Synthesis and Electronic Structure of Platinum-Containing Poly-ynes with Aromatic and Heteroaromatic Rings

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Received August 21, 1997; Revised Manuscript Received November 17, 1997

ABSTRACT: We have studied the dependence of intersystem crossing and the spatial extent of singlet and triplet excitons in platinum-containing poly-yne polymers with the general formula $[Pt(PR_3)_2C{\equiv}CLC{\equiv}C]_n$ (R = Et, ^{n}Bu; L = pyridine, phenylene, or thiophene) as a function of electron delocalization in the spacer group L. We also report the synthesis route of those compounds. The optical absorption, photoluminescence, and photoinduced absorption of the corresponding polymers and monomers have been measured. We find that conjugation is increased but intersystem crossing is reduced by the electron-rich thiophene unit, while the opposite occurs for the electron-deficient pyridine unit as compared to the phenylene unit. For all investigated systems, we find that the singlet excited state and a higher lying T_n triplet excited state extend over more than a repeat unit while the T_1 triplet state remains localized to less then one repeat unit.

1. Introduction

Conjugated polymers such as poly(*p*-pyridine) (PPy), poly(*p*-phenylenevinylene) (PPV), and poly(thiophene) (PT) have attracted much interest for a wide range of applications.[1−6] For a controlled application-aimed synthesis it is necessary to understand how the variation of the chemical structure affects the electronic structure. We have synthesized a series of platinum-containing polymers and monomers where alkynyl units are separated by pyridine, phenylene, or thiophene aromatic ring systems. Figure 1 shows the chemical structure and the synthetic route to the polymers and monomers that have been investigated, together with the abbreviations that are used for them. The triple bonds are abbreviated by T, pyridine rings by P, benzene rings by B, and thiophene rings by Th. Monomers and polymers are differentiated by use of the subscripts 1 and ∞, respectively. This systematic synthetic strategy allows us to compare the effects of the electron-withdrawing ability of the pyridine ring and the electron-donating ability of the thiophene ring with the "neutral" phenylene ring on the optical properties of the reaction products. The inclusion of a heavy metal atom such as platinum in the polymer backbone introduces a strong spin−orbit coupling. This allows us to study optically the triplet excitations which are difficult to measure for hydrocarbon polymers.[7] It also allows the experimental determination of all of the lower energy levels, both triplet and singlet. The results on the phenylene-containing polymer and monomer have already been reported elsewhere[7−12] but are mentioned here for comparison.

In earlier work on $(Pt\text{-}TBT)_\infty$[9,10,13−15] π-conjugation was found to be preserved through the metal atom due to weak hybridization between the π-orbitals of the conjugated ligand, that is the alkynyl groups separated by the aromatic ring, and the platinum 5d orbitals. A stronger hybridization was found between the ligand π^*-orbitals and the platinum 6p-orbitals. However, the heavy metal still forms some barrier to delocalization, so that optical excitations have the character of molecular excited states.

2. Experimental Section

Synthesis. All reactions were performed under an inert nitrogen atmosphere using standard Schlenk techniques. Solvents were freshly distilled, dried, and degassed before use by standard procedures.[16] IR spectra were recorded as dichloromethane solutions, in a NaCl cell, on a Perkin-Elmer 1710 Fourier Transform spectrometer. ^{1}H NMR and ^{31}P spectra were recorded on a Bruker WM-250 spectrometer in appropriate solvents. The chemical shifts were referenced to TMS for ^{1}H NMR and to trimethylphosphite for ^{31}P spectra. Mass spectra were recorded as dichloromethane solutions on a Kratos MS890 spectrometer. Elemental analyses were performed at the Department of Chemistry, University of Cambridge. The metal halides *trans*-$[(Et_3P)_2Pt(Ph)Cl]$ and *trans*-$[(^nBu_3P)_2PtCl_2]$ were prepared by published procedures,[17,18] and 2,5-dibromopyridine, 2,5-dibromothiophene, and the alkyne compounds were obtained from Aldrich and used without further purification. The compound $HC{\equiv}CSiMe_3$ was obtained from the preparation laboratory at the Department of Chemistry. The syntheses of the polymers $(Pt\text{-}TBT)_\infty$ and $(Pt\text{-}TPT)_\infty$ have been reported previously.[8,19]

Preparation of $(Pt\text{-}TThT)_1$. The reaction of the diterminal alkyne $HC{\equiv}C\text{-}2,5\text{-}C_4H_2SC{\equiv}CH$ (1 mmol) (which was prepared in situ by the reaction of $Me_3SiC{\equiv}C\text{-}2,5\text{-}C_4H_2SC{\equiv}CSiMe_3$ with $^nBu_4NF$) with 2 equiv

S0024-9297(97)01267-9 CCC: $15.00

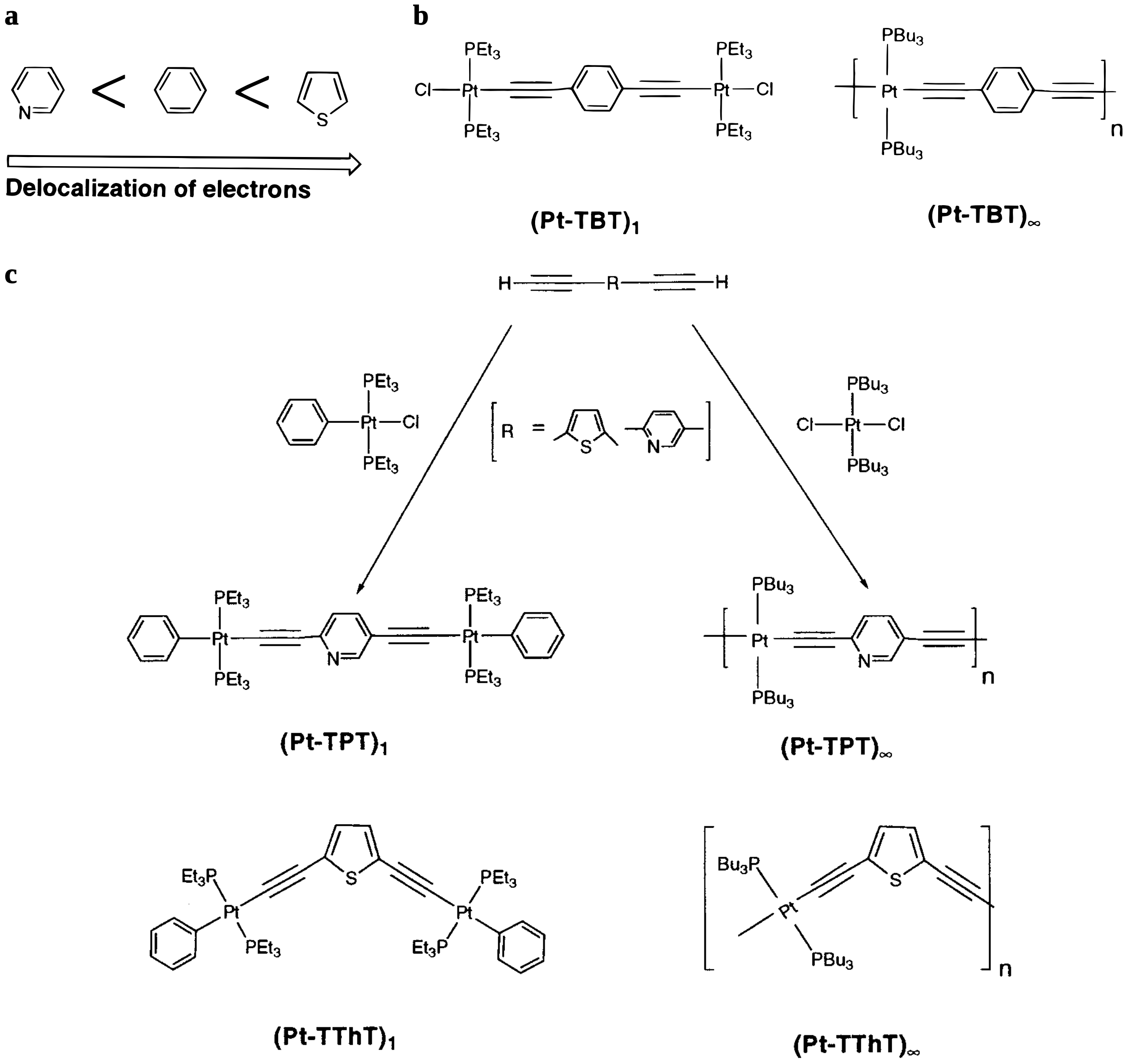

Figure 1. (a) Comparison of π-electron delocalization in the pyridine, phenylene, and thiophene rings. (b) Structural formula of the platinum polymer and monomer with the phenylene ring. (c) Synthesis scheme of the platinum polymers and monomers with the thiophene and pyridine rings.

of *trans*-$[(Et_3P)_2Pt(Ph)Cl]$ (0.10 g, 2 mmol), in the presence of CuI, in CH_2Cl_2/Et_2NH afforded the complex as a light-yellow solid in 65% yield. The product was purified on a silica column using dichloromethane/hexane as eluent. FAB MS: 1146.7 (Calcd M^+ 1146). IR (CH_2Cl_2) ν(C≡C): 2083 cm^{-1}. ^1H NMR ($CDCl_3$, 250 Hz, δ ppm): 1.16 (m, 36H, CH_3), 1.71 (m, 24H, CH_2), 6.78 (t, 2H, C*H*), 6.94 (t, 4H, C*H*), 7.31 (br, 4H, C*H*), 6.60 (s, 2H, C*H*). ^{31}P $\{^1H\}$ NMR ($CDCl_3$, 250 Hz, δ ppm) −131.10 ($^1J_{(Pt-P)}$ = 2677 Hz). Anal. Found: C, 45.71; H, 6.33. Calcd for $C_{44}H_{72}P_4SPt_2$: C, 46.07; H, 6.28.

Preparation of (Pt−TThT)∞. A mixture of *trans*-$[(^nBu_3P)_2PtCl_2]$ (0.2 g, 0.3 mmol) and HC≡C-2,5-C_4H_2-SC≡CH (0.039, 0.3 mmol) in 40 cm^3 of diisopropylamine was allowed to react in the presence of CuI at room temperature for 8 h. The resulting solution was evaporated to dryness. The residue was redissolved in dichloromethane and filtered through a short alumina column. After evaporation of the filtrate a yellow oil was obtained which crystallized after washing with methanol to give a pale-yellow polymer in 87% yield. M_w = 219 937 (n_w = 301) by GPC.[20]; IR (CH_2Cl_2) ν(C≡C): 2088 cm^{-1}. ^1H NMR ($CDCl_3$, 250 Hz, δ ppm): 0.91 (m, 18H, CH_3), 1.40 (m, 12H, CH_2), 1.46 (m, 12H, CH_2), 2.03 (m, 12H, CH_2), 6.57 (s, 2H, C*H*). ^{31}P $\{^1H\}$ NMR ($CDCl_3$, 250 Hz, δ ppm): −137.02 ($^1J_{(Pt-P)}$ = 2383 Hz). Anal. Found: C, 52.66; H, 7.75. Calcd for $C_{32}H_{56}P_2SPt$: C, 52.60; H, 7.60.

Preparation of (Pt−TPT)₁. [PhPt$(PEt_3)_2$C≡C-2,5-C_5H_3NC≡C$(PEt_3)_2$PtPh] was obtained by the reaction of HC≡C-2,5-C_5H_3NC≡CH (0.013 g, 1 mmol) with 2 equiv of *trans*-$[(Et_3P)_2Pt(Ph)Cl]$ (0.109 g), in the presence of CuI, in CH_2Cl_2/Et_2NH. This product was purified on a silica column using dichloromethane/diethyl ether (10:1) as eluent and was obtained as a light-yellow solid in 90% yield. FAB MS: 1142.8 (Calcd M^+ 1141). IR (CH_2Cl_2) ν(C≡C): 2097 cm^{-1}. ^1H NMR ($CDCl_3$, 250 Hz, δ ppm): 1.00 (m, 36H, CH_3), 1.73 (m, 24H, CH_2), 6.76 (t, 2H, C*H*), 6.94 (t, 4H, C*H*), 7.31 (dd, $^3J_{(Pt-H)}$ = 40 Hz, 4H, C*H*), 7.02 (d, 1H, C*H*), 7.33 (d, 1H, C*H*), 8.32 (s, 1H, C*H*). ^{31}P $\{^1H\}$ NMR ($CDCl_3$, 250 Hz, δ ppm): −131.47 ($^1J_{(Pt-P)}$ = 2631.7 Hz). Anal. Found: C, 47.16; H, 6.35. Calcd for $C_{45}H_{73}NP_4Pt_2$: C, 47.32; H, 6.39.

Optical Measurements. Films for optical measurements were spin-coated from dichloromethane solution onto quartz substrates. Optical absorption was measured with a Perkin-Elmer λ-9 spectrometer. Excitation for the photoluminescence (PL) and photoinduced ab-

Table 1. Experimental Values of $S_0 \rightarrow S_1$, $S_0 \rightarrow S_2$, $S_0 \rightarrow S_3$, $S_1 \rightarrow S_0$, $T_1 \rightarrow S_0$, and $T_1 \rightarrow T_n$ Transition Energies, the Energy Difference between the Transition Energies in the Corresponding Monomers and Polymers for the $S_0 \rightarrow S_1$ and $T_1 \rightarrow T_n$ Transitions, the Energy Difference between the $S_1 \rightarrow S_0$ and $T_1 \rightarrow S_0$ Transition Energies, and the Ratio of the Intensities of Singlet Emission to Triplet Emission

energy (eV)	$(Pt\text{-}TThT)_\infty$	$(Pt\text{-}TThT)_1$	$(Pt\text{-}TBT)_\infty$	$(Pt\text{-}TBT)_1$	$(Pt\text{-}TPT)_\infty$	$(Pt\text{-}TPT)_1$
$S_0 \rightarrow S_1$	3.05	3.37	3.26	3.85	3.28	3.56
$S_0 \rightarrow S_2$	4	4.05	4.2	4.35	4.18	4.26
$S_0 \rightarrow S_3$	4.69	4.78	4.6	4.74	4.58	4.66
$S_1 \rightarrow S_0$	2.86	3.11	3.06	3.06	3.2	
$T_1 \rightarrow S_0$	2.06	2.07	2.38	2.39	2.37	2.4
$T_1 \rightarrow T_n$	1.73	2.18	1.48	2.08	1.47	2
$\Delta E_{1,\infty}(S_0 \rightarrow S_1)$	0.32				0.28	
$\Delta E_{1,\infty}(T_1 \rightarrow T_n)$	0.43		0.6		0.53	
$\Delta E_{S_1 \rightarrow S_0, T_1 \rightarrow S_0}$	0.8	1.04	0.68		0.69	0.8
	5 (at 16 K)	0.1 (at 16 K)	80 (at 25 K)		165 (at 18 K)	5 (at 18 K)

sorption (PiA) measurements was provided by the UV lines (334−365 nm) of an Ar^+ laser. To measure transmission (T), the probe beam provided by a monochromated tungsten lamp is mechanically chopped and the signal is detected using a silicon diode connected to a lock-in amplifier. The photoinduced change in transmission (ΔT) of the sample is measured by chopping the pump beam and detecting the resulting modulation of the probe beam transmission as before with the Si diode and the lock-in amplifier. To measure the temperature dependence of PL and PiA, the samples were mounted in a continuous-flow helium cryostat. The temperature was controlled with an Oxford Intelligent Temperature Controller-4 (ITC-4). Photoluminescence spectra were taken either with a monochromator and a Si detector or with a CCD camera coupled to a monochromator. All experiments were conducted under CW illumination.

3. Results

Synthesis. All the platinum-containing poly-ynes have been synthesized by the adaptation of the synthetic route previously reported by Hagihara et al.[21] The reaction products have been characterized by IR and ^1H and ^{31}P NMR spectroscopy, and the molecular weights of the monomeric precursors determined by +FAB mass spectrometry. The molecular weight of the polymer $(Pt\text{-}TThT)_\infty$, which has been determined by gel permeation chromatography, is 219 937 and corresponds to 301 repeat units. All materials are readily soluble in common organic solvents. The spectroscopic data confirm the formulations illustrated in Figure 1 and support the linear "rigid-rod" nature of the $(Pt\text{-}TThT)_\infty$ polymer. The ^1H and ^{31}P NMR data are consistent with those observed for the previously reported platinum-containing poly-yne systems,[7−9] and the $\nu(C{\equiv}C)$ stretching frequency shows little change between the monomeric and polymeric materials.

Optical Absorption. Figure 2 shows the optical absorption spectra of the polymers and corresponding monomers for the thiophene and pyridine materials. The energies of some of the peak positions are summarized in Table 1 including the data of the Pt-TBT system.[7−10] All the materials display three absorption peaks and then a sharp rise with a very weak shoulder at about 5.5 eV. We associate the lowest energy absorption peak with the $S_0 \rightarrow S_1$ transition from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO), which are delocalized π- and π^*-orbitals. In all the polymers the energy of the lowest peak is lowered with respect to that of the corresponding monomer. We therefore associate the first optical transition in the polymers with an electronic excitation that is delocalized over more than one monomer unit.

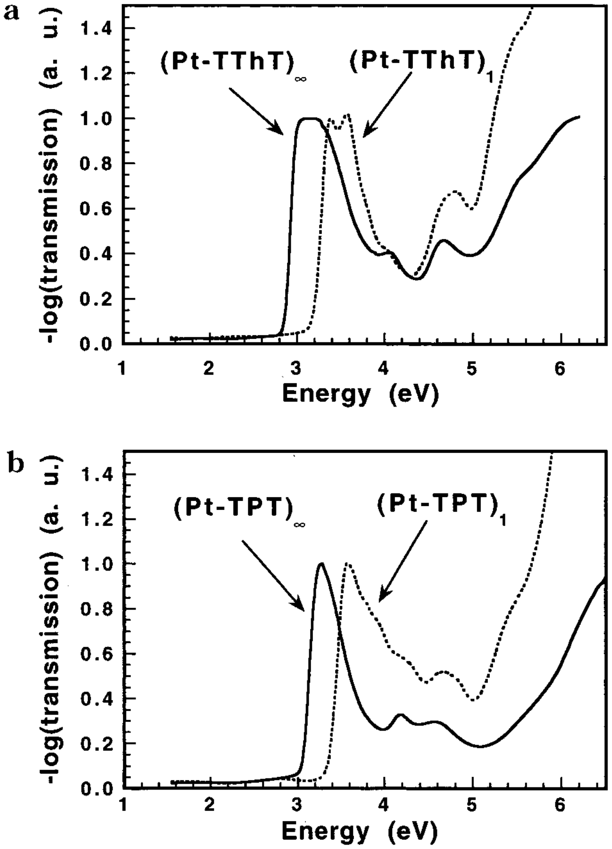

Figure 2. Room-temperature optical absorption spectra of (a) $(Pt\text{-}TThT)_\infty$ and $(Pt\text{-}TThT)_1$ and (b) $(Pt\text{-}TPT)_\infty$ and $(Pt\text{-}TPT)_1$ from a thin solid film.

Quantum chemical calculations have shown that the S_1 singlet state extents over about two repeat units in $(Pt\text{-}TBT)_\infty$.[10] The energy of this first transition follows the order $(Pt\text{-}TThT)_\infty$ < $(Pt\text{-}TBT)_\infty$ < $(Pt\text{-}TPT)_\infty$ (Figure 2). By comparing with the phenylene unit, we conclude that the electron-rich thiophene unit enhances conjugation while the electron-deficient pyridine unit reduces conjugation. The second and third absorption features are affected much less by the chain length. In general, they shift by about 0.08 eV to lower energies. We therefore suggest these excited states to be of a more, but not completely, localized character. The energy difference ΔE between the monomer and the corresponding polymer is lower in the Pt-TThT than in the Pt-TPT (Table 1). This is consistent with a slightly larger extent of the first excited state in the electron-rich Pt-TThT system than in the electron-deficient Pt-TPT system. The phenylene system is not comparable because the monomer $(Pt\text{-}TBT)_1$ shows the energies of the first,

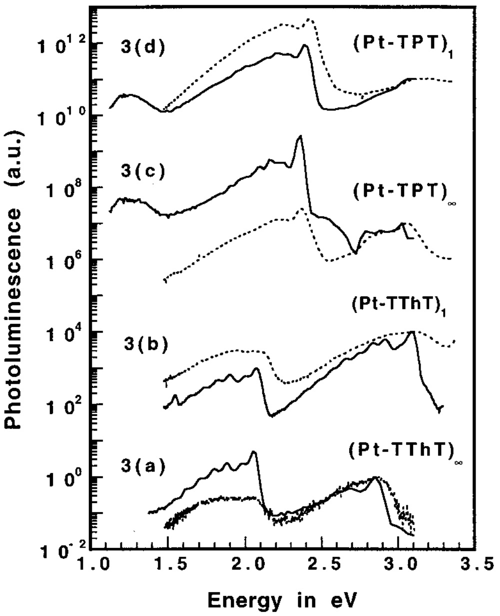

Figure 3. Steady-state photoluminescence spectra of a solid film of (a) (Pt-TThT)$_\infty$, (b) (Pt-TThT)$_1$, (c) (Pt-TPT)$_\infty$, and (d) (Pt-TPT)$_1$. The dotted and the solid lines correspond to room temperature and to 16–18 K, respectively. All spectra are normalized to 1 at the energy of maximum singlet emission. The corresponding plots for different materials are offset for clarity.

second, and third transitions at higher energies than for (Pt-TPT)$_1$. This is due to the lower conjugation length of (Pt-TBT)$_1$ caused by the chlorine atoms at the ends.

Photoluminescence. Figure 3 shows the photoluminescence spectra of the polymers and monomers at room temperature and at 16–18 K. There are two main emission bands, one around 3 eV and the other around 2.0–2.4 eV, which we associate with emission from the S_1 singlet excited state and the T_1 triplet excited state, respectively, in accordance with earlier work on (Pt-TBT)$_\infty$.[7] At room temperature, thermal broadening masks the vibronic structure, and diffusion of the longer-lived triplet excitations (45 μs at 16 K for (Pt-TBT)$_\infty$[7]) to quenching sites reduces the lifetime (to 2 μs at room temperature[26]) and thus the intensity of the triplet emission. We take the peak height ratio from triplet emission to singlet emission at low temperature to indicate the relative efficiency of intersystem crossing and find this increases in the order (Pt-TThT)$_\infty$ < (Pt-TBT)$_\infty$ < (Pt-TPT)$_\infty$ for the polymers (Table 1). According to Wittman et al.,[22] the absolute intersystem crossing efficiency of (Pt-TBT)$_\infty$ is close to 1 at about 16 K. For the monomers, we find the intersystem crossing to be weaker than that for the polymers (see Table 1). In particular for the thiophene monomer (Pt-TThT)$_1$ we find an unusually low efficiency of triplet emission compared to those for the other two monomers and also compared to that for the thiophene polymer (Pt-TThT)$_\infty$. For the pyridine-containing polymer and monomer, there is another weak emission centered at about 1.25 eV. We consider this energy is too low to be reasonable for a singlet d–d transition or charge-transfer transition[23] and speculate whether it might be a triplet d–d transition.

Photoinduced Absorption. On the basis of the extensive optical characterization of Pt-TBT polymer by Wittmann et al.,[7] we assign the peaks displayed in the photoinduced absorption spectra (Figure 4) to the $T_1 \rightarrow T_n$ transition. This transition occurs at about 0.5 eV lower for the polymers than for the monomers (Table 1). The energy of the $T_1 \rightarrow S_0$ transition hardly depends on the chain length (Figure 3). We therefore take this dependence of the $T_1 \rightarrow T_n$ transition energy on the chain length to indicate a triplet T_n state that is delocalized over more than one repeat unit and therefore is significantly more extended than the strongly localized T_1 state. In the spectra for (Pt-TThT)$_\infty$ and (Pt-TPT)$_\infty$ there is an additional shoulder at higher energies which exhibits a different temperature dependence (Figure 4c) and might therefore indicate another electronic transition.

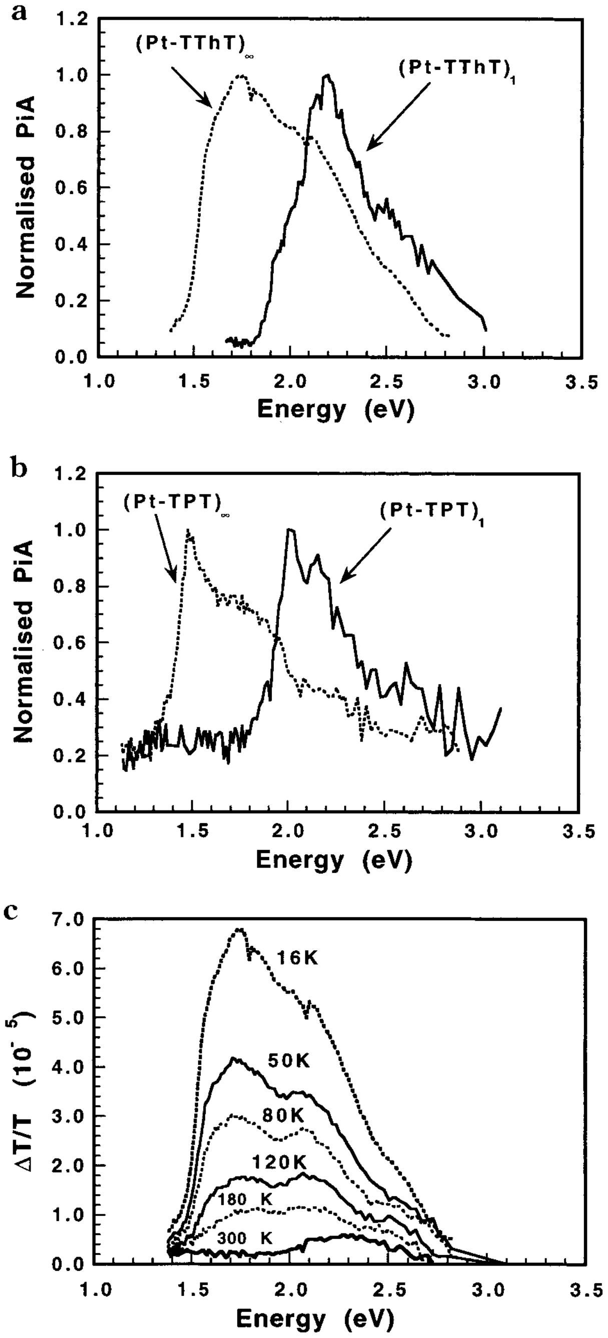

Figure 4. Steady-state photoinduced absorption spectra at 16–18 K from a thin solid film of (a) (Pt-TThT)$_\infty$ and (Pt-TThT)$_1$ and (b) (Pt-TPT)$_\infty$ and (Pt-TPT)$_1$. (c) Temperature dependence of photoinduced absorption peaks at 1.73 and 2.1 eV of (Pt-TThT)$_\infty$.

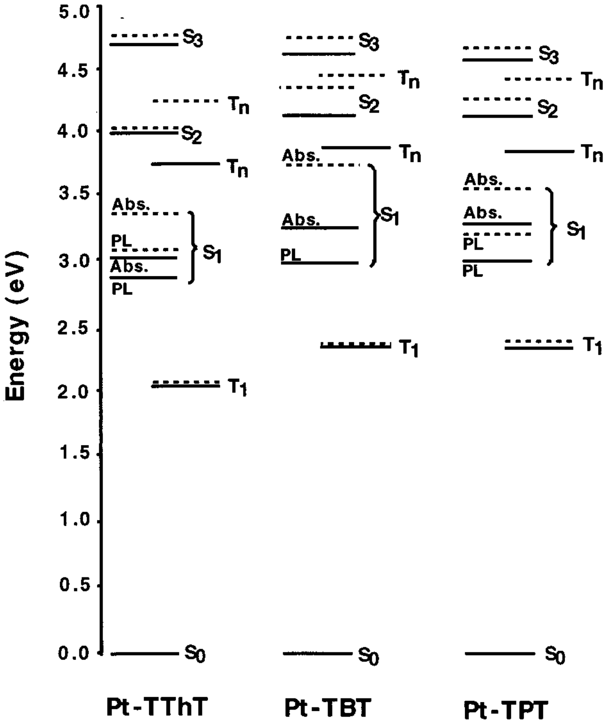

Figure 5. Electronic energy level diagram of Pt-TThT, Pt-TBT, and Pt-TPT. Solid and dashed lines represent polymers and monomers, respectively. The position of the S_1 singlet excited state for the Pt-TBT monomer in PL was not measured because the singlet emission was too weak.

4. Discussion

On the basis of our spectroscopic data we can draw the energy diagram shown in Figure 5 for each of the materials. The energy values shown are absolute values with respect to the S_0 ground state. Monomer and corresponding polymer are shown in the same subdiagram for comparison.

For all three systems, the T_1 triplet state is strongly localized, as can be inferred from the small energy difference between triplet emissions in the monomer and in the polymer. Calculations performed for Pt-TBT have shown the triplet to be confined onto the phenylene ring.[10] Substitution of the ring does not seem to alter this strong confinement. The energy of the S_1 singlet state depends on the nature of the ring and is lowest for the electron-rich thiophene system. However the energy difference ΔE of the S_1 excited state between the respective monomer and polymer varies only by a small amount, indicating a similar extent of the S_1 singlet excited state. The effect of substitution on the triplet states and the intersystem crossing is more complex. In general, we find the intersystem crossing to be larger if the energy difference between singlet and triplet states is lower. For example for the polymers, we find the energy of the S_1 singlet state (and thus the S_1-T_1 energy gap) to be lowered with respect to that of the monomers, and the intersystem crossing rate is higher in the polymers than in the monomers. For the thiophene unit, there are two competing effects. The lowering of the S_1 singlet energy in this polymer is larger than that for the other two systems, but the thiophene unit also lowers the energy of the T_1 excited state by a considerable amount. It thereby increases the energy gap between S_1 singlet and T_1 triplet states and thus reduces the intersystem crossing rate in the thiophene system as compared to those for the other two systems. This reduction of the intersystem crossing rate is particularly drastic for the monomer $(\text{Pt-TThT})_1$.

The strong lowering of the T_n triplet excited state when comparing monomer and corresponding polymer in these systems, that is the dependence of a higher lying triplet state on the polymer chain length, indicates a large delocalization of this state, as previously found for Pt-TBT.[10] We find this strong shift to a different degree for all three rings. It is thus a more general feature of these conjugated systems. This delocalization of the T_n state is at first sight unexpected, because, in a molecular picture, higher lying excitations are usually thought to be more localized, and excitations in these platinum-containing poly-ynes retain a molecular character because of the heavy platinum ion incorporated in the chain. Higher lying electronic excitations on conjugated polymer chains can be extended over several repeat units, as outlined for the case of higher lying singlet excitations in PPV.[24] Obviously the extent or confinement of an excitation depends on the nature of the particular orbitals involved in the respective electronic transition.

5. Conclusion

In this study of the three model aromatic bridging ligands, we have found that the character of the optical excitations remains broadly independent of the particular aromatic ring. For example the T_1 triplet state remains strongly localized, and the T_n triplet state remains strongly delocalized even more than the S_1 singlet state, which also is always delocalized. The efficiency of intersystem crossing is found to be higher for a smaller exchange energy between singlet and triplet, as can be intuitively expected. However the extent of delocalization depends on the particular aromatic ring and is larger for electron-rich groups.

We were able to establish an energy scheme for the lower lying excitation including the triplet states. The extensive spectroscopic characterization of these platinum-containing poly-ynes renders them a suitable model system to probe theoretical calculations. We suggest that the more general features of our results might also apply to conjugated hydrocarbon polymers such as PPV, which are investigated as suitable materials for light-emitting diodes[25] and polymer lasers.[25]

Acknowledgment. We thank D. Beljonne for helpful discussions. Two of us (N.C. and M.Y.) thank the Cambridge Commonwealth Trust for support, and one of us (A.K.) thanks Peterhouse for a research fellowship. We are grateful for the practical assistance of J. A. Stephens.

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MA971267U