



Photophysical properties of free and metallated meso-substituted tetrabenzotriazaporphyrin from density functional theory investigation



Marta E. Alberto, Bruna C. De Simone*, Gloria Mazzone**, Tiziana Marino, Nino Russo

Dipartimento di Chimica e Tecnologie Chimiche, Università della Calabria, I-87036 Arcavacata di Rende, Italy

ARTICLE INFO

Article history:

Received 19 January 2015

Received in revised form

17 April 2015

Accepted 22 April 2015

Available online 8 May 2015

Keywords:

DFT

TDDFT

Electronic spectra

Spin-orbit coupling constants

meso-Substituted

tetrabenzotriazaporphyrins

PDT

ABSTRACT

Density functional theory and its Time-dependent extension have been herein employed to elucidate the photophysical properties of a meso-substituted tetrabenzotriazaporphyrin and its magnesium and zinc complexes. Absorption electronic spectra, singlet-triplet energy gaps and spin-orbit matrix elements, have been provided. The investigated compounds have been found to possess two excited triplet states (T_1 and T_2) lying below the energy of the excited singlet one (S_1). The Spin-Orbit matrix elements for both the radiationless $S_1 \rightarrow T_1$ and $S_1 \rightarrow T_2$ couplings have been thus computed. On the basis of our results, the Zn(II) complex shows *i*) a singlet-triplet energy gap higher than that required to generate the cytotoxic singlet oxygen species, *ii*) a significant coupling between S_1 and T_2 states and, accordingly, it could be proposed as a potential photosensitizer in photodynamic therapy.

© 2015 Elsevier Ltd. All rights reserved.

1. Introduction

The 18π -electron macrocyclic molecules such as porphyrin and phthalocyanine and their metal containing complexes have been the subject of a myriad of theoretical and experimental works since their wide range of applications. Some recent reviews and books well document the past work and highlight future perspectives in this important field of modern chemistry [1].

The substitution of one or more bridging nitrogen atoms of phthalocyanine with sp^2 carbons leads to hybrid structures with new interesting properties [1]. Starting from the seminal works of Dent [2] and Barrett et al. [3] in the 1930s, different porphyrin-like hybrid structures have been proposed [4,5]. Very recently, a series of free and metallated hybrid phthalocyanines have been synthesized and characterized [6,7]. In particular, Mack et al. [6] reported the synthesis and the spectroscopic properties of copper-metallated derivatives of tetrabenzotriazaporphyrin, tetrabenzodiazaporphyrin, tetrabenzomonoozaporphyrin, and tetrabenzoporphyrin derivatives while Diaz-Moscoso et al. [7] have

synthesized and characterized the Mg(II) and Zn(II) complexes of tetrabenzotriazaporphyrin. The knowledge of their photophysical properties allow to predict the possible fields of application including their use as photosensitizers (PS) in photodynamic therapy (PDT). The latter, is a non-invasive treatment for a variety of diseases, which employ a PS able to transfer energy received from a light source to the oxygen present in tissues, generating reactive oxygen species (ROS) [8–10]. To generate the highly cytotoxic singlet oxygen 1O_2 agent, a good photosensitizer must possess: *i*) a red-shifted electronic absorption band falling in the so-called therapeutic window (600–800 nm), to penetrate human tissues allowing the treatment of deeper tumours; *ii*) a high intersystem spin crossing probability between the excited S_1 and the T_1 electronic states; *iii*) a triplet state lying above the $^1\Delta_g$ state of oxygen molecule (0.98 eV), and, consequently, a good singlet oxygen quantum yield (Φ_Δ). These properties can be reliably computed by using density functional theory (DFT) and its time-dependent formulation (TDDFT) [11] allowing not only to predict if a given PS could be employed as PDT drug [12–19], but also to design new and more efficient photosensitizers.

In this paper, we present a careful density functional based study on the free tetrabenzotriazaporphyrin (**1**) and its Mg(II) (**2**) and Zn(II) (**3**) complexes with the aim to better characterize the absorption electronic spectra and other important properties such

* Corresponding author. Tel.: +39 0984 492057.

** Corresponding author. Tel. +39 0984 493342.

E-mail addresses: desimone@unical.it (B.C. De Simone), gloria.mazzone@unical.it (G. Mazzone).

as singlet-triplet energy gaps and spin-orbit coupling constants (see Scheme 1).

2. Computational details

All the computations have been carried out by using Gaussian 09 [20] code at DFT and TDDFT [11] levels of theory.

Although the presence in literature of a series of benchmarks concerning the reliability of the modern exchange-correlation (XC) functionals in the reproduction of both ground and excited state properties of different kinds of molecular systems [21–24], we have performed some preliminary computations on the compound **1** (see Scheme 1) in order to verify the performances of different XC functional in the reproduction of the experimental absorption spectra. The M06, M06-2X [25], ω B97X-D [26], PBE0 [27,28] and B3LYP [29,30] XC functionals, coupled with the 6-31G* basis set, have been used for this purpose. From our results it emerges that M06 functional better reproduces the experimental maximum wavelength (642 versus 684 nm). See Table S1 in the Supporting Information for details.

We have also performed the same calculations considering a larger basis set, 6-31 + G*. Although the presence of a diffuse function slightly enhances the agreement with the experimental λ_{\max} (656 versus 684 nm), the obtained improvement of the results is accompanied by a substantial increase of computational costs. Accordingly, the M06/6-31G* has been adopted as the most suitable computational protocol, as previously done [12–19,21–24], for all the succeeding geometry optimizations and to reproduce the electronic spectra of all the investigated compounds.

The geometrical parameters obtained using the chosen protocol have been compared with the available crystal structure [7], that is compound **2** with a metal coordinated crystallization solvent molecule (ethanol). To have a reliable comparison between experimental and theoretical data, we have optimized compound **2** with a coordinated ethanol molecule, obtaining a quite satisfactory agreement (see Table S2).

All the calculations have been performed in THF to mimic the experimental environment, by using a dielectric constant of 8.93. The integral equation formalism polarizable continuum model (IEFPCM) [31,32], which corresponds to a linear response in non-equilibrium solvation, has been employed.

Spin-orbit matrix elements have been computed by using the atomic-mean field approximation [33] as implemented in DALTON code [34] since our previous experience has demonstrated as Breit-Pauli method [35] and atomic-mean field approximation provide very similar values, the latter of which requires a lower computational cost [12–19]. Because of the presence of only few hybrid functionals available in DALTON to perform these calculations, B3LYP has been selected and used on the previously M06 optimized geometries.

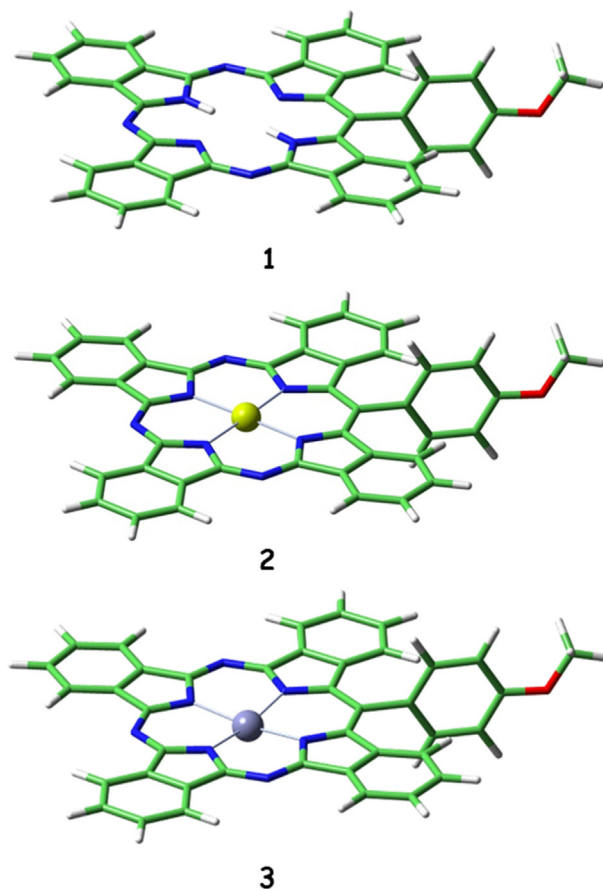


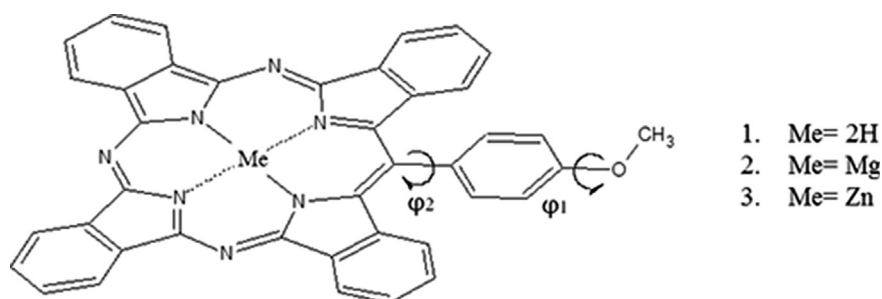
Fig. 1. M06/6-31G* optimized structures of compounds **1–3** computed in THF.

3. Results and discussion

The optimized geometries of the investigated TBTAP **1–3** are reported in Fig. 1. All of them are characterized by a completely planar structure with the meso-substituent oriented at about 90° with respect to the plane of the porphyrin-like ring (see Table S2).

In compounds **2** and **3** the metal ion is lodged in the center of the porphyrin cavity and it is coordinated over the four pyrrolic nitrogen atoms, with very similar distances from them. The presence of metal does not affect the mutual position between the porphyrin-like ring and the meso-substituent.

Table 1 collects the vertical excitation energies for the Q and Soret bands for free and complexed meso-substituted tetrabenzotriazaporphyrin species. The Soret band is characterized by a maximum absorption peak at 364 nm for compound **1** and assumes



Scheme 1.

Download English Version:

<https://daneshyari.com/en/article/175782>

Download Persian Version:

<https://daneshyari.com/article/175782>

[Daneshyari.com](https://daneshyari.com)