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Interchain photoluminescence in poly(phenylene vinylene) derivatives

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We calculate that in cyano-substituted poly(phenylene vinylene), CN-PPV, and poly[2-methoxy, 5-(2′-ethyl-hexyloxy)phenylene vinylene], MEH-PPV, the lowest-energy arrangement has the chains parallel, with the perpendicular distance between chains 3.4 Å in the former case, 4.1 Å in the latter. Although there is evidence that most of the excitations created by above-band-gap light are polaron pairs or excimers in both cases, only those in CN-PPV luminesce because the smaller interchain distance results in a much larger matrix element for emission. [S0163-1829(96)50528-X]

MEH-PPV and CN-PPV are being used in light-emitting diodes[1] and photovoltaic devices[2,3] that show promise for commercial application. It is important to know the nature of the excitations in these materials, particularly those generated by light, because they may affect operation of the devices.

Measurements of picosecond photoinduced absorption (PA) in thin films of PPV, methoxy-PPV, and MEH-PPV revealed a nonradiative photogenerated species with a long lifetime, of the order of nanoseconds and at least several times as long as the radiative lifetime in these materials.[4–6] Direct evidence that these long-lived excitations are not singlet excitons was obtained in experiments that show, by using stimulated emission to identify the excitons, that the long-lived excitations compete with the excitons.[5] Eliminating the possibilities that the excitations are (i) triplet excitons, by the fact that their absorption spectrum is different and (ii) polarons or bipolarons, by the intensity dependence of their decay dynamics, Hsu *et al.* suggested that the long-lived excitations are polaron pairs bound on adjacent chains by their Coulomb attraction.[4] These excitations may also be called indirect excitons[5] or excimers. This identification was strongly reinforced in the case of MEH-PPV, which is soluble, by showing that the long-lived excitations are not generated in dilute solution.[6,7] Additional evidence for the formation of pairs, or excimers, comes from the calculation of the energy levels of such pairs, which gives results for the PA in reasonable agreement with experiment.[8,9]

MEH-PPV is luminescent both in thin films and in solution, with the center of the emission band the same in the two cases,[10] thus due to excitons. The quantum yield of luminescence is much poorer in the films, 0.10, as compared with 0.35 in solution. The poor yield in films can be attributed to photogeneration of nonemissive polaron pairs in preference to excitons.[6] The situation is changed when the MEH-PPV is dispersed in polystryrene, for example. In that case a probe beam receives strong amplification by stimulated emission, indicating a large exciton population, just as it does in a dilute solution of MEH-PPV.[6] In the films it is also found that the luminescence decay is more rapid than in solution.[10]

Recently it was found that luminescence in CN-PPV, which is similar to MEH-PPV in having long side chains that make it soluble (see Fig. 1), has quite different properties. The central frequency of the emission was found to be shifted downward by ~0.45 eV in the film relative to the solution.[11] Unlike PPV, MEH-PPV, and other derivatives, the decay rate of the luminescence is slower by more than a factor of 5 in the film than in the solution.[11] Samuel *et al.* attributed these features to the emission from CN-PPV films being due to an interchain excitation, either a dimer or an excimer.[11] The essential difference between a dimer and an

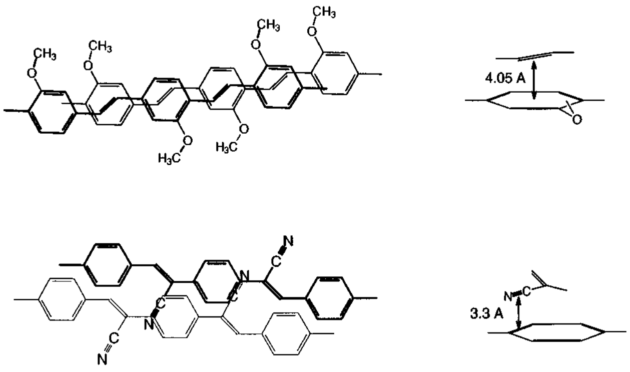

FIG. 1. Schematic of chain packing for the Monte Carlo global minimum in MEH-PPV (top) and CN-PPV (bottom) as viewed perpendicular to the plane of the polymer backbone. Most of the side chains have been removed for clarity. In MEH-PPV, the exocyclic double bond sits over the center of the phenyl ring at 4.05 Å spacing whereas in CN-PPV the cyano group sits over a phenyl ring edge at 3.3 Å spacing.

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excimer is that the former is stable in the ground state. Since there is no evidence that the ground state is stable, we shall refer to the emissive excitation as an excimer. In any case the existence of a stable ground state does not affect the description of the excited state.

By implication, the existence of excimers in PPV and methoxy-PPV, where there is no emission associated with the excimers, was questioned. We show in this paper that the essential difference between the excimers inferred in MEH-PPV and CN-PPV is in the stronger coupling of the chains in the latter case, the result of its high electron affinity. This in turn gives rise to a larger matrix element for emission.

Because of their planar backbones and long alkoxy side groups, low-energy configurations for MEH-PPV or CN-PPV in a film have the planes of the backbones parallel to each other. Although the films are amorphous, determination of the lowest-energy structures in the two cases should give at least the relative values of the average spacing between chains and a good idea of the most typical structures. To determine the minimum energy configuration we apply a Monte Carlo cooling algorithm to a layer of MEH-PPV or CN-PPV consisting of five face-to-face polymers segments, each with three phenyls ($1\frac{1}{2}$ monomers). The algorithm is carried out in two stages. First, an optimized starting geometry for a single polymer chain is found. Then the apparent global and nearby local minima of energy for the polymer layer are found. Free rotations about all the single bonds in the side chains were allowed. The calculations for CN-PPV were simplified by shortening the side chains from OC_6H_{13} to OC_3H_7. This is expected to have negligible effect on the interchain spacing and other properties of the backbone.

The interaction potential, E_t, between polymer molecules in the layer was computed using a classical atom-atom force field (a modified MM2 potential[12]) which includes four terms:

$$E_t = E^{nb} + E^{\mathrm{el}} + (E^{\mathrm{int}} - E^0). \tag{1}$$

In Eq. (1) E^{nb} is the dispersive interaction (van der Waals attractive plus Buckingham repulsive interaction) between the molecules, E^{el} is the electrostatic interaction between the molecules due to residual partial charges on atoms, and $(E^{\mathrm{int}} - E^0)$ is the intramolecular dispersive plus electrostatic plus torsional interaction referenced to a starting geometry for the polymer chain whose energy is E^0. Functional forms for E_t and atom-atom force-field parameters have been given elsewhere.[13,14] In computing E_t for each stage of the simulation, the bond lengths, bond angles, and backbone torsion angles (but not the side chain torsional angles) for the polymer were held fixed.

The reference state E^0 was chosen such that

$$|E^{\mathrm{int}} - E^0| \ll |(E^{nb} + E^{\mathrm{el}})|. \tag{2}$$

Otherwise, most of the simulation time would be spent searching the phase space dominated by the internal degrees of freedom (the side chain torsion geometry) rather than the intermolecular packing. To find a suitable reference state, the initial simulation searched the phase space of the polymer torsion geometry only, looking for low-energy local minima. One of these minima was then used as the reference state for the remainder of the simulation. It is not important that this reference state be the global minimum, only that it satisfy Eq. (2).

Simulation methodology for constructing the polymer layer has been described previously.[15,16] We collected 700 local minima and sorted them according to their packing geometry. For CN-PPV in the lowest-energy structure the perpendicular distance between nearest-neighbor chains was 3.3 Å. However, for a structure with $d = 3.5$ Å the energy of the polymer layer was only 0.001 eV higher. For the next three structures the polymer layer energy was higher by 0.08, 0.12, and 0.13 eV with $d = 3.3$, 3.05, and 4.05 Å, respectively. We chose $d = 3.4$ Å. These structures all have the chains slipped relative to each other, with the cyano group in one chain overlapping the edge of a ring in the nearest-neighbor chain. Such a structure, shown in Fig. 1, is expected because of the high electron affinity of the CN group. For MEH-PPV the lowest-energy structure had $d = 4.05$ Å. The next two structures, with energy 0.18 eV higher, had $d = 4.75$ and 3.32 Å, respectively, while structures 0.21 and 0.22 above the minimum had $d = 3.35$ and 4.63 Å, respectively. We chose $d = 4.1$ Å for MEH-PPV. In this case the lowest-energy structures have a double bond on one chain sitting over a ring of a neighbor, as shown in Fig. 1.

The chain-chain distances in CN-PPV and MEH-PPV are in reasonable accord with typical stacking distances found in molecular complexes of the donor-acceptor type.[17–21] Thus, a distance in the range of 3.25–3.45 Å is characteristic for donors and acceptors of moderate strength, such as cyano-substituted acceptor molecules and phenyl donor groups,[17,19] while distances larger than 3.5 Å are characteristic of negligible donor-acceptor interactions.[17]

Because the important overlap between polarons on adjacent chains is due to the π electrons, whose wave functions decay rapidly with distance, it should be a good first approximation to neglect the horizontal displacements of the chains relative to each other and take the ratio of the matrix elements for optical emission of CN-PPV to MEH-PPV as $e^{-\alpha(3.4-4.1)}$, where α is the decay rate in Å^{-1}. We choose α to match the average decay rate of the overlap of p wave functions centered on carbons with spacing in the range of 3.4–4.1 Å. Using Slater orbitals with exponents[22] $\zeta = 1.625$ we find α is 2.013 Å^{-1}. The square of the matrix element ratio is then 16.8.

For the structures in Fig. 1, the cyano carbon of CN-PPV is horizontally displaced by 0.3 Å relative to the closest ring carbon on the adjacent chain, while the carbons of the vinyl group in MEH-PPV are horizontally displaced by 0.7 Å relative to the closest ring carbon on a neighbor. For these displacements the matrix element ratio squared is 20.7. Using a variety of displacements between 0 and 0.7 Å , to account for a reasonable range of structural fluctuations, leads to other ratios in the range 16.2–20.7. These horizontal displacements correspond to changes in the interchain C-C distances of 3.40 to 3.47 Å for CN-PPV and 4.10 to 4.16 Å for MEH-PPV. Thus, our simple considerations lead to the conclusion that the emission probability for the excimer in CN-PPV should be 16–20 times as large as for the excimer in MEH-PPV. Optimization of the excimer interactions in the excited state would, if anything, increase this ratio because the CN-

PPV, with the shorter chain-chain distances, is likely to benefit more from these interactions than the MEH-PPV.

We conclude that, consistent with inferences from earlier data,[4–7] excimers are formed in large numbers by photons above the absorption edge in MEH-PPV as well as in CN-PPV, but only the latter are emissive because the small matrix element in the former case allows nonradiative interchain transfer processes to be more rapid.

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