Synthesis, characterisation and optical spectroscopy of platinum(II) di-ynes and poly-ynes incorporating condensed aromatic spacers in the backbone

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A series of protected and terminal dialkynes with extended π-conjugation through a condensed aromatic linker unit in the backbone, 1,4-bis(trimethylsilylethynyl)naphthalene, **2a**, 1,4-bis(ethynyl)naphthalene, **2b**, 9,10-bis(trimethylsilyl-ethynyl)anthracene **3a**, 9,10-bis(ethynyl)anthracene **3b**, have been synthesized and characterized spectroscopically. The solid-state structures of **2a** and **3a** have been confirmed by single crystal X-ray diffraction studies. Reaction of two equivalents of the complex *trans*-[Ph(Et₃P)₂PtCl] with an equivalent of the terminal dialkynes 1,4-bis(ethynyl)benzene **1b** and **2b–3b**, in ^{i}Pr₂NH–CH₂Cl₂, in the presence of CuI, at room temperature, afforded the platinum(II) di-ynes *trans*-[Ph(Et₃P)₂Pt–C≡C–R–C≡C–Pt(PEt₃)₂Ph] (R = benzene-1,4-diyl **1c**; naphthalene-1,4-diyl **2c** and anthracene-9,10-diyl **3c**) while reactions between equimolar quantities of *trans*-[(^{n}Bu₃P)₂PtCl₂] and **2b–3b** under similar conditions readily afforded the platinum(II) poly-ynes *trans*-[–(^{n}Bu₃P)₂Pt–C≡C–R–C≡C–]ₙ (R = naphthalene-1,4-diyl **2d** and anthracene-9,10-diyl **3d**). The Pt(II) diynes and poly-ynes have been characterized by analytical and spectroscopic methods, and the single crystal X-ray structures of **1c** and **2c** have been determined. These structures confirm the *trans*-square planar geometry at the platinum centres and the linear nature of the molecules. The di-ynes and poly-ynes are soluble in organic solvents and readily cast into thin films. Optical spectroscopic measurements reveal that the electron-rich naphthalene and anthracene spacers create strong donor–acceptor interactions between the Pt(II) centres and conjugated ligands along the rigid backbone of the organometallic polymers. Thermogravimetry shows that the di-ynes possess a somewhat higher thermal stability than the corresponding poly-ynes. Both the Pt(II) di-ynes and the poly-ynes exhibit increasing thermal stability along the series of spacers from phenylene through naphthalene to anthracene.

Introduction

Conjugated polymers, that have potential electronic and photonic applications, have sparked off an ever increasing interest in academic and industrial research laboratories over the past decade. The synthetic flexibility, ease of processing, and the possibility of tailoring properties to accomplish a desired function make them attractive candidates for manifold applications in materials science. Thus, they are used as laser dyes,[1] scintillators,[1] light emitting diodes (LEDs),[2] sensors,[3] piezoelectric and pyroelectric materials,[4] photoconductors,[5] and are being investigated for use as optical data storage devices,[6] and as optical switches and signal processing devices[7] as well as having nonlinear optical (NLO) applications.[8] Among the variety of conjugated polymers, those composed of alternating aryl and ethynyl units, polyarylene ethynylenes (PAEs) have been the focus of much research with respect to material science applications.[2,9,10] The ease of preparation of PAEs, their photophysical stability and wide usage can be combined with the features of transition metals to give metallo–poly-ynes with novel properties, such as optical nonlinearity, liquid crystallinity, luminescence, electrical and photoconductivity.[11] In organic polymers, light emission occurs from the singlet excited state (S₁) but emission in LEDs can occur from both the excited singlet (S₁) and triplet (T₁) manifolds. It is desirable to understand the photophysics of the triplet excited states and how they change with the chemical structure in order to manipulate the relative separation of the energy

bands and hence, harvest the energy of the triplet excited state.[12] The inclusion of heavy transition metals, such as platinum, in the polymer backbone introduces sufficient spin–orbital coupling to allow light emission from the triplet excited state of the conjugated ligand, by allowing spin-crossover processes to occur.[13] Platinum(II) poly-ynes are considered to be good model systems to study the triplet excited state in conjugated organic polymers.[14] The novel photophysics of the platinum(II) poly-ynes leads to materials that may be used to fabricate high efficiency organic electroluminescent devices,[15] and for application in laser protection.[16]

Recently we have been examining a series of 'rigid rod' platinum(II) poly-ynes of general formula [–(^{n}Bu₃P)₂Pt–C≡C–R–C≡C–]_∞ where R is one of a number of aromatic and hetero-aromatic spacer groups.[17] These materials display varying degrees of donor–acceptor interactions between the metal centres and the conjugated ligands depending on the electronic nature of the spacer group. π-Conjugated polymers with donor–acceptor architectures have generated great interest in recent years because the intra-molecular charge-transfer (ICT) can facilitate manipulation of the electronic structure, leading to small band gap semi-conducting materials.[18]

A strategy towards the design of new PAEs with optimized properties involves intelligent variation of the conjugated spacers. Within the family of platinum(II) poly-ynes, the spacer group has been varied by us and others to include a wide range of carbocyclic, heterocyclic and mixed heterocyclic ring systems, but spacers involving condensed aromatic ring systems have received less

attention. The use of fused-ring spacers has been found to be a powerful approach to the production of some low band gap conjugated polymers.[19] Among the fused aromatic systems, naphthalene and anthracene units are particularly interesting because of their fluorescence, photo- and electroluminescence, liquid crystal, photochromic, hole-transporting and thermal curing properties.[20] Some reports have been concerned with the incorporation of naphthalene and anthracene as bridging chromophores into conjugated di-, oligo- and poly-yne frameworks and studies of intra-molecular electron and energy transfer.[21] The incorporation of electron-rich anthracene units into PAEs has been found to have a marked influence on the luminescence properties of the materials,[22] and they are particularly effective in promoting π-electron delocalisation along the backbone of long-chain Pt(II) poly-ynes.[23]

This background has encouraged us to investigate the chemistry and properties of Pt(II) poly-ynes incorporating naphthalene and anthracene rings in the backbone. In this paper we report the synthesis of series of protected and terminal dialkynes with extended π-conjugation through a condensed aromatic linker unit in the backbone, 1,4-bis(trimethylsilylethynyl)naphthalene, **2a**, 1,4-bis(ethynyl)naphthalene, **2b**, 9,10-bis(trimethylsilylethynyl)-anthracene **3a**, 9,10-bis(ethynyl)anthracene **3b**. The structural characterisation of the protected dialkynes, **2a** and **3a**, and of two dinuclear Pt(II) di-yne complexes, **1c** and **2c**, and a description of the spectroscopic, thermal and optical properties of the Pt(II) di-ynes and poly-ynes **1c–3c, 1d–3d** is also presented.

## Results and discussion

Syntheses

The bis-ethynyl ligands were synthesized by a sequence of coupling and proto–desilylation reactions. The protected alkynyl ligand precursors, 1,4-bis(trimethylsilylethynyl)naphthalene **2a** and 9,10-bis(trimethylsilylethynyl)anthracene **3a** were prepared by improved procedures[24] involving a palladium(II)/copper(I)-catalysed cross-coupling reaction of trimethylsilylethyne with diiodonaphthalene and diiodoanthracene, respectively, in $^{i}Pr_2NH$–THF as illustrated in Scheme 1. The use of diiodonaphthalene and diiodoanthracene, and THF solvent, gave improved yields (80–85%) of the desired bis(trimethylsilylethynyl)carbocycles with a minimum of homo-coupling that would lead to the formation of the side product bis(trimethylsilylethynyl)butadiene. The protected alkynes are indefinitely stable towards light and air at ambient temperature and were fully characterised by IR, NMR (^{1}H and ^{13}C) spectroscopy, EI mass spectrometry, as well as by satisfactory elemental analyses and single crystal X-ray crystallography for both **2a** and **3a**. Conversion of the protected dialkynes **2a** and **3a** into the diterminal alkynes, 1,4-bis(ethynyl)naphthalene **2b** and 9,10-bis(ethynyl)anthracene **3b** was accomplished by cleavage of the trimethylsilyl groups with dilute aqueous KOH in MeOH–THF (Scheme 1). The products were purified by silica gel column chromatography and isolated as orange to red solids in 78–85% yields. The diterminal alkynes **2b** and **3b** are somewhat unstable; storage over a long period of time at ambient temperature and under aerobic conditions led to the formation of dark insoluble material that was presumed to be polymerisation products. Hence, **2b** and **3b** were prepared freshly before reaction with the metal complexes. 1,4-bis(ethynyl)benzene **1b** was also freshly prepared prior to subsequent reaction using previously published procedures.[25]
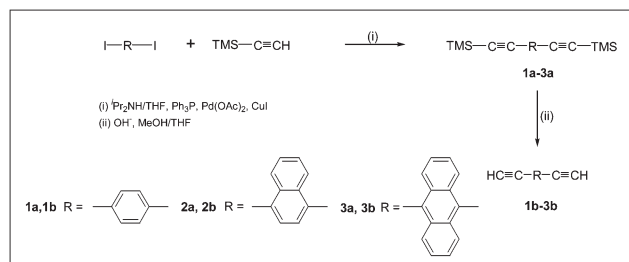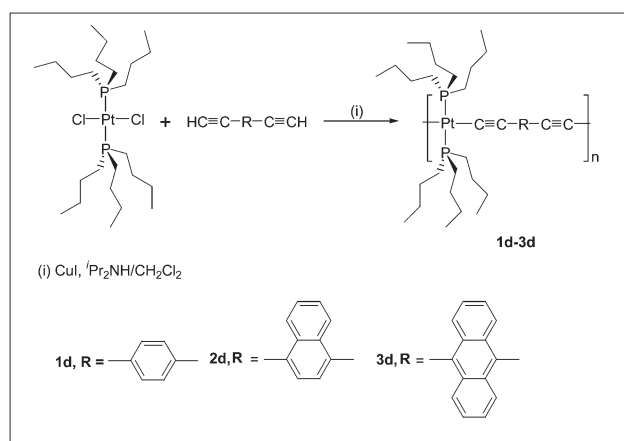
Scheme 1

The dehydrohalogenation reactions between *trans*-[Ph(Et$_3$P)$_2$PtCl] and the diterminal alkynes **1b–3b** in a 2 : 1 stoichiometry, in $^{i}Pr_2NH$–CH$_2$Cl$_2$, in the presence of CuI at room temperature gave the dinuclear Pt(II) di-ynes **1c–3c** (Scheme 2) while the polycondensation reactions between *trans*-[(^{n}Bu$_3$P)$_2$PtCl$_2$] and **2b** and **3b**, respectively, in a 1 : 1 ratio, under similar reaction conditions, readily afforded the platinum(II) poly-ynes **2d** and **3d** (Scheme 3). The synthesis of the phenylene-based Pt(II) poly-yne, [–(^{n}BuP)$_2$Pt–C≡C–(C$_6$H$_4$)–C≡C–]$_∞$ **1d** has been reported previously.[26] The poly-ynes were obtained in yields of 85–90%, pointing to a very high conversion. Purification of the Pt(II) di-ynes was accomplished by column chromatography or preparative TLC on silica while the poly-ynes were purified by chromatography on an alumina column.
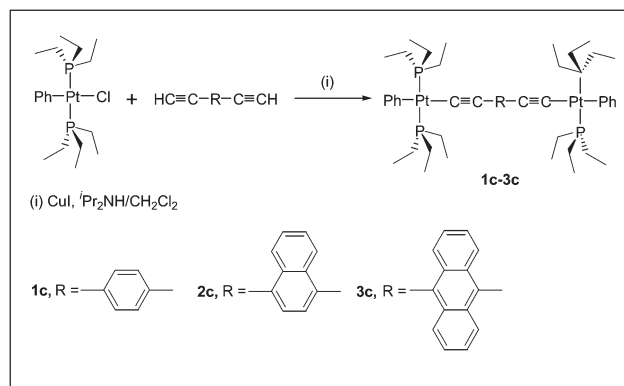
Scheme 2

Scheme 3

Spectroscopic characterization

Initial, systematic characterization of the organic ligand precursors as well as the platinum(II) di-ynes and poly-ynes was achieved by spectroscopic methods. The IR spectra of the Pt(II) di-ynes and poly-ynes show a single sharp $v_{C≡C}$ absorption at around 2095 cm^{-1} consistent with a *trans*-configuration of the ethynylenic units around the Pt(II) centre, and the observed value is similar to that found in a range of related materials.[17] The $v_{C≡C}$ values for the terminal di-ynes **2b–3b** (2107 cm^{-1}) are much lower than those of the trimethylsilyl-protected dialkynes **2a–3a** (2157–2159 cm^{-1}). The fact that terminal ethynes (HC≡C–R) have lower $v_{C≡C}$ frequencies than their protected counterparts RC≡C–R (by about 50 cm^{-1} in this case) is well established.[27] Furthermore, the Pt(II) di-ynes and poly-ynes display lower $v_{C≡C}$ values than those in the corresponding protected or terminal dialkynes. This may be attributed to either metal–yne π-backbonding or the M$^{δ+}$–C$^{δ-}$ polarity.[28] NMR analyses indicate a rigid structure for the Pt(II) di-ynes and poly-ynes. In all cases, ^{1}H NMR resonances arising from the protons of the aromatic ring systems were clearly observed. In addition, two distinct ^{13}C NMR peaks for the individual ethynylenic carbons in the di-ynes and poly-ynes were observed, in accord with their formulations, and they are shifted downfield with respect to the signals in the

Table 1 Bond lengths (Å) and angles (°) for 1,4-bis(trimethylsilylethynyl)-naphthalene **2a**

Si(1)–C(4)	1.834(2)	C(6)–C(11)	1.432(3)
Si(2)–C(17)	1.835(2)	C(9)–C(16)	1.438(3)
C(4)–C(5)	1.205(3)	C(10)–C(15)	1.416(3)
C(5)–C(6)	1.436(3)	C(14)–C(15)	1.360(3)
C(6)–C(7)	1.376(3)	C(16)–C(17)	1.207(3)
C(5)–C(4)–Si(1)	178.0(2)	C(17)–C(16)–C(9)	179.3(2)
C(4)–C(5)–C(6)	179.0(2)	C(16)–C(17)–Si(2)	177.8(2)

Table 2 Bond lengths (Å) and angles (°) for 9,10-bis(trimethylsilylethynyl)-anthracene **3a**

Si(1)–C(4)	1.846(6)	C(6)–C(7)	1.187(6)
Si(2)–C(7)	1.841(5)	C(34)–C(35)	1.205(8)
Si(3)–C(34)	1.839(6)	C(35)–C(36)	1.436(8)
Si(4)–C(54)	1.859(6)	C(54)–C(55)	1.207(8)
C(4)–C(5)	1.191(7)	C(55)–C(56)	1.434(8)
C(5)–C(11)	1.446(6)		
C(5)–C(4)–Si(1)	176.3(6)	C(35)–C(34)–Si(3)	176.8(5)
C(4)–C(5)–C(11)	175.4(6)	C(34)–C(35)–C(36)	176.4(6)
C(7)–C(6)–C(14)	175.9(6)	C(55)–C(54)–Si(4)	175.8(6)
C(6)–C(7)–Si(2)	173.9(4)	C(54)–C(55)–C(56)	176.5(6)

diterminal alkynes. The aromatic region of the ^{13}C NMR spectra reveals a high degree of structural regularity for the main-chain skeleton in the di-ynes and poly-ynes. For example, only 9 well-defined peaks appear in the aromatic region, related to the 18 aromatic carbon atoms of the symmetric dinuclear Pt(II) compound **1c**. Similarly, the ^{13}C NMR spectral features of the Pt(II) poly-ynes agree with the proposed polymer structures. The resonances due to the ethyl and butyl groups are clearly identified. The single resonance in the ^{31}P NMR spectra of the Pt(II) diynes and poly-ynes confirms the *trans* arrangement of the phosphine ligands. The $^1J_{Pt-P}$ values range from 2628 to 2645 Hz for the di-ynes and 2363–2377 Hz for the poly-ynes; the spectral features are similar to other Pt(II) di-ynes and poly-ynes reported previously[13,17] and confirm the all-*trans* configuration of the compounds.

The mass spectrometric results confirm the molecular assignments for the organic precursors and the Pt(II) di-ynes. Gel permeation chromatography (GPC), using a polystyrene (PS) standard shows that the number-average molecular weights of the poly-ynes are in the range of 28000–41000 g mol^{-1}, corresponding to degrees of polymerisation of between 34 and 53 repeat units. The value of poly dispersity index (PDI) varied between 1.8 and 1.9. The narrow poly dispersity (PDI < 2) in the molecular weights is consistent with the proposed linear structure[29] from the condensation polymerisation. GPC data indicate that the number of repeat units per chain for the naphthalene-based poly-yne is higher than that for the anthracene-based poly-yne and the degree of polymerization is significantly reduced in both cases as compared to that found for the related phenylene-based poly-yne.[26] This reduction in chain length with the increasing size of the spacer group may reflect significant steric interactions between adjacent repeat units resulting from a configuration in which naphthalene and anthracene moieties adopt a nearly orthogonal orientation with respect to that of the platinum square plane, but it may also simply reflect a reduction in solubility of the larger species. In addition, the molecular weight values should be viewed with caution in view of the difficulties associated with utilizing 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 to flexible polymers. Therefore, calibration of the GPC with PS standards could inflate the values of the molecular weights of the poly-ynes 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 a high degree of polymerization has been achieved in these organometallic polycondensation reactions.
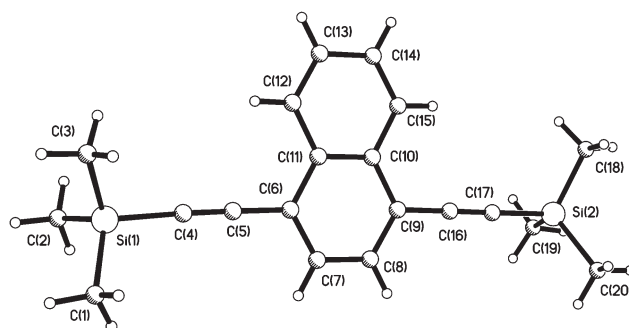
Crystal structure analysis

Single crystals of compounds **2a, 3a, 1c** and **2c** were obtained, and the crystal and molecular structures of these materials were determined in order to confirm the spectroscopic assignments, and investigate the intermolecular interactions in the solid state, with a view to correlating the structure/property relationships in these systems.

The molecular structure of 1,4-bis(trimethylsilylethynyl)-naphthalene **2a** is shown in Fig. 1 while bond parameters are listed in Table 1. This compound crystallises in the orthorhombic space group *Pbca* with one molecule in the asymmetric unit. The molecules show the expected linear geometry (average Si–C≡C, 177.9(2)°, and average C≡C–C, 179.2(2)°) along the two acetylene groups on either side of the planar naphthalene group (maximum

deviation from the ring plane 0.08 Å). The C–C bond lengths within the central naphthalene ring (1.358(3)–1.438(3) Å) lie within the expected range, and the two C≡C bonds have an average length of 1.206(3) Å, consistent with values found in a range of bis-trimethylsilylethynyl derivatives.[17] For the trimethylsilyl groups the (Me)C–Si–C(Me) angles (average 110.83°) are somewhat larger than the (≡C)C–Si–C(Me) angles (average 108.07°).

Fig. 1 The molecular structure of 1,4-bis(trimethylsilylethynyl)-naphthalene **2a** showing the atom numbering scheme adopted.

An examination of the crystal structure of **2a** shows no evidence of graphitic packing between the aromatic components of the molecules, and the closest contacts are between adjacent methyl groups with these distances being close to the sum of the van der Waals radii. Thus, from this evidence, at least, there are no significant intermolecular interactions that, in the polymers, might relate to spectroscopic features assigned to interchain interactions.

The compound 9,10-bis(trimethylsilylethynyl)anthracene, **3a**, crystallises in the monoclinic space group $P2_1/c$, with one unique whole molecule, and two independent half molecules, sitting on centres of symmetry, in the asymmetric unit. The structure of the unique molecule together with the two independent half molecules, and their symmetry related halves, is illustrated in Fig. 2 while bond parameters are presented in Table 2. The crystal structure shows evidence of twinning, giving a pseudo-orthorhombic cell, and there is significant disorder within the trimethylsilyl groups. Therefore, the bond parameters obtained from the structure determination should be treated with caution, but the general nature of the intermolecular interactions is informative. Within the structure the four independent C≡C triple bonds lie in the expected range of 1.187(6)–1.207(8) Å, and the acetylene units are essentially linear with Si–C≡C and C≡C–C angles of 175.6 and 176.1°, respectively. The anthracene rings are planar, with a maximum deviation from planarity of 0.03 Å, and within the ring systems the C–C bond lengths lie in the range 1.334(11)–1.451(7) Å.

As with the crystal structure of **2a**, an examination of the crystal structure of **3a** shows no abnormally short intermolecular contacts or any evidence for graphitic packing. Neither is there evidence of C–H⋯π interactions.

In the crystal structure of [Ph(Et$_3$P)$_2$PtC≡C(C$_6$H$_4$)C≡CPt-(PEt$_3$)$_2$Ph] **1c** the metal complex sits on a crystallographic centre of symmetry, situated at the centre of the central arene ring, and co-crystallises with two chloroform solvent molecules. The molecular structure of **1c** is shown in Fig. 3 which also
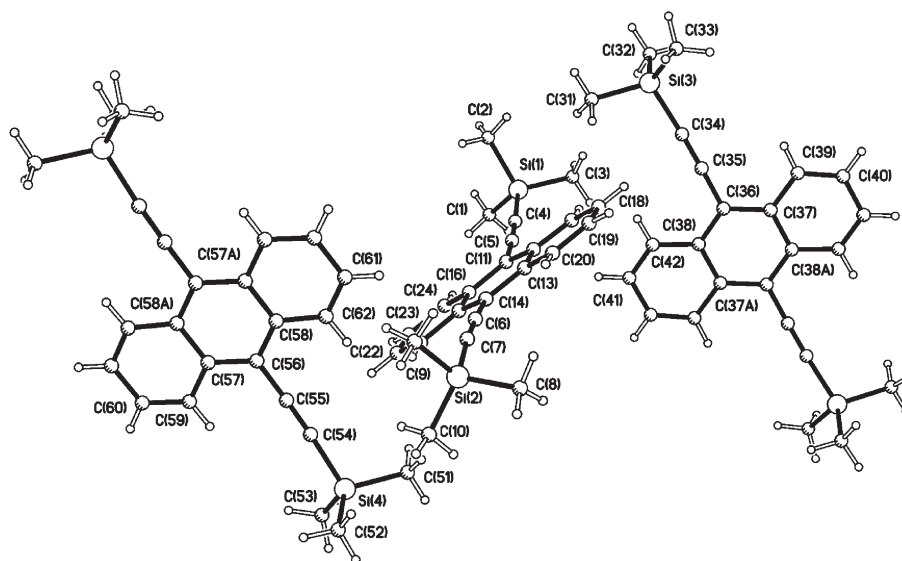
Fig. 2 The molecular structure of 9,10-bis(trimethylsilylethynyl)anthracene **3a** showing the atom numbering scheme adopted. The asymmetric unit contains one whole molecule and two half molecules located on crystallographic centres of symmetry.

shows the hydrogen bond between the hydrogen atom of one of the chloroform molecules and the centre of one of the acetylenic C≡C triple bonds. The hydrogen bond parameters are H···C≡C(centroid) 2.517 Å, C–H···C≡C(centroid), 171.0°, and C···C≡C(centroid), 3.508 Å.
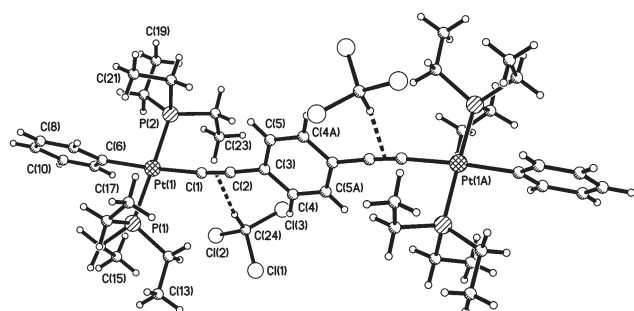

Fig. 3 The molecular structure of [Ph(Et₃P)₂PtC≡C(C₆H₄)C≡CPt(PEt₃)₂Ph] **1c** shown together with one molecules of CHCl₃, with a C–H hydrogen bond interacting with an acetylenic C≡C triple bond.

The complex **1c** can be viewed as the archetypal platinum "rigid rod" di-yne system on which much of the chemistry of the organometallic di-ynes, [Ph(Et₃P)₂PtC≡C–R–C≡CPt(PEt₃)₂Ph], and poly-ynes, [–Pt(ⁿBu₃P)₂–C≡C–R–C≡C–]ₙ, has been based.[13,17] It has not been possible to obtain good single crystals previously, and the inclusion of the hydrogen bonded solvent molecules in the crystal lattice in the present determination indicates the importance of the solvent in stabilising the crystal. In view of the archetypal nature of the complex it is of particular interest to compare the intramolecular bond parameters (Table 3) with those in related complexes. As expected, the alkynylic units are essentially linear, with Pt–C≡C and C≡C–C angles within a few degrees of 180°. The Pt(1)–C(1) (alkynyl) bond, at 2.040(7) Å, is similar to the values (1.96(2)–2.03(2) Å) in the range of di-platinum di-yne complexes characterised previously.[13,17] The Pt–P distances (av. 2.294 Å) also lie in the expected range, 2.27–2.32 Å, by comparison to other structurally characterised systems. The Pt(1)–C(6) (phenyl) distance of 2.074(7) Å, also falls in the previously determined range of 2.05(2)–2.09(3) Å. As expected the geometry at the platinum centre is square planar, and this plane makes an angle of 60.36° with the plane of the central arene ring, and an angle of 82.54° with the terminal phenyl ring. The terminal and central arene rings then make an angle of 37.10° with each other.

The complex [Ph(Et₃P)₂PtC≡C–(C₁₀H₆)–C≡CPt(PEt₃)₂Ph] **2c** crystallises in the triclinic space group *P*1̄ with one unique molecule of the di-platinum species and half a molecule of dichloromethane in the asymmetric unit. The molecular structure

Table 3 Selected bond lengths (Å) and angles (°) for [Ph(Et₃P)₂PtC≡C-(C₆H₄)C≡CPt(PEt₃)₂Ph] **1c**

Pt(1)–C(1)	2.040(7)	C(2)–C(3)	1.449(9)
Pt(1)–C(6)	2.074(7)	C(3)–C(4)	1.393(10)
Pt(1)–P(1)	2.2934(19)	C(3)–C(5)	1.393(10)
Pt(1)–P(2)	2.295(2)	C(4)–C(5A)	1.369(9)
C(1)–C(2)	1.210(10)	C(5)–C(4A)	1.369(9)
P(1)–Pt(1)–P(2)	178.39(6)	C(1)–C(2)–C(3)	175.3(8)
C(1)–Pt(1)–C(6)	173.5(2)	C(4)–C(3)–C(5)	117.3(6)
C(1)–Pt(1)–P(1)	93.4(2)	C(4)–C(3)–C(2)	122.0(7)
C(6)–Pt(1)–P(1)	87.7(2)	C(5)–C(3)–C(2)	120.7(7)
C(1)–Pt(1)–P(2)	87.6(2)	C(3)–C(4)–C(5A)	121.0(7)
C(6)–Pt(1)–P(2)	91.1(2)	C(3)–C(5)–C(4A)	121.7(7)
Pt(1)–C(1)–C(2)	172.9(6)		

Symmetry transformations used to generate equivalent atoms: A: −x + 1, −y + 1, −z.

is displayed in Fig. 4 while selected bond lengths and angles are listed in Table 4. The dichloromethane molecule is disordered over two sites and there is extensive disorder within a number of the ethyl groups of the phosphine ligands. This makes an assessment of the intermolecular interactions less meaningful but, unlike **1c**, there is no short contact between the dichloromethane molecule and the acetylenic triple bonds. The shortest contacts involve hydrogen atoms from the disordered ethyl groups and the chlorine atoms of the dichloromethane molecule {H(22O)···Cl(61), 2.739 Å; H(21I)···Cl(62), 2.711 Å; H(16B)···Cl(61), 2.186 Å}. The molecular geometry of **2c** is related to that of **1c**. The terminal phenyl rings (C(101)–C(106)) and (C(201)–C(206)) make angles of 87.4 and 88.5° with the two platinum-centred square planes (Pt(1), P(11), P(12), C(12), C(101)) and (Pt(2), P(21), P(22), C(42), C(201)), respectively. The central naphthalene unit is essentially planar, with a dihedral angle of 3.6°, between the two fused six-membered rings. The linked ring (C(1), C(2), C(3), C(4), C(5), C(10)) makes angles of 61.9 and 63.9° with the Pt(1)-centred and Pt(2)-centred square planes, respectively.

Optical spectroscopy

Fig. 5 shows the photoluminescence spectra taken at room temperature and at 10 K for the platinum(II) poly-ynes **1d–3d** and di-ynes **1c–3c**. The room-temperature absorption spectra are also shown. For **1d** and **1c**, the first absorption band has been assigned to transitions between the mixed ligand π and platinum 5d orbitals and the ligand π* and platinum 6p orbitals.[14,30] This band shifts to lower energies along the series that suggests an increase in donor–acceptor interaction between the Pt(II) centre and the conjugated ligand in going from benzene, through naphthalene to anthracene

Table 4 Selected bond lengths (Å) and angles (°) for [Ph(Et₃P)₂PtC≡C–(C₁₀H₆)–C≡CPt(PEt₃)₂Ph] **2c**

|			
Pt(1)–C(12)	2.001(4)	C(5)–C(6)	1.428(6)
Pt(1)–C(101)	2.064(4)	C(6)–C(7)	1.358(7)
Pt(1)–P(11)	2.2892(11)	C(7)–C(8)	1.412(7)
Pt(1)–P(12)	2.2865(10)	C(8)–C(9)	1.361(7)
C(11)–C(12)	1.214(6)	C(9)–C(10)	1.438(7)
C(11)–C(1)	1.436(6)	C(4)–C(41)	1.433(6)
C(1)–C(2)	1.387(7)	C(41)–C(42)	1.217(6)
C(2)–C(3)	1.402(6)	C(42)–Pt(2)	2.024(4)
C(3)–C(4)	1.391(7)	Pt(2)–C(201)	2.067(4)
C(4)–C(5)	1.431(6)	Pt(2)–P(21)	2.2923(11)
C(5)–C(10)	1.415(6)	Pt(2)–P(22)	2.2976(12)
C(12)–Pt(1)–C(101)	177.21(19)	C(4)–C(41)–C(42)	175.5(5)
P(11)–Pt(1)–P(12)	174.84(4)	C(41)–C(42)–Pt(2)	177.1(4)
P(11)–Pt(1)–C(12)	90.37(13)	C(42)–Pt(2)–C(201)	178.68(17)
P(11)–Pt(1)–C(101)	91.31(12)	P(21)–Pt(2)–P(22)	173.97(5)
P(12)–Pt(1)–C(12)	86.47(13)	P(21)–Pt(2)–C(42)	87.88(14)
P(12)–Pt(1)–C(101)	91.70(12)	P(21)–Pt(2)–C(201)	90.81(11)
Pt(1)–C(12)–C(11)	174.9(4)	P(22)–Pt(2)–C(42)	94.34(14)
C(12)–C(11)–C(1)	176.5(5)	P(22)–Pt(2)–C(201)	86.97(11)
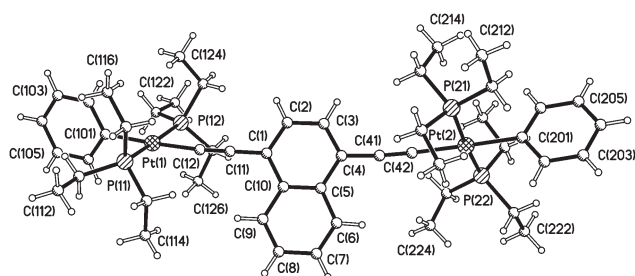
Fig. 4 The molecular structure of [Ph(Et₃P)₂PtC≡C–(C₁₀H₆)–C≡CPt(PEt₃)₂Ph] **2c**. Only one orientation of the disordered PEt₃ groups is shown for clarity, and the CH₂Cl₂ solvent is also omitted.

as the central linker unit. Throughout the series, the absorption of the poly-ynes is shifted to the red compared to the corresponding diynes, although this difference decreases down the series, which indicates that the conjugation of the ligand continues through the metal centre, as has been observed previously.[13,14] The actual band gaps, taken as the onset of the absorption, range from 3.4 eV for **1c**, with the benzene linker, to 2.45 eV for **3c**, with the anthracene linker, for the diplatinum complexes, and from 2.9 eV for **1d** to 2.35 eV for **3d**, for the polymeric systems. These band gaps lie in the region previously observed for this class of platinum-containing, rigid-rod di-ynes and poly-ynes, but since the linker groups are not particularly electron withdrawing, values for the band gap of below 2 eV are not observed, as has been seen for polymers with highly electron withdrawing heteroaromatic rings.[13] The most significant feature, here, is that the band gap is lowered as the electron delocalisation increases through a larger aromatic linker unit.

The photoluminescence spectra of **1d** and **1c** show two emission bands which have previously been assigned to a singlet S_1 state (fluorescence) and a triplet T_1 state (phosphorescence) by lifetime and photoinduced absorption measurements.[13,31] We attribute the emission bands centred around 2.8 eV in **2d** and **2c** and around 2.2 eV in **3d** and **3c** to the singlet S_1 state since this emission is located just beneath the S_1 absorption band and shows little temperature dependence except for a redistribution of the relative weights of the side-peak structure. We assign the emission peaking at 1.96 eV in **2d** and **2c** to a triplet T_1 state since it is at the expected energetic position for the triplet emission,[31] has a strong temperature dependence and shows vibronic structure that excludes it from being an excimer state. The lower relative phosphorescence yield in the di-yne **2c** compared to the poly-yne **2d** is consistent with that found in related compounds.[14]

For compounds **3d** and **3c** that contain an anthracene unit we cannot observe any phosphorescence in thin films. We expect the T_1 state to be at around 1.5 eV, and we have seen a very weak
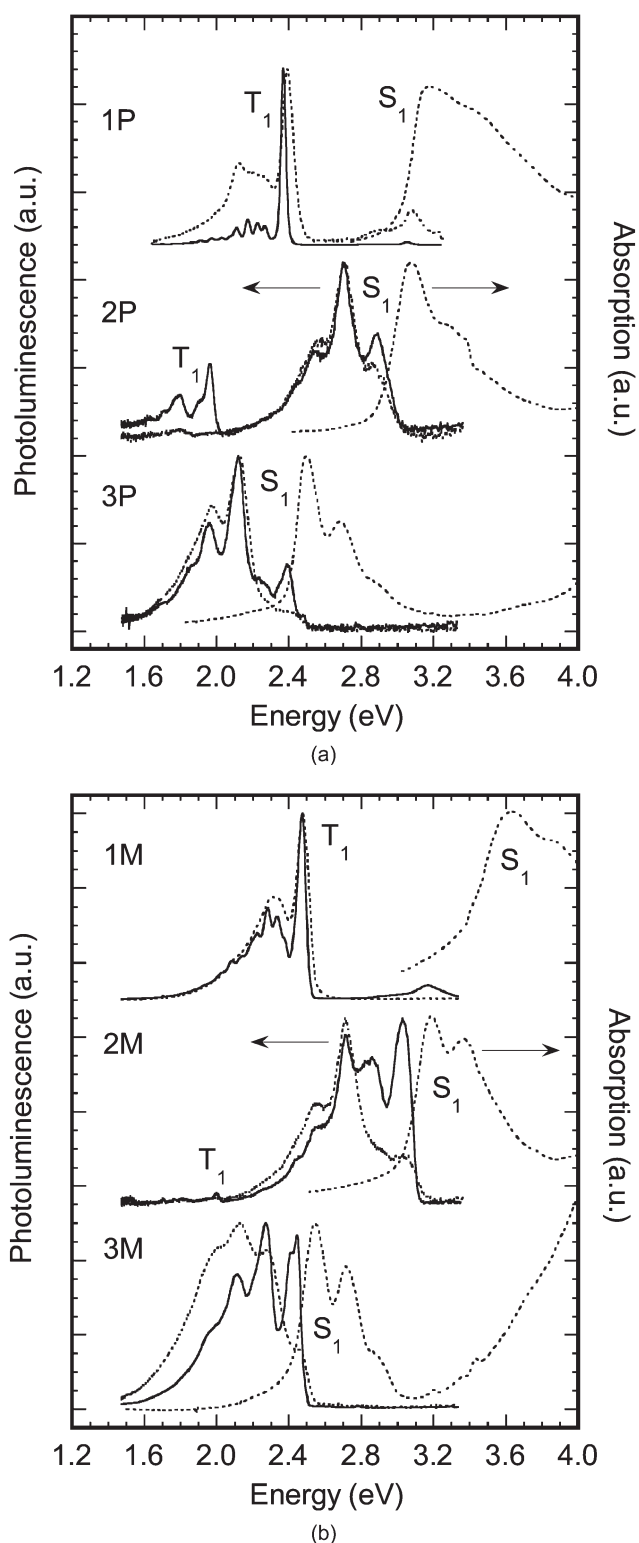

(a)

(b)

Fig. 5 The thin film photoluminescence and absorption spectra of (a) the Pt(II) poly-ynes *trans*-[–(ⁿBu₃P)₂Pt–C≡C–R–C≡C–]ₙ (R = benzene-1,4-diyl **1d**, naphthalene-1,4-diyl **2d** and anthracene-9,10-diyl **3d**) at room temperature (dotted lines) and at 10 K (solid lines) and (b) the diynes *trans*-[Ph(Et₃P)₂Pt–C≡C–R–C≡C–(Et₃P)₂PtPh] (R = benzene-1,4-diyl **1c**; naphthalene-1,4-diyl **2c** and anthracene-9,10-diyl **3c**) at room temperature (dotted lines) and at 10 K (solid lines). The spectra are normalised to unity at the peak of the emission or absorption.

shoulder at this energy in thick drop-cast samples. We note that the platinum atom mainly determines the spin–orbit coupling in these compounds and thus the radiative decay rate k_r should be similar throughout the series. However, the non-radiative decay rate k_{nr} increases exponentially with decreasing T_1 energy and is expected to be three orders of magnitude larger in **3d** than in **1d**,[14] so that the detection of the phosphorescence becomes very difficult.

Thermal analysis

All samples exhibit an exotherm coincident with mass loss due to decomposition. Decomposition onset was defined as a mass loss of 2%. The peak decomposition temperature was defined as the first inflection point in the thermogravimetric curve, corresponding to a peak in the derivative of the TG data. The decomposition exotherms are broad with multiple peaks, and the TG curves suggest a stepwise process. The first decomposition step corresponds to the removal of trialkylphosphine groups from the di-ynes and the poly-ynes. TG traces show that the Pt(II) diynes and poly-ynes have decomposition temperatures of over 300 °C, indicative of good thermal stability. These results are quite encouraging, since decomposition temperatures in excess of 300 °C are needed for the hermetic sealing process commonly used for device fabrication. The DTA peaks show exotherms at these temperatures, indicating that decomposition rather than vaporization is being observed. Poly-yne **3d** exhibits higher decomposition onset and peak temperatures than **2d**, which in turn, exhibits higher thermal stability than the phenylene-containing poly-yne **1d**. A similar trend in thermal stability was also observed for the Pt(II) di-ynes where **1c** showed the lowest and **3c** the highest onset and peak decomposition temperatures. The di-ynes exhibited slightly higher onset and peak decomposition temperatures than the corresponding Pt(II) poly-ynes. The results are shown in Table 5.

Conclusion

The present work provides a convenient entry to a series of Pt(II) di-ynes and poly-ynes incorporating condensed carbocyclic spacer groups in the backbone. Attempts have been made to evaluate how the nature of the central linking unit would influence their spectroscopic, optical, thermal, and structural properties. From the optical spectroscopic measurements it is apparent that the electron-rich naphthalene and anthracene spacers create strong donor–acceptor interactions between the Pt(II) centres and conjugated ligands along the rigid backbone of the polymers. The band gaps decrease as the size of the aromatic linker group increases, consistent with there being greater delocalisation within the anthracene linker group compared to the benzene linker group. Thermogravimetry shows that the di-ynes possess a somewhat higher thermal stability than the corresponding poly-ynes. Both the Pt(II) di-ynes and the poly-ynes exhibit increasing thermal stability along the series of spacers from phenylene through naphthalene to anthracene.

We are currently extending these studies to Pt(II) diynes and poly-ynes incorporating fused heterocyclic spacer groups and further investigation of other properties (such as redox and conducting properties) of these π-conjugated organometallic systems and their organic analogues are now in progress.

Experimental

General procedures

All reactions were performed under a dry argon atmosphere using standard Schlenk or glove-box techniques. Solvents were pre-dried and distilled before use by standard procedures.[32] All chemicals, except where stated otherwise, were obtained from Sigma–Aldrich and used as received. The compounds *trans*-[Ph(Et₃P)₂PtCl],[33] *trans*-[(ⁿBu₃P)₂PtCl₂],[34] 1,4-bis(ethynyl)benzene[25] and diiodonaphthalene/anthracene[35] were prepared by adaptation of 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 trimethyl phosphite. IR 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.

Table 5 Thermal analysis results for decomposition temperatures: all temperatures in °C. Uncertainties are approximately ±8 °C

Compound	T_{decomp} (onset)	T_{decomp} (peak)
1d	302	335
2d	308	342
3d	315	354
1c	309	345
2c	312	349
3c	319	362

Column chromatography was performed either on Kieselgel 60 (230–400 mesh) silica gel or alumina (Brockman Grade II–III).

Molecular weight measurements

Molar masses were determined by GPC method[36] 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 Mocel 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 as GPC LS).

Optical spectroscopy

The polymers and dimeric platinum complexes were dissolved in dichloromethane. Thin films were prepared on quartz substrates using a conventional photoresist spin-coater. Typical film thicknesses were 100–150 nm as measured on a Dektak profilometer. The optical absorption spectra were 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 was measured adjacent to the sample with a calibrated silicon diode. For PL measurements, excitation was provided from a continuous wave (cw) argon ion laser. The UV lines (334–365 nm) of this laser were used for the compounds with benzene and naphthalene spacers and 488 nm was used for the compounds with the anthracene spacer. Typical intensities used were a few mW mm⁻². The emission spectra were recorded using a spectrograph with an optical fiber input coupled to a cooled charge coupled device (CCD) array (Oriel Instaspec IV).

Thermal analysis

Thermal analysis (differential thermal analysis, DTA, and thermogravimetry, TG) of **1d–3d** and **1c–3c** was performed simultaneously in a Stanton-Redcroft model STA-780 Simultaneous Thermal Analyser under flowing N₂. Sample masses were ∼1 mg packed with ∼1 mg Al₂O₃ in open Inconel crucibles. The reference crucible contained Al₂O₃. Samples were heated at 10 °C min⁻¹ to 485 °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.

X-Ray crystallography

The crystals were mounted in inert oil on a glass fibre. Data were measured using graphite-monochromated Mo-Kα radiation, on a Nonius Kappa area detector (**2a, 2c**), and on a Stoe STADI-4 diffractometer (**1c**), or a Bruker AXS SMART CCD area detector on Station 9.8 of the CCLRC Daresbury Laboratory (**3a**) using an X-ray wavelength of $\lambda = 0.6941$ Å, 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).[37] All non-hydrogen atoms were refined anisotropically, except for the disordered ethyl groups in the

Table 6 Crystallographic data

Compound	2a	3a	1c	2c
Formula	$C_{20}H_{24}Si_2$	$C_{24}H_{26}Si_2$	$C_{46}H_{74}P_4Pt_2 \cdot 2CHCl_3$	$C_{50}H_{76}P_4Pt_2 \cdot 0.5CH_2Cl_2$
M_r	320.57	370.6	1379.85	1233.63
Crystal habit	Colourless block	Colourless prism	Yellow plate	Yellow plate
Crystal size/mm	$0.18 \times 0.16 \times 0.09$	$0.18 \times 0.08 \times 0.04$	$0.30 \times 0.24 \times 0.06$	$0.50 \times 0.12 \times 0.03$
Crystal system	Orthorhombic	Monoclinic	Triclinic	Triclinic
Space group	$Pbca$	$P2_1/c$	$P\bar{1}$	$P\bar{1}$
Cell dimensions				
a/Å	17.6525(15)	22.511(16)	9.615(2)	9.2606(1)
b/Å	12.6498(12)	16.794(18)	11.356(4)	16.6595(2)
c/Å	18.3731(15)	11.829(10)	13.277(4)	18.7419(2)
α/°	90	90	83.84(2)	112.549(1)
β/°	90	90.00(7)	84.89(2)	95.470(1)
γ/°	90	90	79.79(2)	94.400(1)
U/Å^3	4102.7(6)	4472(7)	1414.9(7)	2637.82(5)
Z	8	8	1	2
μ/mm^{-1}	0.169	0.163	5.365	5.501
T/°C	−103	−123	−93	−123
θ_{max} /°	25.01	25.00	24.97	30.09
λ/Å	0.71073	0.6941	0.71069	0.71073
No. of reflections				
Measured	6797	24363	9296	96643
Independent	3610	8424	4969	15448
R_{int}	0.034	0.056	0.031	0.084
Parameters	205	480	271	602
Restraints	12	327	0	18
$wR2$ (F^2, all refl.)	0.115	0.266	0.1173	0.0949
$R1$ [$F > 2\sigma(F)$]	0.045	0.085	0.0287	0.0357
GoF	1.045	1.022	1.252	1.063

structures of **1c** and **2c**. The disordered fragments were refined over two sites with the occupancies summing to unity. Disorder was also observed in the dichloromethane molecule in the crystal lattice of **2c**, and this was also refined with partial occupancies. Hydrogen atoms were included using rigid methyl groups or a riding model. The structure of **3a** was found to be twinned, with a pseudo-ortho-rhombic cell. The twin components were refined successfully using the TWIN and BASF commands in SHEXL-97,[37] the TWIN command being TWIN 1 0 0 0 −1 0 0 0 −1. Crystal data are provided in Table 6.

CCDC reference numbers 235526–235529.

See http://www.rsc.org/suppdata/dt/b4/b405070c/ for crystallographic data in CIF or other electronic format.

Ligand synthesis

The ligand precursors were synthesized by following a general procedure outlined below for **2a** and **2b**.

1,4-Diiodonaphthalene. *n*-Butyllithium (8.5 mL, 2.6 M in hexane, 22.1 mmol) was added dropwise over the course of 30 min to a vigorously stirred suspension of 1,4-dibromonaphthalene (2.58 g, 9.0 mmol) in anhydrous diethyl ether (50 cm^3). The mixture was stirred for an additional 10 min after which period iodine (7.5 g, 30 mmol) was added in several portions over 5 min. The reaction mixture was stirred for an additional 15 min until the color was a dark brown. The ethereal solution was washed several times with aqueous sodium thiosulfate (25% w/w), dried over anhydrous magnesium sulfate and the solvent removed under vacuum to obtain a pale yellow solid. The crude product was purified by recrystallization from CCl_4 (100 cm^3) to give off-white solid (1.82 g, 53% yield) identified as the titled compound. ^{1}H NMR (CDCl$_3$): δ 7.55 (dd, 2H, arom.), 8.55 (dd, 4H, arom.). EI MS: *m/z*: 380 (M$^+$). Anal. Calc. for $C_{10}H_6I_2$: C, 31.61; H, 1.59. Found: C, 31.51; H, 1.67%.

9,10-Diiodoanthracene. Similar procedure as described above was adopted using 9,10-dibromoanthracene (3.0 g, 8.93 mmol) to give the title compound as yellow needles in 50% isolated yield. ^{1}H NMR (CDCl$_3$): δ 7.55 (dd, 4H, arom.), 8.55 (dd, 4H, arom.). EI MS: *m/z*: 430 (M$^+$). Calc. for $C_{14}H_8I_2$: C, 39.10; H, 1.88. Found: C, 39.21; H, 1.90%.

1,4-Bis(trimethylsilylethynyl)naphthalene 2a. To a solution of 1,4-diiodonaphthalene (2.0 g, 5.26 mmol) in ^{i}Pr$_2$NH–THF (70 cm^3, 1 : 1 v/v) under nitrogen was added a catalytic mixture of CuI (20 mg), Pd(OAc)$_2$ (20 mg) and PPh$_3$ (60 mg). The solution was stirred for 20 min. at 50 °C and then trimethylsilylethyne (1.68 g, 17.1 mmol) was added. The reaction mixture was left with stirring for 20 h at 75 °C. 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 removed under reduced pressure. The residue was subjected to silica column chromatography using hexane–CH$_2$Cl$_2$ (1 : 1) as eluent to afford **2a** as a salmon coloured crystalline solid in 85% yield (1.43 g). IR (CH$_2$Cl$_2$): ν/cm^{-1} 2155 (–C≡C–). ^{1}H NMR (250 MHz, CDCl$_3$): δ 0.27 (s, 18H, SiMe$_3$), 7.56 (2H, dd, H$_{6,7}$), 7.64 (2H, s, H$_{2,3}$), 8.35 (2H, dd, H$_{5,8}$). ^{13}C NMR (100 MHz, CDCl$_3$): δ 0.04 (s, SiMe$_3$), 101.36, 102.81 (C≡C), 121.54, 126.55, 127.24, 129.31, 133.08 (arom.). EI MS: *m/z*: 320 (M$^+$). Calc. for $C_{20}H_{24}Si_2$: C, 74.97; H, 7.55. Found: C, 75.03; H, 7.63%.

1,4-Bis(ethynyl)naphthalene 2b. The bis-trimethylsilylethynyl derivative **2a** (1.0 g, 3.12 mmol) was proto-desilylated in THF–methanol (50 cm^3, 4 : 1 v/v) using aqueous KOH (0.38 g, 6.86 mmol in 1 cm^3 H$_2$O). The reaction mixture was stirred at room temperature for 2 h, solvent removed and the crude product was purified by silica column chromatography eluting with hexane–CH$_2$Cl$_2$ (2 : 1, v/v). The desired compound **2b** was isolated as an orange–red solid in 80% isolated yield (0.44 g). IR (CH$_2$Cl$_2$): ν/cm^{-1} 2107 (–C≡C–), 3299 (C≡C–H). ^{1}H NMR (250 MHz, CDCl$_3$): δ 3.30 (s, 2H, C≡CH), 7.30 (2H, dd, H$_{6,7}$), 7.56 (2H, s, H$_{2,3}$) 8.35 (2H, dd, H$_{5,8}$). ^{13}C NMR (100.6 MHz, CDCl$_3$): δ 101.36, 102.81 (C≡C), 121.54, 126.55, 127.24, 129.31, 133.08 (arom.). EI-MS: *m/z*: 176.22 (M$^+$). Calc. for $C_{14}H_8$: C, 95.43; H, 4.58. Found: C 95.39; H, 4.61%.

9,10-Bis(trimethylsilylethynyl)anthracene 3a. 9,10-Diiodoanthracene (2.0 g, 4.6 mmol), trimethylsilylethyne (1.46 g, 14.9 mmol) and ^{i}Pr$_2$NH–THF (70 cm^3, 1 : 1 v/v) were mixed with catalytic amounts of CuI (20 mg), Pd(OAc)$_2$ (20 mg) and PPh$_3$ (60 mg). The crude product was worked up, as before, to yield a dark brown residue, which was then applied to a silica column in hexane and eluted with the same solvent. The desired compound **3a** was obtained as a deep red crystalline solid in 78% isolated yield

(1.72 g). IR (CH$_2$Cl$_2$): ν/cm^{-1} 2152 (–C≡C–). ^{1}H NMR (250 MHz, CDCl$_3$): δ 0.27 (s, 18H, SiCH$_3$), 7.63 (dd, 4H, H$_{1–4}$), 8.44 (dd, 4H, H$_{5–8}$). ^{13}C NMR (100.6 MHz, CDCl$_3$): δ 0.20 (s, SiMe$_3$), 101.50, 108.16 (C≡C), 118.44, 127.19, 127.57, 132.36 (arom.). EI-MS: m/z 370 (M$^+$). Calc. For C$_{24}$H$_{26}$Si$_2$: C, 77.81; H, 7.07. Found: C, 78.04; H 6.98%.

9,10-Bis(ethynyl)anthracene 3b. Compound **3a** was proto-desilylated as in **2a** and the crude product was worked up, as before, to yield a dark red solid. Silica column chromatography with hexane–CH$_2$Cl$_2$ (1 : 1 v/v) gave a red solid identified as **3b** (76% yield). IR (CH$_2$Cl$_2$): ν/cm^{-1} 2107 (–C≡C–), 3299 (C≡C–H). ^{1}H NMR (250 MHz, CDCl$_3$): δ 3.30 (s, 2H, C≡CH), 7.63 (dd, 4H, H$_{1–4}$), 8.32 (dd, 4H, H$_{5–8}$). ^{13}C NMR (100.6 MHz, CDCl$_3$): δ 101.50, 108.16 (C≡C), 118.44, 127.19, 127.57, 132.36 (arom.). EI-MS: m/z 226 (M$^+$). Satisfactory microanalysis could not be obtained due to instability of the diterminal alkyne.

Synthesis of Pt(II) di-ynes

The Pt(II) di-ynes **1c–3c** were synthesized by the general procedure outlined below for **1c**.

***trans*-[Ph(Et$_3$P)$_2$Pt–C≡C–R–C≡C–Pt(PEt$_3$)$_2$Ph] (R = benzene-1,4-diyl) 1c.** To a stirred solution of *trans*-[Ph(PEt$_3$)$_2$PtCl] (0.543 g, 1.0 mmol) and 1,4-bis(ethynyl)benzene (0.063 g, 0.5 mmol) in ^{i}Pr$_2$NH–CH$_2$Cl$_2$ (50 cm^3, 1 : 1 v/v) under nitrogen was added CuI (5 mg). 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 CH$_2$Cl$_2$ and passed through a silica column eluting with hexane–CH$_2$Cl$_2$ (1 : 1, v/v). Removal of the solvents *in vacuo* gave the title complex as a pale yellow solid in 70% yield (0.40 g). IR (CH$_2$Cl$_2$): ν/cm^{-1} 2095 (–C≡C–). ^{1}H NMR (250 MHz, CDCl$_3$): δ 7.53 (d, 4H, H$_{ortho}$ of Ph), 7.13 (s, 4H, phenylene spacer), 6.92 (t, 4H, H$_{meta}$ of Ph), 6.77 (t, 2H, H$_{para}$ of Ph), 1.87–1.80 (m, 24H, P–CH$_2$), 1.10 (m, 36H, P–CH$_2$CH$_3$), ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$): δ 156.21, 150.08, 139.22, 137.92, 130.85, 127.45, 126.93, 125.65, 121.13, 118.68 (aromatic), 112.94, 110.76 (C≡C), 14.92, 7.88 (aliph.). ^{31}P{^{1}H} NMR (101.3 MHz, CDCl$_3$): δ –131.17, $^1J_{Pt–P}$ = 2628 Hz. FAB-MS: m/z 1141 (M$^+$). Calc. for C$_{46}$H$_{74}$P$_4$Pt$_2$: C, 48.42; H, 6.54. Found: C, 48.48; H, 6.63%.

***trans*-[Ph(Et$_3$P)$_2$Pt–C≡C–R–C≡C–Pt(PEt$_3$)$_2$Ph] (R = naph-thalene-1,4-diyl) 2c.** This compound was synthesised employing similar reaction conditions to those of 1c but using 2b instead of 1b. The product was purified on preparative TLC plates with hexane–CH$_2$Cl$_2$ (3 : 7, v/v) as eluent giving compound 2c as an orange solid in an isolated yield of 65% (0.39 g). IR (CH$_2$Cl$_2$): ν/cm^{-1} 2095 (–C≡C–). ^{1}H NMR (250 MHz, CDCl$_3$): δ 8.34 (dd, 2H, H$_{5,8}$), 7.44 (dd, 2H$_{6,7}$) 7.38 (s, 2H, H$_{2,3}$), 7.32 (d, 4H, H$_{ortho}$ of Ph) 6.95 (d, 4H, H$_{meta}$ of Ph), 6.80 (t, 2H, H$_{para}$ of Ph), 1.75 (m, 24H, P–CH$_2$), 1.07 (m, 36H, P–CH$_2$CH$_3$), ^{13}C NMR (100 MHz, CDCl$_3$): δ 156.49, 139.26, 137.29, 133.85, 127.47, 124.91, 123.87, 121.16, 119.22 (arom.), 111.01, 108.85 (C≡C), 15.22, 7.90 (aliph.). ^{31}P {^{1}H} NMR (101.3 MHz, CDCl$_3$): δ –131.17, $^1J_{Pt–P}$ = 2643 Hz. FAB-MS: m/z 1191 (M$^+$). Calc. for C$_{50}$H$_{76}$P$_4$Pt$_2$: C, 50.41; H, 6.43. Found: C, 50.69; H, 6.58%.

***trans*-[Ph(Et$_3$P)$_2$Pt–C≡C–R–C≡C–Pt(PEt$_3$)$_2$Ph] (R = anthra-cene-9,10-diyl) 3c.** Treatment of the freshly prepared diterminal alkyne **3b** (0.113 g, 0.50 mmol) with *trans*-[Ph(Et$_3$P)$_2$PtCl] (0.543 g, 1.0 mmol) for 15 h at room temperature, in the presence of a catalytic amount of CuI (5 mg) gave the required complex as an orange solid in 65% isolated yield after purification on a silica column using hexane–CH$_2$Cl$_2$ (3 : 7, v/v) as eluent. IR (CH$_2$Cl$_2$): ν/cm^{-1} 2094 (–C≡C–). ^{1}H NMR (250 MHz, CDCl$_3$): δ 7.72 (dd, 4H, H$_{1,4,5,8}$), 7.40 (dd, 4H, H$_{2,3,6,7}$), 7.25 (d, 4H, H$_{ortho}$ of Ph), 6.99 (t, 4H, H$_{meta}$ of Ph), 6.82 (t, 2H, H$_{para}$ of Ph), 1.77 (m, 24H, P–CH$_2$), 1.12 (m, 36H, P–CH$_2$CH$_3$). ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$): δ 139.37, 131.74, 128.45, 127.28, 33,121, 124.16 (arom.), 110.89,

108.68 (C≡C), 15.36 and 8.05 (aliph.). ^{31}P{^{1}H-NMR (101.3 MHz, CDCl$_3$): δ –131.17, $^1J_{Pt–P}$ = 2645 Hz. FAB-MS: m/z 1241 (M$^+$). Calc. for C$_{54}$H$_{78}$P$_4$Pt$_2$: C, 52.25; H, 6.33. Found: C, 52.53; H, 6.28%.

Synthesis of Pt(II) poly-ynes

The synthesis of Pt(II) poly-yne **1d** has been reported previously.[26] The poly-ynes **2d** and **3d** were synthesized by the general procedure outlined below for **2d**.

***trans*-[–(Bu$_3$P)$_2$Pt–C≡C–R–C≡C–]$_n$, (R = naphthalene-1,4-diyl) 2d.** CuI (5 mg) was added to a mixture of *trans*-[Pt(PBu^n$_3$)$_2$Cl$_2$] (0.670 g, 1.0 mmol) and **2b** (0.176 g, 1.0 mmol) in ^{i}Pr$_2$NH–CH$_2$Cl$_2$ (50 cm^3, 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 CH$_2$Cl$_2$ and passed through a short alumina column. After removal of the solvents by a rotary evaporator, an off-white film was obtained readily which was then washed with methanol to give the polymer **2d** in 85% isolated yield (0.66 g). Further purification can be accomplished by precipitating the polymer solution in methanol from dichloromethane. IR (CH$_2$Cl$_2$): ν/cm^{-1} 2095 (–C≡C–). ^{1}H NMR (250 MHz, CDCl$_3$): δ 8.43 (d, 2H, H$_{5,8}$), 7.36 (d, 2H, H$_{6,7}$), 7.25 (s, 2H, H$_{2,3}$), 2.17 (m, 12H, P–CH$_2$), 1.60 (br, 12H, CH$_2$), 1.41 (sextet, 12H, CH$_2$), 0.92 (t, 18H, CH$_3$), ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$): δ 133.76, 127.89, 127.48, 124.97, 123.74 (arom.), 112.23, 111.16 (C≡C), 53.38, 26.54, 24.29, 13.84 (aliph.). ^{31}P{^{1}H} NMR (101.3 MHz, CDCl$_3$): δ –138.03, $^1J_{Pt–P}$ = 2363 Hz. Calc. for (C$_{38}$H$_{60}$P$_2$Pt)$_n$: C, 58.97; H, 7.81. Found: C, 59.07; H, 7.89%. GPC (THF): M_n = 41020 g mol^{-1} (n = 53), M_w = 78000 g mol^{-1}, PDI = 1.9.

***trans*-[–(Bu$_3$P)$_2$Pt–C≡C–R–C≡C–]$_n$, (R = anthracene-9,10-diyl) 3d.** Red solid (90% yield). IR (CH$_2$Cl$_2$): ν/cm^{-1} 2094 (–C≡C–). ^{1}H NMR (250 MHz, CDCl$_3$): δ 8.30 (br, 4H, H$_{2,3,6,7}$), 7.51 (br, 4H, H$_{1,4,5,8}$), 2.16 (t, 12H, PCH$_2$), 1.68 (m, 12H, CH$_2$), 1.25 (br, 12H, CH$_2$), 0.88 (t, 18H, CH$_3$), ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$): δ 139.37, 131.77, 128.43, 127.28, 124.46 (arom.), 110.28, 108.39 (C≡C), 50.84, 26.76, 24.34 and 13.85 (aliph.). ^{31}P{^{1}H} NMR (101.3 MHz, CDCl$_3$): δ –138.03, $^1J_{Pt–P}$ = 2373 Hz. Calc. for (C$_{42}$H$_{62}$P$_2$Pt)$_n$: C, 61.22; H, 7.58. Found: C, 60.98; H, 7.87%. GPC (THF): M_n = 28000 g mol^{-1} (n = 34), M_w = 50500 g mol^{-1}, PDI = 1.8.

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