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Electronic structures and optical properties of neutral substituted fluorene-based cyclometalated platinum(II)–acetylide complexes: A DFT exploration

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ABSTRACT

We report a combinational DFT and TD-DFT study of the electronic and optical properties of several tridentate cyclometalated mononuclear $[\mathrm{Pt(C{^\wedge}N{^\wedge}N)(C{\equiv}CR)}]$ (**1**–**3**), $[\mathrm{Pt(C{^\wedge}N{^\wedge}N)(C{\equiv}CRC{\equiv}CH)}]$ (**4**), and dinuclear $[\mathrm{Pt(C{^\wedge}N{^\wedge}N)(C{\equiv}CRC{\equiv}C)Pt(C{^\wedge}N{^\wedge}N)}]$ (**5** (C_2 symmetry) and **5′** (C_s symmetry)) platinum(II) complexes with σ-acetylide ligand bearing fluorene substituents, where HC^N^N = 6-aryl-2,2′-bipyridine, R = fluorene-2,7-diyl **1**, **4**, **5** and **5′**, R = 9,9-dimethylfluorene-2,7-diyl **2**, R = 9,9-diethylfluorene-2,7-diyl **3**. The structural and electronic properties of the ground- and lowest triplet state and the EA and IP values of the complexes are discussed. It is found that all of the lowest-lying absorptions are categorized as the LLCT combined with the MLCT transitions. The oscillator strengths of the lowest energy absorptions get a remarkable enhancement for the dinuclear complexes **5** and **5′**compared to **1**–**4** due to the increase of electronic delocalization on the more planar molecular geometry. In general, the phosphorescent emissions of these complexes in CH_2Cl_2 are the reverse process of their lowest energy absorption transitions, except that of **4** is assigned as $^3[\pi^*-\pi]/^3$MLCT transition because of the strengthened electronic localization effect and the interaction with the solvent in the lowest triplet state. In addition, these complexes hold promise as a new kind of nonlinear optical material owing to their large static first hyperpolarizabilities (β_0). The β_0 value has increased in the dinuclear complexes in contrast to those of the mononuclear ones owing to their larger transition moment and smaller transition energy.

1. Introduction

Since the mid-1980s, the study of transition-metal σ-alkynyl complexes has been an intense area of research, because they hold a fascination for synthetic, structural, and material scientists alike [1–11]. The linear geometry of the alkynyl unit and its π-unsaturated character led to metal alkynyls becoming attractive building blocks for molecular wires and polymeric organometallic materials, which can possess interesting properties, such as optical nonlinearity, luminescence, liquid crystallinity, and electrical conductivity [12–26]. Since the applications of organic light-emitting diodes (OLEDs) were tremendously developed by Tang and Van Slyke using the metal–organic Alq_3 (q = hydroxyquinoline) as the fluorescent emitter, the design and synthesis of luminescent transition-metal σ-alkynyl complexes have received much attention [27–33].

Particularly, in recent years, there has been particular interest in platinum(II) alkynyl complexes for molecular photochemical devices manifolds due to their chemical and structural stability, greater conduction bandwidth, as well as the directional nature of the charge transfer (CT) excited states which is ideal for electron–hole creation and separation in square-planar coordination geometry [34,35]. From wide-ranging spectroscopic and magnetic studies, the alkynyl ligand is shown to occupy "strong-field" positions in the spectrochemical series. Thus, alkynyl ligands can be interpreted as good π donors and poor π acceptors. Two classes of platinum(II) σ-alkynyl frameworks have been widely reported: one includes Pt mono-alkynyl and the others consist of Pt dialkynyl with *trans*- and *cis*-modes. Aiming at enhancing the device performances and tuning the photophysical and electroluminescent properties, a vast range of platinum-containing monomers and polymers have been prepared [36–42]. Raithby and co-workers reported a series of blue-luminescent $[\mathrm{Pt(P^nBu_3)_2{-}C{\equiv}C{-}X{-}C{\equiv}C{-}}]$ (X = aromatic spacer) based polymers in the main chain in which the aromatic rings bearing extensive π-conjugation is useful to change the spectroscopic properties [43]. In contrast to hydrocarbon conjugated polymers, the triplet excited states of this kind of polymers are accessible experimentally by various optical methods. The electron-rich fluorene derivatives were recently utilized as the spacer groups, since they showed interesting and unique chemical and physical properties because of the rigid planar biphenyl unit. Furthermore, the facile substitution at the remote C-9 position in fluorene unit can improve the solubility and processability

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of polymers without significantly increasing the steric interactions in the polymer backbone [44–47]. Wong and co-workers studied a group of soluble platinum diyne and polyyne materials consisting of fluorene linking units, and a systematic correlation was made between the effective conjugation length (or conversely, band gap) and the intersystem crossing rate in these polyynes [44,48].

The emission of the aforementioned materials was assigned to triplet intraligand (IL) charge transfer transition perturbed by some ^{3}MLCT transition [15,48]. The low-lying π^* orbitals were strongly localized or delocalized over the main chain. Many spectroscopic and theoretical investigation revealed that many multidentate cyclometalated ligands such as aromatic diimine also features low-lying π^* orbitals [49–53]. Therefore, the luminescent cyclometalated Pt(II) σ-alkynyl species are another way to design and synthesize promising materials in OLEDs as well as photoinduced charge-separation systems. In 1994, Che and co-workers reported the first diimine complexes [Pt(phen)(C≡CPh)$_2$] (phen = 1, 10-phe-

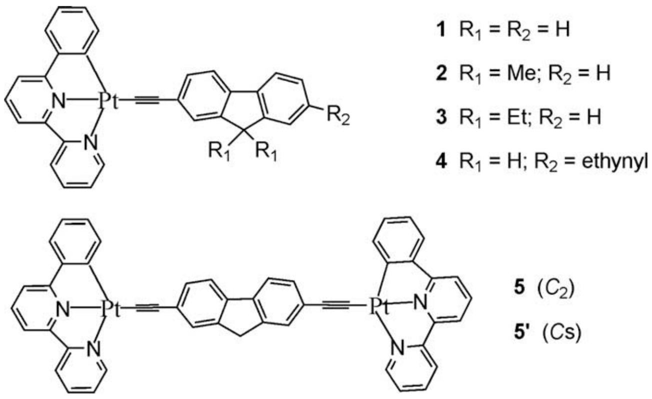

Chart 1.

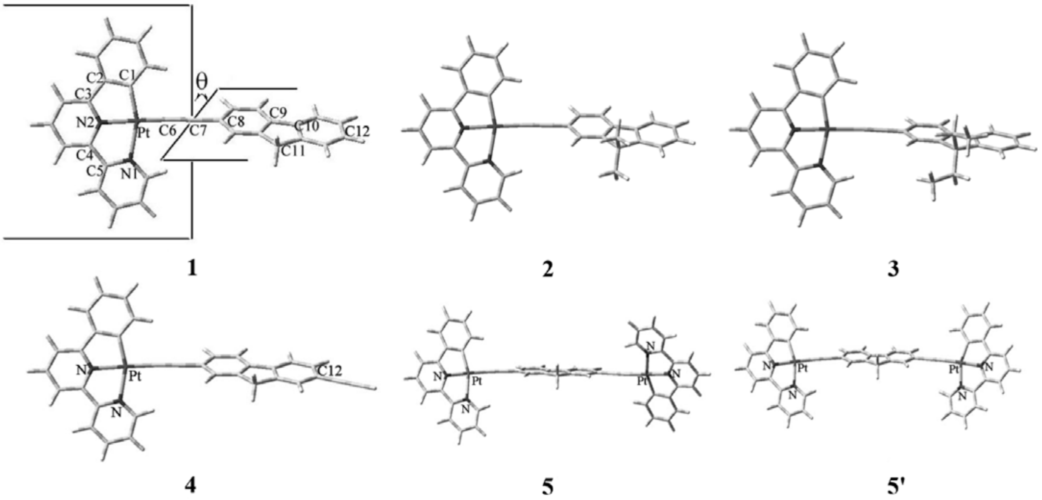

Fig. 1. Optimized molecular structures in the ground state.

Table 1
Partial optimized geometric structural parameters of the complexes in the ground and excited states associated with the experimental values of **2** and the analogues complexes.

	1 State		**2** State		*Exp*[a]	*Exp*	**3** State		**4** State		**5** State		**5′** State	
	^{1}A	^{3}A	^{1}A	^{3}A			^{1}A	^{3}A	^{1}A	^{3}A	^{1}A	^{3}B	^{1}A'	^{3}A''
Bond lengths (Å)														
Pt–N1	2.085	2.127	2.079	2.127	2.042	2.123[b]	2.080	2.126	2.085	2.128	2.085	2.083	2.085	2.087
Pt–N2	2.029	2.046	2.025	2.046	1.984	1.987[b]	2.025	2.045	2.029	2.047	2.028	2.026	2.027	2.022
Pt–C1	2.057	2.070	2.067	2.070	2.069	1.992[b]	2.068	2.071	2.057	2.070	2.056	2.071	2.056	2.068
Pt–C6	1.964	2.006	1.964	2.006	1.956	1.970[b] (2.014[c])	1.965	2.006	1.964	2.009	1.964	1.939	1.963	1.940
C2–C3	1.468	1.478	1.469	1.478	1.472		1.469	1.471	1.468	1.478	1.469	1.472	1.468	1.472
C4–C5	1.485	1.498	1.487	1.498	1.474		1.486	1.499	1.485	1.499	1.485	1.459	1.484	1.461
C6≡C7	1.228	1.220	1.228	1.220	1.210	1.185[b] (1.209[c])	1.228	1.221	1.229	1.214	1.228	1.242	1.229	1.243
C7–C8	1.425	1.397	1.425	1.397	1.433	1.424[c]	1.425	1.398	1.424	1.410	1.425	1.397	1.424	1.396
C9–C10	1.467	1.418	1.467	1.418	1.472	1.472[d]	1.467	1.419	1.464	1.406	1.464	1.434	1.463	1.432
Bond angles (°)														
N1–Pt–N2	77.1	81.5	78.1	81.5	80.9	78.4[b]	78.1	82.5	77.1	76.5	77.1	77.4	77.1	77.5
N2–Pt–C1	81.9	76.5	81.4	76.5	79.8	82.1[b]	81.5	76.5	81.9	81.5	81.9	81.5	81.9	81.7
C1–Pt–C6	100.3	98.8	99.1	99.4	102.2		99.0	98.6	99.2	99.5	98.6	99.1	98.9	99.1
Dihedral angle (°)														
θ[e]	65.2	28.9	66.5	28.9	70.0		71.3	32.7	64.5	75.1	58.8	45.2	38.9	1.1

[a] Experimental values of **2** come from Ref. [63].
[b] From Pt(C^N^N)C≡CPh in Refs. [33,66].
[c] From *trans*-[–Pt(PBu$_3$)$_2$C≡CRC≡C–]$_n$ in Ref. [48].
[d] From polyfluorene in Refs. [99,100].
[e] As shown in Fig 1.