

Polarization of singlet and triplet excited states in a platinum-containing conjugated polymer

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We investigate the polarization of optical transitions associated with the singlet S_1 and triplet T_1 and T_n excited states in a uniaxially aligned platinum-containing conjugated polymer which contains a 2-methoxy-5-(2'-ethyl)-hexyloxy (MEH)-substituted phenyl ring. For the singlet S_1 state, which is extended along the polymer chain, we find the corresponding absorption and emission to be polarized parallel to the chain as seen for other conjugated polymers. However, for the triplet excited states, we find that the emission from the highly localized T_1 state has components both parallel and perpendicular to the polymer chain, while the absorption from T_1 into the delocalized T_n state is polarized entirely parallel to the chain. We discuss this connection between the spatial extent of the excited state and the polarization of the associated optical transitions and consider how the spin-orbit coupling mechanism can influence the polarization of emission from the T_1 state.

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I. INTRODUCTION

In recent years there has been much interest in the alignment of conjugated polymers with a view to producing polarized electroluminescence for display applications¹⁻⁴ and for controlling charge transport in organic thin-film transistors.⁵ Weder and co-workers^{6,7} have also produced polarizing displays that are based on the photoluminescence of conjugated polymers such as alkoxy-substituted phenylene ethynylenes. In their system the energy from a UV back light is absorbed isotropically by sensitizer molecules. These then transfer the energy to aligned polymer chains that subsequently emit polarized light. Such polarizing displays have been shown to be more efficient than their liquid-crystalline counterparts.

The techniques developed for aligning conjugated polymers have also made it possible to investigate many important aspects of the photophysics of these materials.⁸⁻¹³ Polarized absorption spectra, such as those obtained by Miller *et al.* for aligned poly(*p*-phenylene-vinylene) (PPV) and poly(*p*-phenylene) (PPP) derivatives,⁹⁻¹¹ can give detailed information about the one-dimensional delocalization of excited states in conjugated polymers. Doping-induced polarized absorption spectra have also revealed that charged polaron states in these materials are polarized parallel to the chain axis.¹²

However, despite all of this interest in the polarization of optical transitions associated with excited states in conjugated polymers, to our knowledge, the polarization of triplet states in this class of materials has not been investigated. Emission from a triplet excited state to a singlet ground state (phosphorescence) is forbidden by spin selection rules, but can be rendered partially allowed by spin-orbit coupling.¹⁴ However, most organic conjugated materials do not contain heavy atoms and consequently have very little intrinsic spin-orbit coupling,¹⁴ so that it is difficult to detect emission from triplet states in organic conjugated polymers. There are just a few reports of their phosphorescence, and these have only

appeared recently.^{15,16} Consequently, there have been no studies of the polarization of triplet emission in these materials. Here we have investigated the polarization of both singlet and triplet emission and absorption with respect to the polymer backbone by using a polymer that shows triplet-state emission and that can be uniaxially aligned. To circumvent the problem of nonemissive triplet states we used the platinum-containing ethynylene conjugated polymer shown in Fig. 1. Incorporating Pt into the polymer backbone introduces strong spin-orbit coupling while still preserving conjugation, and phosphorescence can be directly observed.¹⁷⁻²³ It is therefore possible to access the triplet state using conventional spectroscopic techniques. Emission and absorption in such Pt-containing polymers are based on π - π^* transi-

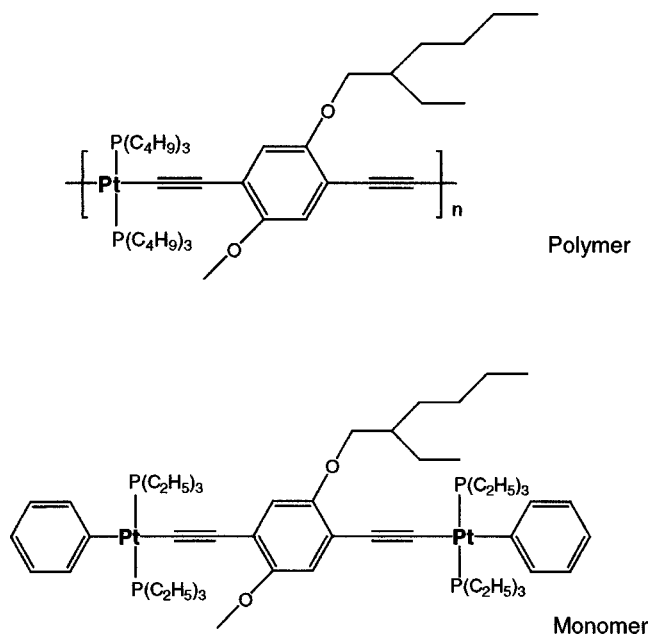


FIG. 1. Chemical structures of the platinum-containing conjugated polymer and monomer investigated.

tions on the organic conjugated unit,^{18,22} and the fluorescence and phosphorescence spectra in a very similar Pt polymer were found to be identical to those of its all-organic analog.²⁴ The Pt-containing polymer shown in Fig. 1 has a thermotropic liquid-crystalline phase transition and therefore can be aligned on a rubbed polyimide substrate.

II. EXPERIMENT

The Pt-containing polymer and monomer were synthesized via the Hagihara route^{22,25} and were readily dissolved in dichloromethane at room temperature. For unpolarized measurements, ~ 100 nm films of polymer and monomer were spun cast onto quartz substrates using a conventional photoresist spin coater. For polarized measurements, films of the polymer were spun cast on top of films of rubbed polyimide on glass substrates. It was found that the best alignment occurred when the films were heated to 180 °C for 5 min in a nitrogen atmosphere and then quenched to a room-temperature liquid-crystalline glass. It was not possible to align the monomer using this technique.

The optical absorption of the aligned films was measured with a Hewlett-Packard ultraviolet-visible spectrometer, with a calcite cube polarizer placed at 45° to the vertical between the lamps and sample. Measurements were made parallel and perpendicular to the rubbing direction and referenced to a blank sample of rubbed polyimide on glass. All the measurements were made at 45° to the vertical in order to eliminate any polarization-dependent effects of diffraction gratings in the detection system so that the intensities of absorption parallel and perpendicular to the polymer chains could be directly compared.

Measurements of photoluminescence (PL) and photoinduced absorption (PIA) were made with the sample oriented such that its rubbing direction was at 45° to the vertical in a continuous-flow helium cryostat. The temperature was controlled with an Oxford-Intelligent temperature controller-4 (ITC-4). For PL measurements, excitation was provided by the UV lines (334–365 nm) of a continuous-wave (cw) argon ion laser. Typical intensities used were a few mW/mm². The polarization of the excitation light was rotated to be at 45° to the vertical and parallel to the rubbing direction using a half wave plate for 355 nm. Any residual excitation light without this polarization was then removed using a calcite cube polarizer at 45° to the vertical placed before the sample. The emission spectra were recorded using a spectrograph with an optical fiber input coupled to a cooled charge-coupled-device array (Oriel Instaspec IV). A calcite cube polarizer was placed between the sample and optical fiber to select the emission either parallel or perpendicular to the rubbing direction. Photoinduced absorption was measured using the UV lines (334–365 nm) of the argon ion laser as a pump beam to photoexcite the sample and monochromated light from a tungsten lamp as a probe beam to measure its absorption in the photoexcited state.²⁶ The probe beam was polarized at 45° to the vertical, either parallel to perpendicular to the rubbing direction, using a calcite cube polarizer placed before the sample.

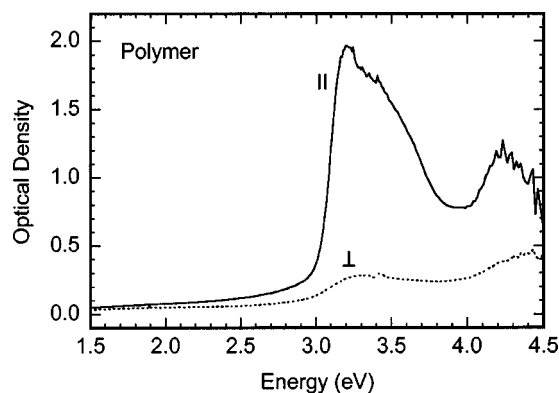


FIG. 2. Absorption spectrum of the polymer measured parallel (solid line) and perpendicular (dotted line) to the alignment direction.

III. RESULTS

A. Polarization of optical transitions

1. Absorption spectroscopy

The absorption spectrum of the Pt polymer aligned on a rubbed polyimide substrate is given in Fig. 2, where the absorption spectra measured both parallel and perpendicular to the alignment direction are compared. The S_0 - S_1 absorption band centred at around 3.2 eV is based on π - π^* transitions on the organic unit of the Pt polymer,^{18,22} and it is polarized parallel to the alignment direction with a dichroic ratio of 7:1. Since the S_0 - S_1 π - π^* optical transitions in analogous alkoxy-substituted phenylene ethynylenes occur parallel to the polymer chain,⁶ we conclude that the long axis of the Pt-polymer chain is parallel to the alignment direction and that good alignment of the polymer chains has been achieved.

2. Photoluminescence spectroscopy

The photoluminescence spectra of the polymer measured parallel and perpendicular to the alignment direction at 290 and 10 K are shown in Fig. 3. There are two emission bands in the spectra. The high- and low-energy bands are from singlet and triplet excited states S_1 and T_1 , respectively. The triplet-state emission of this polymer and similar materials has been well characterized previously by lifetime and photoinduced absorption measurements.^{17,20-23} At both 290 and 10 K the singlet emission is seen to be polarized almost entirely parallel to the polymer chain, as observed for many other conjugated polymers,^{1-3,6,7,27} with a dichroic ratio of 7:1. This is in agreement with the polarization of the absorption spectrum (Fig. 2). In contrast, the triplet emission has components both parallel and perpendicular to the polymer chain with dichroic ratio of 1:2, where the largest component is perpendicular to the polymer backbone. In addition, the same anisotropy is present both at 10 and 290 K. The weight in the vibronic peaks of the triplet emission is different parallel and perpendicular to the chain direction, with 20% more weight in the vibronic sidepeaks for emission parallel to the polymer backbone than perpendicular to it. This is particularly obvious for the 0-1 peak at 2.07 eV, which is a result of the benzene stretching mode.

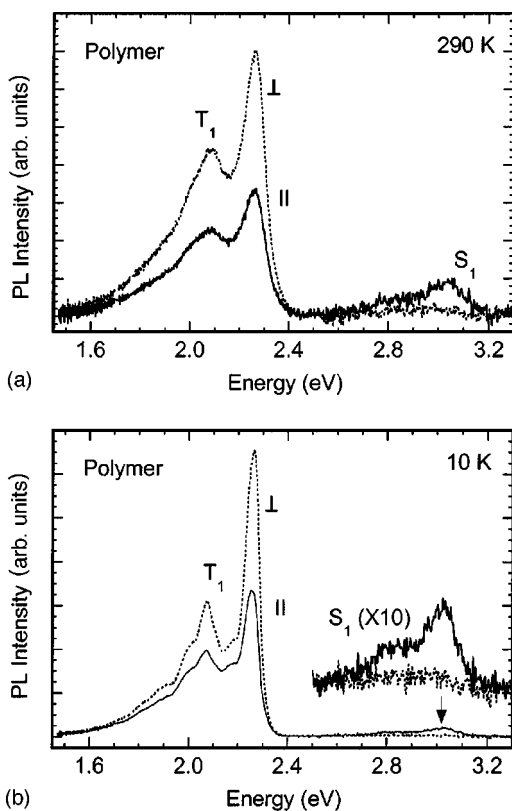


FIG. 3. Photoluminescence spectra of the polymer (a) at 290 K and (b) at 10 K measured parallel (solid lines) and perpendicular (dotted lines) to the polymer chain direction. The emission parallel and perpendicular to the chain direction has been measured in the same configuration so their relative intensities may be directly compared. The inset in (b) shows the singlet emission at 10 K magnified by a factor of 10. The excitation light was parallel to the polymer chain direction.

We note that this triplet emission is produced via intersystem crossing from a singlet state whose absorption is polarized parallel to the polymer chain and that there is negligible absorption directly into the triplet state compared to absorption into the singlet, as can be seen from the absorption spectrum (Fig. 2).

3. Photoinduced absorption

In addition to the T_1 state, we investigated the polarization of absorption into the higher-energy triplet state T_n . The photoinduced absorption spectrum of the Pt polymer is shown in Fig. 4. The absorption peak observed is a result of a photoexcited transition between the T_1 and T_n states. The origin of the transition has been confirmed by its strong temperature dependence, which is characteristic of triplet states, and also by the fact that the absorption intensity has the same lifetime as the triplet T_1 photoluminescence.¹⁸ From Fig. 4 it can be seen that the T_1 - T_n absorption is strongly polarized parallel to the polymer chain direction, with a dichroic ratio of 8:1. This is in contrast to the T_1 - S_0 emission which has components both parallel and perpendicular to the chain.

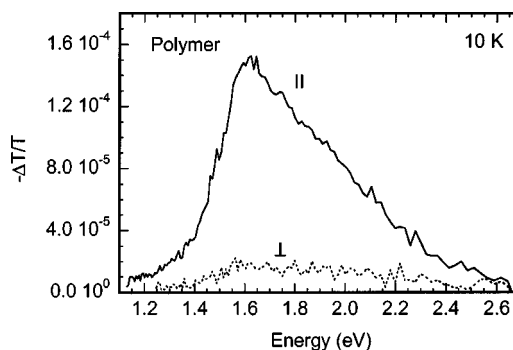


FIG. 4. Photoinduced absorption spectra of the polymer measured parallel (solid line) and perpendicular (dotted line) to the alignment direction at 10 K. The excitation light was parallel to the polymer chain direction.

B. Exciton delocalization

In summary, we have seen that optical transitions associated with the S_1 singlet state are polarized parallel to the polymer chain direction as seen for singlet states in a range of other conjugated polymers.^{2,6,7,12} We also find that absorption from T_1 into the higher-energy triplet state T_n is polarized parallel to the polymer backbone. However, in contrast, we observe that the major component of the T_1 - S_0 emission is polarized perpendicular to the polymer chain.

In order to elucidate the origin of these polarizations we investigated the spatial extent of the T_1 , S_1 , and T_n states in this Pt-MEH polymer by comparing the energies of these states with those in the corresponding monomer (the chemical structure of the monomer is shown in Fig. 1). Figures 5 and 6 compare the photoluminescence and photoinduced absorption spectra of unaligned films of the polymer and corresponding monomer. The energies of the T_1 , S_1 , and T_n states of the polymer and monomer are summarized in Fig. 7 by taking the energy corresponding to the maximum intensity of the photoluminescence and photoinduced absorption spectra. The energies of the T_1 states are very similar for the polymer and monomer. However, the S_1 and T_n states are at

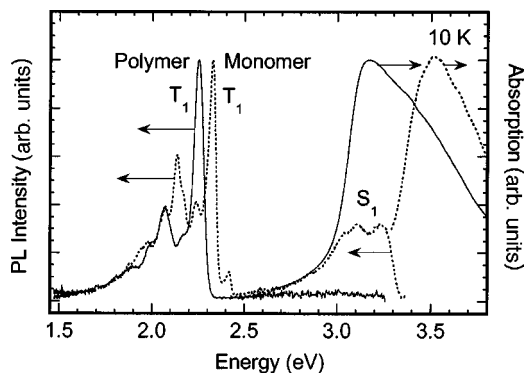


FIG. 5. Photoluminescence spectra of an unaligned film of the polymer (solid line) compared to that of its corresponding monomer (dotted line) measured at 10 K. The corresponding absorption spectra are also shown (as solid and dotted lines, respectively) for comparison. All of the spectra have been normalized to allow comparison of the peak energies.

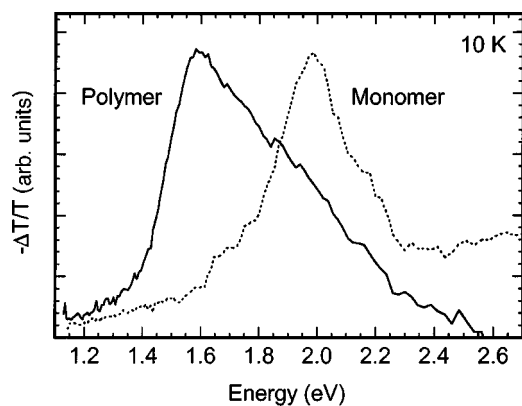


FIG. 6. Photoinduced absorption spectra of the polymer (solid line) compared to that of its corresponding monomer (dotted line) measured at 10 K. The spectra have been normalized to allow comparison of the peak energies.

higher energies in the monomer than in the polymer. By a simple particle in a box argument²⁸ this suggests that the T_n and S_1 states are confined in the monomer and, therefore, extend over more than one repeat unit in the polymer. In contrast, the T_1 state appears to occupy nearly the same space in the polymer and monomer. This agrees well with measurements by Beljonne *et al.*¹⁸ who observed the same trends in energy levels for a Pt-containing polymer and monomer very similar to the materials investigated here. They also calculated the spatial extents of T_1 , S_1 , and T_n states in their Pt-containing polymer and found the T_1 state to be localized to approximately one phenylene ring while the S_1 and T_n states were seen to occupy two and three repeat units of the polymer chain, respectively.¹⁸ The more delocalized character of the higher-energy T_n state is consistent with a gradual transition to bandlike electronic states, as shown previously for singlet excited states.²⁹

IV. DISCUSSION

The polarization of the T_1 -triplet-state emission in small molecules such as benzene and naphthalene, where it is possible to measure phosphorescence directly, was investigated

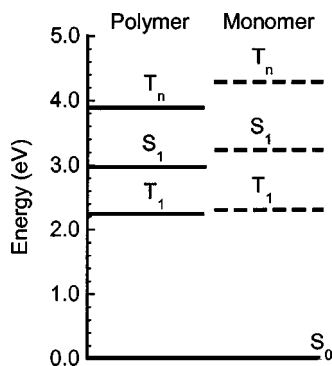


FIG. 7. Summary of the energy levels of the T_1 , S_1 , and T_n states in the polymer and monomer taken from the photoluminescence and photoinduced absorption spectra. The S_0 state has arbitrarily been taken to be at 0 eV.

in the 1960's.³⁰ For π -conjugated systems it was found that the polarization of the triplet-state emission has two components: one out of the molecular plane and the other parallel to the long molecular axis. In planar acenes (such as fluorene, coronene, chrysene, anthracene, and picene) the out-of-plane component was found to be dominant, contributing about 70% of the total emission intensity.³⁰

While the triplet-state emission of small aromatic molecules has been fairly thoroughly investigated, phosphorescence in conjugated polymers has only recently been observed.^{15,16,22,24} In contrast to aromatic molecules, where the excited states are confined by the molecular dimensions, excited states in conjugated polymers are free to extend along the polymer backbone and so can be of various lengths. In the work presented here, we have measured the polarization of the triplet-state emission from a conjugated polymer and compare it to the polarization of the singlet-state emission.

The singlet-state emission in conjugated polymers is usually observed to be polarized along the chain direction,^{1-3,6,7,27} as is the case in the polymer investigated in this work. This polarization can be rationalized within a simple classical model of dipole moments. Optical transitions in organic materials occur because of an oscillating dipole within the material that interacts with the oscillating electric field of light.¹⁴ A dipole transition implies an oscillating region of charge, and if this charge density is extended along the polymer chain, then this will result in a larger dipole moment along the chain than perpendicular to it.

Similarly, in the conjugated polymer investigated here we have shown that the T_n state is elongated, and we find that the absorption from the T_1 to the T_n state occurs only along the polymer chain direction. This is consistent with our dipole moment description since the component of T_n perpendicular to the chain would be significantly weaker than that parallel to the chain. It also indicates that the T_1 state is at least partially polarized along the polymer backbone direction.

In contrast to the S_1 and T_n states, the T_1 state is not extended, but rather localized, so according to our simple classical dipole moment model, we would expect the magnitudes of the dipole moments parallel and perpendicular to the polymer chain direction to both be significant. However, unlike the S_0 - S_1 and T_1 - T_n transitions, the T_1 - S_0 transition involves different spin manifolds and so is formally spin forbidden. Therefore spin-orbit coupling is required in order for the transition to actually occur.

The effect of spin-orbit coupling on an originally unperturbed triplet state is to mix it with one or more singlet states. The resulting state is usually referred to as a nominal triplet state. The same applies to the singlet ground state S_0 , which will acquire some triplet admixture, albeit small. The observed phosphorescence takes its intensity from the allowed transitions between S_0 and the singlets mixed into the triplet state and, to a lesser extent, from the allowed transitions between the triplet excited state and the triplets mixed into S_0 .^{30,31}

For molecules such as the planar acenes, this spin-orbit coupling mechanism also explains the two observed polar-

ization components of the T_1 emission. The x , y , and z components of the spin-orbit coupling operator mix singlet and triplet states of the same parity (u or g), but of different symmetry.^{30,31} Since the different admixtures change the symmetry of the wave function, different polarizations of the T_1 - S_0 emission become possible, depending on the particular symmetries of the admixed singlet states.^{30,31} For some molecules it has been possible to determine exactly which singlet states are mixed with the triplet by spin-orbit coupling. In these cases the observed in-plane and out-of-plane components of the phosphorescence can then be attributed to admixtures of particular singlets according to their symmetry.^{30,31} It is possible that such mixing may also account for the two polarization components that we observe for the phosphorescence in the conjugated polymer that we have investigated here. Yet we stress that detailed quantum chemical calculations are required to clarify this and to reveal which particular singlet states are mixed with the triplet by spin-orbit coupling.

We now address the polarization of the phosphorescence from our conjugated polymer in more detail. A slightly larger proportion of the T_1 emission is observed perpendicular to the alignment direction than parallel, giving a dichroic ratio of 1:2, which suggests that 67% of the emission is polarized perpendicular to the polymer backbone. Yet if we take the π - π^* absorption band to be polarized entirely along the polymer chain,^{1-3,6,7,27} then the dichroic ratio of 7:1 that we find for absorption into S_1 places an upper limit on the fraction of polymer chains that are aligned. It implies that there is one chain perpendicular to the alignment direction for every seven chains that are parallel to it. So if we assume that after excitation the excitons migrate to be equally distributed among aligned and unaligned chains,⁸ then the observed dichroic ratio of 1:2, corresponds to a ratio of 1:2.6 for the case of perfectly aligned chains. This corresponds to 72% of the emission being polarized perpendicular to the polymer back-

bone. It is interesting that this is very similar to the 70% off-axis T_1 emission seen in planar acene molecules.³⁰

V. CONCLUSION

We measured the polarization of optical transitions associated not only with the singlet excited state S_1 , but also with the triplet excited states T_1 and T_n , in a Pt-containing conjugated polymer. The S_1 and T_n states are delocalized along the polymer chain and have optical transitions that are polarized along the polymer backbone direction. In contrast, the T_1 state is localized to approximately one repeat unit, requires spin-orbit coupling for emission to occur, and has a transition to S_0 that is polarized partly parallel and partly perpendicular to the chain.

The fact that the T_1 state has more than half of its emission polarized perpendicular to the polymer chain has important implications for the potential of constructing microcavities with high gain based on phosphorescent polymers. Gain is often limited by reabsorption of the emitted light from the ground state or from charges in the device. Yet not only is the triplet T_1 state shifted by more than 0.7 eV from the singlet ground-state absorption, but it also has emission orthogonal to this ground-state absorption and to the usual direction of charge-induced absorption.¹²

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