Di-, tri-, pseudo-di- and pseudo-tetra-acetylenic polymers of platinum: synthesis, characterization and optical spectra

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Abstract

Reactions of $Me_3Sn-C\equiv C-(C\equiv C-)_m-C\equiv C-SnMe_3$ ($m = 0$, 1) (**1**, **2**), $Me_3Sn-(C\equiv C)_m-p-C_6H_4-(C\equiv C)_m-SnMe_3$ ($m = 1$, 2) (**3**, **4**) with the platinum metal halide complexes, $[Pt(X^nBu_3)_2Cl_2]$ (where X = P (**5**), As (**6**)) afford high molecular weight polymeric species, $\{Pt(X^nBu_3)_2-C\equiv C-(C\equiv C-)_m-C\equiv C\}_n$ (**7–10**), and $\{Pt(P^nBu_3)_2-(C\equiv C)_m-p-C_6H_4-(C\equiv C)_m\}_n$ (**11**, **12**) in excellent yields. Investigations of the optical absorption and photoluminescence spectra of these complexes show extended π-electron conjugation through the metal sites on the chain, with a lower $\pi-\pi^*$ energy gap for triacetylenic than for the diacetylenic polymeric complexes. Well-resolved vibronic structure associated with the $-C\equiv C-$ stretching frequency is observed for both absorption and emission, indicating strong electron-phonon coupling for the di- and triacetylenic polymers.

Introduction

Organometallic polymers in which the transition metal moieties form an integral part of the delocalized π-system of the polyalkyne unit continue to attract much attention. In this regard σ-acetylide complexes of the Group 10 metals, $\{M(P^nBu_3)_2-C\equiv C-(R)_m-C\equiv C\}_n$ (M = Ni, Pd, Pt; R = p-C_6H_4; m = 1, 2), first developed [1] by Hagihara's group, are of great interest owing to their potential applications in the new materials industry. We have recently reported that bis-$SnMe_3$ derivatives of $H-C\equiv C-R-C\equiv C-H$ [R = p-C_6H_4; p-C_6H_4-C_6H_4-p] are versatile precursors of a diverse range of transition metal polyalkyne polymers [2–6]. By this new synthetic route we have now prepared the di-, tri-, pseudo-di- and pseudo-tetra-acetylenic platinum metal-containing polymeric complexes, $\{Pt(X^nBu_3)_2-C\equiv C-(C\equiv C-)_m-C\equiv C\}_n$ (X = P, As; m = 0, 1), and $\{Pt(P^nBu_3)_2-$

$(C\equiv C)_m-p-C_6H_4-(C\equiv C)_m\}_n$ ($m = 1$, 2). Di- and tetra-acetylenic Pt polymers have been obtained previously [7] from the reaction of $[(P^nBu_3)_2Pt(-C\equiv C-C\equiv C-H)_2]$ with $Pt(P^nBu_3)_2Cl_2$, and via oxidative coupling of $[(P^nBu_3)_2Pt(-C\equiv C-C\equiv C-H)_2]$ respectively. The extended metal–polyyne polymers of the tri- and tetra-acetylenes have been suggested [8–10] to be of great importance from studies related to non-linear optical properties of these systems. In this paper we report the synthesis, characterization, and a study of the optical spectra of the platinum-containing di-, tri-, pseudo-di- and pseudo-tetra-acetylenic polymeric complexes. Part of this work has been reported in a preliminary communication [4].
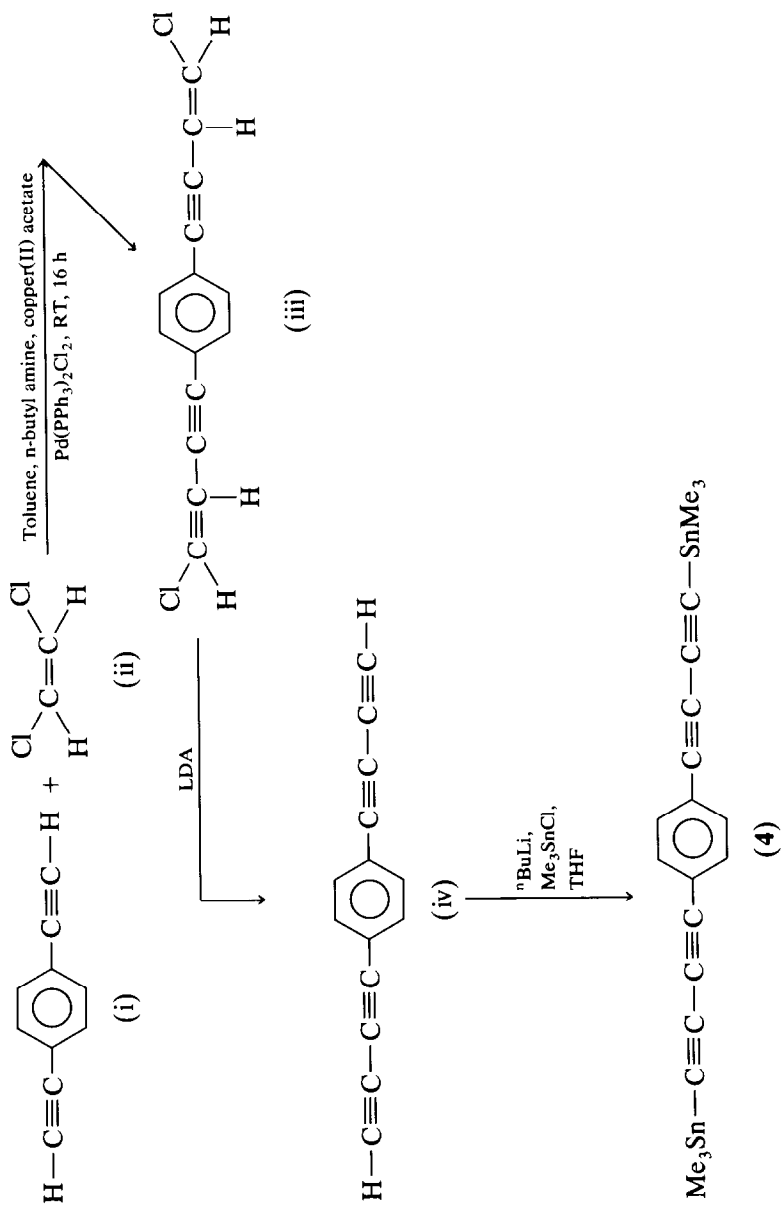
Results and discussion

Synthesis and characterization

Bis-trimethylstannyl alkynylating reagents 1–3 were prepared by modification of published procedures [11–13]. Bis-trimethylstannyl di- and tri-acetylenic compounds (1, 2) are stable solids, which contrasts with the hazardous nature of the corresponding free acetylenes, $H-C\equiv C-(C\equiv C-)_m-C\equiv C-H$ ($m = 0$, 1). The route to the new bis-trimethylstannyl-pseudo-tetracetylene (4) is shown in Scheme 1; it involves coupling of 1,4-bis(ethynyl)benzene with *cis*-1,2-dichloroethylene in the presence of a Pd^{II} catalyst precursor. The chloroenyne thus formed is dehydrohalogenated by lithium diisopropylamide (LDA). This procedure is a modification of the Pd^0-catalysed conversion of terminal acetylenes to chloroenynes followed by dehydrohalogenation with tetra-n-butylammonium fluoride to give off 1,3-diynes [14]. We find that LDA is more effective for the dehydrohalogenation of the chloroenyne compounds. The pseudo-tetrayne is then converted to the corresponding bis-trimethylstannyl derivative by use of butyllithium and trimethylstannyl chloride. Bistrimethylstannyl-pseudo-tetrayne is stable compared with the parent acetylenic compound, and can be stored under nitrogen for long periods without noticeable decomposition. It provides a direct extension of the acetylenic units from the stable benzene-di-ethynyl complex.

A general route to the polymeric species is shown in Scheme 2. In a typical reaction for the preparation of the platinum-containing polyyne polymers, equimolar quantities of $Me_3Sn-C\equiv C-(C\equiv C-)_m-C\equiv C-SnMe_3$ ($m = 0$, 1) (1, 2), or $Me_3Sn-(C\equiv C)_m-p-C_6H_4-(C\equiv C)_m-SnMe_3$ ($m = 1$ (3); $m = 2$ (4)) were treated with $Pt(X-^nBu_3)_2Cl_2$ (X = P (5), As (6)) in the presence of a catalytic amount of CuI in toluene. The crude mixture obtained after evaporation of the solvent was filtered through a column of alumina with dichloromethane as eluant. The product was further purified by repeated precipitations from dichloromethane by methanol. After recrystallization from toluene, polymers 7–12 were obtained as pale to bright yellow solids in very high yields. The conditions required for the polymerization reaction depend on the type of acetylene involved. For di- and tri-acetylenic Pt-polymers, the reaction is complete in 1 h at 30°C, but for the benzeneethynyl derivatives the reaction was carried out at 30–50°C for 12–14 h.

Systematic characterization of these complexes was achieved by analytical and spectroscopic methods (IR, ^1H, ^{13}C, and ^{31}P NMR) and molecular weight determinations. The IR spectrum is dominated by a single intense band ($\nu(C\equiv C)$ stretch) at 1999 cm^{-1} for the diacetylenic complex 7 and at 2096 cm^{-1} for the triacetylenic complex 9. The corresponding peaks for the polymers containing As^nBu_3 as

$H-C\equiv C-H$ +

(i)

(ii)

Cl\C=C/Cl, H, H (structure)

Toluene, n-butyl amine, copper(II) acetate

Pd(PPh$_3$)$_2$Cl$_2$, RT, 16 h

(iii)

LDA

$H-C\equiv C-C\equiv C-H$

(iv)

^{n}BuLi, Me$_3$SnCl, THF

$Me_3Sn-C\equiv C-C\equiv C$ — — $C\equiv C-C\equiv C-SnMe_3$

(4)

Scheme 1

$Me_3Sn-C{\equiv}C-(C{\equiv}C)_m-C{\equiv}C-SnMe_3$
$[m = 0 \ (1); \mathbf{1} \ (2)]$

Toluene, 30°C, 1 h

$Pt(XR_3)_2Cl_2$

$[X = P \ (\mathbf{5});$
$As \ (\mathbf{6}); R = {}^nBu]$

$Me_3Sn-(C{\equiv}C)_m-p\text{-}C_6H_4-(C{\equiv}C)_m-SnMe_3$
$[m = 1 \ (3); \mathbf{2} \ (4)]$

Toluene, 30–50°C, 12–14 h

$+Pt(XR_3)_2+C{\equiv}C-(C{\equiv}C)_m-C{\equiv}O+_n$

$[X = P; m = 0 \ (\mathbf{7});$
$X = As; m = 0 \ (\mathbf{8});$
$X = P; m = 1 \ (\mathbf{9});$
$X = As; m = 1 \ (\mathbf{10})]$

$+(Pt(P^nBu_3)_2+(C{\equiv}C)_m-p\text{-}C_6H_4-(C{\equiv}C)_m+)_n$

$[m = 1 \ (\mathbf{11});$
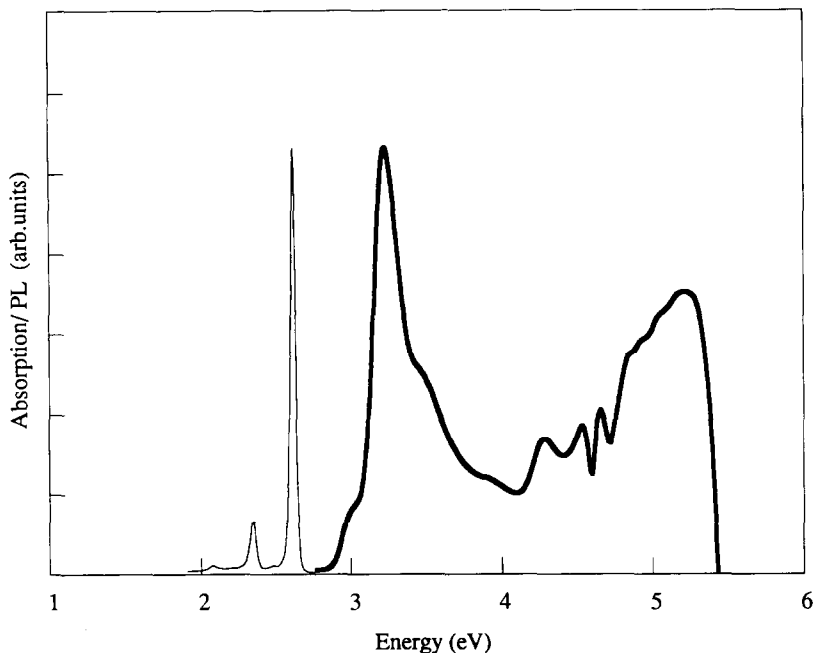$m = 2 \ (\mathbf{12})]$

Scheme 2

Fig. 1. Optical absorption (OA) and photoluminescence (PL) spectra from the diacetylenic polymer. ━━━, OA, diacetylenic, RT; ———— PL, diacetylenic, 28 K.

auxilliary ligands (**8, 10**) are only one or two wavenumbers different from those of their phosphine analogues. The IR spectra of benzeneethynyl polymers (**11, 12**) also contain a single band at 2096 and 2179 cm^{-1} respectively. ^{31}P NMR spectra of these complexes exhibit a single peak at appox. 136 ppm. The spectral data indicate a rigid rod like structure for these complexes. The weight average molecular weights of the polymeric compounds, obtained by gel permeation chromatography (GPC) [15], show a high degree of polymerisation (130000 (n_w = 200) for **7**, 160000 (n_w = 238) for **9** and 210310 (n_w = 277) for **10**, 96000 (n_w = 133) for **11** and 175000 (n_w = 227) for **12**). 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 provides support for the view that there is a high degree of polymerisation in these polymers. Their rigid rod nature has been confirmed by a single crystal X-ray structure of the model compound trans-[Pt(PMe$_2$Ph)$_2$(C≡C-C≡CPh)$_2$ [16].

Absorption and photoluminescence spectra

Optical absorption (OA) and photoluminescence (PL) spectra for the polymers **7, 9, 11** and **12** are shown in Figs. 1–4 with the corresponding data given in Table 1. The spectra show a number of general trends and features; there are strong absorption and luminescence peaks that we ascribe to the π–π^* transitions associated with the acetylenic portions of the chain.

Earlier work [17,18] on the pseudo-diacetylenic polymer **11** and the corresponding oligomer showed that delocalisation does extend over the transition metal
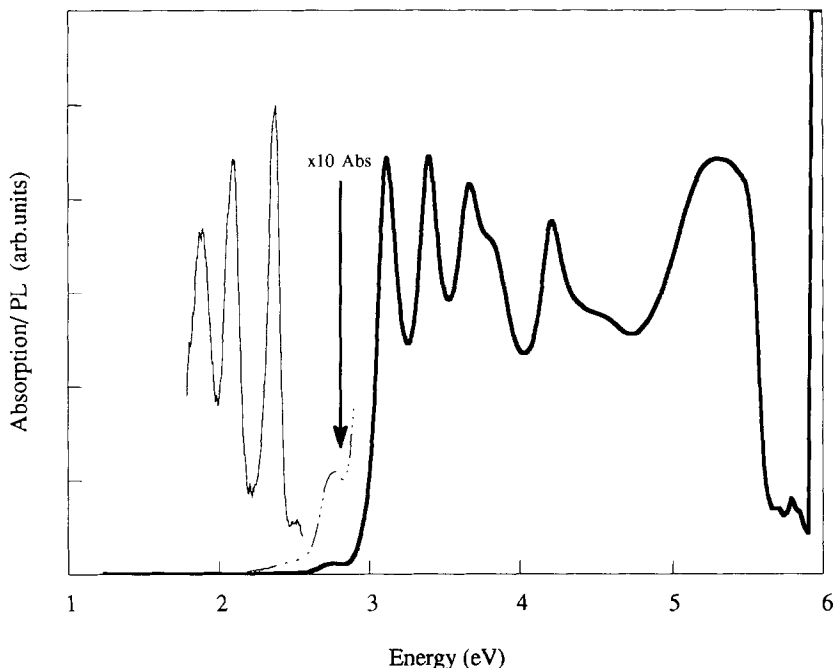
Fig. 2. Optical absorption (OA) and photoluminescence (PL) spectra from the triacetylenic polymer. ——, OA, tri, RT; ———, PL, tri, 21 K; — · · · —, OA×10.

moieties and thus the Pt sites do not hinder the conjugation. Comparison of the oligomer/polymer shift for the di- and tri-acetylenic materials proved more difficult as the monomers readily polymerise in solution. However, the lowest energy absorption bands in these two materials are sufficiently close to those in the pseudo-diacetylenic polymer, where delocalisation is known to occur, to assume that here too, $p\pi$(carbon)-$d\pi$(Pt) hybridisation does occur.

The spectra show a number of very strong features with much smaller peaks often poorly resolved from neighbouring intense bands. We have used simple curve fitting (assuming ideal Gaussian peaks), and derivative calculations to try to determine the precise energy of the low intensity features, but the constraints of these techniques and the low intensity data themselves can provide only limited accuracy. We believe that further work involving Raman spectroscopy and electron-absorption will provide more information for a later, more detailed analysis.

One of the particular advantages of working with the poly-yne spacers between the metal sites (in distinction from earlier work [17] on more complicated spacers such as $-C\equiv C-C_6H_4-C\equiv C-$, in the pseudo-diacetylenic polymer 11) is that the vibrational spectrum of the chain is particularly simple, with a single vibrational mode coupling to the bond dimerisation amplitude; this is the $-C\equiv C-$ stretching frequency at around 2250 cm^{-1} ($= 0.27$ eV) [19]. This accounts for the well-resolved structure in the absorption spectra (more clearly resolved for the tri-acetylenic materials), which is a result of transitions from ground to excited
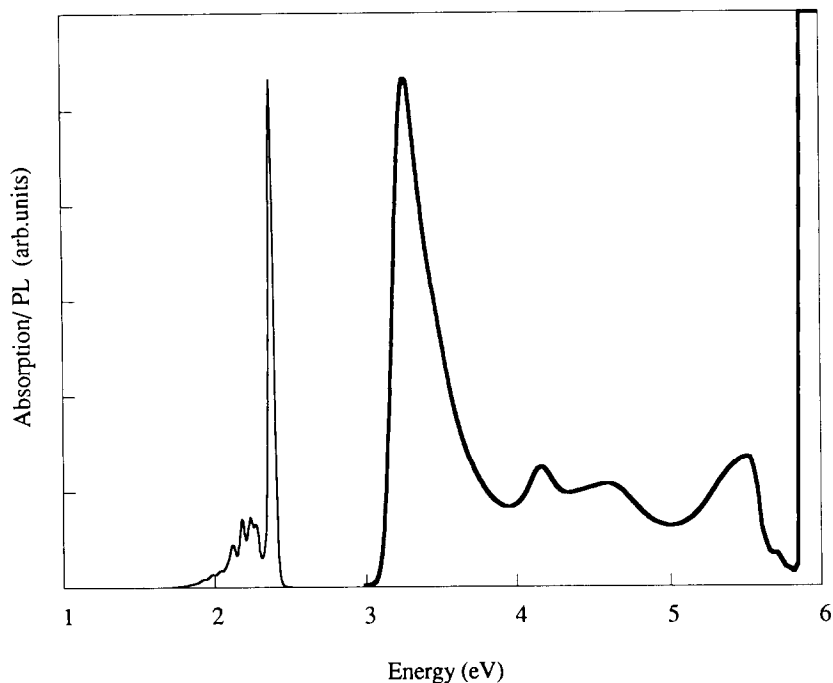
Fig. 3. Optical absorption (OA) and photoluminescence (PL) spectra from the pseudo-di-acetylenic polymer. ━━━, OA, psuedo-di, RT; ────, PL, psuedo-di, 30 K.

electronic state coupled with transitions to the various vibronic levels of the excited state. As seen in Figs. 1–4 and listed in Table 1, many of the energy spacings for all materials studied here are close to 0.27 eV.

All the spectra show strong peaks (at low energy in the OA and high energy in the PL data) which would usually be attributed to ground state transitions, not involving vibrational quanta. The peak energies and the shifts between corresponding peaks in the OA and PL spectra are listed in Table 1. The strongest minimum energy peak is lower for the tri-acetylenic polymer 9 (3.12 eV) than for the diacetylenic polymer (7) (3.23 eV). Similarly, the peak is at lower energy in the pseudo-tetraacetylenic polymer 12 (3.13 eV) than in the pseudo-diacetylenic polymer 11 (3.26 eV). This provides direct evidence for the role of the length and structure of the organic moiety in determining the energy gap for the polymer. In each class of polymer, the longer organic sections provide a smaller energy gap and increase the degree of conjugation and the addition of a phenyl group to the chain lowers the degree of conjugation, as observed in the differences between the di-acetylenic and pseudo-di-acetylenic polymers (3.23 and 3.26 eV respectively).

The Stokes shift between the first strong peaks in the OA and PL data is also listed in Table 1. The shift is much greater for the pseudo-di and pseudo-tetra-acetylenic polymers than for the simpler acetylenic versions and in both cases the shift increases with the length of the organic section of the chain. Thus, it appears that the degree of distortion in the excited states is higher for longer organic segments and is also higher in the phenylcontaining polymers. Excitation to a quinoid type of structure may be possible in the pseudo-di and tetra-acetylenic
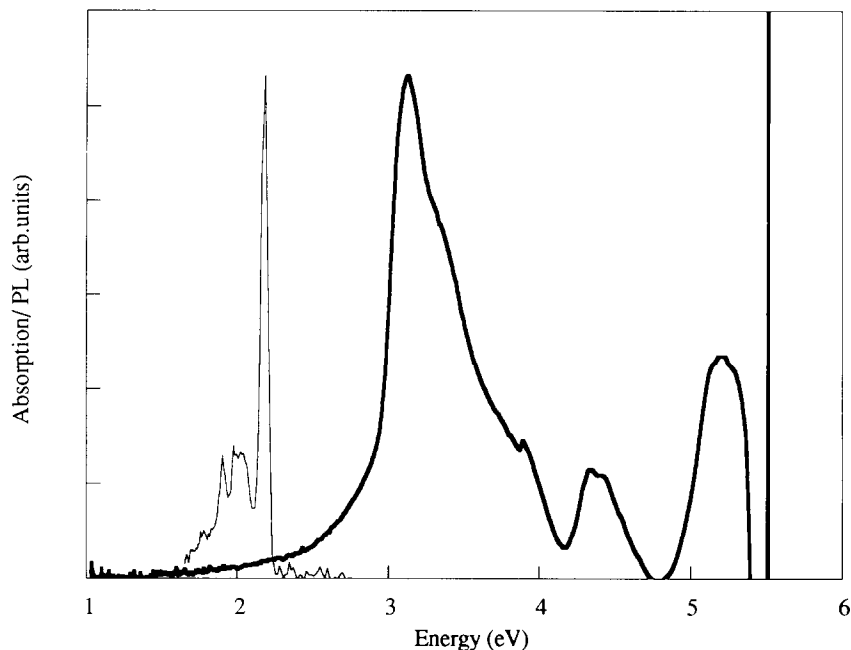
Fig. 4. Optical absorption (OA) and photoluminescence (PL) spectra from the pseudo-tetra-acetylenic polymer. ━━━, OA, pseudo-tetra, RT; ────, PL, pseudo-tetra, 20 K.

polymers and the distortion could also involve some twisting out of the plane by the phenyl group. However, it is clear from the spectra that a straightforward interpretation of the energy gap between the main OA and PL peaks could be misleading as the OA spectra for all the polymers (except the pseudo-tetra) and the PL spectra for the di- and tri-acetylenic versions show one or more weak peaks below the strong absorptions.

The strong vibronic coupling to the electronic transitions, both in absorption and emission, indicates that there is likely to be strong coupling between the π-electron system and the carbon–carbon bond dimerisation amplitude. We infer from this that the dimerisation amplitude for the excited state is weaker than that for the ground state (butatrienic, $C=C=C=C$, or hexapentaenic, $C=C=C=C=C=C$).

PL measurements probe transitions from the lowest vibrational level of the excited state to different vibrational levels of the ground state; we expect that the excited states of the π-electron system will be excitons, and that these will be

Table 1
Principal peaks from optical absorption (OA) and photoluminescence (PL) spectra and corresponding Stoke's shifts

Polymer	OA (eV)	PL (eV)	Shift (eV)
Di-acetylenic	3.23	2.62	0.61
Tri-acetylenic	3.12	2.38	0.74
Pseudo-diacetylenic	3.26	2.39	0.87
Pseudo-tetraacetylenic	3.13	2.18	0.95

localised, probably to within no more than one or two repeat units of the chain, and we can expect to see radiative decay of excitons. The measured PL spectra are characteristic of the decay of such excited states, and we see well resolved bands corresponding to the different levels of the vibrational modes of the ground electronic state; we find again that the energy separation of many of the PL bands is close to 0.27 eV.

The general form of the spectra, and particularly the PL data, show similarities within the two classes of polymers. The PL spectra from the di- and triacetylenic polymers (Figs. 1 and 2) have three strong features, all separated by ∼ 0.27 eV (*i.e.* the C≡C stretching frequency). The PL data from the di-acetylenic material is particularly clear; in addition to the three strong features there are weak shoulders ∼ 0.03 eV below the main peaks and two weak peaks exactly midway between them. The C≡C frequency is thus seen repeatedly in this spectrum. Data from the tri-acetylenic material in PL is less sharp, but the 0.27 eV spacing of the main features is still observed.

Another similarity is shown in the PL spectra from the pseudo-di- and tetra-acetylenic materials (Figs. 3 and 4); these have a virtually identical form but with the tetra-acetylenic version shifted down in energy by ∼ 0.2 eV. There are three small peaks to the left of the main peak (centred at 2.12, 2.19 and 2.25 in di- and at 1.90, 1.98 and 2.04 in tetra-) which have very similar forms in both polymers. The main peak and the lowest energy peak in the PL spectra are separated by 0.27 eV; the spacings of the remaining two peaks indicate lower energy vibrational quanta associated with vibrations of the phenyl group. The OA spectra from the pseudo-acetylenic polymers also show similar forms but the match is not as exact as in the PL data.
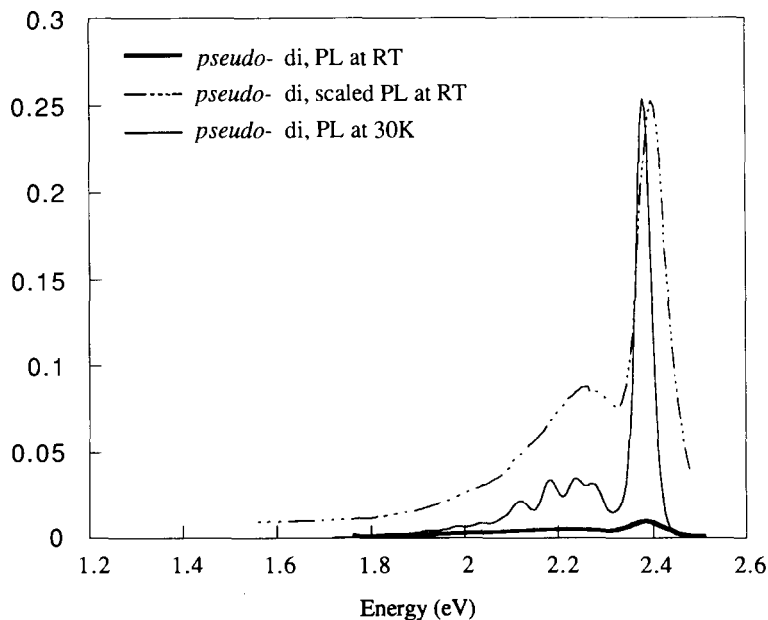

Fig. 5. Temperature dependence of photoluminescence (PL) for the pseudo-di-acetylenic polymer.

The PL spectra were all recorded at low temperature in order to improve the signal and showed a strong increase in intensity with decreasing temperature as illustrated in Fig. 5. In an initial study of the temperature dependence of the spectrum from the pseudo-di-acetylenic polymer (Fig. 5) we found that the relative intensities of the main peak and the lower energy peaks varied from $\sim 2:1$ at room temperature to $\sim 5:1$ at 13 K. The main peak was found to be long lived (of the order of microseconds), indicating that it results from a forbidden transition, possibly involving a triplet state. We note that the large spin–orbit coupling in high atomic number metals such as Pt will facilitate the singlet–triplet conversion and may differentiate this class of polymers from simpler hydrocarbon conjugated polymers. Further work is currently in progress.

Experimental

General

NMR spectra were recorded on a Bruker AM-400 spectrometer. ^{31}P NMR spectra were referenced to external trimethylphosphite and the ^{1}H and ^{13}C NMR spectra were referenced to solvent resonances. The IR spectra were recorded on a Perkin Elmer-1710 Fourier Transform spectrometer. The molecular weights were determined by GPC [15].

Absorption and photoluminescence spectra

Optical absorption spectra were obtained for dilute solutions in dichloromethane. Photoluminescence (PL), measurements were performed on thin films of the polymers which were spin-coated onto spectrosil substrates from solutions in toluene. Excitation was provided by the quadrupled output (266 nm) from a Q-switched Nd:YAG laser, and measurements were made at low temperatures (< 30 K) in order to maximise the intensity and sharpness of the PL features.

Synthesis

The platinum metal dihalide complexes Pt(P^{n}Bu$_3$)$_2$Cl$_2$ (5) and Pt(As^{n}Bu$_3$)$_2$Cl$_2$ (6) were prepared by literature methods [20–21].

$Me_3Sn-C{\equiv}C-C{\equiv}C-$p-$C_6H_4-C{\equiv}C-C{\equiv}C-SnMe_3$ (4). To a solution of bis(ethynyl)benzene (i) (1.26 g, 0.01 mol) in toluene (60 ml), n-butylamine (7.3 g, 0.1 mol), cis-1,2-dichloroethylene (ii) (4.85 g, 0.05 mol), copper(II) acetate (0.545 g, 0.003 mol) and dichloroditriphenylphosphinepalladium (0.701 g, 0.001 mol) were added. The mixture was stirred at room temperature for 16 h, and the solvent was then removed in vacuo. The residue was washed with a minimum of hexane and the catalyst and salts were filtered off by suction. The hexane was removed in vacuo, and the crude product purified on an alumina column using a benzene/hexane (1:1) mixture as an eluant. Bis(1-chloro-but-2-ene-3-yne-yl)benzene (iii) was obtained as a pale yellow solid in 70% yield (1.73 g). To diethylether (50 ml) was added diisopropylamine (4.32 ml, 0.031 mol), the solution mixture was cooled to −40°C in an acetone/dry ice bath, and n-butyllithium (12.4 ml, 2.5 M, 0.031 mol) in hexane was added. The mixture was stirred for 0.5 h to allow the complete formation of LDA and then cooled to −80°C in an acetone/liquid nitrogen bath. Compound (iii) (1.73 g, 0.007 mol) in diethylether (10 ml) was added and the stirred solution allowed to warm to room temperature over a period of 4.5 h. The

reaction was quenched with a cool degassed saturated ammonium chloride solution. The crude product was collected in diethyl ether and washed with ammonium chloride solution. The ether phase was dried over anhydrous magnesium sulphate and the solvent removed *in vacuo* at ice–salt bath temperature. The residue was dissolved in THF (60 ml), cooled to $-80°C$ and n-butyllithium (10 ml, 2.5 M, 0.025 mol) was added. The mixture was stirred for 1 h and a solution of Me_3SnCl (7g, 0.035 mol) in THF (25 ml) was added dropwise. The mixture was warmed to room temperature and stirred for 4 h. THF was removed *in vacuo* and the product taken in hexane (50 ml) and filtered. The hexane solution was cooled to $-80°C$ and bis(trimethylstannylbutadiynyl)benzene (**4**) was obtained as an off-white solid in 70% yield (2.5 g). Anal. Found C, 48.54%, H, 4.46%. Calc. for $C_{20}H_{22}Sn_2$: C, 48.08%; H, 4.40%. Mass spectrum: m/z 499. ^1H NMR (CD_2Cl_2, 400 MHz): 0.30, 7.37, 7.40. ^{13}C NMR (CD_2Cl_2, 100 MHz): -7.63, 73.5, 90.9, 94.2, 122.3, 132.5.

The polymeric complexes (**7–10**) were prepared by the general synthetic procedure outlined for $[-Pt(P^nBu_3)_2-C\equiv C-C\equiv C]_n$ (**7**): to a stirred solution of $Pt(P^nBu_3)_2Cl_2$ (**5**) (0.335g, 0.5 mmol) and bis-$SnMe_3$ acetylide (**1**) (0.188g, 0.5 mmol) in toluene (30 ml) under nitrogen was added a catalytic amount ($\sim$ 3 mg) of CuI. The yellow solution was stirred at 30°C for 1 h and toluene was then removed *in vacuo*. The residue was dissolved in dichloromethane and the solution passed through a short alumina column. The solvent was removed *in vacuo* and the yellow product was further purified by repeated precipitations from a solution in 1:50 mixture of dichloromethane and methanol. After crystallisation from toluene at approx. $-40°C$, compound **7** was obtained in 92% yield (0.3 g) as a pale yellow solid.

$[Pt(P^nBu_3)_2C\equiv C-C\equiv C]_n$ (7). Anal. Found: C, 51.89%; H, 8.47%; P, 9.47%. Calc. for $C_{28}H_{54}P_2Pt$: C, 51.92%; H, 8.40%; P, 9.56%. M_w: 130000; ($n_w = 200$). IR (CH_2Cl_2): $\nu(C\equiv C)$ 1999 cm^{-1}. $^{31}P\{^1H\}$ (CD_2Cl_2, 162 MHz): δ -136.6 ($J(Pt–P) = 2381$ Hz); ^1H (CD_2Cl_2, 400 MHz) δ 0.92, 1.44, 1.51, 2.01.

$[Pt(As^nBu_3)_2-C\equiv C-C\equiv C]_n$ (8). Yellow solid, 89% yield. Anal. Found: C, 45.47%; H, 7.37%. Calc. for $C_{28}H_{54}As_2Pt$: C, 45.66%; H, 7.34%. IR (CH_2Cl_2): $\nu(C\equiv C)$ 1998 cm^{-1}.

$[Pt(P^nBu_3)_2-C\equiv C-C\equiv C-C\equiv C]_n$ (9). Yellow solid, 90% yield. Anal. Found: C, 52.78%, H, 8.12%. Calc. for $C_{30}H_{54}P_2Pt$: C, 53.63%; H, 8.10%. M_w: 160000 ($n_w = 238$). IR (CH_2Cl_2): $\nu(C\equiv C)$ 2096 cm^{-1}. $^{31}P\{^1H\}$ (CD_2Cl_2, 162 MHz): δ -136.3 ($J(Pt–P) = 2300$ Hz); $^{13}C\{^1H\}$ (CD_2Cl_2, 100 MHz) δ 13.8, 24.1, 24.5, 26.5, 59.5, 81.5, 89.4; ^1H (CD_2Cl_2, 400 MHz) δ 0.93, 1.43, 1.51, 2.00.

$[Pt(As^nBu_3)_2-C\equiv C-C\equiv C-C\equiv C]_n$ (10). Bright yellow solid, 88% yield. Anal. Found: C, 46.98%, H, 7.14%. Calc. for $C_{30}H_{54}As_2Pt$: C, 47.41%; H, 7.16%. M_w: 210310 ($n_w = 277$). IR (CH_2Cl_2): $\nu(C\equiv C)$ 2094 cm^{-1}.

Polymers **11–12** were prepared by a similar procedure as described above for **7–10** except that the reaction was carried out at 50°C (**11**) and 30°C (**12**) for 12–14 h.

$[Pt(P^nBu_3)_2-C\equiv C-p-C_6H_4-p-C\equiv C]_n$ (11). Pale yellow solid, 95% yield. Anal. Found: C, 56.62%; H, 8.27%; P, 8.38%. Calc. for $C_{34}H_{58}P_2Pt$: C, 56.42%; H, 8.08%; P, 8.56%. M_w: 96,000; ($n_w = 133$). IR (CH_2Cl_2): $\nu(C\equiv C)$ 2095 cm^{-1}. $^{31}P\{^1H\}$ (CD_2Cl_2, 162 MHz) δ -136.5 ($J(Pt–P) = 2385$ Hz).

$[Pt(P^nBu_3)_2-C\equiv C-C\equiv C-p-C_6H_4-p-C_6H_4-p-C\equiv C-C\equiv C]_n$ (12). Yellow solid,

90% yield. Anal. Found: C, 60.68%; H, 7.59%; P, 8.12%. Calc. for $C_{38}H_{58}P_2Pt$: C, 59.16%; H, 7.52%; P, 8.03%. M_w: 175000 ($n_w = 227$). IR (CH_2Cl_2): $\nu(C\equiv C)$ 2179 cm^{-1}. $^{31}P\{^1H\}$ (CD_2Cl_2, 162 MHz) δ -136.0 ($J(Pt–P) = 2295$ Hz); ^1H (CD_2Cl_2, 400 MHz) δ 0.92, 1.39, 1.57, 2.01, 7.20.

Acknowledgements

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