

Evolution of lowest singlet and triplet excited states with number of thienyl rings in platinum poly-ynes

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Soluble, rigid-rod organometallic polymers $trans\text{-}[-Pt(PBu_3)_2-C\equiv C-R-C\equiv C-]_n$ (R=bithienyl **2**, terthienyl **3**) have been synthesized in good yields by the CuI-catalyzed dehydrohalogenation reaction of $trans\text{-}[Pt(PBu_3)_2Cl_2]$ with one equivalent of the diterminal alkynyl oligothiophenes $H-C\equiv C-R-C\equiv C-H$ in CH_2Cl_2/Pr_2NH at room temperature. We report the thermal properties, and the optical absorption, photoluminescence, and photocurrent action spectra of **1** ($trans\text{-}[-Pt(PBu_3)_2-C\equiv C-R-C\equiv C-]_n$, R=thienyl), **2** and **3** as a function of the number of thiophene rings within the bridging ligand. With increasing thiophene content, the optical gap is reduced and the vibronic structure of the singlet emission changes toward that typical for oligothiophenes. We also find the intersystem crossing from the singlet excited state to the triplet excited state to become reduced, while the singlet-triplet energy gap remains unaltered. The latter implies that, in these systems, the T_1 triplet excited state is extended over several thiophene rings. The photoconducting properties do not depend on the size of the thiophene fragment. We discuss and compare our results with studies on oligothiophenes and related organometallic polymers. © 1999 American Institute of Physics. [S0021-9606(99)51210-5]

I. INTRODUCTION

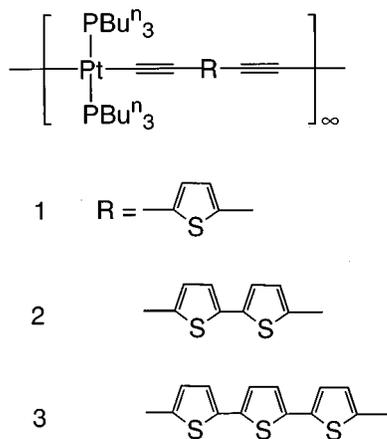
Conjugated polymers are attracting increasing attention as low-cost ready-processed organic semiconductor materials with possible applications in light-emitting diodes,¹ lasers,² and photocells.³ For commercial exploitation of these materials and for direct application-aimed synthesis, a thorough understanding of the relationship between chemical and electronic structure is necessary. In organometallic conjugated polymers, mixing can occur between the metal and ligand orbitals. Thus, the π -conjugation of the ligand is preserved through the metal.⁴⁻⁶ The presence of the heavy metal enhances spin-orbit coupling, so that emission from the triplet excited state, i.e., phosphorescence, can be detected easily.⁴ Another attractive feature of this class of materials is that there is scope for chemical modification of the ligands. For these two reasons organometallic conjugated polymers provide suitable model systems to investigate the relationship between chemical structure and the evolution of singlet and triplet excited states.^{4,6,7} The latter play significant roles in light emitting diodes⁸ and photocells.^{9,10} Here we have investigated the dependence of the first excited singlet and triplet electronic state on the number of thiophene units in the conjugated bridging ligand. By increasing the thiophene

fragment (Fig. 1), we expect to increase π -conjugation in the ligand without changing the nature of the aromatic ring, in contrast to some of our earlier work.⁷

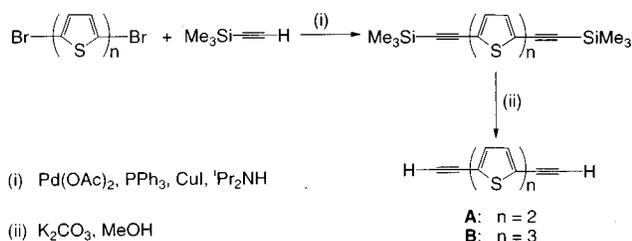
II. EXPERIMENT

A. Synthesis and polymerization

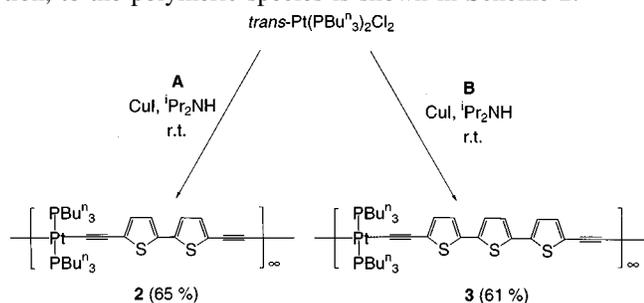
All reactions were performed under an inert nitrogen atmosphere using standard Schlenk techniques. Solvents were predried and distilled before use by standard procedures.¹¹ All chemicals, except where stated otherwise, were obtained from commercial sources and used without further purification. The compound $Me_3SiC\equiv CH$ was obtained from the preparation laboratory in the Department of Chemistry, Cambridge. The platinum complex $trans\text{-}[Pt(PBu_3)_2Cl_2]$ was prepared by the literature method.¹² NMR spectra were recorded on a Bruker WM-250 spectrometer in appropriate solvents. ³¹P{¹H} NMR and ¹H NMR spectra were referenced to external trimethylphosphite and solvent resonances, respectively. Infrared spectra were recorded as CH_2Cl_2 solutions, in a NaCl cell, on a Perkin-Elmer 1710 Fourier Transform IR spectrometer. Microanalyses were performed in the Department of Chemistry. UV/VIS absorption spectra were obtained with a Perkin-Elmer Lambda UV/NIR spectrometer. Column chromatography was performed on alumina (Brockman Grade II-III).

FIG. 1. Chemical structures of polymers **1**, **2**, and **3**.

The preparations of the ligand precursors, 5,5'-di(ethynyl)-2,2'-bithiophene (**A**) and 5,5''-di(ethynyl)-2,2':5',2''-terthiophene (**B**),¹³ and *trans*-[Pt(PBu₃)₂-C≡C-Th-C≡C-]_n (**1**)⁷ have been reported recently (Scheme 1):



A general synthetic route,^{14,15} by dehydrohalogenation reaction, to the polymeric species is shown in Scheme 2:



1. *trans*-[Pt(PBu₃)₂-C≡C-(Th)₂-C≡C-]_n (**2**)

CuI (3 mg) was added to a mixture of *trans*-[Pt(PBu₃)₂Cl₂] (0.10 g, 0.15 mmol) and 1 equivalent of H-C≡C-(Th)₂-C≡C-H (**A**, 0.03 g, 0.15 mmol) in CH₂Cl₂/*i*Pr₂NH (50 cm³, 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, a yellow film was obtained readily, and it was then washed with methanol to give the polymer **2** in 65% yield (0.08 g). Further purification can be accomplished by precipitating the polymer solution in toluene from methanol.

IR (CH₂Cl₂): ν/cm^{-1} 2087 (C≡C). ¹H NMR (250 MHz, CDCl₃): δ 0.93 (*t*, 18H, CH₃), 1.47 [*m*, 24H, (CH₂)₂], 2.08 (*m*, 12H, PCH₂), 6.68 [*d*, 2H, ³J_{3,4(3',4')} = 3.7, H_{3,3'}] and 6.84 [*d*, 2H, ³J_{4,3(4',3')} = 3.7 Hz, H_{4,4'}]. ³¹P{¹H} NMR (101.3 MHz, CDCl₃): δ -137.81, ¹J_{Pt-P} = 2331 Hz. Calcd. for [C₃₆H₅₈P₂S₂Pt]_n: C, 53.25; H, 7.20. Found: C, 54.00; H, 7.33%. *M*_w = 181 900, *M*_n = 56 180 (*n* = 3.238).

2. *trans*-[Pt(PBu₃)₂-C≡C-(Th)₃-C≡C-]_n (**3**)

Similar procedures as in **2** were adopted using H-C≡C-(Th)₃-C≡C-H (**B**, 0.04 g, 0.15 mmol) to produce an orange film of polymer **3** in 61% yield (0.08 g).

IR (CH₂Cl₂): ν/cm^{-1} 2086 (C≡C). ¹H NMR (250 MHz, CDCl₃): δ 0.94 (*t*, 18H, CH₃), 1.48 [*m*, 24H, (CH₂)₂], 2.09 (*m*, 12H, PCH₂), 6.71 [*d*, 2H, ³J_{3,4(3',4'')} = 3.5, H_{3,3''}] and 6.92 [*m*, 4H, H_{3',4'} and H_{4,4''}]. ³¹P{¹H} NMR (101.3 MHz, CDCl₃): δ -137.74, ¹J_{Pt-P} = 2327 Hz. Calcd. for [C₄₀H₆₀P₂S₃Pt]_n: C, 53.73; H, 6.76. Found: C, 53.64; H, 7.04%. *M*_w = 82 860, *M*_n = 64 560 (*n* = 1.283).

B. Molecular weight measurements

Molar masses 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 cm³/min with a Roth Mocol 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).

C. Optical measurements

The polymer films for optical measurements were spin-coated from dichloromethane solutions onto quartz substrates. The optical absorption was measured with a Perkin-Elmer λ-9 spectrometer. Excitation for the photoluminescence studies was provided by the 457 nm line (for **2** and **3**) and UV lines (353–364 nm) (for **1**) of an Ar⁺ laser. The emission spectra were recorded using a spectrograph with an optical fiber input and a CCD (charge coupled diffraction) parallel detection system (Oriol Instaspec IV). For the low temperature luminescence measurements the samples were mounted in a continuous flow helium cryostat.

D. Photocurrent measurements

Sandwich-type photocells in a layer structure of Au/1/Al, ITO/2/Al, and ITO/3/Al (ITO=indium-tin oxide) were fabricated as reported elsewhere.¹⁶ The typical thickness of the film was about 350 nm (**1** and **2**) and 150 nm (**3**), and the active area of the devices, defined by the overlap of the ITO or gold electrode with the aluminum electrode, was about 4 mm². Measurements of the spectral response were made by illuminating the device through the ITO or gold side. Optical excitation was provided by a 100 W tungsten lamp, spectrally resolved by a single grating Bentham M 300 monochromator for **2** and **3**, and a 150 W xenon arc lamp dispersed by a Jobin Yvon H25 monochromator for **1**. A Keithley 237 source-measure unit was used to apply a dc

TABLE I. GPC and some spectroscopic data for polymers **2** and **3**.

Polymer	Yield (%)	M_w	M_n	n	$\nu_{C\equiv C}$ (cm^{-1})	$^{31}\text{P}\{^1\text{H}\}$ NMR (ppm) ^a	λ_{max} in CH_2Cl_2 (nm) ^b
2	65	181 900	56 180	3.238	2087	-137.81 ($^1J_{\text{Pt-P}}=2331$ Hz)	457 (53 000)
3	61	82 860	64 560	1.283	2086	-137.74 ($^1J_{\text{Pt-P}}=2327$ Hz)	470 (62 000)

^aReferenced to P(OMe)₃.^bExtinction coefficient (in $\text{cm}^{-1} \text{M}^{-1}$; molarity is based on the repeating unit) is given in parentheses.

bias voltage to the device and to monitor the current flowing through it. All measurements were taken at room temperature. To correct the photocurrent spectra for the spectral response of the illuminating system, the device was replaced by a silicon photodiode. All of the measurements were taken in air at room temperature immediately after fabrication.

E. Thermal analysis

Thermal analysis (differential thermal analysis, DTA, and thermogravimetry/derivative thermogravimetry, TG/DTG) of **2** and **3** was performed simultaneously in a Stanton–Redcroft model STA-780 Simultaneous Thermal Analyzer under flowing N_2 . Sample sizes were 1–2 milligram in open Inconel crucibles. Samples were redissolved in CH_2Cl_2 that evaporated to form a film. Samples were then immediately heated at $10^\circ\text{C}/\text{min}$ from 15 to 540°C .

III. RESULTS AND DISCUSSION

A. Chemical characterization

The results of a systematic characterization of polymer **2** and **3** by analytical methods (IR, ^1H , and ^{31}P NMR), molecular weight determination, and UV/VIS spectroscopy are shown in Table I. The weight-average molecular weights (M_w) indicate a high degree of polymerization. The number-average molecular weight (M_n) values of **2** and **3** correspond to 69 and 72 repeating units per chain, respectively. The IR and NMR spectral features of **2** and **3** are consistent with the

polymer structures shown above and are similar to other platinum arylene-acetylide polymers previously reported.^{17–19} The IR spectra of the polymers display a single sharp $\nu_{C\equiv C}$ absorption at ca. 2087 cm^{-1} (**2**) and 2086 cm^{-1} (**3**), which together with the singlet signal observed in each ^{31}P NMR spectrum reveal a *trans* configuration of the ligands around $\text{Pt}^{\text{II}}(-\text{C}\equiv\text{C}-)_2$ moieties in these square-planar polymeric species. The $\nu_{C\equiv C}$ stretching frequency for the polymeric complexes **2** and **3** (av 2087 cm^{-1}) is 15 wave numbers lower than for the free ligand precursors **A** and **B** (2102 cm^{-1}),¹³ indicating a higher degree of conjugation in the former.

B. Absorption spectroscopy

Optical absorption spectra were taken in CH_2Cl_2 solutions (Table II) and in thin films (Fig. 2). From Table II, the following trends can be observed:

(i) The energy of the optical gap (i.e., the onset of absorption) of polymers decreases with increasing number of thiophene units (Row 1). We attribute this to an increased delocalization of π -electrons along the polymer backbone. We note that as the number of thiophene units increases, the overall effect on the band gap decreases, and there would probably be little benefit in increasing the number of thiophene units above three.

(ii) Introducing a platinum fragment at each end of the ligands lowers the energies of the transition (compare Row 3 with Row 2). In the same way, the transition energies of the

TABLE II. Optical absorption and optical gap of polymers, **1**, **2**, and **3** and other related compounds.

Row	Compound	Abs. maxima in solid state (eV)	Abs. maxima in solution (eV)	Optical gap in solid state (eV)
	1 : $[-\text{Pt}(\text{PBu}_3)_2-\text{C}\equiv\text{C}-(\text{Th})_1-\text{C}\equiv\text{C}-]_\infty$	3.05 , 4.03, 4.69, 5.53		2.80
1	2 : $[-\text{Pt}(\text{PBu}_3)_2-\text{C}\equiv\text{C}-(\text{Th})_2-\text{C}\equiv\text{C}-]_\infty$	2.78 , 4.12, 4.62, 5.39	2.71	2.55
	3 : $[-\text{Pt}(\text{PBu}_3)_2-\text{C}\equiv\text{C}-(\text{Th})_3-\text{C}\equiv\text{C}-]_\infty$	2.56 , 2.71 , 3.71, 4.56, 5.32	2.64	2.40
2	A : $\text{H}-\text{C}\equiv\text{C}-(\text{Th})_2-\text{C}\equiv\text{C}-\text{H}$		3.51	2.88
	B : $\text{H}-\text{C}\equiv\text{C}-(\text{Th})_3-\text{C}\equiv\text{C}-\text{H}$		3.14	2.42
3	(Ph)Pt(PBu ₃) ₂ -C≡C-(Th) ₂ -C≡C-Pt(PBu ₃) ₂ (Ph)		3.05	
	(Ph)Pt(PBu ₃) ₂ -C≡C-(Th) ₃ -C≡C-Pt(PBu ₃) ₂ (Ph)		2.86	
4	Me ₃ Si-C≡C-(Th) ₂ -C≡C-SiMe ₃			2.93
	Me ₃ Si-C≡C-(Th) ₃ -C≡C-SiMe ₃			2.53

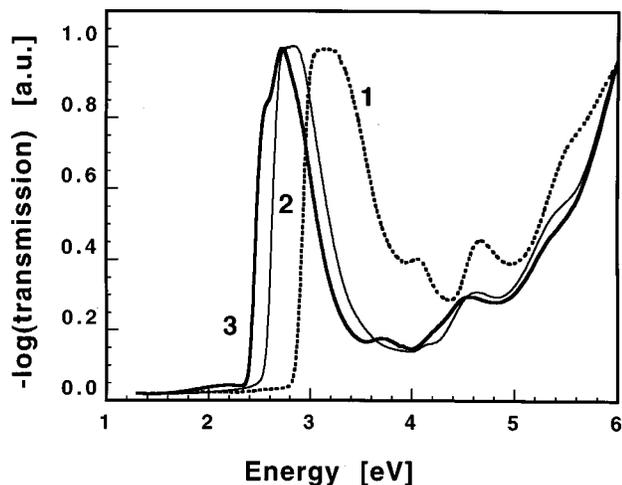


FIG. 2. Optical absorption spectra for polymers 1, 2, and 3 in the solid state.

polymers are lowered compared to the corresponding dimers (Row 1 and 3). This shows that the π -conjugation of the ligands extends into and through the metal center, consistent with our previous results on related systems.⁶ We note that, in contrast, the optical gap increases when introducing trimethylsilyl at the end of the ligands (Row 2 and 4). The latter is produced as an intermediate product during the synthesis route.

Figure 2 shows the solid state absorption spectra of polymers 1–3 up to 6 eV. It is interesting to note that, in general, not only the optical gap shifts with thiophene fragment, but the whole spectrum shifts, including the higher-lying transitions.

C. Photoluminescence spectroscopy

Figure 3 shows the room temperature photoluminescence spectra for polymers 1–3. The emission features are shifted to lower energy with the increasing length of the thiophene segment, analogous to the absorption spectra. We attribute the features peaking at 2.85 eV, 2.44 eV, and 2.28 eV for polymers 1, 2, and 3 to emission from singlet excited

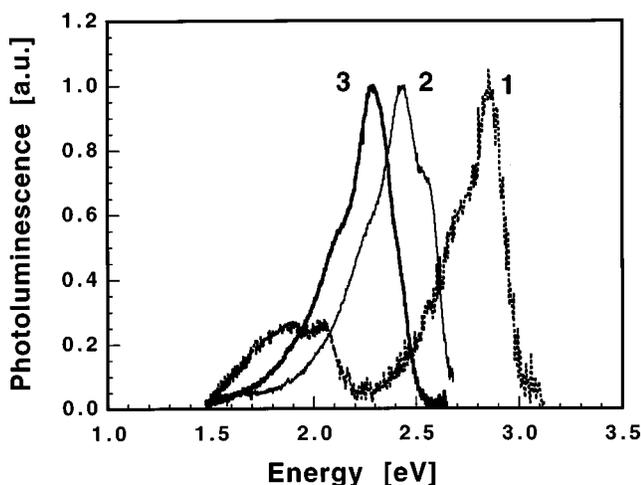


FIG. 3. Room temperature solid-state photoluminescence spectra for polymers 1–3.

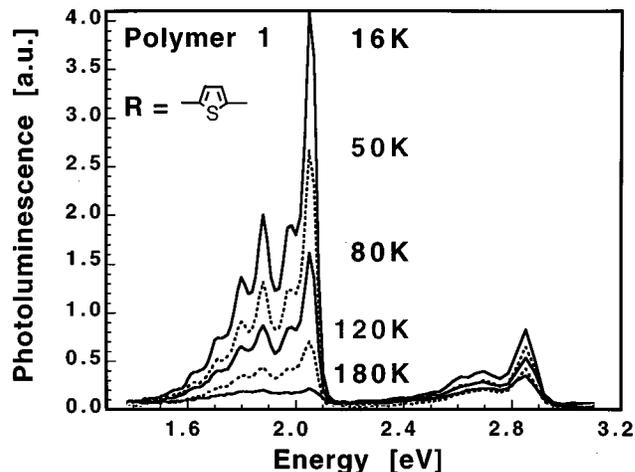


FIG. 4. Temperature dependence of the photoluminescence of polymer 1.

state (fluorescence), due to the small energy shift between absorption and emission features. We note that the singlet $S_0 \leftrightarrow S_1$ transition involves the mixed ligand-metal orbitals, as shown above and discussed in more detail in Refs. 4–6. Without detailed calculations it is difficult to estimate whether the character of this transition is dominated by the intraligand HOMO-LUMO π - π^* transition, as found for related polymers where the thiophene units are replaced by a benzene ring,⁶ namely $[-Pt(PBu_3)_2-C\equiv C-p-C_6H_4-C\equiv C-]_n$, or whether this transition has a predominant charge-transfer type character, as observed for the corresponding related monomer $(Ph)Pt(PBu_3)_2-C\equiv C-p-C_6H_4-C\equiv C-Pt(PBu_3)_2(Ph)$ ⁶ and other platinum (II) acetylide complexes.^{10,20–22} The broad feature between 1.6 eV and 2.2 eV in the emission spectrum of 1 is due to emission from a triplet excited state (phosphorescence). This assignment is discussed below on the basis of the temperature dependence of the emission data. For 2, there is a weak shoulder centered at about 1.67 eV, which we also attribute to a triplet emission, i.e., an emission from the triplet excited state. There is no room temperature triplet emission for 3 over the measured range (1.2–3.0 eV).

We identify the emission feature in 1 peaking at 2.05 eV as a triplet emission for the following reasons: First, this emission is strongly temperature dependent in contrast to the singlet emission (Fig. 4). From 180 K to 16 K, the singlet emission peak increases by a factor of 2.4, while the lower-lying emission increases by a factor of 19.4. This increase of emission intensity indicates a long-living excited state that is quenched by thermally activated diffusion to dissociation sites. Second, for similar systems such as $[-Pt(PBu_3)_2-C\equiv C-p-C_6H_4-C\equiv C-]_n$, we also found a higher-lying singlet emission (at 3.2 eV) and a lower-lying, clearly identified triplet emission (at 2.4 eV).⁴ The latter is also reduced by a factor of about 20 when going from 20 K to 180 K and was found to have a lifetime of 30 μ s at 10 K.¹⁷

Figure 5 shows the emission spectra at 18 K for polymers 1–3, together with the first absorption feature for comparison. In 2 and 3, the origin of the features at 1.67 eV and 1.53 eV, respectively, is not immediately obvious [Fig. 5(b) and 5(c)]. We consider that these emission features have the

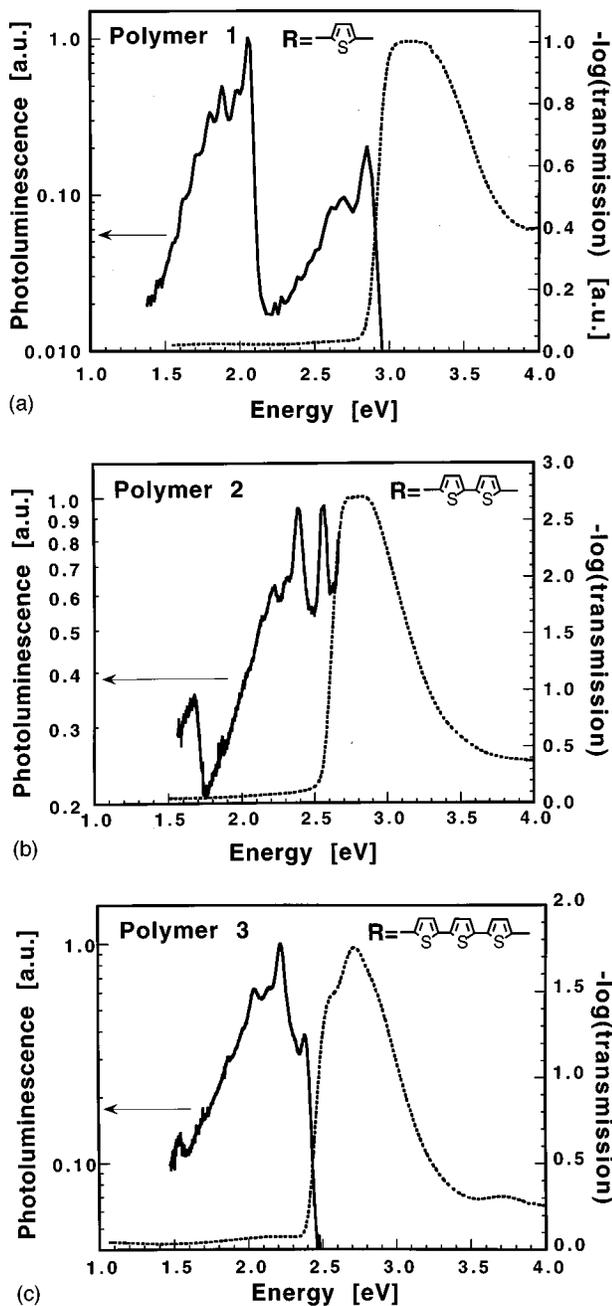


FIG. 5. Absorption and photoluminescence of (a) **1**, (b) **2**, and (c) **3**.

same origin as the emission in **1** at 2.05 eV, namely a triplet state: They are energetically close—in fact, they all lie at 0.80–0.88 eV below the singlet emission (Fig. 6)—and a sudden disappearance of the triplet emission when going from **1** to **2** would be unlikely. Also, origins such as an excimer state or *d-d* transitions appear even more unlikely to us.

There are two unusual features that need attention before assigning these emissions to triplet emissions:

- (1) The intensity of this suspected triplet emission decreases rapidly with increasing number of thiophene units. We rationalize this by the following factors:
 - (i) Increasing the number of thiophene rings in the ligand reduces the influence of the heavy metal

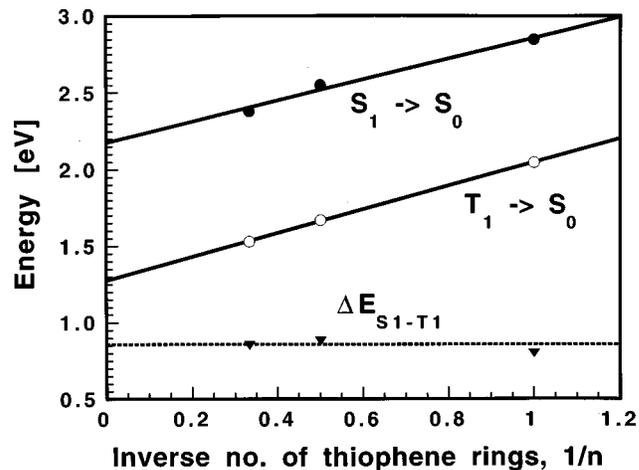


FIG. 6. Evolution of the $S_1 \rightarrow S_0$ and $T_1 \rightarrow S_0$ excitation energies and the singlet–triplet energy gaps $\Delta E_{S_1-T_1}$ with the inverse number of thiophene rings ($1/n$) in the bridging ligand.

center which is mainly responsible for the intersystem crossing.

- (ii) In oligothiophene systems themselves, intersystem crossing (and thus phosphorescence) is reduced with increasing number of thiophene units, as the energy of the singlet excited state drops below the corresponding resonance state for intersystem crossing in those systems.²³
- (2) The energy of the triplet emission shifts (Fig. 6) when adding more thiophene rings in the ligand (from 2.05 eV to 1.53 eV for **1–3**, $\Delta E = 0.52$ eV). This is in contrast to the similar position ($\Delta E \leq 0.03$ eV) of the triplet emission in polymers and corresponding monomers of $[-Pt(PBu_3)_2-C\equiv C-R-C\equiv C-]_n$ with $R = \text{phenyl, pyridine or thiophene}$.^{6,7} Thus in systems studied here, the triplet excited state must be extended over several thiophene rings (i.e., 3 or more), while in those systems^{6,7} the triplet excited state is confined to the aromatic ring only. When comparing these two systems, it is important to be aware that here we increase the conjugation length *within the ligand*, while in those systems^{6,7} the effect of increasing the number of *repeat unit* is studied. This raises the question of whether the triplet excited state is confined *onto* the cyclic ring or whether it is confined *between* the two rigid ethylenic units. If only one ring is considered,⁶ these two cases are identical. Follow-up experiments will investigate this in further detail.

This shift of triplet emission energy observed in **1–3** agrees well with the calculations by Beljonne *et al.* on the evolution of the triplet excitation energy in purely organic oligothiophene systems PT_n (where $PT = \text{oligothiophene}$ and $n = 2–6$).^{23,24} We experimentally find energy shifts of 0.38 eV (**1**→**2**) and 0.15 eV (**2**→**3**). They report a energy shift of 0.14 eV for PT_2 to PT_3 (bithiophene to terthiophene). Extrapolating their data (Fig. 4 of Ref. 23) gives a energy shift of 0.30 eV for PT_1 to PT_2 (monothiophene to bithiophene). Thus from both our and their results,^{23,24} it appears that the triplet excited states in thiophene systems spreads over sev-

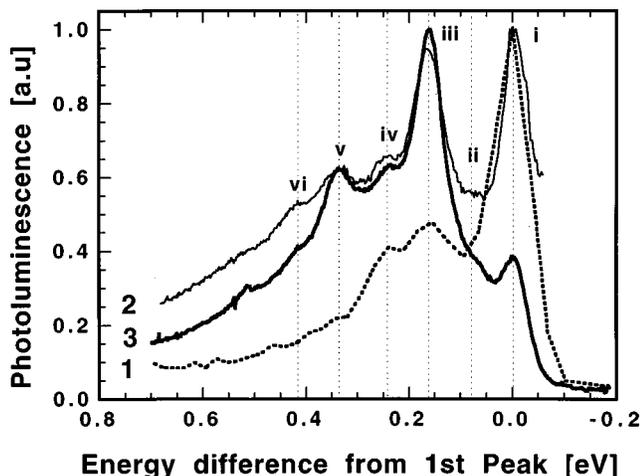


FIG. 7. Singlet emission for polymers 1–3 with the peak emission normalized to unity on the ordinate and with the energy of the first peak set to 0 eV on the abscissa. Numbers are used to label different peaks rather than to assign vibronic transitions.

eral rings. We note that Cornil *et al.* discuss the triplet excited states in oligothiophenes as being confined.²³ This arises because the evolution of triplet excitation energy in oligothiophenes is weak relative to the change in the singlet excitation energy.

We find an almost parallel development of singlet and triplet transition energies here with increasing the number of thiophene unit in the ligand, which is in contrast to the reduction of the singlet–triplet energy gap in oligothiophenes with increasing number of thiophene rings. In our thiophene-containing poly-ynes, the *singlet* emission shifts by only 0.17 eV from 2 to 3, while in the oligothiophenes, this emission shifts by 0.6 eV from PT₂ to PT₃, according to the calculations.^{23,24} We consider that in PT₂ and PT₃, the singlet is spatially confined by the length of the oligomer, so that the excitation is “squeezed in a box.” In contrast, in 2 and 3, the singlet excitation can spread out over the ethylenic units into and through the metal centers so as to occupy its “favored” length along the polymer chain. This explains why the singlet excited state in 2 is at only 2.55 eV while in PT₂ it is calculated to be at 4.2 eV,^{23,24} and also why increasing the number of thiophenes within the ligand does not have such a dramatic effect on the singlet excitation energy than increasing the repeat unit in oligothiophenes from $n=2$ to $n=3$. As a result, the singlet–triplet energy gap remains nearly constant.

Figure 7 shows the singlet emission for polymer 1–3 with the peak emission normalized to unity on the ordinate and with the energy of first peak set to 0 eV on the abscissa. The vibronic sidepeaks display different intensities in polymer 1–3. For 1, the main intensity of the transition occurs for the first vibronic peak; for 2, the third vibronic peak has already acquired a large contribution; and for 3 the third vibronic peak is the dominant transition. In other words, with increasing number of thiophene units the excited state geometry differs more from the ground state geometry and the shape of the emission moves away from the typical $[-Pt(PBu_3)_2-C\equiv C-R-C\equiv C-]_n$ emission^{4,7} to an oligothi-

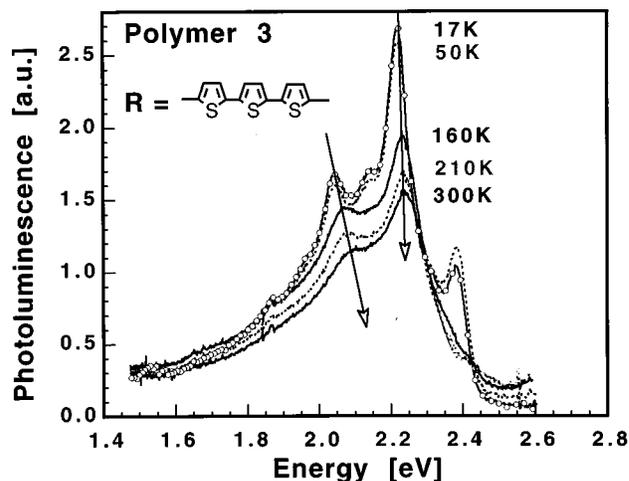


FIG. 8. Temperature dependence of the photoluminescence of polymer 3.

iophene shape.²⁵ According to Beljonne *et al.*,⁶ the ethylenic units are rigid with respect to photoexcitations, so that most of the relaxations must occur on the aromatic ring between the ethylenic units. We consider that this is easier for a larger number of aromatic rings.

In polymer 3, evidence emerges for another electronic transition located at 2.12 eV for 17 K, i.e., at about 0.34 eV below the first transition, from the evolution of the vibronic sidepeaks with temperature (Fig. 8). First, this peak shifts its energetic position by 0.05 eV to lower energy with decreasing temperature in contrast to the other peaks, which shift by only 0.01 eV. Second, for temperatures of 160 K and higher, the vibronic substructure (e.g., peaks 1, 2 and 4) disappears and the fluorescence is dominated by the vibronic transition at 2.26 eV and the transition at 2.12 eV (at 17 K).

This is similar to the observation of a different electronic transition in the phosphorescence signal of the polymer $[-Pt(PBu_3)_2-C\equiv C-p-C_6H_4-C\equiv C-]_n$ ^{4,26} and the monomer $(Ph)Pt(PBu_3)_2-C\equiv C-p-C_6H_4-C\equiv C-Pt(PBu_3)_2(Ph)$,¹⁰ in each case about 0.25 eV below the first peak. In a manner analogous to Fig. 8, this transition contributes to 60% of the phosphorescence signal at room tem-

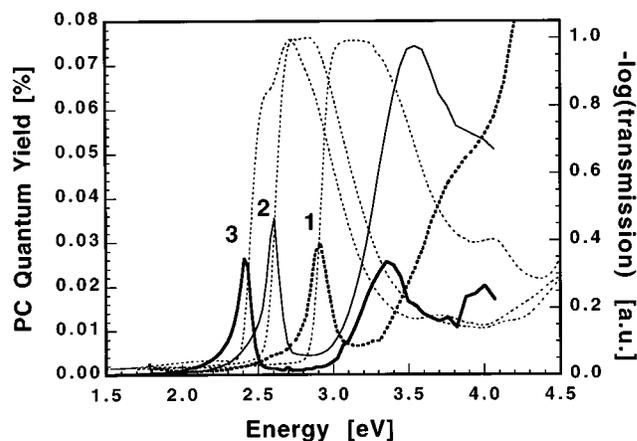


FIG. 9. Photocurrent spectra of the photocells Au/1/Al, ITO/2/Al, and ITO/3/Al. Absorption spectra are also shown for comparison.

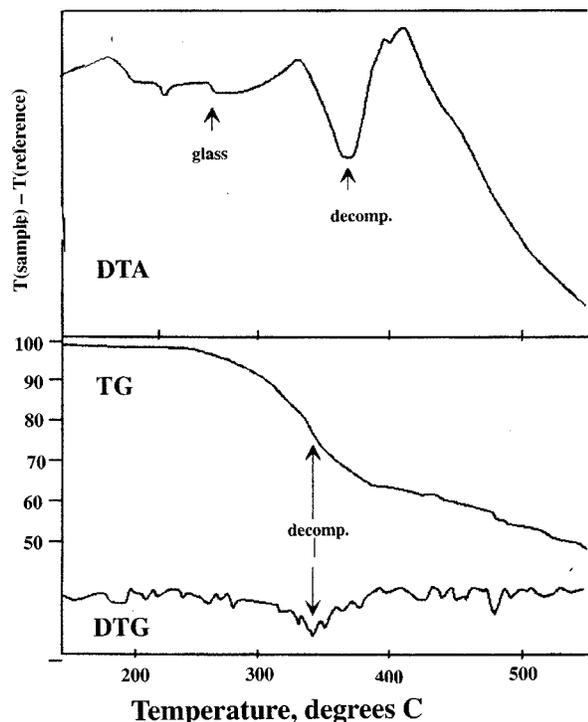


FIG. 10. Simultaneous DTA/TG/DTG data for **2**. The glass transition and decomposition peaks are indicated.

perature (but only 12% to the emission at 18 K).²⁶ Graham, Wittmann, and co-workers speculate on interchain interactions as source for this additional transition.

D. Photocurrent measurements

Figure 9 shows the photocurrent quantum yields as a function of the photon energy in short-circuit mode for illumination through the ITO or gold electrode for polymers **1**, **2**, and **3**. The photocurrent spectra of the Au/1/Al, ITO/2/Al, and ITO/3/Al photocells show two peaks, one at the onset of absorption [2.92 (**1**), 2.64 (**2**), and 2.43 eV (**3**)] and one at higher photon energies [3.81 (**1**), 3.56 (**2**), and 3.38 eV (**3**)]. This is consistent with the UV photocurrent spectra reported for poly(*p*-phenylenevinylene)²⁷ and for platinum poly-yne derivatives containing a thieno-pyrazine ring.¹⁰ Based on comparison with those materials, which have been characterized further into the UV region where they exhibit further photocurrent peaks, we tentatively interpret the second photocurrent peak as caused by absorption into the higher-lying absorption bands. Full discussion of these higher-lying peaks is beyond the range of this paper.^{10,27} The position of the first photocurrent peak at the onset of absorption is determined by factors such as the internal filter effect^{16,28,29} (i.e., the trade-off between the amount and the position of light absorbed in

the device) and increased charge separation at low energy sites.³⁰ All three materials show a short-circuit quantum efficiency of about 0.04% at the first photocurrent peak, which is a common value for single layer devices. There is no difference in quantum efficiency with variation of the thiophene content in the polymer. The quantum efficiency of the second peak is different for **1**, **2**, and **3** and is very sensitive to air exposure. In all three polymers the overall photocurrent increases when exposed to air and is reduced after annealing under vacuum. This process can be cycled reversibly, although the timescales for absorption and desorption of air decrease with repetition. All three materials show a low energy tail which is enhanced by exposure to air in a different manner to the photocurrent at and above the band gap.³¹ We consider this tail might be due to subgap absorption of defect states.³¹ The current-voltage characteristics taken under illumination at intensities of 90 $\mu\text{W}/\text{cm}^2$, 185 $\mu\text{W}/\text{cm}^2$, and 440 $\mu\text{W}/\text{cm}^2$ at the first peak in the spectral response give open-circuit voltages of 0.50, 0.75, and 0.47 and fill-factors of 0.32, 0.35, and 0.30 for **1–3**, respectively. These are typical values for single-layer polymeric photocells.

E. Thermal analysis

All samples exhibited mass loss due to decomposition beginning slightly above their glass transitions. Figure 10 shows the simultaneous DTA/TG/DTG data for **2**. The behavior is qualitatively different from *trans*-[Pt(PBu₃)₂-C≡C-R-C≡C-]_∞ (R=phenyl or substituted phenyl). The DTA peak which accompanies the mass loss is endothermic in the thienyl polymers, not exothermic as in the phenyl analogues.³² It also occurs at somewhat higher temperatures than the DTG peak, whereas the two peaks coincided closely in the phenyl analogues. A minor endotherm was also present in **2** at 227 °C; similar endotherms were observed in phenyl analogues. Decomposition onset was defined as a mass loss of 2%. The results are shown in Table III.

IV. SUMMARY

In order to extend our previous studies on the nature of photoexcited states in organometallic conjugated polymers as a function of π -conjugation in the bridging ligand, we synthesized the platinum poly-ynes [Pt(PBu₃)₂-C≡C-R-C≡C-]_∞ with R=bithienyl, terthienyl, and compared them with [Pt(PBu₃)₂-C≡C-R-C≡C-]_∞ where R=thienyl. We assigned emission features to the first excited singlet and triplet state and discussed their energetic position and the intensity of intersystem crossing in comparison to related platinum poly-yne and oligothiophenes. We consider that these results contribute to the understanding of the relationship between chemical structure and electronic structure in both organic and organometallic conjugated polymers.

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TABLE III. Results of thermal analysis; all temperatures in °C. Uncertainties are standard deviations.

	T_{glass}	T_{decomp} (onset)	T_{decomp} (peak) DTG	T_{decomp} (peak) DTA
2	275 ± 5	278 ± 8	340 ± 4	371 ± 5
3	281 ± 6	290 ± 15	349 ± 7	389 ± 3

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