

Synthesis, characterisation and electronic properties of a series of platinum(II) poly-yne containing novel thienyl-pyridine linker groups

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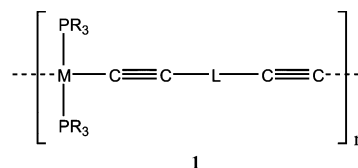
The synthesis and characterisation of a series of novel poly-yne polymers, $trans\text{-}[(P^nBu_3)_2Pt(C\equiv C-L-C\equiv C)]_n$ ($L = 2\text{-}(2'\text{-thienyl})\text{-pyridine (L1)}$, $2,5\text{-bis}(2'\text{-thienyl})\text{pyridine (L2)}$, $6,6'\text{-bis}(2''\text{-thienyl})\text{-}3,3'\text{-bipyridine (L3)}$), and the corresponding platinum dimers $trans\text{-}[(PEt_3)_2(Ph)Pt(C\equiv CLC\equiv C)Pt(Ph)(PEt_3)_2]$ are described. The dimers were prepared by the reaction of two equivalents of $trans\text{-}[Pt(PEt_3)_2(Ph)Cl]$ with one equivalent of the diterminal diyne $HC\equiv C-L-C\equiv CH$, in CuI catalysed dehydrohalogenation reactions in $CH_2Cl_2-Pr^i_2NH$, while the polymers are obtained similarly from the diyne and one equivalent of $trans\text{-}[Pt(P^nBu_3)_2Cl_2]$. The optical absorption and photoluminescence spectra of the polymers with **L1** and **L2** linker groups are reported. The optical gaps are 465 nm (2.67 eV) and 486 nm (2.55 eV), respectively. The photoluminescence spectrum for each polymer exhibits one band at room temperature. At 10 K, low-energy emission bands emerge which are attributed to emission from the triplet excited state. The results of these studies are compared with those obtained for other platinum-containing poly-yne and related organometallic polymers.

Introduction

Over the last decade there has been growing interest in organometallic polymeric materials that contain transition metals in the polymer backbone.¹ The development of effective polycondensation² and ring-opening polymerisation strategies³ has made possible the reliable syntheses and characterisation of high molecular weight organometallic polymers. Such metallo-polymers provide model systems for the study of some of the photophysical processes that occur in conjugated organic polymers,⁴ used in optoelectronic devices such as light-emitting diodes,⁵ lasers,⁶ photocells,⁷ and field-effect transistors.⁸ In organic conjugated polymers, light emission is possible from the singlet excited state (fluorescence) but it is spin-forbidden from the triplet excited state (phosphorescence). This renders the triplet excited state difficult to examine in conjugated organic polymers. In light emitting-diodes, electrical excitation occurs to both singlet and triplet excited states. It is desirable to understand the photophysics of the triplet excited state and in particular how its energy level relates to the chemical structure of the material in order to provide sufficient background for the systematic use of methods that harvest the energy of the triplet state.⁹

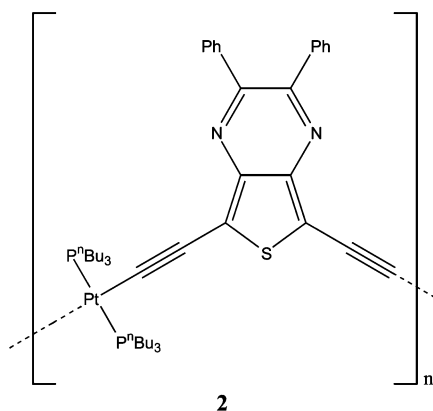
Recently we have been examining a series of 'rigid rod' organometallic poly-yne polymers¹⁰ with the general formula **1** where $M = Ni, Pd, Pt$; $R = Ph, Et, ^nBu$, and **L** is one of a number of aromatic spacer groups.

The inclusion of the transition metal introduces sufficient spin-orbit coupling so as to allow light emission from the triplet excited state of the conjugated ligand thus making this state spectroscopically accessible. The π conjugation of the ligand continues through the metal centres along the polymer chain since there is mixing of the π^* ligand orbitals and the lowest



unoccupied metal 6p states.^{4,11} The electronic properties of the polymers vary with the nature of **L**. Appropriate variation of **L** gives optical gaps in the range from 1.58 to 3.0 eV.^{12,13}

We have recently investigated two series of platinum-containing poly-yne polymers. In one series the conjugated spacer ligand **L** is based on phenylene derivatives.¹² In the second series the ligand was varied from thiophene to bithiophene to terthiophene, thus rendering the ligand increasingly electron rich.¹⁴ In both series the same energy difference between the first excited singlet (S_1) and the triplet (T_1), 0.7 ± 0.1 eV, was found.¹⁵ In an extension to this work, we have investigated a series of systems that contain thienyl-pyridine rings, with adjacent electron donating and accepting units in the main polymer chain. The aim of the investigation is to establish in what way the insertion of a donor-acceptor unit as the spacer ligand, **L**, affects the energies of the singlet and triplet excited states. These results may then be compared with those reported for the novel platinum thienopyrazine polymer **2**,¹⁶ where the spacer group, **L**, consists of an electron donating thiophene ring fused to an electron accepting pyrazine ring, the unit lying perpendicular to the main polymer chain. Copolymers that contain π -conjugated pyridine and thiophene ring systems have already been shown to exhibit novel optical and electronic properties,¹⁷⁻¹⁹ and a ruthenium-containing polythiophene-bipyridine copolymer displays interesting redox properties.²⁰



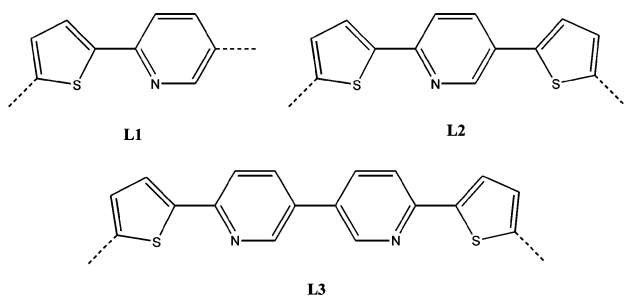
Scheme 1 i CuI, Pd(OAc)₂, PPh₃, ⁱPr₂NH, THF; ii KOH, MeOH, THF.

We now report the synthesis, characterisation and opto-electronic properties of a series of platinum(II) poly-yne polymers that contain novel thienyl-pyridine linker groups.

Results and discussion

Ligand synthesis

Three mixed thienyl-pyridine ring systems, that contain two (**L1**), three (**L2**) and four (**L3**) linked rings, respectively, were initially chosen for incorporation into the 'rigid rod' poly-yne systems, and these are illustrated below:



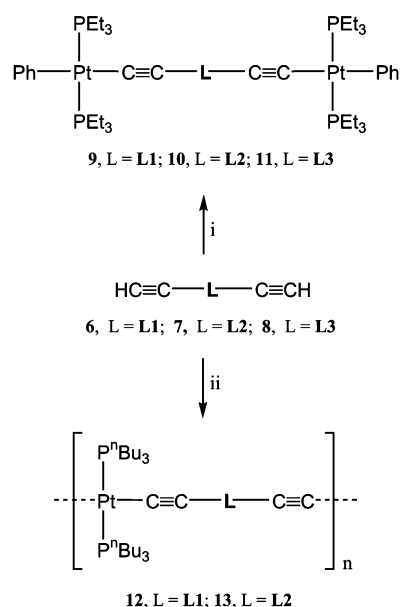
In the compounds with three and four rings, one or two pyridine rings occupy the central positions with a thiophene ring at each end. In each case pyridine rings should act as electron accepting groups and thiophene rings as electron donating groups. Hence, in **3**, there is a donor functionality at one end of the spacer and an acceptor functionality at the other. In **4** and **5** the acceptor group(s) are central with donor groups at either end of the spacer. This provides an adequate range of ligand systems to probe the electronic effects of the different spacer groups in the organometallic polymers. Each of the three compounds, 2-(2'-thienyl)pyridine, 2,5-bis(2'-thienyl)pyridine and 6,6'-bis(2'-thienyl)-3,3'-bipyridine, were dibrominated using NBS in DMF in the absence of light. Then 5,5'-bis(trimethylsilylethynyl)-2-(2'-thienyl)pyridine (**3**), 5',5''-bis(trimethylsilylethynyl)-2,5-bis(2'-thienyl)pyridine (**4**), and 5',5''-bis(trimethylsilylethynyl)-6,6'-bis(2'-thienyl)-3,3'-bipyridine (**5**) were prepared by the Pd^{II}/Cu^I catalysed cross-coupling reaction of the resulting dibromides with trimethylsilylacetylene²¹ as illustrated in Scheme 1. These compounds were isolated as yellow (**3**), and bright yellow (**4** and **5**) solids in yields of 50–70%, and were fully characterised by IR, ¹H and ¹³C NMR, and UV/visible spectroscopy, and by mass spectrometry (Table 1). They are all stable in air and towards light, and are readily soluble in common organic solvents.

These trimethylsilylethynyl derivatives are readily converted into their free diethynyl derivatives, HC≡C-L-C≡CH **6–8**, by desilylation with KOH in MeOH²² (Scheme 1). The products were purified by silica column chromatography, and obtained as pale yellow solids in 70–90% yield. They were characterised spectroscopically (Table 1). All the diterminal diynes are light

and air sensitive and give insoluble brown precipitates on standing. They are significantly less soluble than the trimethylsilyl derivatives, and compound **8** is only sparingly soluble.

Synthesis of dinuclear platinum complexes and polymers

The reaction of each of the diterminal diynes with two equivalents of the platinum complex, *trans*-[Pt(PEt₃)₂(Ph)Cl], in CH₂Cl₂-ⁱPr₂NH, in the presence of CuI, at room temperature, readily affords the dimers *trans*-[(PEt₃)₂(Ph)Pt(C≡CLC≡C)Pt(Ph)(PEt₃)₂] (L = **L1** (**9**), **L2** (**10**), **L3** (**11**)), in good yields (Scheme 2). The bright yellow complexes were characterised by



Scheme 2 i 2[Pt(PEt₃)(Ph)Cl], CuI, ⁱPr₂NH, CH₂Cl₂; ii [Pt(PⁿBu₃)Cl₂], CuI, ⁱPr₂NH, CH₂Cl₂.

IR, ¹H, ¹³C and ³¹P NMR, and UV/visible spectroscopies, and EI mass spectrometry (Table 2), and all gave satisfactory microanalyses.

Similarly, the corresponding polymers *trans*-[Pt(PⁿBu₃)₂](C≡C-L-C≡C)]_n (L = **L1** (**12**), **L2** (**13**)) were prepared by the reaction of one equivalent of *trans*-[Pt(PⁿBu₃)₂Cl₂] with the appropriate diterminal diyne, in CH₂Cl₂-NHⁱPr₂, under reflux, in the presence of CuI. The intense yellow products were purified by passing through an alumina column, and obtained as rubbery materials from CH₂Cl₂-hexane. The polymers were characterised by IR, ¹H, ¹³C and ³¹P NMR, and UV/visible spectroscopies, and their molar masses were determined by Gel Permeation Chromatography (GPC) (Table 2). The microanalyses for these polymers gave somewhat low observed carbon values that reflect the difficulty in isolating completely pure samples of these relatively insoluble materials.

Table 1 Spectroscopic data for the ligand compounds 3–8

Compound	IR/cm ⁻¹ (CH ₂ Cl ₂)	¹ H NMR/ppm (250.13 MHz, CDCl ₃)	¹³ C- ¹ H} NMR/ppm (62.89 MHz, CDCl ₃)	Mass spec. (calc.)	UV-Visible λ_{max} /nm (CH ₂ Cl ₂)
3	2144 (s) 2156 (sh) (C≡C)	8.56 (1H, d, $J_{6,3}$ 1.34 Hz, H-6), 7.67 (1H, dd, $J_{4,6}$ 2.06 Hz, $J_{3,4}$ 8.26 Hz, H-4), 7.49 (1H, d, $J_{3,4}$ 8.25 Hz, H-3), 7.38 (1H, d, $J_{3',4'}$ 3.91 Hz, H-3'), 7.17 (1H, d, $J_{4',3'}$ 3.89 Hz, H-4'), 0.24 (d, J 2.42 Hz, SiMe ₃)	-0.18 (s, SiMe ₃), 97.6, 99.03, 100.83, 101.67 (all s, C≡C), 117.9 (C-5), 118.55 (C-3), 124.8 (C-5'), 125.67 (C-2'), 133.65 (C-4'), 139.34 (C-3') 145.24 (C-4), 150.64 (C-2), 152.51 (C-6)	353.1 (353.11)	353
4	2144 (C≡C)	8.75(d, 1H, $J_{6,3}$ 1.79 Hz, H-6), 7.79 (dd, 1H, $J_{4,6}$ 2.36, $J_{4,3}$ 6.02 Hz, H-4), 7.58 (dd, 1H, $J_{3,6}$ 0.43 Hz, $J_{3,4}$ 7.26 Hz, H-3), 7.41 (d, 2H, $J_{3',4'}$ 3.92 Hz, H-3'), 7.2 (d, 2H, $J_{4',3'}$ 1.33 Hz, H-4'), 0.25 (s, 18H, SiMe ₃)	-0.18 (s, SiMe ₃), 97.69, 97.14, 100.72 (C≡C), 118.81 (C-3), 123.66 (C-5'), 124.38 (C-2'), 133.35, 133.74, 133.82 (C-3' or C-4'), 141.49 (C-4), 146.64, 150.96 (C-2 or C-6). (100.6 MHz)	435.1 (435.7)	379
5	2144 (C≡C)	8.8 (dd, 2H, $J_{2,5}$ 0.98 Hz, $J_{2,4}$ 2.23 Hz, H-2), 7.89 (dd, 2H, $J_{2,4}$ 2.34 Hz, $J_{4,5}$ 8.27 Hz, H-4), 7.7 (dd, 2H, $J_{2,5}$ 0.45 Hz, $J_{5,4}$ 8.44 Hz, H-5), 7.46 (d, 2H, $J_{3',4'}$ 3.86 Hz, H-3'), 7.23 (d, 2H, $J_{4',3'}$ 3.9 Hz, H-4'), 0.26 (s, SiMe ₃)	100.79 (C≡C), 118.98 (C-3 or C-5), 124.62 (C-2' or C-5'), 133.77, 134.55, (C-3' or C-4'), 147.68 (C-4 or C-4'), 151.50 (C-2 or C-6) (100.62 MHz)	512.8 (512.4)	373
6	3300 (C≡CH) 2102.6 (C≡C)	8.61 (1H, d, $J_{6,3}$ 1.36 Hz, H-6), 7.73 (1H, dd, $J_{4,6}$ 2.07 Hz, $J_{3,4}$ 8.27 Hz, H-4), 7.55 (1H, dd, $J_{3,6}$ 0.7 Hz, $J_{3,4}$ 8.27 Hz, H-3), 7.4 (1H, d, $J_{3',4'}$ 3.92 Hz, H-3'), 7.23 (1H, d, $J_{4',3'}$ 3.92 Hz, H-4'), 3.44 (s, 1H, C≡CH), 3.26 (s, 1H, C≡CH).	80.48, 81.34, 82.96, (all s, C≡C), 117.65, 117.99 (C-3 or C-5), 124.58, 124.84 (C-2' or C-5'), 134.15 (C-4'), 139.67 (C-3') 145.47 (C-4), 150.96 (C-2), 152.66 (C-6).	209.0 (209.02)	340
7	3300 (C≡CH) 2101.9 (C≡C)	8.77 (d, 1H, $J_{6,3}$ 1.68 Hz, H-6), 7.82 (dd, 1H, $J_{4,6}$ 2.36, $J_{4,3}$ 6.03 Hz, H-4), 7.62 (dd, 1H, $J_{3,6}$ 0.63 Hz, $J_{3,4}$ 7.71 Hz, H-3), 7.43 (d, 2H, $J_{3',4'}$ 3.84 Hz, H-3'), 7.22 (d, 2H, $J_{4',3'}$ 3.88 Hz, H-4'), 3.43 (s, 2H, C≡CH) (400.13 MHz)	82.79 (C≡C), 118.83 (C-3), 123.79 (C-5'), 124.33 (C-2'), 133.54, 134.20, 134.31 (C-3' or C-4'), 142.0 (C-4), 146.70, 150.91 (C-2 or C-6) (100.62 MHz)	292.0 (291.4)	369
8	3279 (C≡CH) 2093 (C≡C) in Nujol	8.85 (dd, 2H, $J_{2,5}$ 0.48 Hz, $J_{2,4}$ 2.15 Hz, H-2), 8.08 (dd, 2H, $J_{2,4}$ 2.66 Hz, $J_{4,5}$ 8.32 Hz, H-4), 7.87 (d, 2H, $J_{5,4}$ 8.32 Hz, H-5), 7.61 (d, 2H, $J_{3',4'}$ 3.89 Hz, H-3'), 7.24 (d, 2H, $J_{4',3'}$ 3.88 Hz, H-4'), 3.99 (s, 2H, C≡CH) (400.13 MHz, d ₈ -THF)	84.45 (C≡C), 118.75 (C-3 or C-5), 124.62, 125.41, 125.89 (C-2'' or C-5''), 134.69, 135.35, (C-3'' or C-4''), 147.57, 148.46 (C-4 or C-4'), 152.21 (C-2 or C-6)	374 (368.5)	362

Spectroscopic properties

All the organic compounds, the platinum dimers and the platinum polymers show a single strong $\nu(\text{C}\equiv\text{C})$ absorption, that in the metal complexes is consistent with the *trans* configuration for the Pt(II) centres. As observed in other poly-yne compounds there is a lowering of the $\nu(\text{C}\equiv\text{C})$ stretching frequencies in the platinum complexes and polymers compared to the values found in the corresponding trimethylsilyl-substituted diyne compounds.^{14,23} This may be attributed to either metal-yne π -back bonding or the $\text{M}^{\delta+}-\text{C}^{\delta-}$ polarity.²⁴ The ¹H and ¹³C NMR spectra exhibit the expected signals for the systems including resonances around 102 ppm for the acetylenic carbons. The single resonance in the ³¹P NMR for all the platinum(II) dimers and polymers confirms the *trans* arrangement of the phosphine ligands.

The mass spectrometric results confirm the molecular assignments for the organic compounds and the platinum dimer complexes. The weight-average molecular weights (M_w) obtained by GPC for **12** and **13** indicate a high degree of polymerisation. The number-average molecular weight (M_n) values for **12** and **13** correspond to 115 and 159 repeating units per chain, respectively.

The solution electronic absorption spectra of the organic diyne compounds all exhibit one, strong, relatively low-energy $\pi-\pi^*$ transition. There is a shift towards longer wavelength for the trimethylsilyl derivatives when compared to the diterminal diynes, and there is also a shift to longer wavelength in going from the two-ring compounds, **3** and **6**, to the three and four-ring compounds, **4** and **7**, and **5** and **8**, respectively. These shifts presumably reflect higher degrees of conjugation as the number of rings in the central spacer increases. The platinum(II) dimers and the metallo-poly-yne polymers also exhibit absorption spectra that are dominated by $\pi-\pi^*$ transitions, and show fur-

ther red-shifts, such that for ligand **L1**, the absorption for the diterminal diyne, **6**, occurs at 340 nm, that of the corresponding platinum dimer, **9**, at 393 nm, and that of the platinum-containing polymer, **12**, at 430 nm. The dimer and polymer that contain the three-ring spacer, **L2**, show a slightly smaller shift from 420 nm for **10** to 453 nm for **13**. The observed red-shift, as with the poly-thiophene platinum complexes and polymers,^{14,23} is consistent with the platinum fragments acting as net electron donors to the electron withdrawing spacer groups.²⁵

Molecular structure of 4

In order to confirm the linear nature of the compounds and polymers the crystal structure of the *bis*-(trimethylsilylethynyl) derivative of spacer **L2**, compound **4**, has been determined. The molecular structure of **4** is shown in Fig. 1 while selected bond

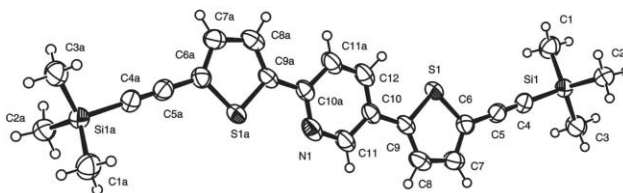


Fig. 1 The molecular structure of **4** showing the atom numbering scheme. Anisotropic displacement parameters are shown at the 50% probability level.

parameters are presented in Table 3. The molecule sits on a crystallographic centre of symmetry, at the centre of the pyridine ring, and as a consequence the two trimethylsilylethynyl substituents are diametrically opposite in the required *pseudo-trans* relationship. The crystallographic symmetry imposes disorder on the central pyridine ring such that the nitrogen atom,

Table 2 Spectroscopic data for the platinum compounds **9–13**

Compound	IR/cm ⁻¹ (CH ₂ Cl ₂)	¹ H NMR/ppm (CDCl ₃)	¹³ C-{ ¹ H} NMR/ppm (CDCl ₃)	³¹ P-{ ¹ H} NMR/ppm (101.3 MHz, CDCl ₃)	Mass spec. (calc.)	UV-Visible λ_{max} /nm (CH ₂ Cl ₂)
9	2084.3 (C≡C)	1.08 (t, 36H, CH ₃), 1.69–1.76 (m, 24H, CH ₂ P), 6.80–6.98 (m, Ph), 7.29 (br, 1H, H-4'), 7.32 (br, 1H, H-3'), 7.42 (br, 1H, H-3), 7.4 (dd, 1H, <i>J</i> _{4,6} 1.7 Hz, <i>J</i> _{4,3} 8.29 Hz, H-4), 8.46 (d, 1H, <i>J</i> _{6,3} 1.12 Hz, H-6) (250.13 MHz)	8.02 (t, CH ₃), 15.14 (t, CH ₂ P), 102.7 (C≡C), 117.32, 119.42 (C-3 or C-5), 121.40, 125.16, (C-2' or C-5'), 127.37, 128.12 (C-4' or C-3'), 138.89 (C-4), 150.37 (C-2 or C-6) (62.896 MHz)	–129.98 ¹ <i>J</i> _{Pt-P} 1315 Hz	1225 (1223)	393
10	2081.3 (C≡C)	1.02–1.15 (m, 36H, CH ₃), 1.69–1.78 (m, 24H, CH ₂ P), 6.96 (t, Ph), 7.12 (d, 2H, <i>J</i> _{4,3'} 3.77 Hz, H-4'), 7.32 (d, 2H, <i>J</i> _{3',4'} 3.34 Hz, H-3'), 7.52 (d, 1H, <i>J</i> _{3,4} 8.4 Hz, H-3), 7.72 (dd, 1H, <i>J</i> _{4,6} 2.33 Hz, <i>J</i> _{4,3} 6.4 Hz, H-4), 8.71 (d, 1H, <i>J</i> _{6,3} 1.93 Hz, H-6) (250.13 MHz)	8.03 (s, CH ₃), 14.99–15.33 (m, PCH ₂), 102.8 (C≡C), 118.1 (C-5), 121.37 (C-3), 123.27, 124.29 (C-2' or C-5'), 127.36–128.21 (Ph), 132.6 (C-3'), 136.42 ((C-4')), 139.06 (C-4), 146.08 (C-2), 150.84 (C-6) (100.62 MHz)	–129.46, ¹ <i>J</i> _{Pt-P} 1313 Hz	1307 (1305)	420
11	2081.4 (C≡C)	1.02–1.13 (m, 36H, CH ₃), 1.70–1.77 (m, 24H, CH ₂ P), 6.86 (d, 2H, <i>J</i> _{4,3'} 3.83 Hz, H-4'), 6.96 (t, Ph), 7.07 (d, 2H, <i>J</i> _{3',4'} 3.88 Hz, H-3'), 7.69 (dd, 2H, <i>J</i> _{2,5} 0.67, <i>J</i> _{5,4} 3.15 Hz, H-5), 7.87 (dd, 2H, <i>J</i> _{2,4} 2.4 Hz, <i>J</i> _{4,5} 8.31 Hz, H-4), 8.76 (d, 2H, <i>J</i> _{2,4} 2.44 Hz, H-2) (400.13 MHz)	8.03 (s, CH ₃), 14.59–15.42 (m, PCH ₂), 102.75 (C≡C), 118.19, 118.38 (C-3 or C-5), 127.75, 128.21 (C-2' or C-5'), 130.04–133.36 (Ph), 134.27 (C-3' or C-4'), 139.01 (C-4 or 4'), 148.43 (C-2 or C-6) (62.89 MHz)	–129.78, ¹ <i>J</i> _{Pt-P} 1312 Hz	1384 (1382)	412
12	2086.7 (C≡C)	0.90 (t, 18H, CH ₃), 1.40–1.57 [m, 24H, (CH ₂) ₂], 1.86–2.14 (m, 12H, PCH ₂), 6.79 (br, 2H, H-4'), 6.99 (br, 2H, H-3'), 7.27 (d, 1H, <i>J</i> = 2.58 Hz, H-3), 7.42 (br, 1H, H-4), 8.4 (br, 1H, H-6) (400.13 MHz)	13.84 (s, CH ₃), 23.78–25.08 {m, (CH ₂) ₂ }, 26.38 (PCH ₂), 102.5 (C≡C), 117.66, 117.78 (C-3 or C-5), 123.18, 123.8, (C-2' or C-5'), 128.58, (C-4'), 137.62 (C-3'), 148.42 (C-4), 151.45, 151.76 (C-2 or C-6).	–136.48, ¹ <i>J</i> _{Pt-P} 1166 Hz	GPC 85420 <i>n</i> _w = 115	430
13	2086.6 (C≡C)	0.94 (t, 18H, CH ₃), 1.43–1.59 [m, 24H, (CH ₂) ₂], 2.12–2.16 (m, 12H, PCH ₂), 6.82 (br, 2H, H-4'), 7.12 (d, 1H, <i>J</i> = 3.34 Hz, H-3'), 7.35 (d, 1H, <i>J</i> = 3.34 Hz, H-3'), 7.52 (d, 1H, <i>J</i> = 8.31 Hz, H-3), 7.72 (d, 1H, <i>J</i> = 7.64 Hz, H-4), 8.71 (br, 1H, H-6) (250.13 MHz)	13.86 (s, CH ₃), 23.86–24.41 {m, (CH ₂) ₂ }, 26.4 (s, PCH ₂), 102 (C≡C), 118.3 (C-5), 123.3, 124.37 (C-3 or C-5'), 128.42, 128.64 (C-2'), 132.08 (C-3'), 132.58 ((C-4')), 136.89 (C-4), 140.62 (C-2), 146.16 (C-6).	–136.02, ¹ <i>J</i> _{Pt-P} 1163 Hz	GPC 141467 <i>n</i> _w = 159	453

Table 3 Selected bond lengths (Å) and angles (°) for **4**^a

Si(1)–C(1)	1.856(3)	Si(1)–C(2)	1.850(3)
Si(1)–C(3)	1.855(4)	Si(1)–C(4)	1.844(4)
C(4)–C(5)	1.202(5)	C(5)–C(6)	1.424(5)
C(6)–C(7)	1.370(4)	C(6)–S(1)	1.731(3)
S(1)–C(9)	1.724(3)	C(7)–C(8)	1.411(5)
C(8)–C(9)	1.365(4)	C(9)–C(10)	1.467(4)
C(10)–C(11)	1.386(4)	C(10)–N(1)	1.349(4)
C(11)–C(12a)	1.373(5)		
C(2)–Si(1)–C(1)	110.52(18)	C(2)–Si(1)–C(3)	109.68(17)
C(3)–Si(1)–C(1)	111.45(19)	C(4)–Si(1)–C(1)	107.64(16)
C(4)–Si(1)–C(2)	109.53(17)	C(4)–Si(1)–C(3)	109.68(17)
Si(1)–C(4)–C(5)	179.7(4)	C(4)–C(5)–C(6)	178.5(4)
C(5)–C(6)–C(7)	129.3(3)	C(5)–C(6)–S(1)	119.8(2)
C(7)–C(6)–S(1)	110.9(3)	C(6)–S(1)–C(9)	92.23(16)
C(6)–C(7)–C(8)	112.4(3)	C(7)–C(8)–C(9)	114.1(3)
C(8)–C(9)–C(10)	129.9(3)	C(8)–C(9)–S(1)	110.4(3)
C(10)–C(9)–S(1)	119.7(2)	N(1)–C(10)–C(11)	119.6(3)
N(1)–C(10)–C(9)	119.1(3)	C(11)–C(10)–C(9)	121.3(3)
C(10)–N(1)–C(11a)	119.8(3)	C(10)–C(11)–C(12a)	120.6(3)

^a Symmetry transformation used to generate the equivalent atoms "a" is $-x + 2, -y, -z + 1$.

N(1), and the ring carbon, C(12), are disordered over the two sites in a 50 : 50 ratio. The dihedral angle between the pyridine ring and the unique thiophene ring is 6.1° (12.2° between thiophene rings), the twist reducing the unfavourable steric interaction between the hydrogen atoms on the adjacent pyridine and thiophene rings. This twist angle is similar to that found in 2-(2'-thienyl)pyridine, **L1**, and in a number of related molecules.²⁶ A search of the Cambridge Structural Database²⁷ revealed no structures containing the **L2** unit.

No solid-state π - π stacking between adjacent molecules, nor short intermolecular contacts below 3 Å are present, presumably due to the presence of the bulky trimethylsilyl groups.

Absorption spectroscopy

The electronic absorption spectra of the polymers were also investigated in the solid state, the materials were spun into films. Fig. 2 shows the normalised electronic absorption spectra of the platinum-containing polymers **12** and **13**, respectively. The spectra of **12** and **13** both comprise of two prominent

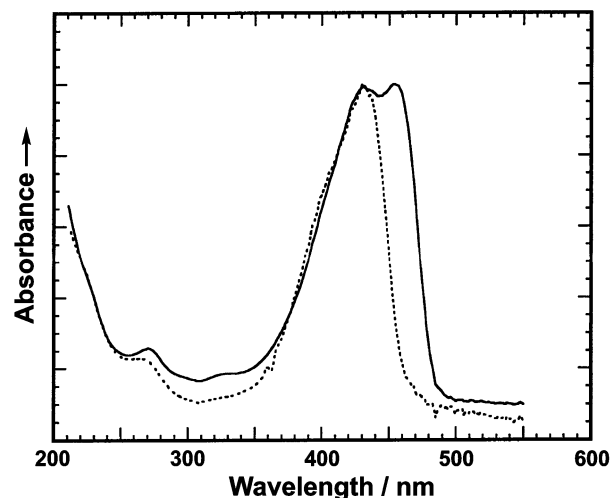


Fig. 2 Thin film absorption spectra of polymer **12** (dotted line) and **13** (solid line).

absorption bands in the visible region. Bands of similar intensity are observed at 430 and 455 nm for **12**, whereas **13** also possesses a band at 430 nm with an additional high-energy shoulder centred at *ca.* 405 nm. The optical gaps for **12** and **13** are at 465 nm (2.67 eV) and 486 nm (2.55 eV). This compares to the corresponding polymers containing a bithiophene or terthiophene spacer which have optical gaps of 486 (2.55 eV) and 516 nm (2.40 eV).¹⁴ This represents a blue-shift of 0.12 and 0.15 eV, respectively.

Photoluminescence spectroscopy

The solid-state photoluminescence spectra of the polymers as spun films recorded at 10 K and room temperature are illustrated in Fig. 3 for **12** and Fig. 4 for **13**, respectively. The spectra

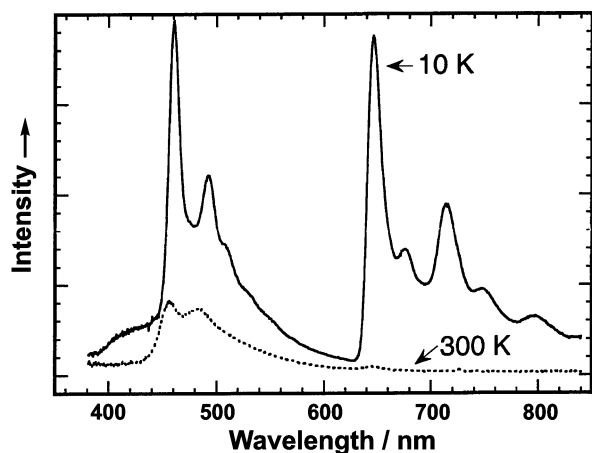


Fig. 3 Photoluminescence spectra of a thin film of polymer **12** at 10 and 300 K.

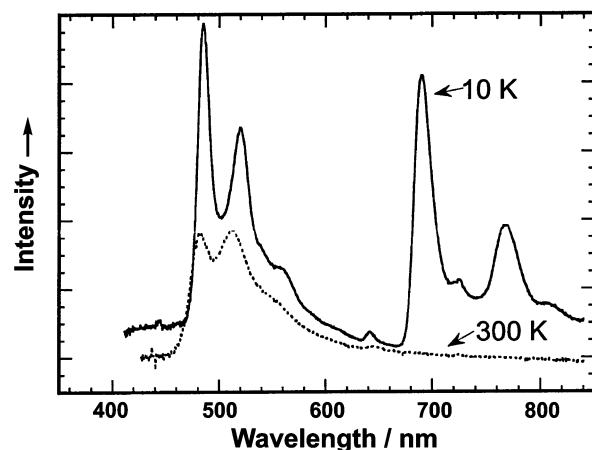


Fig. 4 Photoluminescence spectra of a thin film of polymer **13** at 10 and 300 K.

were taken on the same sample, in each case, with the same experimental geometry and set-up. They are comparable in intensity except for changes in the absorbance at the excitation wavelength that may occur, and this factor does not significantly alter the general spectral features. The low temperature spectra show two emission bands, one from about 450 to 600 nm, and one from about 630 or 670 to beyond 850 nm. We attribute the first (higher energy) band to emission from the first singlet excited state, S_1 , (fluorescence) while we attribute the second (lower energy) band to emission from the first triplet excited state, T_1 , (phosphorescence) due to its strong temperature dependence, energetic position and line shape.^{11–16} The energetic separation of the peak for the triplet state at 646 nm (1.92 eV) for **12** and at 691 nm (1.79 eV) for **13** from the peak for the singlet excited state at 460 nm (2.70 eV) for **12** and at

485 nm (2.56 eV) for **13** is 0.78 and 0.77 eV, respectively. These gaps fall in the same range as the values obtained for the S_1 – T_1 energy gaps in related polymeric materials.^{11–16}

There are three noteworthy features in these results. The first is the markedly smaller (0.14 eV) S_1 to S_0 gap observed for polymer **13** over **12**. In order to understand the electronic structures of the bridging groups we have performed preliminary density functional theory (DFT) calculations on the diethynyl functionalised **6** and **7** bridging groups, respectively, using the Gaussian 98 program,²⁸ employing the B3LYP^{29–31} functional in conjunction with the 6–31G* basis set for H, C, N and S.³² Representations of the HOMO and LUMO levels for **6** (C_s) and **7** (C_1) are given in Fig. 5. When the second thiophene ring is

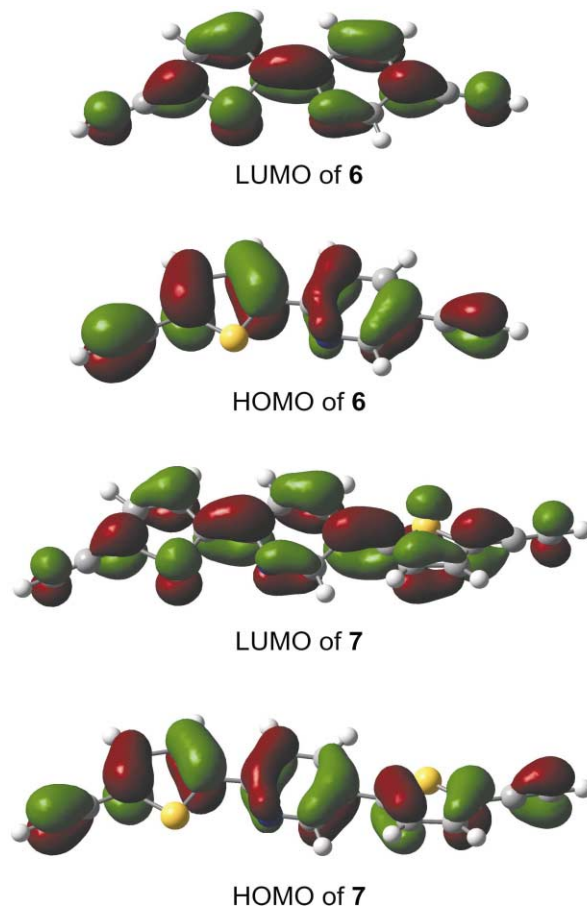


Fig. 5 Molecular orbital plots for the HOMO and LUMO of **6** and **7**.

introduced into the then planar **6** molecule the HOMO–LUMO energy gap is reduced by *ca.* 0.3 eV, which is inherently a consequence of greater conjugation in the longer bridging ligand. However, the magnitude of that “reduction” is reduced as the optimised ground state structure of **7** contains a twist of *ca.* 24° between the pyridine and second thiophene ring (see Fig. 5), which mediates unfavourable intramolecular interactions between hydrogen atoms on adjacent rings, and is consistent with the twist seen in the crystal structure described earlier in the paper. Due to the similarity in the natures of the HOMO and LUMO levels for **6** and **7**, similar situations can be envisaged when the ethynyl protons are exchanged for linking $Pt(PR_3)_2$ groups, and hence there again the HOMO–LUMO gap for **13** should be smaller than for **12**, and polymer **13** should be twisted.

The second feature is the blue-shift of the singlet state compared to the corresponding bi- and tri-thiophene-containing systems. If there was any charge-transfer-like electronic interaction between the electron-rich thiophene ring and the electron-poor pyridine ring, this should result in increased conjugation and thus lead to a red-shift with respect to an

analogous system consisting only of thiophene rings. The observed blue-shift indicates the absence of such a charge-transfer interaction. Instead, exchange of a thiophene ring by a pyridine ring seems to reduce any donor–acceptor interaction between the metal and the ligand. This can be rationalised by considering that the pyridine ring might withdraw electron density from the polymer backbone towards the lone pair. This reduction in electron density compared to a purely thiophene-containing system manifests itself in reduced conjugation and thus higher optical gaps. Indeed, the calculated HOMO–LUMO energy gaps for **6** and **7** are *ca.* 0.2 eV higher than those of their corresponding bi- and tri-thiophene analogues (*C*₂), which is mainly a consequence of the HOMOs of **6** and **7** being higher in energy than those of their thiophene counterparts, whereas the energy levels of the corresponding LUMOs are comparable.

The last important feature is the observation of a S₁–T₁ energy gap that is identical to the values observed for other platinum-containing polymers with phenylene or thiophene-based spacer ligands.^{11–16} Earlier work has shown that the triplet excited state in these materials is localised within one spacer unit^{4,14} while the singlet excited state extends over one or two repeat units.⁴ It is, therefore, reasonable to speculate that intra-ligand charge-transfer interactions between the thiophene and pyridine units might shift the energy of the triplet excited state with respect to the singlet state. However, there is no such effect on the position of the triplet state, consistent with the lack of any charge-transfer effect on the energetic position of the singlet state.

Conclusions

In summary, it has been shown that it is possible to prepare a series of platinum poly-yne polymers that contain mixed heterocyclic ring linker groups in good yields, by CuI catalysed dehydrohalogenation reactions. Polymers with molar masses in the range 85,000–140,000 that contain the 2-(2'-thienyl)pyridine (**12**) and 2,5-bis(2'-thienyl)pyridine (**13**) linking groups have been fully characterised. The optical gaps for the two polymers, **12** and **13**, are 2.67 and 2.55 eV, respectively, which compare to gaps of 2.55 and 2.40 eV observed for the corresponding polymers that contain bi and tri-thiophene linker groups,¹⁴ and represents blue-shifts of 0.12 and 0.15 eV, respectively. This result is consistent with a reduction in the donor–acceptor interaction between the metal and the ligand. The photoluminescence spectra exhibit both triplet (phosphorescence) and singlet (fluorescence) emission. In both cases the triplet emission is *ca.* 0.8 eV below the singlet emission, a feature that has been similarly observed in the spectra of related systems.^{11–16} These results have stimulated a study of organometallic polymers that contain spacer groups with significantly different intra-ligand charge transfer properties, and this work is in progress.

Experimental

All reactions were performed under an inert nitrogen atmosphere using standard Schlenk techniques. Solvents were pre-dried and distilled before use by standard procedures.³³ All chemicals, except where stated otherwise, were obtained from commercial sources and used without further purification. Trimethylsilyl acetylene was obtained from the preparation laboratory in the Department of Chemistry, University of Cambridge. The platinum complex *trans*-[Pt(PⁿBu₃)₂Cl₂] was prepared by the literature method,³⁴ as were each of the three compounds, 2-(2'-thienyl)pyridine,¹⁷ 2,5-bis(2'-thienyl)pyridine¹⁷ and 6,6'-bis(2''-thienyl)-3,3'-bipyridine,¹⁹ 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 CH₂Cl₂ solutions, in a NaCl cell, using a Perkin–Elmer 1710 Fourier Transform IR spectrometer. Mass spectra were recorded using a Kratos MS890 spectrometer with electron impact (EI) techniques. Microanalyses were performed in the Department of Chemistry. UV/visible absorption spectra were obtained using a Perkin–Elmer Lambda UV/NIR spectrometer. Column chromatography was performed on alumina (Brockman Grade II–III).

Synthesis of the spacer groups

5,5'-Dibromo-2-(2'-thienyl)pyridine (BrL₁Br). The compound was synthesised by following the literature method.³⁵ ¹H NMR (250.13 MHz, CDCl₃): δ = 8.58 (1H, d, *J*_{6,3} 1.35 Hz, H-6), 7.70 (dd, 1H, *J*_{4,6} 2.05, *J*_{3,4} 8.28 Hz, H-4), 7.52 (d, 1H, *J*_{3,4} 8.26 Hz, H-3), 7.39 (d, 1H, *J*_{3,4'} 3.91 Hz, H-3'), 7.20 (d, 1H, *J*_{4',3'} 3.89 Hz, H-4'). EI-mass spectrum: *m/z* 319.3; Calc. 319.2. Calc for C₉H₅NSBr₂: C, 33.86; H, 1.58; N, 4.39. Found: C, 33.91; H, 1.65; N, 4.47%.

5',5''-Dibromo-2,5-bis(2'-thienyl)pyridine (BrL₂Br). In the absence of light, NBS (2.66 g, 15 mmol) was added portionwise at 20 °C to a solution of 2,5-bis(2'-thienyl)pyridine (1.80 g, 7.4 mmol) in DMF (25 mL). The reaction mixture was stirred for 3 h, poured onto ice forming a yellow–brown precipitate. The solid was filtered off, washed several times with water and dried *in vacuo* over P₂O₅. The crude product was purified by column chromatography on alumina using CH₂Cl₂–hexane (4 : 1 v/v) to yield a yellow solid. Recrystallisation from ethanol afforded 2.12 g (88% yield) as a bright yellow solid. ¹H NMR (250.13 MHz, CDCl₃): δ = 8.74 (d, 1H, *J*_{6,3} 1.74 Hz, H-6), 7.75 (dd, 1H, *J*_{4,6} 2.37, *J*_{4,3} 6.01 Hz, H-4), 7.60 (dd, 1H, *J*_{3,6} 0.55 Hz, *J*_{3,4} 7.64 Hz, H-3), 7.42 (d, 2H, *J*_{3,4} 3.88 Hz, H-3'), 7.21 (d, 2H, *J*_{4,3'} 2.33 Hz, H-4'). EI-mass spectrum: *m/z* 401.3; Calc. 401.3. Calc for C₁₃H₇NS₂Br₂: C, 38.90; H, 1.76; N, 3.49. Found: C, 38.98; H, 1.74; N, 3.53%.

5'',5'''-Dibromo-6,6'-bis(2''-thienyl)-3,3'-bipyridine (BrL₃Br). In the absence of light, NBS (0.356 g, 2 mmol) dissolved in DMF (10 mL), was rapidly added to a vigorously stirred solution of 6,6'-bis(2''-thienyl)-3,3'-bipyridine (0.32 g, 1 mmol) in DMF (50 mL) at 80 °C. After 2 h the reaction mixture was cooled to room temperature and poured onto ice. The crude product was purified by column chromatography using CH₂Cl₂–hexane (2 : 1 v/v) on alumina to yield a bright yellow solid, 0.37 g (76%). ¹H NMR (250.13 MHz, CDCl₃): δ = 8.78 (dd, 2H, *J*_{2,5} 0.78 Hz, *J*_{2,4} 2.19 Hz, H-2), 8.01 (dd, 2H, *J*_{2,4} 2.44, *J*_{4,5} 8.29 Hz, H-4), 7.82 (dd, 2H, *J*_{2,5} 0.48 Hz, *J*_{5,4} 8.49 Hz, H-5), 7.46 (d, 2H, *J*_{3',4'} 3.88 Hz, H-3''), 7.25 (d, 2H, *J*_{4',3'} 3.89 Hz, H-4''). EI-mass spectrum: *m/z* 478.5; Calc. 478.4. Calc for C₁₈H₁₀N₃S₂Br₂: C, 45.19; H, 2.11; N, 5.86. Found: C, 45.23; H, 2.14; N, 5.95%.

5',5''-Bis(trimethylsilylethynyl)-2,5-bis(2'-thienyl)pyridine (4). 5',5''-Dibromo-2,5-bis(2'-thienyl)pyridine (3g, 7.48 mmol) was dissolved in freshly distilled THF–³Pr₂NH (700 cm³, 6 : 1 v/v) at room temperature under nitrogen. Me₃SiC≡CH (1.83 g, 18.69 mmol) was then added followed by the catalysts CuI (17.8 mg, 0.093 mmol), Pd(OAc)₂ (16.9 mg, 0.075 mmol) and PPh₃ (97.7 mg, 0.37 mmol). The solution mixture was stirred at room temperature for 1 h then slowly heated to reflux for 48 h. The reaction was monitored by IR spectroscopy and TLC until completion was established. The solution was allowed to cool to room temperature, Et₂O (100 cm³) was added and the precipitate was filtered off. The volatiles were removed from the yellow filtrate under reduced pressure and the residue was dissolved in Et₂O (100 cm³) and washed sequentially with 10% HCl (3 × 100 cm³), H₂O (3 × 100 cm³), NaHCO₃ (3 × 100 cm³),

and H₂O (3 × 100 cm³). The resulting organic phase was then dried (MgSO₄) and the volatiles removed once again to leave a yellow residue. The residue was dissolved in the minimum amount of CH₂Cl₂ and subjected to column chromatography on silica using toluene–CH₂Cl₂ (2 : 1 v/v). The product eluted as a bright yellow band which was further purified by recrystallisation from warm 2 : 1 toluene–CH₂Cl₂ to afford **4** as glistening yellow flakes in 67% yield (2.2 g). Calc. for C₂₃H₂₅Si₂S₂N: C, 63.4; H, 5.78; N, 3.21. Found: C, 61.9; H, 5.62; N, 3.03.

5,5'-Bis(trimethylsilylethynyl)-2-(2'-thienyl)pyridine (3). Similar procedures as for **4** were adopted using 5,5'-dibromo-2-(2'-thienyl)pyridine (2.0 g, 6.27 mmol) (except that the solvent used in this reaction was ¹Pr₂NH) to produce light yellow **3** in 60% yield (0.66 g). Calc. for C₁₉H₂₃Si₂S₂N: C, 64.50; H, 6.6; N, 3.96. Found: C, 64.47; H, 6.61; N, 3.93%.

5',5''-Bis(trimethylsilylethynyl)-6,6'-bis(2''-thienyl)-3,3'-bipyridine (5). Similar procedures as for **3** were adopted using 5',5''-dibromo-6,6'-bis(2''-thienyl)-3,3'-bipyridine (1.2 g, 2.51 mmol) to produce bright yellow **5** in 52% yield (0.66 g). Calc. for C₂₈H₂₈Si₂S₂N₂: C, 65.50; H, 5.50; N, 5.46. Found: C, 64.10; H, 5.22; N, 5.29%.

5',5''-Di(ethynyl)-2,5-bis(2'-thienyl)pyridine (7). The trimethylsilylethynyl-derivative **4** (145 mg, 0.33 mmol) was desilylated by dissolving in freshly distilled THF–MeOH (70 cm³, 6 : 1 v/v) and adding dropwise a solution of KOH (92 mg, 1.65 mmol) in a minimum amount of H₂O. The reaction was completed by stirring for 1 h at room temperature. The volatiles were then removed under reduced pressure to afford a light yellow residue which was washed with H₂O and extracted with CH₂Cl₂. The solution was dried (MgSO₄) and filtered and the volatiles removed under reduced pressure. The residue was subjected to column chromatography on silica using toluene–CH₂Cl₂ (2 : 1 v/v) affording the desired product as a light yellow solid in 77% yield (75 mg). Calc. for C₁₇H₉S₂N: C, 70.10; H, 3.11; N, 4.81. Found: C, 68.96; H, 3.43; N, 4.47%.

5,5'-Di(ethynyl)-2-(2'-thienyl)pyridine (6). Compound **6** was synthesised from **3** adopting a similar procedure to that described above for **7**. The product was obtained as a pale yellow solid in 84% yield after purification using a silica column and CH₂Cl₂–hexane (1 : 2) as eluent. Calc. for C₁₃H₇SN: C, 74.6; H, 3.37; N, 6.69. Found: C, 74.58; H, 3.50; N, 6.60%.

5',5''-Di(ethynyl)-6,6'-bis(2''-thienyl)-3,3'-bipyridine (8). Compound **8** was synthesised from **5** adopting the similar procedure as above for **7**. However, the product **8** was only sparingly soluble in organic solvents which made purification difficult. It was purified by passing a THF (sparingly soluble) solution through a silica column and washing the residue with hexane. The product was not sufficiently pure for use with organometallic polymerisation reactions where an accurate 1 : 1 reactant ratio is required.

Synthesis of the platinum complexes and polymers

Trans-[(PEt₃)₂(Ph)Pt(C≡C–L1–C≡C)Pt(Ph)(PEt₃)₂] (9). Treatment of the diterminal diyne compound **6** (29.1 mg, 0.14 mmol) with 2 equivalents of *trans*-[Pt(PEt₃)₂(Ph)Cl] (151 mg, 0.277 mmol) for 20 h at room temperature, in the presence of CuI (3 mg), in CH₂Cl₂–¹Pr₂NH (60 cm³, 1 : 1 v/v), gave the required complex as a bright yellow solid in 39% yield (0.15 g) after purification on a silica column using toluene–CH₂Cl₂ (2 : 1) as eluent and subsequent recrystallisation from a hot solution of hexane–CH₂Cl₂ (2 : 1). Calc. for C₄₉H₇₅P₄Pt₂SN: C, 48.07; H, 6.18; N, 1.14. Found: C, 48.67; H, 6.13; N, 1.44%.

Trans-[(PEt₃P)₂(Ph)Pt(C≡C–L2–C≡C)Pt(Ph)(PEt₃)₂] (10). Complex **10** was synthesised using the same conditions as

described for **9** by the reaction of **7** (41.38 mg, 0.142 mmol) with 2 equivalents of *trans*-[Pt(PEt₃)₂(Ph)Cl] (154.5 mg, 0.284 mmol). Calc. for C₅₃H₇₇P₄Pt₂S₂N: C, 48.7; H, 5.94; N, 1.07. Found: C, 48.98; H, 5.91; N, 1.04%.

Trans-[(PEt₃P)₂(Ph)Pt(C≡C–L3–C≡C)Pt(Ph)(PEt₃)₂] (11). Complex **11** was synthesised using the similar method to that described for **9** from the reaction of **8** (55.9 mg, 0.15 mmol) and *trans*-[Pt(PEt₃)₂(Ph)Cl] (165 mg, 0.303 mmol) in THF–¹Pr₂NH (80 cm³, 1 : 1 v/v) because of limited solubility of **8** in CH₂Cl₂. Calc. for C₅₈H₈₀P₄Pt₂S₂N₂: C, 50.35; H, 5.83; N, 2.02. Found: C, 49.33; H, 5.22; N, 2.79%.

Trans-[-Pt(PⁿBu₃)₂(C≡C–L1–C≡C)-]_n (12). To a mixture of *trans*-[Pt(PⁿBu₃)₂Cl₂] (0.19 g, 0.28 mmol) and one equivalent of HC≡C–L1–C≡CH (**6**, 59.3 mg, 0.28 mmol) in CH₂Cl₂–¹Pr₂NH (60 cm³, 1 : 1 v/v) was added CuI (3 mg). The mixture was stirred at room temperature for 18 h, after which all volatiles were removed under reduced pressure. The residue was redissolved in CH₂Cl₂ and filtered through a short alumina column. After removal of volatiles once again a yellow residue was obtained which was purified by precipitation from CH₂Cl₂–hexane to produce a deep yellow polymer **12** in 94% yield (0.2 g). Calc. for [C₃₇H₅₉SNP₂Pt]_n: C, 59.65; H, 7.98; N, 1.88. Found: C, 54.76; H, 7.35; N, 1.76%.

Trans-[-Pt(PⁿBu₃)₂(C≡C–L2–C≡C)-]_n (13). The diterminal diyne **7** (17.3 mg, 0.06 mmol) was dissolved in 100 ml ¹Pr₂NH and heated at 95 °C for 30 min. *Trans*-[Pt(PⁿBu₃)₂Cl₂] (39.8 mg, 0.06 mmol) was added followed by CuI (2 mg). The reaction mixture was then heated under reflux for a further 24 h, after which all volatile components were removed under reduced pressure. The mixture was worked up as described for **12** to produce a deep yellow rubbery polymer **13** in 75% yield (0.04 g). Calc. for [C₄₁H₆₁S₂NP₂Pt]_n: C, 55.38; H, 6.92; N, 1.57. Found: C, 53.51; H, 6.64; N, 1.46%.

X-Ray crystallography

A colourless, plate-like crystal of **4** was obtained by slow evaporation of a CH₂Cl₂–hexane solution. Crystal data were collected on a Rigaku R-Axis II imaging plate diffractometer equipped with a molybdenum rotating anode target, a graphite monochromator, and an Oxford Cryosystems crystal cooling apparatus.

Crystal data: Crystal size 0.40 × 0.25 × 0.10 mm, monoclinic, *P*2₁/*c*, *a* = 17.605(3), *b* = 5.744(2), *c* = 11.719(2) Å, β = 96.42(1)°, *V* = 1177.6 Å³, *Z* = 2, ρ_{calc} = 1.229 Mg m⁻³, μ = 0.337 mm⁻¹, 2θ_{max} = 50.38°, MoK_α radiation, λ = 0.71073 Å, *T* = –93 °C, two orientations: 18 frames, 10° per frame, 100 s per frame and 23 frames, 8° per frame, 80 s per frame, 3641 reflections measured, 1999 (*R*_{int} = 0.0627) independent reflections; data corrected for Lorentz polarization and for absorption (min. and max. transmission 0.877, 0.967); structure solved by direct methods (TEXSAN),³⁶ and refined by full matrix least-squares based on *F*² (SHELXL97).³⁷ 131 parameters. H atoms in calculated positions, *R*₁ = 0.0550 for 1397 observed reflections, and *wR*₂ = 0.137 (all data), *S* = 0.995; final residual electron density 0.268 and –0.306 e Å⁻³. C(12) and N(1) disordered of two sites with 50% occupancies.

CCDC reference number 148650.

See <http://www.rsc.org/suppdata/dt/b2/b201073a/> for crystallographic data in CIF or other electronic format.

Molecular weight determinations

Molar masses were determined by Gel Permeation Chromatography (GPC) using two PL Gel 30 cm, 5 micron mixed C columns at 30 °C running in THF at 1 cm³ min⁻¹ 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).

Photophysical 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 UV lines (334–364 nm) of an Ar⁺ laser; the samples were mounted in a continuous flow helium cryostat. The emission spectra were recorded using a spectrograph with an optical fibre input and a CCD (charge coupled device) parallel detection system (Oriel Instaspec IV).

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