Triplet states in a series of Pt-containing ethynylenes

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By use of optical steady state and time resolved spectroscopy, we studied the evolution of the triplet excited state in a series of six ethynylenic polymers of the structure $[\text{-Pt}(\text{PBu}_3^n)_2\text{-C}\equiv\text{C-}R\text{-C}\equiv\text{C-}]_n$ where the spacer unit R is systematically varied to give optical gaps from 1.7–3.0 eV. The inclusion of platinum in the polymer backbone induces a strong spin-orbit coupling such that triplet state emission (phosphorescence) associated with the conjugated system can be detected. Throughout the series we find the S_1-T_1 (singlet-triplet) energy splitting to be independent of the spacer R, such that the T_1 state is always 0.7 ± 0.1 eV below the S_1 state. With decreasing optical gap, the intensity and lifetime of the triplet state emission were seen to reduce in accordance with the energy gap law. © *2000 American Institute of Physics.* [S0021-9606(00)71641-2]

I. INTRODUCTION

Intensive studies of conjugated polymers over the last ten years have made it possible to clarify some fundamental questions about the nature of the singlet excited state[1–3] yet still little is known about the nature of triplet excited states in conjugated polymers. Since emission from triplet excited states is spin-forbidden, they can usually only be investigated indirectly, for example by photoinduced absorption,[4,5] optically detected magnetic resonance,[6,7] or energy transfer[8] measurements. Consequently, even basic information such as their energy level and extent is sparse. Nevertheless, a thorough understanding of triplet photophysics is essential if one intends to develop a full picture of basic excitations in conjugated polymers which takes into account the effect of spin on the electronic interactions.

An understanding of such issues is also necessary for further progress in the technological development of optoelectronic devices based on conjugated polymers. For example, in light-emitting diodes (LEDs), it is not clear what fraction of the electron-hole pairs formed after charge injection is in a (nonemissive) spin triplet state rather than in an (emissive) spin singlet state.[9–14] Yet the percentage of emissive singlet excitons determines the overall efficiency of the LED. Higher efficiencies can only be realized by harvesting the energy of the nonemissive triplet excitons.[15–17] This again requires detailed knowledge of the energy levels of the triplet excited state.

To study the triplet excited state in conjugated polymers directly, we have used a model system where the triplet excited state has been made emissive thus rendering it easily accessible by optical spectroscopy.[18–22] This is achieved by including platinum in the main polymer chain. The heavy metal atom introduces spin-orbit coupling, and radiative transitions between singlet and triplet states therefore become possible.

Platinum (II) takes a square planar configuration and forms stable bonds with ethynylenes, so that organometallic polymers of the general structure $[-\text{Pt}(\text{PBu}_3^n)_2\text{-C}\equiv\text{C-}R\text{-C}\equiv\text{C-}]_n$ can be synthesized. The two nonconjugated phosphine ligands allow for solubility. The two conjugated ligands consisting of the ethynylenic groups bridged by a conjugated spacer, R, form the backbone of the polymer. Conjugation is preserved through the metal site, as a result of mixing between the frontier orbitals of the metal and the conjugated ligands. Previous theoretical investigations for such a polymer have shown that the mixing is primarily between the metal $6p$ orbital and the ligand π^* orbital.[19] The resultant optical gap in these polymers is determined by a number of factors. The fundamental optical transition is between the mixed $5d/\pi$ and $6p/\pi^*$ orbitals of the metal/ligand conjugated system.[19,20] The extent of mixing depends on the overlap between ligand and metal orbitals and so may vary from ligand to ligand. Also the size of the spacer in the ligand and the original extent of conjugation on
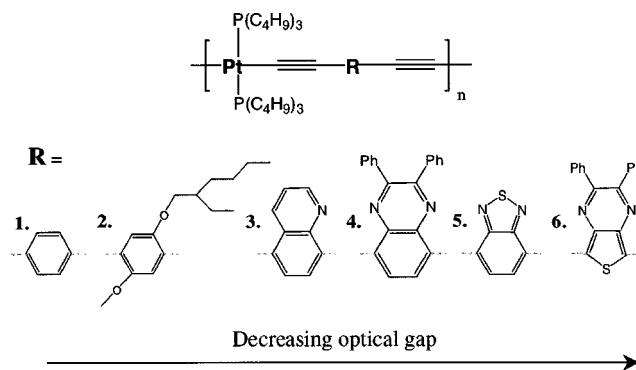

FIG. 1. The general chemical structure of the polymers investigated and the spacer units, R, that were used. The trend in optical gap from polymer **1** to polymer **6** is shown.

TABLE I. Synthetic and other characterization data for polymers **2–5**.

Polymer	Yield (%)	M_w	M_n	n	$\nu_{c\equiv c}$ (cm^{-1})	$^{31}P\{^1H\}$ NMR (ppm)[a]
2	85	210 110	156 870	1.282	2095	138.08(^1JPt-P=2331 Hz)
3	78	169 700	114 660	1.480	2089	138.50(^1JPt-P=2327 Hz)
4	84	150 900	96 230	1.568	2092	137.52(^1JPt-P=2340 Hz)
5	88	150 910	113 640	1.328	2091	138.05(^1JPt-P=2337 Hz)

[a]Referenced to P(OMe)$_3$.

it will affect the energies of the ligand orbitals, and thus the energies of the polymer orbitals. Furthermore, platinum is electron rich in comparison to the conjugated ligands and should therefore act as an electron donor within the polymer. The resulting donor acceptor interaction is expected to lower the overall optical gap, depending on the acceptor strength of the ligand.[20,23]

We have systematically varied the spacer R between six polymers (Fig. 1) so as to tune the onset of the singlet absorption from 1.7 to 3.0 eV. The polymer backbone, consisting of platinum, carbon–carbon triple bonds, and phenyl (for **6** thiophene) rings, is kept constant along the series while the groups attached to the phenyl ring are varied. Here we report on the corresponding development of the triplet state emission (phosphorescence).

II. EXPERIMENT
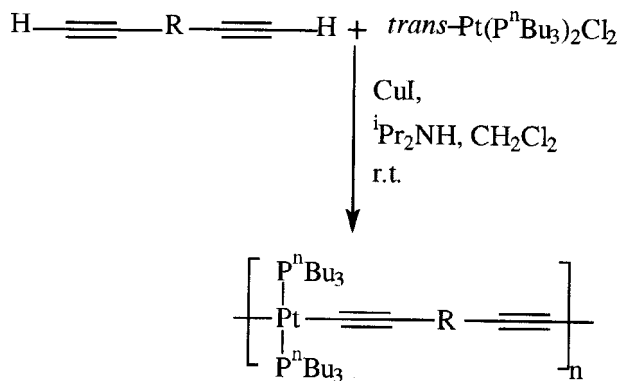
A. Synthesis and polymerization

All reactions were performed under an inert nitrogen atmosphere using standard Schlenk techniques. Solvents were pre-dried and distilled before use by standard procedures.[24] All chemicals, except where stated otherwise, were obtained from Sigma Aldrich and checked for purity by GC/MS prior to use. The NMR spectra were recorded on a Bruker WM-250 spectrometer in appropriate solvents. $^{31}P\{^1H\}$ NMR and ^1H NMR spectra were referenced to external trimethylphosphite and solvent resonances, respectively. Infrared spectra were recorded as CH$_2$Cl$_2$ solutions, in a NaCl cell, on a Perkin-Elmer 1710 fourier transform infrared (FTIR) spectrometer. Microanalyses were performed in the Department of Chemistry, University of Cambridge. Column chromatography was performed on alumina (Brockman Grade II-III). Molecular weights of the polymers were determined by gel permeation chromatography (GPC) using two PL Gel 30 cm, 5 μm mixed C columns at 30 °C running in THF at 1 cm^3/min with a Roth Mocel 200 high precision pump. A DAWN DSP (Wyatt Technology) multi-angle laser light scattering (MALLS) apparatus with 18 detectors and auxiliary Viscotek model 200 differential refractometer/viscometer detectors was used to calculate the absolute molecular weights (referred to GPC LS). GC-MS analyses were performed on a Hewlett-Packard 5890 Series II/5971A MSD instrument equipped with an HP 7673A autosampler and a fused silica column (30 cm×0.25 mm×0.25 μm, cross linked 5% phenylmethyl silicone). The following operating conditions were used: injector, 260 °C, detector, 280 °C, oven temperature was ramped from 70 to 260 °C at the rate of 20 °C/min; helium (UHP grade) was used as the carrier gas; toluene (BDH, 99.7%) was used as an internal integration standard.

The platinum complex *trans*-[Pt(P^{n}Bu$_3$)$_2$Cl$_2$] was prepared by the literature method.[25] The syntheses of the ligand precursors, 1,4-diethynylbenzene, 2,3-diethynyl-5,7-thieno[3,4-b]pyrazine, and their Pt polymers *trans*-[−Pt(P^{n}Bu$_3$)$_2$-C≡C-R-C≡C]$_n$ (**1**) and (**6**) have been reported.[26,20] The synthesis of the new diterminal alkynes, 2,5-diethynyl-1-(2-ethylhexyloxy)-4-methoxybenzene, 5,8-diethynylquionoline, 2,3-diphenyl-5,8-diethynylquinoxaline, 4,7-diethynyl-2,1,3-benzothiadiazole will be reported elsewhere[27] (scheme 1).

(i)   Pd(OAc)$_2$, PPh$_3$, CuI, ^{i}Pr$_2$NH

(ii)   KOH, MeOH, THF
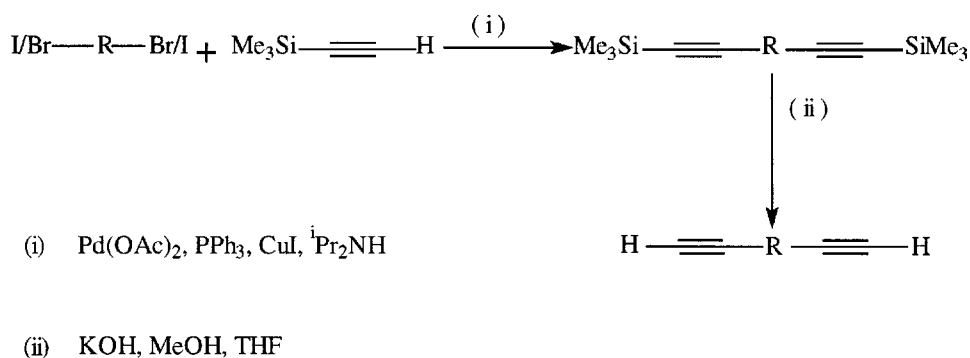
The polymeric complexes (scheme 2)

were synthesized by adaptation of the dehydrohalogenation route developed originally by Hagihara.[28,29] A typical polymerization reaction involved the reaction of equimolar quantities of the diterminal alkynes and $trans$-$[Pt(P^nBu_3)_2Cl_2]$ in dichloromethane/diisopropylamine (1:1 v/v) in the presence of a catalytic amount of CuI. The crude mixture obtained after evaporation of the solvents was filtered through a column of alumina with dichloromethane as eluant. The product was further purified by repeated precipitations from dichloromethane by methanol.

$$trans\text{-}[-Pt(P^nBu_3)_2\text{-}C\equiv C\text{-}R\text{-}C\equiv C\text{-}]_n. \qquad (2)$$

$R = 1\text{-}(2\text{-ethylhexyloxy})\text{-}4\text{-methoxybenzol}$

CuI (10 mg) was added to a mixture of $trans$-$[Pt(P^nBu_3)_2Cl_2]$ (0.670 g, 1.0 mmol) and 2,5-diethynyl-1-(2-ethylhexyloxy)-4-methoxybenzene (0.284 g, 1.0 mmol) in CH_2Cl_2/Pr_2NH (50 cm^3, 1:1 v/v). The yellow solution was stirred at room temperature over a period of 15 h, after which all volatile components were removed under reduced pressure. The residue was redissolved in dichloromethane and filtered through a short alumina column. After removal of solvent by rotary evaporator, yellow solid of polymer **2** was obtained in 85% yield (0.750 g). Further purification can be accomplished by precipitating the polymer solution in dichloromethane from methanol.
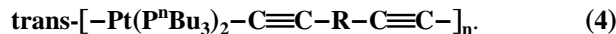
IR(CH_2Cl_2):v/cm^{-1} 2095 ($C\equiv C$). ^1H NMR (250 MHz,CDCl$_3$):δ 0.88(t,24H,**CH$_3$**), 1.27–1.60 (m,32H,**CH$_2$**), 1.72 (hep, 1H, **CH**), 2.16(brs,12H,**PCH$_2$**), 3.70(s,3H,**OCH$_3$**) and 3.73(s,2H,**OCH$_2$**), 6.68(s,1H,**H$_3$**) and 6.69(s,2H,**H$_6$**). $^{31}P\{^1H\}$ NMR (101.3 MHz,CDCl$_3$):δ −138.08,$J_{Pt\text{-}P}$=2330 Hz. Calculated for $[C_{43}H_{76}P_2O_2Pt]_n$: C, 58.57; H, 8.63. Found: C, 58.63: H, 8.59%. M_w = 201 110,M_n=156 870 (n=1.282).

$$trans\text{-}[-Pt(P^nBu_3)_2\text{-}C\equiv C\text{-}R\text{-}C\equiv C\text{-}]_n. \qquad (3)$$
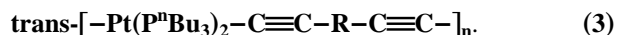
Similar procedures as for (**2**) were adopted using 5,8-diethynylquionoline to produce a light orange solid of polymer **3** in 78% yield.

IR(CH_2Cl_2):v/cm^{-1} 2089 ($C\equiv C$). ^1H NMR (250 MHz,CDCl$_3$):δ 0.87(t,18H,**CH$_3$**). 1.40(sex,12H, **CH$_2$**), 1.65(brs,12H,**CH$_2$**), 2.25(m,12H,**PCH$_2$**), 7.28(brs, 1H,**H$_3$**) and 7.33(brs,1H,**H$_6$**), 7.54(brs,1H,**H$_7$**), 8.74(brs,1H,**H$_4$**) and 8.83(brs,1H,**H$_2$**). $^{31}P\{^1H\}$ NMR (101.3 MHz,CDCl$_3$):δ−138.50,$J_{Pt\text{-}P}$=2347 Hz. Calculated

for $[C_{37}H_{59}NP_2Pt]_n$: C, 57.35; H, 7.67. Found: C, 57.64; H, 7.64%. M_w=169 700,M_n=114 660 (n=1.48).

$$trans\text{-}[-Pt(P^nBu_3)_2\text{-}C\equiv C\text{-}R\text{-}C\equiv C\text{-}]_n. \qquad (4)$$

Orange solid, 84% yield. IR(CH_2Cl_2):v/cm^{-1} 2092 ($C\equiv C$). ^1H NMR (250 MHz,CDCl$_3$):δ 0.75(t,18H,**CH$_3$**), 1.24(sex,12H,**CH$_2$**), 1.52(brs,12H,**CH$_2$**), 2.20(brs, 12H,**PCH$_2$**), 7.23–7.57 (m, 12H, aromatic). $^{31}P\{^1H\}$ NMR (101.3 MHz,CDCl$_3$):δ− 137.52,$J_{Pt\text{-}P}$= 2350 Hz. Calculated for $[C_{48}H_{66}N_2P_2Pt]_n$: C, 62.12; H, 7.17. Found: C, 62.24; H, 7.14% M_w=150 900,M_n=96 230 (n=1.568).

$$trans\text{-}[-Pt(P^nBu_3)_2\text{-}C\equiv C\text{-}R\text{-}C\equiv C\text{-}]_n. \qquad (5)$$
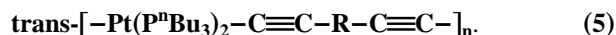
$R = 2,1,3\text{-benzothiadiazolyl}$

Red solid, 88% yield. IR (CH_2Cl_2):ν/cm^{-1} 2091 ($C\equiv C$). ^1H NMR (250 MHz, CDCl$_3$): δ0.87(t,18H,**CH$_3$**), 1.42(sex,12H,**CH$_2$**), 1.62(brs,12H,**CH$_2$**), 2.29(brs,12H, **PCH$_2$**), and 7.30(s,2H,**H$_{5,6}$**). $^{31}P\{^1H\}$ NMR (101.3 MHz, CDCl$_3$): δ− 138.05, $J_{Pt\text{-}P}$= 2337 Hz. Calculated for $[C_{34}H_{56}N_2SP_2Pt]_n$: C. 52.27; H, 7.22. Found: C, 52.24; H. 7.14%. M_w=150 910, M_n=113 640 (n=1.328).

B. Optical measurements

All of the polymers were readily dissolved in dichloromethane at room temperature and polymer films were produced on quartz substrates using a conventional photoresist spin-coater. 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 (UV-VIS) spectrometer. Measurements of photoluminescence (PL) and photoluminescence lifetimes were made with the sample 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/mm^2. The emission spectra were recorded using a spectrograph with an optical fiber input coupled to a cooled charge coupled device (CCD) array (Oriel Instaspec IV). For the lifetime measurements, the tripled output from a Q-switched YAG laser was used (355 nm, ~15 ns pulses). The emission was recorded using a photomultiplier tube and a digital oscilloscope. The temporal resolution of this setup was found to be around 70 ns.

III. RESULTS

A. Chemical characterization

Systematic characterization of the polymeric complexes was achieved by analytical and spectroscopic methods (IR, ^1H and ^{31}P NMR) and molecular weight determination; the results are shown in Table I. The IR spectra of the organometallic polymers display a single sharp $\nu_{C\equiv C}$ absorption at ~2090 cm^{-1} (for **2**, 2095 cm^{-1}) which indicates a trans-configuration of the ethynylene ligands around $Pt^{II}(P^nBu_3)_2$ moieties in these square-planar polymeric species. ^{31}P NMR spectra of the complexes exhibit a singlet peak at approximately −138.0 ppm which confirms a trans- configuration of
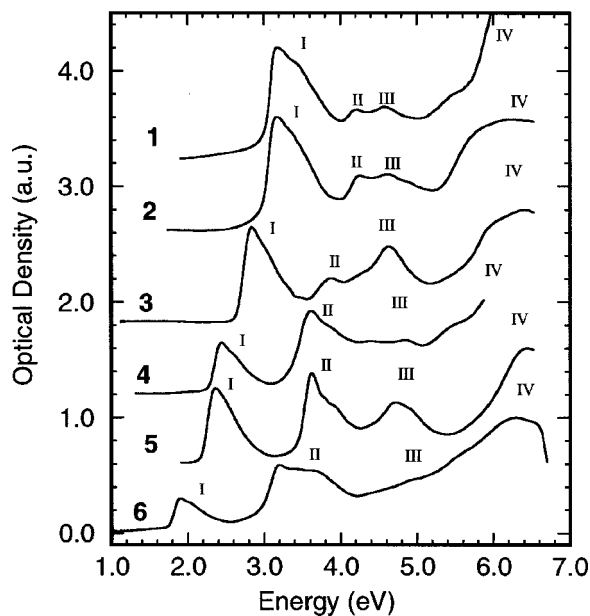
FIG. 2. The absorption spectra of films of polymers **1–6**. The spectra have been displaced on the vertical axis for clarity.

the coordinated trialkylphosphines around $Pt^{II}(-C\equiv C-R-C\equiv C-)_2$ moieties. The spectral data imply a "rigid-rod" like structure for **2–5** as illustrated in Fig. 1 and are similar to other platinum arylene-acetylide polymers previously reported.[21,22,30] The weight-average molecular weights (M_w) of the polymeric compounds, obtained by GPC, show a high degree of polymerization [201 110 (n_w = 228) for **2**, 169 700 (n_w = 219) for **3**, 150 900 (n_w = 163) for **4**, and 150 910 (n_w = 193) for **5**]. The molecular weights should be viewed with caution in view of the difficulties associated with utilizing GPC for rigid-rod polymers. The lack of discernible resonances which could be attributed to end groups in the NMR spectra provide support for the view that there is a high degree of polymerization in these polymers.

B. Absorption spectroscopy

The thin film absorption spectra are shown in Fig. 2. We compare the absorption bands observed for this series of Pt-containing polymers with those of poly(phenylene-vinylene)s (PPVs).[31] For PPVs, the absorption consists of several bands. Bands I and II are attributed to transitions from delocalized occupied orbitals to delocalized unoccupied orbitals (such as the π and π^* orbitals), bands III and V involve transitions from delocalized to localized orbitals and vice versa, and band IV is a result of transitions between localized orbitals.

We note that for the Pt-containing polymers, the optical transitions are not centered on the platinum site. In particular, they are not associated with intraplatinum d-d transitions, but, as mentioned above, they originate from the mixed metal/conjugated ligand orbitals and as such can be compared with an organic polymer. We find that the following experimental trends emerge for compounds **1–6**:
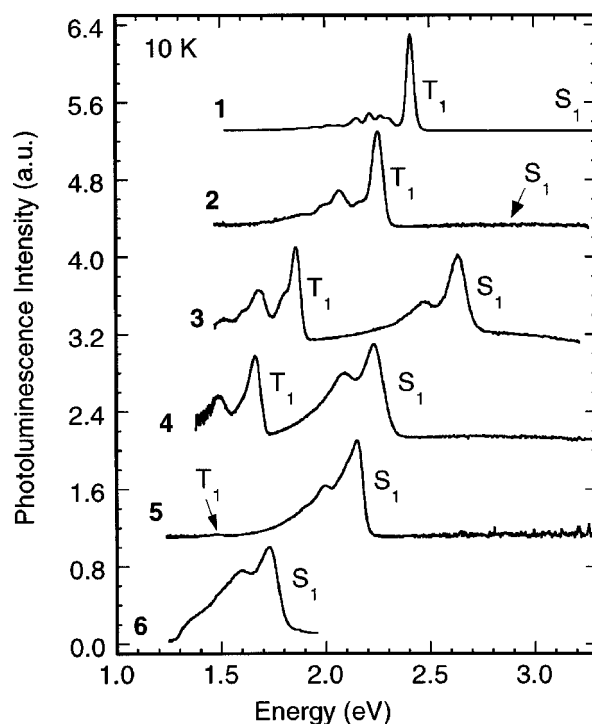

FIG. 3. The photoluminescence spectra of films of polymers **1–6** taken with UV excitation at 10 K. The spectra are displaced on the vertical axis for clarity.

(1) Bands I and II both shift to lower energy along the series. Their onsets remain at a constant separation of 1.3 eV. We consider that bands I and II might therefore be of a similar origin here as in PPV, that is they originate from transitions between delocalized orbitals. In particular we note that the conjugated π-orbitals must also play a role in the creation of band II, since this band shifts in energy to the same degree as band I.

(2) The oscillator strength in band I is reduced along the series. The reason for this is unclear.

(3) In band I the 0-0 vibronic transition is dominant even in absorption.

The consistent weight in the 0-0 transition of the first absorption band for **1–6** is different to that generally found for organic conjugated polymers. It indicates a very similar geometry between the singlet ground state and the singlet excited state, and therefore a small Huang–Rhys parameter (a measure of the number of phonons required to move from the S_0 to the S_1 state). This confirms quantum chemical calculations of the S_0 and S_1 geometries in compounds closely related to polymer **1**.[19] A small Huang–Rhys parameter is usually associated with an exciton which is well delocalized, which suggests that the conjugation does indeed extend through the Pt in these polymers.

C. Photoluminescence spectroscopy

The PL was measured at various temperatures for each of the polymers using the UV lines of the laser to excite into the first absorption band for polymers **1**, **2**, and **3** and into the second band for polymers **4**, **5**, and **6**. PL spectra were also
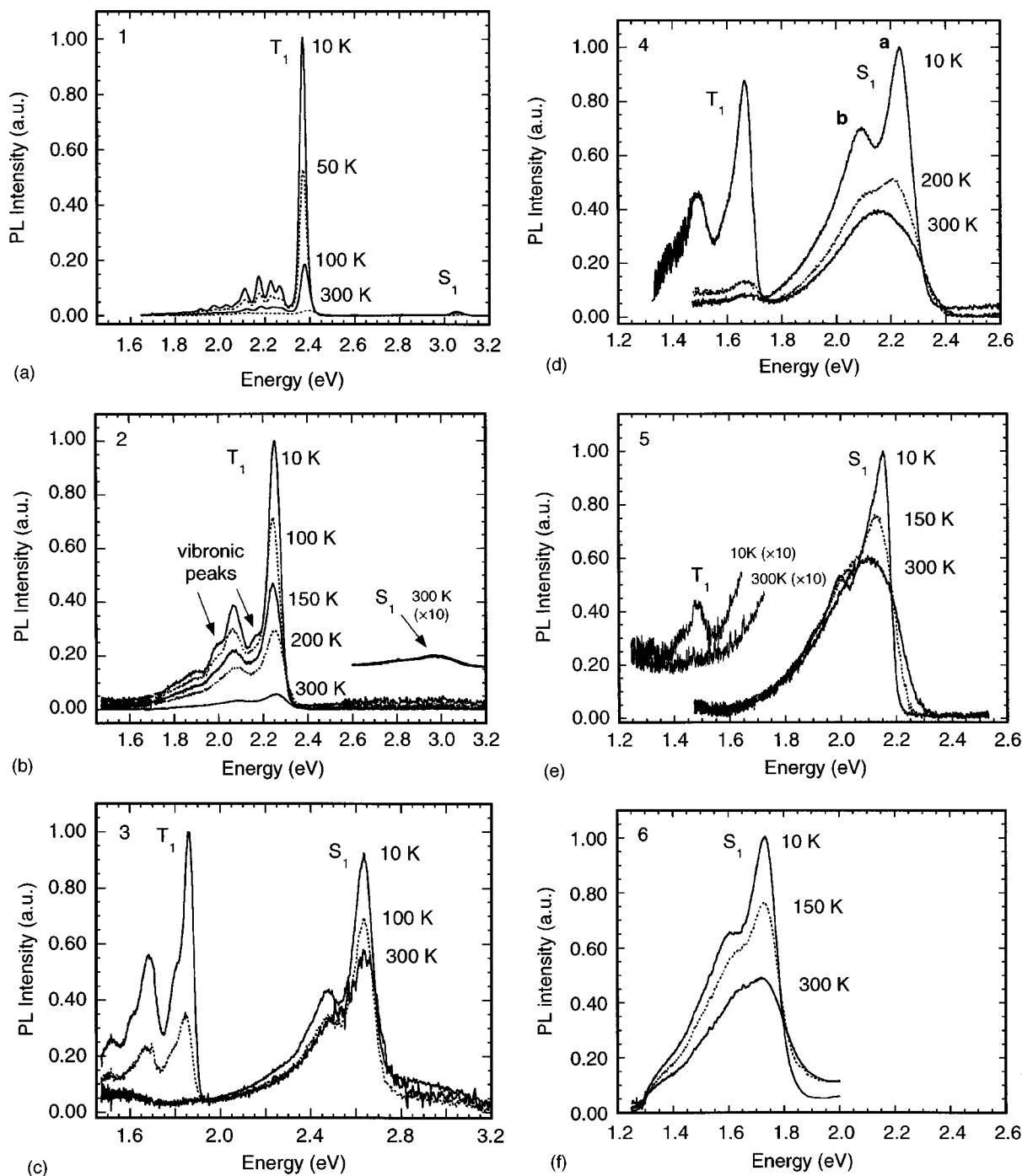
FIG. 4. (a)–(f) Temperature dependencies of the PL of polymers **1**–**6**. The polymer number is given in the top left corner of the plots.

taken with excitation energies of 488 and 457 nm to excite into the first absorption bands of **4** and **5**, but these gave the same spectra as those taken with 365 nm excitation. Figure 3 summarizes the photoluminescence spectra of polymers **1**–**6** at 10 K.

All of the spectra (with the exception of that of polymer **6**) show two characteristic emissions. For polymers **1** and **2**, the higher energy emission cannot be seen on this scale, but can be seen on the scale used in Fig. 4. The higher energy emission is due to the same singlet excited state as band I in the absorption spectra. The lower energy emission is attributed to that of a triplet excited state for the following rea-

sons. The triplet state emission of polymer **1** has been well-characterized previously[18] by lifetime and photoinduced absorption measurements. The lower energy emissions from polymers **2**–**5** have similar lifetimes, temperature dependencies (see below), and energies to those of polymer **1**. In addition, the emissions do not change in dilute solutions, which excludes an excimer origin.

For all six polymers the energies of both the singlet and the triplet peaks reduce along with the optical gap of the polymer. The energy difference between the onset of singlet and triplet emission remains constant at 0.7 ± 0.1 eV. The intensity of triplet emission is reduced relative to the singlet
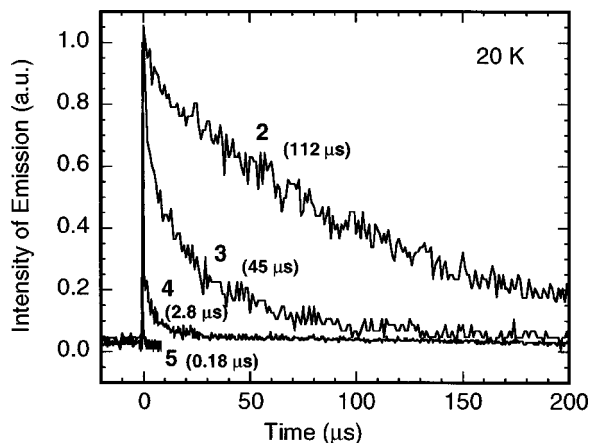
FIG. 5. The decaying intensity of triplet emission signals from films of polymers **2–5** at 20 K. The laser pulse occurs at 0 μs on this time scale and lasts for 50 ns. The values for the triplet lifetimes are also given.

emission when going from polymer **1** to polymer **5**. It was not possible to detect any triplet emission for polymer **6** between 1.0 and 3.3 eV.

The temperature dependencies of the PL spectra are displayed in Fig. 4. We consider that the strong temperature dependence of the triplet arises from the fact that it is a long-lived excited state and as such is more sensitive to thermally activated nonradiative decay mechanisms.

Vibronic structure can be seen in the triplet emission at low temperatures [Fig. 4(b)]. The singlet and triplet peaks also appear to have second peaks on the low energy side of them. These have a different temperature dependence to the main peaks. For example, by comparing *a* and *b* in Fig. 4(d), it can be seen that *a* increases in weight relative to *b* as the temperature is reduced. At room temperature, the low energy side peaks are particularly dominant for compounds **4–6**, which have a bulky spacer and a low optical gap. The side peaks might have a different electronic origin to the main peaks since for compound **1**, the side peak has a different lifetime[18] and does not correspond to any of the normal Raman modes or overtones.[32,33]

D. Triplet exciton lifetime measurements

Triplet lifetimes for organic polymers such as poly(phenylene vinylene)s are typically a few hundred microseconds at low temperature.[34,35] The triplet lifetimes in these organometallic polymers are shorter. They reduce from 112 to 0.18 μs for polymer **2** to polymer **5** at 20 K (Fig. 5). Assuming that the decay was mono- or bimolecular, the emission signals have been fitted to biexponential curves to determine these integrated lifetimes.

Lifetimes measured at room temperature were an order of magnitude smaller than those at 20 K as increased thermal energy assists the nonradiative decay. The lifetimes were still seen to decrease with triplet energy, and were 24, 11, 0.4, and 0.23 μs for polymers **2–5**.

IV. DISCUSSION

A. The S_1-T_1 energy gap

Recently there has been increasing experimental and theoretical attention focusing on the energy levels of singlet and triplet states in conjugated polymers.[36–39] The relative positions of singlet and triplet states strongly affect the intersystem crossing into the triplet manifold. For organic polymers this provides a major nonradiative decay mechanism and reduces the luminescence efficiency.[39–41] The intersystem crossing rate depends exponentially on the energy gap to the nearest triplet excited state.[42] It would therefore be very useful to understand what controls the relative positions of the singlet and triplet energy levels in order to chemically tailor the singlet-triplet gap.

For polymers **1–5** a constant S_1-T_1 energy gap of 0.7 eV is observed which is surprising considering that the optical gap is shifted over about 1.3 eV using a range of different spacers. Moreover, a constant S_1-T_1 gap of 0.7 eV has also been observed in systems similar to polymers **1–5** but with $R=$ thiophene, bithiophene, and terthiophene.[21] In the thiophene systems, the π-conjugation in the spacer was increased without changing the nature of the aromatic ring, whereas in polymers **1–5**, changing R increases the π-conjugation *and* changes the nature of the spacer. We therefore find that for the Pt-containing ethynylenes, the S_1-T_1 energy gap is not affected by the amount of π-conjugation on the spacer nor by the particular type of spacer.

It is difficult to directly compare this result to organic conjugated polymers since most do not have direct emission from the triplet state, and so there are not many systems available for comparison.

Organic systems which have been investigated are a ladder-type poly-(para-phenylene) and an analogous oligomer,[43] oligo(thiophene)s[36,39,44] and oligo(phenylene vinylene)s.[38] There the S_1-T_1 gap is seen to depend strongly on the oligomer chain length since the S_1 and T_n states evolve strongly with chain length while the T_1 state is only weakly dependent on chain length (T_n denotes a higher lying triplet state that is coupled to T_1 via a large oscillator strength). This is because the T_n and S_1 excitons are very extended while the T_1 exciton is more localized. As a consequence, their energy levels are raised to different degrees by confinement effects such as a limited chain length in an oligomer. As a result, the energy splitting between S_1, T_n, and T_1 states changes when the π-delocalized system is increased. Thus for oligomers the singlet-triplet energy gap will usually have both a contribution from the singlet-triplet exchange energy and a variable contribution from the effects of the chain length.

Moving from oligomers to polymers the chain length should no longer produce confinement effects. However, as pointed out above, the orbitals involved in the Pt-containing polymers contain an admixture of metal orbitals, and the influence of the platinum on the energy levels of the excited states is difficult to assess. We have already mentioned that the small Huang–Rhys parameter found for the S_0-S_1 transition indicates a well extended singlet excited state, and this
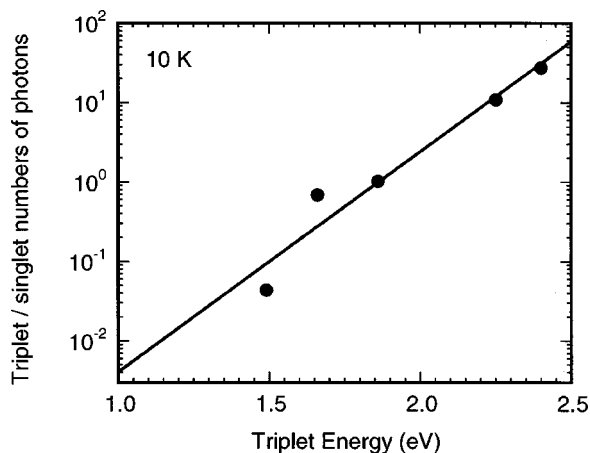
FIG. 6. The ratio of total number of photons emitted from the T_1 state at 10 K to total number of photons emitted from the S_1 state, plotted against the energy of the T_1 state for polymers **1–5**. The data have been fitted to an exponential.

FIG. 7. The energy levels determined for polymers **1–6** from absorption and PL using the maxima of the absorption and PL spectra. The integrated triplet lifetimes measured are also given. The S_0 levels are arbitrarily shown to be of equal energy.

seems to imply that there are no confinement effects on the S_1 state introduced by the metal site. However, at the present stage it cannot be excluded that the mixing of the metal orbitals may shift the energy levels of the resulting singlet and triplet excited states to different degrees. In this case the energy gap of 0.7 eV might consist of the exchange energy plus some offset that is constant along the series of polymers **1–5**. Thus for analogous organic materials,[45,46] we would expect a similarly constant S_1-T_1 gap, although probably with a different absolute value.

We note that the S_1-T_1 gap of 0.7 eV found for these Pt polymers is close to the gap of 5000 cm^{-1} (0.62 eV) for a ladder-type poly-(para-phenylene) polymer determined from phosphorescence measurements.[43] It also compares well with the 0.6–0.7 eV estimated by Beljonne for an infinite PPV chain.[38] It is, however, smaller than the value of 1.1 eV found by Monkman for a soluble PPV derivative (MEH-PPV) using energy transfer.[8]

B. The phosphorescence intensity

The decreasing intensity of triplet emission relative to singlet emission (Fig. 3) down the series of polymers **1–5** is more closely examined in Fig. 6. Here the ratio of the integrated area of photon emission from the T_1 state to the integrated area of photon emission from the S_1 state is plotted against the energy of the T_1 state. Since the spin-orbit coupling in this series of materials is determined by the heavy metal it can be taken as constant along the series. Similarly, the S_1-T_1 gap is constant. Therefore the intersystem crossing, and thus the relative intensity and the lifetime of the phosphorescence, ought to be approximately constant.[39] However, it can be seen that they reduce with the energy of the $T_1 - S_0$ emission.

This is consistent with the energy gap law which states that the nonradiative decay rate increases slightly more than exponentially with decreasing energy gap between the two electronic states.[47–49] This relationship arises as the radiationless decay depends on the vibrational overlap between the two states involved, so that the nonradiative decay rate
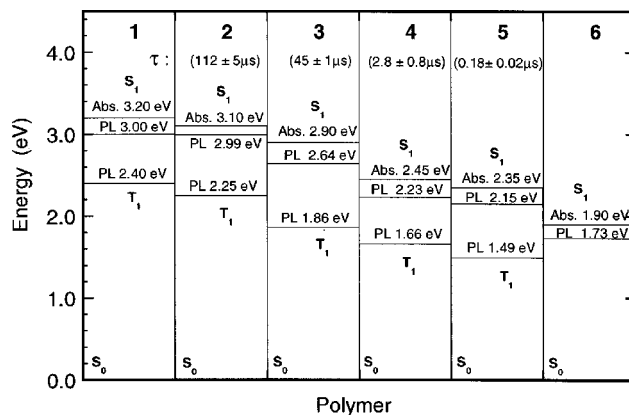
becomes a function of the Franck–Condon factor and of the vibrationally induced electronic coupling term.[42,48,50] The energy gap law has been extensively investigated and applied for both organic molecules and rare earth ions and methods for reducing the nonradiative decay have been established.[40,49,51] One approach is to avoid high energy vibrations, such as those of C–H bonds, within the molecule.[40,52] For high energy vibrations fewer quanta are required to match a given electronic gap with vibrational energy, therefore increasing the probability of nonradiative decay.[40,49]

In conjugated polymers, the phosphorescence has a long radiative lifetime compared to the fluorescence, so the nonradiative decay rate becomes significant. We consider that the decay mechanisms already established for rare earth ions and organic molecules may warrant further investigation of the phosphorescence of conjugated polymers in this context.

The nonradiative lifetime does not always depend solely on the energy gap law, as it would appear to for polymers **1–5**, but may also be further affected by the particular nature of the chromophore R.[51] Nevertheless, this implies that efficient phosphorescence is easier to obtain for higher S_0-T_1 energy gaps since the red emitters will always be subject to a higher rate of nonradiative decay.

C. Summary of trends

The measured energies of the absorption and PL peaks, and the lifetimes of polymers **1–6**, are summarized in Fig. 7. It is seen that, going from polymer **1** to polymer **6**,

(1) The energy of the S_1 singlet excited state reduces as expected.
(2) The S_1-T_1 energy gap remains constant at 0.7 ± 0.1 eV.
(3) The lifetimes and intensities of triplet emission are drastically reduced with decreasing triplet energy as a result of increasing nonradiative recombination.

The series of triplet energies and intensities suggests that the triplet in polymer **6** may be at an energy of around 1.0 ± 0.1 eV and, according to Fig. 6, the number of photons involved in this triplet transition should be around 5×10^{-3}

times the number in the singlet. We consider this emission to be below our detection limit, since the fluorescence yield of compound **6** is already low (0.08%).

The difficulty of observing phosphorescence from the triplet states in most conjugated polymers has meant that previous investigations of S_1-T_1 energy gaps have concentrated on the limited number of systems where triplet emission does occur, usually oligomer systems. However, a limited chain length means there are inherent confinement effects for oligomer systems. We have been able to establish the S_1-T_1 energy gap for a series of polymers. We found a constant S_1-T_1 energy gap of 0.7 ± 0.1 eV which we attribute to the exchange energy and possibly some additional constant contribution due to the admixture of the platinum orbitals.

This work also demonstrates the importance of radiationless decay from the triplet excited state. We suggest that the energy gap law established for organic molecules and rare earth ions might be applied to the T_1-S_0 transition in conjugated polymers.

Note added in proof. Similar S_1-T_1 gaps of 0.62–0.84 eV have now also been observed for four poly(paraphenylene)-derivatives by D. Hertel, S. Setayesh, H. Nothofer, U. Scherf, K. Müllen, and M Bässler, Adv. Mater. (in press).

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