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Review

The triplet state in Pt-acetylide oligomers, polymers and copolymers☆

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Contents

Abstract

Platinum acetylide oligomers and polymers are π-conjugated materials that display luminescence from the triplet exciton. This property makes platinum acetylides useful for exploring the properties of the triplet state in π-conjugated systems. In the present review we describe the excited state properties of a series of Pt-acetylide oligomers and polymers with an emphasis placed on understanding structure–property relationships for the triplet state in π-conjugated systems.

Keywords: Platinum-acetylide; Triplet state; Phosphorescence; π-Conjugated polymers

1. Introduction

Conjugated materials have been the focus of considerable research during the past several decades [1]. This field has been stimulated by the large number of potential applications for conjugated materials in electronic and electro-optical devices [2]. Although most of the work in this field has focused on conjugated materials that are comprised of organic building blocks, there has been increasing interest in the properties of organometallic conjugated materials [3]. This interest derives from the fact that incorporation of heavy metals into an organic conjugated framework can elicit large effects on the electronic and optical properties of the materials. In many cases the effects are predictable and tunable, allowing one to use structure to control the properties of a desired material [4–7].

Organometallic materials are of particular interest in applications that require light emission, for example as the active materials in light emitting diodes (LEDs) [4,8–11] and optical oxygen sensors [12,13]. The propensity of heavy transition metals such as Ir and Pt to mix singlet and triplet excited states via spin-orbit coupling leads to molecule-based

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materials, which feature high phosphorescence yields and relatively long emission lifetimes. These properties are particularly useful in LEDs and oxygen sensing. In particular, in LEDs, the ability to harvest light emission from both singlet and triplet excitons leads to devices that operate with high quantum efficiency [8,9].

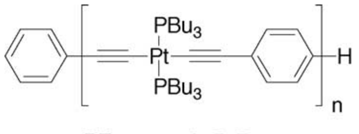
Another application which has received interest is nonlinear absorption and reverse saturable absorption [14]. In particular, in a recent study it was shown that a Pt-acetylide oligomer is an effective optical limiter for nanosecond pulses of visible light [15,16]. Optical limiting is believed to arise via reverse saturable absorption due to the triplet state. This observation has stimulated interest in investigation of the factors that control the yield and absorption of the triplet excited state in Pt-acetylide materials [17,18].

Our group has carried out a number of investigations which seek to develop structure–property relationships for the optical properties of Pt-acetylide materials [19–21]. In the course of this work we have prepared and characterized the optical properties of a variety of Pt-acetylide based oligomers and polymers, with particular emphasis being placed on understanding how structure controls the properties of the triplet excited state. In the present review we provide an overview of some of the recent work that we have carried out in this area.

2. Monodisperse platinum-acetylide oligomers

Excited-state structure and electronic delocalization in Pt-acetylide based π-conjugated polymers have been investigated considerably [22–27]. While these studies have provided much insight into the optical and photophysical properties of these materials, there are several inherent difficulties in using polymers for careful photophysical studies. First, synthetic polymers are by nature polydisperse – any given polymer sample includes a variety of chain lengths. In addition, polymer chains may have defects in their backbones that are not easily detected by normal structural characterization techniques, but which may influence the photophysical properties of the polymer.

Our group has been interested in using conjugated oligomers as models for large conjugated polymer systems [20,28–32]. The oligomer-based approach allows systematic investigation of the changes in optical properties that accompany an increase in conjugation length. Despite its utility in providing an understanding of the relationship between structure and optical properties, until now very few studies have focused on structurally well-defined Pt-acetylide oligomers [33]. Recently, we completed a systematic photophysical study of a series of mono-disperse Pt-acetylide oligomers [34]. This investigation was carried out with the objective of providing insight concerning electronic delocalization in Pt-acetylide polymers. The series of Pt-acetylide oligomers (PAOs) that were the focus of this work are shown in Scheme 1 [20].

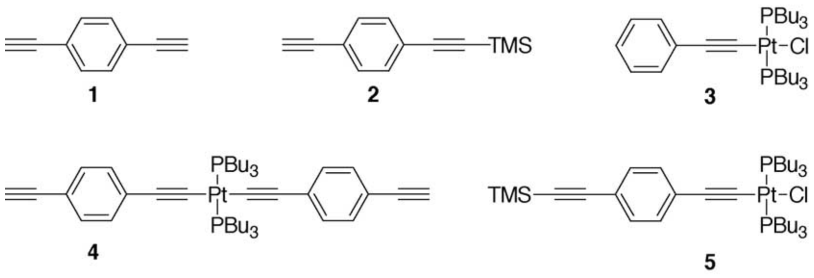


PE-n n = 1- 5, 7

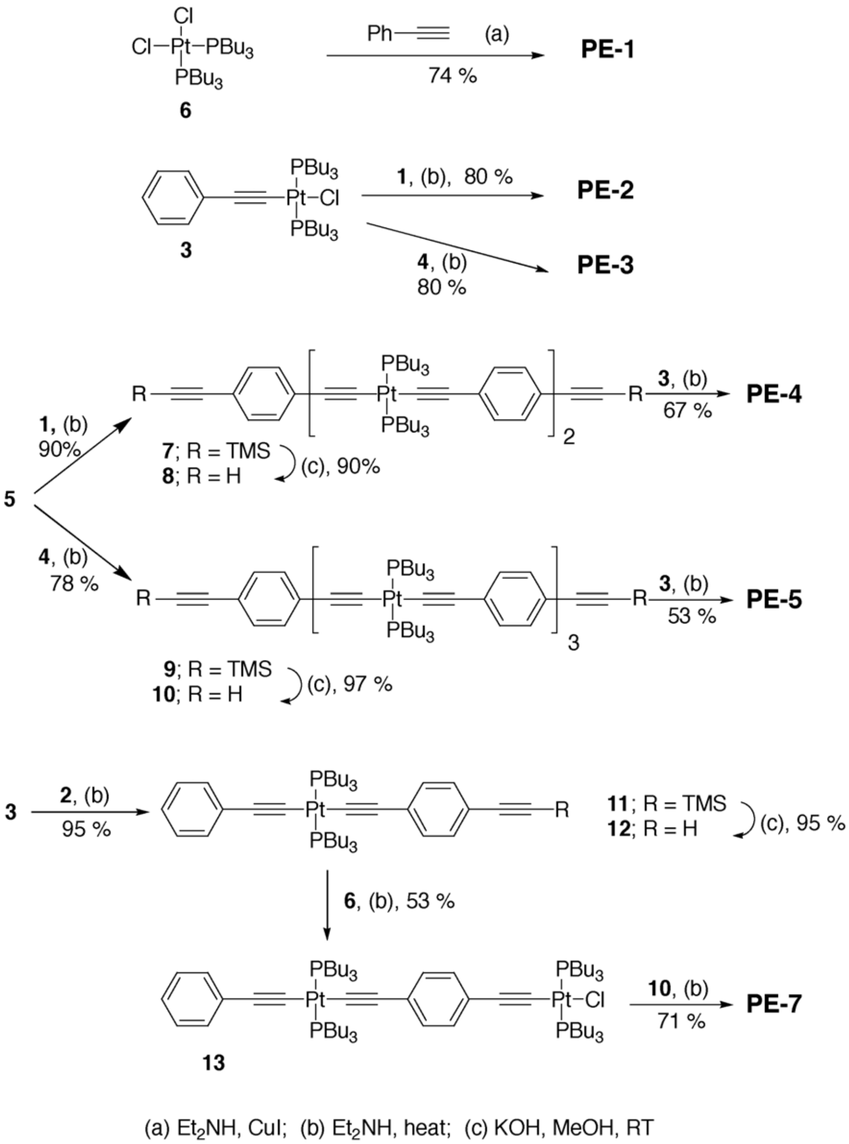
Scheme 1. Structure of PAOs.

Schemes 2 and 3 illustrate the overall synthetic route used to prepare the PAOs. Aryl acetylide building blocks such as **1** and **2** were obtained by Pd(0)-mediated Sonogashira coupling reactions. Trimethylsilyl protected terminal acetylene groups allowed the selective coupling of one side of the molecule with platinum containing building blocks. Oligomers PE-1 to PE-7 were prepared in good yields by the sequential Hagihara coupling of aryl acetylides with *bis*(tributylphosphine)platinum(II) chloride. The reactions were carried out in the presence of an amine base (typically diethylamine) at or slightly above room temperature. Without the presence of catalyst, the major product of these reactions is the mono-substituted platinum acetylide complex, whereas the *bis*-acetylide complex is typically obtained in the presence of a catalytic amount of CuI.

The PAOs were structurally characterized by spectroscopic analyses including ^{31}P NMR. ^{31}P NMR spectra allow us to confirm that the oligomers have the all-*trans* geometry (with respect to the Pt center). Moreover, it is possible to distinguish the phosphines on the terminal and internal Pt units, and therefore by integrating the peaks in the ^{31}P NMR spectrum it is possible to confirm that the ratio of internal to terminal units is consistent with the length of the each oligomer. The length of each oligomer was also confirmed



Scheme 2. Pt-acetylide building blocks.



Scheme 3. Synthesis of PAOs.

by ^{1}H NMR and by time-of-flight mass spectrometry (MS-TOF) by using desorption ionization on silicon mode (DIOS) [35,36].

Photophysical investigations of PE-1 to PE-7 were carried out to explore the effect of oligomer length on the oligomers' excited state properties. Fig. 1a displays the absorption spectra, which are dominated by three absorption bands. The strong band I arises from the long-axis π–π^* transition and its λ_{max} red-shifts continuously as the chain length is increased. However, the shift in λ_{max} becomes negligible between PE-5 and PE-7, indicating that conjugation in the lowest singlet excited state (S_1) is effective through approximately five or six Pt-acetylide repeat units. Photoluminescence spectra of PE-2 to PE-7 (PE-1 is non-emissive at room temperature) were obtained at ambient temperature in vacuum-degassed THF solutions (Fig. 1b). Each of the PAOs exhibits a very weak fluorescence band and a relatively intense phosphorescence band. Note that the fluorescence intensity is magnified 100× as compared to phosphorescence. The small Stokes-shift of the fluorescence band indicates that it arises from S_1. Both absorption and fluorescence maxima red-shift with increasing oligomer length, indicating an increase in the delocalization of singlet excited states in PAOs. On the other hand, the phosphorescence maximum red-shifts by only 2 nm from PE-2 to PE-7, revealing that the triplet excited state is more spatially confined and consequently its energy is not strongly influenced by the chain length. This observation is in good agreement with previous work which investigated the evolution of lowest singlet (S_1) and triplet excited states (T_1) of Pt-acetylides linked through various numbers of thienyl rings. This work suggested that T_1 in Pt-acetylide is considerably less delocalized than S_1 [24].

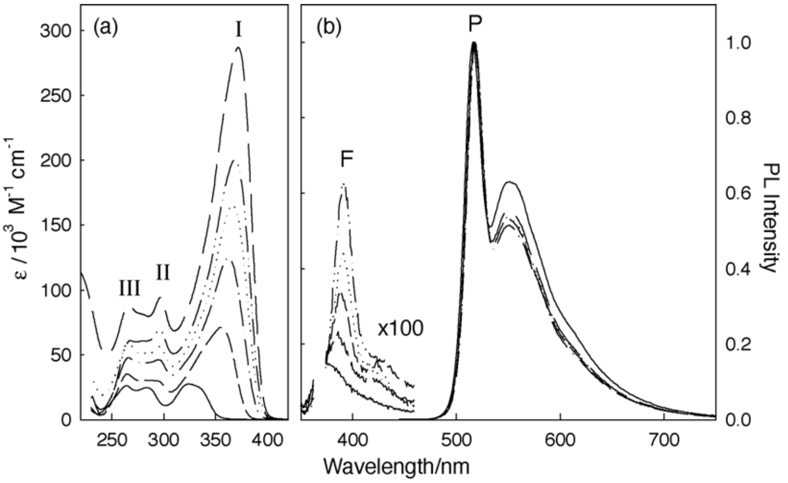


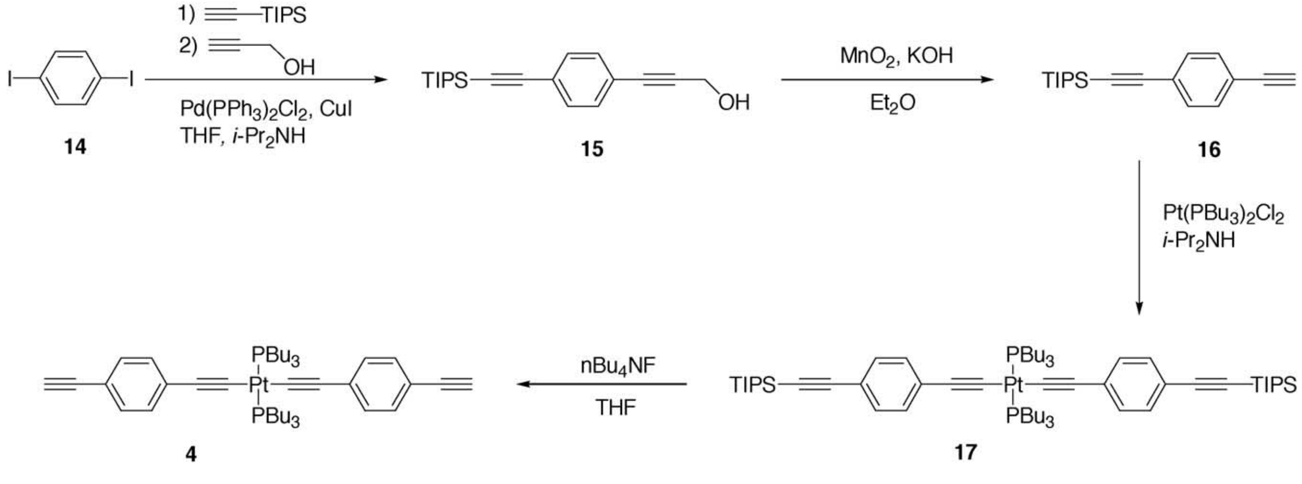
Fig. 1. (a) UV–visible absorption spectra of PAOs in THF in order of increasing intensity: PE-1, PE-2, PE-3, PE-4, PE-5 and PE-7. (b) Photoluminescence spectra in deoxygenated THF. F and P are fluorescence and phosphorescence, respectively, in order of increasing intensity: PE-2, PE-3, PE-4, PE-5 and PE-7. (Figure reprinted with permission of the American Chemical Society).

3. Poly(phenylene ethynylene)-co-(platinum-acetylide) random copolymers

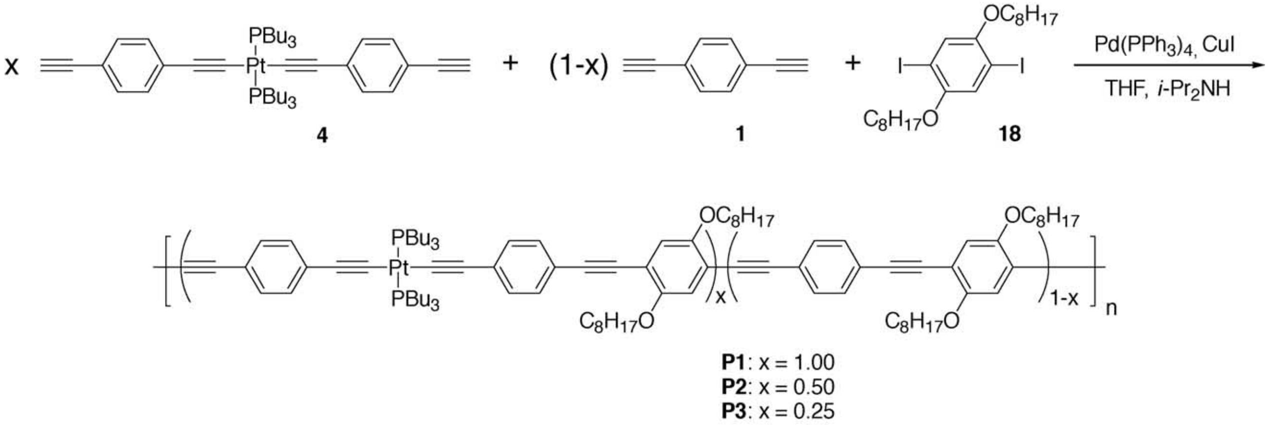
Spin-orbit coupling in Pt-acetylides induced by the Pt(II) center plays an important role in determining the excited state properties of the materials. In particular, the rates of $S_1 \rightarrow T_1$ intersystem crossing and $T_1 \rightarrow S_0$ radiative decay (k_{isc} and k_r, respectively) are significantly enhanced in Pt-acetylides compared to the structurally analogous all-organic poly(phenylene ethynylene) (PPE) materials. Thus, we sought to obtain information regarding how variation of the amount of Pt(II) in a PPE-type polymer would influence the excited state properties. In particular we were interested in exploring how decreasing the content of Pt(II) in the chain would influence the triplet yield and the phosphorescence efficiency.

In order to meet this objective, a series of platinum containing PPE-type polymers was prepared in which the content of Pt-acetylide repeat unit was varied. The synthesis of the copolymers required the preparation of the *bis*-terminal acetylene functionalized platinum acetylide complex **4** (Scheme 4). A one-pot double Sonogashira [37] coupling reaction between 1,4-diiodobenzene and two orthogonally protected acetylenes afforded compound **15**. Deprotection of the hydroxymethyl group afforded **16** which was subsequently reacted with *cis*-*bis*-(tributylphosphine)-dichloroplatinum(II) [38] to afford compound **17**. Removal of the triisopropylsilyl (TIPS) protecting groups with tetrabutylammonium fluoride gave the required Pt-acetylide monomer **4**.

Copolymers P1, P2, and P3 were prepared in AA/BB type polymerization reactions effected by Sonogashira coupling between 2,5-dioctyloxy-1,4-diiodobenzene **18** and the



Scheme 4. Synthesis of monomeric units.



Scheme 5. Synthesis of polymers P1–P3.

bis-terminal acetylene functionalized monomers **4** and 1,4-diethynylbenzene **1** (Scheme 5). Homopolymer P1, which contains a Pt-acetylide moiety in every repeat unit of the polymer chain, was prepared by polymerizing with stochiometric amounts of comonomers **4** and **18**. Copolymer P2, which contains an average of one Pt-acetylide center per two repeat units, was prepared in a polymerization reaction that contained one equivalent of **18** and 0.5 equivalents of **1** and **4**. Finally, to prepare copolymer P3, which contains one Pt-aceylide center per four repeat units, 0.25 equivalents of **4** and 0.75 equivalent of **1** were polymerized with comonomer **18**. The structure of the polymers and loading of the Pt-acetylide repeat units were characterized by using ^{1}H NMR. The ^{1}H chemical shifts of the methylene unit adjacent to phosphorous (e.g., $-CH_2-P$) and the methylene adjacent to oxygen in the alkoxy side chains (e.g., $-CH_2-O-Ar$) are well resolved in the spectra and therefore it is possible to use the relative integrals for these groups to confirm the relative amounts of the comonomers that are present in the polymers. In addition, molecular weight and polydispersity of the polymers were determined by GPC and their physical properties are presented in Table 1.

The absorption and photoluminescence spectra of P1–P3 measured in THF solution are shown in Fig. 2. The absorption spectra feature a strong band that is centered at approximately 410 nm. This absorption is assigned to the long-axis polarized π, π* absorption of the PPE-co-Pt-acetylide conjugated chain. Interestingly, the absorption band is red-shifted in P3

Table 1
Physical properties of polymers P1–P3

Polymer	% of Pt-containing repeat units	Yield (%)	M_n	M_w	PDI (M_w/M_n)
P1	100	75	16300	79605	4.88
P2	50	76	11453	32152	2.81
P3	25	77	140982	281045	1.99

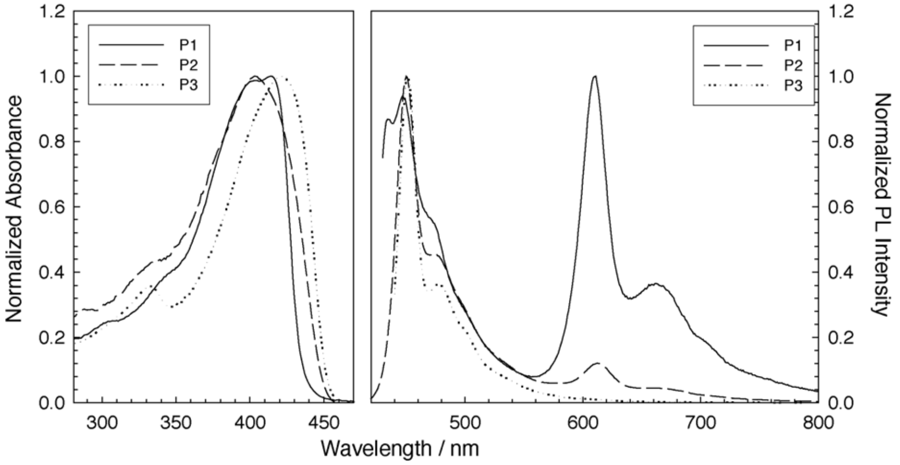


Fig. 2. UV–visible absorption (left) and photoluminescence spectra (right) of polymers P1–P3 in THF solution.

relative to P1 and P2, suggesting that the conjugation length of the polymers increases with decreasing Pt-acetylide content. This finding is consistent with two lines of evidence. First, Godt and co-workers prepared a series of mono-disperse phenylene ethynylene oligomers, and they demonstrated that the conjugation length in this family of conjugated materials is ≥10 phenylene ethynylene repeats [39,40]. Second, in the work described in the above section, we have demonstrated that the conjugation length in Pt-acetylide chains is ≤6 repeat units. Taken together, these findings reveal that in the singlet excited state, conjugation through a Pt-acetylide repeat unit is less than through a structurally analogous phenylene ethynylene chain that does not contain a Pt-acetylide unit. Apparently, the $d\pi/p\pi$ overlap that gives rise to conjugation through the Pt-acetylide center is less effective compared to the $p\pi/p\pi$ overlap along the all-organic segments. The poorer overlap likely arises because of the large mismatch in size and energy between the 5d Pt orbitals and the 2p carbon orbitals.

The photoluminescence (PL) spectra of P1–P3 were obtained in deoxygenated THF solutions and they are shown in the right panel of Fig. 2. Note that there is a significant difference in the PL spectra as the loading of Pt-acetylide in the polymer chain varies. The spectrum of P1 features two emission bands with maxima at 450 and 611 nm which arise, respectively, from the singlet (fluorescence) and the triplet (phosphorescence) excited states. The spectrum of P2 is dominated by the fluorescence ($\lambda_{max} = 447$ nm) and it shows only a small phosphorescence band ($\lambda_{max} = 612$ nm). Finally, P3 exhibits only fluorescence ($\lambda_{max} = 451$ nm) at room temperature; however a PL spectrum of P3 recorded at 80 K (not shown) does show a weak phosphorescence at $\lambda_{max} = 628$ nm. These emission spectra are all independent of the excitation wavelength.

The quantum yields of fluorescence [41] and inter-system crossing (measured by time resolved photo-acoustic spectroscopy [42]) of P1–P3 were also measured, and the results (listed in Table 2) are in good agreement with the expected effects of platinum loading. In particular, several trends are clearly evident in the data. As the Pt-acetylide content in the polymers decreases: (1) the fluorescence quantum efficiency increases; (2) the quantum efficiency for $S_1 \rightarrow T_1$ intersystem crossing decreases; (3) the relative phosphorescence efficiency decreases. All of these effects clearly arise due to the decrease in spin-orbit coupling that occurs as the loading of Pt-acetylide in the polymer decreases. The decrease in $S_1 \rightarrow T_1$ ISC likely arises because k_{isc} decreases; this results in a decreased ISC quantum yield, and an increase in the fluorescence yield.

Despite the fact that the triplet yield decreases with Pt-acetylide content in the PPE chains, the yield nevertheless remains relatively high even in P3 ($\phi = 0.40$), which contains only one Pt-center in every four repeat units. By comparison, the triplet yield in all-organic PPE type polymers is ≤0.10. This indicates that efficient $S_1 \rightarrow T_1$ ISC can be achieved in materials without necessitating a high loading of an expensive platinum complex in the polymer backbone. This idea is important in the context of non-linear optical applications, which rely on the triplet state [16].

4. Triplet energy transfer in platinum acetylide copolymers doped with thiophene

As discussed earlier in this review, we have demonstrated that the triplet exciton in Pt-acetylide chains is spatially localized, even in long oligomers and polymers. This is in contrast to the singlet exciton in the all-organic polymer analog (PPE), which is quite delocalized (as noted above, the singlet is delocalized over ≥10 phenylene ethynylene repeats) [43]. Energy transport in PPEs is known to be rapid and efficient, a property which is believed to be largely due to their extended π-delocalization [44]. As part of the investigation of the photophysical properties of Pt-acetylide materials, we have undertaken to determine if these molecules exhibit efficient triplet energy transport, despite the localized nature of the triplet. In this section of the review we report preliminary results of this investigation.

In order to understand the nature of triplet energy transport in Pt-acetylides, five random copolymers with varying amounts of 2,5-thienylene units in the backbone were synthesized. The thiophene moiety was chosen for this study because its triplet energy is known to be lower than that of the 1,4-phenylene-based repeats in Pt-acetylide chains [27]. The structure of the thiophene-containing copolymers is outlined in Scheme 6. The abbreviated nomenclature adopted for these polymers is P_xT_y, where the subscript x is the percentage of 1,4-phenylene repeat units in the polymer, and the subscript y is the percentage of 2,5-thienylene repeat units. Note that the distribution of thienylene units in these polymers is completely random, as evidenced by the sharp resonances of the thiophene protons in ^{1}H NMR.

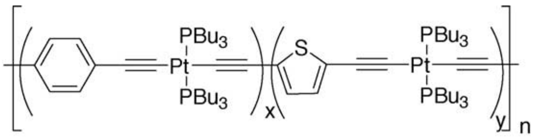
Table 2
Photophysical properties of polymers P1–P3

Polymer	UV–vis	Photoluminescence		Φ_F (%)	Φ_{ISC} (%)	τ_P[a] (μs)
	λ_{max} (nm) (log ε)	λ^F_{max} (nm)	λ^P_{max} (nm)			
P1	414 (4.94)	450	611	1.1	79.5	275
P2	404 (4.87)	447	612	9.5	53.1	340
P3	421 (–)[b]	451	628[c]	16.2	40.3	245

[a] Computed from phosphorescence decay.

[b] Molar absorptivity not determined due to incomplete polymer dissolution.

[c] Emission at 80 K in 2-methyltetrahydrofuran glass.



x = 1, y = 0 $P_{100}T_0$
x = 0.95, y = 0.05 $P_{95}T_5$
x = 0.85, y = 0.15 $P_{85}T_{15}$
x = 0.75, y = 0.25 $P_{75}T_{25}$
x = 0, y = 1 P_0T_{100}

Scheme 6. Structure of platinum-acetylide phenylene thiophene copolymers.

Fig. 3 (left panel) shows the absorption spectra of the series of P_xT_y copolymers. The all-phenylene polymer, $P_{100}T_0$ exhibits an absorbance maximum at 341 nm. As the amount of thiophene in the polymers is increased, the most striking feature is the appearance of a new band at longer wavelength ($\lambda_{max} \approx 398$ nm). Interestingly, the maximum of this band corresponds closely to the absorption maximum of the all-thienylene polymer, P_0T_{100}, and on this basis it is assigned to absorption of the thiophene-containing segments in the copolymers. In accord with this assignment, the relative intensity of the long wavelength absorption band increases with increasing fraction of thienylene units in the copolymers.

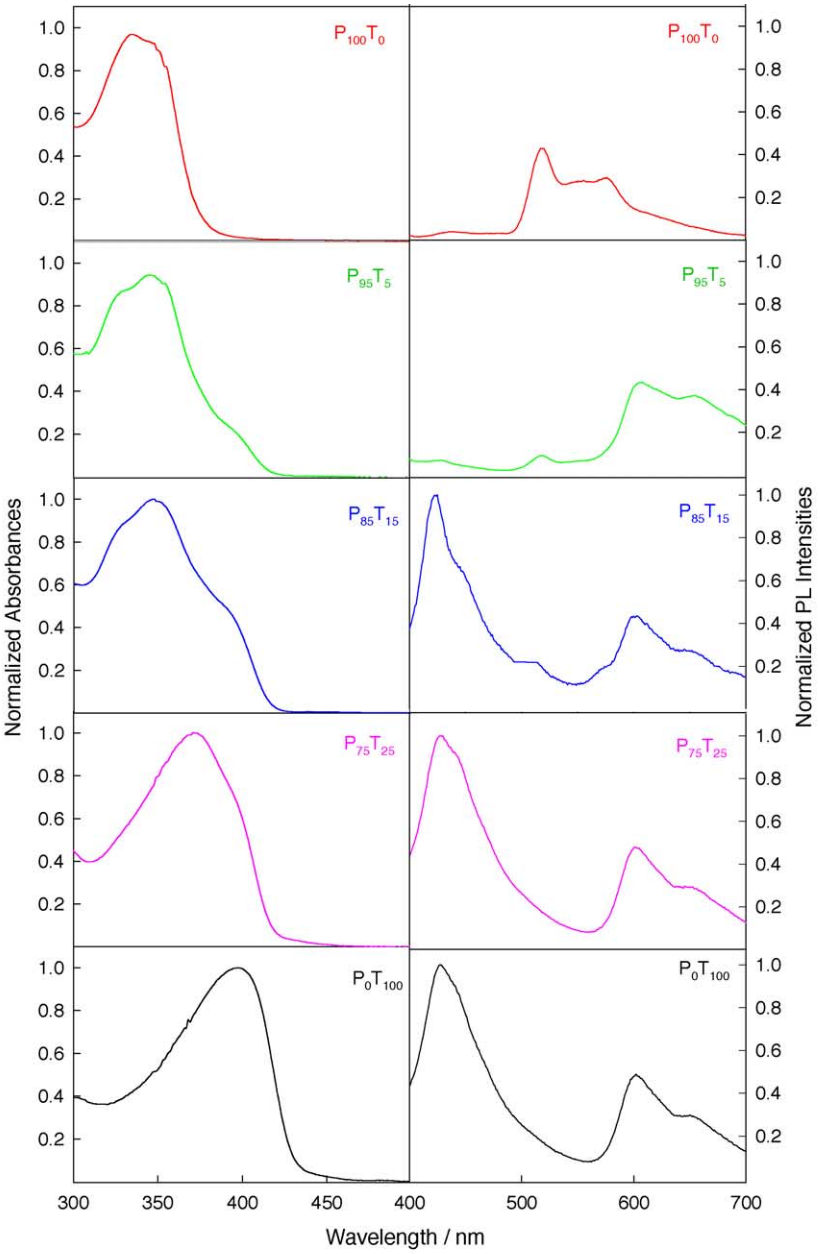


Fig. 3. Left: UV–visible absorption spectra of Pt-acetylide copolymers in THF solution. Right: photoluminescence spectra of Pt-acetylide copolymers in THF solution, excitation wavelength 350 nm.

Close inspection of the short wavelength absorption band which is due to the phenylene repeat units shows that the maximum is nearly constant for $P_{100}T_0$, $P_{95}T_5$ and $P_{85}T_{15}$, but then it is red-shifted significantly in $P_{75}T_{25}$. The red-shift in the phenylene transition is believed to arise due to the effect of adjacent thienylene segments on the absorption of the phenylene containing units. In essence, due to π-delocalization effects, once the loading of the thienylene repeats reaches 25% in the copolymer, there is at least one thienylene unit within every "chromophore" on the polymer chain. This is consistent with the notion that the singlet state is delocalized over more than four repeat units in the Pt-acetylide polymers.

Information concerning the triplet exciton is obtained by investigation of the photoluminescence of the copolymers (Fig. 3, right panel). The all-phenylene polymer, $P_{100}T_0$, only exhibits phosphorescence emission with $\lambda_{max} = 514$ nm. Note that the energy of this emission is in close correspondence with the emission observed from the Pt-acetylide oligomers described above in Section 2, which indicates that it arises from the $[-Pt-C{\equiv}C-C_6H_4-C{\equiv}C-]$ repeat units. The all-thienylene polymer, P_0T_{100}, exhibits fluorescence with $\lambda_{max} = 420$ nm, in addition to a broad phosphorescence band with $\lambda_{max} = 614$ nm. (The assignment of the two emission bands in P_0T_{100} is made on the basis of emission lifetimes.)

From the spectra of the copolymers, $P_{75}T_{25}$, $P_{85}T_{15}$, and $P_{95}T_5$, it is apparent that the phenylene-based phosphorescence ($\lambda_{max} = 514$ nm) is quenched almost entirely, and it is replaced by thienylene-based phosphorescence ($\lambda_{max} = 614$ nm). In fact, no phenylene-based phosphorescence is apparent at thiophene doping levels of 15 and 25% ($P_{85}T_{15}$ and $P_{75}T_{25}$, respectively), although other experiments have indicated that there is in fact a very weak band corresponding to phenylene-based phosphorescence that is obscured by the more intense fluorescence from the thienylene segments. In $P_{95}T_5$, while some phenylene-based phosphorescence is observed, its intensity is <5% of the thiophene-based phosphorescence.

The striking feature with respect to the photoluminescence data is that it indicates that energy transfer from the phenylene segments to the thienylene segments is quite efficient, even when the fraction of thienylene repeats in the chains is low. There are two possible mechanisms, which can be considered to explain the efficient energy transfer to the thienylene traps. In the first (Mechanism A), energy transfer occurs *prior* to intersystem crossing. In this situation, energy transfer would occur via the singlet exciton. This process is expected to be relatively rapid, since the singlet is relatively delocalized, and it may also be able to diffuse rapidly along the chain via dipole–dipole coupling (i.e., Förster transfer) [45].

Mechanism A:

$$\mathrm{P}\cdots\mathrm{T} + h\nu \rightarrow {}^1\mathrm{P}^*\cdots\mathrm{T} \qquad \text{(A1)}$$

$$^1\mathrm{P}^*\cdots\mathrm{T} \rightarrow \mathrm{P}\cdots{}^1\mathrm{T}^* \qquad \text{(A2)}$$

$$\mathrm{P}\cdots{}^1\mathrm{T}^* \rightarrow \mathrm{P}\cdots{}^3\mathrm{T}^* \qquad \text{(A3)}$$

Mechanism B:

$$\mathrm{P}\cdots\mathrm{T} + h\nu \rightarrow {}^1\mathrm{P}^*\cdots\mathrm{T} \qquad \text{(B1)}$$

$$^1\mathrm{P}^*\cdots\mathrm{T} \rightarrow {}^3\mathrm{P}^*\cdots\mathrm{T} \qquad \text{(B2)}$$

$$^3\mathrm{P}^*\cdots\mathrm{T} \rightarrow \mathrm{P}\cdots{}^3\mathrm{T}^* \qquad \text{(B3)}$$

(In these equations P and T represent phenylene and thienylene repeats, respectively.)

The second possible energy transfer pathway (Mechanism B) involves a sequence in which intersystem crossing to afford a triplet exciton localized on a phenylene segment precedes energy transfer. This transfer mechanism is likely to occur on a slower timescale, because of the localized nature of the triplet exciton and due to the fact that intra-chain exciton hopping, which is mediated by exchange interactions, is likely to be relatively slow.

While the available information does not allow us to draw a clear conclusion as to which mechanism dominates, the data suggests that both pathways may be operating. First, evidence that mechanism A is operative is provided by the fact that relatively strong fluorescence is observed from the thienylene units, regardless of excitation wavelength. For example, excitation of $P_{85}T_{15}$ at 350 nm, where absorption is dominated by the phenylene-based repeat units gives rise to the fluorescence from the thiophene-based segments. This observation supports the notion that singlet–singlet energy transfer occurs from the phenylene segment which is initially photoexcited to a nearby thienylene-containing segment.

Although the evidence described above supports energy transfer via Mechanism A, experiments using time resolved emission spectroscopy to monitor the phosphorescence from

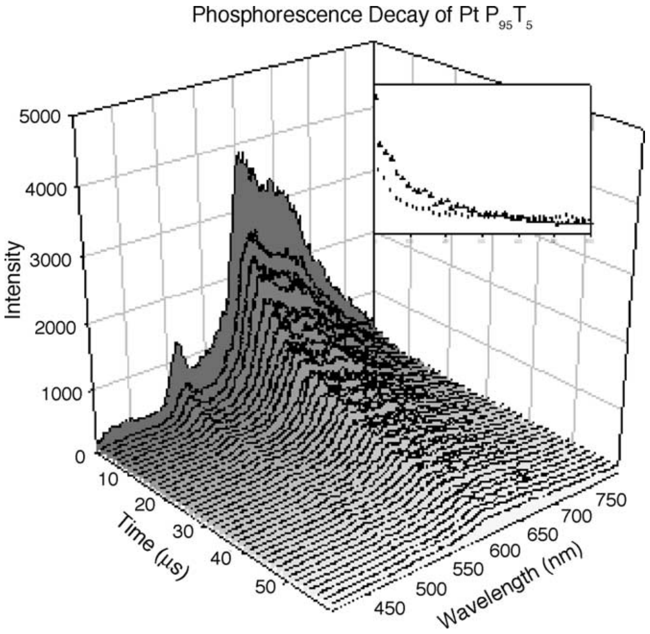


Fig. 4. Time resolved emission spectrum of $P_{95}T_5$ in THF solution at room temperature, excitation wavelength 355 nm. Inset: normalized emission decay at 514 nm (circles) and 605 nm (triangles).

the phenylene and thienylene segments suggest that energy transfer via Mechanism B also occurs on a longer timescale. For example, Fig. 4 shows the time resolved emission of $P_{95}T_5$ at room temperature over the timescale from 0 to 40 μs. At early times following excitation, emission from the phenylene segments is observed at 515 nm along with the thienylene-based emission at 605 nm. The interesting feature is that the higher energy emission from the phenylene segments decays considerably more rapidly (i.e., within 5 μs) than the low energy emission from the thienylene units, which decays over a timescale of ≈30 μs. This observation suggests that energy transfer between the phenylene and thienylene units takes place within the lifetime of the triplet excited state, and that the process competes with phosphorescence. More detailed investigations on the dynamics of intra-chain triplet energy transfer in these copolymers are underway in our laboratory, and the results will be reported in a forthcoming paper.

5. Summary and conclusions

The optical properties of a series of Pt-acetylide oligomers and polymers have been investigated. The materials absorb in the near-UV due to optical transitions having π, π* character. The singlet exciton in the Pt-acetylides is delocalized over several repeat units, however, the triplet state is spatially confined on a chromophore consisting of approximately two [$-Pt-C{\equiv}C-C_6H_4-C{\equiv}C-$] units. The study of co-polymers in which the loading of the Pt-acetylide unit is varied demonstrates that the effect of spin-orbit coupling induced by the Pt-center decreases rapidly as the loading of the metal in the chains decreases. Preliminary investigations which seek to explore the mechanism of intra-chain exciton transfer suggest that the singlet exciton migrates rapidly, whereas the triplet exciton migrates more slowly. The triplet exciton diffuses more slowly due to the fact that it is spatially confined and coupling between the chromophore segments by exchange interactions is comparatively weak.

Acknowledgments

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