



Photophysical, photochemical and aggregation behavior of novel peripherally tetra-substituted phthalocyanine derivatives

Ece Tuğba Saka^a, Cem Göl^b, Mahmut Durmuş^b, Halit Kantekin^{a,*}, Zekeriya Bıyıklıoğlu^a

^a Department of Chemistry, Faculty of Sciences, Karadeniz Technical University, 61080 Trabzon, Turkey

^b Gebze Institute of Technology, Department of Chemistry, PO Box 141, Gebze 41400, Kocaeli, Turkey

ARTICLE INFO

Article history:

Received 27 February 2012

Received in revised form 26 April 2012

Accepted 23 May 2012

Available online 1 June 2012

Keywords:

Phthalocyanine

Zinc

J-aggregation

Photophysical

Photochemical

Singlet oxygen

ABSTRACT

In this study, the novel metal-free (**4**) and zinc (II) (**5**) phthalocyanine compounds substituted with four 1-(2-oxyethyl)-4-piperidone ethylene ketal functional groups at peripheral positions have been prepared. These new phthalocyanine compounds have been characterized by IR, ¹H NMR, ¹³C NMR spectroscopy, MS spectral data and elemental analysis. The synthesized phthalocyanine compounds exhibited excellent solubility in common organic solvents and the zinc (II) phthalocyanine complex (**5**) showed J-type aggregation in chloroform. The photophysical and photochemical properties of metal-free (**4**) and zinc (II) (**5**) phthalocyanine complexes were also investigated in DMSO. The investigation of the photophysical and photochemical properties of photosensitizers is very useful for photodynamic therapy (PDT) applications.

© 2012 Elsevier B.V. All rights reserved.

1. Introduction

Metallophthalocyanine (MPC) complexes are being extensively researched because of their diverse applications. These include their uses in electronic devices, non-linear optics, electrochromic devices, Langmuir–Blodgett films, as gas sensors and photosensitizers in photodynamic therapy (PDT) of cancer [1,2]. The exceptional chemical and physical properties of phthalocyanines can be because of various substituents on the phthalocyanine framework. Over 70 elements can be included into the phthalocyanine core and its chemical versatility allows the introduction of many different substituents at peripheral positions [3,4].

Metallophthalocyanines are known to have low solubility in most organic solvents. The solubility of these compounds can be improved via substitution of different groups on the phthalocyanine skeleton. It has been documented that tetra-substituted phthalocyanines are more soluble than their octa-substituted counterparts due to formation of constitutional isomers and their high dipole moments [5,6].

Aggregation of the phthalocyanine compounds is an important phenomenon. The substituted metallophthalocyanines could be form two types of aggregations which affect on electronic and optical properties, namely face-to-face H-aggregation and

side-to-side J-aggregation [1,2]. Typically, phthalocyanine aggregation results in a decrease in intensity of the Q band corresponding to the monomeric species, meanwhile a new, broader and blue-shifted band is seen to increase in intensity. This shift to lower wavelengths indicates to H-type aggregation among the phthalocyanine molecules. Rare cases red-shifted bands have been observed corresponding to J-type aggregation of the phthalocyanine molecules. Generally, J-aggregates of Pc occurred by utilizing the coordination of the side substituent from one Pc molecule to the central metal ion in a neighbor [7–11]. The substituted zinc Pcs in non-coordinated organic solvents, e.g. chloroform and dichloromethane exhibit J-aggregation [12,13]. The addition of coordinating solvents such as methanol or ethanol caused dissociation of the dimers, which implies that the absence of coordinating solvents is essential for J-aggregation of Pc [14]. UV–vis and MALDI–TOF–MS spectra could be used for determination presence of J-aggregation for Pc compounds [15].

Furthermore, owing to their extensively planar aromatic π system, phthalocyanines exhibit a high aggregation tendency which leads to insolubility in the case of unsubstituted parent derivatives or hinders purification and characterization of compounds in many respects together with a lower efficiency in their use in PDT [16,17]. PDT is a binary therapy that involves the combination of visible light and a photosensitizer [18]. Diamagnetic ions such as Zn²⁺, Al³⁺, Ga³⁺ and Ti⁴⁺ give phthalocyanine complexes comprising both high triplet yields and long triplet lifetimes which are suitable for photodynamic therapy (PDT) applications [19]. Due to the intense absorption in the visible region, high efficiency to generate

* Corresponding author at: Department of Chemistry, Karadeniz Technical University, 61080 Trabzon, Turkey. Tel.: +90 462 3772599; fax: +90 462 3253196.

E-mail address: halit@ktu.edu.tr (H. Kantekin).

reactive oxygen species (such as singlet oxygen), and low dark toxicity, phthalocyanines have been used in this avenue for the treatment of various cancers and photoinactivation of viruses [18,20].

Our previous studies have already reported synthesis, photophysical and photochemical properties of various substituted phthalocyanines [21–25]. These phthalocyanine complexes show interesting photophysical and photochemical properties especially high singlet oxygen quantum yields which are very important for PDT of cancer. In this work, we have been synthesized new metal-free (**4**) and zinc (**5**) phthalocyanines substituted with four 1-(2-oxyethyl)-4-piperidone ethylene ketal groups as potential PDT agents. Aggregation behavior, photophysical (fluorescence lifetime and quantum yields) and photochemical (singlet oxygen and photodegradation quantum yields) properties were investigated. This work has also been reported the effects of the substituents and the nature of the metal on the photophysical and photochemical parameters of 1-(2-oxyethyl)-4-piperidone ethylene ketal substituted phthalocyanine derivatives in DMSO. This work also explores the effects of substituents and nature of the central metal ions on the fluorescence properties of the phthalocyanines and on the quenching of the phthalocyanines by 1,4-benzoquinone (BQ) using the Stern–Volmer relationship.

2. Experimental

2.1. Materials

All phthalocyanine reactions were carried out under nitrogen atmosphere using standard Schlenk techniques. 1,3-Diphenylisobenzofuran (DPBF) and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) were purchased from Fluka. All solvents were dried and purified as described by reported procedure [26]. 1-(2-Hydroxyethyl)4-piperidone ethylene ketal (**1**) [27], 4-nitrophthalonitrile (**2**) [28] were prepared according to the literature procedure.

2.2. Equipment

FT-IR spectra were obtained on a Perkin Elmer 1600 FTIR spectrophotometer with the samples prepared as KBr pellets. NMR spectra were recorded on a Varian Mercury 200 MHz spectrometer in CDCl₃, and chemical shifts were reported (δ) relative to TMS as an internal standard. Mass spectra were recorded on a Micromass Quatro LC/ULTIMA LC-MS/MS spectrometer. The elemental analyses were performed on a Costech ECS 4010 instrument. The formation of J-aggregation for zinc (II) Pc complex (**5**) was determined by positive ion and linear mode MALDI-MS in dihydroxybenzoic acid as MALDI matrix using nitrogen laser accumulating 50 laser shots using Bruker Microflex LT MALDI-TOF mass spectrometer. Melting points were measured on an electrothermal apparatus. Domestic microwave oven was used synthesis of zinc (II) Pc complex (**5**). Absorption spectra in the UV–vis region were recorded with a Shimadzu 2001 UV spectrophotometer. Fluorescence excitation and emission spectra were recorded on a Varian Eclipse spectrofluorometer using 1 cm pathlength cuvettes at room temperature. Photo-irradiations were done using a General Electric quartz line lamp (300 W). A 600 nm glass cut off filter (Schott) and a water filter were used to filter off ultraviolet and infrared radiations, respectively. An interference filter (Intor, 670 nm with a band width of 40 nm) was additionally placed in the light path before the sample. Light intensities were measured with a POWER MAX5100 (Molelectron detector incorporated) power meter.

2.3. Photophysical parameters

2.3.1. Fluorescence quantum yields and lifetimes

Fluorescence quantum yields (Φ_F) were determined in DMSO by the comparative method using equation 1 [29,30].

$$\Phi_F = \Phi_F(\text{Std}) \frac{F \cdot A_{\text{Std}} \cdot n^2}{F_{\text{Std}} \cdot A \cdot n_{\text{Std}}^2}, \quad (1)$$

where F and F_{Std} are the areas under the fluorescence emission curves of the samples (**4** and **5**) and the standard, respectively. A and A_{Std} are the respective absorbances of the samples and standard at the excitation wavelengths, respectively. n^2 and n_{Std}^2 are the refractive indices of solvents used for the sample and standard, respectively. Unsubstituted ZnPc (in DMSO) ($\Phi_F = 0.20$) [31] was employed as the standard. The absorbance of the solutions at the excitation wavelength ranged between 0.04 and 0.05.

Natural radiative life times (τ_0) were determined using PhotochemCAD program [32] which uses the Strickler–Berg equation. The fluorescence lifetimes (τ_F) were evaluated using Eq. (2).

$$\Phi_F = \frac{\tau_F}{\tau_0}. \quad (2)$$

2.4. Photochemical parameters

2.4.1. Singlet oxygen quantum yields

Singlet oxygen quantum yield (Φ_Δ) determinations were carried out using the experimental set-up described in the literature [33–35]. Typically, a 3 ml portion of the respective unsubstituted, metal-free Pc (**4**) and zinc Pc complex (**5**) solutions ($C = 1 \times 10^{-5}$ M) containing the singlet oxygen quencher was irradiated in the Q band region with the photo-irradiation set-up described in references [33–35]. Singlet oxygen quantum yields (Φ_Δ) were determined in DMSO using the relative method with unsubstituted ZnPc as reference. DPBF was used as chemical quencher for singlet oxygen in DMSO. Eq. (3) was employed for the calculations:

$$\Phi_\Delta = \Phi_\Delta^{\text{Std}} \frac{R \cdot I_{\text{abs}}^{\text{Std}}}{R^{\text{Std}} \cdot I_{\text{abs}}}, \quad (3)$$

where Φ_Δ^{Std} is the singlet oxygen quantum yield for the standard unsubstituted ZnPc ($\Phi_\Delta^{\text{Std}} = 0.67$ in DMSO)[36]. R and R^{Std} are the DPBF photobleaching rates in the presence of the samples (**4** and **5**) and standard, respectively. I_{abs} and $I_{\text{abs}}^{\text{Std}}$ are the rates of light absorption by the samples (**4** and **5**) and standard, respectively. To avoid chain reactions induced by DPBF in the presence of singlet oxygen, the concentration of quenchers (DPBF) was lowered to $\sim 3 \times 10^{-5}$ mol dm⁻³ [37]. Solutions of sensitizer ($C = 1 \times 10^{-5}$ M) containing DPBF were prepared in the dark and irradiated in the Q band region using the photoirradiation setup. DPBF degradation at 417 nm was monitored. The light intensity 7.3×10^{15} photons s⁻¹ cm⁻² was used for Φ_Δ determinations.

2.4.2. Photodegradation quantum yields

Photodegradation quantum yield (Φ_d) determinations were carried out using the experimental set-up described in the literature [33–35]. Photodegradation quantum yields were determined using Eq. (4),

$$\Phi_d = \frac{(C_0 - C_t) \cdot V \cdot N_A}{I_{\text{abs}} \cdot S \cdot t}, \quad (4)$$

where C_0 and C_t are the samples (**4** and **5**) concentrations before and after irradiation respectively, V is the reaction volume, N_A is the Avogadro's constant, S is the irradiated cell area and t is the irradiation time. I_{abs} is the overlap integral of the radiation source light intensity and the absorption of the samples (**4** and **5**). A

Download English Version:

<https://daneshyari.com/en/article/26960>

Download Persian Version:

<https://daneshyari.com/article/26960>

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