Global Science Press

Theoretical studies on one-photon and two-photon absorption properties of platinum acetylide complexes

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Abstract. The one-photon and two-photon absorption properties of platinum acetylide complexes that feature hightly π-conguated ligands substituted with π-donor or π-acceptor moieties are investigated by use of the analytic response theory at DFT level. The numerical results show that these molecules have relatively strong two-photon absorption activities. While the platium insert into the ligands, TPA cross sections of the metal compounds are significantly enhanced. Metal clusters can also extend the π-conjugated length, which plays an important role in increasing the TPA cross section. Moreover, the NLO properties of metal clusters can be enhanced by the introduction of metal→ligand and ligand→metal charge-transfer states. The charge-transfer process is analyzed when the molecule is excited from the ground state to charge-transfer state.

1. Introduction

For several decades there has been extensive research in the area of two-photon absorption (TPA) both theoretically and experimentally. TPA process is one which occurs through the simultaneous absorption of two photons via virtual state in a medium. Materials possessing large TPA response have opened up a number of unique applications in photonics and biophotonics[1-6], such as two-photon excited fluorescence microscopy[2], optical limiting[3], upconverted lasing[4], three-dimensional optical datastorage [5], and microfabrication [6]. Lots of experimental synthesis and theoretical calculations have been carried out to find non-linear optical materials with strong TPA. Extensive research efforts have been centered on organic complexes owing to low density, mechanical flexibility, and high nonlinear response [7-9]. However, Metal clusters are reported to be excellent candidates for NLO materials [10,11], since their high damage threshold and fast respons time in comparison to organic compounds, and they involve dπ–pπ delocalized systems and dπ–dπ conjugated systems[12], These compounds have a large variety of structures and diverse electronic properties that can be tuned by virtue of the coordinated metal[13-15]; thus the opportunity exists to tune the NLO properties of metal complexes. Metal clusters can also extend the π-conjugated length, which plays an important role in increasing the TPA cross section. Moreover, the NLO properties of metal clusters can be enhanced by the introduction of metal→ligand and ligand→metal charge-transfer states [16]. Although many methods can be used to promote the NLO properties of metal clusters, the origination of the NLO properties is the delocalization of the π-electron cloud [17-19]. This delocalization in metal clusters is mainly brought about by metal ions constructing the skeleton and organic ligands fixing the skeleton, thus both the metal ions and the organic ligands should be important for the nonlinear optical properties of the clusters. Many early studies confirm that heavy-metal ions play very important roles on the third-order NLO properties of metal

clusters because their incorporation introduces more sublevels into the energy hierarchy, which permits more allowed electronic transitions to take place and hence a larger NLO effect to be produced [20,21].

Recently, Rogers et al synthesized a series of platinum acetylide complexes that feature hightly π-conguated ligands (noted as L1-L3) substituted with π-donor or π-acceptor moieties, and measured their one-photon and two-photon excitation spectra [22]. The design of new two-photon absorbing chromophores (noted as Pt1- Pt4) coupled with Pt complexes to produce materials that exhibit large intrinsic 2PA cross-sections, coupled with efficient intersystem crossing to afford long-lifetime triplet states.

Metal ions can assemble organic ligands in a variety of multipolar arrangements which show interesting electronic and optical properties [23-26]. The systems which are the focus of this investigation incorporate one or more platinum centers. Platium is used because of its large spin-orbit coupling which gives rise to rapid intersystem crossing and high effective triplet yields. In order to understand optical properties of these compounds, and the effect of the metal ions on the NLO properties, a theoretical analysis for their one-photon absorption (OPA) and TPA properties by means of the response theory at density functional theory (DFT) level is provided.

2. Computational methods

The one-photon absorption (OPA) strength between the ground $|0\rangle$ and excited $|f\rangle$ state is described by the oscillator strength

$$\delta_{op} = \frac{2\omega_f}{3} \sum_\alpha |\langle 0|\mu_\alpha|f\rangle|^2,$$

Where ω_f is the excited energy and μ_α is the dipole moment operator. The summation runs over the molecular axes: $\alpha\epsilon(x,y,z)$.

The TPA cross sections of randomly oriented systems can be directly related to the imaginary part of the third susceptibility. Alternatively, the TPA cross section can be obtained by computing the individual TP transition matrix elements $S_{\alpha\beta}$ between the initial state $|0\rangle$ and final state $|f\rangle$,

$$S_{\alpha\beta} = \sum_i \left[\frac{\langle 0|\mu_\alpha|i\rangle\langle i|\mu_\beta|f\rangle}{\omega_i - \omega_f/2} + \frac{\langle 0|\mu_\beta|i\rangle\langle i|\mu_\alpha|f\rangle}{\omega_i - \omega_f/2} \right], \qquad (1)$$

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where $\alpha, \beta \epsilon(x, y, z)$, ω_i and ω_f are the excitation energy to the intermediate state $|i\rangle$ and the final state ω_f, respectively. The summation here includes all intermediate, initial, and final states.

The TPA cross section is given by orientational averaging over the two-photon absorption probability [27]

$$\delta_{tp} = \sum_{\alpha\beta}\left[F \times S_{\alpha\alpha}S_{\beta\beta}^* + G \times S_{\alpha\beta}S_{\alpha\beta}^* + H \times S_{\alpha\beta}S_{\beta\alpha}^* \right], \quad (2)$$

The coefficients F, G and H are related to the incident radiation. For the linearly polarized light, F, G and H are 2, 2 and 2, but for the circular case, they are −2, 3, and 3, respectively. The summation goes over the molecular axes $\alpha, \beta = (x, y, z)$.

The TPA cross section that can be directly compared with the experiment is defined as

$$\sigma_{tp} = \frac{4\pi^2 a_0^5 \alpha}{15 c_0} \times \frac{\omega^2 g(\omega)}{\Gamma_f}\delta_{tp}, \quad (3)$$

where a_0 is the Bohr radius, c_0 is the speed of light in vacuo, α is the fine structure constant, ω is the photon energy of the incident light, $g(\omega)$ denotes the spectral line profile that is assumed to be a δ function here, and the level broadening Γ_f of final state is assumed to have the commonly used value Γ_f=0.1 eV [28], corresponding to a lifetime of a few femtoseconds.

The straightforward application of Eq. (1) to calculate the TP transition matrix elements is limited since it requires the knowledge of all excited states. Another rigorous method to calculate the TP transition matrix elements is by using of response theory [29]. In this framework the summation over excited states is substituted by the solution of a set of coupled response equations, where the TP transition matrix elements can be identified from the residue of the quadratic response function.
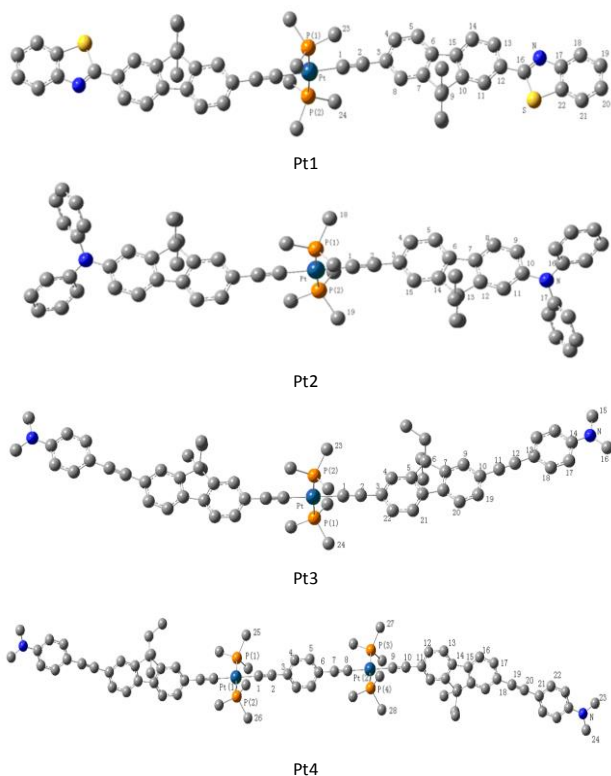

Figure 1: Optimized geometries of molecule Pt1-Pt4

3. Results and discussion

A. Computational details

The geometries of molecules are optimized using GAUSSIAN03 program [29] combined with basis sets 6-31G* for C, N, S, P and H atoms, and LANL2DZ for Pt atom, along with corresponding pseudopotential. The OPA and TPA calculations have been obtained using response theory at DFT/B3LYP level under the basis set of 6-31G* for C, N, S, P and H atoms, and ecp-sdd-pseudo for Pt atom, implemented with DALTON program. For purpose of assuring the convergence of numerical results, larger basis sets of 6-31G**, and hybrid functions B3PW91 and B3P86 are employed.

B. Molecular structures

The molecule structures optimized by DFT method are shown in **Figure 1**. In **Table 1** we list some selective bond lengths and angles of the platinum acetylide complexes. From **Table 1**, one can see that the bond lengths of Pt-C(1) (noted as B) in Pt1, Pt2, Pt3, and Pt4 are 2.0403Å , 2.0523 Å , 2.0405 Å and 2.0519 Å respectively. And we can obtain the trace that B(Pt1)<B(Pt3)<B(Pt4)<B(Pt2). The same trend is happened in the bond length of the axetylene bonded to the platinum. This demonstrates that molecule Pt1 has a better conjugation from ligands to platinum. The backbones of both four molecules possesses perfect planarity, for instance, the angle of Pt–C(1)–C(2) in Pt1, Pt2, Pt3, and Pt4 are all 179.9°. And the atoms Pt, P(1) and P(2) also nearly on the same plane, the angles of Pt–P(1)–P(2) are ~ 176°. In compound Pt2, we noted that the angle between the fluorenyl carbon-nitrogenphenyl carbon atoms is ~120°, for example the angles are respective 119.9°, 119.9° and 120.2°, it is consistent with the experimental results [22], showing that the lone pair of electrons on the nitrogen has sp² hybidization, resulting in conjugation with the fluorenyl group and the attached phenyls.

C. One-photon absorption

The excitation energies and oscillator strengths of the states are calculated at the DFT/B3LYP level in gas phase as listed in **Table 2**. As shown in **Table 2**, our calculated results are in agreement with the experimental values. For the studied molecules, the transition to the first excited state dominates the OPA spectrum. As the platinum insert into the ligands, the maximum OPA wavelength of the molecules are successively red-shifted, For instance, the maximum OPA wavelength is form L1 (346.3 nm) to Pt1 (399.6 nm), L2 (363.5 nm) to Pt2 (376.7 nm), and from L3 (378.7 nm) to Pt3 (399.2 nm) Pt4 (394.9 nm). The singlet of state energy of the ligands follow the trend E(L3)<E(L2)<E(L1), while that of the platinum compounds follow the trend E(Pt1)<E(Pt3)≈E(Pt4)< E(Pt2). The magnitude of the

Table 1. The selective bond lengths and dihedral angle of the metal compounds.

Pt1		Pt2		Pt3		Pt4	
Pt-P(1)	2.4121	Pt-P(1)	2.4112	Pt-P(1)	2.4114	Pt(1)-P(1)	2..4107
Pt-P(2)	2.4121	Pt-P(2)	2.4112	Pt-P(2)	2.4115	Pt(1)-P(2)	2.4105
Pt-C(1)	2.0403	Pt-C(1)	2.0523	Pt(1)-C(1)	2.0405	Pt(1)-C(1)	2.0519
C(1)-C(2)	1.2129	C(1)-C(2)	1.2140	C(1)-C(2)	1.2130	C(1)-C(2)	1.2139
C(2)-C(3)	1.4338	C(2)-C(3)	1.4358	C(2)-C(3)	1.4344	C(2)-C(3)	1.4360
P(1)-C(23)	1.8687	P(1)-C(18)	1.8716	P(1)-C(23)	1.8687	C(7)-C(8)	1.2142
P(2)-C(24)	1.8687	P(2)-C(19)	1.8716	P(2)-C(24)	1.8687	Pt(2)-P(3)	2.4107
N-C(16)	1.2756	N-C(10)	1.4235	N-C(10)	1.1996	Pt(2)-P(4)	2.4110
N-C(17)	1.3952	N-C(16)	1.4208	C(11)-C(12)	1.4324	Pt(2)-C(9)	2.0530
S-C(16)	1.8422	N-C(17)	1.4210	N-C(14)	1.4520	C(9)-C(10)	1.2142
S-C(22)	1.8054	Pt-C(1)-C(2)	179.9	N-C(15)	1.4520	Pt(1)-C(1)-C(2)	179.9
Pt-C(1)-C(2)	179.9	C(1)-C(2)-C(3)	179.9	Pt-C(1)-C(2)	179.9	C(1)-C(2)-C(3)	179.9
C(1)-C(2)-C(3)	179.9	Pt- P(1)- P(2)	176.3	C(1)-C(2)-C(3)	179.9	Pt(1)- P(1)-P(2)	176.1
Pt- P(1)- P(2)	176.3	C(10)-N-C(16)	119.9	Pt-P(1)-P(2)	176.3	P-P(1)-P(2)	176.3
C(16)-N-C(17)	114.3	C(10)-N-C(17)	119.9	C(10)-C(11)-C(12)	179.9	C(8)-Pt(2)-C(9)	179.9
C(16)-S-C(22)	87.3	C(16)-N-C(17)	120.2	C(11)-C(12)-C(10)	179.9	C(18)-C(19)-C(20)	179.9