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The synthesis, crystal structure and photophysical properties of mononuclear platinum(II) 6-phenyl-[2,2′]bipyridinyl acetylide complexes

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ABSTRACT

The synthesis, structural, electrochemical and photophysical properties of a series of 4,6-diphenyl-2,2′-bipyridine platinum(II) complexes bearing σ-alkynyl ancillary ligands were studied. Absorption bands were observed in UV–Vis absorption spectra (maximum peaks range from 431 to 455 nm) and phosphorescence emission maxima varied from 554 nm to 577 nm. Both the UV absorption and photoluminesence emission maxima of the complexes were red-shifted in accordance with not only the electron-donating ability of the *para*-substituent on the phenylacetylide ligand, but also the extension of the π-conjugated length of the oligo phenylacetylide ligand. The photoluminescent and electrochemical properties as well as crystal structure were investigated with the aim of providing the basis for elucidating structure-physical property relationships in the context of light-emitting materials.

1. Introduction

Cyclometalated square-planar platinum(II) complexes have attracted a great deal of attention owing to their use in optoelectronic devices, chemosensors, photovoltaic cells and photocatalysis [1–10]. The square-planar Pt(II) coordination geometry discourages D_{2d} distortion which is likely to result in radiationless decay and their photophysical properties can be modulated by structurally modifying the ligands employed [11,12]. Of these, square-planar platinum(II) σ-alkynyl complexes have been extensively investigated and in the context of organic light-emitting diodes (OLEDs), nonlinear optical materials, low-dimension conductors and photovoltaic devices by virtue of their chemical and structural stability [13–19]. As rigid π-conjugated bridging components of these complexes, acetylide moieties facilitate a wide range of photorelated processes, including triplet energy transfer, electron (or hole) transfer, photon migration, and electron delocalization, while maintaining strict stereochemical integrity.

Che and co-workers [13,14] synthesized a series of 6-aryl-2,2′-bypyridine tridentate cyclometalated platinum(II) complexes containing σ-alkynyl auxiliaries, and showed that the σ-alkynyl component can act as photophysically ’active’ ligand which constitutes an integral part of the electronic structure through Pt-(alkynyl) π-conjugation. Additionally, the anionic σ-alkynyl ligand lends neutrality to the [Pt(C^N^N)] moiety and is envisaged to modulate their photophysical properties by measn of variation of the substituent in the acetylide moiety. The metal-to-ligand charge transfer (^{1}MLCT) absorption band and the emission maximum of the complexes can be systematically altered in accordance with the electron-donating or electron- withdrawing ability of the *para*-substituent in the phenylacetylide ligand. In this context, the development of novel, tridentate, cyclometalated platinum(II) complexes containing various σ-alkynyl moieties and their photophysical properties and structure-property relationships are feasible, challengeable and potentially valuable.

This paper concerns a series of novel, mononuclear platinum(II) 6-phenyl-[2,2′]bipyridinyl acetylide complexes, that contain various arylacetylide substituents (Scheme 1). Their photophysical properties were investigated with the aim of understanding structure-physical property relationships in the context of novel organic light-emitting materials.

2. Experimental

2.1. Materials

All reagents were purchased from Sinopharm Chemcial Reagent Co. Ltd. Dichloromethane, chloroform and acetonitrile were

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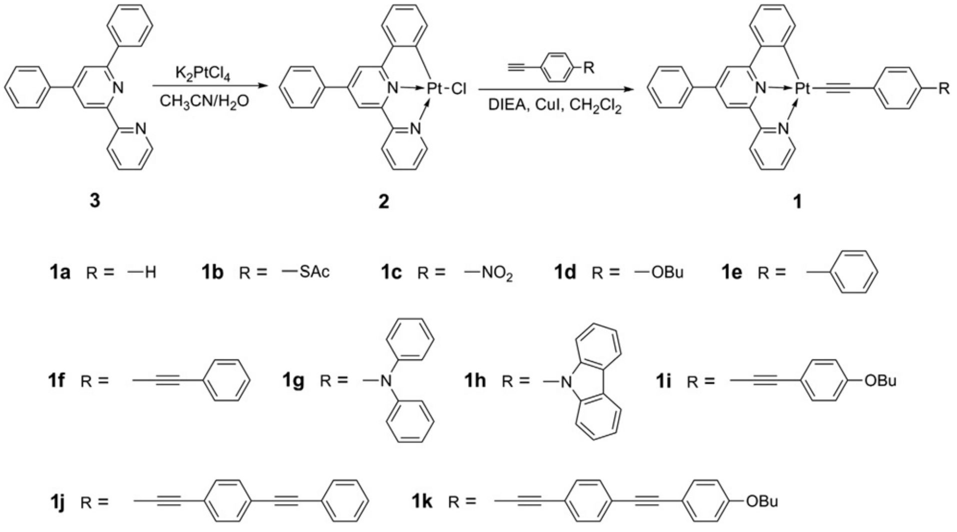

Scheme 1. Synthesis of Pt(II) complexes (**1a**–**1k**).

purified by redistillation. Tetrahydrofuran (THF) and *N,N*-diisopropylethylamine (DIEA) were distilled under N_2 over sodium benzophenone ketyl. Tetra-*n*-butylammonium perchlorate (TBAP) and ferrocene were purified by recrystallization twice from ethanol. All other reagents were used as received. 4,6-Diphenyl-2,2′-bipyridine (**3**) [13] and phenylacetylide ligands [20–25] were synthesized according to literature methods.

2.2. Measurements

^{1}H NMR and ^{13}C NMR spectra were recorded on either a Bruker AV-500 or AV-300 spectrometer using DMSO-d_6 as the solvent, with tetramethylsilane as internal standard. The elemental analyses were performed with a Vario El III elemental analyzer. High resolution mass (HRMS) analyses were performed at an AutoSpec Premier mass spectrometer (Waters). Optical absorption spectra were obtained by using a Cary 5000 UV/Spectrophotometer (Varian). PL spectra were carried out on a LS-55 spectrofluorometer (Perkin-Elmer). The X-ray crystallographic analysis was performed on a Nonius CAD4 single-crystal diffractometer. The electrochemical experiments were carried out using a CHI 660C electrochemistry workstation (CHI USA). A standard one-compartment three-electrode cell was used with a Pt electrode as the working electrode, a Pt wire as the counter electrode and a Ag/Ag$^+$ electrode (Ag in 0.1 M $AgNO_3$ solution, from CHI, Inc) as the reference electrode. TBAP (0.1 M) was used as the supporting electrolyte and the scan rate was 100 mV s^{-1}.

2.3. Synthesis

2.3.1. Synthesis of complex (C^N^N)PtCl (**2**)

4,6-Diphenyl-2,2′-bipyridyl (0.31 g, 1.0 mmol, 1.0 equiv.), K_2PtCl_4 (0.41 g, 1.0 mmol, 1.0 equiv.), acetonitrile and water (v/v = 1:1, 40 mL) were mixed in a round-bottom flask and refluxed for 48 h under a dry atmosphere of N_2. The mixture was cooled to ambient and filtered; the precipitate was rinsed with acetonitrile (20 mL) and water (20 mL) to afford 0.33 g orange solid complex **2** in 61.0% yield [13]. ^{1}H NMR (DMSO-d_6, 300 MHz): δ ppm 8.92 (d, J = 5.1 Hz, 1H), 8.76 (d, J = 8.0 Hz, 1H), 8.53 (s, 1H), 8.38 (t, J = 7.8 Hz, 1H), 8.28 (s, 1H), 8.12 (d, J = 6.8 Hz, 2H), 7.93 (d, J = 7.3 Hz, 1H), 7.83 (d, J = 7.5 Hz, 1H), 7.61–7.50 (m, 4H), 7.18–7.07 (m, 2H).

2.3.2. General procedure for synthesis of complexes **1a**–**1k**

A mixture of **2** (0.54 g, 1 mmol, 1.0 equiv.), phenylacetylide (3 mmol, 3.0 equiv.), DIEA (0.45 g, 3.5 mmol, 3.5 equiv.) and CuI (0.019 g, 10 mol %) in degassed CH_2Cl_2 (30 mL) was stirred for 12 h under a nitrogen atmosphere at room temperature in the absence of light. The mixture was then quenched with water, extracted with CH_2Cl_2 (3 × 30 mL). The organic layer was washed with water (50 mL), dried over anhydrous magnesium sulfate and evaporated to dryness. Then the crude product was purified by recrystallization from CH_2Cl_2/Et_2O (v/v = 3:1, 20 mL) to afford to give the desired product.

*2.3.2.1. Complex [(C^N^N)PtC≡CC$_6$H$_5$] (**1a**).* Yield was 62.1% as orange solid [11]. ^{1}H NMR (DMSO-d_6, 300 MHz): δ ppm 9.10 (d, J = 4.5 Hz, 1H), 8.77 (d, J = 8.2 Hz, 1H), 8.59 (s, 1H), 8.40 (t, J = 7.2 Hz, 1H), 8.35 (s, 1H), 8.12 (d, J = 8.0 Hz, 2H), 7.92–7.89 (m, 2H), 7.79 (d, J = 6.5 Hz, 1H), 7.63–7.60 (m, 3H), 7.38 (d, J = 7.4 Hz, 2H), 7.29 (t, J = 7.5 Hz, 2H), 7.19–7.09 (m, 3H).

*2.3.2.2. Complex [(C^N^N)PtC≡CC$_6$H$_4$-4-SAc] (**1b**).* Yield was 58.8% as orange solid. ^{1}H NMR (DMSO-d_6, 300 MHz): δ ppm 9.05 (d, J = 5.5 Hz, 1H), 8.75 (d, J = 8.1 Hz, 1H), 8.58 (s, 1H), 8.38 (t, J = 7.2 Hz, 1H), 8.33 (s, 1H), 8.11 (d, J = 6.0 Hz, 2H), 7.88 (t, J = 6.6 Hz, 2H), 7.75 (d, J = 7.1 Hz, 1H), 7.60–7.62 (m, 3H), 7.43 (d, J = 8.2 Hz, 2H), 7.32 (t, J = 8.2 Hz, 2H), 7.14–7.09 (m, 2H), 2.43 (s, 3H). ^{13}C NMR (DMSO-d_6, 300 MHz): δ ppm 193.8, 164.3, 157.4, 154.7, 151.3, 142.2, 140.1, 137.6, 136.5, 134.2, 131.7, 130.2, 130.1, 129.0, 128.7, 127.6, 125.4, 124.4, 123.6, 123.3, 117.0, 116.4, 30.0. HRMS *m/z* [M]$^+$ Calcd. for $C_{32}H_{22}N_2OPtS$: 677.1101. Found: 677.1098. Anal. Calcd. (%) for $C_{32}H_{22}N_2OPtS$: C, 56.72; H, 3.27; N, 4.13. Found: C, 56.69; H, 3.30; N, 4.12.

*2.3.2.3. Complex [(C^N^N)PtC≡CC$_6$H$_4$-4-NO$_2$] (**1c**).* Yield was 63.3% as orange solid. ^{1}H NMR (DMSO-d_6, 300 MHz): δ ppm 9.02 (d, J = 4.5 Hz, 1H), 8.76 (d, J = 7.6 Hz, 1H), 8.59 (s, 1H), 8.39 (t, J = 8.2 Hz, 1H), 8.25 (d, J = 8.5 Hz, 1H), 8.17 (s, 1H), 8.14–8.10 (m, 3H), 7.8 (s, 2H), 7.71 (d, J = 7.2 Hz, 1H), 7.62–7.56 (m, 5H), 7.14–7.09 (m, 2H). ^{13}C NMR (DMSO-d_6, 300 MHz): δ ppm 165.2, 158.3, 156.6, 154.3, 151.5, 151.3, 146.8, 142.6, 138.6, 138.5, 137.3, 132.9, 131.1, 129.8, 129.4, 127.3, 124.5, 123.6, 122.4, 121.5, 117.5, 116.2, 114.2, 105.5. HRMS *m/z* [M]$^+$ Calcd. for $C_{30}H_{19}N_3O_2Pt$: 648.1125. Found: 648.1103. Anal. Calcd. (%) for $C_{30}H_{19}N_3O_2Pt$: C, 55.56; H, 2.95; N, 6.48. Found: C, 55.51; H, 2.99; N, 6.44.