

Structural characterisation of a series of acetylide-functionalised oligopyridines and the synthesis, characterisation and optical spectroscopy of platinum di-yne and poly-yne containing oligopyridyl linker groups in the backbone

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Received 20th November 2001, Accepted 15th January 2002

First published as an Advance Article on the web 26th February 2002

A series of trimethylsilyl-protected bis(ethynyl)oligopyridine derivatives $\text{Me}_3\text{SiC}\equiv\text{C}-\text{R}-\text{C}\equiv\text{C}-\text{SiMe}_3$ ($\text{R} = 2,2'$ -bipyridine-5,5'-diyl (**1a**), 2,2'-bipyridine-6,6'-diyl (**2a**), 2,2':6',2''-terpyridine-6,6''-diyl (**3a**), 4'-phenyl-2,2':6',2''-terpyridine-6,6''-diyl (**4a**)) has been synthesised and **2a–4a** have been characterised by single crystal X-ray crystallography. The corresponding terminal di-yne $\text{H}-\text{C}\equiv\text{C}-\text{R}-\text{C}\equiv\text{CH}$ (**1b–4b**) and their dinuclear platinum(II) complexes *trans*- $[(\text{Et}_3\text{P})_2(\text{Ph})\text{Pt}-\text{C}\equiv\text{C}-\text{R}-\text{C}\equiv\text{C}-\text{Pt}(\text{Ph})(\text{Et}_3\text{P})_2]$ (**1M–4M**) have been characterised spectroscopically and by single-crystal X-ray crystallography for **2M**. Novel platinum(II) poly-yne polymers *trans*- $[\text{Pt}(\text{PBu}^n)_2-\text{C}\equiv\text{C}-\text{R}-\text{C}\equiv\text{C}]_n$ (**1P–4P**) containing the oligopyridyl linker groups in the backbone have been synthesised by the CuI-catalysed dehydrohalogenation polycondensation reaction of **1b–4b** and *trans*- $[(\text{Bu}_3\text{P})_2\text{PtCl}_2]$ in $\text{Pr}^i_2\text{NH}-\text{CH}_2\text{Cl}_2$. The polymeric materials exhibit decreasing thermal stability with increasing number of pyridine units in the linker group. In the absorption and phosphorescence spectra, the platinum(II) poly-yne and di-yne complexes **1P**, **1M** show red shifts whereas the complexes **2P–3P**, **2M–3M** show blue shifts of the S_1 and T_1 states. At room temperature, the phosphorescence spectra indicate some excimer formation whereas at 10 K, only intra-chain emission occurs. The results of the photophysical studies are compared with those obtained for other platinum(II)-containing poly-yne and related organometallic polymers.

Introduction

The last decade has witnessed a great deal of interest in the scientific community towards organometallic polymers that contain transition metals in the main chain.¹ Among the variety of organometallic polymers, conjugated metal-containing poly-yne *trans*- $[(\text{L})_x\text{M}-\text{C}\equiv\text{C}-\text{R}-\text{C}\equiv\text{C}]_n$ ($\text{M} = \text{group 8 or 10 metal}$, $\text{L} = \text{phosphine}$, $x = 4$ for group 8, 2 for group 10 metals; $\text{R} = \text{one of a number of aromatic/heteroaromatic spacer groups}$) constitute a particularly important class of new materials for basic and applied research, since the various acetylide-functionalised ligands can be easily synthesised and the alkynyl ligands can be readily incorporated into metal-containing polymers. These materials show a wide variety of properties useful for application in modern technology. For example, the metal-containing poly-yne provide model systems for the study of some of the photophysical processes that occur in conjugated organic polymers,² are used in optoelectronic devices such as light emitting diodes (LEDs),³ lasers,⁴ photocells,⁵ and field-effect transistors (FETs).⁶ Group 10 metal-containing polymers with a rigid conjugated backbone also show interesting alignment properties in magnetic and electric fields,⁷ fast and reproducible response to relative humidity variations in surface acoustic wave (SAW) sensors,⁸ and molecular orientation even when

spin deposited in thick layers.⁹ Metal-containing poly-yne are also potential candidates as low-dimensional conductors¹⁰ and non-linear optical materials.¹¹

Within this framework, we have been working on the design, synthesis, chemistry and photophysics of 'rigid-rod' platinum(II) poly-yne. The conjugation of the ligand continues through metal centres along the polymer chain since there is mixing of π^* ligand states and the lowest unoccupied metal 6p states.¹² The inclusion of platinum(II) in the polymer chain introduces sufficient spin-orbit coupling to allow light emission from the triplet excited state of the conjugated ligand.^{13–15} For commercial exploitation of these materials and for controlled application-oriented synthesis, a thorough understanding of the structure–property relationship is necessary such that suitable modifications of the chemical structures may fine-tune the electronic properties of the polymers.

We have recently investigated two series of platinum(II)-containing poly-yne. In one series the conjugated spacer R is based on phenylene derivatives where little donor–acceptor interaction occurs between the phenylene ring and platinum centres along the rigid backbone of the organometallic polymers.¹⁶ In the second series the spacer unit is based on electron-rich oligothiényl rings which act as electron donors and the platinum moieties act as electron acceptors.^{14,17} In an extension

to this work, we have investigated a series of platinum(II) di-ynes and poly-ynes with oligopyridyl linker groups in the backbone; the di-ynes can be considered as the molecular models and building blocks for the high molecular weight poly-ynes. The aim of the investigation is to establish in what way the insertion of an oligopyridyl spacer unit affects the optical and electronic properties of the platinum(II) poly-ynes compared to related organometallic polymers.

A few recent reports have concerned the incorporation of pyridine and its derivatives into conjugated polymeric frameworks.¹⁸ Compared to benzene or thiophene, pyridine is electron-deficient; consequently, the derived polymers have increased electron affinity and improved electron-transporting properties.¹⁹ The increase in the number of pyridine units may enhance the electron-accepting ability of the polymers making the oligopyridyl-containing polymers more suited for application in electronic devices. It was therefore envisaged that oligopyridines would constitute an interesting class of new spacer units in the novel platinum(II) poly-yne systems. There is also considerable interest in the solid-state structures of the polymeric materials because of evidence for interchain interactions that influence their electronic properties. In this context an analysis of the intermolecular interactions in the crystal structures of the ligand systems and of the model complexes may lead to a better understanding of the interactions in the polymers.²⁰ Bearing these concepts in mind we set out to synthesize a series of bis(acetylide)-functionalised oligopyridines which can give dimeric and polymeric platinum(II) complexes. Here, we report the structural characterization of a series of bis(trimethylsilylethynyl)oligopyridine ligands **2a–4a** and the synthesis, characterisation and optoelectronic properties of a series of platinum(II) poly-ynes containing oligopyridyl linker groups. The synthesis and characterisation of related dimeric model complexes are also reported. The crystal structure of a selected diplatinum complex **2M** is also described.

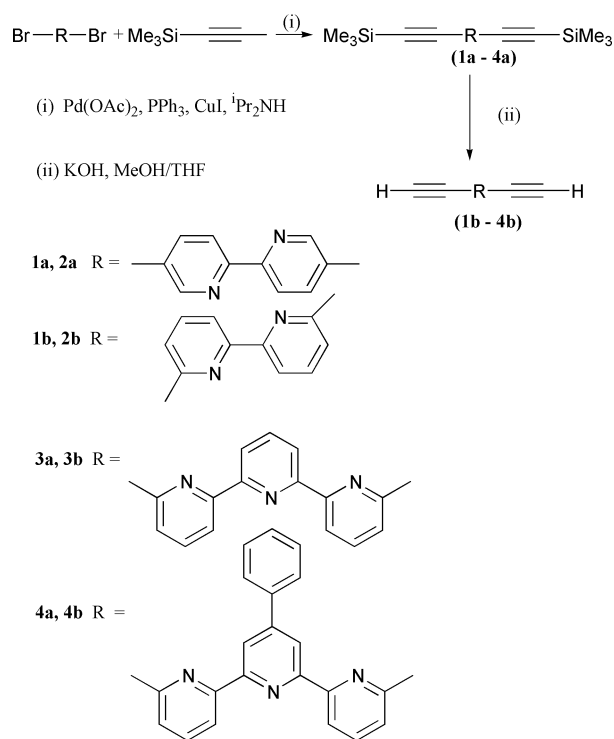
Results and discussion

Syntheses

The bis(ethynyl)oligopyridine ligands were synthesised by a sequence of coupling and proto-desilylation reactions. The trimethylsilyl-protected ligand precursors **1a–4a** were synthesised by adopting improved procedures²¹ for the palladium-catalyzed coupling of trimethylsilylethyne with dibromo-substituted oligopyridines (Scheme 1). The protected di-ynes are indefinitely stable towards light and air and were fully characterised by IR, NMR (¹H and ¹³C) spectroscopy, EI mass spectrometry as well as by satisfactory elemental analyses and single crystal X-ray crystallography for **2a–4a**.

Conversion of the protected ligand precursors into their terminal di-ynes **1b–4b** was accomplished by smooth removal of the trimethylsilyl protecting groups with dilute aqueous KOH in MeOH–THF (Scheme 1). The products were purified by silica column chromatography and characterised by elemental analyses and by IR, NMR (¹H and ¹³C) spectroscopy and mass spectrometry. The terminal di-ynes are relatively stable at low temperature in the absence of light and air; however, in the presence of light and/or air they undergo a slow colour change. Long storage times at ambient temperature and under aerobic condition led to the formation of some insoluble material (<5%), which was presumed to be a polymerisation product.

The synthesis of the platinum(II) di-yne complexes is outlined in Scheme 2 and that of the platinum(II) poly-yne polymers is outlined in Scheme 3. The reaction of each of the di-ynes with two equivalents of the platinum complex *trans*-[Pt(Ph)(PEt₃)₂Cl], in CH₂Cl₂–NHPr^t₂, in the presence of CuI, at room temperature, readily affords the dimeric complexes *trans*-[(Et₃P)₂(Ph)Pt–C≡C–R–C≡C–Pt(Ph)(Et₃P)₂] (**1M–4M**), in good yields. The related mono-nuclear Pt(II) σ-acetylide complexes



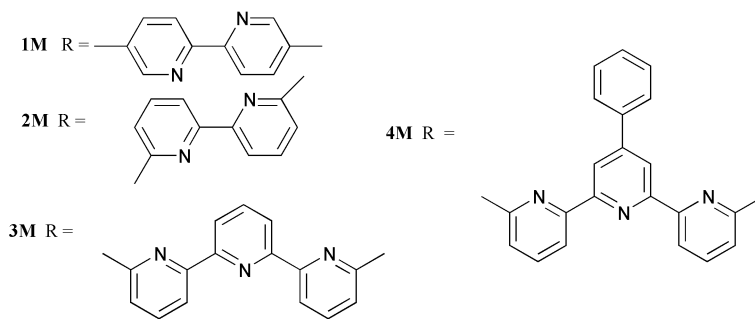
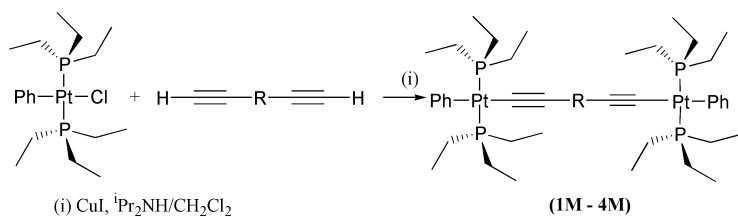
trans-[Pt(PBu₃)₂{C≡C–R'}₂] (R' = 2,2'-bipyridine-4-yl or 2,2':6',2''-terpyridine-4-yl) have been reported previously.²²

The corresponding polymers *trans*-[Pt(PBu₃)₂–C≡C–R–C≡C–]_n (**1P–4P**) were prepared by the reaction of one equivalent of *trans*-[(Bu₃P)₂PtCl₂] with the appropriate di-yne under similar reaction conditions. Purification of the dimers **1M–4M** was accomplished by silica column chromatography while the polymers **1P–4P** were purified by alumina column chromatography followed by precipitation from dichloromethane solution into methanol.

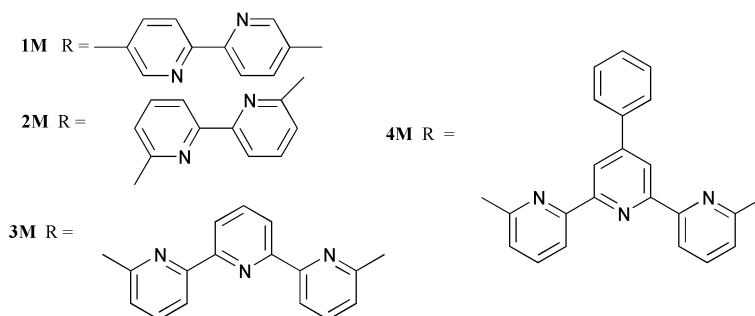
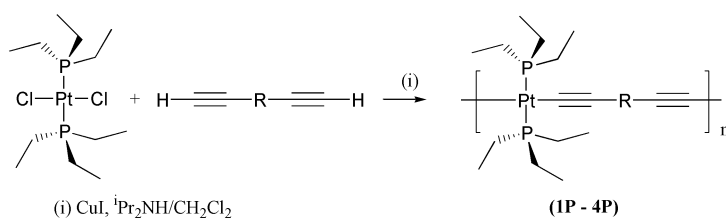
Spectroscopic characterisation

Systematic characterisation of the platinum(II) di-ynes and poly-ynes was achieved by spectroscopic methods (IR, ¹H, ¹³C and ³¹P NMR). The IR spectra of the Pt(II) di-ynes and poly-ynes show a single sharp ν_{C≡C} absorption at around 2095 cm⁻¹ consistent with a *trans*-configuration of the acetylenic units around the Pt(II) centre. The ν_{C≡C} values for the terminal di-ynes **1b–4b** (2107 cm⁻¹) are much lower than those of the trimethylsilyl-substituted di-ynes **1a–4a** (2157–2159 cm⁻¹). The fact that terminal ethynes (HC≡C–R) have lower ν_{C≡C} frequencies than their protected counterparts RC≡C–R (by about 50 cm⁻¹ in this case) is well established.²³ Furthermore, the platinum(II)-containing compounds display lower ν_{C≡C} values than those in the corresponding trimethyl-substituted or terminal di-ynes. This may be attributed to either metal-yne π-back bonding or the M^{δ+}–C^{δ-} polarity.²⁴ The ¹H and ¹³C NMR spectra of all the compounds exhibit the expected signals for the systems including resonances for the acetylenic carbons. The single resonance in the ³¹P NMR spectra of all the platinum(II) dimers and polymers confirms the *trans* arrangement of the phosphine ligands. From the ³¹P{¹H} NMR spectral data, it is clearly seen that the ¹J_{Pt–P} coupling constants for the di-ynes **1M–4M** are larger than those of the poly-ynes **1P–4P** by about 300 Hz.

The mass spectrometric results confirm the molecular assignments for the organic ligands and the platinum(II) di-yne complexes. The weight-average molecular weights (M_w) of the poly-ynes **1P–4P** indicate high degree of polymerisation. The number average molecular weight (M_n) values are in the range of 60 000 to 87 000 g mol⁻¹, corresponding to between 75 and 91 repeating units per chain. The polydispersity (M_w/M_n) varies



Scheme 2



Scheme 3

between 1.3 and 1.8. The molecular weights should be viewed with caution in view of the difficulties associated with utilizing gel permeation chromatography (GPC) for rigid-rod polymers. GPC does not give absolute values of molecular weights but provides a measure of hydrodynamic volume. Rod-like polymers in solution possess very different hydrodynamic properties than flexible polymers. Therefore, calibration of the GPC with PS standards is likely to inflate the values of the molecular weights of the poly-yne to some extent. However, the lack of discernable resonances that could be attributed to end groups in the NMR spectra provides support for the view that there is high degree of polymerization in these poly-yne.

Optical spectroscopy

Fig. 1 shows the thin film absorption spectra of the platinum(II) di-yne complexes **1M–4M** and the corresponding poly-yne complexes **1P–4P**. We compare these spectra to those reported for analogous platinum(II) di-yne and poly-yne ($\text{R} = \text{pyridine-2,5-diyl}$) with an onset of absorption at 3.3 eV (376 nm) and 3.0 eV (413 nm), respectively.^{12b} In **1P** and **1M**, the alkynyl groups are at the 5,5'-positions and the compounds are fully conjugated, while in **2P–4P** and **2M–4M**, the alkynyl groups occur at the 6,6'- or 6,6''-positions hindering conjugation between the pyridine rings. Correspondingly, for **1P** and **1M** the addition of a second pyridine ring shifts the onset of absorp-

tion to the red compared to the monopyridine analogues by 0.1 and 0.2 eV, respectively, while for **2P–4P** and **2M–4M**, the onset of absorption is blue-shifted compared to the pyridine analogues by 0.3 and 0.1 eV, respectively.

We note that even in the fully conjugated platinum(II) poly-yne containing pyridine-2,5-diyl^{12b} or 2,2'-bipyridine-5,5'-diyl (**1P**), the onset of absorption is not as low as in the analogous platinum(II) poly-yne $\text{trans}[\text{Pt}(\text{P}^n\text{Bu}_3)_2\text{-C}\equiv\text{C-R-C}\equiv\text{C}]_n$ ($\text{R} = \text{thiophene-2,5-diyl}$; 2,2'-bithiophene-5,5'-diyl).¹⁴ This suggests stronger donor-acceptor interactions in the platinum(II) poly-yne containing thiophene spacers than for pyridine spacers.

Comparing the poly-yne with their corresponding di-yne complexes, we find the onset of absorption in **1P** is 0.2 eV lower than in **1M** consistent with the extended conjugation in the poly-yne compared to the di-yne complex. Similarly, the onset of absorption in **2P–4P** is 0.1 eV lower than in **2M–4M** because even in these kinked poly-yne, a conjugated segment is still longer than in the di-yne complexes. In the di-yne complexes, the conjugation extends only from one oligopyridine ring to the end-capping phenylene while the poly-yne is conjugated from one oligopyridine ring over the platinum site to another oligopyridine ring where the conjugation then terminates. The spectral shapes of **1P** and **1M** are very similar to those of the pyridine analogues and the first absorption band at 3–3.5 eV is more intense than the higher-lying bands at and above 4 eV.

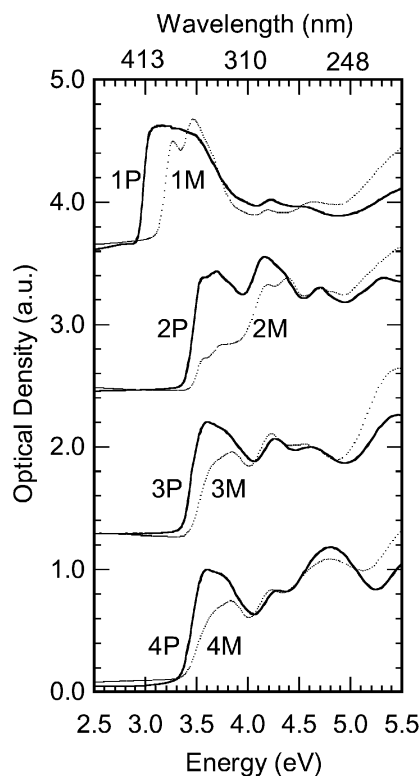


Fig. 1 The absorption spectra of films of the Pt(II) poly-yne complexes **1P–4P** (solid lines) and corresponding Pt(II) di-yne complexes **1M–4M** (dotted lines). The spectra are normalised to unity at the peak of the first absorption band and they are displaced on the vertical axis for clarity.

The first absorption band is mainly due to the $\pi\text{--}\pi^*$ transition in the organic system, possibly with some admixture of metal d orbitals which may alter the overall energy of the transition.^{12b,25} Consequently, the intensity of the first band is reduced in comparison to the higher-lying bands when the conjugation is interrupted by the kinked-spacers in **2P–4P**. The even shorter conjugation length in the di-yne complexes **2M–4M** further reduces the relative intensity of the first band.

The photoluminescence (PL) spectra of the platinum(II) di-yne complexes **1M–3M** and poly-yne complexes **1P–3P**, measured at 300, 200, 100, 50 and 10 K are shown in Fig. 2. We find the two emission bands with the 0–0 vibrational peaks of the 10 K emissions at 2.91 eV (426 nm) and 2.18 eV (569 nm) for **1P** and at 3.10 eV (400 nm) and 2.22 eV (559 nm) for **1M**. The higher energy emission is fluorescence from the same singlet excited state as the first band in the absorption spectra, and is denoted S_1 . We attribute the lower energy band to phosphorescence from a triplet excited state T_1 for the following reasons. The lower energy band has been assigned previously to phosphorescence in related poly-yne and di-yne on the basis of lifetime and photoinduced absorption measurements.^{12a,15,25} It was shown that for Pt-poly-yne with many different spacers R the 0–0 vibrational peak of the phosphorescence always occurs 0.7 eV below the 0–0 vibrational peak of the fluorescence.^{14,15,25} For **1P**, the low energy band is 0.7 eV below the fluorescence, and the 10 K spectrum shows a well-resolved vibronic structure and a spectral shape similar to the phosphorescence in related compounds.^{12b,25} For **1M**, the phosphorescence band is at almost the same energy as in **1P** in agreement with analogous compounds.¹⁵ The extended conjugation in the linear bipyridine-containing compounds shifts the phosphorescence to the red by 0.18 eV compared to the pyridine containing analogues.

For the kinked bi and terpyridine-containing compounds **2P**, **3P**, **2M** and **3M** we observe no fluorescence band but only the phosphorescence band. It is interesting to note that the 0–0

vibrational peak of the phosphorescence band is 0.6 eV below the onset of absorption as for the fully conjugated Pt-poly-yne,^{14,15} even though these compounds have their conjugation disrupted by the unfavourable disposition of the alkyne groups. The reduced conjugation shifts the phosphorescence band to the blue by 0.3 eV compared to the linear bipyridine-containing analogues, so that the 0–0 vibrational peaks of the 10 K emissions are located around 2.68 eV (462 nm). In this class of materials, this is the highest energy at which phosphorescence has been observed so far and correspondingly, according to the energy gap law, it should be associated with the lowest rate of non-radiative decay from the T_1 state at 10 K. Compared to linear bipyridine or *p*-phenylene-containing analogues, the non-radiative decay rate should be reduced by a factor of 10.¹⁵

For Pt-poly-yne and di-yne with a T_1 state at 2.2 eV or higher the lifetime of the T_1 emission is around or above 100 μs .¹⁵ This long lifetime allows for temperature-activated diffusion of the T_1 excitation to lower energy sites such as aggregate sites or excimer sites which are only weakly emissive.²⁶ From Fig. 2, there is some evidence for such diffusion. For example, for **3P**, the spectrum at 10 K has a well-resolved vibronic structure with most weight in the 0–0 vibrational peak at 2.69 eV. This spectral shape is characteristic of Pt-poly-yne.^{12b,15} In contrast, at room temperature the emission is broad and unstructured. The 0–0 vibrational peak has disappeared, and the emission is now centred further red at 2.2 eV. This broad, unstructured, red-shifted low-intensity emission is characteristic of an aggregate or excimer site.²⁶ Similar progressions occur for **1P**, **2P** and, to a weaker extent, for **2M** and **3M**.

In summary, using linear and kinked oligopyridine spacers in the polymer backbone we obtain both red and blue shifts, respectively, of the S_1 and T_1 states in platinum(II) di-yne and poly-yne complexes. The blue shifts are associated with a loss of oscillator strength in the first absorption band. The high energy of the T_1 state obtained by using the non-linear linkage in the oligopyridine is expected to be associated with a low non-radiative decay rate from the T_1 state. This is desirable for applications that harvest the T_1 state for light emission.^{27–29}

Thermal characterisation

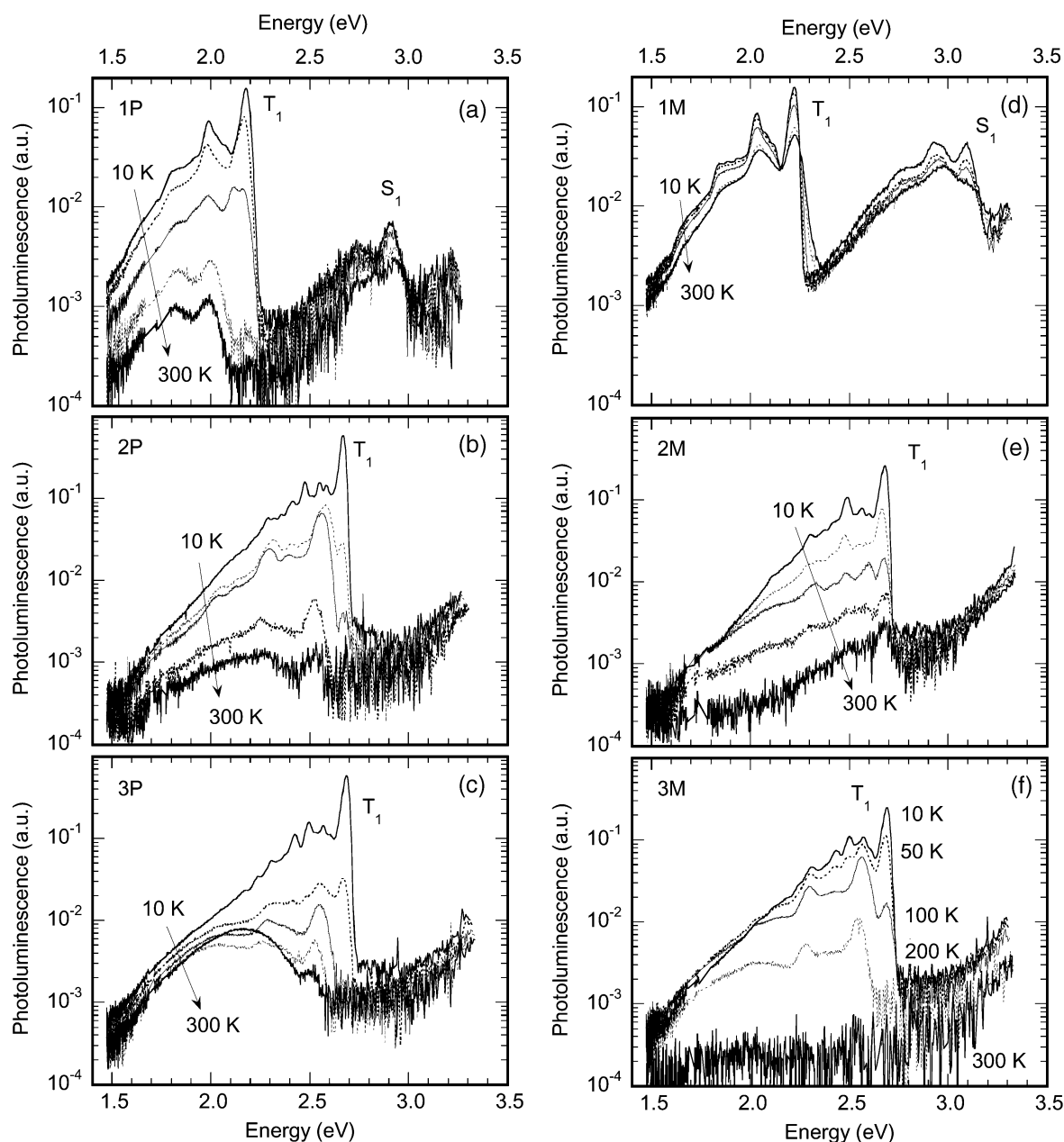
Unlike the platinum(II) poly-yne containing phenylene and thienylene spacers, these materials did not exhibit discernable glass transitions.^{14,16} A clear trend of decreasing decomposition temperature was observed as the number of pyridine units was increased from two to three. The differential thermal analysis (DTA) data varied from material to material: the decomposition peak was an exotherm for **1P** and **2P**, an endotherm for **3P**, and was too broad to be clearly discernable in **4P**. A minor endotherm was also present in **1P** at 151 °C; similar endotherms were observed in thienylene and phenylene analogues at somewhat higher temperatures.^{14,16} The thermogravimetric (TG) data also showed variation. The mass loss in **3P** was particularly sharp and over 50% of the sample mass was lost as the temperature rose from 170 to 250 °C. Onset of decomposition in **4P** was difficult to establish, in that mass loss began almost immediately in most samples tested, and occurred over a broad range of temperature. Decomposition onset was defined as a mass loss of 2%. The results are shown in Table 1.

Structural characterisation

Contents of the unit cell. The four structures reported show a range of packing arrangements within the unit cell, some employing the symmetry of the crystal lattice. 6,6'-Bis(2-trimethylsilyl-1-ethynyl)-2,2'-bipyridine, **2a**, crystallised with two half molecules in the asymmetric unit. The central carbon–carbon bond connecting the pyridine rings in each of the two molecules lies on an inversion centre. The trimethylsilyl group of one of these molecules shows disorder, the SiMe_3 group was refined over two sites with partial occupancies summing to

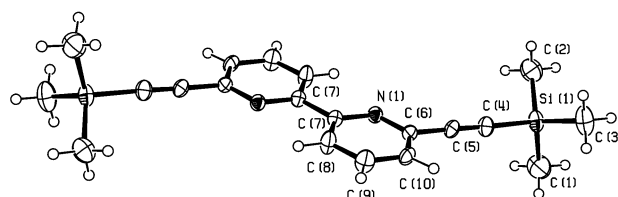
Table 1 Results of thermal analysis; temperatures in °C

Compound	T_{decomp} (onset)	T_{decomp} (peak) DTG	T_{decomp} (peak) DTA
1P	274	325	326
2P	287	343	344
3P	169	236	234
4P	—	212	—

**Fig. 2** The photoluminescence spectra of films of the Pt(II) poly-yne **1P–3P** (a–c) and the corresponding Pt(II) di-yne complexes **1M–3M** (d–f) plotted on a logarithmic scale. All of the photoluminescence spectra give the correct relative intensities at 300 K, 200 K, 100 K, 50 K and 10 K.

unity. 6,6''-Bis(2-trimethylsilyl-1-ethynyl)-2,2':6',2''-terpyridine, **3a**, crystallised with one molecule and 6,6''-bis(2-trimethylsilyl-1-ethynyl)-4'-phenyl-2,2':6',2''-terpyridine, **4a**, with two independent but structurally similar molecules in the asymmetric unit. In contrast to the bis-trimethylsilyl derivative, *trans*-[(Et₃P)₂(Ph)Pt–C≡C–(2,2'-bipyridine-6,6'-diyl)–C≡C–Pt(Ph)(PEt₃)] **2M** crystallises with one independent molecule in the asymmetric unit.

Molecular constitution. The molecular structures of the compounds **2a–4a** and **2M** are shown in Figs. 3–6, respectively,

**Fig. 3** The molecular structure of one of the two independent half molecules of **2a** (with the symmetry related half). Only one orientation of the disordered trimethylsilyl fragment is shown for clarity.

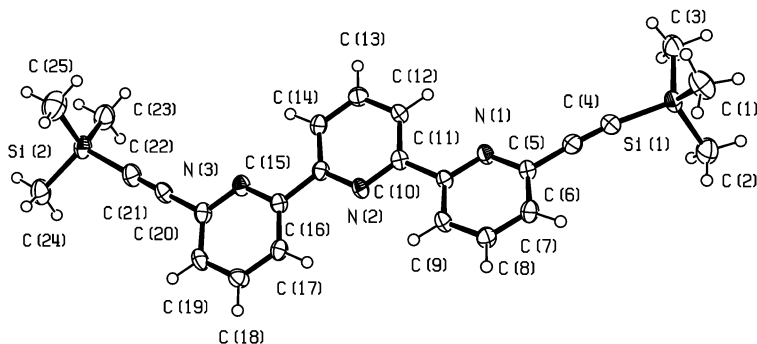


Fig. 4 The molecular structure of **3a** showing the atom numbering scheme adopted.

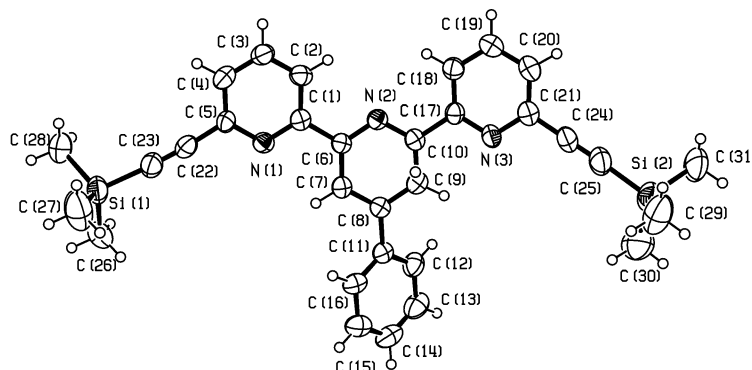


Fig. 5 The molecular structure of one of the two independent molecules of **4a** showing the atom numbering scheme.

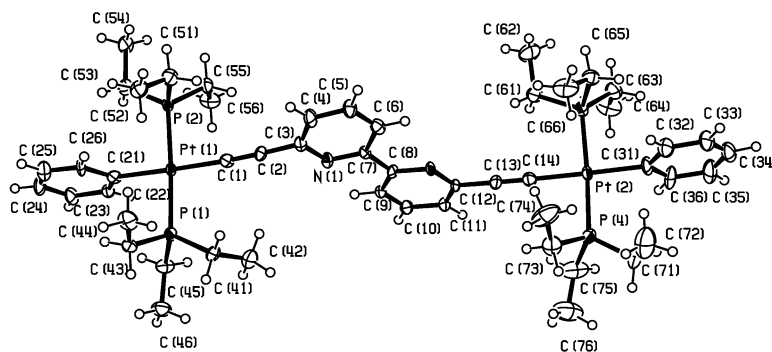


Fig. 6 The molecular structure of **2M** showing the atom numbering scheme.

Table 2 Selected bond lengths [Å] and angles [°] for **2a**

N(1)–C(6)	1.341(4)	N(1)–C(7)	1.344(4)
C(4)–C(5)	1.195(4)	C(5)–C(6)	1.457(4)
C(7)–C(7)#1	1.482(7)	N(11)–C(16)	1.346(4)
N(11)–C(17)	1.346(4)	C(14)–C(15)	1.199(4)
C(15)–C(16)	1.457(4)	C(17)–C(17)#2	1.485(7)
C(6)–N(1)–C(7)	117.7(3)	C(5)–C(4)–Si(1)	177.5(3)
C(4)–C(5)–C(6)	178.9(3)	C(16)–N(11)–C(17)	117.3(3)
C(14)–C(15)–C(16)	178.2(4)	C(15)–C(14)–Si(11)	175.5(4)

Symmetry transformations used to generate equivalent atoms: #1 $-x + 1, -y + 1, -z + 2$; #2 $-x + 2, -y + 2, -z + 2$.

Table 3 Selected bond lengths [Å] and angles [°] for **3a**

C(4)–C(5)	1.206(3)	C(5)–C(6)	1.457(3)
N(1)–C(10)	1.343(3)	N(1)–C(6)	1.345(3)
C(10)–C(11)	1.494(3)	N(2)–C(11)	1.343(3)
N(2)–C(15)	1.343(3)	C(15)–C(16)	1.489(3)
N(3)–C(20)	1.338(3)	N(3)–C(16)	1.347(3)
C(20)–C(21)	1.453(3)	C(21)–C(22)	1.199(3)
C(5)–C(4)–Si(1)	171.6(2)	C(4)–C(5)–C(6)	176.6(2)
C(10)–N(1)–C(6)	117.43(18)	C(11)–N(2)–C(15)	117.72(19)
C(20)–N(3)–C(16)	118.0(2)	C(21)–C(22)–Si(2)	177.2(3)
C(22)–C(21)–C(20)	177.8(3)		

and selected intramolecular bond parameters are listed in Tables 2–5.

The nitrogen–carbon bond lengths in **2a**, **3a** and **4a** are in the range of 1.331(3)–1.351(5) Å. These bond lengths are similar to those in 6,6'-bis(2-phenyl-1-ethynyl)-2,2'-bipyridine (= ph-A-bipy), (1.337(4) and 1.351(4) Å),³⁰ or in 2,2':6',2'':6'',2'''-quaterpyridine (1.333(2)–1.340(2) Å).³¹ The C–N–C angles in **2a–4a** (116.9(4), 117.7(3)°) are equivalent to those in the uncoordinated ph-A-bipy compound (117.6(3)°)³⁰ or in quater-

pyridine (117.3(2), 118.5(1)°).³¹ The carbon–carbon bonds between the pyridine rings in **2a–4a** (1.482(7)–1.496(6) Å) are typical for a single bond between sp²-hybridized carbons, as in quaterpyridine (1.485(2), 1.482(3) Å),³¹ in ph-A-bipy (1.496(6) Å)³⁰ or in terpy (1.474(9)–1.479(9) Å).³² The carbon–carbon bonds between the sp²-hybridized pyridine ring and the sp-hybridized ethynyl group are shorter (1.447(7)–1.457(4) Å in **2a–4a**). These bond lengths are also in good correspondence with those in ph-A-bipy (1.438(5) Å).³⁰ The carbon–carbon triple bonds in **2a–4a** correspond to the expected value

Table 4 Selected bond lengths [Å] and angles [°] for **4a**

N(1)–C(1)	1.344(5)	N(1)–C(5)	1.347(5)
N(2)–C(6)	1.338(5)	N(2)–C(10)	1.343(5)
N(3)–C(17)	1.338(5)	N(3)–C(21)	1.351(5)
N(4)–C(36)	1.343(5)	N(4)–C(32)	1.343(5)
N(5)–C(41)	1.337(5)	N(5)–C(37)	1.349(5)
N(6)–C(48)	1.344(5)	N(6)–C(52)	1.345(5)
C(5)–C(22)	1.449(6)	C(1)–C(6)	1.496(6)
C(10)–C(17)	1.492(6)	C(8)–C(11)	1.480(6)
C(21)–C(24)	1.447(7)	C(22)–C(23)	1.204(6)
C(24)–C(25)	1.208(6)	C(39)–C(42)	1.486(6)
C(32)–C(37)	1.491(6)	C(52)–C(55)	1.451(7)
C(36)–C(53)	1.445(7)	C(41)–C(48)	1.495(6)
C(53)–C(54)	1.203(6)	C(55)–C(56)	1.212(6)
C(1)–N(1)–C(5)	117.3(3)	C(6)–N(2)–C(10)	117.8(3)
C(17)–N(3)–C(21)	116.9(4)	C(36)–N(4)–C(32)	117.6(4)
C(41)–N(5)–C(37)	117.0(3)	C(48)–N(6)–C(52)	117.6(3)
C(23)–C(22)–C(5)	176.0(5)	C(22)–C(23)–Si(1)	176.3(4)
C(25)–C(24)–C(21)	178.9(6)	C(24)–C(25)–Si(2)	177.3(5)
C(54)–C(53)–C(36)	177.3(6)	C(53)–C(54)–Si(3)	178.0(5)
C(56)–C(55)–C(52)	176.4(5)	C(55)–C(56)–Si(4)	175.1(5)

Table 5 Selected bond lengths [Å] and angles [°] for **2M**

Pt(1)–P(1)	2.291(2)	Pt(1)–P(2)	2.287(2)
Pt(1)–C(1)	2.022(9)	Pt(1)–C(21)	2.074(9)
Pt(2)–P(3)	2.292(3)	Pt(2)–P(4)	2.286(3)
Pt(2)–C(14)	2.026(10)	Pt(2)–C(31)	2.086(10)
C(1)–C(2)	1.199(13)	C(13)–C(14)	1.195(14)
C(2)–C(3)	1.433(13)	C(12)–C(13)	1.452(12)
C(3)–N(1)	1.352(13)	C(12)–N(2)	1.354(12)
C(3)–C(4)	1.387(15)	C(11)–C(12)	1.398(14)
C(4)–C(5)	1.384(14)	C(10)–C(11)	1.377(13)
C(5)–C(6)	1.396(15)	C(9)–C(10)	1.375(14)
C(6)–C(7)	1.386(13)	C(8)–C(9)	1.387(13)
N(1)–C(7)	1.357(11)	N(2)–C(8)	1.356(11)
C(7)–C(8)	1.498(13)		

(1.195(4)–1.212(6) Å, *cf.* 1.189(5) Å in ph-A-bipy).³⁰ The ethynyl groups in **2a–4a** show the expected linear arrangement (C–C≡C 176.0(5)–178.9(6)°, Si–C≡C 171.6(2)–178.0(5)°, *cf.* 175.5(4), 180.0(4)° in ph-A-bipy).

The bond parameters within the organic spacer groups in the diplatinum complex **2M** does not show any significant differences from those in the organic precursors. The Pt–C(acetylenic) distances lie in the range 2.022(9)–2.026(10) Å, which is within the range of values, 1.96(2)–2.05(2) Å, found in related platinum di-yne complexes when the spacer group consists of one or two thiophene rings.¹⁷ However, the distances are consistently longer than the Pt–C(acetylenic) distances of 1.940(19) and 1.947(17) Å in the *cis*-complex [Pt(C≡CC₆H₄Me)₂(^tBu₂bipy)].³³ The Pt–C(Ph) distances, range 2.074(9)–2.086(10) Å, and the Pt–P(phosphine) distances, range 2.286(7)–2.292(3) Å, are also quite similar to those observed in the thiophene derivatives.¹⁷

Molecular conformation. **2a**, **3a** and **4a**, and the metal complex, **2M**, showed the expected transoid conformation for uncoordinated oligopyridines (torsion angles N–C–C–N 162.2(4)–180.0°).

The bipyridine moiety in the two independent molecules in **2a** is exactly coplanar due to symmetry. The Si–C≡C– groups lie nearly within the bipyridine planes, Si deviation 0.217(8) and –0.141(8) Å. The pyridine rings in the terpyridine moiety of **3a** are also twisted in respect of each other, showing dihedral angles of 14.75(14) and 2.49(16)°. These dihedral angles differ significantly from those in terpyridine (5.1, 7.2°).³⁴ As in **2a**, both Si–C≡C– lie nearly within the plane of the attached pyridine rings (Si deviation 0.223(6) and 0.278(6) Å). The terpyridine moieties in the two independent molecules in **4a** show similar dihedral angles as in **3a** (17.8(2), 3.1(2) and 15.0(2), 2.7(2)°). In contrast to **3a**, the middle pyridine rings in

4a are slightly folded with respect to the N–*p*-C axis: the dihedral angle between the two planes (N–*o*/*m*/*p*-C) in **4a** are 3.5(4) and 2.8(4)°, *cf.* 0.8(3)° in **3a**, the mean deviations from the pyridine ring plane are 0.018 and 0.015 Å in **4a**, *cf.* 0.007 Å in **3**. This is probably due to the phenyl ring attached to the pyridine ring in *para* position in **4a**. The dihedral angles between the phenyl ring plane and the plane of the pyridine ring are 31.35(12) and 30.68(12)°. This twist reduces the steric interactions between the hydrogen atoms attached to the phenyl- and pyridine ring and is notably larger than in 4'-phenyl-2,2':6',2''-terpyridine (10.9°) or the corresponding Ni²⁺ complex (16.7, 17.8°).³⁵

Crystal packing. From the nature of the molecules **2a** to **4a** one could expect to find C–H ⋯ N hydrogen bonds or π ⋯ π interactions in the crystal packing. However, with C ⋯ N distances in the range of 3.522(6)–3.774(6) Å and the C–H ⋯ N angles generally below 150° (see Table 6) the assumption of a hydrogen bond, even a non-classical, is, at least, arguable. A proposed upper value for C ⋯ N distances for this type of hydrogen bond is 3.5 Å,³⁶ *cf.* sum of the van der Waals radii 3.25 Å.³⁷ On the other hand, as the resulting hydrogen bonding motifs are meaningful, we favour the concept of hydrogen bonds over pure van der Waals interactions in the most cases.

Except for **2a** π ⋯ π interactions were present in the crystal packing (interlayer distances smaller than 3.5 Å).³⁸

The molecules in **2a** form criss-crossed, interlinked layers perpendicular to (0 0 1). Within the layers weak C–H ⋯ N hydrogen bonds are present (N ⋯ H 2.80, 2.91 Å). The combination of those two hydrogen bonds forms a chain, motif C₂²(8).³⁹ The smallest interlayer distance between parallel aromatic systems within one of the layers perpendicular to (0 0 1) is 5.581(12) Å.

In **3a** the shortest C ⋯ N distance of 3.624(3) Å (angle 160.2°) is in direction of the stacks parallel to (1 0 0). Those stacks also show small interplanar distances of 2.397(5) Å. Between neighbouring stacks only weak forces are present. The interplanar distance of 5.838(5) Å shows no indication of π ⋯ π interactions. On the other hand, two stacks could be considered to be linked by weak C–H ⋯ N hydrogen bonds (C_{Me} ⋯ N 3.683(3) Å, C_{Ph} ⋯ N 3.761(4) Å, angles 131.7 and 149.4°). These hydrogen bonds show ring motifs [N₁: R₂²(26) and R₂²(12), respectively]. The combination of these hydrogen bonds results in the motif R₂²(13).

In **4a** the combination of π ⋯ π interactions and weak non-conventional hydrogen bonds results in a zigzag ribbon arrangement parallel to the plane with trace (1 1 0) on the *ab*-plane. Within this ribbon small interplanar distances of 3.297(9) and 3.302(10) Å between symmetry related phenyl rings of the two independent molecules could be found. Additionally, those dimers are stabilised by C–H ⋯ N hydrogen bonds [C ⋯ N 3.593(6), 3.554(6) Å, angles 148.9, 143.4°, motif R₂²(20)]. Between two dimers additional, weak, non-conventional hydrogen bonds are present, linking molecules that are not related by symmetry [C ⋯ N 3.522(6), 3.774(6) Å, angles 129.8, 157.1°, combined motif R₂²(18)].

In the crystal structure of **2M** weak C–H ⋯ N hydrogen bonds are also observed (Table 6). However, the presence of the bulky platinum-phosphine groups prevents π ⋯ π interactions from occurring.

Experimental

General procedures

All reactions were performed under a dry nitrogen atmosphere using standard Schlenk or glove box techniques. Solvents were pre-dried and distilled before use by standard procedures.⁴⁰ All chemicals, except where stated otherwise, were obtained from Sigma Aldrich and used as received. The compounds *trans*-[(Ph)(PET₃)₂PtCl]₂,⁴¹ *trans*-[(PBuⁿ)₂PtCl₂],⁴² 6,6'-dibromo-2,2'-bipyridine,⁴³ 5,5'-dibromo-2,2'-bipyridine,⁴⁴

Table 6 C–H...N hydrogen bonds and contacts, not corrected

Structure	Bond	D–H/Å	H...A/Å	D...A/Å	D–H...A/°
2a	C20–H20...N1	0.95	2.80	3.619(4)	144.8
2a	C10–H10...N11 ⁱ	0.95	2.91	3.660(4)	137.0
3a	C8–H8...N1 ⁱⁱ	0.95	2.72	3.624(3)	160.2
3a	C13–H13...N1 ⁱⁱⁱ	0.95	2.98	3.683(3)	131.7
3a	C3–H3...N3 ⁱⁱⁱ	0.98	2.88	3.761(4)	149.4
4a	C14–H14...N1 ^{iv}	0.95	2.75	3.593(6)	148.9
4a	C45–H45...N6 ^v	0.95	2.75	3.554(6)	143.4
4a	C34–H34...N1 ⁱⁱ	0.95	2.84	3.522(6)	129.8
4a	C50–H50...N3 ⁱⁱ	0.95	2.88	3.774(6)	157.1
2M	C43–H43b...N1 ^{vi}	0.99	2.92	3.878(7)	164.2
2M	C62–H62b...N1 ^{vii}	0.98	2.77	3.375(7)	120.7

Symmetry operators: i 1 + x, y, z; ii x – 1, y, z; iii 1 – x, 1 – y, 1 – z; iv –1 – x, 1 – y, 1 – z; v –x, –y, 1 – z; vi x, y + 1, z; vii x, y – 1, z.

6,6'-dibromo-2,2':6',2''-terpyridine, and 6,6'-dibromo-4'-phenyl-2,2':6',2''-terpyridine⁴⁵ were prepared *via* literature procedures. The NMR spectra were recorded on a Bruker WM-250 or AM-400 spectrometer in CDCl₃. The ¹H and ¹³C{¹H} NMR spectra were referenced to solvent resonances and ³¹P{¹H} NMR spectra were referenced to external trimethylphosphite. Infrared spectra were recorded as CH₂Cl₂ solutions, in a NaCl cell, on a Perkin-Elmer 1710 FT-IR spectrometer, mass spectra on a Kratos MS 890 spectrometer by the electron impact (EI) and fast atom bombardment (FAB) techniques. Microanalyses were performed in the University Chemical Laboratory, University of Cambridge. Preparative TLC was carried out on commercial Merck plates with a 0.25 mm layer of silica. Column chromatography was performed either on Kieselgel 60 (230–400 mesh) silica gel or alumina (Brockman Grade II–III).

Optical characterisation

Thin films of the poly-ynes **1P–4P** and of the dinuclear complexes **1M–4M** were spun from dichloromethane solution onto quartz substrates using a conventional photoresist spin-coater. Films were typically 100–150 nm in thickness as measured on a Dektak profilometer. The optical absorption was measured with a Hewlett-Packard ultraviolet-visible (UV-VIS) spectrometer. Measurements of photoluminescence (PL) were made with the sample in a continuous-flow Helium cryostat. The temperature was controlled with an Oxford-Intelligent temperature controller-4 (ITC-4) and a calibrated silicon diode adjacent to the sample. For PL measurements, excitation was provided by the UV lines (334–365 nm) of a continuous wave (CW) Argon ion laser. Typical intensities used were a few mW mm⁻². The emission spectra were recorded using a spectrograph with an optical fibre input coupled to a cooled charge coupled device (CCD) array (Oriel Instaspec IV).

X-Ray crystallography

For crystal data, see Table 7. *Data collection and reduction*: the crystals were mounted in inert oil on a glass fibre. Data were measured using Cu-K α radiation ($\lambda = 1.54178$ Å) with a Stoe STADI4 diffractometer (**2a**), or Mo-K α radiation ($\lambda = 0.71073$ Å) with a Nonius Kappa area detector (**3a**, **4a**), or a Bruker AXS SMART CCD area detector on Station 9.8 of the CLRC Daresbury Laboratory (**2M**), all fitted with an Oxford Cryostream low-temperature attachment. *Structure solution and refinement*: structures were solved by direct methods and subjected to full-matrix least-squares refinement on F^2 (program SHELXL-97).⁴⁶ All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included using rigid methyl groups or a riding model.

CCDC reference numbers 174647–174650.

See <http://www.rsc.org/suppdata/dt/b1/b110658a/> for crystallographic data in CIF or other electronic format.

Thermal characterizations

Thermal analysis (DTA, and TG) of **1P–4P** was performed simultaneously in a Stanton-Redcroft model STA-780 Simultaneous Thermal Analyser under flowing N₂. Sample masses were ~1 mg packed with ~2 mg Al₂O₃ in open Inconel crucibles. The reference crucible contained Al₂O₃. Samples were heated at 10 °C min⁻¹ to 465 °C. The thermocouple readings were calibrated using a series of DTA standard materials: KNO₃, In, Sn, Ag₂SO₄ and K₂SO₄ as well as Pb and Al as secondary standards, using the same heating rates as the samples.

Molecular weight measurements

Molar masses were determined by GPC⁴⁷ using two PL Gel 30 cm, 5 μ m 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 molecular weights (referred to GPC LS).

Ligand synthesis

Bis(trimethylsilylethynyl)oligopyridines **1a–4a** were prepared by following a general procedure outlined below for **1a**.

5,5'-Bis(trimethylsilylethynyl)-2,2'-bipyridine (1a). To a solution of 5,5'-dibromo-2,2'-bipyridine (2.0 g, 6.37 mmol) in diisopropylamine–THF (60 cm³, 1 : 1 v/v) under nitrogen was added a catalytic mixture of CuI (15 mg), Pd(OAc)₂ (16 mg) and PPh₃ (50 mg). The solution was stirred for 20 min at 50 °C and then trimethylsilylethyne (2.24 cm³, 15.92 mmol) was added and the mixture stirred for another 20 min. The temperature was then raised to 75 °C and the reaction left under reflux with stirring for 20 h. The completion of the reaction was determined by silica TLC and IR spectroscopy. The solution was allowed to cool to room temperature, filtered and the solvent mixture was removed. The residue was subjected to silica column chromatography using hexane–CH₂Cl₂ (1 : 2, v/v) as eluent to afford **1a** as pale yellow needles (1.77 g, 80% yield). IR (CH₂Cl₂): ν /cm⁻¹ 2159 (–C \equiv C–). ¹H NMR (250 MHz, CDCl₃): δ 8.70 (dd, $J = 2.0, 0.7$ Hz, 2H, H_{6,6'}), 8.34 (t, $J = 8.2, 0.76$ Hz, 2H, H_{3,3'}), 7.84 (dd, $J = 8.1, 2.1$ Hz, 2H, H_{4,4'}), 0.27 (s, 18H, SiMe₃ \times 2). ¹³C NMR (100 MHz, CDCl₃): δ 154.18 (C_{2,2'}), 152.04 (C_{6,6'}), 139.73 (C_{3,3'}), 120.44 (C_{4,4'}), 120.32 (C_{5,5'}), 101.75, 99.42 (C \equiv C), –0.18 (SiMe₃). EI-mass spectrum: m/z 349 (M⁺). Calc. for C₂₀H₂₄Si₂N₂: C, 68.94; H, 6.94; N, 8.04. Found: C, 68.88; H, 6.91; N, 7.98%.

6,6'-Bis(trimethylsilylethynyl)-2,2'-bipyridine (2a). Off-white solid (72% yield). IR (CH₂Cl₂): ν /cm⁻¹ 2159 cm⁻¹ (–C \equiv C–). ¹H NMR (250 MHz, CDCl₃): δ 8.40 (2H, dd, $J = 8.0, 1.0$ Hz, H_{3,3'}),

Table 7 Crystallographic data

Compound	2a	3a	4a	2M
Formula	C ₂₀ H ₂₄ N ₂ Si ₂	C ₂₅ H ₂₇ N ₃ Si ₂	C ₃₁ H ₃₁ N ₃ Si ₂	C ₅₀ H ₇₆ N ₂ P ₄ Pt ₂
<i>M_r</i>	348.59	425.68	501.77	1219.19
Crystal habit	Colourless block	Colourless prism	Colourless plate	Yellow needle
Crystal size/mm	0.40 × 0.30 × 0.20	0.28 × 0.16 × 0.07	0.20 × 0.18 × 0.06	0.10 × 0.02 × 0.01
Crystal system	Monoclinic	Triclinic	Triclinic	Monoclinic
Space group	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 1̄	<i>P</i> 1̄	<i>P</i> 2 ₁ / <i>c</i>
<i>a</i> /Å	11.024(3)	6.3543(8)	11.389(6)	23.540(7)
<i>b</i> /Å	10.645(4)	10.844(2)	13.353(11)	9.389(3)
<i>c</i> /Å	17.768(4)	17.722(4)	19.540(16)	25.662(7)
<i>α</i> ^o	90	84.891(8)	94.69(3)	90
<i>β</i> ^o	92.68(3)	86.268(10)	99.71(5)	116.005(14)
<i>γ</i> ^o	90	82.049(10)	90.48(5)	90
<i>U</i> /Å ³	2082.8(11)	1202.8(4)	2918(4)	5097(3)
<i>Z</i>	4	2	4	4
<i>μ</i> /mm ⁻¹	1.556	0.163	0.145	5.642
<i>T</i> ^o C	-93	-123	-93	-123
2 θ _{max} ^o	110	55	45	50
Wavelength/Å	1.54178	0.71073	0.71073	0.68980
No. of reflections measured	4267	7566	13311	26831
Independent	2016	5373	7470	9734
<i>R</i> _{int}	0.017	0.041	0.064	0.069
Parameters	223	277	649	535
Restraints	18	14	0	0
<i>wR</i> 2 (<i>F</i> ² , all refl.)	0.142	0.1248	0.209	0.1508
<i>R</i> 1 [<i>F</i> > 2 σ (<i>F</i>)]	0.052	0.056	0.070	0.0611
GoF	1.079	0.937	1.024	1.286

7.74 (2H, t, *J* = 7.80 Hz, H_{4,4'}), 7.45 (2H, dd, *J* = 7.7, 1.0 Hz, H_{5,5'}), 0.28 (18H, s, SiMe₃ × 2). ¹³C NMR (100 MHz, CDCl₃): δ 155.70 (C_{2,2'}), 142.34 (C_{6,6'}), 136.91 (C_{3,3'}), 127.77 (C_{4,4'}), 121.09 (C_{5,5'}), 103.95, 94.51 (C≡C), -0.31 (SiMe₃). EI-mass spectrum: *m/z* 348 (M⁺). Calc. for C₂₀H₂₄Si₂N₂: C, 68.94; H, 6.94; N, 8.04. Found: C, 69.10; H, 6.89; N, 8.07%.

6,6'-Bis(trimethylsilylethynyl)-2,2':6',2''-terpyridine (3a). Off-white solid (75% yield). IR (CH₂Cl₂): *v*/cm⁻¹ 2159 (C≡C-). ¹H NMR (250 MHz, CDCl₃): δ 8.53 (dd, *J* = 8.0, 0.9 Hz, 2H, H_{3,3'}), 8.51 (d, *J* = 7.8 Hz, 2H, H_{3,5'}), 7.92 (t, *J* = 7.8 Hz, 1H, H₄), 7.78 (t, 2H, *J* = 8.0 Hz, H_{4,4'}), 7.49 (dd, 2H, *J* = 7.8, 0.9 Hz, H_{5,5'}), 0.28 (s, 18H, SiMe₃ × 2). ¹³C NMR (100 MHz, CDCl₃): δ 156.29 (C_{2,6'}), 154.38 (C_{2,2'}), 142.30 (C_{6,6'}), 137.67 (C₄), 136.69 (C_{4',4'}), 127.41 (C_{5,5'}), 121.67 (C₅), 120.42 (C_{3,3'}), 103.84, 94.34 (C≡C), -0.10 (SiMe₃). EI-mass spectrum: *m/z* 426 (M⁺). Calc. for C₂₅H₂₇N₃Si₂: C, 70.57; H, 6.40; N, 9.88. Found: C, 70.42; H, 6.48; N, 9.91%.

6,6'-Bis(trimethylsilylethynyl)-4'-phenyl-2,2':6',2''-terpyridine (4a). White solid (90% yield). IR (CH₂Cl₂): *v*/cm⁻¹ 2159 (C≡C-). ¹H NMR (250 MHz, CDCl₃): δ 8.74 (s, 2H, H_{3,5'}), 8.56 (dd, *J* = 8.0, 1.0 Hz, 2H, H_{3,3'}), 7.88 (td, *J* = 6.7, 1.6 Hz, 2H, H_{ortho} for Ph), 7.80 (t, *J* = 8.0 Hz, 2H, H_{4,4'}), 7.50 (dd, *J* = 8.0, 1.0 Hz, 2H, H_{5,5'}), 7.4-7.5 (m, 3H, H_{meta} and *para* for Ph), 0.39 (s, 18H, SiMe₃ × 2). ¹³C NMR (100 MHz, CDCl₃): δ 156.41 (C_{2,6'}), 155.00 (C_{2,2'}), 150.43 (C₄), 142.33 (C_{6,6'}), 138.42 (C_{para} for Ph), 136.80 (C_{4',4'}), 128.79 (C_{ortho} for Ph), 127.56 (C_{5,5'}), 127.35 (C_{meta} for Ph), 121.08 (C₅), 120.77 (C_{3,3'}), 103.96, 94.47 (C≡C), -0.30 (CH₃). EI-mass spectrum: *m/z* 501 (M⁺). Calc. for C₃₁H₃₁N₃Si₂: C, 74.22; H, 6.23; N, 8.38. Found: C, 74.19; H, 6.27; N, 8.29%.

Bis(ethynyl)oligopyridines **1b-4b** were prepared by the general procedure outlined below for **1b**.

5,5'-Bis(ethynyl)-2,2'-bipyridine (1b). 5,5'-Bis(trimethylsilylethynyl)-2,2'-bipyridine (**1a**) (0.696 g, 2.0 mmol) was protodesilylated in THF-methanol (50 cm³, 4 : 1, v/v) using aqueous KOH (0.36 g, 6.6 mmol in 1 cm³ water). The reaction mixture was stirred at room temperature for 2 h during which time IR and TLC showed that all protected compound had been converted to the terminal alkyne. The solvent mixture was then removed and the residue was dissolved in CH₂Cl₂ and subjected

to column chromatography on silica using hexane-CH₂Cl₂ (1 : 1, v/v) as eluent to afford a white solid identified as **1b** (0.31 g, 76%). IR(CH₂Cl₂): *v*/cm⁻¹ 3300 (C≡C-H), 2107 (C≡C-). ¹H NMR (250 MHz, CDCl₃): δ 8.74 (dd, *J* = 2.0 Hz, 2H, H_{6,6'}), 8.36 (t, *J* = 8.2 Hz, 2H, H_{3,3'}), 7.88 (dd, *J* = 8.2, 2.1 Hz, 2H, H_{4,4'}), 3.16 (s, 2H, C≡NC-H). ¹³C NMR (100 MHz, CDCl₃): δ 155.66 (C_{2,2'}), 152.30 (C_{6,6'}), 140.60 (C_{3,3'}), 120.79 (C_{4,4'}), 120.42 (C_{5,5'}), 83.14 (C≡C). EI-mass spectrum: *m/z* 204 (M⁺). Calc. for C₁₄H₈N₂: C, 82.33; H, 3.95; N, 13.72. Found: C, 82.29; H, 3.98; N, 13.69%.

6,6'-Bis(ethynyl)-2,2'-bipyridine (2b). White solid, 60% yield. IR (CH₂Cl₂): *v*/cm⁻¹ 2107 (C≡C-), 3299 (C≡C-H). ¹H NMR (250 MHz, CDCl₃): δ 8.46 (dd, 2H, *J* = 8.0, 0.99 Hz, H_{3,3'}), 7.76 (t, 2H, *J* = 7.81 Hz, H_{4,4'}), 7.50 (dd, 2H, *J* = 7.68, 1.03 Hz, H_{5,5'}), 3.16 (s, 2H, C≡C-H). ¹³C NMR (100 MHz, CDCl₃): δ 155.66 (C_{2,2'}), 141.60 (C_{6,6'}), 137.11 (C_{3,3'}), 127.79 (C_{4,4'}), 121.32 (C_{5,5'}), 82.94 (C≡C). EI-mass spectrum: *m/z* 204 (M⁺). Calc. for C₁₄H₈N₂: C, 82.33; H, 3.95; N, 13.72. Found: C, 82.28; H, 3.99; N, 13.76%.

6,6'-Bis(ethynyl)-2,2':6',2''-terpyridine (3b). White solid, 65% yield. IR(CH₂Cl₂): *v*/cm⁻¹ 3298 (C≡C-H), 2105 (C≡C-). ¹H NMR (250 MHz, CDCl₃): δ 8.56 (dd, *J* = 8.0, 1.0 Hz, 2H, H_{3,3'}), 8.54 (d, 2H, *J* = 7.9 Hz, H_{3,5'}), 7.95 (t, *J* = 7.9 Hz, 1H, H₄), 7.81 (t, 2H, *J* = 8.0 Hz, H_{4,4'}), 7.51 (2H, dd, *J* = 7.8, 0.9 Hz, H_{5,5'}), 3.2 (s, 2H, C≡C-H). EI-mass spectrum: *m/z* 28 (M⁺). Calc. for C₁₉H₁₁N₃: C, 81.12; H, 3.94; N, 14.94. Found: C, 81.09; H, 3.99; N, 14.98%.

6,6'-Bis(ethynyl)-4'-phenyl-2,2':6',2''-terpyridine (4b). White solid, 85% yield. IR(CH₂Cl₂): *v*/cm⁻¹ 3298 (C≡C-H), 2106 (C≡C-). ¹H NMR (250 MHz, CDCl₃): δ 8.75 (s, 2H, H_{3,5'}), 8.61 (dd, *J* = 8.0, 1.0 Hz, 2H, H_{3,3'}), 7.86 (td, 2H, *J* = 6.7, 1.6 Hz, H_{ortho} for Ph), 7.83 (2H, t, *J* = 8.0 Hz, H_{4,4'}), 7.52 (2H, dd, *J* = 8.0, 1.0 Hz, H_{5,5'}), 7.46-7.44 (3H, m, H_{meta} and *para* for Ph), 3.20 (s, 2H, C≡C-H). ¹³C NMR (100 MHz, CDCl₃): δ 156.61 (C_{2,6'}), 155.02 (C_{2,2'}), 150.63 (C₄), 141.66 (C_{6,6'}), 138.33 (C_{para} for Ph), 136.98 (C_{4',4'}), 128.94 (C_{ortho} for Ph), 127.61 (C_{5,5'}), 127.46 (C_{meta} for Ph), 121.19 (C₅), 119.69 (C_{3,3'}), 83.12 (C≡C). EI-mass spectrum: *m/z* 357 (M⁺). Calc. for C₂₅H₁₅N₃: C, 84.01; H, 4.23; N, 11.76. Found: C, 83.92; H, 4.18; N, 11.81%.

Complex preparations

The di-yne complexes **1M–4M** were synthesized by the general procedure outlined below for **1M**.

trans-[(Ph)(Et₃P)₂Pt–C≡C–R–C≡C–Pt(PEt₃)₂(Ph)] (R = 2,2'-bipyridine-5,5'-diyl, **1M).** To a stirred solution *trans*-[(PEt₃)₂(Ph)-PtCl] (0.543 g, 1.0 mmol) and 5,5'-bis(ethynyl)-2,2'-bipyridine (**1b**) (0.102 g, 0.50 mmol) in CH₂Cl₂-iPr₂NH (50 cm³, 1 : 1 v/v) under nitrogen was added a catalytic amount (~5 mg) of CuI. The yellow solution was stirred at room temperature for 15 h, after which all volatile components were removed under reduced pressure. The residue was dissolved in CH₂Cl₂ and passed through a silica column eluting with hexane-CH₂Cl₂ (1 : 1, v/v). Removal of the solvents *in vacuo* gave the title complex as off-white solid (0.43 g, 70%). IR (CH₂Cl₂): ν/cm⁻¹ 2093 (–C≡C–). ¹H NMR (250 MHz, CDCl₃): δ 8.57 (d, 2H, *J* = 7.8, 0.99 Hz, H_{6,6'}), 8.18 (dd, 2H, *J* = 8.2, 0.76 Hz, H_{3,3'}), 7.60 (dd, 2H, *J* = 8.2, 2.1 Hz, H_{4,4'}), 7.31 (t, 4H, *J* = 7.7 Hz, H_{ortho} Ph), 6.95 (t, 4H, *J* = 7.4 Hz, H_{meta} Ph), 6.80 (t, 4H, *J* = 7.3 Hz, H_{para} Ph), 1.75 (m, 24H, PCH₂), 1.10 [(t, 36H, P(CH₂)CH₃)]. ¹³C NMR (100 MHz, CDCl₃): δ 155.80 (C_{2,2'}), 151.46 (C_{6,6'}), 139.02 (C_{3,3'}), 137.94–121.37 (C Ph), 120.14 (C_{4,4'}), 119.80 (C_{5,5'}), 117.13, 107.41 (C≡C), 15.08 (PCH₂CH₃), 8.00 (CH₃). ³¹P{¹H} NMR (101.3 MHz, CDCl₃): δ –131.17, ¹J_{Pt-P} = 2677 Hz. FAB-MS: 1219 (M⁺). Calc. for C₅₀H₇₆N₂P₄Pt₂: C, 49.25; H, 6.28; N, 2.30. Found: C, 49.18; H, 6.34; N, 2.28%.

trans-[(Ph)(Et₃P)₂Pt–C≡C–R–C≡C–Pt(PEt₃)₂(Ph)] (R = 2,2'-bipyridine-6,6'-diyl, **2M).** Pale yellow solid (70% yield). IR (CH₂Cl₂): ν/cm⁻¹ 2095 (–C≡C–). ¹H NMR (250 MHz, CDCl₃): δ 8.22 (d, 2H, *J* = 7.8, 0.99 Hz, H_{3,3'}), 7.56 (t, 2H, *J* = 7.81 Hz, H_{4,4'}), 7.33 (d, 4H, *J* = 7.0 Hz, H_{ortho} for Ph), 7.16 (d, 2H, *J* = 7.6 Hz, H_{5,5'}), 6.87 (t, 4H, *J* = 7.4 Hz, H_{meta} Ph), 6.80 (t, 2H, *J* = 7.4 Hz, H_{para} Ph), 1.79 (m, 24H, PCH₂), 1.12 [(t, 36H, P(CH₂)CH₃)]. ¹³C NMR (100 MHz, CDCl₃): δ 155.93 (C_{2,2'}), 146.72 (C_{6,6'}), 139.13 (C_{3,3'}), 135.83 (C Ph), 127.32 (C_{4,4'}), 125.67 (C Ph), 121.29 (d, C_{5,5'}), 118.13 (C Ph), 117.47, 110.40 (C≡C), 13.62 (PCH₂CH₃), 8.20 (CH₃). ³¹P{¹H} NMR (101.3 MHz, CDCl₃): δ –131.10, ¹J_{Pt-P} = 2657 Hz. FAB-MS: 1219 (M⁺). Calc. for C₅₀H₇₆N₂P₄Pt₂: C, 49.25; H, 6.28; N, 2.30. Found: C, 49.18; H, 6.34; N, 2.26%.

trans-[(Ph)(Et₃P)₂Pt–C≡C–R–C≡C–Pt(PEt₃)₂(Ph)] (R = 2,2':6',2''-terpyridine-6,6''-diyl, **3M).** Off-white compound (65% yield). IR (CH₂Cl₂): ν/cm⁻¹ 2096 (–C≡C–). ¹H NMR (250 MHz, CDCl₃): δ 8.48 (d, 2H, *J* = 7.8 Hz, H_{3,3'}), 8.35 (dd, 2H, *J* = 7.7, 0.7 Hz, H_{3',5'}), 7.86 (t, 1H, *J* = 7.8 Hz, H₄), 7.63 (t, 2H, *J* = 7.80 Hz, H_{4,4'}), 7.33 (dd, 2H, *J* = 7.7, 0.7 Hz, H_{5,5'}), 7.21 (dd, 4H, *J* = 7.6, 0.7 Hz, H_{ortho} for Ph), 6.97 (t, 4H, *J* = 7.4 Hz, H_{meta} for Ph), 6.80 (t, 2H, *J* = 7.4 Hz, H_{para} for Ph), 1.82 (m, 24H, PCH₂), 1.11 [(t, 36H, P(CH₂)CH₃)]. ¹³C NMR (100 MHz, CDCl₃): δ 156.24 (C_{2',6'}), 155.59 (C_{2,2'}), 146.94 (C_{6',6''}), 139.08 (C_{4'}), 136.77 (C_{4',4'}), 127.84 (C_{5',5'}), 127.31–125.92 (C Ph), 121.87 (C₅), 120.80 (C_{3,3'}), 116.60, 111.37 (C≡C), 15.16 (t, PCH₂CH₃), 7.87 (CH₃). ³¹P{¹H} NMR (101.3 MHz, CDCl₃): δ –131.27, ¹J_{Pt-P} = 2659 Hz. FAB-MS: 1297 (M⁺). Calc. for C₅₅H₇₉N₃P₄Pt₂: C, 50.96; H, 6.14; N, 3.24. Found: C, 51.13; H, 6.21; N, 3.27%.

trans-[(Ph)(Et₃P)₂Pt–C≡C–R–C≡C–Pt(PEt₃)₂(Ph)] (R = 4'-phenyl-2,2':6',2''-terpyridine-6,6''-diyl, **4M).** White solid (55% yield). IR (CH₂Cl₂): ν/cm⁻¹ 2095 (–C≡C–). ¹H NMR (250 MHz, CDCl₃): δ 8.81 (s, 2H, H_{3',5'}), 8.40 (dd, 2H, *J* = 7.8, 0.9 Hz, H_{3,3'}), 7.89 (td, 2H, *J* = 8.0, 1.5 Hz, H_{ortho} for 'Ph), 7.66 (t, 2H, *J* = 7.8 Hz, H_{4,4'}), 7.48 (tt, 2H, *J* = 7.0, 1.3 Hz, H_{meta} for 4'-Ph), 7.42 (tt, 1H, *J* = 7.2, 1.3 Hz, H_{para} for 4'-Ph), 7.34 (d, 2H, *J* = 7.8 Hz, H_{5,5'}), 7.23 [(dd, 4H, *J* = 7.7, 1.32 Hz, H_{ortho} for Pt(Ph)), 6.97 [(t, 4H, *J* = 8.0 Hz, H_{meta} for Pt(Ph)), 6.79 [(t, 2H, *J* = 7.2 Hz, H_{para} for Pt(Ph)), 1.8 (m, 2H, PCH₂), 1.12 [(t, 36H, P(CH₂)CH₃)]. ¹³C NMR (100 MHz, CDCl₃): δ 156.13 (C_{2',6'}), 155.67 (C_{2,2'}), 149.20 (C_{6',6''}), 146.89 (C_{4'}), 139.27

(C Ph), 136.10 (C_{4',4'}), 128.70, 127.20 (C Ph), 125.82 (C_{5',5'}), 121.30 (C₅), 118.77 (C_{3,3'}), 116.54, 111.46 (C≡C), 15.11 (t, PCH₂CH₃), 8.06 (CH₃). ³¹P{¹H} NMR (101.3 MHz, CDCl₃): δ –131.12, ¹J_{Pt-P} = 2659 Hz. FAB-MS: 1373 (M⁺). Calc. for C₆₁H₈₃N₃P₄Pt₂: C, 53.38; H, 6.09; N, 3.06. Found: C, 53.65; H, 5.98; N, 3.03%.

Polymer preparations

The poly-yne complexes **1P–4P** were synthesized by the general procedure outlined below for **1P**.

trans-[-(Bu₃P)₂Pt–C≡C–R–C≡C-]_n (R = 2,2'-bipyridine-5,5'-diyl, **1P).** CuI (5 mg) was added to a mixture of *trans*-[Pt-(PBu₃)₂Cl₂] (0.670 g, 1.0 mmol) and **1b** (0.204 g, 1 mmol) in PrⁱNH–CH₂Cl₂ (50 cm³, 1 : 1 v/v). The solution was stirred at room temperature for 15 h, after which all volatile components were removed under reduced pressure. The residue was dissolved in CH₂Cl₂ and passed through a short alumina column. After removal of the solvent by a rotary evaporator, an off-white film was obtained readily which was then washed with methanol to give the polymer **1P** in 85% isolated yield (0.680 g). Further purification can be accomplished by precipitating the polymer from dichloromethane solution in methanol. IR (CH₂Cl₂): ν/cm⁻¹ 2096 (–C≡C–). ¹H NMR (250 MHz, CDCl₃): δ 8.54 (s, 2H, H_{6,6'}), 8.18 (d, 2H, *J* = 7.2 Hz, H_{3,3'}), 7.50 (d, 2H, *J* = 7.2 Hz, H_{4,4'}), 2.13 [m, 12H, PCH₂(CH₂)₂(CH₃)], 1.64 [(br s, 12H, PCH₂(CH₂)₂(CH₃)], 1.44 [(sextet, 12H, PCH₂(CH₂)₂(CH₃)], 0.91 [(t, 18H, P(CH₂)₃CH₃)]. ¹³C NMR (100 MHz, CDCl₃): δ 154.86 (C_{2,2'}), 151.42 (C_{6,6'}), 138.06 (C_{3,3'}), 120.61 (C_{4,4'}), 120.30 (C_{5,5'}), 116.68, 108.40 (C≡C), 28.72–23.71 (PCH₂CH₂CH₂CH₃), 13.78 (CH₃). ³¹P{¹H} NMR (101.3 MHz, CDCl₃): δ –137.87, ¹J_{Pt-P} = 2353 Hz. Calc. for (C₃₈H₆₀N₂P₂Pt)_n: C, 56.91; H, 7.54; N, 3.49. Found: C, 57.02; H, 7.67; N, 3.52%. GPC (THF): *M*_n = 68,900 g mol⁻¹ (*n* = 86), *M*_w = 89,570 g mol⁻¹, polydispersity = 1.3.

trans-[-(Bu₃P)₂Pt–C≡C–R–C≡C-]_n (R = 2,2'-bipyridine-6,6'-diyl, **2P).** Off-white solid (85% yield). IR (CH₂Cl₂): ν/cm⁻¹ 2095 (–C≡C–). ¹H NMR (250 MHz, CDCl₃): δ 8.33 (d, 2H, *J* = 7.0 Hz, H_{3,3'}), 7.27 (t, 2H, *J* = 7.0 Hz, H_{4,4'}), 6.98 (d, 2H, *J* = 7.6 Hz, H_{5,5'}), 2.09 [m, 12H, PCH₂(CH₂)₂(CH₃)], 1.55 [m, 12H, PCH₂(CH₂)₂(CH₃)], 1.40 [m, 12H, PCH₂(CH₂)₂(CH₃)], 0.90 [(t, 18H, P(CH₂)₃CH₃)]. ¹³C NMR (100 MHz, CDCl₃): δ 155.86 (C_{2,2'}), 146.42 (C_{6,6'}), 135.69 (C_{3,3'}), 125.61 (C_{4,4'}), 121.05 (C_{5,5'}), 116.47, 110.24 (C≡C), 29.72–22.71 (PCH₂CH₂CH₂CH₃), 14.13 (CH₃). ³¹P{¹H} NMR (101.3 MHz, CDCl₃): δ –138.07, ¹J_{Pt-P} = 2357 Hz. Calc. for (C₃₈H₆₀N₂P₂Pt)_n: C, 56.91; H, 7.54; N, 3.49. Found: C, 56.82; H, 7.61; N, 3.51%. GPC (THF): *M*_n = 60,100 g mol⁻¹ (*n* = 75), *M*_w = 102,170 g mol⁻¹, polydispersity = 1.7.

trans-[-(Bu₃P)₂Pt–C≡C–R–C≡C-]_n (R = 2,2':6',2''-terpyridine 6,6''-diyl, **3P).** Off-white product (80% yield). IR (CH₂Cl₂): ν/cm⁻¹ 2095 (–C≡C–). ¹H NMR (250 MHz, CDCl₃): δ 8.49 (d, 2H, *J* = 7.8 Hz, H_{3,3'}), 8.37 (d, 2H, *J* = 7.8 Hz, H_{3',5'}), 7.84 (t, 1H, *J* = 7.8 Hz, H₄), 7.65 (t, 2H, *J* = 7.80 Hz, H_{4,4'}), 7.18 (d, 2H, *J* = 7.4 Hz, H_{5,5'}), 2.25 [m, 12H, PCH₂(CH₂)₂(CH₃)], 1.67 [m, 12H, PCH₂(CH₂)₂(CH₃)], 1.49 [m, 12H, PCH₂(CH₂)₂(CH₃)], 0.93 [(t, 18H, P(CH₂)₃CH₃)]. ¹³C NMR (100 MHz, CDCl₃): δ 155.76 (C_{2',6'}), 155.44 (C_{2,2'}), 146.70 (C_{6',6''}), 137.00 (C_{4'}), 136.07 (C_{4',4'}), 125.86 (C_{5',5'}), 120.99 (C₅), 120.19 (C_{3,3'}), 116.81, 110.43 (C≡C), 28.14–24.26 (PCH₂CH₂CH₂CH₃), 13.85 (CH₃). ³¹P{¹H} NMR (101.3 MHz, CDCl₃): δ –138.28, ¹J_{Pt-P} = 2350 Hz. Calc. for (C₄₃H₆₃N₃P₂Pt)_n: C, 58.75; H, 7.22; N, 4.78. Found: C, 58.86; H, 7.33; N, 4.81%. GPC (THF): *M*_n = 72,100 g mol⁻¹ (*n* = 82), *M*_w = 129,780 g mol⁻¹, polydispersity = 1.8.

trans-[-(Bu₃P)₂Pt–C≡C–R–C≡C-]_n (R = 4'-phenyl-2,2':6',2''-terpyridine-6,6''-diyl, **4P).** Off-white product, 70% yield. IR (CH₂Cl₂): ν/cm⁻¹ 2095 (–C≡C–). ¹H NMR (250 MHz, CDCl₃): δ 8.76 (s, 2H, H_{3',5'}), 8.43 (d, 2H, *J* = 7.8 Hz, H_{3,3'}), 7.84 (d, 2H,

$J = 7.1$ Hz, H_{ortho} for Ph), 7.67 (t, 2H, $J = 7.7$ Hz, $H_{4,4'}$), 7.49 (t, 2H, $J = 7.1$ Hz, H_{meta} for Ph), 7.44 (t, 1H, $J = 7.0$ Hz, H_{para} for Ph), 7.24 (d, 2H, $J = 7.7$ Hz, $H_{5,5'}$), 2.24 [m, 12H, $PCH_2-(CH_2)_2(CH_3)$], 1.65 [(br s, 12H, $PCH_2(CH_2)_2(CH_3)$], 1.47 [(sextet, 12H, $PCH_2(CH_2)_2(CH_3)$], 0.87 [(t, 18H, $P(CH_2)_2CH_3$]. ^{13}C NMR (100 MHz, $CDCl_3$): δ 156.07 ($C_{2',6'}$), 155.82 ($C_{2',2}$), 149.75 ($C_{6',6}$), 146.75 (C_4), 139.39 (C Ph), 136.08 ($C_{4',4}$), 128.70 (C Ph), 127.35 (C Ph), 126.02 ($C_{5',5}$), 119.05 (C_5), 117.47 ($C_{3,3'}$), 116.78, 109.48 ($C=C$), 29.71–24.15 ($PCH_2CH_2CH_2CH_3$), 13.83 (CH_3). $^{31}P\{^1H\}$ NMR (101.3 MHz, $CDCl_3$): δ -137.58, $^1J_{Pt-P} = 2357$ Hz. Calc. for ($C_{49}H_{67}N_3P_2$) $_n$: C, 61.61; H, 7.07; N, 4.40. Found: C, 61.87; H, 6.97; N, 4.37%. GPC (THF): $M_n = 86800$ ($n = 91$), $g\ mol^{-1}$ ($n = 82$), $M_w = 156240\ g\ mol^{-1}$, polydispersity = 1.8.

Acknowledgements

We gratefully acknowledge Sultan Qaboos University (SQU) Research Grant No. IG/SCI/CHEM/02/02. M. S. K. acknowledges EPSRC, UK for a Visiting Fellowship and SQU for a research leave. The award of a DAAD grant (Gemeinsames Hochschulsonderprogramm III von Bund und Ländern) (to B. A.) is gratefully acknowledged. A. K. thanks Peterhouse, Cambridge for a Research Fellowship and the Royal Society for a University Research Fellowship. The support of the EPSRC for project funding and for the purchase of the X-ray diffractometers is gratefully acknowledged.

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