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Triplet Emission in Platinum-Containing Poly(alkynylsilanes)

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ABSTRACT: Synthetic routes to novel oligomeric and polymeric platinum(II)-containing alkynylsilanes were developed. Soluble and thermally stable platinum(II) poly(alkynylsilanes) *trans*-$[-Pt(PBu_3)_2C{\equiv}C(p\text{-}C_6H_4)C{\equiv}CSiPh_2C{\equiv}C(p\text{-}C_6H_4)C{\equiv}C-]_n$ were prepared in good yield by CuI-catalyzed condensation polymerization of *trans*-$[PtCl_2(PBu_3)_2]$ with $HC{\equiv}C(p\text{-}C_6H_4)C{\equiv}CSiPh_2C{\equiv}C(p\text{-}C_6H_4)C{\equiv}CH$. The regiochemical structure of the polymer was studied by NMR (^{1}H, ^{13}C, ^{29}Si, and ^{31}P) spectroscopy. We report the optical absorption and photoluminescence spectra of such metal-based organosilicon polymer and compare the data with their oligomeric model complexes *trans*-$[Pt(Ph)(PEt_3)_2C{\equiv}C(p\text{-}C_6H_4)C{\equiv}CSiPh_2C{\equiv}C(p\text{-}C_6H_4)C{\equiv}CPt(Ph)(PEt_3)_2]$ and *trans*-$[Pt(Ph)(PEt_3)_2C{\equiv}C(p\text{-}C_6H_4)C{\equiv}CSiPh_2C{\equiv}C(p\text{-}C_6H_4)C{\equiv}CPt(PBu_3)_2C{\equiv}C(p\text{-}C_6H_4)C{\equiv}CSiPh_2C{\equiv}C(p\text{-}C_6H_4)C{\equiv}CPt(Ph)(PEt_3)_2]$. Our studies indicate that such organometallic poly(alkynylsilanes) show a strong triplet emission with a very high efficiency of intersystem crossing from the S_1 singlet excited state to the T_1 triplet excited state. The dependence of intersystem crossing and the spatial extent of singlet and triplet excitons as a function of the central spacer group is discussed in polymetallaynes possessing $SiPh_2$, C_6H_4 and $Pt(PR_3)_2$ (R = Et, Bu) linkers. The photoconducting properties of such silicon-linked platinum polyyne are described.

Introduction

Fluorescent and phosphorescent materials continue to attract commercial and scientific interest because of their potential applications in light-emitting diodes (LEDs) and large area flexible displays.[1−5] One of the major issues in organic LEDs is the ratio of 3:1 for the generation of (nonemissive) triplet to (emissive) singlet excitons based on the spin statistics.[6] Yet the percentage of emissive singlet excitons determines the overall efficiency of the LED. Higher efficiencies can only be realized by harvesting the energy of the nonemissive triplet excitons.[3,4,7,8] This requires detailed knowledge of the energy levels of the triplet state. To study the triplet excitons directly, conjugated polymers of the type *trans*-$[-Pt(PBu_3)_2C{\equiv}CRC{\equiv}C-]_n$ have been used by us and others as model systems to obtain a clear picture of the spatial extent of the singlet and triplet manifolds.[9−17] Strong spin−orbit coupling associated with the heavy transition metals renders the spin-forbidden triplet emission (phosphorescence) partially allowed.[9−13] The prototypical polymer for much of this work is *trans*-$[-Pt(PBu_3)_2C{\equiv}C(p\text{-}C_6H_4)C{\equiv}C-]_n$,[18] and more recently, a wide variety of derivatives have been prepared where alkynyl units are connected to a variety of aromatic ring systems.[9−17] Recent observations in this area demonstrate that the intersystem crossing rate from the singlet excited state to the triplet excited state is notably enhanced when conjugation is decreased.[9,11,13]

In the other context, the chemistry of molecular systems composed of silicon atoms and acetylene units has received much current attention.[19] It was envisaged that the lower ionization energy of the silicon atom compared with carbon can enhance the through-bond interaction of ethynyl units along the backbone.[20] These organosilicon substances have good potential as functional materials in the area of electronics and material science.[19] The electrical and optical properties associated with these materials are generally attributed to the delocalization of electrons through the silylene linkages via $\pi-d_{Si}$ interaction[21] and $\sigma-\pi$ conjugation.[20,22] π-Conjugated organosilicon systems incorporating phenylene, anthrylene, or oligothienylene bridges have been extensively studied regarding their applications to optoelectronic devices.[19]

Recently, we have extended our research efforts to the synthesis of oligoacetylenic compounds containing main-group elements[23,24] and have reported a systematic synthetic approach to some oligoacetylenic silanes exhibiting through-Si conjugation along the backbone.[25] In contrast to the body of work on luminescent polymetallaynes with π-electron unit,[9−18] no reports were known for similar systems having silylene units in the backbone. Although a number of researchers have contributed to the areas of poly(silylacetylenes) containing organometallic carbonyl moieties,[26,27] little research on rigid-rod transition-metal σ-alkynylsilane polymers has been carried out. In light of the findings in some conjugated polymers (e.g., poly(fluorenes)) that the light-emitting performance can be improved by the deliberate inclusion of conjugation-interrupting units[28−31] and introduction of disorder to the conjugated system,[32,33] we envisioned that the sp^3 silicon unit can be a good choice of spacer group in metal polyynes. To address this issue, in the present work we report the first examples of platinum(II)-containing oligomeric and polymeric σ-alkynylsilanes in order to evaluate how the metal center and the silyl moiety would influence the electronic and optical properties of this class of materials. The significance of the silicon residue in this class of materials in comparison to other conjugated linking units will be discussed.

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Experimental Section

General. 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 GF_{254}) prepared in our laboratory. The compounds $HC\equiv C(p\text{-}C_6H_4)C\equiv CSiPh_2C\equiv C(p\text{-}C_6H_4)C\equiv CH$ (**I**),[25] *trans*-$[PtCl(Ph)(PEt_3)_2]$,[34] *cis*-$[PtCl_2(PEt_3)_2]$,[35] and *trans*-$[PtCl_2(PBu_3)_2]$[36] were prepared by literature methods. Infrared spectra were recorded as CH_2Cl_2 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 TMS and ^{31}P chemical shifts relative to an 85% H_3PO_4 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 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. 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. The solvent in all measurements was deoxygenated CH_2Cl_2, and the supporting electrolyte was 0.1 M $[Bu_4N]PF_6$. 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 weights of the polymers were determined by GPC (HP 1050 series HPLC with visible wavelength and fluorescent detectors) using polystyrene standards, and thermal analyses were performed with Shimadzu DSC-50 and Perkin-Elmer TGA6 thermal analyzers. Good optical quality polymer films of **4** for photocurrent measurements were prepared by casting the polymer solution from 1,1,2,2-tetrachloroethane onto ITO-coated glass substrates. Measurements of the spectral response were made by illuminating the device through the ITO side, and optical excitation was provided by a xenon arc lamp at 370 nm.

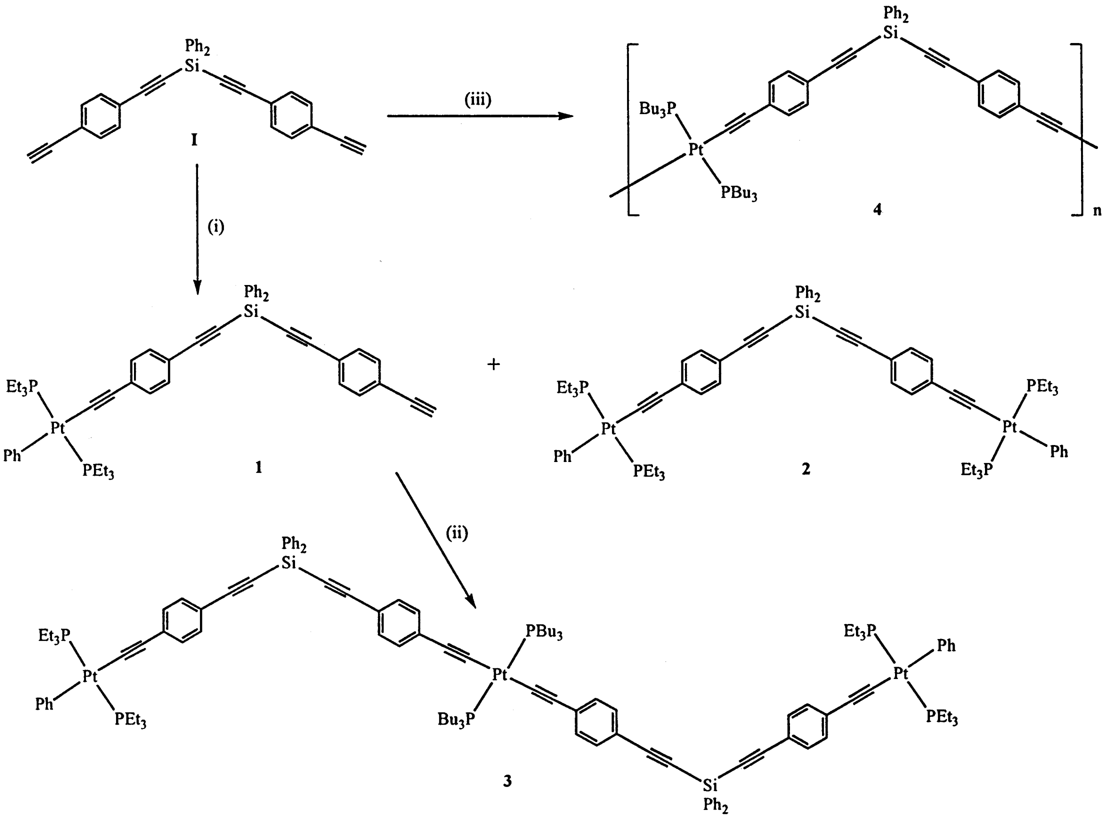
***trans*-$[Pt(Ph)(PEt_3)_2C\equiv C(p\text{-}C_6H_4)C\equiv CSiPh_2C\equiv C(p\text{-}C_6H_4)C\equiv CH]$ (1) and *trans*-$[Pt(Ph)(PEt_3)_2C\equiv C(p\text{-}C_6H_4)C\equiv CSiPh_2C\equiv C(p\text{-}C_6H_4)C\equiv CPt(Ph)(PEt_3)_2]$ (2).** A slight excess of $HC\equiv C(p\text{-}C_6H_4)C\equiv CSiPh_2C\equiv C(p\text{-}C_6H_4)C\equiv CH$ (**I**, 68.0 mg, 0.16 mmol) was combined with *trans*-$[PtCl(Ph)(PEt_3)_2]$ (81.3 mg, 0.15 mmol) in $^iPr_2NH$ (5 mL) and CH_2Cl_2 (10 mL) followed by the addition of CuI (4 mg). The solution was stirred at room temperature for 15 h, after which all volatile components were removed under reduced pressure. The crude product was taken up in CH_2Cl_2 and separated on preparative silica TLC plates using hexane/CH_2Cl_2 (3:2, v/v) as eluent. Analytically pure **1** and **2** were obtained as white solids from two colorless bands ($R_f = 0.51$ and 0.34, respectively), and the respective yields are 44% (62.4 mg) and 24% (26.0 mg). The ratio of mono- to dinuclear complexes was increased when a larger amount of the ligand was employed in the synthesis. Compound **2** was the only isolable product (69%) when 2 mol equiv of *trans*-$[PtCl(Ph)(PEt_3)_2]$ was used. **1**: IR (CH_2Cl_2): $\nu(\equiv CH)$ 3296, $\nu(C\equiv C)$ 2156, 2092 cm^{-1}. ^1H NMR ($CDCl_3$): δ (ppm) 7.88 (m, 4H, Ph or C_6H_4), 7.56−7.27 (m, 16H, Ph or C_6H_4 + H_{ortho} of Ph−Pt), 6.99 (t, J = 6.8 Hz, 2H, H_{meta} of Ph−Pt), 6.83 (t, J = 6.8 Hz, 1H, H_{para} of Ph−Pt), 3.20 (s, 1H, $C\equiv CH$), 1.77 (m, 12H, CH_2), 1.11 (m, 18H, CH_3). ^{29}Si NMR ($CDCl_3$): δ (ppm) −48.33. ^{31}P {^1H} NMR ($CDCl_3$): δ (ppm) 10.95 ($^1J_{P-Pt}$ = 2631 Hz). FAB-MS (m/z): 940 [M^+]. Anal. Calcd for $C_{50}H_{54}P_2PtSi$: C, 63.88; H, 5.79. Found: C, 63.68; H, 5.75. **2**: IR (CH_2Cl_2): $\nu(C\equiv C)$ 2154, 2093 cm^{-1}. ^1H NMR ($CDCl_3$): δ (ppm) 7.87 (d, J = 7.2 Hz, 4H, C_6H_4), 7.44−7.39 (m, 10H, Ph), 7.32 (d, J = 7.2 Hz, 4H, C_6H_4), 7.22 (m, 4H, H_{ortho} of Ph−Pt), 6.97 (t, J = 7.2 Hz, 4H, H_{meta} of Ph−Pt), 6.81 (t, J = 7.2 Hz, 2H, H_{para} of Ph−Pt), 1.75 (m, 24H, CH_2), 1.09 (m, 36H, CH_3). ^{29}Si NMR ($CDCl_3$): δ (ppm) −48.48. ^{31}P {^1H} NMR ($CDCl_3$): δ (ppm) 10.95 ($^1J_{P-Pt}$ = 2633 Hz). FAB-MS (m/z): 1447 [M^+]. Anal. Calcd for $C_{68}H_{88}P_4Pt_2Si$: C, 56.42; H, 6.13. Found: C, 56.21; H, 6.04.

***trans*-$[Pt(Ph)(PEt_3)_2C\equiv C(p\text{-}C_6H_4)C\equiv CSiPh_2C\equiv C(p\text{-}C_6H_4)C\equiv CPt(PBu_3)_2C\equiv C(p\text{-}C_6H_4)C\equiv CSiPh_2C\equiv C(p\text{-}C_6H_4)C\equiv CPt(Ph)(PEt_3)_2]$ (3).** A mixture of **1** (76.0 mg, 0.08 mmol) and *trans*-$[PtCl_2(PBu_3)_2]$ (26.8 mg, 0.04 mmol) in a 2:1 molar ratio in $^iPr_2NH/CH_2Cl_2$ (20 mL, 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 CH_2Cl_2, and the filtrate was subjected to preparative TLC on silica eluting with hexane/CH_2Cl_2 (3:2, v/v) to afford a pale yellow band (R_f = 0.44). Compound **3** was isolated as a light yellow solid in 26% yield (26.0 mg). IR (CH_2Cl_2): $\nu(C\equiv C)$ 2154, 2096 cm^{-1}. ^1H NMR ($CDCl_3$): δ (ppm) 7.87 (m, 8H, Ph or C_6H_4), 7.41−7.16 (m, 32H, Ph or C_6H_4 + H_{ortho} of Ph−Pt), 6.99 (t, J = 7.2 Hz, 4H, H_{meta} of Ph−Pt), 6.83 (t, J = 7.2 Hz, 2H, H_{para} of Ph−Pt), 2.13 (m, 12H, PCH_2 of Bu), 1.77 (m, 24H, CH_2 of Et), 1.61 (m, 12H, PCH_2CH_2 of Bu), 1.49 (m, 12H, $P(CH_2)_2CH_2CH_3$ of Bu), 1.11 (m, 36H, CH_3 of Et), 0.93 (m, 18H, CH_3 of Bu). ^{29}Si NMR ($CDCl_3$): δ (ppm) −49.32. ^{31}P {^1H} NMR ($CDCl_3$): δ (ppm) 10.95 (PEt_3, $^1J_{P-Pt}$ = 2634 Hz), 4.28 (PBu_3, $^1J_{P-Pt}$ = 2344 Hz). FAB-MS (m/z): 2478 [M^+]. Anal. Calcd for $C_{124}H_{160}P_6Pt_3Si_2$: C, 60.11; H, 6.51. Found: C, 60.01; H, 6.39.

***trans*-$[-Pt(PBu_3)_2C\equiv C(p\text{-}C_6H_4)C\equiv CSiPh_2C\equiv C(p\text{-}C_6H_4)C\equiv C-]_n$ (4).** CuI (3 mg) was added to a mixture of **I** (43.2 mg, 0.10 mmol) and *trans*-$[PtCl_2(PBu_3)_2]$ (67.0 mg, 0.10 mmol) in $^iPr_2NH/CH_2Cl_2$ (20 mL, 1:1, v/v). The yellow solution was stirred at room temperature over a period of 15 h, after which all solvents were evaporated off. The residue was redissolved in CH_2Cl_2, and filtered through a silica column using the same eluent. After removal of solvent, a viscous off-white solid was obtained, and it was then washed with MeOH to provide polymer **4** in 80% yield (82.0 mg). Further purification can be accomplished by precipitating the polymer solution in toluene from MeOH. IR (CH_2Cl_2): $\nu(C\equiv C)$ 2154, 2096 cm^{-1}. ^1H NMR ($CDCl_3$): δ (ppm) 7.85 (d, J = 8.0 Hz, 4H, C_6H_4), 7.42 (m, 10H, Ph), 7.19 (d, J = 8.0 Hz, 4H, C_6H_4), 2.11 (m, 12H, PCH_2), 1.58 (m, 12H, PCH_2CH_2), 1.44 (m, 12H, $P(CH_2)_2CH_2CH_3$), 0.91 (m, 18H, CH_3). ^{13}C NMR ($CDCl_3$): δ (ppm) 134.89, 134.42, 133.42, 131.96, 130.50, 130.30, 130.08, 127.99 (arom C), 125.01, 118.35, 109.43, 87.93 ($C\equiv C$), 26.32, 24.36, 24.10, 13.77 (Bu). ^{29}Si NMR ($CDCl_3$): δ (ppm) −48.16. ^{31}P {^1H} NMR ($CDCl_3$): δ (ppm) 4.30 ($^1J_{P-Pt}$ = 2343 Hz). GPC (THF as eluent): M_w = 146 000, M_n = 82 700, polydispersity = 1.77. Anal. Calcd for $(C_{56}H_{72}P_2PtSi)_n$: C, 65.28; H, 7.04. Found: C, 65.14; H, 6.95.

***trans*-$[HC\equiv C(p\text{-}C_6H_4)C\equiv CPt(PEt_3)_2C\equiv C(p\text{-}C_6H_4)C\equiv CH]$ (II).** To a chilled solution of 1,4-diethynylbenzene (176.4 mg, 1.40 mmol) in dried THF (30 mL) at −15 °C, ^nBuLi (1.0 mL, 1.60 mmol, 1.6 M in hexane) was added dropwise under a nitrogen atmosphere. The mixture was stirred for 30 min at this temperature and then 15 min at room temperature. The resulting solution was again cooled to −15 °C; a solution of *cis*-$[PtCl_2(PEt_3)_2]$ (350.0 mg, 0.70 mmol) in THF (10 mL) was added dropwise over 15 min, and the reaction mixture was stirred for a further 30 min before stirring was continued for another 15 min at room temperature. The volatile components were evaporated, and the residue was extracted with CH_2Cl_2. The filtrate was concentrated and subjected to preparative TLC isolation using silica plates and hexane/CH_2Cl_2 (1:1, v/v) as eluent. From the second band (R_f = 0.52), the title compound was obtained as a light yellow solid with a yield of 20% (95.0 mg) based on 1,4-diethynylbenzene. The starting 1,4-diethynylbenzene was also recovered in a pure form from the top band (20%), which can be employed as a precursor for the synthesis of more **II**. IR (CH_2Cl_2): $\nu(\equiv CH)$ 3232, $\nu(C\equiv C)$

Scheme 1. Synthesis of 1–4[a]



[a] Reagents and conditions: (i) *trans*-[PtCl(Ph)PEt$_3$)$_2$], CuI, ^{i}Pr$_2$NH–CH$_2$Cl$_2$, r.t.; (ii) *trans*-[PtCl$_2$(PBu$_3$)$_2$] (0.5 equiv), CuI, ^{i}Pr$_2$NH–CH$_2$Cl$_2$, r.t.; (iii) *trans*-[PtCl$_2$(PBu$_3$)$_2$] (1 equiv), CuI, ^{i}Pr$_2$NH–CH$_2$Cl$_2$, r.t.

2096 cm^{-1}. ^{1}H NMR (CDCl$_3$): δ (ppm) 7.34 (d, J = 8.0 Hz, 4H, C$_6$H$_4$), 7.21 (d, J = 8.0 Hz, 4H, C$_6$H$_4$), 3.12 (s, 2H, C≡CH), 2.15 (m, 12H, CH$_2$), 1.21 (m, 18H, CH$_3$). ^{31}P {^{1}H} NMR (CDCl$_3$): δ (ppm) 12.34 ($^1J_{\mathrm{P-Pt}}$ = 2356 Hz). FAB-MS (m/z): 681 [M$^+$]. Anal. Calcd for C$_{32}$H$_{40}$P$_2$Pt: C, 56.38; H, 5.91. Found: C, 56.01; H, 5.65.

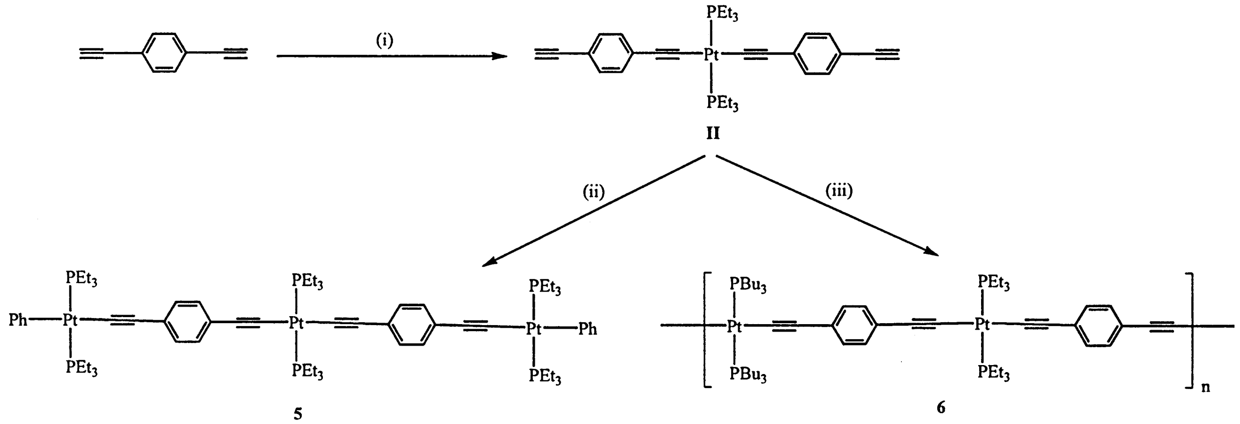
***trans*-[Pt(Ph)(PEt$_3$)$_2$C≡C(p-C$_6$H$_4$)C≡CPt(PEt$_3$)$_2$C≡C-(p-C$_6$H$_4$)C≡CPt(Ph)(PEt$_3$)$_2$] (5).** Treatment of 2 mol equiv of *trans*-[PtCl(Ph)(PEt$_3$)$_2$] (54.0 mg, 0.10 mmol) with **II** (34.0 mg, 0.05 mmol) in ^{i}Pr$_2$NH/CH$_2$Cl$_2$ (15 mL, 1:2, v/v) with a catalytic amount of CuI (3 mg) produced the desired triplatinum complex **5** following the same workup procedures as for **2** accompanied by TLC separation (R_f = 0.42) using hexane/CH$_2$Cl$_2$ (3:1, v/v) as eluent. Compound **5** was isolated as a pale yellow solid in 76% yield (64.5 mg). IR (CH$_2$Cl$_2$): ν(C≡C) 2100 cm^{-1}. ^{1}H NMR (CDCl$_3$): δ (ppm) 7.33 (d, J = 6.4 Hz, 4H, C$_6$H$_4$), 7.13–7.10 (m, 8H, C$_6$H$_4$ + H$_{\mathrm{ortho}}$ of Ph), 6.96 (t, J = 7.2 Hz, 4H, H$_{\mathrm{meta}}$ of Ph), 6.80 (t, J = 7.2 Hz, 2H, H$_{\mathrm{para}}$ of Ph), 2.13 (m, 12H, CH$_2$), 1.74 (m, 24H, CH$_2$), 1.25 (m, 18H, CH$_3$), 1.08 (m, 36H, CH$_3$). ^{31}P {^{1}H} NMR (CDCl$_3$): δ (ppm) 11.85 ($^1J_{\mathrm{P-Pt}}$ = 2377 Hz), 10.80 ($^1J_{\mathrm{P-Pt}}$ = 2638 Hz). FAB-MS (m/z): 1696 [M$^+$]. Anal. Calcd for C$_{68}$H$_{108}$P$_6$Pt$_3$: C, 48.14; H, 6.42. Found: C, 47.90; H, 6.14.

***trans*-[–Pt(PBu$_3$)$_2$C≡C(p-C$_6$H$_4$)C≡CPt(PEt$_3$)$_2$C≡C-(p-C$_6$H$_4$)C≡C–]$_n$ (6).** Equimolar amounts of complex **II** (61.5 mg, 0.09 mmol) and *trans*-[PtCl$_2$(PBu$_3$)$_2$] (60.5 mg, 0.09 mmol) were combined in a ^{i}Pr$_2$NH/CH$_2$Cl$_2$ mixture (60 mL, 2:1, v/v). Upon adding CuI (3 mg), the mixture was stirred for 15 h. The resulting pale yellow solution was filtered through a silica column using CH$_2$Cl$_2$ as eluent to remove the catalyst residue and amine salt. The product was further purified by precipitation from a MeOH/toluene mixture to give **5** as a yellow powder in 60% yield (69.0 mg). IR (CH$_2$Cl$_2$): ν(C≡C) 2099 cm^{-1}. ^{1}H NMR (CDCl$_3$): δ (ppm) 7.11 (m, 8H, C$_6$H$_4$), 2.16 (m, 24H, PCH$_2$ of Bu and Et), 1.59 (m, 12H, PCH$_2$CH_2 of Bu), 1.42 (m, 12H, P(CH$_2$)$_2$CH_2CH$_3$ of Bu), 1.21 (m, 18H, CH$_3$ of Et), 0.91 (m, 18H, CH$_3$ of Bu). ^{31}P {^{1}H} NMR (CDCl$_3$): δ (ppm) 11.95 (PEt$_3$, $^1J_{\mathrm{P-Pt}}$ = 2379 Hz), 4.02 (PBu$_3$, $^1J_{\mathrm{P-Pt}}$ = 2360 Hz). GPC (THF as eluent): M_w = 102 200, M_n = 89 400, polydispersity = 1.14. Anal. Calcd for (C$_{56}$H$_{92}$P$_4$Pt$_2$)$_n$: C, 52.57; H, 7.25. Found: C, 52.19; H, 7.02.

Results and Discussion

Synthesis. The general synthetic pathways to the new complexes and polymers are outlined in Schemes 1 and 2. The silicon- and platinum-linked oligoalkyne precursors, HC≡C(p-C$_6$H$_4$)C≡CRC≡C(p-C$_6$H$_4$)C≡CH (R = SiPh$_2$ **I**, Pt(PEt$_3$)$_2$ **II**), were obtained by condensation reaction of Ph$_2$SiCl$_2$ or *cis*-[PtCl$_2$(PEt$_3$)$_2$] with the components prepared in situ from a HC≡C(p-C$_6$H$_4$)C≡CH/^{n}BuLi mixture in THF.[25] The structure of **II** was ascertained by single-crystal X-ray analysis. Following the dehydrohalogenating route using the CuI/^{i}Pr$_2$NH catalytic system,[9–11] the reaction of *trans*-[PtCl(Ph)-(PEt$_3$)$_2$] with **I** afford the monoplatinum complex *trans*-[Pt(Ph)(PEt$_3$)$_2$C≡C(p-C$_6$H$_4$)C≡CSiPh$_2$C≡C(p-C$_6$H$_4$)-C≡CH] (**1**) and the dinuclear complex *trans*-[Pt(Ph)-(PEt$_3$)$_2$C≡C(p-C$_6$H$_4$)C≡CSiPh$_2$C≡C(p-C$_6$H$_4$)C≡CPt-(Ph)(PEt$_3$)$_2$] (**2**), depending on the stoichiometry of the reactants used. The yields of these transformations are fairly high. Complex **1** can be utilized as key starting material for access to the triplatinum system *trans*-[Pt-(Ph)(PEt$_3$)$_2$C≡C(p-C$_6$H$_4$)C≡CSiPh$_2$C≡C(p-C$_6$H$_4$)C≡CPt-(PBu$_3$)$_2$C≡C(p-C$_6$H$_4$)C≡CSiPh$_2$C≡C(p-C$_6$H$_4$)C≡CPt(Ph)-(PEt$_3$)$_2$] (**3**), and the chain length is doubled in this synthetic procedure. All these new complexes were isolated as off-white to light yellow solids by preparative TLC plates on silica. Organometallic polymers *trans*-[–Pt(PBu$_3$)$_2$C≡C(p-C$_6$H$_4$)C≡CRC≡C(p-C$_6$H$_4$)C≡C–]$_n$ (R = SiPh$_2$ **4**, Pt(PEt$_3$)$_2$ **6**) were synthesized by CuI-catalyzed polymerization involving the dehydrohaloge-

Scheme 2. Synthesis of 5 and 6[a]



[a] Reagents and conditions: (i) *cis*-[$PtCl_2(PEt_3)_2$], ^nBuLi, −15 °C. THF; (ii) *trans*-[PtCl(Ph)($PEt_3)_2$] (2 equiv), CuI, $^iPr_2NH-CH_2Cl_2$, r.t.; (iii) *trans*-[$PtCl_2(PBu_3)_2$] (1 equiv), CuI, $^iPr_2NH-CH_2Cl_2$, r.t.

Table 1. Structural and Thermal Properties of the Polymers

polymer	M_w	M_n	M_w/M_n	T_g (°C)	T_{decomp}(onset) (°C)
4	146 000	82 700	1.77	216 ± 4	366 ± 5
6	102 200	89 400	1.14	n.d.[a]	357 ± 5

[a] n.d. = not detected.

nating coupling of *trans*-[$PtCl_2(PBu_3)_2$] and **I** or **II** with a feed mole ratio of 1:1. Purification of the polymers was effected by silica column chromatography using CH_2Cl_2 as eluent, and they were obtained as creamy white to yellow powders in high purity and yields. The model complex of **6**, *trans*-[Pt(Ph)$(PEt_3)_2C{\equiv}C(p\text{-}C_6H_4)C{\equiv}CPt(PEt_3)_2C{\equiv}C(p\text{-}C_6H_4)C{\equiv}CPt(Ph)(PEt_3)_2$] (**5**), can be prepared by reacting **II** with *trans*-[PtCl(Ph)$(PEt_3)_2$] in a 1:2 molar ratio. All these platinum complexes are stable to air and can be stored without any special precautions. They generally exhibit good solubility in aromatic solvents, chlorocarbons, and ethers but are insoluble in hydrocarbons. Similar to other known platinum(II) polyynes, we found that both polymers **4** and **6** can cast tough, free-standing thin films of good optical quality from appropriate solvents. The molecular weight data of both polymers, as determined in THF by gel permeation chromatography (GPC), are tabulated in Table 1. The M_w values indicate a high degree of polymerization, and the degrees of polymerization calculated from M_n are 80 and 70 for **4** and **6**, respectively. Indexes of polydispersity (M_w/M_n) around 2 have been calculated, which is a common value for polycondensates. It should be noted that GPC does not give absolute values of molecular weights but provides a measure of hydrodynamic volume. Rodlike polymers in solution possess different hydrodynamic properties than flexible polymers. So, calibration of the GPC with polystyrene standards is likely to inflate the values of the molecular weights of the polyynes to some extent. However, the lack of discernible 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 **4** and **6**, in line with the observations reported in the literature.[10,11,13]

Spectroscopic and Redox Properties. Systematic characterization of these new complexes was achieved by analytical and spectroscopic methods. The IR spectra of **1**−**4** are each dominated by two intense ν(C≡C) bands (ca. 2092 and 2154 cm^{-1}) and those of **5** and **6** by a single absorption band. The terminal acetylenic C−H signal is also apparent at 3296 cm^{-1} for **1**. The ν(C≡C) stretching frequencies for **1**−**4** are lower than those for the free silyl ligand **I** (2157 cm^{-1}),[25] in line with a higher degree of conjugation in the former. The single $^{31}P\ \{^1H\}$ NMR signal flanked by platinum satellites for **1**, **2**, and **4** as well as the two $^{31}P\ \{^1H\}$ singlets for **3**, **5**, and **6** are consistent with a trans geometry of the $Pt(PR_3)_2$ (R = Et or Bu) unit in such square-planar geometry. The $^1J_{P-Pt}$ values in **1**−**4** range from 2631 to 2634 Hz for the PEt_3 groups and 2343 to 2344 Hz for the PBu_3 moieties, typical of those for related *trans*-PtP_2 systems.[9−17] The formulas of the mono-, di-, and trimetallic species were also established by appearance of the intense molecular ion peaks in the respective positive FAB mass spectra. ^1H NMR analyses clearly demonstrate a well-defined structure for each compound. In all cases, ^1H NMR resonances stemming from the protons of the organic moieties were observed. The ^{13}C NMR spectral data in the aromatic region with eight well-defined peaks for **4** show a high degree of structural regularity and symmetry in the polymer. The distinct ^{13}C NMR peaks in the range 88−125 ppm for the sp carbons in **4** are shifted downfield with respect to the free alkyne **I**.[25] Each of **1**−**4** exhibits a single ^{29}Si NMR resonance which is related to a simple nuclear environment of silicon in these compounds. The chemical shifts, however, remain relatively unshifted as compared to **I** (δ −48.49).[25]

The electrochemical nature of our platinum compounds was investigated in CH_2Cl_2 by cyclic voltammetry (Table 2). Within the measured scan range, each of **1**−**3** only displayed a single irreversible oxidation wave at ca. 0.80−0.94 V due to the one-electron oxidation of the Pt residue, but we observe no reduction prior to the solvent limit. Two irreversible waves were observed for **4**, which in an analogous manner to other related systems, probably arises from the stepwise two-electron oxidation at the Pt center [$Pt^{2+} \rightarrow Pt^{3+} + e^- \rightarrow Pt^{4+} + 2e^-$].[13] There is no particular trend in the electrochemical data of **1**−**4** apart from an anodic shift in the oxidation potential when going from polymer **4** to the shorter-chain oligomers **1**−**3**. Two irreversible oxidation events associated with the central and terminal Pt centers took place for the trimetallic complex **5**. We also note that when the conjugation is increased, oxidation is favored by the delocalization of charge along the system which renders the platinum oxidation easier in **6** as compared to the silyl counterpart **4**.

Table 2. Absorption, Emission, and Redox Data for 1−6

	λ_{max} (nm)[a] CH$_2$Cl$_2$	λ_{max} (nm) film	E_g (eV)[b]	λ_{em} (nm) film (290 K)	λ_{em} (nm) film (11 K)	ΔE(T$_1$→S$_0$, S$_1$→S$_0$)[c]	E_{ox} (V)[d]
1	273 (4.8), 289 (5.2), 306 (2.5), 339 (4.0)	280 292 309 339	3.39	507*[e]	377*, 418*, 507, 537*, 550*, 564*	13.1	+0.94
2	308 (5.6) 344 (9.0)	307 343	3.32	508*	376*, 404*, 509, 540*, 551*, 567*	18.9	+0.81
3	273 (5.0), 289 (5.8), 306 (6.8), 347 (13.6)	306 349	3.14	425*	425*, 510, 542*, 552*, 568*	19.4	+0.80
4	303 (4.3) 355 (8.7)	304 360	3.10	394*, 513*, 575*	394*, 423*, 512, 555*, 575*	170.4	+0.55 +0.86
5	271 (1.9), 300 (2.4), 365 (6.0)	273 301 365	3.15	394*, 515*	394*, 513, 535*, 546*, 559*	67.0	+0.44 +0.75
6	271 (3.6), 299 (4.1), 383 (14.9)	272 300 384	3.05	402*, 522*	402*, 520, 552*, 565*, 581*	125.4	+0.43

[a] Extinction coefficients are shown in parentheses. [b] Estimated from the onset wavelength of the solid-state optical absorption. [c] Ratio of the intensities of triplet emission to singlet emission at 11 K. [d] Irreversible waves. [e] Emission peaks appear as shoulders or weak bands.

Thermal Analysis. The thermal properties of both polymers were examined by thermal gravimetry (TG) and differential scanning calorimetry (DSC) under nitrogen (Table 1). Analysis of the TG trace (heating rate 20 °C/min) for **4** and **6** shows that they have decomposition temperatures in excess of 350 °C and thus exhibit excellent thermal stability. Decomposition commences at 366 and 357 °C for **4** and **6**, respectively, and these onset temperatures appear higher than those in *trans*-[−Pt(PBu$_3$)$_2$C≡CRC≡C−]$_n$ (R = phenylene, thienylene, pyridyl, substituted fluorenylene).[10,11,13,14,37] Introduction of the SiPh$_2$ unit has the added effect of enhancing the thermal stability of platinum(II) polyynes. We observe a sharp weight loss of 38% between 366 and 444 °C for **4** whereas 32% of the weight was lost for **6** as the temperature rose from 357 to 406 °C. The decomposition step is ascribed to the elimination of two PBu$_3$ groups from the polymers. The glass transition temperature (T_g) was determined to be 216 °C for **4**, but polymer **6** did not exhibit a discernible glass transition. Like the platinum polyynes containing phenylene and thienylene spacers, a minor endotherm was present at a somewhat higher temperature (326 °C) for **4**.[11]

Optical Absorption and Photoluminescence Spectroscopy. Optical absorption spectra of new platinum(II)-containing alkynylsilanes were taken at room temperature in CH$_2$Cl$_2$ solutions and as thin films. Relevant data are shown in Table 2. For **1**−**6**, they display absorption peaks in the near-UV region (ca. 271−383 nm). In each case, the first absorption band is mainly due to the $\pi-\pi^*$ transition in the organic system, possibly with some admixture of metal d orbitals which may alter the overall energy of the transition. We associate the lowest energy peak with the (0,0) vibronic peak of a S$_0$ → S$_1$ transition from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO), which are mainly delocalized π and π^* orbitals. As compared to the band at 290 nm for **I**,[25] we find that the position of the lowest energy absorption band is red-shifted after the inclusion of platinum fragment in **1**−**4**. This reveals that π-conjugation of the ligands continues through metal sites along the main chain, in line with previous results on the related systems.[13,14] The transition energies of **4** are lowered with respect to those of **1**−**3**, indicating that the first optical absorption transition in **4** arises from an electronic excitation that is delocalized over more than one repeat unit.[11,13] Likewise, polymer **6** possesses a well extended singlet excited state. This agrees with the results of *trans*-[−Pt(PBu$_3$)$_2$C≡C(p-C$_6$H$_4$)C≡C−]$_n$ and other platinum polyynes having (hetero)aromatic spacers.[11] We observe that the solution λ_{max} follows the order **6** (383 nm) ≈ *trans*-[−Pt(PBu$_3$)$_2$C≡C(p-C$_6$H$_4$)C≡C−]$_n$ (380 nm) > **4** (355 nm) and **5** > **2**, indicating that SiPh$_2$ is less effective than the phenylene and Pt(PEt$_3$)$_2$ units in electronic conjugation in the present system, and thus the energy of the S$_1$ singlet state is highest for the silicon-linked derivatives. Moreover, it is obvious that the HOMO−LUMO gaps (E_g) gradually decrease in the order **1** > **2** > **3** > **4** with increasing chain length, and that of **4** (3.10 eV) is remarkably larger than what we observe for the anthrylene and thienylene analogues *trans*-[−Pt(PBu$_3$)$_2$C≡C(p-C$_6$H$_4$)C≡CRC≡C(p-C$_6$H$_4$)C≡C−]$_n$ (R = 9,10-anthrylene, 2.48; R = 2,5-thienylene 2.70 eV).[38]

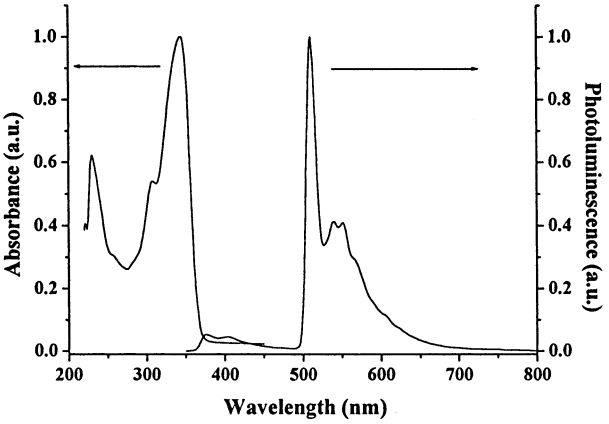


Figure 1. Room temperature optical absorption spectrum and the photoluminescence (PL) spectrum (11 K) of **2** in solid.

The thin film photoluminescence (PL) spectra of **1**−**6** were measured at various temperatures, and the results are gathered in Table 2. In general, two characteristic emission bands are observed at 11 K in each case, and the spectra for **2**, **4**, and **6** are depicted in Figures 1−3, respectively. The higher energy emission of very low intensity near 400 nm is due to fluorescence from the singlet excited state (S$_1$ → S$_0$), which is in line with the small Stokes shift observed between the bands in the

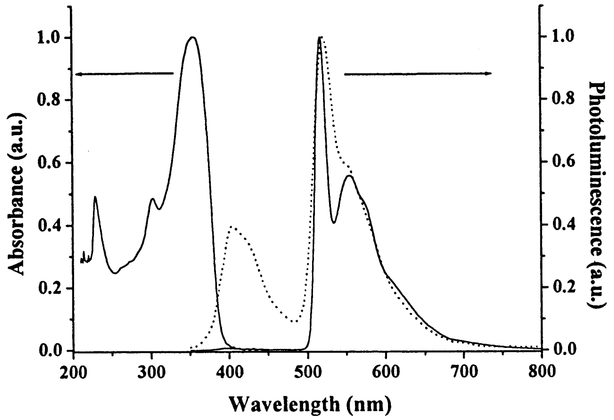


Figure 2. Room temperature optical absorption spectrum and the PL spectrum (11 K) of **4** in solid (solid line). The dotted line corresponds to the PL spectrum in CH_2Cl_2 solution at 290 K.

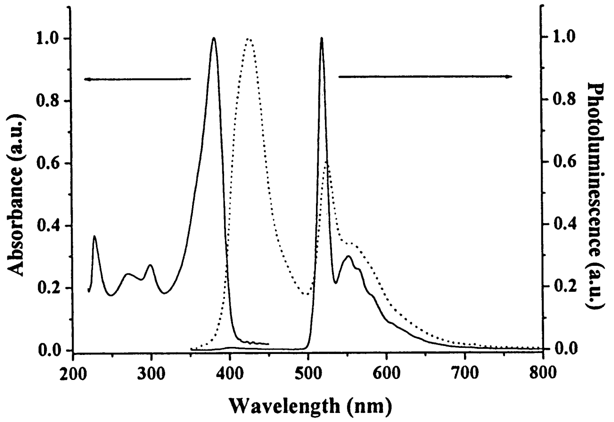


Figure 3. Room temperature optical absorption spectrum and the PL spectrum (11 K) of **6** in solid (solid line). The dotted line corresponds to the PL spectrum in CH_2Cl_2 solution at 290 K.

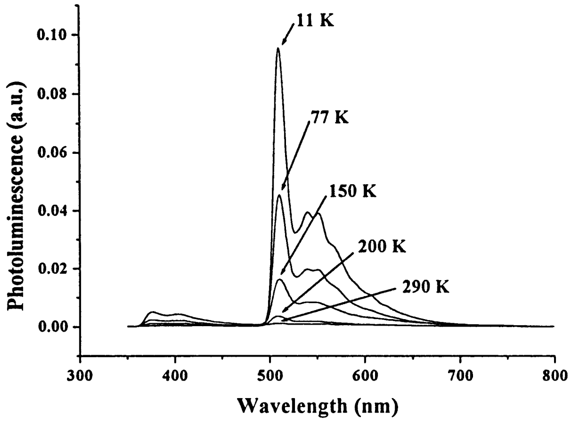


Figure 4. Temperature dependence of the PL of **2**.

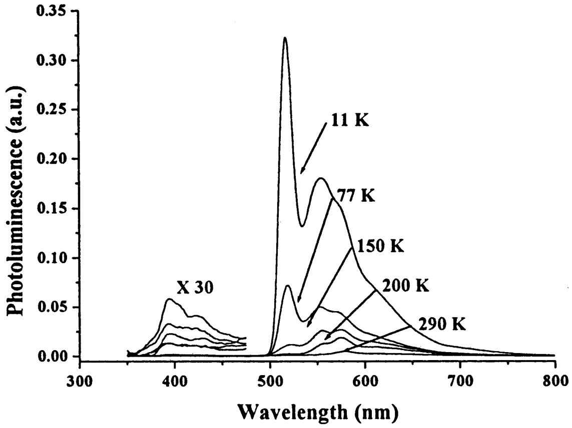


Figure 5. Temperature dependence of the PL of **4**.

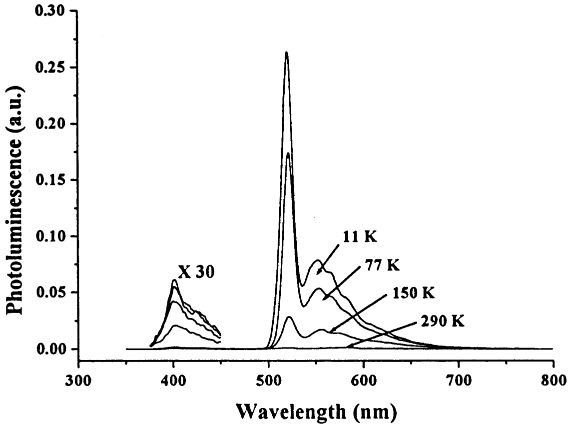


Figure 6. Temperature dependence of the PL of **6**.

absorption and the emission spectra (e.g., ca. 0.30 eV for **4**).[11,13] The lower-lying emission beyond 500 nm is attributed to that of a triplet excited state (phosphorescence $T_1 \rightarrow S_0$) due to the substantial Stokes shift measured (e.g., ca. 1.02 eV for **4**). In addition, the emissions do not show a marked shift in dilute solutions (ca. 404 and 520 nm for **4**, 428 and 525 nm for **6** in CH_2Cl_2 at 290 K), which excludes an excimer origin (Figures 2 and 3). Vibronic structure with most weight in the 0–0 vibrational peak can be seen in the triplet emission at low temperatures for **1**–**6**, and the spectral shape is similar to the phosphorescence in related compounds.[9,11,13,37] The assignment can best be rationalized in terms of the observed temperature dependence of the emission data, in accordance with earlier work on platinum polyynes.[9,11,13] The temperature dependencies of the PL spectra for **2**, **4**, and **6** are displayed in Figures 4–6. In all cases, the triplet photoluminescence band shows a strong temperature dependence, in contrast to the higher-lying singlet emission. From 290 to 11 K, the singlet emission peak intensity increases only by a factor of 10.0 and 4.3 for **2** and **4**, respectively. However, the intensity of the corresponding lower-lying emission increases by a factor of 109.3 (for **2**) and 246.2 (for **4**), and such an increase in emission intensity indicates a long-lived excited state that is more sensitive to thermally activated nonradiative decay mechanisms.[9–13] Similarly, the intensity of the singlet and triplet peaks for **6** increases by a factor of 3.0 and 240.0, respectively, as the temperature is lowered from 290 to 11 K. The S_1–T_1 energy gaps for **4** and **6** are found to lie within the constant range of 0.7 ± 0.1 eV for similar conjugated metal polyynes[9,12] and are close to the gap of ca. 0.62 eV for a ladder-type poly(*p*-phenylene) polymer determined from phosphorescence measurements.[39] The gap also compares well with the 0.6–0.7 eV estimated by Beljonne for an infinite PPV chain.[40] We attribute such a constant S_1–T_1 energy gap to the exchange energy and possibly some additional constant contribution due to the admixture of the platinum orbitals.[9] For both **4** and **6**, the T_1 state appears strongly localized, as shown from the small energy difference between triplet emissions in the respective dimers (**2** and **5**) and in the polymers (**4** and **6**). On the basis of the spectroscopic

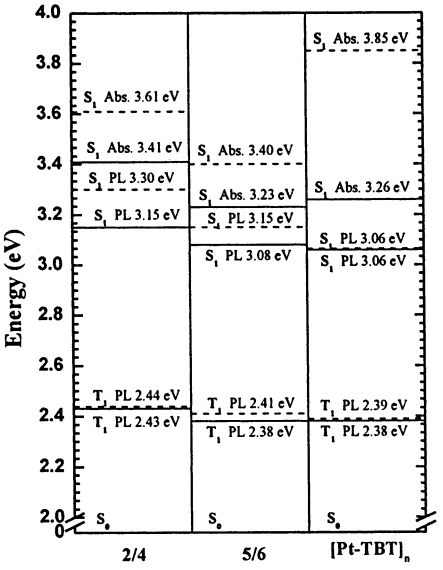


Figure 7. Electronic energy level diagram of **2**, **4**, **5**, and **6** determined from absorption and PL data. Solid and dashed lines represent polymers and dimers, respectively, and the S_0 levels are arbitrarily shown to be of equal energy. $[Pt-TBT]_n$ refers to the Pt polyyne and diyne containing *p*-phenylene spacer, and the data were taken from ref 12.

data, we can draw the energy level diagram shown in Figure 7 for the new polymers and the dimeric congeners. The energy values are absolute values with respect to the S_0 ground state. We observe that in all instances the energy levels in the left column appear blue-shifted relative to those in the middle and right columns.

To assess the relative efficiency of intersystem crossing, the peak height ratio from triplet emission to singlet emission at 11 K, $\Delta E(T_1 \rightarrow S_0, S_1 \rightarrow S_0)$, was used as a probe (Table 2).[11,13] Clearly, the intersystem crossing is much stronger in polymer **4** than in the corresponding oligomers **1**−**3** since the energy of the S_1 state (and thus the S_1-T_1 energy gap) is lower for the former. We note a very high efficiency of triplet emission for **4**, and the order of S_1-T_1 crossover efficiency is **4** (170) > **6** (125) > *trans*-$[-Pt(PBu_3)_2C{\equiv}C(p\text{-}C_6H_4)C{\equiv}C-]_n$ (80 at 25 K). This also agrees with the solution PL data in which the ratio of integrated intensities of phosphorescence to fluorescence is greater than unity for **4** but is less than unity for **6**. These data reveal that the intensity of phosphorescence reduces with the energy of the T_1-S_0 emission, and the efficiency of intersystem crossing is higher for the metal polyyne system with a larger optical gap as in the alkynylsilane derivative **4**. The use of conjugation-interrupting silyl segment in such metal polyynes can fine-tune the effective conjugation length and gives rise to efficient crossover between S_1 and T_1 states, especially at low temperatures.

Photocurrent Measurements. We also studied the photoconducting properties of the polymer film of **4**. Fabrication of the ITO/**4**/Al photocell (ITO = indium−tin oxide) was possible, and the typical film thickness was 0.1−0.5 μm. The experiment was performed by using a lock-in amplifier to measure the voltage drop across a resistor resulting from the photocurrent through the polymer film so that the signal due to the dark current can be eliminated. Excitation was made at 370 nm, close to the absorption edge of **4**, and Figure 8 depicts the logarithmic plot of the photocurrent of such photocell against the applied electric field across the polymer for illumination through the ITO anode. Our results showed that the photocell displayed a moderate photoconductivity in ambient air. At forward bias, the photocurrent of the devices is field-dependent, and it increases with increasing bias voltage. The curve is steeper at higher voltages, typical of other known organometallic photoconductors and recently reported platinum polyynes with oligothienylene and fluorene entities.[10,13,14] Similar to *trans*-$[-Pt(PBu_3)_2C{\equiv}C(p\text{-}C_6H_4)C{\equiv}C-]_n$ or alike, it is conceived that the excited states are mostly strongly bound triplet excitons in such Pt−polyyne upon photoexcitation, and these are confined to one monomer unit.[41] Polymer **4** showed a photocurrent quantum yield of approximately 0.01% at 370 nm, which compares well with other single-layer devices.[10] Alternate substitution of the $Pt(PBu_3)_2$ unit in *trans*-$[-Pt(PBu_3)_2C{\equiv}C(p\text{-}C_6H_4)C{\equiv}C-]_n$ by $SiPh_2$ as in **4** preserves the photoconducting properties of this class of platinum polyynes while increasing the flexibility of the polymers.

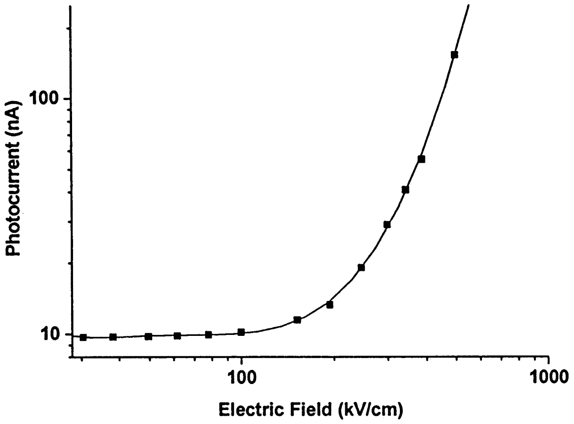


Figure 8. Photocurrent vs external electric field logarithmic plot for **4**.

Concluding Remarks

In summary, we have outlined the synthesis and characterization of a new structural class of well-defined platinum-containing poly(alkynylsilanes) with excellent thermal stability. While the silyl segment hinders conjugation, these materials display strong triplet emission and the intersystem crossing efficiency is enhanced. We consider that the silyl functionality is an effective conjugation interrupter to limit the conjugation length in metal polyynes. Our results indicate that efficient phosphorescence is easier to obtain for higher S_0-T_1 energy gaps. These new polymer systems serve as a good model to study the relationship between chemical structure and the evolution of singlet and triplet excitons in conjugated polymers, and such an investigation is desirable for applications that harvest the T_1 state for light emission. The pursuit of new alkynylsilanes of higher generations in such metal polyynes is currently underway in an attempt to achieve better optical and electrical performance. It is also worthwhile to investigate the suitability of this type of organometallic polymers as precursors to transition-metal-containing ceramics, and extension of these synthetic methodologies to other group 14 elements would warrant further examination.

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Supporting Information Available: Absorption and PL spectra of **1**, **3**, and **5**, perspective drawing, and tables of X-ray crystal data for **II**. This material is available free of charge via the Internet at http://pubs.acs.org.

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