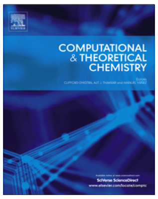
Computational and Theoretical Chemistry 1027 (2014) 26–32

Contents lists available at ScienceDirect

Computational and Theoretical Chemistry

journal homepage: www.elsevier.com/locate/comptc



Computational study on second-order nonlinear optical properties of a series of axially substituted zinc porphyrin

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ARTICLE INFO

Article history:
Received 11 August 2013
Received in revised form 13 October 2013
Accepted 14 October 2013
Available online 23 October 2013

Keywords:
Metal complex
Zinc porphyrin
Nonlinear optical property
Hyperpolarizability
Density functional theory
Finite field method

ABSTRACT

The second-order nonlinear optical (NLO) property of a series of axially substituted zinc porphyrin has been studied based on the density functional theory calculations. Our calculations show that they possess considerable second-order NLO property. The static first hyperpolarizability of these zinc porphyrins can be finely tuned by electron donor strength and the position and number of porphyrin core. Meanwhile, the two-dimensional second-order NLO properties of the axially subsumed zinc porphyrin also have been studied. Introduction of the donor–acceptor branch along radial direction is better than axial direction for their two-dimensional second-order NLO properties according to our hyperpolarizability calculations.

1. Introduction

Because of their potential application in optical fibers [1], data storage [2], optical limiting [3], optical computing [4], optical switching [5], signal processing [6], molecules with second-order nonlinear optical (NLO) property have received much attention in the recent years. The large second-order NLO responses of molecular materials arise from highly delocalized π-electron systems. Porphyrins and metalloporphyrins were considered as NLO molecular materials in this regard. The NLO properties of porphyrin, metalloporphyrin, and relative compounds via covalent bonding the strong donor and the acceptor at the porphyrin edge have been extensively studied in the past two decades [7–15]. They exhibit numerous advantages, such as high stability, versatility, processability, and architectural flexibility, which provide a very good basis to finely tune their NLO responses. For the metalloporphyrin, the nature of metal atom is also very important because the nd configuration, oxidation state, spin state of metal center will significantly affect their physical and chemical properties. A number of metal atoms have been successfully introduced into porphyrin core. Zinc porphyrins as one of them are especially well studied in various science communities because of their broadly tunable light absorption bonds and flexible edge-functionalization chemistry [16–20]. Moreover, the zinc center has capability to coordinate the axial ligand with modest equilibrium bonding constants. The synthesis of axially substituted zinc porphyrin is more facile than assembly via covalent bonds at the porphyrin edge [21]. However, to the best of our knowledge, the second-order NLO property of axially substituted zinc porphyrin has not been reported.

The molecule with large first hyperpolarizability β, is always one-dimensional (1-D) π-conjugated system ended with electron donor and acceptor. However, there are some obvious problems in the second-order NLO properties of the 1-D system. One is the centrosymmetric arrangement in crystal [22]. Most 1-D NLO molecules have large dipole moment. They tend to align in an anti-parallel formation in their crystal because of the strong dipole-dipole intermolecular interaction. This will lead to no macroscopic second-order NLO responses. Another problem is that an optimal molecular orientation in the crystal is essential to obtain efficient phase-matched second harmonic generation (SHG) [23], which is so-called phase-matching condition. For the 1-D NLO molecule, the phase-matching orientation always leads to low macroscopic NLO responses. It has been reported that the macroscopic second-order NLO response of a 1-D push-pull molecule only recovered 38% of its microscopic response because of the phase-matching arrangement [24]. These facts suggest that it may be appropriate to reconsider the new tenets of NLO chromophore design. Some new types of NLO molecule should be examined in this

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2210-271X/$ - see front matter
http://dx.doi.org/10.1016/j.comptc.2013.10.016

regard if significant advances are to be realized. Toward such goals, octupole molecules have been proposed as an alternative as they have little or no dipole moment [25]. Unfortunately, it is difficult to obtain noncentrosymmetrical arrangement for octupole molecules [26]. Besides octupole systems, the two-dimensional (2-D) chromophore with two charge transfer (CT) axes also has been explored. It has been reported that these 2-D chromophores possessed considerable NLO responses and better phase-matching than 1-D chromophores because of their large off-diagonal β-tensor components [27–31]. In addition, the noncentrosymmetric crystal packing also has been reported for 2-D organic compounds [32]. However, the available data for 2-D NLO chromophore are very scarce when compared with the 1-D molecules currently.

In the present paper, the second-order NLO properties of the series of axially substituted zinc porphyrins have been studied by using density functional theory (DFT) combined with finite field (FF) method. Due to the capability of coordinate to the axial ligand, the zinc porphyrin has been assign as a linker to attach ligands along radial and axial direction to design the 2-D structure.

2. Computational details

All of the calculations, including geometry optimization, vibrational frequencies, excited-state property, and first hyperpolarizability were run using GAUSSIAN 09 program [33]. Molecular geometries were optimized with the B3LYP hybrid exchange correlation functional [34–36]. A mixed-basis-set approach has been employed for the geometry optimization. The LanL2DZ basis set containing effective core potential (ECP) representations of electrons near the nuclei was applied for zinc atom [37–40], the 6-31g(d) basis set was used on all other atoms. The frequency calculations were run at the same level. No imaginary frequencies were obtained in vibrational calculations, conforming that the optimized structures reside at potential-energy-surface minimal point.

FF method [41,42] was broadly applied because it can be used in concert with electronic structure method to compute the first hyperpolarizability β. When a molecule is subjected to a static electric field (F), the energy (E) of the molecule is expressed by the following equation:

$$E = E^{(0)} - \mu_i F_i - \frac{1}{2}\alpha_{ij}F_iF_j - \frac{1}{6}\beta_{ijk}F_iF_jF_k - \frac{1}{24}\gamma_{ijkl}F_iF_jF_kF_l - \ldots \qquad (1)$$

In this expression, $E^{(0)}$ is the energy of molecule in the absence of an electronic field, μ_i is the components of dipole moment vector, and α is linear polarizability tensor, β and γ are first and second hyperpolarizability tensor, respectively. i, j, and k are donated as x, y and z components. When numerical FF procedure was carried out, the static hyperpolarizability tensors are evaluated as

$$\beta_L^{e,0,k}(0;0,0) = \lim_{F_L \to 0} \frac{E(-2^{k+1}F_L) - 2E(-2^kF_L) + 2E(2^kF_L) - E(2^{k+1}F_L)}{2(2^kF_L)^3} \qquad (2)$$

where E is the field dependence of the energy. The field amplitudes are given by 2^kF_L with $k = 0, 1, 2, \ldots, 6$. The field dependence of the energy was generated from the GAUSSIAN 09/SCI calculation in this work. It is clear that the numerical accuracy of the FF equation is associated with the precision in the field dependence of energy calculations. In order to reduce the error from the energy calculations, an appropriate choice of field amplitude is important. In the present paper, the field amplitudes of 0.0010 a.u., which was demonstrated to be effective for calculation of the static first hyperpolarizability in many literatures, has been chosen to calculate the first hyperpolarizability. For improving the accuracy of the calculated first hyperpolarizability, the high-order hyperpolarizability contaminations have been removed by using the iterative Romberg formula in GAUSSIAN 09 program [33].

For the first hyperpolarizability, β, the vector component along the dipole moment has been calculated by using the following equation:

$$\beta_{vec} = \sum_i \mu_i\beta_i/|\mu| \quad i = x, y, z \qquad (3)$$

The above component is defined by the equation:

$$\beta_i = \beta_{iii} + \frac{1}{3}\sum_{i \neq j}(\beta_{ijj} + \beta_{jij} + \beta_{jji}) \qquad (4)$$

The Hatree-Fock (HF) method has been firstly employed to calculate the static first hyperpolarizability in this work [43]. And then the electron correlation effect has been considered by using DFT. It should be stressed that the conventional DFT-derived results always overestimates the first hyperpolarizability of the donor-π-conjugated bridge-acceptor (D-π-A) systems because of the incorrect description of long-range charge transfer behaviors between donor and acceptor [44]. Recently, some new long-rang-corrected functionals have been developed specifically to overcome the defects of the conventional DFT [45]. They have been proposed as a good candidate to evaluate the first hyperpolarizability. In the present paper, two long-rang-corrected functionals, CAM-B3LYP [46] and ωB97XD [47,48], have been employed to calculate the first hyperpolarizability. The basis sets containing diffuse and polarized functions are necessary for accurate predictions of electronic hyperpolarizability according to many literatures [49–52]. The 6-31+g* basis set including polarized diffuse functions on the main group atoms (C, N, and O), is an appropriate choice for hyperpolarizability computations of relatively large molecules and thus has been employed for the first hyperpolarizability calculations in this work.

In order to get more insights of the second-order NLO response, the excited-state properties of the series of zinc porphyrins were also calculated using time dependent(TD)DFT with the CAM-B3LYP functional and the 6-31+g(d) basis set (LanL2DZ basis set on metal atom). It has been proved that TDDFT is a usefully accurate approach for calculation of low-lying single excitations [53].

3. Results and discussion

In order to obtain good second-order NLO responses, the electron donor and acceptor have been introduced into our studied systems along the axial direction. As shown in Fig. 1, three types of electron donor have been considered in this work, $[Ru^{II}(NH_3)_5]^{2+}$ group, tetrathiafulvalene (TTF) unit, and dimethylamino group were denoted as **1**, **2**, and **3**, respectively. The second-order NLO properties of these zinc porphyrins have been calculated at HF, CAM-B3LPY, and ωB97XD methods with 6-31+g(d) basis sets (LanL2DZ basis set on zinc atom) in this work. The calculated static first hyperpolarizabilities β values have been listed in Table 1. For the axially substituted zinc porphyrin **1**, **2**, and **3**, the introduction of the electron correlation at the CAM-B3LPY and ωB97XD levels increases β value relative the HF-derived result. Moreover, the ratio between the DFT-derived β values and the relative HF values differs from molecule to another. The CAM-B3LYP calculation leads to this ratio for the β_{vec} value in the range of 1.76 for **3**, 2.10 for **2**, and 3.73 for **1**, respectively. All the hyperpolarizability calculation with three methods shows that the diagonal tensor β_{zzz} is the dominant component of the total β value (β_{vec}), which displays a significant 1-D second-order NLO feature. According to HF calculations, the β values with in the series of zinc porphyrins evolve following the order **1** > **3** > **2**. And considering the results obtained by the two long-range-functional calculations, the β values evolve