ADVANCED MATERIALS

Transfer Processes in Semiconducting Polymer–Porphyrin Blends**

By *Vicki Cleave*, *Goghan Yahioglu*, *Pierre Le Barny*, *Do-Hoon Hwang*, *Andrew B. Holmes*, *Richard H. Friend*,* and *Nir Tessler**

Organic light-emitting diodes (LEDs) have been gaining prominence in the past few years.[1–4] Triplet excitons, which are statistically predicted to be generated in such devices with three times the efficiency of singlet excitons, have been hard to detect. However, they may be accessed through the use of a phosphorescent emitter blended into the semiconductor, as demonstrated in several recent reports.[5–7] Here, we present a study of a variety of electroluminescent polymer blends with a phosphorescent porphyrin, PtOEP. We are able to predict and study interactions between blend components which may be based on the transfer of charged or neutral species, and result in either emission or quenching of the guest molecule phosphorescence. Where triplet exciton transfer either to or from the porphyrin is observed, we may use this as a technique to reveal properties of the host polymer. For instance, triplet excitons from the guest porphyrin transfer to dialkoxy poly(*p*-phenylenevinylene) (PPV) derivatives, and can be detected in them through the triplet optical absorption near 1.4 eV. An optical cross-section of 3×10^{-15} cm^2 for the absorption can then be calculated, and we also find that the triplet excitons are stabilized with respect to singlet excitons by at least 0.15 eV.

Excited states (excitons) in molecular and polymeric semiconductors are mobile for the systems studied here, and are able to reach guest–host heterojunctions. At such a heterojunction, a range of interactions is possible. For any energy transfer to occur from donor to acceptor, several criteria must be satisfied. Firstly, the exciton energy must be lower in the guest than in the host. Secondly, it must be favorable for both electron and hole to transfer together from the host polymer to the guest molecule to prevent charge separation between blend components. Fulfillment of the second requirement may be assessed via measurement of the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) levels, which tell us about the hole and electron levels of the materials. If HOMO and LUMO energies of the blend components are sufficiently offset to overcome the exciton binding energy, charge transfer can occur, which results in exciton dissociation,[8] and energy transfer will not be observed.

Figure 1 shows the relative positions of the HOMO and LUMO levels of the guest molecule, the triplet-emitting platinum octaethyl porphyrin (PtOEP), and the various host polymers we have studied, as measured by cyclic voltammetry. We show that the polymer blends may be classified by the interactions expected between the blend components, which may be caused by either energy or charge transfers, and result in either phosphorescence or quenching of emission. We illustrate these four combinations below:

a) *Energy Transfer to Guest with Phosphorescence*: This example is provided by blends of the polymer poly[4-(*N*-4-vinylbenzyloxyethyl, *N*-methylamino)-*N*-(2,5-di-*tert*-butylphenyl naphthalimide)] (PNP) and PtOEP. As reported in a previous publication,[5] in addition to singlet exciton transfer in this blend, we have also observed direct transfer of PNP triplet excitons to PtOEP. We have shown that the Dexter (triplet–triplet) transfer in LEDs has two signatures. Firstly, an enhanced emission from the guest PtOEP under electrical excitation as compared with photoexcitation. Secondly, a prolonged rise in the electroluminescence (EL) response occurs after the excitation pulse has finished. This is attributed to the transport and transfer of long-lived triplet excitons from host to guest, followed by radiative decay on the guest molecule. The relative positions of HOMO and LUMO for this system shown in Figure 1 demonstrate why this combination functions in this way. The guest has HOMO and LUMO levels which function as only shallow traps for both electrons and holes, so that electron–hole recombination occurs predominantly in the bulk (host) polymer and not by sequential carrier trapping on the PtOEP molecules.

b) *Charge Recombination at Guest, with Phosphorescence*: Phosphorescence from the guest PtOEP molecule may also result from charge recombination at the guest molecule. We expect this when the guest acts as a deep trap for one or other charge, as is the case for holes in blends of PtOEP with PFO, for which the trap energy is 0.5 eV. Work by Wolf et al.[9] predicts a critical dopant concentration of 0.0001 % for hole trapping to become a significant effect at a trap energy of 0.5 eV. The comparison of the current dependence of the slow rise time from the time-resolved EL of blends of PtOEP in PFO to PNP shown in Figure 2b does indeed indicate a difference between the responses of the two host polymer blends. Whilst the PNP blend shows the slow rise attributed to triplet exciton migration to a porphyrin site from the lowest measurable currents, the rise time in PFO is not discernable until higher currents are reached. Trapping on the PtOEP molecule in PFO

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[**] We thank Cambridge Display Technology (CDT) for the PFO and help with CV measurements, Covion for the OC_1C_{10}–PPV, and Dr. Anna Köhler for fruitful discussions and assistance. We also thank the Commission of the EU under Brite-Euram Contract BRPR-CT97-0469 "OSCA" and EPSRC for financial support of the project.

0935-9648/01/0101-0044 $ 17.50+.50/0

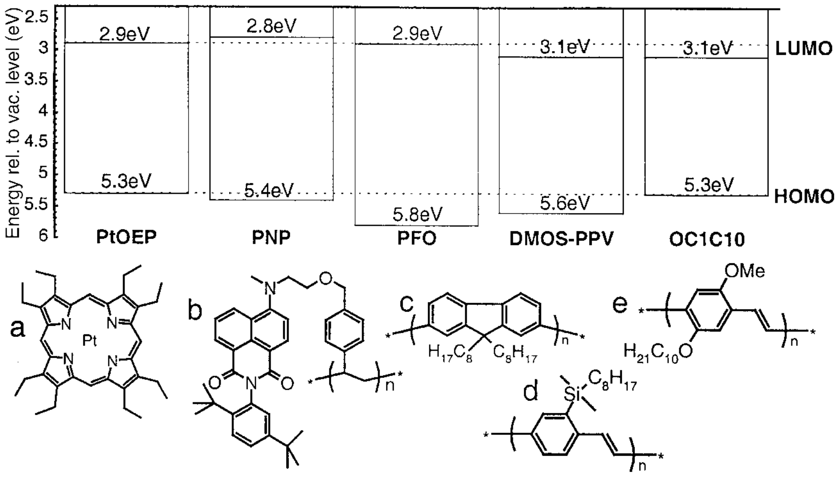

Fig. 1. HOMO and LUMO levels for the polymers and porphyrin used in this work. Oxidation potentials were determined using cyclic voltammetry, using a Ag/AgCl standard reference, a platinum working, and a platinum wire counter electrode. 0.1 M Bu_4NClO_4 in MeCN was used as the cell solution and a nitrogen purge maintained inert conditions. LUMO levels were obtained from combination of the CV-determined HOMO energy and the optical band gap for each material. The chemical structures of the materials are also shown: a) PtOEP; b) PNP; c) PFO; d) DMOS–PPV; and e) OC_1C_{10}–PPV (see text for systematic names).

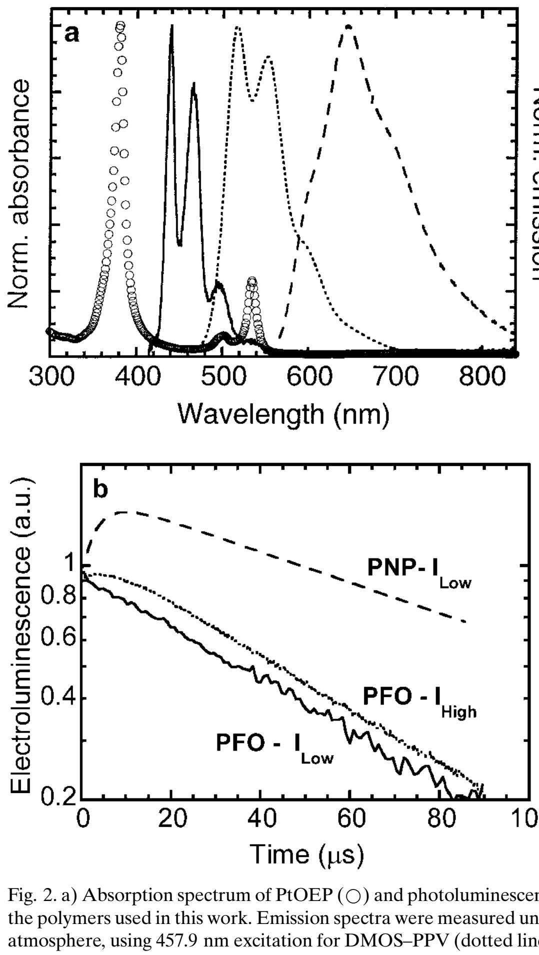

Fig. 2. a) Absorption spectrum of PtOEP (○) and photoluminescence spectra for the polymers used in this work. Emission spectra were measured under a nitrogen atmosphere, using 457.9 nm excitation for DMOS–PPV (dotted line), UV excitation for the PFO (solid line), and 501 nm excitation for OC_1C_{10}–PPV (dashed line). All doping levels are quoted as wt.-%. b) The effect of changing current on the Dexter transfer observed in LEDs made from blends of PNP and PFO with 0.1 % PtOEP. The LEDs were excited with an electrical pulse of a few hundred ns, and the transient electroluminescence recorded with a photomultiplier tube with 10 ns resolution. All LEDs consisted of an indium tin oxide anode, covered with a hole-transporting layer of approx. 75 nm, and then the emissive blend (~80 nm thick). Cathodes consisted of ~200 nm Ca covered in 200 nm+ Al, and were evaporated under a 10^{-6} mbar vacuum. All devices were tested under a 10^{-5} mbar vacuum. LEDs made with PFO blended with PtOEP have reached efficiencies of 0.6 lm/W due primarily to the PtOEP acting as a recombination centre for charge carriers in a wide bandgap host.

seems to dominate the response of the LED until, at high charge and exciton concentrations, the PtOEP sites are partially filled and some excitons are generated in the polymer and not directly on the PtOEP. When this occurs, we observe a small signature of the transfer of the fraction of triplets that were not generated on the PtOEP site. Our findings suggest that charge trapping may be an important factor in producing high efficiency phosphorescent LEDs, since triplet excitons formed in this way are still offered a radiative decay channel.

c) *Excited-State Charge-Transfer and Phosphorescence Quenching*: Charged interactions in blends may also lead to emission quenching if charge carriers are energetically favored to lie on different components.[10] Blends of poly(2-dimethyloctylsilyl-1,4-phenylenevinylene) (DMOS–PPV)[11] with PtOEP demonstrate this phenomenon, where, as Figure 1 shows, both the HOMO and LUMO levels are offset, and exciton dissociation is therefore expected so long as this offset is sufficient to overcome the exciton binding energy. Photoluminescence from blends of PtOEP in DMOS–PPV show no phosphorescence from the guest, despite overlap of the host emission and guest absorption. Indeed, quenching of the host polymer emission by a factor of 20 at a 5 % PtOEP doping level is also observed. Charge separation is indeed confirmed by photoinduced absorption (PiA) measurements, as shown in Figure 3, where both a pure polymer and a blend sample are photoexcited and the absorptions of the excited states are probed. The pure sample shows only a peak at 1.45 eV attributed to triplet (T_1–T_n) absorption, whereas, the blend shows a large additional absorption at 1.6 eV with a complex lifetime that we attribute[12] to separated charges in the blend. We consider that charge transfer occurs prior to intersystem crossing to the triplet state on the porphyrin, since the triplet level of the porphyrin is sufficiently stabilized with respect to the host LUMO to make exciton dissociation energetically unfavored.

d) *Triplet Energy Transfer from Guest to Host, Phosphorescence Quenching*: Neither singlet energy transfer or exciton dissociation is expected in blends of PtOEP with the polymer poly[(2-methoxy-5-(3,7-dimethyl)-octyloxy)-1,4-phenylenevi-

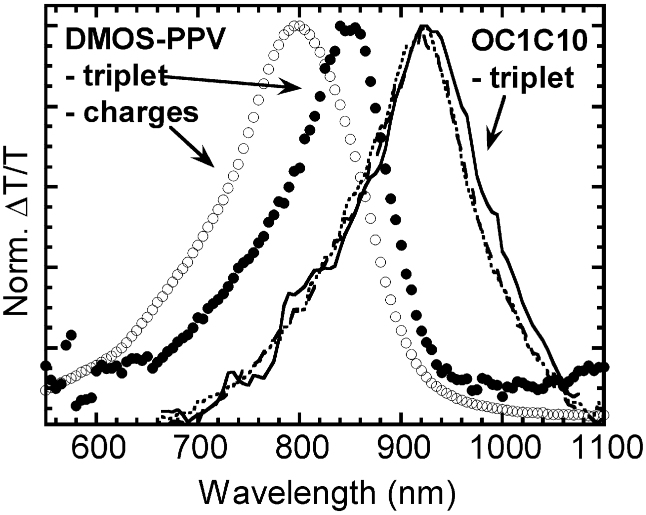

Fig. 3. Photo-induced absorption spectra of DMOS–PPV and OC_1C_{10}–PPV blends with PtOEP. Unblended DMOS–PPV (●); 1 % PtOEP in DMOS–PPV (○); unblended OC_1C_{10} (solid line); 1 % PtOEP in OC_1C_{10} (dashed line); and 5 % PtOEP in OC_1C_{10}–PPV (dotted line). All spectra recorded at 50 K, at a pump wavelength of 501 nm and chop frequencies of 237 Hz and 167 Hz for the DMOS–PPV blends and OC_1C_{10} blends respectively.

nylene] (OC_1C_{10}–PPV), since the polymer emission is too low in energy to coincide with the PtOEP absorption, and the HOMO and LUMO levels are not offset. However, the porphyrin phosphorescence is strongly quenched in a 5 % blend of PtOEP in OC_1C_{10}–PPV. This quenching is detected by the reduced lifetime for emission and is found to be temperature dependent. The porphyrin emission lifetime is quenched by more than a factor of 50 at room temperature (from 75 µs to 1.2 µs), but only a factor of 1.5 at 50 K (from 150 µs to 100 µs).

PiA measurements on both pure and blended OC_1C_{10}–PPV (Fig. 3) show the same feature in all cases, which has been attributed to the T_1 to T_n absorption in the very similar polymer MEH–PPV,[13] and indicate that exciton dissociation does not occur. However, the fate of the quenched PtOEP triplet excitations is also indicated by these measurements. The measured lifetime of the OC_1C_{10}–PPV triplet exciton (Table 1) is seen to increase with the doping level as a larger fraction of light is absorbed by the PtOEP which transfers triplet excitons directly to the polymer. The polymer triplet absorption intensity also increases on addition of PtOEP, though the modest increase is indicative of the low quenching level observed at 50 K. A similar variation in lifetime is observed in a given blend when the excitation wavelength is changed to 465 nm where the relative absorption of the PtOEP is less. These two observations confirm that triplet transfer from the PtOEP is occurring.

Table 1. PiA data for blends of PtOEP in OC_1C_{10}–PPV. Data was extracted from the measurements shown in Figure 3, and triplet lifetimes were evaluated by monitoring the pump beam chop frequency dependence of the PiA signal.

Blend (% of PtOEP)	λ_{ex} [nm]	% absorption by PtOEP	PiA intensity at 920 nm [a]	OC_1C_{10} triplet lifetime [ms]
0%	501	0%	1.0	0.14
1%	501	0.2%	1.7	0.21
5%	501	1.0%	1.3	0.23
5%	465	0.4%	–	0.18

[a] Estimated error ±30 %.

As the long-lived triplet excitons transfer from guest to host, the apparent triplet lifetime of the host is extended. This situation is analogous to that shown in Figure 2b, where excitons were transferred from host to guest over a relatively extended period. It can be seen that the transfer extends the apparent lifetime, that is, the time taken for the intensity to fall to e^{-1} of its maximum. The greater the proportion of delayed transfer, the longer the measured lifetime becomes.

This transfer mechanism can be expressed using differential rate equations. We show below the solution obtained for the time dependence of the triplet density in the host after a certain population has been created at $t = 0$.

$$T^{OC} = T_0^{OC}\exp(-k_{OC}t) + \frac{k_{Tr}T_0^{Pt}}{(k_{Pt}+k_{Tr}-k_{OC})}\left[\exp(-k_{OC}t) - \exp(-[k_{Pt}+k_{Tr}]\,t)\right] \qquad (1)$$

where T^{OC} is the OC_1C_{10}–PPV triplet exciton density, T_0^{Pt} and T_0^{OC} are the densities at $t = 0$, and k_{OC} and k_{Pt} are the rates of decay of OC_1C_{10}–PPV and PtOEP triplet excitations respectively, and k_{Tr} is the rate of transfer from PtOEP to OC_1C_{10}–PPV. It is assumed that the intersystem crossing on both host and guest is "instantaneous" relative to the timescale of the ongoing guest–host triplet transfer, and that the transfer and decay rates are dependent on the population of the donor and emitting levels respectively. Using the data in Table 1, columns 3 and 5, we were able to model the effect of the transfer of PtOEP triplets on the polymer triplet exciton lifetime and verify that transfer to the OC_1C_{10}–PPV triplet dominates the quenching of the PtOEP phosphorescence. This method also allows us to quantify the fraction of triplets generated directly in the OC_1C_{10}–PPV (the inherent number of triplet excitons created on the host by intersystem crossing, T_0^{OC}). We find that approximately 0.2 % of the photo-excitation of the OC_1C_{10}–PPV undergoes intersystem crossing from the polymer singlet to triplet manifold. From this we may estimate the absorption cross-section for the T_1–T_n transition, which we calculate to be 3×10^{-15} cm^2.

The direct evidence for triplet energy transfer in cases a, b, and d, and knowledge of the energy of PtOEP T_1 level from its phosphorescence enable us also to comment on the triplet energy levels of the host polymers. Dexter energy transfer can only be operational if the triplet energy levels of the two molecules involved are appropriately placed. That is, the energy level of the acceptor molecule must lie below that of the donor molecule for the tunneling mechanism to be operational. The direction of triplet energy transfer between the porphyrin and polymer therefore provides us with a tool with which we can place limits on the energy of the triplet exciton in the polymer.

In cases a and b, the observations of triplet energy transfer from host polymer to guest molecule places a lower limit of 1.9 eV on the energy of the triplet exciton above the ground

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state in both PNP and PFO. From scenario d we can deduce an upper limit of 1.9 eV for the OC_1C_{10}–PPV triplet level from the triplet energy transfer from PtOEP to the host polymer. A similar approach has been used to deduce a triplet energy of 1.27 ± 0.07 eV for the polymer MEH–PPV, using the observations of triplet energy transfer to or from a variety of sensitizers in solution.[14] A concentration-dependent molar absorption coefficient for the polymer in solution was also deduced from the same work. The triplet exciton energy of PPV was also deduced in a recent study,[15] using a different technique based on the observation of a singlet fission channel involved in the creation of triplet excitons.

Placing a limit on the triplet exciton energy, and combining this with singlet exciton energies of the polymers known from photoluminescence, also allows us to place a lower limit on the exchange energy between the S_1 and T_1 states. The energy of the singlet 0–0 emission of the exciton in OC_1C_{10}–PPV is seen to be 2.05 eV, indicating that the exchange energy between singlet and triplet excitons in the polymer is not less than 0.15 eV. In the cases of PNP and PFO, the exchange energy is calculated to be not more than 0.5 eV and 0.9 eV respectively. These values are in accord with calculations reported by Beljonne et al.

The guest–host studies reported here illustrate the complexity of the possible charge and energy transfers at heterojunctions, and, by accessing the triplet channel through the use of a phosphorescent guest, we are able to measure a range of properties of the triplet excitons in the host polymers. These techniques make possible the detailed studies which will be needed in order to reveal the full role played by triplet excitons in organic LEDs.[16] For example, our measurement of the triplet–triplet optical cross-section for OC_1C_{10}–PPV makes the measurement of triplet exciton concentrations possible through their excited state absorption. These and other observations, such as an estimation of singlet to triplet exciton ratio in tris(8-hydroxyquinoline) aluminum (Alq_3),[17] made possible by the use of a phosphorescent dopant, show that through careful use, the technique is becoming an important tool for the investigation of organic electroluminescent materials.

Received: January 17, 2000
Final version: August 16, 2000

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Micropatterns of Poly(4,4′-dimethoxy-2,2′-bithiophene) Generated by the Scanning Electrochemical Microscope[**]

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The scanning electrochemical microscope (SECM) is a novel surface analysis tool that combines the principles of scanning tunneling microscopy (STM) and the ultramicroelectrode (UME) technique.[1,2] The central piece of the microscope is a UME, which is moved in an electrolyte above the surface. This UME measures a current produced by the oxidation or reduction of the electrochemical species dissolved in the electrolyte, which varies with the chemical nature of the surface and with the tip–sample distance. The two fields of application of this new microscopy technique are surface analysis and micromodification. In fact, scanning the UME at constant height provides precious information about local surface conductivity, morphology, concentration profiles, and maps of reactive sites. This explains why the SECM is an excellent analytical tool.[3] The SECM and its high-resolution microstructuring possibilities have also attracted the interest of the microelectronics industry, where well-defined, localized changes in chemical or physical properties have important technological implications.[4] High-resolution surface etching and deposition, in particular, have potential in the fabrication of microelectronic devices.

On the other hand, conducting polymers such as polyaniline (PANI), polythiophene (PT), and polypyrrole (PPy) have attracted considerable attention in the microelectronics industry over the last decade. This new generation of synthetic

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[**] We gratefully acknowledge the financial support of the BMBF and the DFG.