

# Time-dependent density functional theory investigate the effect of arylacetylide chain length of cyclometalated Pt(II) complexes

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## ABSTRACT

Time-dependent density functional theory (TDDFT) method was used to investigate the effect of arylacetylide chain length on the geometrical structures, electronic properties, electroluminescent properties, absorption and emission spectra of four cyclometalated Pt(II) complexes [Pt(*t*Bu)<sub>3</sub>(tpy){C≡C(C<sub>6</sub>H<sub>4</sub>C≡C)<sub>*n*-1</sub>}C<sub>6</sub>H<sub>5</sub>]<sup>+</sup> (*n* = 1–4). The ωB97XD functional which includes long range corrections and empirical dispersion proved to be suitable for calculating the characters of the lowest singlet excited state (S<sub>1</sub>) and the lowest triplet excited state (T<sub>1</sub>) in TDDFT calculations. With the arylacetylide chain increasing, the energy levels of the occupied molecular orbitals could be raised orderly, while the unoccupied molecular orbitals had little changes. Moreover, both the absorption and emission wavelengths were red-shifted with the arylacetylide introduction. The difficulties of hole and electron injection gradually decreased. When there were four arylacetylide ligand, the complex had the best performance for electron and hole transport.

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## 1. Introduction

Phosphorescent transition metal complexes have been attracting an upsurge in interest for the design and synthesis of new functional molecular materials. The main potential applications of these complexes include organic light-emitting devices, sensors, nonlinear optical devices and photovoltaic cells [1–8]. Usually, the transition metal ions with d<sup>6</sup> and d<sup>8</sup> electronic configuration are employed, such as Re(I), Os(II), Ir(III), Pt(II) and Au(III) [9–13]. Because these transition metal ions can introduce strong spin-orbit coupling (SOC) effect, which increase the rate of singlet–triplet intersystem crossing (ISC). The Pt(II) complexes are typical phosphorescent materials with d<sup>8</sup> electronic configuration, which have dsp<sup>2</sup> hybridization and square-planar structure, and the planar structure is conducive to producing and separating electron–hole. Then attachment of Pt(II) to acetylide ligands is a good method to synthesize phosphorescent materials. The p<sub>π</sub>-orbitals of acetylide ligand mixed with d<sub>π</sub>(Pt)-orbitals through π-conjugation facilitates charge migration and energy transfer.

The performance of a transition metal complex depends on its electronic structure, which can be modified by the changes in coordinating ligands. Nowadays, time-dependent density functional theory (TDDFT) [14–16] has emerged as the ‘work-horse’ of

quantum chemistry for the calculation of excited state properties of large molecules [17–19]. The computational cost is an intermediate between semiempirical theories and wave function approaches. But there is an important drawback: the quality of the obtained results is profoundly functional-dependent [20,21]. So the appropriate selection of the exchange–correlation functional is crucial to gain sound conclusions.

The effects of arylacetylide chain length on the spectroscopic and photophysical properties have attracted much attention [22–25]. Recently, Che and co-workers have synthesized a series of luminescent Pt(II) complexes, [Pt(*t*Bu)<sub>3</sub>(tpy){C≡C(C<sub>6</sub>H<sub>4</sub>C≡C)<sub>*n*-1</sub>}C<sub>6</sub>H<sub>5</sub>]<sup>+</sup> [(*t*Bu)<sub>3</sub>tpy = 4,4',4''-trityl-2,2',6',2''-terpyridine] [26]. In this paper, we tested a few functionals under TDDFT method to gain reliable excited state properties. We carried out the present work with two goals: (1) to provide an in-depth theoretical understanding about the effect of arylacetylide chain length on the spectroscopic and photophysical properties. (2) To gain a sound process for calculating the excited states of p<sub>π</sub>-orbitals mixed with d<sub>π</sub>(Pt)-orbitals through π-conjugation.

## 2. Computational details

The structures of complexes 1–4 are depicted in Fig. 1. By taking into account the possible maximum π conjugative effect between the π electron-rich planes, the total molecule should be coplanar, so the complexes were symmetry-restricted to C<sub>2v</sub> group. To

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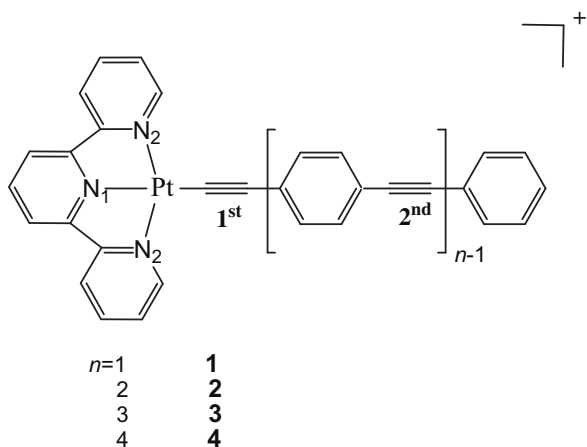


Fig. 1. Schematic structures of the investigated complexes.

save computational resources, we used hydrogen atom to replace  $(t\text{Bu})_3$  in real complex. To test the influence of this change, we calculated the absorption spectra of complexes **1** and **2** in the real structure. The results showed that the differences between the two situations were very small and the oscillator strengths only have small increases. The similar model had been proved that it is appropriate to calculate heavy organometallic complexes [27]. All the calculations were accomplished by using the Gaussian 09 software package [28] with the polarized continuum model (PCM) [29].

To find the sound calculation method, we used four methods to calculate the phosphorescence wavelength of complex **1** and the results were listed in Table 1. The 6-31+G(d,p) basis sets were adopted for C, N and H atoms, and the LANL2DZ basis sets [30,31] associated with the pseudopotential were adopted for Pt. The B3LYP functional [32–34] were employed in DFT and TDDFT methods. From Table 1, we could see the signed error (SE, calculation minus experiment) of HF/CIS/TDDFT method [27] (HF for the ground state optimization, CIS for the lowest triplet state optimization and TDDFT for the electron transition calculation between the two states) was the smallest and TDDFT tended to outperform the rest approaches. However, the HF/CIS/TDDFT method has some drawbacks, which is not perfect and may not be consistent. Therefore, we used the TDDFT method which has great promise in our calculations.

To explain the rationality of LANL2DZ/6-31+G(d,p) basis sets, complex **1** and complex **2** were selected to do the calculation tests at TDDFT/B3LYP level. Table 2 shows that the SE obtained by double-zeta basis set is closed to triple-zeta basis set. For saving computational resources, we chose the LANL2DZ/6-31+G(d,p) basis sets.

As we know, the functional is crucial to TDDFT calculation results. To find appropriate functionals, we calculated vertical excitation energies for the  $T_1$  state of complexes **1**, **2** and **3** with different functionals. The results were listed in Table 3 and Fig. 2. As we expected, the functionals  $\omega\text{B97X}$  [35], CAM-B3LYP [36] and  $\omega\text{B97XD}$  [37], which include long range corrections, provided relatively accurate descriptions for charge-transfer excitations. These range-separated functionals partially account for long range charge-separation effects by adding a growing fraction of exact exchange when the interelectronic distance increases. The  $\omega\text{B97XD}$  functional gave the best estimates for the experimental transition energies and numerical stability, which includes 100% long-range exact exchange, a small fraction (about 22%) of short-range exact exchange, a modified B97 exchange density functional for

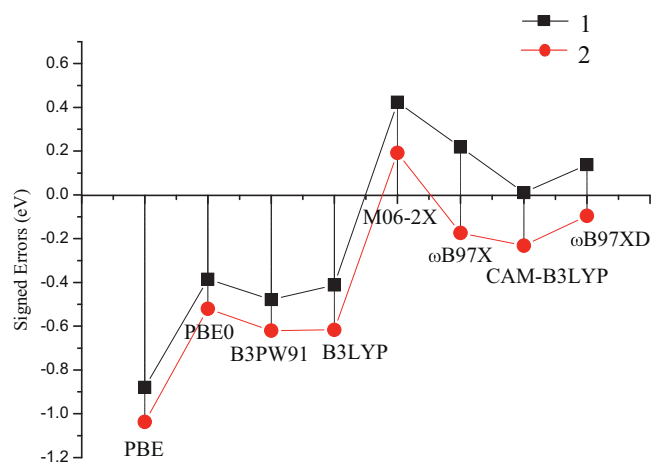


Fig. 2. Signed errors (calculation minus experiment) for complexes **1** and **2** under TDDFT calculations with different functionals.

short-range interaction, the B97 correlation density functional, and empirical dispersion corrections. It provides a dispersion energy

$$E_{disp}^{DFT-D} = - \sum_{i=1}^{N_{at}-1} \sum_{j=i+1}^{N_{at}} \frac{C_6^{ij}}{R_{ij}^6} f_{damp}(R_{ij}), \quad (1)$$

$$f_{damp}(R_{ij}) = \frac{1}{1 + a(R_{ij}/R_r)^{-12}}, \quad (2)$$

where  $N_{at}$  is the number of atoms in the system,  $C_6^{ij}$  is the dispersion coefficient for atom pair  $ij$ ,  $R_{ij}$  is an interatomic distance,  $R_r$  is the sum of vdW radii of the atomic pair  $ij$ , and  $a$  controls the strength of dispersion corrections [37]. The M06-2X [38] functional tended to outperform other conventional hybrid functionals and PBE [39,40] functional in our TDDFT calculations, since the weak interaction is considered in this functional. Therefore,  $\omega\text{B97XD}$  is appropriate for calculating the effects of arylacetylide chain length.

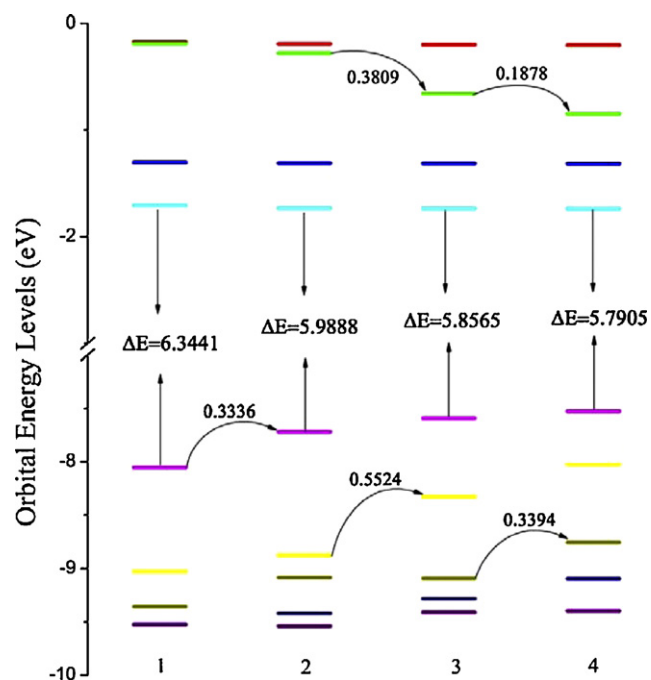


Fig. 3. Energy levels diagrams of partial molecular orbitals for the complexes **1–4**.

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