



Self-assembling novel phthalocyanines containing a rigid benzothiazole skeleton with a 1,4-benzene linker: Synthesis, spectroscopic and spectral properties, and photochemical/photophysical affinity

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ABSTRACT

A novel benzothiazole containing phthalonitrile derivative and its peripherally tetra substituted metal free (**4**), Ni(II) (**5**), Zn(II) (**6**), Cu(II) (**7**) and Ti(IV) (**8**) phthalocyanines have been synthesized. The novel compounds were characterized by elemental analysis, IR, UV–Vis, ¹H NMR, ¹³C NMR and mass spectroscopy. Zn(II)Pc (**6**) showed monomeric behavior in THF up to 7×10^{-5} mol dm⁻³ concentration and in various solvents (pyridine, dichloromethane, DMF and DMSO) up to 4×10^{-5} mol dm⁻³ concentration. On the other hand, Cu(II)Pc (**7**) formed aggregates in THF at concentrations higher than 3.6×10^{-5} mol dm⁻³ and showed monomeric behavior in THF, DMF and DMSO at 2.4×10^{-5} mol dm⁻³. Furthermore, the photochemical and photophysical properties of the metal free (**4**), Zn(II) (**6**) and Ti(IV) (**8**) phthalocyanines were investigated in THF. All the investigated phthalocyanines showed similar fluorescence behavior in THF. The synthesized Ni(II) (**5**) and Cu(II) (**7**) phthalocyanines were not evaluated for this purpose because of the paramagnetic behavior of the central metals in the cavity of these complexes. Singlet oxygen generation properties of these phthalocyanine compounds were also investigated and the order of singlet oxygen quantum yields were found as: Zn(II) Pc (**6**) > Ti(IV) Pc (**8**) > unsubstituted Zn(II) Pc (ZnPc) > metal free Pc (**4**). The degradation of the studied compounds was studied under light irradiation and the oxotitanium (IV) phthalocyanine derivative was found to be very sensitive to light irradiation. The fluorescence quenching behavior of the studied novel peripherally tetra 4-(1,3-benzothiazol-2-yl)phenoxy substituted metal free (**4**), Zn(II) (**6**) and Ti(IV) (**8**) phthalocyanines by the addition of 1,4-benzoquinone was also studied.

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1. Introduction

Phthalocyanines (Pcs) have been under systematic study for more than 70 years due to their glorious functional properties [1]. Pcs are used in a number of applications due to their high stability, diverse coordination properties and improved spectroscopic characteristics. Possible application areas of Pcs are electrophotography, molecular electronics, photovoltaic and solar cells, Langmuir–Blodgett films, gas sensors, electrochromic display devices, NLO, optical discs and photosensitizers in photodynamic therapy of cancer (PDT) [2,3].

On the other hand, nitrogen and sulfur containing aromatic heterocyclic compounds, called benzothiazole and its derivatives, are very important species [4]. They are popular molecules due to their pharmaceutical and biological activities, such as antitumor [5], local anesthetic [6], antimicrobial [7] and antiglutamate/antiparkinson agents. Recently, these compounds have been

widely used for the preparation of anti-inflammatory drugs and analgesics [8], organic optoelectronic materials, second-order non-linear optical (NLO) materials [9], calcium channel antagonists [10], liquid crystals [11], fluorophores [12], inhibitors of several enzymes, azo dyes [13,14] and corrosion inhibitors [15–17].

Pcs are useful photosensitizers due to their high molar absorption coefficients, long lifetimes of the photoexcited triplet states and photostabilities [18,19]. One of the most important problems related to Pcs is their low solubility in common organic solvents, such as chloroform, methanol, acetone, THF, diethylether and ethyl acetate. Their insolubility does not allow scientists to investigate them. Locating bulky groups or long alkyl, alkoxy or alkylthio chains to peripheral areas or quaternary ion formation enhances the solubility of phthalocyanine products in many solvents [20]. In view of the biological importance of both benzothiazoles and phthalocyanines, it is worthwhile to combine these two functional structures into a single compound.

In the last decade, microwave heating technology has arisen as a strategic alternative to thermal energy due to advantages such as selectivity, rapidity in heating and cooling, decreased reaction

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time, increased yields and easy improved controllability [21–23]. From this perspective, microwave assisted synthesis of phthalocyanines is even more important [23–25].

In this study, the synthesis, characterization and structural investigation of metal-free and Ni(II), Zn(II), Cu(II) and Ti(IV) metallo phthalocyanines containing nitrogen, sulfur and oxygen donor atoms on the periphery are described. They are discussed below on the basis of their spectroscopic characteristics. The photophysical and photochemical properties of the novel metal-free (**4**), Zn(II) (**6**) and Ti(IV) (**8**) phthalocyanines were also investigated in THF and results are compared.

2. Experimental

2.1. Materials

4-(1,3-Benzothiazol-2-yl)phenol (**1**) [26] and 4-nitrophthalonitrile (**2**) [27] were prepared according to literature procedures. All reactions were carried out under an atmosphere of dry, oxygen-free nitrogen, using standard Schlenk techniques. All solvents were dried and purified as described by Perrin and Armarego [28].

2.2. Equipment

¹H NMR and ¹³C NMR spectra were recorded on a Varian XL-200 NMR spectrophotometer in CDCl₃, and chemical shifts are reported (δ) relative to Me₄Si as an internal standard. FT-IR spectra were recorded on a Perkin-Elmer Spectrum one FT-IR spectrometer using KBr pellets. The mass spectra were measured with a Micromass Quattro LC/ULTIMA LC-MS/MS spectrometer equipped with chloroform-methanol as the solvent. All experiments were performed in the positive ion mode. Elemental analyses were performed on a Costech ECS 4010 instrument and the obtained values agreed with the calculated ones. A Beko MD 1500, 2.45 MHz domestic microwave oven was used in the synthesis of all the phthalocyanines, except for metal-free and Ti(IV) Pc. Melting points were measured on an electrothermal apparatus and were uncorrected. UV-Vis spectra were recorded by means of Unicam UV2-100 and Shimadzu 2101 UV-Vis spectrophotometers, using 1 cm path length cuvettes at room temperature. Fluorescence excitation and emission spectra were recorded on a Varian Eclipse spectrofluorometer using 1 cm path length cuvettes at room temperature. A General Electric quartz line lamp (300 W) was used for photo-irradiation studies. A 600 nm glass cut off filter (Intor) 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 by the comparative method using Eq. (1) [29].

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

where F and F_{Std} are the areas under the fluorescence emission curves of the samples (metal-free (**4**), Zn(II) (**6**) and Ti(IV) (**8**) phthalocyanines) and the standard, respectively. A and A_{Std} are the respective absorbances of the samples and standard at the excitation wavelengths, respectively. n and n_{Std} are the refractive indices of solvents used for the sample and standard, respectively. Unsubstituted ZnPc ($\Phi_F = 0.20$) [30] was employed as the standard

in DMSO. The absorbance of the solutions at the excitation wavelength ranged between 0.04 and 0.05.

Natural radiative lifetimes (τ_0) were determined using the PhotochemCAD program [31] 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 [32–34] in THF. Typically, a 3 mL portion of the respective substituted phthalocyanine (metal-free (**4**), Zn(II) (**6**) and Ti(IV) (**8**)) 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 the references [32–34].

Singlet oxygen quantum yields (Φ_Δ) were determined in air using the relative method with unsubstituted ZnPc (in THF) as the reference. DPBF was used as a chemical quencher for singlet oxygen in THF. 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 ($\Phi_\Delta^{\text{Std}} = 0.53$ in THF) [35], R and R_{Std} are the DPBF photobleaching rates in the presence of the respective samples (metal-free (**4**), Zn(II) (**6**) and Ti(IV) (**8**) phthalocyanines) and standards, respectively. I_{abs} and $I_{\text{abs}}^{\text{Std}}$ are the rates of light absorption by the samples and standard, respectively. To avoid chain reactions induced by DPBF in the presence of singlet oxygen [36], the concentration of the quencher was lowered to $\sim 3 \times 10^{-5}$ M. Solutions of sensitizer (1×10^{-5} M) containing DPBF was prepared in the dark and irradiated in the Q band region using the setup described above. DPBF degradation at 417 nm was monitored. A light intensity of 6.39×10^{15} photons $\text{s}^{-1} \text{cm}^{-2}$ 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 [32–34]. 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 sample (metal-free (**4**), Zn(II) (**6**) and Ti(IV) (**8**) phthalocyanines) concentrations before and after irradiation respectively, V is the reaction volume, N_A is Avogadro's constant, S is the irradiated cell area, t is the irradiation time and I_{abs} is the overlap integral of the radiation source light intensity and the absorption of the samples. A light intensity of 2.13×10^{16} photons $\text{s}^{-1} \text{cm}^{-2}$ was employed for Φ_d determination.

2.4.3. Fluorescence quenching studies by 1,4-benzoquinone [BQ]

Fluorescence quenching experiments on the substituted phthalocyanine compounds (metal-free (**4**), Zn(II) (**6**) and Ti(IV) (**8**)) were carried out by the addition of different concentrations of BQ to a fixed concentration of the compounds, and the concentrations of BQ in the resulting mixtures were 0, 0.008, 0.016, 0.024, 0.032 and 0.040 M. The fluorescence spectra of the substituted phthalocyanine compounds at each BQ concentration were recorded, and the changes in fluorescence intensity were related

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