



# Synthesis and aggregation behavior of zinc phthalocyanines substituted with bulky naphthoxy and phenylazonaphthoxy groups: An experimental and theoretical study



İbrahim Özçeşmeci<sup>a,\*</sup>, Adem Tekin<sup>b,\*</sup>, Ahmet Gül<sup>a</sup>

<sup>a</sup> Department of Chemistry, Istanbul Technical University, 34469 Maslak, Istanbul, Turkey

<sup>b</sup> Informatics Institute, Istanbul Technical University, 34469 Maslak, Istanbul, Turkey

## ARTICLE INFO

### Article history:

Received 19 December 2013

Accepted 6 January 2014

Available online 1 February 2014

### Keywords:

Phthalocyanine

Azobenzene

β-Naphthol

Red shifts

Aggregation

Density functional theory

## ABSTRACT

Zinc (II) phthalocyanines, bearing peripherally β-naphthol and (1-[(Z or E)-phenylazo]-2-naphthyl)oxy) have been synthesized and characterized. Aggregation properties of these compounds were investigated in different concentration ranges. The molecular orbital properties and ultraviolet–visible spectra of these phthalocyanines were studied using density functional and time-dependent density functional theories. The computed electronic spectra are in good agreement with the experimental data. Moreover, dimerization of these phthalocyanine complexes in solvent (tetrahydrofuran) medium was investigated by counterpoise corrected interaction energy calculations employing dispersion corrected Becke's 1997 hybrid functional with valence triple-zeta basis set. These calculations revealed that aggregation in these complexes are prevented due to the strong solvent–phthalocyanine interactions and this finding was supported by our experiments.

© 2014 Elsevier B.V. All rights reserved.

## 1. Introduction

Phthalocyanines (Pcs) are 18  $\pi$ -electron conjugated macrocyclic systems which attract great interest due to their diverse applications in medicinal and materials chemistry [1]. A number of modifications can be made in the macrocycle either by the introduction of different central ions or by the substitution of functional groups at the peripheral sites of the ring [2]. The addition of substituents to the peripheral ( $\beta$ ) positions of the Pc ring is expected to give an enhanced solubility in numerous organic solvents [3,4] and affects the electronic spectrum depending on their properties. In addition, solvents may also lead to changes in photochemical and photophysical behavior of Pcs [5].

Recently, phthalocyanine complexes have found potential as photosensitisers in photodynamic therapy (PDT) due to the presence of a since diamagnetic central metals, such as Zn or Mg which enhances the phototoxicity of phthalocyanines [6,7]. Zinc phthalocyanine complexes have attracted much interest because of their appreciably high triplet state quantum yields and long triplet lifetimes [8,9].

Azo compounds, which are aromatic compounds with one or more  $-N=N-$  groups, constitute the largest class of synthetic dyes [10] used in commercial applications. These compounds belong to one of the most intensively studied groups for non-linear optics (NLO) [11], optical information storage [12], and optical switching [13]. Moreover, they find increasing accessibility in photoresponsive biomaterials [14] and supramolecular systems [15]. Although many kinds of azo dyes have been synthesized, phthalocyanines containing azo groups are relatively rare [16]. They combine their optical and electronic properties with good chemical stability and solution processability [17], which makes them interesting for applications.

In this work, we have synthesized the peripherally tetra- $\beta$ -naphthol and tetra-naphthyl-azobenzene substituted zinc (II) phthalocyanine compounds. We explored the effects of substituents on the spectroscopic and aggregation properties of zinc (II) phthalocyanine derivatives in tetrahydrofuran (THF) in different concentration ranges. Furthermore, we performed density functional theory (DFT) and time-dependent density functional theory (TDDFT) calculations to obtain the electronic absorption spectrum and the molecular orbital properties of the experimentally considered phthalocyanines. In addition, counterpoise (CP) corrected interaction energy computations were carried out to investigate the aggregation behavior of these complexes. Since  $\pi$ - $\pi$  interaction is one of the dominant forces stabilizing the phthalocyanine dimer, the effect of dispersion to the optimized geometry and the interaction energy was also discussed.

\* Corresponding authors. Tel.: +90 212 285 69 52/212 285 73 08.

E-mail addresses: [ozcesmecii@itu.edu.tr](mailto:ozcesmecii@itu.edu.tr), [ozcesmeci@hotmail.com](mailto:ozcesmeci@hotmail.com) (İ. Özçeşmeci), [adem.tekin@be.itu.edu.tr](mailto:adem.tekin@be.itu.edu.tr) (A. Tekin).

## 2. Experimental and computational details

### 2.1. Equipment and materials

IR spectra were recorded on a Perkin-Elmer Spectrum One FT-IR spectrometer, electronic spectra on a Scinco Neosys-2000 double-beam ultraviolet–visible (UV–vis) spectrophotometer using 1 cm path length cuvettes at room temperature. Elemental analyses were performed by the Instrumental Analysis Laboratory of the TUBITAK Marmara Research Center.  $^1\text{H}$  NMR spectra were recorded on a Bruker 250 MHz spectrometer using TMS as internal reference. Mass spectra were performed on Ultima Fourier Transform and Varian 711 mass spectrometer. All solvents were dried and purified according to the procedure described in Ref. [18]. The homogeneity of the products was tested in each step by TLC ( $\text{SiO}_2$ ). 4-Nitrophthalonitrile **1** was synthesized following the reported route [19]. 4-(2-Naphthol)phthalonitrile **4** [20] Tetrakis(2-naphthoxy)phthalocyaninatozinc (II) **6** was prepared according to the reported procedure [21].

### 2.2. Preparation of 4-({1-[(Z or E)-phenylazo]-2-naphthyl}oxy)phthalonitrile (**5**)

4-Nitrophthalonitrile (**1**) (0.310 g, 1.25 mmol) was dissolved in dry DMF under  $\text{N}_2$  atmosphere, and 1-[(Z or E)-phenylazo]-2-naphthol (**1**) (0.216 g, 1.25 mmol) was added at room temperature. After stirring for 15 min, anhydrous  $\text{K}_2\text{CO}_3$  (0.345 g, 2.5 mmol) was added portion-wise during 2 h with efficient stirring. The reaction mixture was stirred for 7 days. Then the mixture was poured into an ice-water. The resulting dark red solid was collected by filtration and washed with water until the washings were neutral. Then it was dried in vacuo at  $100^\circ\text{C}$ , and crystallized from ethanol to produce the red, crystalline powder. The yield was 197 mg (42.01%). M.p.  $200^\circ\text{C}$ . Anal. calc. for  $\text{C}_{24}\text{H}_{14}\text{N}_4\text{O}$ : C, 76.99; H, 3.77; N, 14.96. Found: C, 76.89; H, 3.64; N, 14.75%; IR ( $\text{cm}^{-1}$ ): 3103–3075–3040 (Ar–H), 2232 ( $\text{C}\equiv\text{N}$ ), 1587–1568 (Ar  $\text{C}=\text{C}$ ), 1483, 1248 (Ar–O–Ar), 850, 756;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ - $d_6$ ),  $\delta$ : 8.51 (d, 1H, Ar–H), 8.01–7.94 (m, 6H, Ar–H), 7.69–7.61 (m, 2H, Ar–H), 7.50–7.47 (m, 3H, Ar–H), 7.31–7.08 (m, 2H, Ar–H); MS:  $m/z$  375.20 [ $\text{M}+1$ ] $^+$ , 376.20 [ $\text{M}+2$ ] $^+$ .

### 2.3. Preparation of tetrakis({1-[(Z or E)-phenylazo]-2-naphthyl}oxy)phthalocyaninato-zinc (II) (**7**)

A mixture of 0.25 mmol (0.0936 g) of compound **5** and 0.0625 mmol (0.008 g) of anhydrous  $\text{Zn}(\text{OAc})_2$  in 2 ml of N,N-(dimethyl amino)ethanol was fused in a glass tube. The mixture was heated and stirred at  $145^\circ\text{C}$  for 24 h under  $\text{N}_2$ . The resulting green suspension was cooled to ambient temperature and the crude product was precipitated by addition of ethanol–water mixture. It was filtered off. The residue was dissolved in THF and was precipitated first with hexane then diethyl ether and then dried in vacuo. Purification of the product was accomplished by column chromatography on silica gel first with THF/hexane (3:2) and then acetone/hexane (2:1) as eluent. Yield was 30 mg (30.73%). M.p.  $>200^\circ\text{C}$ . Anal. calc. for  $\text{C}_{96}\text{H}_{56}\text{N}_{16}\text{O}_4\text{Zn}$ : C, 73.77; H, 3.61; N, 14.34. Found: C, 73.85; H, 3.77; N, 14.15; IR ( $\text{cm}^{-1}$ ): 3098 (Ar–H), 1600–1585–1564 (Ar  $\text{C}=\text{C}$ ), 1481, 1248 (Ar–O–Ar), 826, 759;  $^1\text{H}$  NMR ( $\text{DMSO}-d_6$ ),  $\delta$ : 9.24 (m, 28H, Ar–H), 7.95 (m, 20H, Ar–H), 7.55 (m, 4H, Ar–H), 7.31 (m, 2H, Ar–H), 7.18 (m, 2H, Ar–H); MS:  $m/z$  1563.5 [ $\text{M}+1$ ] $^+$ .

### 2.4. Computational setup

All geometry optimizations have been performed using TURBOMOLE V6.1 [22] quantum chemistry package utilizing Perdew, Burke and Ernzerhof (PBE) [23] and B97-D DFT functionals with

valence triple-zeta basis set (TZVP). Since the dimer configurations contain many atoms, for all geometry optimizations the resolution of identity (RI) [24] approximation was switched on and all atomic positions were relaxed. Interaction energy computations were performed at B97-D level (and in some cases at B3LYP-D, PBE-D, TPSS-D and TPSS) using TZVP and in some cases TZVPP basis sets. Due to the complexity of the dimers, it is not feasible to compute binding energies using high accurate methods such as second-order Møller–Plesset (MP2), spin-component scaled MP2 (SCS-MP2) and B2PLYP-D (even if it is a DFT functional, it requires MP2 calculations). Very recently, it has been shown that [25] interaction energies obtained from B97-D level are in a good agreement with MP2, SCS-MP2 and B2PLYP-D. Based on this fact, only B97-D was employed for the calculation of the interaction energies.

In our calculations, interaction energies were corrected against to the basis set superposition error (BSSE) using the counterpoise (CP) method [26]. The negative binding energies were obtained using the following formula:

$$E_{\text{int}} = E_{\text{dimer}} - (E_{\text{monomer A}} + E_{\text{monomer B}})$$

where  $E_{\text{int}}$  is the interaction energy,  $E_{\text{dimer}}$ ,  $E_{\text{monomer A}}$  and  $E_{\text{monomer B}}$  are the total energies of dimer, monomer A and monomer B, respectively. Since experiments were carried out in the existence of THF, geometry optimization of dimers were also performed by the implicit inclusion of THF (the dielectric constant  $\epsilon$  was set to 7.426) using the COSMO module of TURBOMOLE. Default parameters (solvent radius and optimized atomic radii) of COSMO were used for the cavity construction of each atom. In addition, explicit THF molecules were also considered for dimers of **6**. TDDFT was employed for the calculation of excitation energies and the simulation of UV–vis electronic spectra of both monomers and dimers of **6** and **7** using the relaxed structures at PBE/TZVP.

## 3. Results and discussion

### 3.1. Synthesis

The first step in the synthetic procedure was to obtain 4-(2-naphthol)phthalonitrile **4** and 4-({1-[(Z or E)-phenylazo]-2-naphthyl}oxy)phthalonitrile **5**. They were prepared from 4-nitrophthalonitrile **1** and 2-naphthol **2** in DMSO for 4-(2-naphthol)phthalonitrile **4** [20] and 4-[(Z or E)-phenylazo]-1-naphthol **3** in DMF for 4-({1-[(Z or E)-phenylazo]-2-naphthyl}oxy)phthalonitrile **5**;  $\text{K}_2\text{CO}_3$  was used as the base for these nucleophilic aromatic displacement (Scheme 1) [27,28]. Conversion of **4** and **5** into the corresponding zinc (II) phthalocyanines **6** and **7** was accomplished in high-boiling solvents (N,N-(dimethylamino)ethanol) in the presence of metal salts ( $\text{Zn}(\text{OAc})_2$ ). All of these new compounds were characterized by elemental analysis, IR, UV–vis, Mass and NMR spectroscopy techniques.

The spectroscopic data of the new compounds were in accordance with the structures. FT-IR spectra were recorded on crude participated for phthalonitrile derivatives **4–5** and phthalocyanine derivatives **6–7**. IR spectrum of **4** and **5** have characteristic vibrations corresponding to the ether groups (C–O–C) at  $1246\text{--}1248\text{ cm}^{-1}$ , aromatic C–H stretching at  $3080\text{ cm}^{-1}$  for **4**,  $3103\text{--}3075\text{--}3040\text{ cm}^{-1}$  for **5**, aromatic  $\text{C}=\text{C}$  stretching at  $1570\text{ cm}^{-1}$  for **4** and  $1587\text{--}1568\text{ cm}^{-1}$  for **5**. Expected characteristic chemical shifts were obtained from the NMR investigation of the compounds **4** and **5**. In the  $^1\text{H}$  NMR analysis of all phthalonitrile compounds **4** and **5** in deuterated chloroform, the aromatic protons appear as multiple at 7.17 and 7.97 ppm for **4** and as doublet at 8.51 ppm and, multiple at 8.01–7.94, 7.69–7.61, 7.50–7.47, 7.31–7.08 ppm for **5**. In the mass spectra of these

Download English Version:

<https://daneshyari.com/en/article/1441045>

Download Persian Version:

<https://daneshyari.com/article/1441045>

[Daneshyari.com](https://daneshyari.com)