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Synthesis, spectroscopy, structures and photophysics of metal alkynyl complexes and polymers containing functionalized carbazole spacers

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Abstract

A new class of soluble and thermally stable group 10 platinum(II) poly-yne polymers functionalized with 9-arylcarbazole moiety *trans*-[-Pt$(PBu_3)_2C{\equiv}CRC{\equiv}C$-]$_n$ (R = 9-arylcarbazole-3,6-diyl; aryl = *p*-methoxyphenyl, *p*-chlorophenyl) were prepared in good yields by the polycondensation polymerization of *trans*-[$PtCl_2(PBu_3)_2$] with $HC{\equiv}CRC{\equiv}CH$ under ambient conditions. The optical absorption and emission properties of these polymetallaynes were investigated and compared with their bimetallic molecular model complexes *trans*-[$Pt(Ph)(PEt_3)_2C{\equiv}CRC{\equiv}CPt(Ph)(PEt_3)_2$] as well as their group 11 gold(I) and group 12 mercury(II) neighbors [$(PPh_3)AuC{\equiv}CRC{\equiv}CAu(PPh_3)$] and [$MeHgC{\equiv}CRC{\equiv}CHgMe$]. The structures of all the compounds were confirmed by spectroscopic methods and by X-ray crystallography for selected model complexes. The influence of the heavy metal atom and the 9-aryl substituent of carbazole on the evolution of lowest electronic singlet and triplet excited states is critically characterized. It was shown that the organic-localized phosphorescence emission can be triggered readily by the heavy-atom effect of group 10–12 transition metals (viz., Pt, Au, and Hg) with the emission efficiency generally in the order Pt > Au > Hg. These carbazole-based organometallic materials possess high-energy triplet states of 2.68 eV or higher which do not vary much with the substituent of 9-aryl group.

Keywords: Acetylide; Carbazole; Gold; Mercury; Platinum; Phosphorescence

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1. Introduction

The use of carbazole chromophores offers exciting perspectives for the design of new molecular and polymeric materials for various optoelectronic applications [1]. Many carbazole derivatives have a sufficiently high triplet energy to be able to host red [2–5], green [6,7], and in some cases even blue [8,9] triplet emitters. Poly(carbazole) homopolymers and their copolymers are highly promising materials for applications in light-emitting devices because they contain a rigid biphenyl unit which can lead to a large band gap with efficient blue emission, and the facile substitution at the remote *N*-position offers the possibility of improving the solubility and processability of polymers without remarkably increasing the steric interactions in the polymer backbone [1].

While developments based on the exploitation of 9-arylcarbazole as the building unit for the synthesis of branched molecules, oligomers, polymers or even dendrimers have been extensive, most of them are restricted to purely organic systems [10]. Carbazole-based coordination/organometallic compounds have been much less explored [11]. To our knowledge, carbazole-containing

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metal alkynyl compounds are still scarce. Literature examples are exclusively confined to 2,7-diethynyl-9-butylcarbazolediyl-spaced metal di-, oligo- and polymers [12]. However, there has been no report of 9-arylcarbazolyl-derived metal complexes, and the chemistry of such compounds would be interesting within the realm of materials science and optoelectronics. There are also very few reports in the sensitization of carbazole's triplet emission using heavy-metal effects [10h]. According to the energy gap law, the rate of phosphorescence emission is increased by interruption of the π-conjugation, i.e. a compound with high-energy triplet state is desirable [13]. With this in mind, we report here the synthesis, spectroscopic characterization, crystal structures and photophysical properties of some luminescent group 10–12 dinuclear and polynuclear platinum(II), gold(I) and mercury(II) complexes functionalized with some 9-arylcarbazole spacers. The influence of the heavy metal center and the 9-aryl substituent of carbazole ring on the photoluminescence behavior will be elucidated in this contribution.

2. Results and discussion

2.1. Synthesis

The synthesis of 3,6-diethynyl-9-arylcarbazole, **Ia** and **Ib**, are outlined in Scheme 1. First, the *N*-arylation of carbazole was achieved by the modified Ullmann condensation between carbazole and the corresponding *p*-iodoarene under the CuI/phen/KOH catalytic medium [14]. The corresponding *N*-arylated 3,6-dibromocarbazole precursors were obtained in good yields by bromination of 9-arylcarbazole derivatives with *N*-bromosuccinimide (NBS). An alternative synthetic method can also be used to produce 3,6-dibromo-9-arylcarbazoles in a similar yield by condensing the commercially available 3,6-dibromocarbazole with the corresponding *p*-iodoarene. The 3, 6-bis(trimethylsilylethynyl)-functionalized 9-arylcarbazole compounds were formed from the Sonogashira-type coupling reaction between the dibromo derivatives and trimethylsilylacetylene and they were then converted to the diethynyl counterparts **Ia** and **Ib** in very good yields (88–94%) using K_2CO_3 in MeOH as the deprotecting reagent [15]. The crude products from these reaction mixtures were purified by passage through silica gel column and were recrystallized where necessary.

All the metal alkynyl complexes and polymers were obtained in good yields by the general alkynylation routes as described in Scheme 1. The diplatinum complexes can be considered the geometrical molecular models for the long chain organometallic polymers. Organic ligands **Ia** and **Ib** were employed as versatile synthons in the present study to form a series of group 10–12 metal acetylide complexes and polymers by adaptation of the classical dehydrohalogenation procedures reported in the literature [16]. **1a**, **1b**, **2a** and **2b** were synthesized by CuI-catalyzed dehydrohalogenating coupling of *trans*-$[PtCl_2(PBu_3)_2]$ or *trans*-$[PtCl(Ph)(PEt_3)_2]$ with **Ia** or **Ib** at room temperature (r.t.), respectively. The feed mole ratios of 2:1 and 1:1 for the platinum chloride precursors and the diethynyl ligand were adopted for the model complex and polymer syntheses, respectively. Purification of the polymers **1a** and **1b** were accomplished by silica column chromatography using CH_2Cl_2 as the eluent whereas the diplatinum complexes **2a** and **2b** were isolated by preparative TLC on silica. We have also prepared the d^{10} digold(I) diacetylide counterparts **3a** and **3b** by reaction of $Au(PPh_3)Cl$ with **Ia** or **Ib** in a 2:1 stoichiometry in the presence of a base [17]. Similarly, complexes **4a** and **4b**, the isoelectronic and isolobal analogues of **3a** and **3b**, were synthesized by treatment of **Ia** and **Ib** with two equivalents of MeHgCl under similar basic medium [18]. The yields of these transformations are generally high in each case. All the new complexes and polymers are air-stable solids which can be stored without demanding any special precautions. They display good solubility in chlorocarbons such as CH_2Cl_2 and $CHCl_3$, but are insoluble in hydrocarbons. Estimates of the molecular weights using gel permeation chromatography (GPC) in THF indicate that the degrees of polymerization calculated from M_w are 8–16 for **1a** and **1b** (Table 1). It should be noted that the GPC method used does not give absolute values of molecular weights but can only measure the hydrodynamic volume. Rod-like polymers in solution possess different hydrodynamic properties than flexible polystyrene standard. So, calibration of the GPC with polystyrene is likely to inflate the values of the molecular weights of the poly-ynes to some extent.

2.2. Spectroscopic properties

The IR, NMR (^1H, ^{13}C and ^{31}P) and fast-atom bombardment (FAB) mass spectral data of our compounds agree with their chemical structures. The solution IR spectra are each characterized by a single sharp $\nu(C{\equiv}C)$ absorption band at ca. 2092–2134 cm^{-1}. The IR spectrum of each compound shows no $\nu({\equiv}CH)$ band in the range 3200–3300 cm^{-1}, in line with the fact that **Ia** and **Ib** are completely being capped by the metal groups via σ bonds. The single $^{31}P\{1H\}$ NMR signals flanked by platinum satellites for **1a**, **1b**, **2a** and **2b** are consistent with a *trans* geometry of the square-planar Pt unit. The room-temperature ^{31}P NMR spectrum of **3a** and **3b** display a sharp singlet at δ 43.91, indicative of a symmetrical arrangement of $PAuC{\equiv}C$ groups in solution. ^1H NMR resonances arising from the protons of the organic and phosphine moieties were clearly observed. The formulas of the model complexes **1a**, **1b**, **3a**, **3b**, **4a** and **4b** were also characterized by the presence of intense molecular ion peaks in their respective positive FAB mass spectra.

2.3. Crystal structure analyses

The three-dimensional molecular structures of **2a**, **3a** and **4b** were analyzed by X-ray crystallography and are