



# Spectroscopic investigations and theoretical calculations of DABCO induced xanthene bridged self-assembled zinc(II) porphyrin dimer

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**ABSTRACT:** An in-depth study of the electronic structure of a 1,4-diazabicyclo[2.2.2]octane (DABCO) induced molecular self-assembled xanthene-bridged and amide-bonded porphyrin dimer is reported. Density functional theory (DFT) and time-dependent DFT (TD-DFT) calculations are used to identify trends in the optical spectroscopic properties. B3LYP geometry optimization predicts the formation of an almost perfectly eclipsed structure with respect to the two porphyrin rings with the analogous pyrrole nitrogens separated by 7.7–8.1 Å. The observed distinctive derivative-shaped band morphology of the pseudo-Faraday- $A_1$  terms in the MCD spectra has been used to identify the main electronic Q and B-bands and to validate the TD-DFT calculations. The absence of a discernible splitting of the redox steps or a quenching of the fluorescence demonstrates that there is no significant exciton coupling between the two porphyrin rings.

**KEYWORDS:** porphyrin dimer, self-assembly, spectroscopy, TD-DFT calculations.

## INTRODUCTION

In recent years, there has been considerable interest in the synthesis and properties of cofacial porphyrin dimers [1–4], since these compounds provide a possible pathway for mimicking the electron transfer properties of the bacteriochlorophyll dimer in photosystem II, which is often referred as the “special pair” [5]. Self-assembly of Zn(II)-porphyrins is particularly important in this regard, since axial ligation of the metal-center from above and below the porphyrin ring occurs readily in the presence of a nitrogen-containing Lewis base guest molecule such as pyridine, 4,4-bipyridine, piperazine, or 1,4-diazabicyclo[2.2.2]octane (DABCO) [6]. DABCO is more suitable in this

system, since there are stronger host–guest molecule interactions due to the lone pair electrons of the nitrogen atoms. Upon titration with the guest-molecules, the spectroscopic properties of the Zn(II) porphyrin host changes significantly due to the “host–guest” and “host–host” interactions. Generally, Zn(II) porphyrin dimers can be readily formed from porphyrin monomers through inter-molecular coordination upon addition of 0.0–1.0 eq guest molecules [7], or polymerized by the host–guest molecule interaction at higher concentrations [8]. It is noteworthy that porphyrin dimers with differently-sized bridging spacers exhibit significantly different electronic structure [9]. To the best of our knowledge, no in-depth studies have been reported that focus on changes in the electronic structure when Zn(II)porphyrin dimers are linked by flexible non-aromatic-bridging moieties. In this study, an in-depth study of the electronic structure of a 1,4-diazabicyclo[2.2.2]octane (DABCO) induced molecular self-assembled xanthene-bridged and amide-bonded porphyrin dimer will be described.

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