



Synthesis, photophysics and pyrolytic ceramization of a platinum(II)-containing poly(germylacetylene) polymer

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ABSTRACT

A synthetic route to a new polymeric platinum(II)-containing germylacetylene has been developed. Soluble and thermally stable platinum(II) polyynyl polymer *trans*-[Pt(PBu₃)₂C≡CGePh₂C≡C]_n (**P1**) was prepared in good yield by CuI-catalyzed polymerization of *trans*-[Pt(PBu₃)₂Cl₂] and Ph₂Ge(C≡CH)₂. We report the optical absorption and photoluminescence spectra of **P1** and the results are compared with platinum(II) polyynes with purely acetylenic and other (hetero)aromatic conjugated units. Harvesting of organic triplet emission harnessed through the strong heavy-atom effect of Pt and Ge was examined. Polymer **P1** was found to have a high optical bandgap (ca. 3.84 eV). The influence of metal and sp³-hybridized germyl-based conjugation interrupter on the intersystem crossing rate and the spatial extent of the lowest singlet and triplet excitons were fully elucidated. Our investigations indicate that a high-bandgap polymer **P** intrinsically gives rise to a very efficient phosphorescence with fast radiative decay. Remarkably, a simple single-step method was also established for the synthesis of platinum–germanium (PtGe) alloy nanoparticles using **P1** as the polymer precursor and the resulting ceramic metal alloys have been characterized by powder X-ray diffraction, energy dispersive X-ray analysis and transmission electron microscopy.

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1. Introduction

In contrast to the large body of work on luminescent poly-metallaynes with π-electron units [1–5], similar systems having germylene units in the backbone have been reported, and little research on rigid–rod transition metal σ-alkynylgermane polymers has been carried out [6,7]. 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 [8–17] and introduction of

disorder to the conjugated system [18,19], we envisioned that the sp³-germanium unit can be a good choice of spacer group in metal polyynes. In addition, inclusion of the sp³-Ge linker can limit the effective conjugation length and trigger the triplet light emission by taking advantage of the heavy-atom effect of Ge atoms [6,7]. Therefore, the key feature of this study is to evaluate how the metal center and the germyl moiety would influence the electronic and optical properties of this class of materials.

On the other hand, metallic nanoparticles (NPs) have attracted great interest over the years due to their unique optical, electrical, magnetic and catalytic properties [20]. Properties of the NPs differ from those of the bulk since the quantum size effects dominate their unique characteristics [21]. In particular, platinum NPs have been widely used in many applications, for example, catalysts [22,23], fuel cells [22–24], electro-optical devices [25] and magnetic devices [26], etc. The properties of Pt NPs depend strongly on the particle size, shape, composition, and structure [27,28].

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Platinum is also known to have high catalytic activity for hydrogenation and dehydrogenation [29]. However, the very high activity of Pt would generate a large amount of undesired methane during the process of hydrogenolysis [30]. To reduce the activity of Pt NPs, intermetallic compounds such as Pt₃Ge and PtGe have been used [30,31]. The lower activity of Pt–Ge NPs reduces the generation of undesired methane for the hydrogenation than Pt NPs but is associated with their higher selectivity to specific alkenes.

There are several reports on the synthesis of Pt–Ge type NPs [30–34]. Most of them require an arc melting of the mixture of pure Pt and Ge granular metals under extreme conditions (high pressure and high temperature) or vaporization of Ge(acac)₂Cl₂ (acac = acetylacetonate) on Pt loaded substrate prepared by calcination with Pt(NH₃)₄Cl₂ at high temperature. The Pt/Ge molar ratio was varied by changing the relative amount of metals or ionic metal precursors charged into the system. Although Pt–Ge NPs are still predominantly prepared by physical methods, there is a desire to prepare the materials by chemical techniques. Chemical routes are generally simpler and less expensive and have the advantages of improved stoichiometric control and intimate mixing [35].

In this paper, we report full details of our studies on the synthesis, characterization and photophysical properties of a Pt(II)-containing poly(germylacetylene) polymer **P1**. Their optical and emission properties will be discussed in comparison to those systems having purely acetylenic and other (hetero)aromatic spacers. The effect of adding the heavy metal and the germanium residue on the phosphorescence decay rate of **P1** is also investigated. Furthermore, we have developed a new approach for a 'one-pot' synthesis of PtGe NPs by the pyrolysis of **P**. A study of such ceramic composites made from **P1** was also described.

2. Experimental

2.1. General information

All reactions were performed under nitrogen. Solvents were carefully dried and distilled from appropriate drying agents prior to use. Commercially available reagents were used without further purification unless otherwise stated. All reagents for the chemical syntheses were purchased from Aldrich or Acros Organics. The Pt(II) precursor *trans*-[PtCl₂(PBU₃)₂] was prepared according to the literature method [36]. All reactions were monitored by thin-layer chromatography (TLC) with Merck pre-coated glass plates. Flash column chromatography and preparative TLC were carried out using silica gel from Merck (230–400 mesh). Fast atom bombardment (FAB) mass spectra were recorded on a Finnigan MAT SSQ710 system. NMR spectra were measured in CDCl₃ on a Varian Inova 400 MHz FT-NMR spectrometer and chemical shifts are quoted relative to tetramethylsilane for ¹H and ¹³C nuclei and an 85% H₃PO₄ external standard for ³¹P nucleus. Infrared spectra were recorded as CH₂Cl₂ solutions on the Nicolet Magna 550 Series II FTIR spectrometer, using CaF₂ cells with a 0.05 mm path length.

2.2. Physical measurements

UV–vis spectra were obtained on a HP-8453 spectrophotometer. The photoluminescent properties and lifetimes of the compounds were probed on the Photon Technology International (PTI) Fluorescence Master Series QM1 system. The quantum yields were determined in CH₂Cl₂ solutions at 293 K against quinine sulfate in 1.0 N H₂SO₄ (Φ = 0.40) as a reference [37]. For solid-state 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 K to 330 K. For lifetime measurements, the third harmonics, 355 nm line of a Q-switched Nd:YAG laser was used as the excitation light source. The emission was recorded by using a PMT and a HP54522A 500 MHz oscilloscope. 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 a Perkin–Elmer TGA6 thermal analyzer [2,3].

2.3. Preparation of compounds

2.3.1. Synthesis of **L1-TMS**

To a chilled solution of Me₃SiC≡CH (104 mg, 1.05 mmol) in dried THF (20 ml) at –78 °C, ⁿBuLi (0.8 ml, 1.28 mmol) was added dropwisely under N₂. The mixture was stirred for 0.5 h at this temperature and then 0.5 h at room temperature. The resulting solution was again cooled to –78 °C and a solution of Ph₂GeCl₂ (142 mg, 0.4 mmol) was added dropwise over 20 min and the reaction mixture was stirred for a further 0.5 h before stirring was continued for another 1 h at room temperature. The volatile components were evaporated and the residue was extracted with CH₂Cl₂. The filtrate was concentrated and subjected to preparative TLC isolation on silica plates using *n*-hexane/CH₂Cl₂ (1:2, v/v) as the eluent. From the first band, compound **L1-TMS** was obtained as a white solid with 60% yield (121 mg). *Spectral data*: IR (CH₂Cl₂): 2038 cm⁻¹ (ν_{C≡C}); ¹H NMR (CDCl₃): δ 7.71–7.74 (m, 4H, Ar), 7.43–7.46 (m, 6H, Ar), 0.28 (s, 18H, TMS); ¹³C{¹H} NMR (CDCl₃): δ 134.34, 133.70, 129.76, 128.41 (Ar), 116.37, 104.91 (C≡C), –0.16 (TMS); FAB-MS: *m/z* = 345 (M–Ph)⁺. Anal. Calc. for C₂₂H₂₈Si₂Ge: C, 62.73; H, 6.70. Found: C, 62.55; H, 6.79%.

2.3.2. Synthesis of **L1**

A mixture of compound **L1-TMS** (121 mg, 0.3 mmol) and K₂CO₃ (55 mg, 0.4 mmol) in Et₂O/MeOH (30 ml 2:1, v/v) was stirred at room temperature overnight. Infrared spectroscopy showed that all the starting materials had been consumed. Solvent was removed under reduced pressure to a leave colorless residue. This residue was dissolved in the minimum amount of CH₂Cl₂ and subjected to TLC on silica using *n*-hexane/CH₂Cl₂ (4:1 v/v) as eluent to afford a major colorless but UV–visible product identified as **L1** (68.8 mg, 87%). *Spectral data*: IR (CH₂Cl₂): 2039 cm⁻¹ (ν_{C≡C}), 3282 cm⁻¹ (ν_{C≡CH}); ¹H NMR (CDCl₃): δ 7.73–7.75 (m, 4H, Ar), 7.43–7.50 (m, 6H, Ar), 2.64 (s, 2H, C≡CH); ¹³C{¹H} NMR (CDCl₃): δ 133.60, 132.78, 130.18, 128.62 (Ar), 82.41 (C≡C), 98.67 (C≡CH); FAB-MS: *m/z* = 277 (M)⁺. Anal. Calc. for C₁₆H₁₂Ge: C, 69.41; H, 4.37. Found: C, 69.65; H, 4.54%.

2.3.3. Synthesis of **P1**

CuI (1.2 mg) was added to a mixture of **L1** (250 mg, 0.90 mmol) and *trans*-[PtCl₂(PBU₃)₂] (606 mg, 0.90 mmol) in ^tPr₂NH/CH₂Cl₂ (30 ml, 1:1, v/v) [2,3]. The pale 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 CH₂Cl₂, and filtered through a silica column using the same eluent. After removal of solvent, a pale yellow oily solid was obtained, and it was then washed with MeOH. Further purification can be accomplished by precipitating the polymer solution in toluene from MeOH to afford **P1** as a pale yellow solid in 76% yield (600 mg). *Spectral data*: IR (CH₂Cl₂): 2026 cm⁻¹ (ν_{C≡C}); ¹H NMR (CDCl₃): δ 7.72 (m, 4H, Ar), 7.23 (m, 6H, Ar), 1.99 (m, 12H, PCH₂ of Bu), 1.39 (m, 12H, PCH₂CH₂ of Bu), 1.26 (m, 12H, CH₂CH₃ of Bu), 0.80 (m, 18H, CH₃ of Bu); ¹³C{¹H} NMR (CDCl₃): δ 139.88, 135.03, 128.19, 126.32 (Ar), 107.27, 93.70 (C≡C), 26.36, 24.17, 23.32, 13.94 (Bu); ³¹P{¹H} NMR (CDCl₃): δ 3.86

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