



MCD spectroscopy and TD-DFT calculations of a naphthalene-ring-bridged coplanar binuclear phthalocyanine dimer

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Dedicated to Professor Özer Bekaroğlu on the occasion of his 80th birthday

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ABSTRACT: Magnetic circular dichroism (MCD) spectroscopy and TD-DFT calculations are used to analyze the electronic structure and optical properties of an alkyl-substituted naphthalene-ring-bridged coplanar binuclear phthalocyanine dimer. An analysis of the MCD spectrum of the naphthalene-ring-bridged dimer relative to those of benzene-bridged compounds reported previously, demonstrates that there is a significantly weaker interaction between the two phthalocyanine rings. TD-DFT results obtained using the B3LYP functional with 6–31G basis sets were found to be problematic. Closer agreement with the experimental data is obtained when the CAM-B3LYP functional is used instead. The naphthalene-ring-bridged compound is found to be unsuitable for use as a photosensitizer for the formation of singlet oxygen, because the Φ_T values are negligible.

KEYWORDS: phthalocyanine, MCD spectroscopy, TD-DFT calculations.

INTRODUCTION

In recent years, there has been considerable interest in the synthesis and properties of planar binuclear phthalocyanines due to their potential use in non-linear optical [1] and data storage devices, and as laser dyes [2]. Intense absorption has been reported in the near IR-region for planar binuclear phthalocyanines with a shared benzene ring [3]. There is a 200 nm red shift of the Q band relative to the corresponding phthalocyanine monomer, due to the extension of the π -conjugation system. This makes these compounds

potentially suitable for use as solid and liquid phase color filters as well as IR-region labels. The first attempt to increase the size of the aromatic bridge from benzene to naphthalene was reported by Yang *et al.* [2]. However, the target compound was obtained in only 6% yield and the optical properties in the near IR-region were not reported. In subsequent research, the data obtained were somewhat contradictory [1, 2, 4]. The Moscow group recently reported the synthesis in high yield of peripherally alkyl- and phenyl-substituted coplanar binuclear phthalocyanines sharing a common naphthalene ring [5, 6] and examined their electrochemical, spectroelectrochemical and physicochemical properties [5, 6]. In this paper, magnetic circular dichroism (MCD) spectroscopy and TD-DFT calculations are used to further analyze the electronic

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