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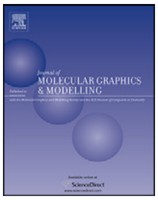

The origin of the unusual broad and intense visible absorption of tetrathiafulvalene-annulated zinc porphyrazine: A density functional theory study

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ABSTRACT

The vertical excitation energies of tetrathiafulvalene (TTF)-annulated zinc porphyrazine (ZnPzTTF) were investigated using time-dependent density functional theory (TDDFT) calculations and compared to the experimental UV–vis spectra. To examine the effects of the aza substitutions and TTF groups on the molecular properties, zinc complexes of porphyrin (ZnP), porphyrazine (ZnPz) and tetraTTF-annulated porphyrin (ZnPTTF) were also selected for comparison. It was shown that numerous electronic transitions with TTF-to-porphyrin or porphyrazine charge transfer character exist and the Q band of ZnPzTTF is dominated by TTF-to-porphyrazine charge transfer transition mixed with porphyrazine core unit itself except for classic porphyrazine $\pi \rightarrow \pi^*$ transitions. The Q band of ZnPzTTF mixes with other configurations, which breaks down the Gouterman's classic four-orbital model for the spectral interpretation. The data suggest that TDDFT/SAOP performs best for Q and B bands of ZnPzTTF with the maximum error in excitation energy being 0.17 eV. The CAM-B3LYP, ωB97XD and M06-2X calculations qualitatively predict that the low-lying electronic transitions of ZnPzTTF with TTF-to-porphyrazine charge transfer character located below the Q band. The broad and intense red-shifted Q band suggests that ZnPzTTF can be a candidate for dye-sensitized solar cells.

1. Introduction

Metal complexes of porphyrins, porphyrazines and their related tetrapyrrole ligands, have been of great importance as model compounds due to their biological functions such as photosynthesis, and as important functional materials in organic photoelectronic devices such as organic light-emitting diodes, organic photovoltaics and organic field-effect transistors [1]. The redox-active tetrathiafulvalene (TTF) is also an excellent π-electron donor with three different stable redox states (TTF, TTF^{+}, TTF^{2+}). TTF derivatives have been widely known as charge transporting and superconducting materials [2–4]. Recently, TTF-containing porphyrins [5–10], porphyrazines [11], phthalocyanines [12] and their analogues represent an exciting class of macrocyclic compounds because of their important applications such as electrochemical sensing of anions and second-order nonlinear optical (NLO)response. As to the photophysical properties, the absorption spectrum of the TTF-containing porphyrins shows a strong Soret band and two or three weak Q bands [6,9]. To our surprise, the absorption spectrum of the TTF-containing metalloporphyrazines or metallophthalocyanines shows a broad, red-shifted and intense Q band [11,12]. Experimentally, the appearance of the broad, red-shifted and intense Q band was attributed to a transition from the nonbonding sulfur and nitrogen electrons (n) to the porphyrazine (phthalocyanine) rings (π^*) ($n \rightarrow \pi^*$) and aggregation of the macrocyclic system. However, the origin of this intense Q band has not been demonstrated convincingly. The character of UV–vis spectra of TTF-containing metalloporphyrazines or metallophthalocyanines is similar to meso (ferrocenyl)-containing porphyrins [13,14] in which the redox-active ferrocene is also a good donor. The reasons for broadening of the Q band of the meso (ferrocenyl)-containing porphyrins could be the presence of ferrocene-centered molecular orbitals (MOs) located between the classic Gouterman-type porphyrin-centered π and π^* MOs ($\pi \rightarrow \pi^*$). So we hypothesize TTF-centered MOs are located between the Gouterman-type π and π^* MOs. Such a situation could potentially result in numerous TTF-to-porphyrazine (phthalocyanine) charge transfer transitions thus complicating the absorption spectra of the TTF-to-porphyrazine (phthalocyanine).

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It is well recognized that density functional theory (DFT) and time-dependent DFT (TDDFT) methods have been employed successfully to explore both electronic structures and spectral properties on porphyrins and related tetrapyrrole ligands [15–26]. For example, Nguyen and Rosa carried out TDDFT/B3LYP and TDDFT/SAOP calculations on the excitation energies of zinc complexes of porphyrin (ZnP), porphyrazine (ZnPz) and phthalocyanine (ZnPc), respectively [15,16]. The results show that the TDDFT/SAOP results give satisfactory results. However, up to now, theoretical investigations on the photophysical properties of TTF-annulated metallotetrapyrroles were sparse. Our group has recently reported the electron spectra and second-order NLO properties of monoTTF–metalloporphyrins by means of DFT calculation [27].

In this paper, our initial interest focused on the ambiguous assignment of the electronic spectra of TTF-annulated tetrapyrrole derivatives. Here, in order to shed light on the role of tetraaza substitutions and tetraTTF annulations, electronic structure and absorption spectra of tetraTTF-annulated zinc porphyrazine (ZnPzTTF) and its parent compounds (tetraTTF-annulated zinc porphyrin (ZnPTTF), ZnPz and ZnP) were systematically investigated in detail using DFT and TDDFT calculations. In addition, we also employed some representative (meta)-hybrid functionals and long range corrected functionals in an attempt to explore the prediction of the low-lying CT states of ZnPzTTF. TDDFT results suggest that the Q band of ZnPzTTF are dominated by TTF-to-porphyrazine charge transfer character mixed with porphyrazine core unit itself except for classic porphyrazine $\pi \rightarrow \pi^*$ transitions and conformational inhomogeneity is also likely to contribute to the broadening of the Q band of ZnPzTTF to some extent. ZnPzTTF is able to harvest light over a wide spectral range, so they are potential sensitizers for dye-sensitized solar cells (DSSCs). We hope that our investigation of the electronic spectra of TTF-annulated tetrapyrrole derivatives can provide guidance to the design novel tetrapyrrole sensitizers for DSSCs.

2. Computational details

The models of ZnP, ZnPz, ZnPTTF and ZnPzTTF are shown in Fig. 1. The ground state geometry of the four complexes was optimized at the DFT/BP86 level [28,29] using ADF2008.01 program [30–32] with triple-ξ plus polarization Slater-type orbital basis sets (TZP). The numerical integration of 6.0 and the scalar relativistic effects via the zero-order regular approximation (ZORA) [33] have been used to provide accurate results. Vertical singlet excitation energies and oscillator strengths of the lowest dipole and spin allowed excited states of the four complexes were calculated at the scalar relativistic TDDFT level using the asymptotically correct statistical-average-of-orbital potentials (SAOP) [34,35] along with the TZP basis sets. SAOP is widely and reliably used for the prediction of electronic structures and absorption spectra of porphyrins and related tetrapyrrole ligands [16,18,19,22,23,36,37]. The solvation was modeled through the conductor-like screening model (COSMO) [38,39] as implemented in ADF programs [40] with chloroform as solvent.

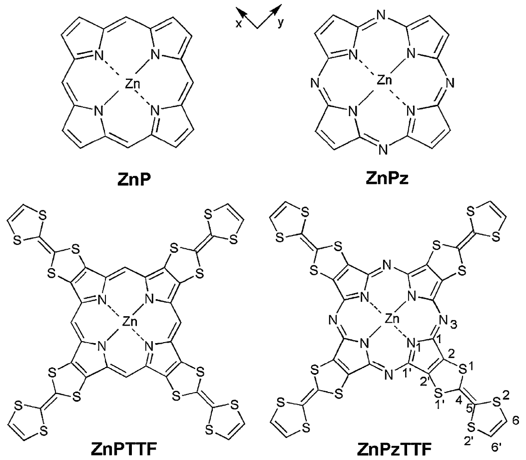

Fig. 1. Molecular structures of ZnP, ZnPz, ZnPTTF and ZnPzTTF.

The theoretical description of the absorption spectra of ZnPTTF and ZnPzTTF is complicated due to the introduction of charge transfer excited states upon incorporation of TTF units. In general, the conventional TDDFT methods notoriously underestimate the excitation energy of charge transfer (CT) transitions [41–43]. To this end, we also performed geometric optimization and frequency analysis of ZnPzTTF at DFT/PBE0 level [44] using Gaussian09 program [45] with 6-31G* basis set for C, H, O, N, S and def2-TZVP basis set [46] for zinc atom. In particular, based on the optimized ZnPzTTF geometry, vertical singlet excitation energies were calculated using PBE0, B3LYP [47–49], LC-ωPBE [50–53], CAM-B3LYP [54], ωB97XD [55], M06-HF [56,57] and M06-2X [58], because the hybrid functionals (PBE0 and B3LYP) with some fraction of the non-local Hartree–Fock (HF) exchange can alleviate, partly or satisfactorily, the CT problem of TDDFT. Recently, the long-range corrected (LC) functionals (LC-ωPBE, CAM-B3LYP and ωB97XD) was widely and accurately used to improve the CT states in porphyrins [17,20,59]. M06-HF is a full Hartree–Fock exchange functional with adapting to long-range properties and that performs well for Rydberg and CT excitations. M06-2X with double amount of nonlocal exchange was designed for valence and Rydberg excitations. The solvent effect of chloroform was simulated using the integral equation formalism of the polarized continuum model (IEFPCM) in Gaussian suite of program [60].

Molecular orbital compositions were analyzed using the AOMix program [61,62] and the absorption spectra were simulated by the SWizard program [61,63] using the Gaussian model with a half-bandwidth of 4000 cm^{-1}.

3. Results and discussion

3.1. Geometrical structures

The geometrical structures of ZnP and ZnPz in the ground state were both optimized under D_{4h} symmetry [15]. The optimized geometries were subsequently verified to be local minima by frequency calculations. According to the crystal structure of analogous bisTTF–porphyrin [9], where the TTF fragments are bowed, C_s, C_{2h}, C_{4v} and D_{2d} symmetry structure of ZnPzTTF were checked (Fig. S1). The lowest energy was found for the C_{4v} conformer, though the energy difference between other conformers was found to be small in the range of 0.01–0.65 kcal/mol (Table 1). The frequency calculations showed that the C_{2h} and C_{4v} structures are true minima (all positive frequencies) and that the C_s and D_{2d} structures contain imaginary frequencies and hence are not local minima (Supporting information pp. S5–S15). Therefore, the C_{4v} structure of ZnPTTF and ZnPzTTF is mainly considered. These four molecules lay in the xy plane with the x and y axes passing through pyrrolic nitrogens (Fig. 1). The selected optimized structure data at BP86 and PBE0 level are summarized in Table 2, and the available experimental values of ZnP are also included.

Table 1
Relative energies ΔEr (in kcal/mol) of the ZnPzTTF conformers calculated by BP/TZP.

Symmetry	C_{4v}	C_{2h}	C_s	D_{2d}	D_{4h}
ΔE_r	0	0.01	0.16	0.22	0.65