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Density functional theory study on photophysical properties of the porphyrins derivatives with through-bond energy transfer characters

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ABSTRACT

Density functional theory (DFT) calculations have been carried out on the electronic structures, electronic spectra, carrier injection and transport properties of a series of porphyrin derivatives, 5,15-di(R)porphyrin, 5,10,15,20-tetra(R)porphyrin, and Zn-5,10,15,20-tetra(R)-porphyrin, namely, DCP, TCP, and ZCP (where R = carbazole); DMP, TMP, and ZMP (where R = N,N-dimethyl-phenyl); DQP, TQP, and ZQP (where R = 2,3,6,7-tetrahydro-1H,5H-benzo[*ij*]puinolizine). The through-bond (TB) energy transfer process in these porphyrin derivatives has been verified by three aspects of characters, i.e. electronic structures, Dexter-type and Förster-type energy transfer. Moreover, the reasons for their high efficiency as red emitting materials have been revealed by the investigations of the ionization potential (IP), electron affinity (EA), reorganization energy (λ), and exciton binding energy (E_b). These structure–property relationships provide a valuable guide for the design and synthesis of highly efficient red light-emitting materials based on porphyrin derivatives.

1. Introduction

During the past decade, the design and synthesis of highly efficient green, blue, and red emitters have become one of the foremost topics in science and industry due to their potential application in large area flat-panel displays. To date, the green and blue emitters have basically met the requirements for the commercial application. Nevertheless, achieving pure red emitter with high quantum efficiency is still a great challenge in the field [1, 2]. Generally, red emitter is achieved by through-space (TS) energy transfer between the doping red dyes [3,4] and the host materials. Unfortunately, the optimum dopant concentration is usually very low [5–7]. And the red organic light-emitting diodes (OLEDs) based on dopant materials are difficult to adapt for mass production process [2,8]. To overcome these problems, a series of porphyrin derivatives bearing fluorene arms were synthesized [9–11] and reported as efficient non-doped red light-emitting materials [10]. The idea in the above works is to bond the porphyrin (acceptor) and fluorene (donor) with conjugated chemical connection, which would lead to through-bond (TB) energy transfer. Normally, the rate of TB energy transfer is hundred times faster than that of TS energy transfer [13,14]. Furthermore, these kinds of structures should also help to form homogeneous amorphous films and prevent the porphyrin rings from aggregating and self-quenching of fluorescence [9]. Consequently, Paul-Roth's group reported that this type of porphyrin derivatives displayed higher fluorescence quantum yield than many other porphyrins [12].

In contrast to the considerable experimental studies, the theoretical investigations on the origin of their high-efficiency are surprisingly limited [15]. In view of this, to establish the structure–property relationships, we provide a detailed theoretical investigations on the ground and

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Table 1
The emission spectra (nm) of donors (C–H, M–H, and Q–H) calculated by TD-B3LYP/6-31G(d) method using Turbomole suite.

Molecules	TD-B3LYP/6-31G(d)	Experiment
C–H	317.2	350[a]
M–H	261.4	
Q–H	311.4	

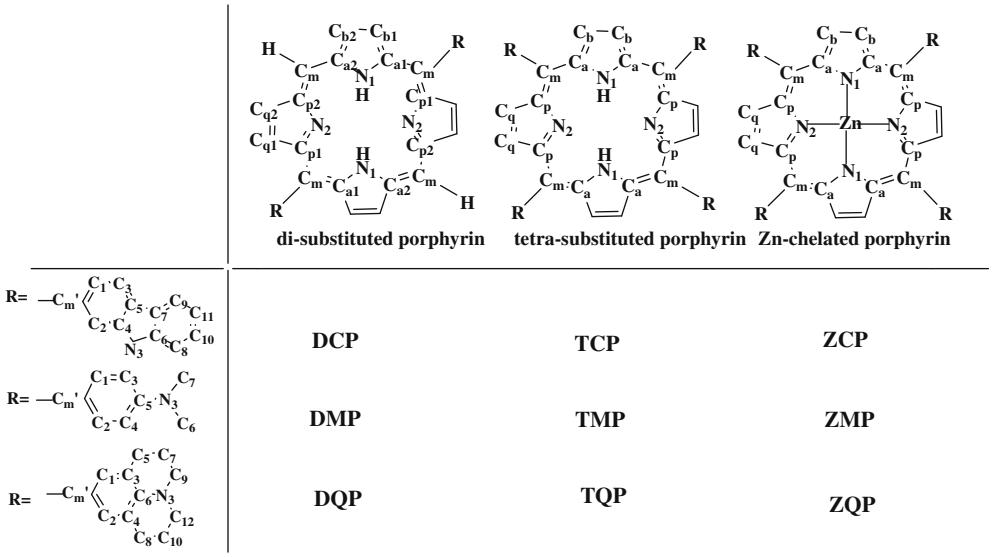
[a] Ref. [19], measured in acetonitrile at 298 K under nitrogen atmosphere.

excited states properties of this type of porphyrin derivatives. The moieties of C (carbazole), M (N,N-dimethyl-phenyl), and Q (2,3,6,7-tetrahydro-1H,5H-pyrido[3,2,1-*ij*]quinoline) are chosen as energy transfer donors because of their wide application in red OLEDs [16,17,1]. Moreover, their emission peaks are in the region of 300–350 nm (predicted by TDDFT/B3LYP/6-31G(d) using Turbomole suite [18] in Table 1), which are similar with the fluorescence spectra of fluorene arms [11]. Accordingly, these moieties are linked to meso-sites of the porphyrin ring, that is, 5,15-di(R)porphyrin, 5,10,15,20-tetra(R)porphyrin, and Zn-5,10,15,20-tetra(R)porphyrin, namely, DCP, TCP, and ZCP (where R = C); DMP, TMP, and ZMP (where R = M); DQP, TQP, and ZQP (where R = Q), as shown in Scheme 1. The main aim of this work is twofold: (1) to testify if these porphyrin derivatives have TB energy transfer features; (2) to reveal the origin of their improved efficiency as red light-emitting materials. In addition, the experimental synthesized compounds such as tetraphenylporphyrin (TPP), 5,15-difluorenylporphyrin (DFP), 5,10,15,20-tetrafluorenylporphyrin (TFP), and Zn-5,10,15,20-tetrafluorenylporphyrin (FPZ) [15] will be used for comparative studies. This work is expected to provide valuable insight into the structure–photophysical property relationship for designing efficient red emitters with TB energy transfer features.

2. Computational methods

Recent studies [20–22] had confirmed that DFT theory can predict relatively accurate electronic structure for porphyrins derivatives. So, the DFT-B3LYP [23–25] level of theory with 6-31G(d) basis set was employed to optimize the ground-state geometries of 5,15-di(R)porphyrin, 5,10,15,20-tetra(R)porphyrin, and Zn-5,10,15,20-tetra(R)porphyrin, where R = carbazole, N,N-dimethyl-phenyl, and 2,3,6,7-tetrahydro-1H,5H-pyrido[3,2,1-*ij*]quinoline, as well as their ions structures. The free based porphyrin (FBP), Zn porphyrin (ZnP), and di-substituted porphyrins (DCP, DMP, and DQP) were optimized with D_{2h}, D_{4h}, and C_i symmetry constraint, respectively. Tetra-substituted porphyrins (TCP, TMP, TQP, and TPP) and Zn-chelated porphyrins (ZCP, ZMP, and ZQP) were restricted with C_{2h} point group constraint. On the basis of these optimized geometries, the ionization potentials (IP), electron affinity (EA), hole extraction potentials (HEP), electron extraction potentials (EEP), and reorganization energy (λ) [26] were calculated by the method as described in Refs. [15,27]. On the basis of the optimized ground-state geometries, the absorption spectra of these compounds were predicted by the TD-DFT//B3LYP/6-31G(d) method. This kind of calculation level had been proven to be reliable for porphyrin derivatives [15,23,24].

In order to facilitate the computation for large molecules, the lowest singlet excited-state (S_1) geometries of studied complexes were optimized by singlet configuration interaction CIS [28] with 3-21G(d) basis sets, which had been proved to be suitable for model the excited states of porphyrin derivatives [29]. Based on our previous report



Scheme 1. The studied porphyrin derivatives: 5,15-di(R)porphyrin, 5,10,15,20-tetra(R)porphyrin, and Zn-5,10,15,20-tetra(R)porphyrin, namely, DCP, TCP, and ZCP (where R = carbazole); DMP, TMP, and ZMP (where R = N,N-dimethyl-phenyl); DQP, TQP, and ZQP (where R = 2,3,6,7-tetrahydro-1H,5H-benzo[*ij*]puinolizine), together with the schematic structures of porphyrins fragment and meso-substitutions.