Journal of Organometallic Chemistry 708-709 (2012) 65–74

Contents lists available at SciVerse ScienceDirect

Journal of Organometallic Chemistry

journal homepage: www.elsevier.com/locate/jorganchem

Synthesis, characterization and comparative studies on the photophysical and photochemical properties of peripherally and non-peripherally tetra-substituted zinc(II) phthalocyanines

İrfan Acar [a], Zekeriya Bıyıklıoğlu [b,*], Mahmut Durmuş [c], Halit Kantekin [b]

[a] Department of Woodworking Industry Engineering, of Faculty of Technology, Karadeniz Technical University, 61830 Trabzon, Turkey
[b] Department of Chemistry, Faculty of Sciences, Karadeniz Technical University, 61080 Trabzon, Turkey
[c] Gebze Institute of Technology, Department of Chemistry, PO Box 141, Gebze, 41400 Kocaeli, Turkey

ARTICLE INFO

Article history:
Received 19 January 2012
Received in revised form
18 February 2012
Accepted 21 February 2012

Keywords:
Phthalocyanine
Zinc
Singlet oxygen
J-aggregation
Photodynamic therapy
Photosensitizer

ABSTRACT

In this study, the novel peripherally and non-peripherally tetra-substituted zinc(II) phthalocyanines were synthesized for the first time by cyclotetramerization reactions of corresponding four different phthalonitriles. All of these new zinc phthalocyanines were characterized by the spectral data (IR, ^{1}H NMR, ^{13}C NMR, UV–Vis and mass spectroscopies) as well as elemental analysis. These new zinc(II) phthalocyanines showed excellent solubility in many organic solvents. Surprisingly, the non-peripherally substituted zinc (II) phthalocyanine complexes (**9** and **10**) formed J-aggregates in non-coordinating solvents such as chloroform, dichloromethane and toluene. The formation of the J-aggregation was proved by UV–Vis and MALDI-TOF mass spectra of these complexes. The photophysical and photochemical properties of zinc 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.

1. Introduction

Phthalocyanines (Pcs), a family of aromatic macrocycles based on an extensive delocalized 18 π-electron system, have been extensively studied due to their unique optical, electronic, catalytic and structural properties. They have been used in very different areas of technology and medical applications, i.e., gas sensor [1–3], solar cell [4,5], liquid crystal [6], catalyst [7], electrochromic display [8], photodynamic therapy (PDT) of cancer [9–11]. They have also found different applications in many fields ranging from industrial [12], technological [13,14], to medical [15,16].

Applications of phthalocyanines are restricted owing to their insolubility in common organic solvents and water. It has been found that suitable functional groups on the peripheral benzene rings of the phthalocyanine structure can improve the solubility in protic or non-protic solvents [17,18].

Metallophthalocyanine derivatives are photoactive and may be employed in photosensitization [19,20]. In this regard, it is worth emphasizing the Pcs' application as photosensitizers in the PDT of tumors. Pcs are known to be useful photosensitizers due to their high molar absorption coefficient in the red part of the spectrum, photostability and long lifetimes of the photoexicited triplet states [21–23]. Especially, ZnPcs have been extensively studied because of d^{10} configuration of the central Zn^{2+} ion results in optical spectra that are not complicated by additional bands, as in transition-metal Pc complexes. ZnPcs have intensive red-visible region absorption and high singlet and triplet yields, which make them valuable photosensitizer for PDT applications.

The aggregation behavior of phthalocyanine compounds has been extensively investigated [24,25]. The aggregation formation among the phthalocyanine molecules involves ligand–metal coordination [26,27], π-stacking [28,29], hydrogen bonding [27] and donor–acceptor [30] interactions. The phthalocyanine compounds have two types of aggregations which affect on electronic and optical properties of these compounds. One of them namely face-to-face H-aggregation and another one is side-to-side J-aggregation [1,31].

In H-aggregates, the phthalocyanine molecules are arranged into a face-to-face conformation, and transition dipoles are perpendicular to the line connecting their centers. In contrast, in J-aggregates, the phthalocyanine molecules adopt a side-by-side conformation, and their transition dipoles are parallel to the line connecting their centers. In general, J-aggregates are highly desirable to maximize the optical properties of the phthalocyanines.

* Corresponding author. Tel.: +90 462 512 76 39; fax: +90 462 325 31 96.
E-mail address: zekeriya_61@yahoo.com (Z. Bıyıklıoğlu).

0022-328X/$ – see front matter © 2012 Elsevier B.V. All rights reserved.
doi:10.1016/j.jorganchem.2012.02.028

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 molecules occurred by utilizing the coordination of the side substituent from one Pc molecule to the central metal ion in a neighbor molecule [32–36]. The substituted zinc Pcs in non-coordinated organic solvents, e.g. chloroform and dichloromethane exhibit J-aggregation [37,38]. The addition of coordinating solvents such as methanol or pyridine caused dissociation of the dimers, which implies that the absence of coordinating solvents is essential for J-aggregation of Pc compounds [39]. UV–vis and MALDI-TOF-MS spectra could be used for determination presence of J-aggregation for Pc compounds [40].

Recently, we reported that ZnPc derivatives functionalized with substituents such as 4-(quinolin-6-yloxy) and crown ether groups in peripheral and non-peripheral positions on the phthalocyanine ring, compounds offered PDT properties due to their interesting photophysical properties [41,42]. Herein, we report on the synthesis, characterization and spectroscopic behavior as well as photophysical (fluorescence quantum yields and lifetimes) and photochemical (singlet oxygen and photodegradation quantum yields) properties of zinc phthalocyanine complexes substituted with four 2-[2-(1-naphthyloxy)ethoxy]ethanol and 2-[2-(2-naphthyloxy) ethoxy]ethanol groups (Schemes 1 and 2). The aggregation behavior of the synthesized zinc (II) phthalocyanine complexes are investigated in different solvents. The non-peripherally substituted complexes (**9** and **10**) showed J-type aggregation in non-coordinating solvents such as chloroform, dichloromethane and toluene. The formation of J-aggregation among the phthalocyanine molecules was determined using by UV–Vis spectra of these complexes in non-coordinating solvents as well as MALDI-TOF spectra.

2. Experimental

2.1. Materials

All reagents and solvents were of reagent grade quality and were obtained from commercial suppliers. All solvents were dried and purified as described by Perrin and Armarego [43]. 1,3-diphenylisobenzofuran (DPBF) and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) were purchased from Fluka. Unsubstituted zinc (II) phthalocyanine was purchased from Aldrich. 2-[2-(1-naphthyloxy) ethoxy]ethanol (**1**) [44], 2-[2-(2-naphthyloxy)ethoxy]ethanol (**6**) [44], 3-nitrophthalonitrile [45], 4-nitrophthalonitrile [46], 4-{2-[2-(1-naphthyloxy)ethoxy]ethoxy}phthalonitrile (**2**) [47] and 2(3),9(10), 16(17),23(24)-tetrakis {2-[2-(1-naphthyloxy)ethoxy]ethoxy} phthalocyaninato zinc (II) (**4**) [47] were synthesized and purified according to well known literature.

2.2. Equipment

The IR spectra were recorded on a Perkin Elmer 1600 FT-IR spectrophotometer using KBr pellets. ^{1}H-and ^{13}C NMR spectra were recorded on a Varian Mercury 200 MHz spectrometer in $CDCl_3$. Chemical shifts were reported (δ) relative to Me_4Si as internal standard. Mass spectra were measured on a Micromass Quatro LC/ULTIMA LC-MS/MS spectrometer. The formation of J-aggregation for non-peripherally substituted zinc (II) Pc complexes (**9** and **10**) were 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. The elemental analyses were performed on a Costech ECS 4010 instrument. Melting points were measured on an electrothermal apparatus and are uncorrected. 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. Photoirradiations 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) [48,49].

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

where F and F_{Std} are the areas under the fluorescence emission curves of the samples (**4**, **5**, **9** and **10**) 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^2_{Std} are the refractive indices of solvents used for the sample and standard, respectively. Unsubstituted ZnPc (in DMSO) ($\Phi_F = 0.20$) [50] was employed as the standard. The absorbance of the solutions at the excitation wavelength ranged between 0.04 and 0.05.

Natural radiative lifetimes (τ_0) were determined using PhotochemCAD program [51] which uses the Strickler–Berg equation. The fluorescence lifetimes (τ_F) were evaluated using equation (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 [52,53]. 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. Typically, a 3 ml portion of the respective unsubstituted zinc phthalocyanine (**ZnPc**) and substituted zinc phthalocyanine (**4**, **5**, **9** and **10**) solutions ($C = 1 \times 10^{-5}$ M) containing the singlet oxygen quencher were irradiated in the Q band region with the photo-irradiation set-up described in references [52,53]. Equation (3) was employed for the calculations:

$$\Phi_\Delta = \Phi^{\mathrm{Std}}_\Delta\frac{R\cdot I^{\mathrm{Std}}_{\mathrm{abs}}}{R_{\mathrm{Std}}\cdot I_{\mathrm{abs}}} \quad (3)$$

where $\Phi^{\mathrm{Std}}_\Delta$ is the singlet oxygen quantum yield for the standard unsubstituted ZnPc ($\Phi^{\mathrm{Std}}_\Delta = 0.67$ in DMSO) [54]. R and R_{Std} are the DPBF photobleaching rates in the presence of the samples (**4**, **5**, **9** and **10**) and standard, respectively. I_{abs} and $I^{\mathrm{Std}}_{\mathrm{abs}}$ are the rates of light absorption by the samples (**4**, **5**, **9** and **10**) and standard, respectively. To avoid chain reactions induced by DPBF in the presence of singlet oxygen, the concentration of quencher (DPBF) was lowered