The singlet–triplet energy gap in organic and Pt-containing phenylene ethynylene polymers and monomers

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We have studied the evolution of the T_1 triplet excited state in an extensive series of phenylene ethynylene polymers and monomers with platinum atoms in the polymer backbone and in an analogous series of all-organic polymers with the platinum(II) tributylphosphonium complex replaced by phenylene. The inclusion of platinum increases spin–orbit coupling so T_1 state emission (phosphorescence) is easier to detect. For both, the platinum-containing polymer series and for the all-organic polymers, we find the T_1 state to be at a constant separation of 0.7 ± 0.1 eV below the singlet S_1 state. It is not possible to change this singlet–triplet splitting by altering the size or the charge-transfer character of the polymer repeat unit or by changing the electron delocalization along the polymer backbone. The $S_1 - T_1$ gap can be increased by confining the S_1 state in oligomers and monomers. © *2002 American Institute of Physics.* [DOI: 10.1063/1.1473194]

I. INTRODUCTION

Conjugated polymers are a class of materials that are now well investigated due to their commercial potential. However, attention is mostly paid to the singlet excited state S_1 while little is known about the triplet excited state T_1. In organic conjugated polymers, the T_1 state is difficult to study as it is usually nonemissive. Emission from a triplet excited state to the singlet ground state requires a spin flip which does not occur in an optical transition. Yet, knowledge of the T_1 state is important for an understanding of the basic photophysics of conjugated polymers[1–3] and for their technological applications such as organic light-emitting diodes.[4–9]

Since triplet states are usually nonemissive, the most common ways of investigating them include triplet–triplet absorption measurements,[10–12] energy transfer onto phosphorescent dyes,[8,9,13–15] optically detected magnetic resonance,[16] or delayed fluorescence measurements.[17,18] However, these methods can only give partial information while direct measurement of triplet-state emission (phosphorescence) readily gives access to the energy, vibrational structure, and lifetime of the triplet state.

Here, we use direct measurements of fluorescence and phosphorescence to determine the S_1 and T_1 energies in a series of conjugated polymers. Phosphorescence can be measured when the T_1 emission becomes partially allowed by spin–orbit coupling. In organic conjugated polymers, spin–orbit coupling is extremely weak giving a low radiative decay rate for emission from the triplet state in comparison with the much larger nonradiative decay rate.[19] In addition, there is little intersystem crossing from S_1 to T_1 in organic conjugated polymers. Intersystem crossing occurs by vibrational coupling where suitable modes result in a change in orbital angular momentum that compensates the spin flip.[20,21] This process is known to be weak for aromatic molecules[20] and is probably even weaker for polymers with large delocalized π-electron systems since a significant amount of energy is required to deform an extended π-electron cloud. The measurement of phosphorescence in organic conjugated polymers therefore requires a very sensitive time-resolved detection technique.[22,23]

The amount of spin–orbit coupling in a molecule can be greatly increased by introducing heavy atoms such as platinum into the chemical structure, so that the radiative decay rate of the T_1 state is increased to become comparable with the intrinsic nonradiative decay rate.[19] In this case, emission from the T_1 state can be readily detected with conventional steady-state spectroscopic techniques.[24–26] Here, we used an extensive model system of platinum-containing conjugated polymers and monomers to investigate the relationship between singlet- and triplet-energy levels (Fig. 1). Platinum is incorporated in a square planar Pt(II) configuration and mixing of the $5d$ and $6p$ orbitals of the platinum with the π and π^* orbitals of the organic unit preserves conjugation along the polymer chain.[27] We then compare our results with the S_1 and T_1 energy levels which we measure for some analogous conjugated polymers and monomers without the Pt metal inclusion by using time-resolved detection. We find excellent agreement of the $S_1 - T_1$ energy gap measured for the organic compounds with that of the metal-containing model system.

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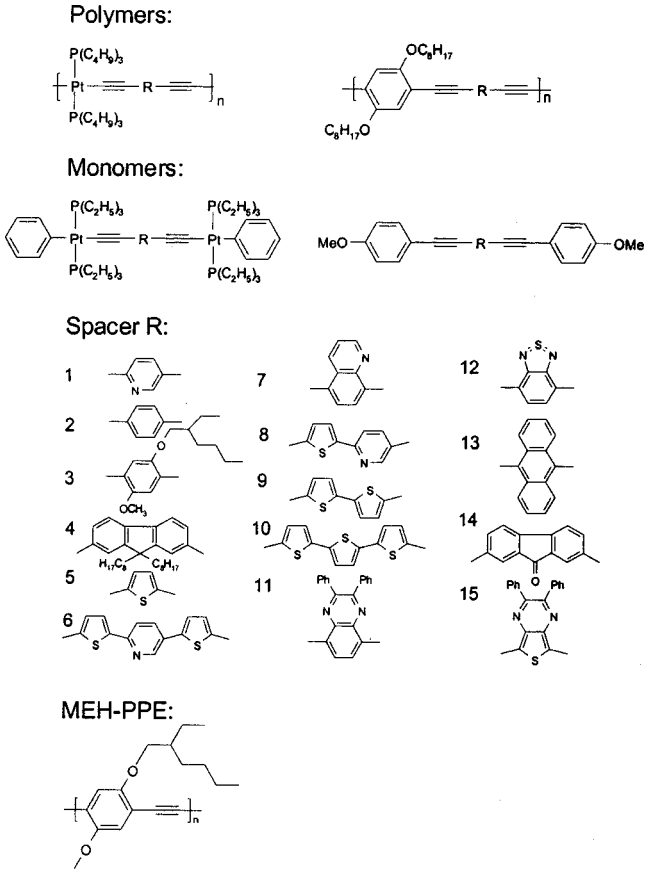

FIG. 1. General chemical structures of the platinum-containing and organic polymers and monomers investigated and the spacer units, *R*, that were used. The spacers are labeled in order of decreasing S_1 energy for the platinum-containing polymers. The structure of the organic polymer MEH-PPE is also shown.

II. EXPERIMENT

The Pt-containing polymers and monomers were synthesized by adaptation of the dehydrohalogenation route developed originally by Hagihara.[24–26,28–31] Defect-free all-organic polymers and monomers were synthesized by a one-pot reaction.[32] All of the polymers and monomers were readily dissolved in dichloromethane at room temperature and thin films were produced on quartz substrates using a conventional photoresist spincoater. Films were typically 100–150 nm in thickness as measured on a Dektak profilometer. The optical absorption was measured with a Hewlett–Packard ultraviolet-visible spectrometer.

Measurements of steady-state photoluminescence (PL) were made with the sample in a continuous-flow helium cryostat. The temperature was controlled with an Oxford-Intelligent temperature controller-4 and measured with a calibrated silicon diode adjacent to the sample. Excitation was provided by the UV lines (334–365 nm) of a continuous wave argon ion laser. Typical intensities used were a few mW/mm^2. The emission spectra were recorded using a spectrograph with an optical fiber input coupled to a cooled charge coupled device array (Oriel Instaspec IV).

For time-resolved PL measurements, the organic polymers were dissolved in anhydrous methyltetrahydrofuoran (Me-THF) to give a 10^{-5} M solution which forms a glassy matrix at 77 K. The solutions were filled in a sealed cuvette and cooled to 77 K in a nitrogen cryostat. The frozen solutions were excited by a tunable parametric oscillator pumped by the tripled output of a *Q*-switched Nd:YAG laser with a pulse duration of 7 ns and a repetition rate of 10 Hz. The emission was dispersed by a monochromator and recorded by an optical multichannel analyzer (PAR model 1460) with a gated intensified diode array detector. It was possible to vary the detection time (gate width) and the delay after excitation. At a delay of 0 ns, a gate width of 100 ns was used to record prompt fluorescence while for other delay times, a gate width of 10 ms was used to maximize the signal intensity.

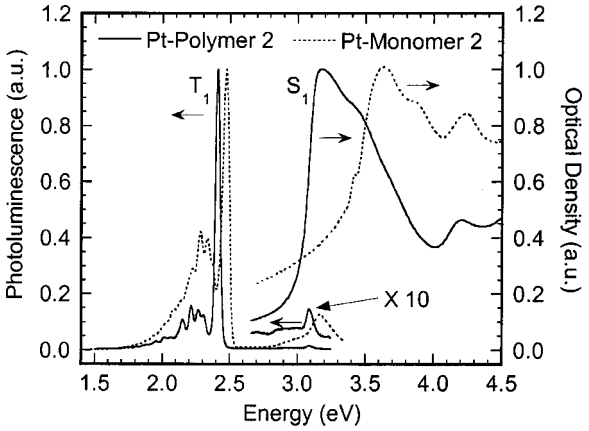

FIG. 2. PL spectra at 10 K and absorption spectra at room temperature of thin films of the Pt-containing polymer and monomer with spacer 2. The singlet S_1 emission from the polymer has been magnified by a factor of 10.

III. RESULTS

A. Pt-containing polymers

The thin-film PL and absorption spectra of a typical Pt-containing polymer and monomer are given in Fig. 2. The first absorption band and the high energy emission band around 3 eV are associated with the S_1 singlet excited state, while the low energy emission band arises from a T_1 triplet excited state, as shown previously by time-resolved PL and photoinduced absorption spectroscopy.[33] These singlet and triplet excited states involve π–π^* transitions. In both absorption and low-temperature emission, the maximum intensity is seen in the 0-0 vibrational peak.[24]

We observe the S_1 state to be at a significantly lower energy in the polymer than in the monomer, as can be seen from the shift of the 0-0 peak in the first absorption band by 0.4 eV from the monomer to the polymer. In contrast, the T_1 state is located at very similar energies in the polymer and monomer (since the excitation was at 3.4 eV, only the vibronic sidebands of the S_1 emission can be seen in this monomer).

Taking a simple particle-in-a-box model, the energy of a state decreases with increasing oligomer size since the associated delocalized π-electron system extends until it reaches its maximum length after which a further increase of oligomer size does not reduce the energy of the state any more.[20,34] A monomer and a polymer obviously represent

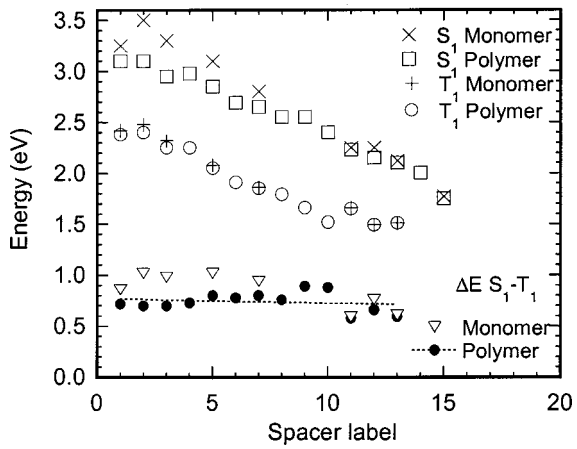

FIG. 3. Energy levels of the singlet S_1 and triplet T_1 excited states and their energy difference $\Delta E_{S_1-T_1}$ for the platinum-containing polymers and monomers with spacers labeled 1–15. [Note that the labels are in order of decreasing singlet-exciton energy for the polymers.] The dotted line is a straight line fit to $\Delta E_{S_1-T_1}$ for the Pt polymers. The energies plotted correspond to the observed energies of the 0-0 peaks of the 10 K PL spectra except for S_1 of the monomers with spacers 1–3. For these, the 0-0 emission peak was estimated by adding the energy difference between the 0-0 absorption peaks in polymer and monomer to the 0-0 emission peak in the polymer.

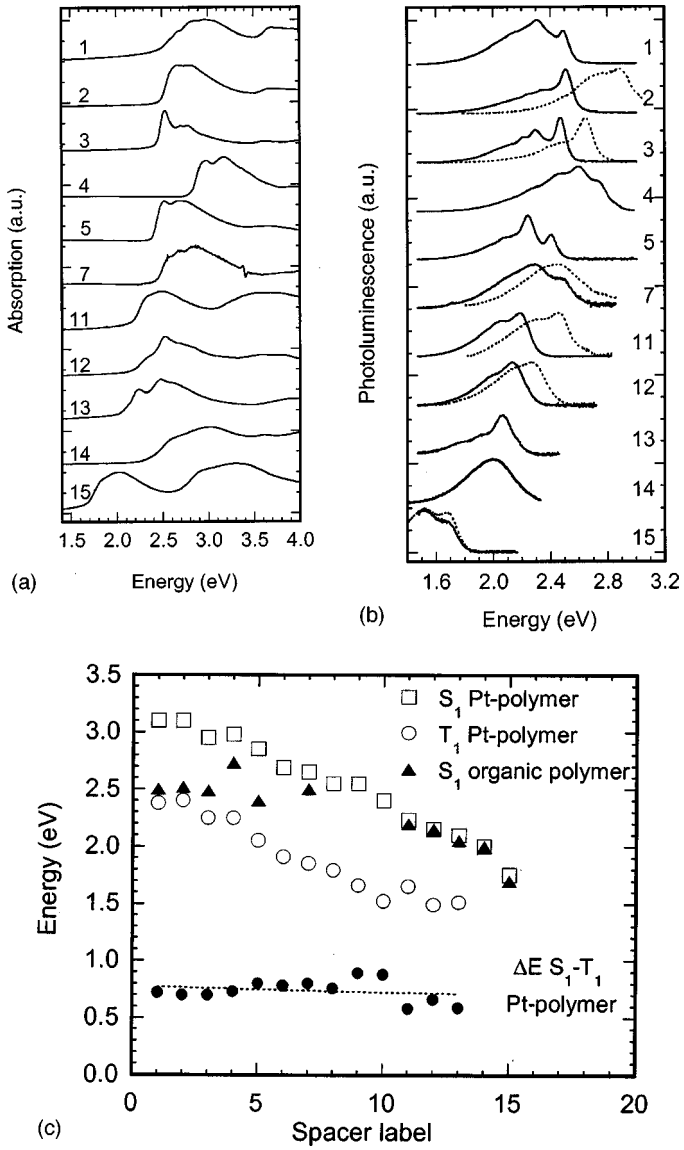

FIG. 4. (a) The absorption spectra at 300 K of thin films of the organic polymers with spacers 1–15 as labeled. (b) The PL spectra at 300 K from thin films of the organic polymers (solid lines) with spacers 1–15 and of the organic monomers (dotted lines) with spacers 2, 3, 7, 11, 12, and 15 as labeled. (c) The energy levels of the S_1 excited state for the organic polymers (triangles) with spacers 1–15 and of the S_1 (open squares) and T_1 (open circles) excited states and the energy difference $\Delta E_{S_1-T_1}$ (solid circles) for the platinum-containing polymers, plotted as a function of the spacer group label, as described in the caption to Fig. 3. The dotted line is a straight line fit to $\Delta E_{S_1-T_1}$. The energies plotted correspond to the 0-0 peaks of the 10 and 300 K thin-film PL spectra of the Pt-containing and organic polymers, respectively.

two extreme cases of oligomer length. Accordingly, the large energy gap between the S_1 states in the polymer and monomer suggests that S_1 is delocalized in the polymer, while the smaller energy difference for the T_1 state points to a state which is more localized in the polymer. These observations are in agreement with quantum chemical calculations.[27]

Similar results were obtained for the other Pt-containing polymers and monomers containing the spacers shown in Fig. 1.[24–26] We have labeled the different "spacer" groups shown in Fig. 1 in order of decreasing singlet-exciton energy for the platinum-containing polymer (as measured from the PL peak), and we show the variation of the their S_1 and T_1 states and the corresponding S_1-T_1 energy gaps as a function of "spacer label" in Fig. 3, both for the polymers and for their corresponding monomers. A localized T_1 state is suggested by the energetic proximity of this state in all the polymer and monomer pairs. According to the differences in S_1 energy for corresponding polymer and monomer pairs, the S_1 state is more extended than the monomer size for compounds 1, 2, 3, and 5, while it can be accommodated on a single monomer unit for compounds 7, 11, 12, 13, and 15. There are two effects which might contribute to this. Firstly, the lower energy of the S_1 state in compounds 7–15 suggests a significant donor–acceptor interaction between the electron-rich platinum and the organic spacers which may cause the singlet state to have a more localized, charge-transfer-type character. Secondly, compounds 1–5 only contain a single ring in the spacer, while compounds 7–15 contain two or more rings to accommodate charge density.

We now consider the energy difference $\Delta E_{S_1-T_1}$ between the S_1 and T_1 states. When spacer substitution lowers the S_1 energy in the polymer, the T_1 energy reduces by the same amount to give a constant energy gap of about 0.7 eV for all polymers, as shown earlier for a subset of these polymers.[24] For the spacers 1–7, we find a larger S_1-T_1 energy gap for the monomers than in the polymers, which is mostly due to the higher S_1 energy in the monomers.

B. Organic polymers

We have investigated the analogous organic polymers and monomers shown in Fig. 1 to establish whether the trends observed for the Pt-containing model system also occur in organic systems. Figures 4(a) and 4(b) show the room-temperature absorption spectra of the polymers and PL spec-

tra of the polymers and monomers. The onsets of the polymer absorption and emission overlap so the emission can be associated with the S_1 state.

The difference in the energy of the S_1 emission between polymer and monomer pairs reduces less along the series than for the platinum-containing pairs. A less localized S_1 state in these organic polymers than in the Pt-containing polymers is consistent with the weaker donor strength of the alkoxy-substituted phenyl ring and therefore a reduced charge-transfer character of the S_1 state.

The S_1 energy levels of organic polymers are compared to the S_1 and T_1 energy levels of the corresponding Pt-containing polymers in Fig. 4(c). For the spacers 11–15, the S_1 energies of the organic and the Pt-containing polymers coincide, while they differ by about 0.5 eV for compounds 1, 2, 3, and 5.

It is not obvious whether the admixture of platinum orbitals will affect the S_1 and T_1 states in the same way. In particular, for the organic polymers with spacers 1–5, it is questionable whether the T_1 state will be about 0.7 eV below the S_1 state, as is the case for the Pt-containing polymers. Since the energy of the T_1 triplet excited state is more difficult to determine in organic polymers than in Pt-containing polymers, we concentrate on polymers with high S_1 energy, i.e., polymers 2, 3, 4, and poly(2-methoxy-5-(2′-ethyl-hexyloxy)-*p*-phenylene ethynylene) (MEH-PPE). The reason for this choice is that our study of the nonradiative decay from the T_1 state in the Pt-containing compounds has shown that the nonradiative decay rate increases exponentially with decreasing T_1-S_0 energy gap.[19] Higher energy T_1 states are therefore much easier to detect.

Emission spectra of organic polymers 2, 3, 4, and MEH-PPE were taken in dilute frozen solutions of Me-THF at 77 K after pulsed excitation. Figures 5(a)–5(c) show the spectra taken from the phenylene ethynylene polymers with a delay with respect to the pulse of 0 and 150 ns. After 0 ns delay, prompt fluorescence from the S_1 singlet excited state is seen, with an energy and spectral shape consistent with the thin-film room-temperature emission spectra shown in Fig. 4(b). After a 150 ns delay, there are two emission bands with similar spectral shapes, one lower energy band with a 0-0 peak centered around 1.9 eV, and one higher energy band with a 0-0 peak congruent with the prompt fluorescence. The low-energy band is long lived. After a delay of 10 ms, this band in compound 3 has decayed to only one third of its initial value, while the high-energy band has decayed by three orders of magnitude. We attribute the low-energy emission centered around 1.9 eV to phosphorescence from a T_1 triplet-excited state because of the similar spectral shapes of the low- and high-energy emissions, the long lifetime of the low-energy emission, and the energy separation of about 0.6–0.7 eV between the high- and low-energy band. We consider the high-energy emission to be delayed fluorescence. The same is observed for the fluorene-containing polymer 4 [Fig. 5(d)].

Figure 5(e) compares the delayed emission from the organic polymer with spacer 2 with the emission from the analogous Pt-containing polymer. The emission bands have been normalized and for the Pt polymer the energy axis was shifted by 0.55 eV. The spectra of the organic polymer and the Pt-containing polymer are remarkably similar, suggesting that the emission in the Pt-platinum containing polymer is indeed associated with the organic spacer group. From the identical S_1-T_1 energy splitting in both polymers, it is also evident that for spacer 2 the admixture of platinum orbitals affects the singlet- and triplet-energy levels to the same extent, shifting both by 0.55 eV.

Figure 6 shows the dependence of the phosphorescence and the delayed fluorescence signals on the intensity of the exciting laser pulse for the organic polymer 3. Both signals show a power-law dependence with exponents of 0.8 and 1.6, respectively. We therefore consider the delayed fluorescence in the organic polymer 3 to be caused by triplet–triplet annihilation. Since we used dilute solutions (10^{-5} M), the triplet–triplet annihilation is likely to arise from triplet transport within one polymer chain, rather then between different polymer chains. The small deviation from the expected exponents of 1 and 2 might be caused by some singlet–singlet annihilation prior to intersystem crossing.

In Fig. 7, we finally compare the S_1 and T_1 energies of the Pt-containing polymers and the organic polymers 2, 3, 4, and MEH-PPE. The energy levels of singlet S_1 and triplet T_1 states are lowered in the organic compounds compared to the Pt-containing compounds, but they are lowered by the same amount, so that the energy gap $\Delta E_{S_1-T_1}$ is the same for both organic and Pt-containing polymers.

IV. DISCUSSION

We have measured the S_1-T_1 gap in Pt-containing and organic ethynylenic polymers and monomers. The spacers have been systematically varied to form three series. In one series formed by pyridine, benzene, and thiophene (spacers 1, 2, and 5 in Fig. 1), the electron density on the spacer ring increases along the series.[26] In a second series formed by thiophene, bithiophene, and terthiophene spacers (5, 9, and 10), the physical length and conjugation length of the spacer increases.[25] In a third series, we increased the acceptor strength of the spacer to shift the S_1 energy in the Pt-containing polymers from 3.0 to 1.7 eV (spacers 2, 3, 7, 11, 12, and 15).[24] For each of these different series, we find a constant S_1-T_1 energy splitting of 0.7 eV. It is also not possible to reduce this energy gap by using spacers that have a planarized π-electron system along (4) or orthogonal (13) to the chain, strong internal donor–acceptor interactions (6 and 8) or the possibility of mixing with *n* orbitals (14).

Our finding of a constant S_1-T_1 energy separation of 0.7 eV for both the platinum-containing polymers and for the all-organic polymers is a very striking result. Its constancy can not therefore be due to a specific feature of the platinum electronic structure. So this work shows that we can use results and trends obtained from this extensive range of platinum-containing materials as being representative of the corresponding all-organic analogues. We also note that the few values reported for the S_1-T_1 energy gap in other organic conjugated polymers are consistent with the value we report here.[15,23] It is surprising that such a range of conju-

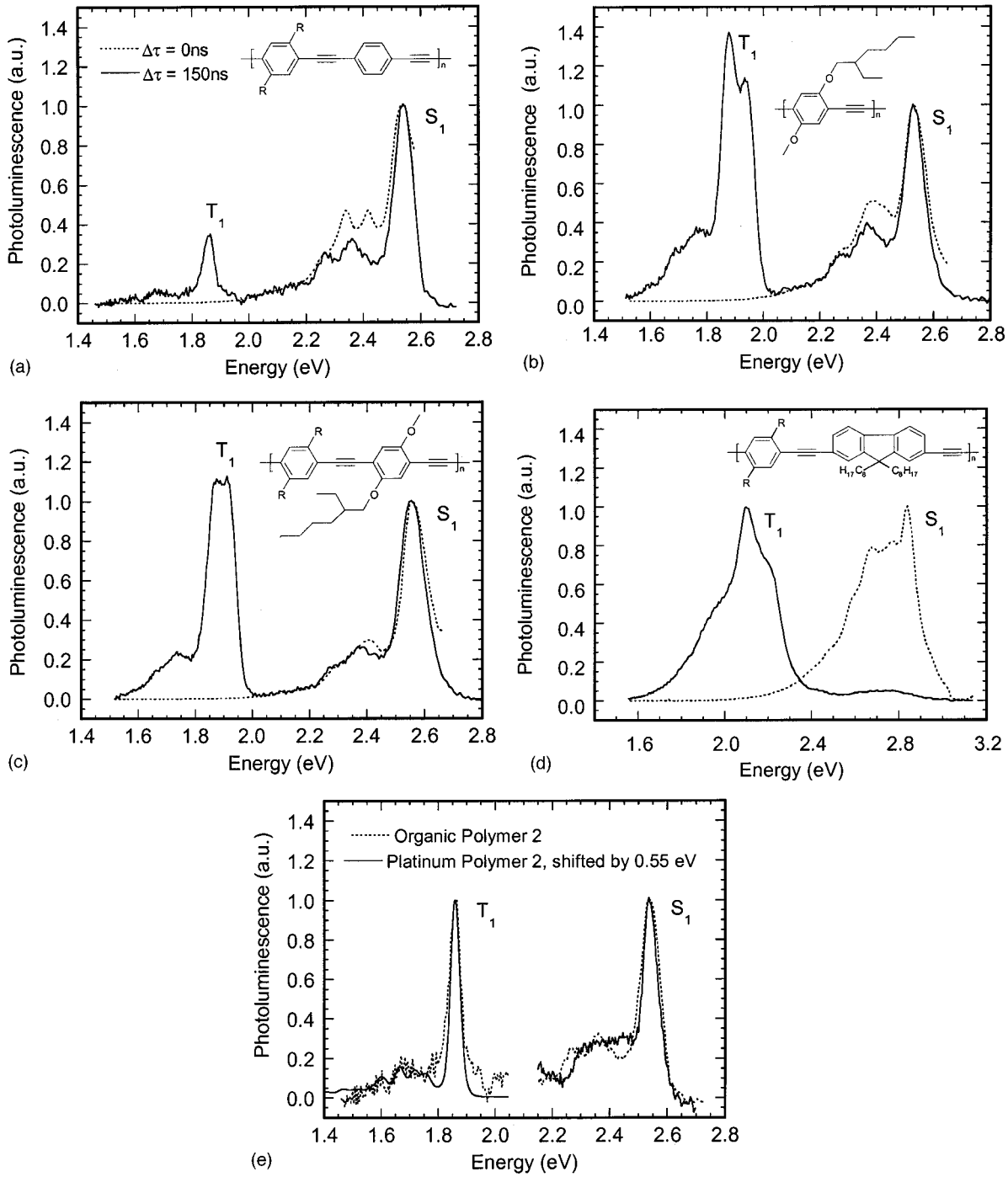

FIG. 5. (a)–(d) PL spectra of frozen solutions of organic phenylene ethynylene polymers with spacer 2–4 and MEH-PPE at 0 ns (dotted line) and at 150 ns (solid line) after excitation. The chemical structures are shown as insets. (e) The organic polymer with spacer 2 after a delay of 150 ns (dotted line) together with the thin-film steady-state emission spectrum of the Pt-containing polymer with spacer 2 (solid line). The emission spectra are normalized and the spectrum of the Pt-containing polymer has been shifted by 0.55 eV to the red.

gated polymers have the same value for the S_1-T_1 separation while a large spread of values is found for other conjugated materials such as 0.3 eV for porphyrenes and C_{60},[8,35] 0.6 to 1.0 eV for the Pt-containing monomers as shown in Fig. 3, about 1.3 eV for polyacenes (from benzene to pentacene)[36] and 1.75 eV for terthiophene.[1]

In many conjugated polymers, such as the poly(phenylene ethynylene)s that we have investigated, the first excited state arises from transitions between π and π^* orbitals which are both delocalized along the polymer backbone. So for all these compounds, the spatial overlap of the π and π^* orbitals, and the mean electron–hole separation, may be fairly similar. Yet the effective conjugation length of the resulting state, that is the distance which the electron–hole wave packet explores, may be larger for some polymers (spacers 1–5) than for others (spacers 11–15). In polymers, the S_1-T_1 energy gap is controlled by the exchange energy, which is determined by the spatial overlap of the π and π^* orbitals involved. A similar $\pi-\pi^*$ overlap would therefore explain the similar exchange energy that has been observed

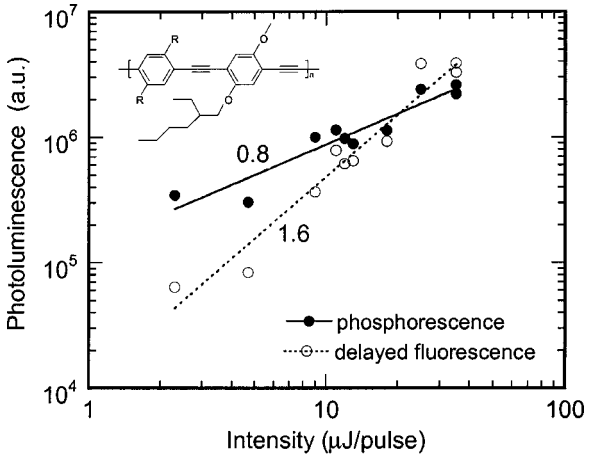

FIG. 6. The dependence of the delayed fluorescence (open circles) and the phosphorescence (solid circles) on the pump laser intensity for the organic polymer with spacer 3. Straight line fits on the double-logarithmic plot indicate a power-law dependency with exponents of 0.8 and 1.6.

for conjugated polymers even though their degree of conjugation may vary considerably as discussed herein. Detailed quantum chemical calculations may give more insight into this.

While in polymers the extended π-conjugation allows for different sizes of the singlet and triplet excited states, the situation changes when monomers (or oligomers) are considered. Additional Coulombic effects due to the confinement of the excitation by the size of the molecule need to be taken into account. As shown here, and as is evident from calculations, the triplet exciton is more spatially localized, whereas the singlet exciton tends to be more extended (because electrons are better correlated via the exchange interaction in the triplet state than in the singlet state).[1,37] Consequently, the S_1 energy is raised more than the T_1 energy when going from a polymer to its corresponding monomer and as a result the S_1-T_1 gap is larger for the monomer than for its polymer. This is shown in Fig. 3 for spacers 1–5 and agrees with

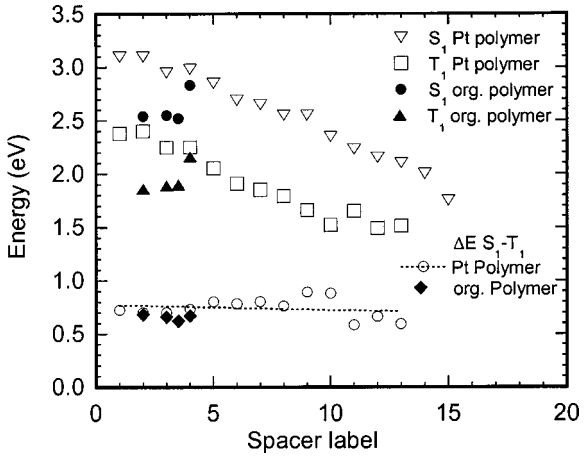

FIG. 7. The energy levels of the S_1 and T_1 excited states and the energy difference $\Delta E_{S_1-T_1}$ for the Pt-containing polymers with spacers 1–15 and the organic polymers with spacers 2, 3, 4, and MEH-PPE. The values for MEH-PPE are listed between spacer labels 3 and 4. The energies plotted correspond to the 0-0 PL peaks at 10 K in thin films for the Pt-containing polymer and at 77 K in frozen solution for the organic polymers.

quantum chemical calculations.[21] This confinement effect has also been reported for phenylene and thiophene oligomers.[1,23] The absence of such confinement effects in polymers implies that their S_1-T_1 splitting can be considerably smaller than that of systems in which the singlet state can not delocalize, such as acenes, and this may account for the value of 0.7 eV that we have found.

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