substituents of the neighbor molecules.

The conformation around the double bond that bears the cyano group is different from that found in other OPV crystals studied so far. The introduction of the cyano group has caused an almost  $180^\circ$  rotation around the single bond to the central ring and results in the molecular backbone and octyloxy tail being in close proximity.

**Ooct-OPV5-CN’’.** Orange-red crystals of Ooct-OPV5-CN’’ were obtained from a chloroform/*n*-hexane mixture. This compound, which has its cyano substituents at the *outer* position of the central vinylene linkages, has a  $P\bar{1}$  crystal packing which is very different from that of Ooct-OPV5-CN’. As Figure 5B illustrates, nearest-neighbor molecules exhibit only an axial displacement of little more than a phenyl ring. In a view perpendicular to the central ring, the aromatic systems overlap to a large extent. Since the distance between the conjugated backbones is approximately  $3.5 \text{ \AA}$ , significant  $\pi$ - $\pi$  interactions between neighboring molecules are to be expected ( $\pi$ -stacking).



**FIGURE 5.** Views of two nearest-neighbor molecules in the crystal lattice: (A) Ooct-OPV5-CN’, (B) Ooct-OPV5-CN’’. In each case, the top picture presents a view perpendicular to the plane of the central ring, while the bottom picture shows a side view in the plane. Atom colors: light and dark gray, carbon atoms of the front and rear molecule, respectively; white, oxygen atoms; black, nitrogen atoms.

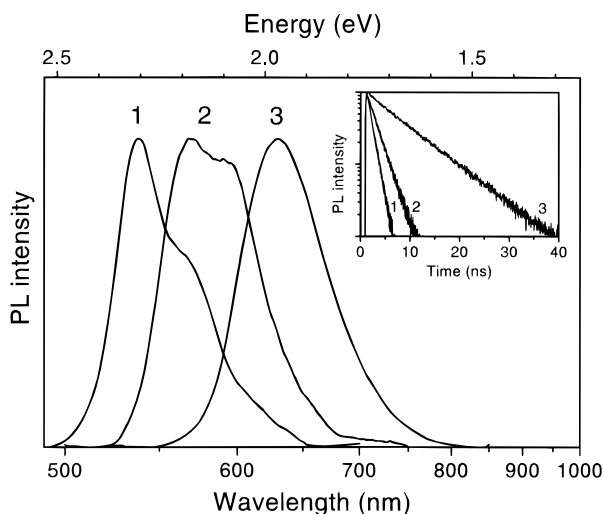


FIGURE 6. Normalized photoluminescence spectra of (1) Ooct-OPV5, (2) Ooct-OPV5-CN', and (3) Ooct-OPV5-CN'' single crystals. Inset: corresponding PL decay curves.

The octyloxy chains are extended nearly perpendicular to the molecular axis, in the plane of the aromatic backbone.

**Optical Properties of Single Crystals.** For the three octyloxy-substituted five-ring oligomers, the normalized photoluminescence spectra of the single crystals are depicted in Figure 6. For Ooct-OPV5 and Ooct-OPV5-CN', the PL spectra show vibrational structure characteristic of single-molecule luminescence. The PL lifetimes, 1.0 and 2.2 ns, respectively, are typical values for small organic dyes. For both oligomers, no significant  $\pi$ - $\pi$  interactions were expected on the basis of the molecular packing in the crystal structure. The observation of luminescence originating from an intramolecular excitation agrees with these conclusions.

For Ooct-OPV5-CN'', the molecular organization in the single-crystal lattice is favorable for  $\pi$ - $\pi$  interactions between neighboring molecules. This is in line with the emission properties of the Ooct-OPV5-CN'' single crystals, which differ significantly from those of the other two oligomers. The luminescence spectrum is featureless and red-shifted in comparison with that of its isomer Ooct-OPV5-CN'. The PL lifetime,  $\sim 8$  ns, is significantly longer. This behavior is similar to that reported for cyano-PPV films, which was attributed to excimer luminescence originating from interchain excitations.<sup>8</sup> An excimer is a pair of identical planar molecules in a cofacial arrangement, formed as a result of attractive interactions arising upon excitation of one of the molecules, which have a repulsive interaction in the ground state. Typically, excimer formation occurs when the aromatic planes of the molecules are separated by 3–4 Å. The absence of vibronic features is one of the characteristics of excimer luminescence. Another is the long radiative lifetime, caused by the symmetry-forbidden nature of the transition. In the case of conjugated polymers, the excimer is thought to be formed by planar chain segments of two or more polymer chains.

Our study shows that molecular  $\pi$ -stacking in the solid leads to excimer-type emission; a similar arrangement of

chain segments may be the origin of the long-lived luminescence from cyano-alkoxy-PPVs.

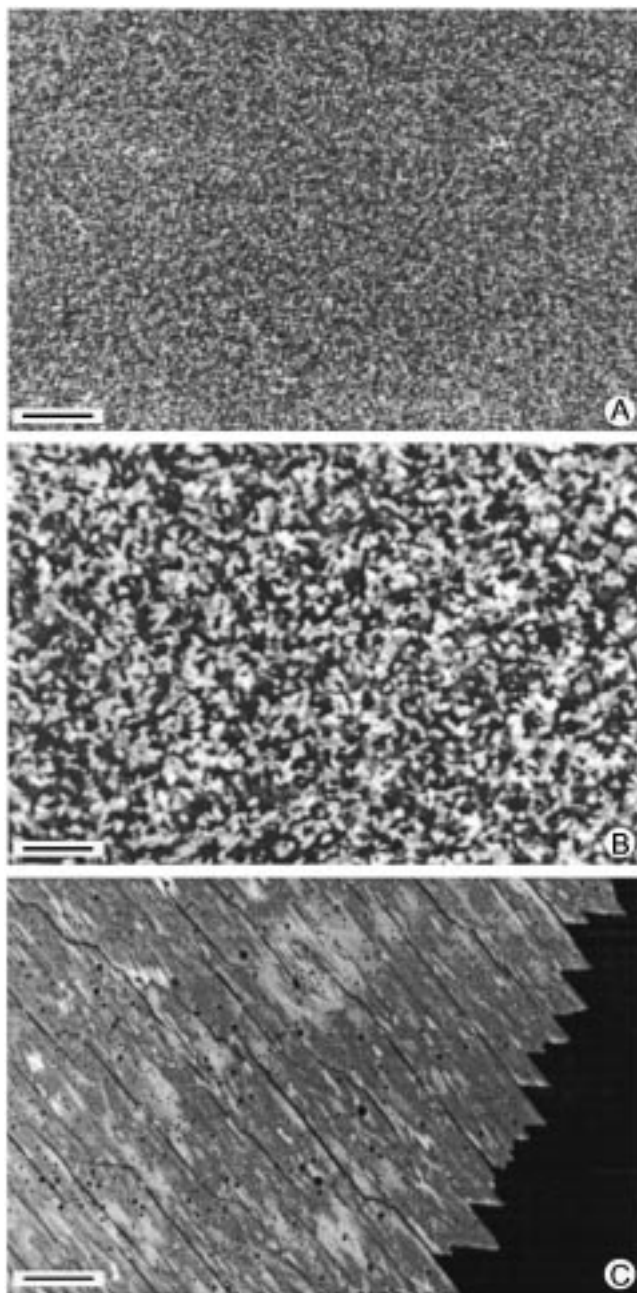
## Light Emission Applications of OPV Thin Films

Thin films of conjugated oligomers with well-defined chain length have recently become of considerable interest for the preparation of, for example, field-effect transistors and light-emitting diodes. Films prepared by vacuum sublimation/deposition are generally highly crystalline, as a result of low molecular weight and high purity. By controlling the processing conditions, such as evaporation rate and substrate temperature, the thin-film morphology can be varied. Order may be at least partially induced by interactions with the substrate surface in the case of an interactive substrate.

Films on glass substrates were prepared by evaporation from a molybdenum boat at  $10^{-6}$  mbar and at a temperature just above the melting point of the oligomer. The film was deposited at a rate of 2–4 Å s<sup>-1</sup>. The as-deposited layer showed a fine-grained polycrystalline structure when observed in the optical microscope. Heating the films resulted in a morphological change, which was not reversible upon cooling. This morphological change occurred below the first melting point of the oligomer and manifested itself in an increase of the domain size. In the case of Ooct-OPV5, annealing the film at 120 °C caused an abrupt recrystallization, resulting in an increase of the domain size from a few micrometers to approximately 20  $\mu$ m (Figure 7A,B). X-ray diffraction studies indicated enhancement of the molecular orientation. Crystallization of the film from the isotropic melt at 210 °C resulted in the formation of domains with dimensions up to several millimeters (Figure 7C).

**Light-Emitting Diodes: Influence of Morphology.** Single-layer light-emitting diodes were realized in the configuration ITO/Ooct-OPV5/Al. Thin (ca. 200 nm) films of Ooct-OPV5 were deposited onto an ITO (indium–tin oxide) electrode on glass, by vacuum sublimation at a deposition rate of 2–4 Å s<sup>-1</sup>. These films showed similar morphologies in the optical microscope as layers deposited onto glass substrates. The cathode consisted of a 100 nm aluminum layer deposited directly onto the organic layer at a pressure of  $2 \times 10^{-6}$  mbar. Clear light emission could be visually observed over the whole active area ( $7 \times 10^{-2}$  cm<sup>2</sup>) of the device.

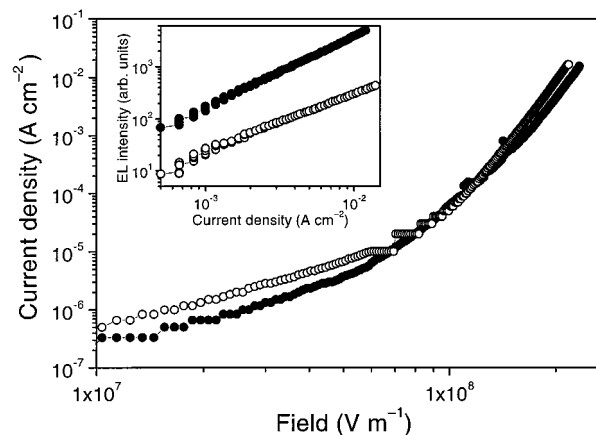
The influence of the thin-film morphology on the device performance was investigated for Ooct-OPV5 by means of annealing (Figure 8). The external efficiency of an annealed LED amounted to  $1.2 \times 10^{-2}\%$  photon/electron, 1 order of magnitude higher than that of a pristine LED ( $0.1 \times 10^{-2}\%$ ). Annealing of Ooct-OPV5 film was found to result in a 20% increase of the photoluminescence quantum yield as measured under laser illumination in an integrating sphere. This 20% rise in PL efficiency alone cannot account for the increase in EL efficiency. Figure 8 shows that the cell current hardly changes upon annealing. Since the majority charge car-



**FIGURE 7.** Polarized-light optical micrographs of Ooct-OPV5 films: (A) as deposited, (B) after annealing at 120 °C, (C) after crystallization from the isotropic melt at 210 °C. The scale bar is 100  $\mu\text{m}$ .

riers in these devices are holes, we conclude that the hole current is the same for both morphologies.

The electron current in such devices is much smaller than and fully masked by the current of the majority carriers. For this reason, Al/Ooct-OPV5/Ca devices were prepared, which can be considered as “electron-only” devices. In annealed electron-only devices, the current was approximately 1 order of magnitude higher. Hence, the increase in efficiency upon annealing is attributed to an increase of the electron mobility. The improvement of molecular orientation and the reduction of the density of grain boundaries upon annealing may be considered as possible explanations for the enhanced electron mobility.



**FIGURE 8.**  $J$ – $E$  characteristics for single-layer ITO/Ooct-OPV5/Al devices: as-deposited (open circles); annealed (120 °C, 5 min; filled circles). Inset: luminance as a function of cell current for both thin-film morphologies.

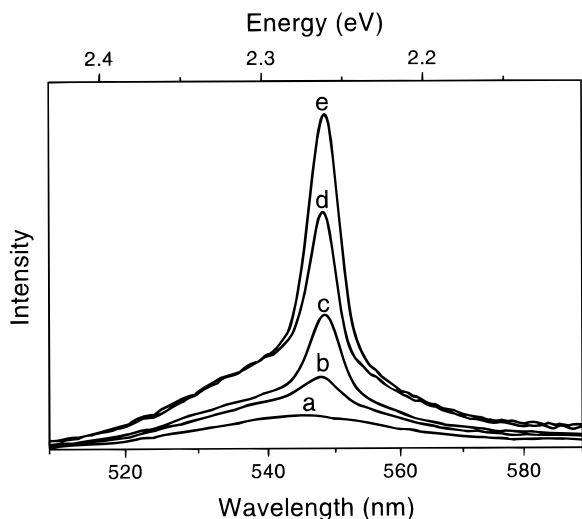
The influence of the oligomer–metal interface on the electron drift mobility could be important as well.

Whereas chemical and device-oriented strategies have generally been invoked to tune the balance of hole and electron currents in LEDs, our results demonstrate that this balance is also affected by the microstructure of the active layer.

**Stimulated Emission.** Recently, light amplification under pulsed optical excitation, with conjugated polymers as active medium, has been demonstrated in neat thin films.<sup>26–30</sup> Laser-like (spectral narrowing) phenomena have also been observed in photopumped neat films without external feedback.<sup>28,29,31</sup> The observation of stimulated emission from photopumped neat films shows that singlet intrachain excitons can be generated with high yields in the condensed phase. Since it is well-established that electroluminescence from polymer LEDs originates from excited states identical to those created by photoexcitation, this suggests the possibility of an electrically pumped polymer laser. An important question to be answered is whether it is possible to obtain electrically induced net gain. On the basis of the lasing threshold under optical excitation, it is estimated that current densities in excess of  $10^3 \text{ A cm}^{-2}$  are needed to establish net gain in such devices, which is substantially higher than currently achieved in polymer LEDs. The low current densities in polymer LEDs, especially for electron transport, are the result of the low charge carrier mobilities, high trap densities, and poor charge injection in conjugated polymers.

Ordered conjugated organic materials exhibit low trap densities and high charge carrier mobilities, for both electrons and holes. As an example, in single crystals of anthracene,<sup>32</sup> the hole and electron mobilities are approximately  $1 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  and the crystal photoluminescence quantum yield at room temperature is almost unity. Both electroluminescence<sup>32</sup> and stimulated emission<sup>33</sup> have been demonstrated in anthracene single crystals. Hence, single crystals of OPVs are potentially interesting for electrically driven devices. For practical applications





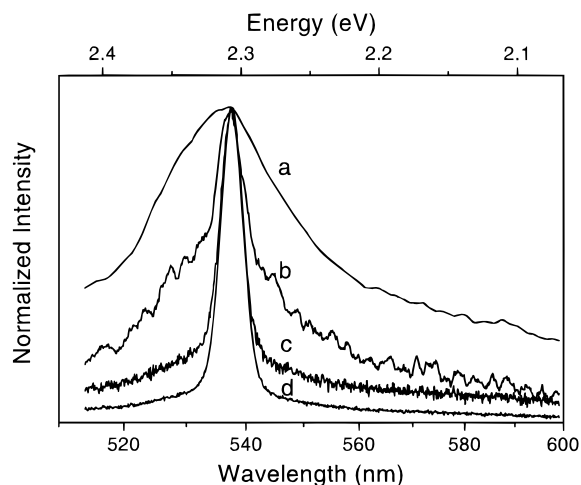
**FIGURE 9.** Emission spectra of an annealed thin (300 nm) film of Ooct-OPV5. Excitation energy: (a) 0.9, (b) 1.6, (c) 2.1, (d) 3.1, and (e) 3.9 eV. Excitation beam diameter  $\sim 1.8$  mm.

in devices, however, single crystals are not convenient. We have therefore investigated vapor-deposited films, for which the desired geometry can be easily obtained. We report light emission spectra of Ooct-OPV5 thin films under intense optical excitation with the third harmonic of a nanosecond Nd:YAG laser, measured in an integrating sphere.<sup>34,35</sup>

The as-deposited films (300 nm on glass substrate) showed no spectral narrowing at any pump energy up to the damage threshold. Emission spectra of an annealed Ooct-OPV5 film are shown in Figure 9. At low excitation energy, only the ordinary broad luminescence spectrum was observed. Above a well-defined excitation threshold, a sharp emission peak (fwhm  $\approx 5$  nm) appeared, centered around 548 nm and surrounded by a broad luminescence tail. The higher the excitation energy, the more dominant the spectrally narrow emission became. The wavelength of the narrow peak at high pump energies is near the maximum of the luminescence emission spectrum.

The appearance of a spectrally narrow peak above a well-defined energy threshold and the relative suppression (sublinear growth) of the broad luminescence tails together with a linear dependence of the integrated total intensity on input energy, indicating the spectral energy redistribution within the emitted light, are a signature of light-induced net gain due to stimulated emission. The observed behavior can be explained in terms of amplified spontaneous emission (ASE).<sup>31</sup>

The energy threshold for line width collapse is approximately  $60 \text{ mJ cm}^{-2}$ , which is 3 orders of magnitude higher than that of conjugated polymers.<sup>26–31</sup> We attribute this to the polycrystalline structure of the thin films. Amplification occurs only within the individual crystalline domains, which, in the annealed film, have average dimensions of  $20 \mu\text{m}$ . Scattering at grain boundaries results in high optical losses, which prevents sufficient net gain to be realized over multiple domains. Hence, the amplification length is restricted by the size of the individual crystalline domains. Their size in as-deposited



**FIGURE 10.** Normalized emission spectra of a melt-crystallized thin (300 nm) film of Ooct-OPV5. Excitation energy: (a) 1, (b) 10, (c) 50, and (d)  $70 \mu\text{J}$ . Excitation beam diameter  $\sim 1$  mm.

films, approximately  $4 \mu\text{m}$ , is too small to achieve observable gain at all. Since some positive feedback might result from such light scattering mechanisms, and the observed spectral evolution might be assigned to “true” lasing, we think it is appropriate to note that mode structure was not observed in any of our measurements.

Since the amplification length is restricted by the size of the crystalline domains, increasing the domain size will likely result in an ASE threshold comparable to that reported for conjugated polymer films, which is typically in the range of  $10 \mu\text{J cm}^{-2}$  to a few hundred  $\mu\text{J cm}^{-2}$ , using nanosecond pulses. This was checked experimentally with Ooct-OPV5 films crystallized from the isotropic melt (Figure 7C). The normalized emission spectra as a function of excitation energy for a melt-crystallized film are shown in Figure 10. The lowest measured energy threshold for line width collapse corresponded to a fluence of  $\sim 500 \mu\text{J cm}^{-2}$ , which is substantially lower than that measured for the annealed films. Unlike in the annealed films, in the melt-crystallized ones the energy threshold was dependent on the excitation spot size at constant pump intensity, which indicated that amplification occurred over the whole illuminated area.

Spectral gain narrowing has been observed in thin oligomer films. Although the polycrystalline nature of the films is disadvantageous for laser applications, it clearly helped demonstrating the key role of morphology to optical amplification in the solid state.

## Summary and Outlook

The optical properties of PPV and related (co)polymers can be tuned by variation of the chromophores, e.g., type of side chains or length of the chromophore. To understand relationships between substitution pattern, solid-state structure, and emission properties, we have studied a variety of five-ring oligo(*p*-phenylenevinylene)s that closely resemble those chromophores. In many cases, single crystals have been obtained, and the molecular arrangement could be derived from a crystallographic

analysis. In this paper, attention has been paid to the influence of the position of cyano substituents. Intermolecular  $\pi$ -stacking was found when the cyano group was placed not directly adjacent to the central ring, and this resulted in strongly red-shifted, excimer-type emission.

Optical absorption and photoluminescence spectra of vapor-deposited thin films are significantly different from dilute solution spectra, which indicates that intermolecular interactions play an important role. The molecular orientation and crystal domain size can be increased by thermal annealing of the films. This control of the microstructure is essential for the use of such films in optoelectronic devices. The influence of the morphology of the active layer on LED performance has been investigated. Annealed layers showed a higher efficiency; this was attributed to enhanced electron mobility. Amplification of spontaneous emission has also been observed in thin films of oligomers. Scattering losses at the domain boundaries in these polycrystalline films prevent amplification across those boundaries, and the domain size therefore limits the length of interaction. For net gain to be observable, the domain size must exceed a critical value at a given fluence.

Luminescence from the solid state is strongly subject to packing effects. Some are related to molecular conformation; some result from electronic interactions between molecules. Clear-cut relationships have not been established, and admittedly, the gap between model oligomers and polymers has not (yet) been bridged. What the studies of oligomer films have clearly pointed out is the importance of the structural organization at higher levels for the optical and electrical properties. Film morphology should therefore be of primary concern to anyone working on the optimization of light-emitting devices based on films of organic materials.

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