



Mechanistic study and design of porphyrin derivatives for inducing the triplet state of perylene bismide



Krishanthi C. Weerasinghe^a, Tianyang Wang^{a,b,c}, Junpeng Zhuang^a, Dongzhi Liu^{b,c}, Wei Li^b, Xueqin Zhou^{b,c,*}, Lichang Wang^{a,*}

^a Department of Chemistry and Biochemistry and the Materials Technology Center, Southern Illinois University Carbondale, Carbondale, IL 62901, USA

^b School of Chemical Engineering and Technology, Tianjin University, Tianjin 300072, China

^c Collaborative Innovation Center of Chemical Science and Engineering, Tianjin 300072, China

ARTICLE INFO

Article history:

Received 5 July 2016

Received in revised form 8 September 2016

Accepted 19 September 2016

Keywords:

Porphyrin
Perylene bismide
Donor-acceptor
Triplet state
DFT

ABSTRACT

Density functional theory (DFT) and time-dependent DFT (TDDFT) calculations based on B3LYP functional were carried out to understand the experimentally observed photophysical processes in the porphyrin-peryrene bisimide (**HPPP-PDI**) dyad that exhibited long-lived triplet states. The results indicate that breaking the rigidity of **PDI** in **HPPP-PDI** is responsible to the generation of long-lived triplet states. Furthermore, six porphyrin derivatives were designed by introducing a 4,4'-dicarboxybutadienyl functional group to the porphyrin moiety and studied to investigate the substituent effects on the non-coplanarity, molecular orbital, and excitation wavelength of the porphyrin donor. This work showed that the functional group at β 2-pyrrole- or meso-substitution tends to reduce the HOMO, LUMO, and the HOMO-LUMO gap of porphyrins. The results indicate that five of the six proposed porphyrin derivatives are promising donors in the **HPPP-PDI** dyad to replace **HPPP** for its potential use in photodynamic therapy.

© 2016 Elsevier B.V. All rights reserved.

1. Introduction

N-(1-hexylheptyl)-N'-phenyl perylene-3,4,9,10-tetracarboxylbismide (**PDI**) has a long-lived triplet state, which is a desirable property for use in photodynamic therapy (PDT) applications [1,2]. However, upon photoexcitation, **PDI** molecules decay to the ground electronic state through solvation relaxation rather than intersystem crossing to the triplet state. By linking **PDI** to porphyrin through a triazine linker to form a **HPPP-PDI** dyad, we succeeded in partially directing the relaxation process to the intersystem crossing pathway [3]. Specifically, our photophysical studies of the **HPPP-PDI** molecules showed that about 18% of the decay went towards the intersystem crossing. It would be interesting and important to improve upon the previous system so that the new systems can provide a better decay ratio, i.e., more than 18%, towards the intersystem crossing pathway. One strategy to increase the decay ratio to benefit the intersystem crossing is to

tune the porphyrin moiety in the **HPPP-PDI** system to longer absorption wavelengths with an enhanced absorbance.

Chlorophyll is the centerpiece of the photosynthesis process chosen by nature to provide us brilliant green color associated with living plants [4–7]. It participates directly in key steps of solar energy conversion such as light harvesting, energy transfer, and electron transfer [6–8]. This inspires researchers to investigate “artificial photosynthesis” which generally involves artificial molecular architectures with the aim of achieving efficient and direct energy transfer [6,9]. Porphyrins especially have attracted considerable attention and have been used in PDT applications, mimicking enzymes, catalytic reactions, molecular electronic devices, sensors or probes [10–13], and conversion of solar energy [6,9,14]. Moreover, numerous porphyrin based artificial light-harvesting antennae [15,16], and donor-acceptor systems [17,18] have been prepared and tested to improve our understanding of the photochemical aspect of natural photosynthesis.

The porphyrin ring is an aromatic system containing 22π electrons, but only 18 of them are involved in delocalization pathway [5,19]. In particular, electronic transitions of the two closely packed highest occupied molecular orbitals (HOMO and HOMO–1) to the lowest unoccupied molecular orbital (LUMO) strongly interact to produce a high energy excited state, S_2 , with strong

* Corresponding authors at: School of Chemical Engineering and Technology, Tianjin University, Tianjin 300072, China (X. Zhou) and Department of Chemistry and Biochemistry and the Materials Technology Center, Southern Illinois University Carbondale, Carbondale, IL 62901, USA (L. Wang).

E-mail address: lwang@chem.siu.edu (L. Wang).

absorbance around 420 nm called the “Soret band”, and a lower energy excited state, S_1 , with a weak absorbance band between 500 nm and 650 nm denoted as the “Q-band” [9,20]. Substitutions at two different types of positions, meso- and β -pyrrole-, on the macrocycle can alter these molecular orbitals and therefore change the electronic properties of porphyrin derivatives. The compounds with meso-substitutions are widely present in natural products while those with β -pyrrole-substitutions have no counterpart in nature and were developed as functional artificial models. For instance, Campbell and coworkers designed an extended porphyrin π -system by substituting the β -pyrrole position with an olefin-linked electron acceptor and reported a high photoelectric conversion efficiency of 7.1% [21]. Ma et al. designed and calculated various meso-substituted porphyrins with different donor–acceptor combinations. According to their analysis, a higher efficiency than 7.1% may be obtained with those novel porphyrin systems [22]. Through a molecular rational design strategy, record high efficiencies of 12% and 13% were achieved by GY50 and SM315 porphyrin dyes, respectively [23,24].

These successes illustrate that tuning the HOMO and LUMO levels as well as the HOMO–LUMO energy gaps of porphyrin derivatives plays a crucial role in optimizing the performance of devices involving porphyrin. In an effective rational molecular design and engineering of materials for an optimized device performance, computational predictions or assessments of the designed materials as the first step would be a desirable strategy. With the advancement of the computational chemistry, such a practice has become more feasible. Since 2004 we have practiced such a strategy in the design and engineering of functional materials and applied it successfully in the development of fluorescence sensors for detecting Zn^{2+} [25]. Further, we have published a series of donor–acceptor systems which were successfully characterized with experimental and calculated results [26,27].

More encouragingly, other researchers have utilized computational predictions to guide their materials designs related to porphyrin derivatives. Santhanamoorthi, et al. utilized the DFT and time-dependent DFT (TDDFT) approach to investigate a series of porphyrin sensitizers with different electron-donating and withdrawing substituents and revealed that those new systems should have a better performance than the existing efficient dyes due to their improved optical properties [28]. Another successful work was performed by Kim and coworkers using AMI and DFT calculations [8]. Based on the DFT and TDDFT results, Shahroosvand, et al. observed higher stabilization of the LUMO level compared to the HOMO when a bromine substitute at the β -pyrrole position in the porphyrin that explains the enhancement of the solar cell efficiency [29]. Ambre and coworkers revealed a superior performance of meso-para-carboxyphenyl porphyrin derivatives compared to the meso-meta-derivatives according to the observed dipole moments (μ) and electron density distribution based on their DFT calculations [30]. These examples demonstrated DFT and TDDFT calculations are very helpful to study the molecular orbitals and the photophysical properties and predict the efficiency of many porphyrin derivatives [31–34].

As such, we have employed DFT and TDDFT calculations to predict the properties of six designed porphyrin derivatives to replace the porphyrin in the porphyrin–perylene bisimide dyad. Specifically, the designed molecules allow us to systematically investigate the substituent effects relative to the properties of the PDI moiety. The other objective of the current study is to calculate the photophysical processes described in our work [3] to further understand the experimental observations and the mechanism of generating long-lived triplet states. Before presenting these results, in Section 2 we have made comparisons between the theoretical and experimental results of the porphyrin systems from the previous experiments [3] to ensure the accuracy of the computational tools

that are also presented in the section. The results of the physical processes for the porphyrin–perylene bisimide dyad, the structures and electronic properties of the six designed porphyrin derivatives are presented in Section 3 together with selected frontier orbital contours. In Section 3, discussion is also made on the correlation between the substituents and the functional group positions and the structures and electronic properties of the porphyrin derivatives. The predicted suitable porphyrin derivatives to replace porphyrin in the original porphyrin–perylene bisimide dyad are also presented.

2. Computational details and accuracy analysis

All calculations were performed using the three-parameter functional of Becke and correlation functional of Lee, Yang and Parr (B3LYP) [35–38]. Fully geometry optimizations were carried out in dichloromethane without any symmetry constraints with the 6-31G(d,p) basis set. There were eleven systems being studied in this work: 5,10,15,20-tetraphenylporphyrin (**HTPP**), 5-(4-Aminophenyl)-10,15,20-triphenylporphyrin (**HTPPa**), 5-(4-(3,5-dichlorotriazine)amino phenyl)-10,15,20-triphenylporphyrin hydrochloride (**HTPPt**), N-(1-hexylheptyl)-N'-(4-amino)phenylperylene-3,4,9,10-tetracarboxylbisimide (**PDIa**), 5-{4-[3-chloro-5-(N-(1-hexylheptyl)-N'-(4-amino)phenylperylene-3,4,9,10-tetracarboxylbisimide)triazine]aminophenyl}-10,15,20 triphenylporphyrin (**HTPP-PDI**), 2-(4,4'-dicarboxy-butadienyl)-5,10,15,20-tetra(p-toyl) porphyrin (**HTPP-A**), 2-(4,4'-dicarboxybutadienyl)-5,15-di(p-toyl)porphyrin (**HTPP-B**), 2-(4,4'-dicarboxybutadienyl)-5-(p-toyl)-15-(2,4,6-trimethylphenyl)porphyrin (**HTPP-C**), 2-(4,4'-dicarboxybutadienyl)-5,15-di(2,4,6-trimethylphenyl)porphyrin (**HTPP-D**), 2-(4,4'-dicarboxy butadienyl)-5,15-di(p-toyl)porphyrin (**HTPP-E**), 5-(p-toyl)-10-(4,4'-dicarboxybutadienyl)-15-(2,4,6-trimethylphenyl)porphyrin (**HTPP-F**). The polarized continuum model (PCM) [39–41] framework was used to describe the solvent interaction of the system. In order to confirm the optimized geometry is a minimum energy structure, frequency calculations at the same level were performed. All geometry optimizations were obtained with the default SCF, gradient, and energy convergence of 10^{-8} , 10^{-4} , and 10^{-5} a.u., respectively. The optimized structures of these molecules in Cartesian coordinates are provided in the [Supporting Information](#).

The absorption spectra of the molecules were calculated using TDDFT [42,43] with a 6-31+G(d,p) basis set. In the TDDFT calculations, six states were used to calculate excitation energies of all the molecules except for the **PDIa** and **HTPP-PDI** dyad, where twelve states and twenty-four states were used, respectively. All the above mentioned DFT and TDDFT calculations were performed using the Gaussian03 or Gaussian 09 package [44].

B3LYP functional has been used to provide reliable results for organic molecules that were reported in our previous publications [45–47] and others [8,22,43]. However, porphyrins are more complicated and we resort to firstly investigate the accuracy of B3LYP and TD-B3LYP calculations on three porphyrin compounds: **HTPP**, **HTPPa** and **HTPPt** by comparing them with our experimental data.

Specifically, we compared the excitation energies and depicted the results in Fig. 1. The calculated absorption spectrum of **HTPP** (Fig. 1a) has four significant excitations, 409 nm, 355 nm, 534 nm, and 578 nm. Among those, the peak at 409 nm shows the highest oscillator strength, which agrees well with the experimental data of 420 nm [3]. The weak absorption peaks at 534 nm and 578 nm also agree well with the experimental measurements of the Q band [3]. Similar observations can be seen in the calculated absorption spectra of **HTPPa** and **HTPPt** (Fig. 1b and c).

Comparisons were also made to the UV–vis spectra for **PDI** and **HTPP-PDI** systems. As this study focused on porphyrin

Download English Version:

<https://daneshyari.com/en/article/5453557>

Download Persian Version:

<https://daneshyari.com/article/5453557>

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