



Theoretical investigation on quinoline-based platinum (II) complexes as efficient singlet oxygen photosensitizers in photodynamic therapy

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ABSTRACT

Geometry optimizations of the quinoline-based platinum (II) complexes (1-R, 2-R) and their related calculations on excited state energies, electronic absorption spectra and orbital populations have been carried out by the hybrid density functional theory (DFT) and its time-dependent approach (TD-DFT). The solvent effects on excitation energies are taken into account using the conductor-like polarizable continuum model (C-PCM). The red-shifted level of absorption bands, energy gaps between the singlet ground state (S_1) and the first triplet excited state (T_1) for each examined complex have been elaborated thoroughly as well. We find that the quinoline-8-thioil (ligand 2) induces much more significant red-shifted level than 8-hydroxyquinoline (ligand 1), and singlet-triplet splitting energy gaps of all examined complexes are bigger than threshold energy to yield singlet oxygen. It is revealed that the electronic red-shifted absorption bands originate from metal-to-ligand charge transfer (MLCT) transitions, and also shown that the quinoline-based Pt (II) complexes with strong donor groups could be considered as potential candidates for unearthing of novel photosensitizers in photodynamic therapy (PDT).

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1. Introduction

Singlet molecular oxygen (1O_2) has been of importance for scientific research due to its unique properties. Much attention to the physical, chemical, and biological properties of singlet oxygen have been indeed attracted for the past few decades [1–5]. Up to now it has been demonstrated that 1O_2 can react with many kinds of biological molecules such as DNA, proteins and lipids [6]. The sensitized singlet oxygen also has shown many significant applications in various aspects from photooxidation, DNA damage to photodynamic therapy (PDT) of cancer. A large number of photosensitizers together with their generating mechanisms of singlet oxygen have also been discussed in detail [7–9]. Among these studies, the types of photosensitizers generating singlet oxygen mostly concentrate on the organic molecules, such as organic dyes, porphyrins, phthalocyanines, and some macrocycles systems etc. However, many of transition metal complexes have been found to be more efficient as the singlet oxygen producers than the well-studied organic systems. For example, some complexes of ruthenium (II) and platinum (II) can be the efficient photosensitizers to induce singlet oxygen [10,11]. Especially, it is investigated

extensively that Pt (II) mix-ligand complexes contain donor and acceptor ligands as a 1O_2 producer [12,13]. These studies show that the reasons of Pt(II) mix-ligand complexes as efficient photosensitizers are that platinum atom facilitates intersystem crossing and improves the triplets yields and MLCT transition, and platinum(II) (d^8) always adopts to square planar coordination which enhances the rigidity of molecular structure and significantly decreases the nonradiation decay. Recently, Obata and co-workers have found that Pt (II) complexes with porphyrin-based ligands have higher singlet oxygen yields and bigger photocytotoxicity than porphyrin ligands [14]. Shavaleev et al. also found that platinum (II) complexes with quinoline-based ligands can efficiently produce singlet oxygen [15]. We are intrigued by these experiment results which suggested that platinum atom has an important effect on generating singlet oxygen. Thus, we embark on a theoretical study of the photophysical properties of these platinum (II) complexes with a great effort to ascertain the generating mechanisms of singlet oxygen. To our best knowledge, there is even no theoretical investigation for possible application of platinum (II) complexes as photosensitizers so far. Therefore, it is worthy investigating possible applications of platinum (II) complexes as photosensitizers. Although a lot of efforts to porphyrin-like systems as photosensitizers have been paid experimentally and theoretically, they usually exhibit lower tumor selectivity and higher toxicity in PDT [16]. So our research goal is to aim at photophysical properties

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of platinum (II) complexes with quinoline-based ligands, and try to provide a theoretical proof for development of next generation efficient photosensitizers applied in PDT.

Although the accurate calculation of transition energies for large molecules remains a challenge in quantum chemistry, the time-dependent density functional theory (TD-DFT) is often viewed as a valid tool to solve the contradiction between computational effort and obtained accuracy [17]. In this work, the optimized structures, transition energies and singlet-triplets energy gaps of seven quinoline-based complexes (five experimentally reported and two designed) have been performed through DFT/TD-DFT calculations. Four 8-hydroxyquinoline-based complexes and three quinoline-8-thiol-based ones are included as follows: 8-hydroxyquinoline-2-phenylpyridineplatinum(II)(1-H), 5,7-dimethyl-8-hydroxyquinoline-2-phenylpyridineplatinum(II)(1-CH₃), 5,7-dichloro-8-hydroxyquinoline-2-phenylpyridineplatinum(II)(1-Cl), 5,7-dimethyl-8-hydroxyquinoline-8-thiol-2-phenylpyridineplatinum(II)(2-H), 5,7-dimethylquinoline-8-thiol-2-phenylpyridineplatinum(II)(2-CH₃), 5,7-diaminoquinoline-8-thiol-2-phenylpyridineplatinum(II)(2-NH₂). Two newly designed complexes (2-CH₃ and 2-NH₂) are taken into account for a comparison on the red-shifted ability of ligand 1 and 2, and also for a theoretical direction to the synthesis of photosensitized complexes. This work is expected to provide a “proof-of-principle” for development of novel photosensitizers in PDT.

2. Computational methods

Density functional theory (DFT) with the B3LYP [18] exchange-correlations is employed to optimize geometry structures, calculate vibration frequency and analyze electronic structures at the ground states throughout this work. Vibration frequency analyses are used to confirm the character of minima on the optimized structures. The lowest-lying triplet state geometries were optimized with the unrestricted B3LYP method (UB3LYP). There is no symmetry constraints on these complexes studied in this work. Electronic excitation energies and oscillator strengths are

computed within the adiabatic approximation of time-dependent density functional theory (TD-DFT) [19]. For ground state structural optimizations, the split valence plus polarization basis sets 6-31G(d) for nonmetal (H, C, N, S, O) atoms, and a double- ξ quality LANL2DZ basis sets are used for metal atoms Pt with 28 core electrons being replaced by the relativistic effective core potential (ECP) of Hay and Wadt [20]. For electronic absorption spectra calculations, nonempirical PBEPBE [21] and PW91 [22] hybrid functionals together with polarized valence triple- ξ basis set (TZVP) [23] and split valence plus diffusion basis sets 6-31 + G(d, p) have been employed to verify the B3LYP/6-31G(d) results in TD-DFT calculations. Solvent effects are evaluated using the conductor-like approach within the framework of the polarizable continuum method (C-PCM) [24–26]. Since the experimental absorption spectra have been recorded in dichloromethane (CH₂Cl₂) solution [15], vertical excitation energies of the singlet and triplet states are obtained by B3LYP/6-31G(d) approach (LANL2DZ assigned to metal atoms) in both dichloromethane (with C-PCM model) and vacuum, respectively. The dielectric constant of dichloromethane ($\epsilon = 8.93$) and solvent radius are determined with C-PCM module. All calculations above are implemented in Gaussian03 software package [27] on the Origin/2950 servers. The UV–vis spectra are simulated by convolution of the first 100 excitation energy roots and corresponding oscillator strengths using SWizard program code [28], and the peak half-width in the UV–vis spectra is set in 0.209 eV(1685.83 cm⁻¹) at its half height.

3. Results and discussions

3.1. Geometrical structures at ground-and excited-states

Two kinds of quinoline-based complexes (1-R and 2-R) have been studied in this work. 8-hydroxyquinoline-2-phenylpyridineplatinum(II)(1-H), 5,7-dimethyl-8-hydroxyquinoline-2-phenylpyridineplatinum(II)(1-CH₃), 5,7-dichloro-8-hydroxyquinoline-2-phenylpyridineplatinum(II)(1-Cl), 5,7-dimethyl-8-hydroxyquinoline-8-thiol-2-phenylpyridineplatinum(II)(2-H), 5,7-dimethylquinoline-8-thiol-2-phenylpyridineplatinum(II)(2-CH₃) and quinoline-8-thiol-2-

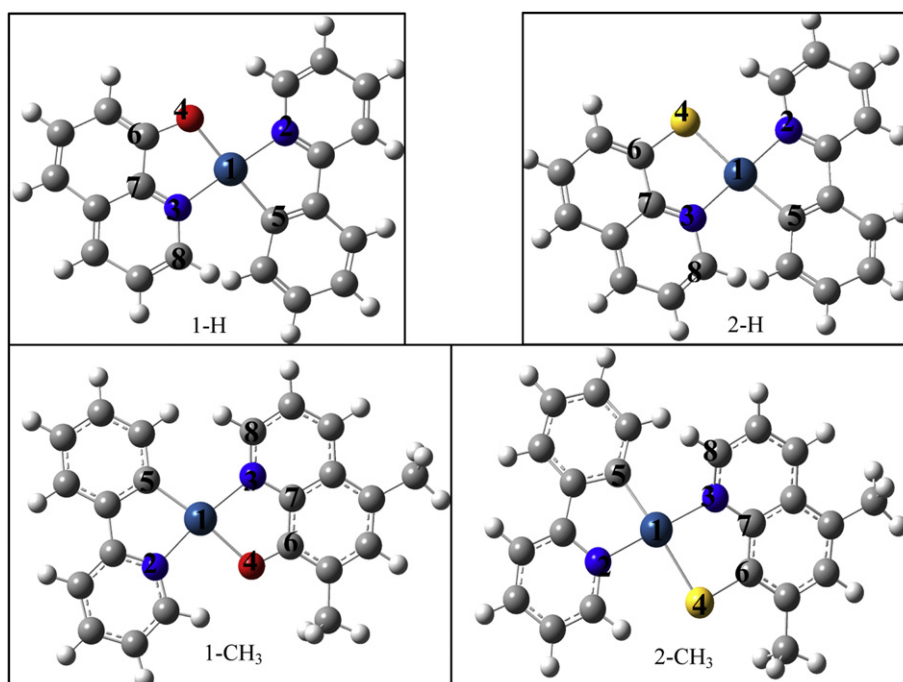


Fig. 1. Optimized structures by B3LYP/6-31G(d) (lanl2dz for Pt) for 1-H, 1-CH₃, 2-H, 2-CH₃.

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