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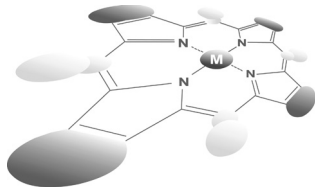

MCD spectroscopy and TD-DFT calculations of magnesium tetra-(15-crown-5-oxanthreno)-phthalocyanine

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Dedicated to Professor Kevin M. Smith on the occasion of his 70th birthday

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ABSTRACT: An analysis of the MCD spectroscopy and TD-DFT calculations of magnesium tetra-(15-crown-5-oxanthreno)-phthalocyanine is reported. This study provides a reassessment of an earlier study on the nature of the bands in UV-visible absorption spectra of magnesium and zinc tetra-(15-crown-5-oxanthreno)-phthalocyanine that was based on an analysis of TD-DFT calculations for a series of model complexes with the B3LYP functional. A detailed analysis of MCD spectral data and TD-DFT calculations with the CAM-B3LYP functional for the complete Mg(II) complex provides an additional insight into the optical properties and electronic structures of tetra-(15-crown-5-oxanthreno)-phthalocyanines. Thus, the bands in the Q-band region are reassigned as being due exclusively to the Q transition of Gouterman's 4-orbital model, since intense pseudo-A_1 terms are observed in the MCD spectrum in a spectral region that had previously been assigned as charge transfer bands.

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

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INTRODUCTION

Safonova *et al.* recently reported the synthesis and properties of novel radially-symmetric fused-ring expanded magnesium and zinc phthalocyanine (MgPc and ZnPc) analogues with four peripheral electron-rich 15-crown-5-oxanthrene moieties (Fig. 1) [1]. The goal of the study was to prepare Pc analogs with electron-donating tetra-oxy-benzene units that lie coplanar with the Pc core, leading to an expansion of the π-system. The peripheral crown ether moieties were shown to enable reversible switching between aggregated and disaggregated forms, due to the alkali metal coordination properties [2], in a manner that could facilitate the development of organic field effect transistors [3]. A series of charge transfer bands were predicted to lie slightly to red of the phthalocyanine Q-band on the basis of TD-DFT calculations with the B3LYP functional for a series of model complexes [1]. The use of the B3LYP functional in TD-DFT calculations has previously been shown to be problematic, since transitions with significant charge transfer character tend to be underestimated [4]. In this study, a detailed analysis of the theoretical calculations and magnetic circular dichroism (MCD) spectroscopy of magnesium tetra-(15-crown-5-oxanthreno)-phthalocyanine (**1**) is reported, and its optical properties are reassessed on this basis.

EXPERIMENTAL

The magnesium tetra-(15-crown-5-oxanthreno)-phthalocyanine (**1**) was obtained according to the previously

◊ SPP full member in good standing

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