



Facile synthesis, spectroscopic and electrochemical properties, and theoretical calculations of porphyrin dimers with a bridging amide-bonded xanthene moiety

Xu Liang^{a,b}, Li Xu^a, Minzhi Li^a, John Mack^{*c}, Justin Stone^c, Tebello Nyokong^c,
Yu Jiang^a, Nagao Kobayashi^{*b} and Weihua Zhu^{*a}

^aSchool of Chemistry and Chemical Engineering, Jiangsu University, Zhenjiang 212013, P. R. China

^bDepartment of Chemistry, Graduate School of Science, Tohoku University, Sendai 980-8578, Japan

^cDepartment of Chemistry, Rhodes University, Grahamstown 6140, South Africa

Received 22 December 2014

Accepted 13 February 2015

ABSTRACT: A free base porphyrin dimer bridged by a flexible amide-bonded xanthene moiety and its binuclear zinc(II) complex were synthesized and characterized. Structural characterization by MS and ¹H NMR spectroscopy confirmed the bridged porphyrin dimer structure. The properties of the dimers were characterized by IR, UV-visible absorption, fluorescence and magnetic circular dichroism (MCD) spectroscopy, and electrochemistry studies. Theoretical calculations were carried out to analyze the electronic structures of porphyrin dimers with a bridging amide-bonded xanthene moiety.

KEYWORDS: xanthene, porphyrin dimers, spectroscopy, TD-DFT calculations, electrochemistry.

INTRODUCTION

Porphyrin oligomers with macrocyclic rings that are covalently linked in a cofacial configuration have received considerable attention in recent years due to their unique electronic structures and novel optical properties [1]. Several types of conjugated porphyrin oligomers have been reported such as, doubly- or triply-fused co-planar porphyrins [2], alkyne-bridged porphyrin strands [3], and π -phenylene-bridged twisted/planar porphyrin dimers [4]. Interest of porphyrin dimers with linking moieties, especially those that adopt a face-to-face manner has been increasing in recent years. Porphyrin dimers with face-to-face conformations exhibit an increased ability to bind two metal ions in a suitable geometry, opening up the possibility of mimicking the activity of heme and nonheme iron and copper-binding bioproteins such as oxidase, oxygenase, and oxygen transport proteins, which have binuclear active sites [5]. Xanthenes, have found widespread use as

synthetic dyes in a wide range of applications, and their spectroscopic properties have been extensively studied [6]. Xanthene moieties have usually been introduced to porphyrin arrays through direct C–C bonds at the *meso*-positions and the electronic structures, and optical and magnetic properties of these compounds have been studied in depth [7]. In contrast, porphyrin xanthenes with flexible bridges such as alkyl chains and amines have received considerably less attention [8], and their spectroscopic properties and electrochemical properties have not been reported. Given the progress that has been made in xanthene-bridged cofacial porphyrin dimers, the goal of this study was to synthesize new compounds with flexible amide bridging units and to investigate their spectroscopic and electrochemical properties to develop an in-depth understanding of their electronic structures.

EXPERIMENTAL

Chemicals

Spectral grade *o*-dichlorobenzene for electrochemical measurements was purchased from the

[†]SPP full member in good standing

*Correspondence to: Weihua Zhu, email: sayman@ujs.edu.cn, tel/fax: +86 511-8879-1928; John Mack, email: j.mack@ru.ac.za, fax: +27 46-622-5109; Nagao Kobayashi, email: nagaok@m.tohoku.ac.jp, fax: +81 22-795-7719.