



Cyclometalated NCN platinum(II) acetylide complexes – Synthesis, photophysics and OLEDs fabrication



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ABSTRACT

The novel cyclometalated NCN platinum(II) acetylide complexes were synthesized. As precursors of acetylide ligands were used 9,9-dibutyl-2-ethynylfluorene, 9-butyl-3-ethynylcarbazole, and 5-ethynyl-2,2'-bithiophene, whereas 1,3-di(2-pirydylyl)benzene derivatives were cyclometalating NCN ligands. Variable character of ligands allowed to prepare a series of novel platinum(II) complexes, which showed light emission in a wide wavelength range from 410 to 625 nm. The optical and electrochemical properties of new complexes were examined and compared with theoretical DFT calculations. Complexes containing fluorenyl and carbazol motif were used as emitters in an organic light-emitting diodes. The applicability of these Pt(II) complexes for electroluminescence was examined.

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1. Introduction

Square-planar NCN cyclometalated Pt(II) complexes ([Pt(NCN)X]) consist of covalent (Pt-C) and coordinative (N-Pt) bonds between ligands and platinum. 1,3-Di(2-pirydylyl)benzene derivatives as precursors of main ligands, contain carbon atom being enormously strong δ donor, while nitrogen in pyridine ring acts as π acceptor. The character of atoms in such kind of ligands directly affects the photophysical properties of Pt(II) complexes. The presence of strong field ligands influences the excited state and the photophysical properties of Pt(II) complexes. Compared to analogical [Pt(NNN)X], the distance of Pt-C in NCN complexes is smaller than Pt-N (middle ring in NNN complexes) [1] resulting mostly in considerable increase of the energy required for deactivating DMSO- d_6 states by NCN ligands. Furthermore, complexes with 1,3-di(2-pirydylyl)benzene exhibited emission in solid state, contrary to terpyridine complexes showing poor emission in room

temperature. It is due to efficient non-radiative decay processes of terpyridine complexes [2].

In addition, the exchange of coordination environment, for instance replacement of chloride atom to strong field acetylide ligand, has tuned the energetic states. The occurrence of acetylide motif has lead to significant increase of energy of deactivating DMSO- d_6 states. The existence of acetylide fragment in platinum(II) complexes has significantly affected the photophysical properties of platinum complex owing to ethynyl derivatives being superior π conjugated molecules. In addition, the triple bond in these derivatives causes rigidity of molecule and the flatness, which directly impacts both the external and internal interactions [3].

Hence, over recent years ethynyl derivatives containing fluorene, carbazole, and 2,2'-bithiophene motifs have been widely synthesized as potential materials applied in organic electronics. Ethynyl derivatives of carbazole and fluorene were used for construction of high efficient Bulk-Heterojunction small organic solar cells [3]. Ethynyl motif in organic compounds provokes interesting luminescence properties, including strong fluorescence in a solid state of such materials [4]. For instance, ethynyl bithiophene is well-known π -linkage used in the synthesis of compounds widely

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applied in photovoltaics [5].

The phosphorescent platinum(II) complexes with ligands being itself luminophores are widely investigated as a potential active layers in organic light emitting diodes (OLED) [6,7]. Therefore, platinum(II) complexes with ethynyl ligand have recently emerged as very promising nonlinear optical (NLO) materials due to their extended delocalized π -electron structure leading to enhancement of reverse saturable absorption [8–10]. Platinum(II) complexes based on ethynyl carbazoles ligands with various coordinative surroundings such as phosphine [11], bipyridine [12], and NNC cyclometalating derivatives [13], have been recently described. Complexes of 9-(prop-2-ynyl)-9H-carbazole as ethynyl ligand and 2,6-bis(benzothiazol-2'-yl)benzene have showed absorption in the range of 295–440 nm and maximum of emission at around 600 nm [6]. However, NCN cyclometalated complexes based on 9-alkyl-3-ethynylcarbazole are not known.

Nowadays, acetylide platinum(II) complexes with ethynyl bithiophene ligand are extensively studied, though there are mainly phosphine complexes containing two ethynyl motifs that have been described [14]. Polyynyle platinum(II) complexes are also often synthesized [15,16], where electron donor ability of ethynylbithiophene ligand is mostly responsible for efficient charge mobility via intramolecular charge transfer (ICT). On the other hand, polymeric Pt(II) complexes based on ethynylbithiophene ligands exhibiting broad absorption and large molar coefficient are efficient sensitizers in the organic polymer solar cells [17]. It is worth mentioning that cyclometalated or NN type Pt(II) complexes with ethynyl fragment (considering ethynylbithiophene) have not been described so far. A number of acetylide Pt(II) complexes based on fluorene motif are known, mainly diimine complexes with *N,N*-bipyridine coordinative ligands which were mostly tested with regard to their NLO properties [8–10]. Cyclometalated Pt(II) complexes of NNC type with 9-alkyl-2-ethynylfluorene as acetylide ligand have been recently synthesized and their optical properties were characterized [13]. Aforementioned compounds have demonstrated a strong solubility dependence on the length of alkyl chain at 9,9 position in fluorene [13]. Recently, NCN cyclometalated Pt(II) complexes based on 3-(*N,N*-diethylamino)-propyl)-2-ethynylfluorene have been described and investigated as the cathode interlayer for polymer solar cells [18].

Herein, we report on synthesis and optical properties of a series of novel Pt(II) complexes with the variation of strong field ligands, namely NCN cyclometalating: 1,3-bis(piryd-2-yl)benzene and 1,3-difluoro-2,6-bis(piryd-2-yl)benzene, and ethynyl aromatic ligands: 9,9-dibutyl-2-ethynylfluorene, 9-butyl-3-ethynylcarbazole, and 5-ethynyl-2,2'-bithiophene. The photophysical, electrochemical, electrical properties and theoretical calculations of all Pt(II) complexes were thoroughly investigated. In addition, complexes **Pt-1**, **Pt-3**, **Pt-4** and **Pt-6** (Fig. 1) were used as emissive layer in OLEDs giving devices emitting orange-red or yellow-greenish light.

2. Experimental

Experimental details, synthesis of ligands L1 and L2, and spectroscopic data (^1H NMR and ^{13}C NMR spectra) for **Pt-1-Pt-6** were collected in Supporting Information. 1,3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzene and 1,3-difluoro-4,6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzene were prepared according to the literature procedure [19].

2.1. Synthesis of [PtL1Cl]

To a round-bottom flask, 1.58 g (6.81 mmol) 1,3-di(pyrid-2-yl)benzene and 3.10 g (7.49 mmol) $\text{K}_2[\text{PtCl}_4]$ were added. Next 50 ml of

glacial acetic acid was added and the flask was purged by argon for 30 min. The mixture was heated by 72 h at 130 °C under argon atmosphere. After cooling, the particulate was filtered and washed by water, ethanol and diethyl ether and dried under vacuum. The **[PtL1Cl]** was obtained as a yellow solid (2.18 g, 69%). ^1H NMR (400 MHz, DMSO) δ 9.25–8.87 (m, 2H), 8.22 (m, 2H), 8.15 (d, $J = 8.0$ Hz, 2H), 7.78 (d, $J = 7.7$ Hz, 2H), 7.57 (m, 2H), 7.31 (t, $J = 7.7$ Hz, 1H). ^{13}C NMR (101 MHz, DMSO) δ 166.71, 161.21, 151.44, 140.76, 140.65, 125.12, 124.22, 123.30, 120.58.

2.2. Synthesis of [PtL2Cl]

The procedure was the similar to that of **[PtL1Cl]**, except used 0.78 g (2.94 mmol) 1,3-difluoro-4,6-di(pyridin-2-yl)benzene and 1.33 g (3.23 mmol) $\text{K}_2[\text{PtCl}_4]$ in 32 ml of glacial acetic acid. **[PtL2Cl]** was obtained as an orange solid (1.31 g, 90%). ^1H NMR (400 MHz, CDCl_3) δ 9.40–9.17 (dd, $J_{\text{H-Pt}} = 20.4$ Hz, $J_{\text{H-H}} = 5.6$ Hz, 2H), 8.00–7.92 (m, 2H), 7.92–7.83 (m, 2H), 7.33–7.26 (m, 2H), 6.65 (t, $J = 11.2$ Hz, 1H). ^{13}C NMR (126 MHz, CDCl_3) δ 164.39, 160.90, 158.75, 152.14, 139.59, 124.45, 123.14, 122.63, 99.35. HRMS: calcd. $[\text{M} - \text{Cl}]^+ = 462.0381$, found. $[\text{M} - \text{Cl}]^+ = 462.0390$.

2.3. General method of synthesis of ethynyl platinum complexes (Pt-1-Pt-6)

To a round-bottom two-necked flask, 10 eq. of NaOH was placed and 5 ml of MeOH was added. The mixture was stirred at room temperature by 30 min under argon atmosphere. Next, through rubbish septum, 3 eq. of ethynylarene (ethynyl ligand), dissolved in CH_2Cl_2 was added. The mixture was stirred by 30 min at 35 °C. Further, 1 eq. of **[PtLCl]**, dissolved in CH_2Cl_2 was added, and the mixture was stirred by 48 h at 50 °C. After cooling, the mixture was evaporated to dryness. The crude product was dissolved in CH_2Cl_2 . The inorganic precipitate was filtered. The filtrate was collected and evaporated to a small amount of CH_2Cl_2 , and hexane was added. The crude product was precipitated, then filtered and dried under vacuum. The crude product was purified on column chromatography on Al_2O_3 .

Pt-1 Product was purified by column chromatography ($\text{CH}_2\text{Cl}_2/\text{NEt}_3$, 100:1) and obtained as yellow solid. Yield = 49%. ^1H NMR (400 MHz, CDCl_3) δ 9.67–9.30 (m, 2H), 7.94 (td, $J = 7.8$, 1.6 Hz, 1H), 7.71–7.64 (m, 1H), 7.64–7.60 (m, 1H), 7.58 (dt, $J = 3.2$, 1.4 Hz, 1H), 7.53 (d, $J = 7.7$ Hz, 1H), 7.34–7.29 (m, 1H), 7.25–7.19 (m, 1H), 1.97 (s, 2H), 1.09 (s, 2H), 0.65 (d, $J = 34.1$ Hz, 5H). ^{13}C NMR (101 MHz, CDCl_3) δ 178.76, 169.67, 155.68, 150.91, 150.45, 143.17, 141.30, 138.55, 136.10, 130.51, 126.77, 126.62, 126.45, 126.20, 123.78, 123.46, 123.09, 122.77, 119.41, 119.27, 119.20, 113.30, 77.22, 54.86, 40.31, 25.94, 23.14, 13.86. HRMS: calcd: $[\text{M} + \text{H}]^+ = 727.2520$, found: $[\text{M} + \text{H}]^+ = 727.2532$.

Pt-2 was purified by column chromatography ($\text{CH}_2\text{Cl}_2/\text{NEt}_3$, 100:1) and obtained as orange solid. Yield = 18%. ^1H NMR (400 MHz, CDCl_3) δ 9.57–9.34 (d, $J_{\text{H-Pt}} = 23.2$ Hz, 2H), 7.94 (ddd, $J = 8.0$, 7.6, 1.6 Hz, 2H), 7.69 (d, $J = 7.6$ Hz, 2H), 7.51 (d, $J = 7.6$ Hz, 2H), 7.23 (m, 3H), 7.17 (dd, $J = 5.1$, 1.0 Hz, 1H), 7.15 (dd, $J = 3.6$, 1.0 Hz, 1H), 7.04–7.01 (m, 2H), 7.00 (dd, $J = 5.1$, 3.6 Hz, 1H). ^{13}C NMR (101 MHz, CDCl_3) δ 178.18, 169.56, 155.48, 144.26, 143.14, 138.65, 138.08, 134.30, 129.26, 127.74, 123.80, 123.68, 123.50, 123.43, 123.26, 123.01, 119.36, 103.35. HRMS: calcd.: $[\text{M} + \text{H}]^+ = 616.0475$; found: $[\text{M} + \text{H}]^+ = 616.0161$.

Pt-3 was purified by column chromatography ($\text{CH}_2\text{Cl}_2/\text{NEt}_3$, 100:1) and obtained as orange solid. Yield = 39%. ^1H NMR (400 MHz, CDCl_3) δ 9.75–9.47 (m, 2H), 8.36 (s, 1H), 8.09 (d, $J = 7.6$ Hz, 1H), 7.93 (m, 2H), 7.74 (d, $J = 8.4$ Hz, 1H), 7.68 (d, $J = 7.2$ Hz, 2H), 7.53 (d, $J = 7.6$ Hz, 2H), 7.49–7.36 (m, 2H), 7.38–7.30 (d, $J = 8.0$ Hz, 1H), 7.25–7.14 (m, 3H), 4.30 (t, $J = 6.8$ Hz, 2H), 1.94–1.77 (m, 2H), 1.42 (m, 2H), 0.95 (t, $J = 7.2$ Hz, 3H). ^{13}C NMR (101 MHz,

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