FULL PAPER

Synthesis, structures and optical spectroscopy of photoluminescent platinum-linked poly(silylacetylenes)

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Synthetic routes to a series of novel oligomeric and polymeric platinum(II)-containing silylacetylenes have been developed. The CuI-catalyzed reaction of *trans*-[Pt(PEt₃)₂PhC] with the alkynylsilane Ph₂Si(C=CH)₂, in a basic medium, afforded the mononuclear *trans*-[Ph(Et₃P)₂PtC=CSiPh₂C=CH] (1) and the dinuclear *trans*-[Ph(Et₃P)₂PtC=CSiPh₂C=CPt(PEt₃)₂Ph] (2). Complex 1 can be utilized as a key starting material for access to the triplatinum(II) system *trans*-[Ph(Et₃P)₂PtC=CSiPh₂C=CPt(PBu₃)₂C=CSiPh₂C=CPt(PEt₃)₂Ph] (3). Attempted oxidative coupling of 1 only led to the isolation of the triacetylenic species *trans*-[Ph(Et₃P)₂PtC=CC=CC=CPt(PEt₃)₂Ph] (5), involving cleavage of Si–C(alkyne) bonds. Soluble and thermally stable platinum(II) poly-yne silane polymer *trans*-[-Pt(PBu₃)₂C=CSiPh₂C=C-]_n (4) was prepared in good yield by CuI-catalyzed polymerization of *trans*-[Pt(PBu₃)₂Cl₂] and Ph₂Si(C=CH)₂. The single-crystal X-ray structural analyses and DFT calculations were performed on 1, 2 and 5. We report the optical absorption and photoluminescence spectra of these new metal-based oligomeric and polymeric silylacetylenes and the results are compared with platinum(II) poly-ynes with purely acetylenic and (hetero)aromatic conjugated units.

Introduction

With the realization of polyacetylenes and other conjugated heteronuclear polymers as potentially important electronic and optically active materials, research on electron delocalized organic and metalloorganic polymers has received increased attention in the scientific community.¹ Among them, organosilicon polymers are becoming important in many aspects of device technology and play an increasingly vital role in the electronic industry today.² In particular, the molecular design and synthesis of linear, cyclic or dendritic systems composed of silicon atoms and acetylene units have attracted enormous research interest.^{2,3} The lower ionization energy of the silicon atom compared with carbon is expected to enhance the through-bond interaction of ethynyl units along the backbone.^{4,5} These organosilicon compounds can act as functional materials such as semiconductors, hole-transporting and heatresistant materials and ceramic precursors.² The electrical and optical properties associated with these materials are generally attributed to the delocalization of electrons through the silylene linkages via π -d_{si} interaction⁶ and σ - π conjugation.^{4,7} π -Conjugated organosilicon systems have been extensively studied regarding their applications to electro- and optical devices.8

There is a long-term interest in the design, synthesis and photophysics of rigid-rod organometallic poly-ynes of the general formula *trans*-[$-Pt(PBu_3)_2C\equiv CRC\equiv C-]_n$ (R = aromatic or heteroaromatic spacer groups) and these metal-based polymers contribute a particularly important class of new materials for basic and applied research.⁹ One of the merits in the present system is that incorporation of a heavy platinum centre in the polymer chain induces strong spin–orbit coupling to allow light emission from the triplet excited state of the conjugated ligand and higher quantum efficiencies may be achieved in the light-emitting devices by harvesting the energy of the nonemissive triplet excitons.^{9a-e} These metal-containing poly-vnes also provide model systems for the study of some of the photophysical processes that occur in conjugated organic polymers.¹⁰ For commercial exploitation of these materials and for controlled application-aimed synthesis, a fundamental and thorough understanding of the structure-property relationship is crucial such that suitable modifications of the chemical structures and geometries may fine-tune the electronic and optical properties of the polymers. Recent works by us and others have investigated the dependence of the intersystem crossing rate from the singlet excited state to the triplet excited state as a function of the extent of π -conjugation along the backbone.9a-e While considerable effort has been devoted to the use of (hetero)aromatic or carbon-rich acetylenic spacer units, much less is known for the silicon-linked system and related studies on platinum(II) alkynylsilanes remain relatively unexplored. Here we report the first synthesis, structural characterization and luminescence behaviour of a series of novel platinum-containing oligo- and poly-(silylacetylenes). Their optical and theoretical properties will be discussed in comparison to those systems having purely acetylenic and other (hetero)aromatic spacers.

Results and discussion

Synthesis

The preparations of new complexes and polymers are shown in Scheme 1. Using the well-established dehydrohalogenation route under the CuI- ${}^{i}Pr_{2}NH$ catalytic system, ${}^{9a-k}$ trans- $[Pt(PEt_{3})_{2}PhCl]$ reacts with Ph₂Si(C=CH)₂ (I) to produce the

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 $\begin{array}{l} \textbf{Scheme 1} \quad \text{Reagents and conditions: (i) } \textit{trans-[Pt(PEt_3)_2PhCl], CuI, } ^{i}Pr_2NH-CH_2Cl_2, rt; (ii) } \textit{trans-[Pt(PBu_3)_2Cl_2] (0.5 equiv.), CuI, } ^{i}Pr_2NH-CH_2Cl_2, rt; (iii) } \textit{trans-[Pt(PBu_3)_2Cl_2] (1 equiv), CuI, } ^{i}Pr_2NH-CH_2Cl_2, rt; (iv) Cu(OAc)_2 (1.5 equiv.), pyridine, O_2, CH_2Cl_2. \\ \end{array}$

mono-platinum complex trans-[Ph(Et₃P)₂PtC=CSiPh₂C=CH] (1) and the dinuclear species trans- $[Ph(Et_3P)_2PtC=CSiPh_2C=$ CPt(PEt₃)₂Ph] (2), the product distribution of which depends on the stoichiometry of the reactants used. Starting from 1 with a free alkyne unit, this can provide an easy entry to the triplatinum compound trans-[Ph(Et₃P)₂PtC=CSiPh₂C=CPt-(PBu₃)₂C=CSiPh₂C=CPt(PEt₃)₂Ph] (3) accompanied by a doubling of the chain length. However, attempted oxidative homocoupling of 1 in Cu(OAc)₂-O₂-pyridine¹¹ has met with little success and only a complicated mixture was obtained from which we were able to isolate the triacetylenic complex trans-[Ph(Et₃P)₂PtC=CC=CPt(PEt₃)₂Ph] (5). The formation of 5 involves the cleavage of Si-C(alkyne) bonds and this kind of bond breaking was also observed when [Au(PPh₃)Cl] was allowed to react with I in a NaOMe-MeOH mixture to furnish the known complex [(Ph₃P)AuC≡CAu(PPh₃)].¹² All these new complexes were isolated as off-white to light yellow solids from preparative TLC plates on silica. Organometallic polymer $trans-[-Pt(PBu_3)_2C\equiv CSiPh_2C\equiv C-]_n$ (4) was synthesized by CuIcatalyzed polycondensation polymerization between equimolar quantities of *trans*-[Pt(PBu₃)₂Cl₂] and I.^{9a-k} Purification by silica column chromatography using CH₂Cl₂ as eluent gives 4 in high purity and yield (78%) and the product appears oily at room temperature.

All these platinum complexes are air-stable and can be stored without any special precautions. They have good solubility in common organic solvents except hydrocarbons. The $M_{\rm w}$ value determined by gel permeation chromatography (GPC) in THF indicates a high degree of polymerization for 4 and the number of repeat units per chain calculated from M_n is 63, which is lower than that for the totally linear *trans*-[-Pt(PBu₃)₂C=CC=CC=C-]_n.¹³ The polydispersity index (M_w/M_n) of 1.51 for 4 is a common value for polycondensation polymers. It should be noted that GPC does not give absolute values of molecular weights but provides a measure of hydrodynamic volume. The hydrodynamic properties of rigid-rod type polymers in solution are quite different from those for flexible polymers. In view of this, calibration of the GPC with polystyrene standards is likely to inflate the molecular weight values of our metal poly-yne. The lack of discernible NMR resonances attributable to the end groups confirms a high degree of polymerization in 4.

Spectroscopic and redox properties

The IR, NMR, MS and elemental analysis data shown in the Experimental section are consistent with the chemical structures of our new compounds 1–5. The IR spectra of 1–4 are each dominated by a sharp $v_{C=C}$ absorption band (*ca.* 2025–2031)

cm⁻¹) and the peaks are lower than that for the free silvl ligand precursor I (2041 cm⁻¹), in line with π -conjugation through the platinum group. The terminal acetylenic C-H absorption is also located at 3260 cm^{-1} for 1. The triacetylenic species 5 shows a strong $v_{C=C}$ stretch at 2087 cm⁻¹, which compares well with the value (2096 cm⁻¹) for the polymeric analogue trans- $[-Pt(PBu_3)_2C \equiv CC \equiv CC \equiv C-]_n^{13}$ but the frequency is significantly larger than that for 2. The ¹H NMR spectra of all the compounds exhibit the expected signals for the systems and clearly demonstrate a well-defined structure for each compound. Except for the trinuclear complex 3, the unique singlets in the ³¹P-{¹H} NMR spectra flanked by platinum satellites for the mono- and di-platinum complexes and the polymer confirm the trans arrangement of the phosphine ligands in such squareplanar geometry. Two distinct ³¹P signals are observed for the terminal and central phosphine groups in 3. The ${}^{1}J_{P-Pt}$ coupling constants are normal for related *trans*-PtP₂ systems.^{9a-k} The ${}^{13}C$ NMR spectral data for polymer 4 also give precise information about the regiochemical structure of the main-chain skeleton and show a high degree of structural regularity in the polymer. The two ¹³C NMR peaks for the sp carbons in 4 are shifted downfield with respect to those for I ($\delta = 83.37$ and 97.36). For 1-4, the ²⁹Si NMR chemical shifts appear at more downfield positions in comparison to I ($\delta = -48.42$) and do not differ significantly from those for related polymers consisting of silvlacetylene and π -conjugated organic groups.¹⁴

The electrochemical nature of our compounds was investigated in CH_2Cl_2 by cyclic voltammetry (Table 1). Within the measured scan range, each only showed a single irreversible wave in the range of *ca*. 0.53–0.90 V due to the one-electron $Pt^{2+} \rightarrow Pt^{3+}$ oxidation but we observe no reduction prior to the solvent limit. Ligand I is electrochemically silent in our measurements. There is no particular trend in the electrochemical data of these complexes apart from a slight anodic shift of the oxidation potential when going from the polymer to the monomeric, dinuclear and trinuclear species. Similar shifts were also observed in some fluorene- and carbazole-based platinum poly-ynes.^{9e}

Structural and theoretical studies

The regiochemical structure of the polymer has been ascertained by single-crystal X-ray analysis on the model complexes 1 and 2 and the solid-state structure of 5 was also determined in comparison to that of 2. Perspective views of 1, 2 and 5 are shown in Figs. 1–3, respectively, and important bond distances and angles are given in Tables 2–4. There are two structurally independent but similar molecules per asymmetric unit in the unit cell of 2. In each case, the coordination geometry at the Pt

 Table 1
 Absorption, emission and electrochemical data for 1–5

	$\lambda_{\max}{}^a/nm$	$\lambda_{\rm max}/{\rm nm}$		$\lambda_{ m em}/ m nm$		
	CH ₂ Cl ₂	Film	E_{g}^{b}/eV	Film (290 K)	Film (11 K)	E_{ox} ^c /V
1	266 (1.0), 308 (0.5)	265 307	3.87			+0.90
2	268 (1.5), 308 (0.8)	264 309	3.81	Very weak	401, ^{<i>d</i>} 443, 484, 505, 535, ^{<i>d</i>} 561 ^{<i>d</i>}	+0.88
3	261 (1.6), 275 (1.8), 310 (1.8)	262 275	3.78	421, ^{<i>d</i>} 504 ^{<i>d</i>}	421, ^{<i>d</i>} 462, ^{<i>d</i>} 504, 542 ^{<i>d</i>}	+0.90
4	261 (1.4), 277 (1.7), 312 (2.0)	261 278 314	3.70	418, ^d 510 ^d	419, ^{<i>d</i>} 508	+0.53
5	272 (0.24), 288 (0.22), 317 (0.16), 344 (0.05), 370 (0.02)	273 289 319 345 271	3.25	500, 561, 634 ^{<i>d</i>}	500, 561, 634	

^{*a*} Extinction coefficients ($10^4 \text{ M}^{-1} \text{ cm}^{-1}$) are shown in parentheses. ^{*b*} Estimated from the onset wavelength of the solid-state optical absorption. ^{*c*} Irreversible waves. ^{*d*} Emission peaks appear as shoulders or weak bands.



Fig. 1 A perspective view of complex **1**. Thermal ellipsoids are drawn at the 25% probability level.



Fig. 2 A perspective view of complex **2**. Thermal ellipsoids are drawn at the 25% probability level.

centre is square-planar and the two PEt₃ groups are positioned *trans* to each other. To our knowledge, complex **2** is the first structurally characterized example of a silylacetylene-linked diplatinum complex. The internal C=C bond lengths lying within the narrow range 1.196(9)–1.226(10) Å are typical of metal-acetylide σ bonding and the C=CH bond [1.181(7) Å] in **1** shows a slight shortening due to the libration effect.¹⁵ The Si–C(sp) single bond lengths are 1.792(5)–1.838(5) Å, which

 Table 2
 Selected bond lengths (Å) and angles (°) for 1

Pt(1)–P(1) Pt(1)–C(19) Si(1)–C(20) C(21)–C(22)	2.2895(12) 2.009(4) 1.792(5) 1.181(7)	Pt(1)–P(2) C(19)–C(20) Si(1)–C(21)	2.3019(12) 1.217(6) 1.838(5)
P(1)-Pt(1)-C(19) Pt(1)-C(19)-C(20) Si(1)-C(21)-C(22)	92.06(12) 173.7(4) 179.3(5)	P(2)-Pt(1)-C(19) Si(1)-C(20)-C(19) C(20)-Si(1)-C(21)	88.93(13) 171.5(4) 109.6(2)



Fig. 3 A perspective view of complex **5**. Thermal ellipsoids are drawn at the 25% probability level.

appear to be slightly shorter than those found in other silylacetylene compounds in the literature.^{3c,16} These data, together with the observed C=C bond lengths, are suggestive of partial through-Si conjugation along the molecule. For **5**, the fourcoordinate platinum atoms are bridged by a virtually linear C_6^{2-} chain with the crystallographic symmetry located at the centre of the hexatriynediyl unit. The structural data for bridging acetylenic units in **5** compare well with those reported by Gladysz, Bruce, Lapinte, Akita and Che.^{11,17} The bond angles close to 180° for the fragment Pt–C=C confirm the rigid-rod nature of all complexes. All of the remaining structural parameters are comparable to those found for other crystal structures of platinum(II) acetylide compounds in the literature.^{9e-g}

To study the electronic structures of platinum diynyl complexes which differ in the central unit that bridges the two metal fragments, we have carried out molecular orbital calculations on 1, 2, 5 and *trans*-[Ph(Et₃P)₂PtC=CRC=CPt(PEt₃)₂Ph] (R = 2,5-thienyl)¹⁸ at the B3LYP level of density functional theory based on their experimental geometries obtained from X-ray data. Examining the characteristics of the molecular orbitals in the frontier region, we find that the highest occupied (HOMO)

	Molecule 1	Molecule 2		Molecule 1	Molecule 2
Pt(1)–P(1)	2.295(2)	2.297(2)	Pt(1)–P(2)	2.276(2)	2.282(2)
Pt(2)-P(3)	2.275(2)	2.268(2)	Pt(2) - P(4)	2.276(2)	2.278(3)
Pt(1)-C(19)	2.019(7)	2.011(8)	Pt(2) - C(34)	2.027(7)	2.000(8)
C(19) - C(20)	1.210(10)	1.221(11)	Si(1) - C(20)	1.807(8)	1.810(8)
Si(1)-C(33)	1.821(7)	1.814(8)	C(33) - C(34)	1.196(9)	1.226(10)
P(1)-Pt(1)-C(19)	91.66(19)	91.6(2)	P(2)-Pt(1)-C(19)	90.93(19)	87.7(2)
P(3)-Pt(2)-C(34)	89.8(2)	90.5(3)	P(4) - Pt(2) - C(34)	87.7(2)	86.5(3)
Pt(1) - C(19) - C(20)	177.6(6)	177.5(8)	Pt(2) - C(34) - C(33)	177.3(7)	177.7(8)
C(20) - Si(1) - C(33)	114.7(3)	112.2(4)			~ /

Table 4Selected bond lengths (Å) and angles (°) for 5

Pt(1)-P(1)	2.295(2)	Pt(1)–P(2)	2.292(2)
Pt(1)-C(19)	2.002(7)	C(19) - C(20)	1.217(10)
C(20)–C(21)	1.370(10)	C(21)–C(21A)	1.208(14)
P(1)-Pt(1)-C(19)	87.0(2)	P(2)-Pt(1)-C(19)	93.2(2)
Pt(1)-C(19)-C(20)	174.7(8)	C(19)-C(20)-C(21)	178.3(11)
C(20)–C(21)–C(21A)	179.3(9)		
Symmetry transformat	ions used to a	enerate equivalent ator	$ms \cdot -r + 2$

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

and lowest unoccupied molecular orbitals (LUMO) are mainly related to orbitals from the metal centres and π/π^* from the conjugate organic structural units. The HOMOs correspond to the linear combination of π orbitals from the conjugate organic units and also mix slightly with the metal d orbitals in an antibonding fashion. The LUMOs contain mainly the vacant p₁ orbitals of the Pt centre mixed with π^* orbitals of the organic bridge. Here, p₁ stands for the p orbitals perpendicular to the square planes around Pt, *i.e.*, p_z when each coordination plane is specifically defined as the xy plane. From the contour plots,¹⁹ shown in Fig. 4, the calculated HOMO-LUMO gap follows the order 5 (4.18 eV) \approx trans-[Ph(Et_3P)_2PtC=CRC=CPt(PEt_3)_2Ph] $(R = 2,5-thienyl) (4.30 eV) \le 2 (5.22 eV) \le 1 (5.38 eV)$, in line with the extent of π -delocalization in the conjugated chain. Apparently, the triple bond and thiophene units are able to extend π -conjugation effectively while the SiPh₂ group does not since the two metallic moieties are separated by two Si-C single bonds. The small difference in the optical gaps between 1 and 2 agrees with the almost identical lowest energy band in their absorption spectra (vide infra).

Thermal analysis

Polymer 4 showed a very good thermal stability as confirmed by thermogravimetric analysis (heating rate 20 °C min⁻¹ under N₂) and no decomposition took place up to 381 °C. Such an onset temperature is higher than those in related polymers *trans*- $[-Pt(PBu_3)_2C\equiv CRC\equiv C-]_n$ (R = phenylene, thienylene, pyridyl, substituted fluorenylene),^{9b,e,f,i,k} suggesting that use of the SiPh₂ unit can increase the thermal stability of platinum(II) poly-ynes. The mass loss in 4 was quite sharp and 48% of the sample mass was lost as the temperature rose from 381 to 423 °C. The decomposition step is assigned to the removal of two PBu₃ groups from the polymer. Although glass transition temperatures can be located for platinum(II) poly-ynes containing phenylene and thienylene spacers,^{9b} polymer 4 did not exhibit discernable glass transition, reminiscent of the recently reported oligopyridyl analogues.^{9k} In addition, this polymeric material decomposes without melting.

Optical spectroscopy

Optical absorption spectra of our new platinum(II)-containing silylacetylenes were taken at room temperature in CH_2Cl_2 solutions and as thin films. Relevant data are shown in Table 1. For 1–4, they display similar structured absorption bands (*ca.* 266–312 nm) in the near UV region in solution. In each case, the first absorption band arises mainly from the π - π * transition in the organic system, possibly with some admixture of metal d orbitals which may change the overall energy of the transition.^{9a-c} We associate the lowest energy peak with the S₀ \rightarrow S₁ transition from the HOMO to the LUMO, which are mainly delocalized π and π * orbitals. Well-resolved structure in the absorption spectrum is apparent in 5, which is a result of



Fig. 4 Contour plots of the frontier molecular orbitals for 1, 2, 5 and *trans*-[Ph(Et₃P)₂PtC=CRC=CPt(PEt₃)₂Ph] (R = 2,5-thienyl). (1 au = 27.2114 eV).

Table 5 Optical gaps (in eV) for platinum di-ynes and poly-ynes with aseries of spacer groups

	Decreasing delocalization of electrons→				
Spacer	≡	$\langle s \rangle$	$\langle \rangle$		SiPh ₂
Di-yne Poly-yne	3.22 2.82	3.22 2.85	3.34 2.98	3.38 3.05	3.81 3.70

transitions from ground to excited electronic states coupled with transitions to the various vibronic levels of the excited state. The spectral pattern is similar to that of its polymeric counterpart *trans*- $[-Pt(PBu_3)_2C \equiv CC \equiv CC \equiv C-]_n$.¹³ With reference to the value at 272 nm for I, we note a red shift of the position of the lowest energy absorption band in 1-4 after the inclusion of platinum fragment. This reveals that π -conjugation of the ligand is preserved through the metal site. The apparent lack of an energy shift in the $S_0 \rightarrow S_1$ transition among 1–4 shows that the lowest singlet excited state is confined to a single repeat unit, which is in contrast to *trans*- $[-Pt(PBu_3)_2C \equiv CRC \equiv C-]_n$ (R = 1,4-phenylene, 2,5-thienylene, 2,5-pyridyl) with a wellextended singlet excited state.9a-c The experimentally determined HOMO-LUMO energy gaps (E_g) as measured from the onset wavelength in the solid film are tabulated in Table 5 for a series of spacer groups in platinum di-ynes and poly-ynes. The degree of electronic conjugation roughly follows the order: $C \equiv C \approx 2,5$ -thienyl > 1,4-phenylene > 2,5-pyridyl > SiPh₂.^{9b-d,13} In other words, the energy of the S_1 singlet state is highest for the silicon-linked derivatives among them. It is obvious from Table 1 that the E_{g} values show a gradual decrease in the order 1 > 2 > 3 > 4 with increasing chain length.

The thin film photoluminescence (PL) spectra of 2–5 were measured at various temperatures and the results are gathered in Table 1. For these silicon-linked compounds, we observe no fluorescence band but only the phosphorescence bands associated with the mixed ligand-metal orbitals. We consider that the emission peaks arise from a triplet excited state (*i.e.* $T_1 \rightarrow S_0$) based on the observed temperature dependence of emission data and the lifetime measurements, in accordance with earlier work on platinum(II) poly-ynes.^{9a-e,k} The temperature dependencies of the PL spectra of 3 and 4 are shown in Figs. 5 and 6, respectively.



Fig. 5 Temperature dependence of the photoluminescence of 3.

In each case, the triplet photoluminescence band shows a strong temperature dependence and there is a strong increase in intensity with decreasing temperature. From 290 to 11 K, the intensity of the triplet emission increases by a factor of 38.0 and 58.3 for **3** and **4**, respectively, typical of this class of metal poly-ynes, and such an increase in emission intensity indicates a triplet exciton that is quenched by thermally activated diffusion



Fig. 6 Temperature dependence of the photoluminescence of 4.

to dissociation sites at room temperature. At 11 K, the principal emissive peak occurs at *ca.* 484, 504 and 508 nm for **2**, **3** and **4**, respectively. Lifetime (τ) data suggest that the main emission peak for **3** and **4** is rather long-lived. The τ values are found to be 37.7 ± 0.2 (**3**) and 11.0 ± 0.1 (**4**) µs at 290 K and 45.0 ± 0.3 (**3**) and 40.2 ± 0.1 (**4**) µs at 11 K, which can be compared to $\tau = 30$ µs at 10 K for *trans*-[-Pt(PBu₃)₂C=C(*p*-C₆H₄)C=C-]_n.²⁰ Vibronic substructure is seen for the emission bands of **2** and **3** as the temperature is lowered but the emission pattern for **4** appears broad and unstructured even at low temperatures. The substantial Stokes' shift between the strongest bands in the absorption and the emission spectra in the narrow range 1.50 ± 0.05 eV supports the π - π * character of the phosphorescent triplet state for the emission bands (Fig. 7).^{9*a*-e,20} The hindered conjugation



Fig. 7 The room temperature optical absorption spectrum and the photoluminescence spectrum (11 K) of 4 in the solid state.

in the poly(silylacetylene) derivative **4** shifts the phosphorescence (at 2.44 eV) to the blue by 0.06 and 0.38 eV, respectively, compared to the 1,4-phenylene and 2,5-thienylene containing counterparts.^{9c}

In the solid state, complex **5** is emissive both at 290 and 11 K and sharp vibronically structured emissions are observed with λ_{0-0} lines appearing at 500 nm. The large Stokes' shift from the absorption spectrum suggests triplet emission, reminiscent of its polymeric analogue (Fig. 8).²¹ With reference to the recent work by Che and Friend,^{9d,m,17f} such triplet emissions are ascribed to the lowest-energy acetylenic ${}^3(\pi\pi^*)$ excited states associated with the (C=C)₃²⁻ chain. The single vibronic progression of 2087 cm⁻¹ in the emission spectrum of **5** is attributed to the $v_{C=C}$ mode.^{13,17/21} While *trans*-[-Pt(PBu₃)₂C=CC=CC=C-]_n is phosphorescent at 1.88, 2.09 and 2.37 eV,²¹ we observe a blue shift of the phosphorescence band in **4** after replacement of the C=C unit by the SiPh₂ group.



Fig. 8 The room temperature optical absorption spectrum and the photoluminescence spectrum (11 K) of 5 in the solid state.

Concluding remarks

Our present work reports the synthesis and characterization of a novel class of platinum(II)-containing oligo- and poly-(silylacetylenes) with interesting electronic and phosphorescence properties. Optical spectroscopy and theoretical calculations suggest that while the silyl group is weak in electronic conjugation, the resulting organometallic materials exhibit strong triplet emission with negligible fluorescence intensity at low temperatures. The reduced conjugation in the presence of the SiPh₂ unit shifts the optical gap and the phosphorescence band to the blue compared to other platinum poly-ynes with aromatic and heteroaromatic spacers. These new polymer systems enable the study of the relationship between chemical structure and triplet energy levels in conjugated polymers and such an investigation is desirable for optoelectronic applications that harvest the triplet excited state for light emission. Further investigations of light-emitting devices and photocells fabricated from these materials are planned and work is currently in progress to examine similar systems based on other Group 14 elements.

Experimental

General procedures

All reactions were carried out under a nitrogen atmosphere with the use of standard Schlenk techniques, but no special precautions were taken to exclude oxygen during workup. Solvents were predried and distilled from appropriate drying agents. All reagents and chemicals, unless otherwise stated, were purchased from commercial sources and used without further purification. Preparative TLC was performed on 0.7 mm silica plates (Merck Kieselgel 60 GF₂₅₄) prepared in our laboratory. The compounds trans-[Pt(PEt₃)₂PhCl],²² trans-[Pt(PBu₃)₂Cl₂]²³ and Ph₂Si(C=CH)₂ (I)²⁴ were prepared by literature methods. Infrared spectra were recorded as CH₂Cl₂ solutions using a Perkin-Elmer Paragon 1000 PC or Nicolet Magna 550 Series II FTIR spectrometer. NMR spectra were measured in appropriate solvents on a Jeol EX270 or a Varian Inova 400 MHz FT-NMR spectrometer, with ¹H NMR chemical shifts quoted relative to SiMe4 and ³¹P chemical shifts relative to an 85% H₃PO₄ external standard. Electron impact (EI) and fast atom bombardment (FAB) mass spectra were recorded on a Finnigan MAT SSQ710 mass spectrometer. Electronic absorption spectra were obtained with a HP 8453 UV-VIS spectrometer. For emission spectral measurements, the 325 nm line of a He-Cd laser was used as an excitation source. The luminescence spectra were analyzed by a 0.25 m focal length double monochromator with a Peltier cooled photomultiplier tube (PMT) and processed with a lock-in-amplifier. For the low temperature experiments, samples were mounted in a closed-cycle cryostat (Oxford CC1104) in which the temperature can be adjusted from 10 to 330 K. For the lifetime measurements, the third harmonic, 355 nm line of a Q-switched Nd:YAG laser was used as the excitation light source. The emission was recorded using a PMT and a HP54522A 500 MHz oscilloscope. Cyclic voltammetry experiments were done with a Princeton Applied Research (PAR) model 273A potentiostat. A conventional three-electrode configuration consisting of a glassy-carbon working electrode and a Pt-wire as the counter and reference electrodes was used at a scan rate of 100 mV s⁻¹ The solvent in all measurements was deoxygenated CH₂Cl₂ and the supporting electrolyte was 0.1 M [Bu₄N]PF₆. Ferrocene was added as a calibrant after each set of measurements and all potentials reported were quoted with reference to the ferrocene-ferrocenium couple. The molecular weight of the polymer was determined by GPC (HP 1050 series HPLC with visible wavelength and fluorescent detectors) using polystyrene standards and thermal analyses were performed with a Shimadzu DSC-50 and Perkin-Elmer TGA6 thermal analyzers. For density functional calculations at the B3LYP level, the basis set used for C and H atoms was 6-31G²⁵ while effective core potentials with a LanL2DZ basis set²⁶ were employed for P, S, Si and Pt atoms. The Gaussian 98 program was used for the calculations.²⁷ Polarization functions were added for P, S and Si atoms $[\zeta_d(\mathbf{P}) = 0.340, \zeta_d(\mathbf{S}) = 0.421, \zeta_d(\mathbf{S}i) = 0.262].$

Synthetic procedures

trans-[Ph(Et₃P)₂PtC=CSiPh₂C=CH] (1) and trans-[Ph(Et₃P)₂-PtC=CSiPh2C=CPt(PEt3)2Ph] (2). To a stirred mixture of Ph₂Si(C=CH)₂ (I, 63.0 mg, 0.27 mmol) and trans-[Pt(PEt₃)₂-PhCl] (130.0 mg, 0.24 mmol) in ⁱPr₂NH (5 cm³) and CH₂Cl₂ (10 cm³) was added CuI (6 mg). The solution was stirred at room temperature over a period of 15 h, after which all volatile components were removed under vacuum. The crude product was taken up in CH₂Cl₂ and purified on preparative silica TLC plates with hexane– CH_2Cl_2 (1 : 1, v/v) as eluent. From the first colorless band ($R_f = 0.66$) 1 was obtained as a white solid (103.0 mg, 58%) while 2 was isolated as a white powder from another band at $R_{\rm f} = 0.43$ with a yield of 20% (30.0 mg). An improved yield of 1 was achieved at the expense of 2 when a larger sample size of the ligand was used. However, when the reaction was carried out using two molar equivalents of trans- $[Pt(PEt_3)_2PhCl]$, the dimeric species 2 was obtained as the sole product in 75% yield.

For 1. (Found: C, 55.02; H, 6.10. $C_{34}H_{46}P_2PtSi$ requires C, 55.20; H, 6.27%). IR (CH₂Cl₂): 3260 ($v_{\equiv CH}$) and 2031 cm⁻¹ ($v_{C\equiv C}$). ¹H NMR (CDCl₃): δ 7.84 (m, 4H, Ph), 7.41–7.26 (m, 8H, Ph + H_{ortho} of Ph–Pt), 6.98 (t, J = 7.2 Hz, 2H, H_{meta} of Ph–Pt), 6.82 (t, J = 7.2 Hz, 1H, H_{para} of Ph–Pt), 2.60 (s, 1H, C=CH), 1.72 (m, 12H, CH₂) and 1.06 (m, 18H, CH₃). ²⁹Si NMR (CDCl₃): δ -54.27. ³¹P{¹H} NMR (CDCl₃): δ 11.28 (¹J_{P-Pt} = 2623 Hz). MS (FAB): m/z 740 (calc. M^+ 740).

For 2. (Found: C, 49.90; H, 6.14. $C_{52}H_{80}P_4P_1_2Si$ requires C, 50.07; H, 6.46%). IR (CH₂Cl₂): 2027 cm⁻¹ ($\nu_{C=C}$). ¹H NMR (CDCl₃): δ 7.84 (m, 4H, Ph), 7.27 (m, 10H, Ph + H_{ortho} of Ph–Pt), 6.93 (t, J = 7.2 Hz, 4H, H_{meta} of Ph–Pt), 6.77 (t, J = 7.2 Hz, 2H, H_{para} of Ph–Pt), 1.69 (m, 24H, CH₂) and 1.03 (m, 36H, CH₃). ²⁹Si NMR (CDCl₃): $\delta - 58.10$. ³¹P{¹H} NMR (CDCl₃): $\delta 11.94$ (¹ $J_{P-Pt} = 2630$ Hz). MS (FAB): *m*/*z* 1247 (calc. *M*⁺ 1247).

trans-[Ph(Et₃P)₂PtC=CSiPh₂C=CPt(PBu₃)₂C=CSiPh₂C=

CPt(PEt₃)₂Ph] (3). A mixture of **1** (148.0 mg, 0.20 mmol) and *trans*-[Pt(PBu₃)₂Cl₂] (67.0 mg, 0.10 mmol) in a 2 : 1 molar ratio in ⁱPr₂NH–CH₂Cl₂ (20 cm³, 1 : 1, v/v) was allowed to react in the presence of CuI (3 mg) at room temperature for 15 h. The resulting solution was evaporated to dryness. The residue was redissolved in CH₂Cl₂ and the filtrate was subjected to preparative TLC on silica eluting with hexane–CH₂Cl₂ (3 : 2, v/v) to

	1	2	5
Empirical formula	C34H46P2PtSi	$C_{52}H_{80}P_4Pt_2Si$	$C_{42}H_{70}P_4Pt_2$
M	739.83	1247.31	1089.04
Crystal system	Monoclinic	Triclinic	Orthorhombic
Space group	$P2_1/c$	$P\overline{1}$	Fdd2
aľÅ	12.0760(7)	9.9773(6)	16.1148(13)
b/Å	15.3158(9)	13.7256(8)	65.387(5)
c/Å	18.5935(11)	43.156(2)	9.1219(8)
$a/^{\circ}$		85.6250(10)	
βľ°	92.5910(10)	84.4180(10)	
γl°		76.4340(10)	
$U/Å^3$	3435.4(3)	5709.1(6)	9611.8(14)
Z	4	4	8
μ (Mo-K α)/mm ⁻¹	4.232	5.058	5.973
No. reflections collected	19872	33832	13649
Unique reflections (R_{int})	7710 (0.0359)	24553 (0.0295)	4852 (0.0386)
Observed reflections $[I > 2\sigma(I)]$	5328	16782	4642
R indices $[I > 2\sigma(I)]$	R1 = 0.0399	R1 = 0.0494	R1 = 0.0346
	wR2 = 0.1029	wR2 = 0.1158	wR2 = 0.0891
<i>R</i> indices (all data)	R1 = 0.0648	R1 = 0.0770	R1 = 0.0365
	wR2 = 0.1151	wR2 = 0.1284	wR2 = 0.0902
$R1 = \sum F_{o} - F_{c} / \sum F_{o} , \ wR2 = \{\sum [w(F_{o}^{2} - F_{c}^{2})^{2}] / \sum [w(F_{o}^{2})^{2}] \}^{1/2}.$			

afford a pale yellow band ($R_{\rm f} = 0.26$). Compound **3** was isolated as a light yellow solid in 27% yield (54 mg). (Found: C, 53.01; H, 6.69. C₉₂H₁₄₄P₆Pt₃Si₂ requires C, 53.19; H, 6.99%). IR (CH₂Cl₂): 2026 cm⁻¹ ($v_{C=C}$). ¹H NMR (CDCl₃): δ 7.81 (m, 8H, Ph), 7.27–7.20 (m, 16H, Ph + H_{ortho} of Ph–Pt), 6.92 (t, J = 7.2 Hz, 4H, H_{meta} of Ph–Pt), 6.76 (t, J = 7.2 Hz, 2H, H_{para} of Ph–Pt), 2.03 (m, 12H, CH₂ of Bu), 1.69 (m, 24H, CH₂ of Et), 1.48 (m, 12H, CH₂ of Bu), 1.32 (m, 12H, CH₂ of Bu), 1.01 (m, 36H, CH₃ of Et) and 0.82 (m, 18H, CH₃ of Bu). ²⁹Si NMR (CDCl₃): δ –57.75. ³¹P{¹H} NMR (CDCl₃): δ 11.55 (PEt₃, ¹J_{P-Pt} = 2640 Hz) and 4.06 (PBu₃, ¹J_{P-Pt} = 2373 Hz). MS (FAB): m/z 2077 (calc. M^+ 2077).

trans-[-Pt(PBu₃)₂C=CSiPh₂C=C-]_n (4). Polymerization was carried out by mixing the di-yne I (23.2 mg, 0.10 mmol), trans-[Pt(PBu₃)₂Cl₂] (67.0 mg, 0.10 mmol) and CuI (3 mg) in ⁱPr₂NH- CH_2Cl_2 (30 cm³, 1 : 1, v/v). After stirring at room temperature for 15 h, the solution mixture was evaporated to dryness. The residue was redissolved in CH2Cl2, and filtered through a silica column using the same eluent to remove ionic impurities and catalyst residues. After removal of the solvent, the crude product was purified by precipitation in toluene from MeOH. Subsequent washing with hexane and drying in vacuo gave an oily solid of **4** (65.0 mg, 78%). (Found: C, 57.55; H, 7.80. (C₄₀H₆₄P₂PtSi)_n requires C, 57.88; H, 7.77%). IR (CH₂Cl₂): 2025 $cm^{-1}(v_{C=C})$. ¹H NMR (CDCl₃): δ 7.75 (m, 4H, Ph), 7.20 (m, 6H, Ph), 1.97 (m, 12H, PCH₂), 1.43 (m, 12H, PCH₂CH₂), 1.27 [m, 12H, P(CH₂)₂CH₂CH₃] and 0.80 (m, 18H, CH₃). ¹³C NMR (CDCl₃): δ 139.95, 134.87, 127.89, 126.81 (arom C), 107.38, 94.40 (C=C), 26.36, 24.14, 23.33 and 13.96 (Bu). ²⁹Si NMR (CDCl₃): δ -57.50. ³¹P{¹H} NMR (CDCl₃): δ 4.14 (¹J_{P-Pt} = 2377 Hz). GPC (THF as eluent): $M_{\rm w} = 78700$, $M_{\rm n} = 52000$, polydispersity = 1.51.

trans-[Ph(Et₃P)₂PtC=CC=CPt(PEt₃)₂Ph] (5). The monoplatinum complex 1 (22.2 mg, 0.03 mmol) and 1.5 equivalents of Cu(OAc)₂·H₂O (10 mg, 0.045 mmol) were refluxed in pyridine (30 cm³) under air for 16 h. After removal of all volatile components, the resulting dark residue was purified by silica TLC plates, eluting with hexane-CH₂Cl₂ (1 : 1, v/v), to give 5 in low yield ($R_f = 0.56$, 3 mg, 18%) along with some unidentified products. (Found: C, 46.10; H, 6.34. C₄₂H₇₀P₄Pt₂ requires C, 46.32; H, 6.48%). IR (CH₂Cl₂): 2087 cm⁻¹ ($v_{C=C}$). ¹H NMR (CDCl₃): δ 7.24 (m, 4H, H_{ortho} of Ph), 6.94 (t, J = 7.2 Hz, 4H, H_{meta} of Ph), 6.78 (t, J = 7.2 Hz, 2H, H_{para} of Ph), 1.70

(m, 24H, CH₂) and 1.05 (m, 36H, CH₃). ³¹P{¹H} NMR (CDCl₃): δ 11.87 (¹J_{P-Pt} = 2619 Hz). MS (FAB): *m*/*z* 1089 (calc. *M*⁺ 1089).

X-Ray crystallography

Colorless crystals of 1, 2 and 5 suitable for X-ray diffraction studies were grown by slow evaporation of their respective solutions in hexane-CH2Cl2 mixtures at room temperature. Geometric and intensity data were collected at 293 K using graphite-monochromated Mo-K α radiation ($\lambda = 0.71073$ Å) on a Bruker AXS SMART 1000 CCD area-detector. The collected frames were processed with the software SAINT^{28a} and an absorption correction was applied (SADABS)^{28b} to the collected reflections. The structure was solved by direct methods (SHELXTL)²⁹ in conjunction with standard difference Fourier techniques and subsequently refined by full-matrix least-squares analyses on F^2 . All non-hydrogen atoms were assigned with anisotropic displacement parameters. The hydrogen atoms were generated in their idealized positions and allowed to ride on the respective carbon atoms. Crystal data and other experimental details are summarized in Table 6.

CCDC reference numbers 191134–191136.

See http://www.rsc.org/suppdata/dt/b2/b207575j/ for crystallographic data in CIF or other electronic format.

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