

## Full Length Article

## Investigation of self-aggregation properties of amino functionalized zinc chlorins

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## ABSTRACT

Zinc chlorin derivatives consisting of primary, secondary and tertiary amine unit were prepared and their aggregation properties have been studied both in solution and in solid state in order to investigate the influence of the amine moiety on the formation of self-assembled nanostructures. The supramolecular organization ability of these derivatives have been investigated on the solid substrate, namely, highly oriented pyrolytic graphite (HOPG) by using AFM (atomic force microscopy) and STM (scanning tunneling microscopy) spectroscopy. The supramolecular organization of zinc chlorin derivatives in solution has been further supported by UV–vis spectroscopy. Zinc chlorins bearing primary, secondary amine exhibit well-ordered *J*-type aggregation in solution and well-defined self-organization on HOPG. On the other hand, the self-organization of tertiary amine substituted zinc chlorin both in solution and in solid state was less pronounced.

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## 1. Introduction

Research based on the preparation of self-assembled nanostructures has gained considerable attention due to its utility in wide variety of photonic applications. The natural photosynthetic system which based on highly organized supramolecular assemblies is the most successful process for the conversion and storage of solar energy [1–3]. The use of supramolecular interaction for the construction of self-organizing system present fundamental scientific importance in terms of mimics the analogous natural system [4–6]. Supramolecular nanostructures have been constructed through non-covalent interactions such as hydrogen bond,  $\pi$ – $\pi$  and van der Waals interactions [7]. Within them, metal-directed self-assembly has become an important tool to prepare large and elaborate complex ensembles from structurally simpler components [8]. Among the tetrapyrrolic macrocycles employed for the preparation of self-assembled nano-structures metallochlorin hold a privileged position due to excellent light harvesting ability resulted from non-covalent supramolecular interactions [9,10].

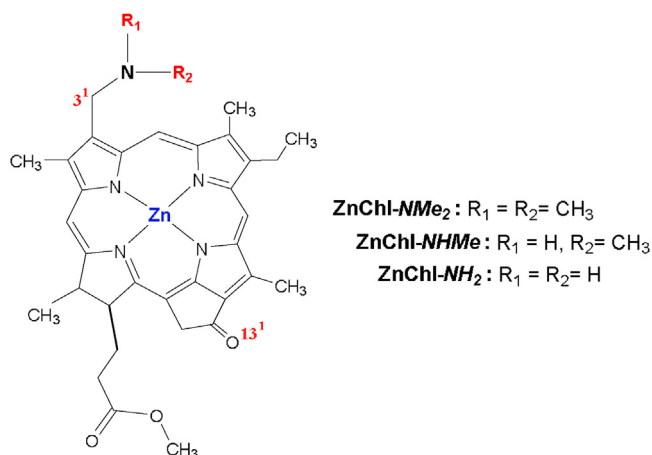
Up to date, a large variety of supramolecular systems based on metallo chlorin have been described and their photophysical properties studied both in solution and in solid state with the

aim of integrating these systems in a variety of electronic applications [11–14]. For example, our group reported that a novel bio-mimetic supramolecular nanostructured light harvesting system using synthetically modified zinc chlorin units self-assembled inside a solid-state Anodic Aluminum Oxide (AAO) nano-template have been prepared which bear great potential for efficient light harvesting modules in many photonic applications like photovoltaic, photocatalytic devices [15]. The self-organization features of the synthetic bacteriochlorophyll (BChl) derivatives are strongly affected by the chemical structure [11–14]. Bacteriochlorophylls generally exhibit well-ordered *J*-type aggregation are characterized by a remarkable bathochromic shift of the absorption which is mainly the result of metal-ligand interaction between the central metal ion and the functional groups, hydrogen bonding metal-ligand interaction and  $\pi$ – $\pi$  interaction between chlorin  $\pi$  systems. In particular, *J*-type aggregation formation of BChls-c, d and e bearing peripheral 3<sup>1</sup>-OH and 13-C=O substituents and central magnesium atom, results from hydrogen bonding between OH and C=O units and coordination bonding between Mg and 3<sup>1</sup>-OH [16].

To date the self-aggregation of the synthetic zinc and magnesium bacteriochlorophyll has been extensively studied by several groups and especially by Würthner and Tamiaki groups [10,11]. In most of the cases, the formation of rod-shaped aggregates of bacteriochlorophyll (metallochlorin) as a result of metal-ligand interaction between hydroxy group of chlorophyll and central metal atom have been observed, thus paving the way for the utilization of these materials for light harvesting systems [16–18]. Not only the hydroxy groups at the 3<sup>1</sup>-position but also the –NH2

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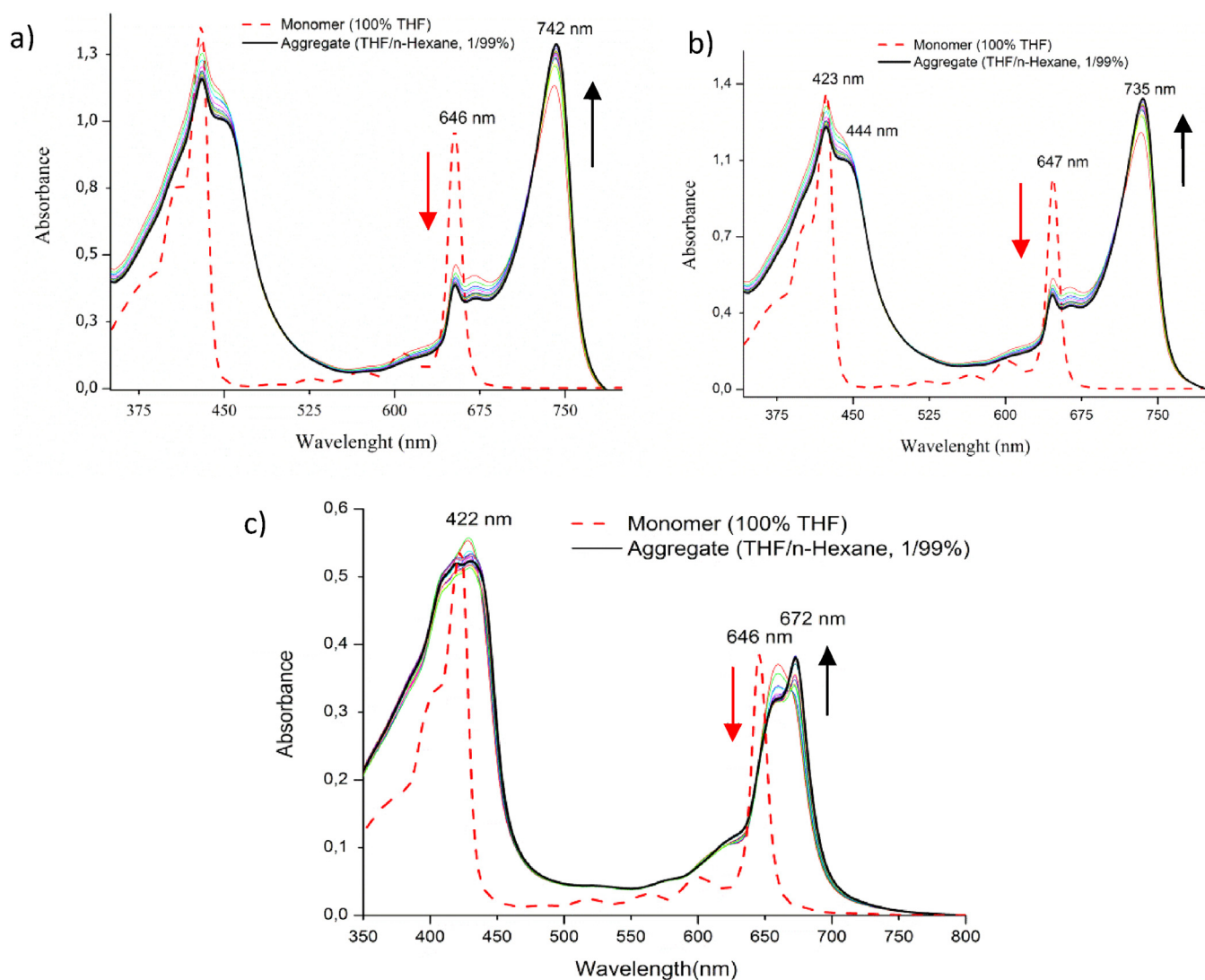
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**Fig. 1.** Molecular structures of synthetically modified zinc aminochlorin derivatives of Chl *a*.

groups provide the desired supramolecular arrangement of zinc chlorin derivatives by means of *J*-type self-aggregation. Recently, some zinc chlorophyll derivatives bearing an amino group in the 3<sup>1</sup>-substituent have been prepared and their self-aggregation properties examined [19,20]. For example, Watanabe et al. have reported the self-aggregates of zinc chlorophyll derivatives bearing either a substituted or unsubstituted dimethyl aminomethyl group at the C3 position. Self aggregation studies show that zinc chlorophyll having a tertiary amino group exhibit *J*-type aggregation owing to interaction between central Zn–N atom of the dimethylamino group. On the other hand, the other derivatives consisting of the bulky 3-ethylmethylamino/diamino groups could not form remarkable supramolecular arrangement due to the fact that more than one carbon atoms around the nitrogen atom increases the steric hindrance, which reduces the intermolecular Zn–N interaction [21].

By virtue of these results, we investigated the self-organization of amine-functionalized zinc chlorins (see Fig. 1) with the aim of building stable sophisticated nanostructure systems. The supramolecular organization ability of zinc aminochlorins aggregates have been investigated on a variety of solid substrates



**Fig. 2.** UV/Vis Absorption spectra of ZnChl-NH<sub>2</sub> (a), ZnChl-NHMe (b) and ZnChl-NMe<sub>2</sub> (c) in THF (red dashed line) and various spectra of the mixture of THF/*n*-hexane (1:99%) (solid lines) were taken at 5 min interval up to one hour after injecting the above solution in *n*-hexane at 293 K (30  $\mu$ L of  $1.3 \times 10^{-5}$  mol L<sup>-1</sup> THF solution of ZnChl-NH<sub>2</sub>, ZnChl-NHMe and ZnChl-NH<sub>2</sub> injected into 3 mL of *n*-hexane). The cuvette was not removed from the spectrophotometer throughout the measurements. The arrows indicate the changes upon various time intervals. The red arrows represented decreasing of the monomer bands and the black arrows increasing of the aggregates bands upon increasing time (~1 h). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

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