



Metal-free, zinc(II) and lead(II) phthalocyanines functioning with 3-(2H-benzo[d][1,2,3]triazol-2-yl)-4-hydroxyphenethyl methacrylate groups: Synthesis and investigation of photophysical and photochemical properties

Ümit Demirbaş^a, Mehmet Pişkin^b, Burak Barut^c, Rıza Bayrak^d, Mahmut Durmuş^e, Halit Kantekin^{a,*}

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

^b Çanakkale Onsekiz Mart University, Vocational School of Technical Sciences, Department of Food Technology, Çanakkale, 17100, Turkey

^c Karadeniz Technical University, Faculty of Pharmacy, Department of Biochemistry Trabzon, 61080, Turkey

^d Sinop University, Vocational School of Health Services, Department of Medical Laboratory Techniques, 57000 Sinop, Turkey

^e Gebze Technical University, Department of Chemistry, 41400, Kocaeli, Turkey

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ABSTRACT

In this study, the synthesis and characterization of 3-(2H-benzo[d][1,2,3]triazol-2-yl)-4-hydroxyphenethyl methacrylate substituted novel phthalonitrile compound and its peripherally substituted zinc(II) lead(II) and metal-free phthalocyanine derivatives were performed for the first time. This novel compounds were characterized by obtained data from general spectroscopic methods such as FT-IR, ¹H NMR, ¹³C NMR and mass. The photophysical and photochemical properties of these phthalocyanines were investigated in *N,N*-dimethylformamide solutions for determination of their photosensitizing abilities in photocatalytic applications such as photodynamic therapy. The lead(II) phthalocyanine complex did not produce any fluorescent in *N,N*-dimethylformamide because of the heavy atom effect of bigger lead atom. The fluorescence quantum yields of studied zinc(II) and metal-free phthalocyanines were found to quite higher than unsubstituted zinc(II) phthalocyanine due to substitution of the phthalocyanine skeleton. The influence of substituent and variety of the central metal ions on spectroscopic, photophysical and photochemical properties were also determined and compared.

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1. Introduction

Thanks to their strong delocalized 18 π -electronic structure, thermal stabilities and optical properties in visible area, phthalocyanines (Pcs) have many potential applications in different areas like as chemical sensors [1–3], electrochromic displaying systems, liquid crystals [4], non-linear optics [5], solar cells [6], photo-voltaic optics, molecular electronics [7], semiconductors [8], optical storage devices [9], laser dyes [10], catalyst [11] and photodynamic therapeutic agents (PDT) [12].

Benzotriazole derivatives are used as corrosion inhibitors [13], drug precursors [14], heating and cooling systems, hydraulic fluids

and vapor phase inhibitors [15]. In addition, different triazole derivatives are used as photosensitizer in some studies and their photophysical and photochemical properties have been discussed [16–18].

To best of our knowledge, although photophysical and photochemical properties of phthalocyanine ring has widely known the investigation of photophysical and photochemical properties were done first the time for benzotriazole bearing phthalocyanine.

In this study, we designed and prepared novel phthalonitrile compound (**3**) and its peripherally substituted zinc(II) (**4**), lead(II) (**5**) and metal-free (**6**) Pc derivatives bearing 3-(2H-benzo[d][1,2,3]triazol-2-yl)-4-hydroxyphenethyl methacrylate moieties.

The photophysical and photochemical properties of novel Pcs were investigated in *N,N*-dimethylformamide (DMF) solutions

* Corresponding author.

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

because the determination of photophysical and photochemical properties is worthy for usability of these Pcs as photosensitizers for photocatalytic applications such as photodynamic therapy (PDT) in cancer treatment. The effects of the 3-(2H-benzo[d][1,2,3]triazol-2-yl)-4-hydroxyphenethyl methacrylate groups on the phthalocyanine skeleton and the nature of the central metal ions in the Pc cavity on the photophysical and photochemical properties were also performed.

2. Experimental

2.1. Materials

All used chemicals were of reagent grade quality. 1,3-diphenylisobenzofuran (DPBF) and metal salts were purchased from Fluka or Merck and used as received. The solvents were purified, dried and stored over molecular sieves (4 Å). Column chromatography was performed on silica gel 60 (0.04–0.63 mm) purchased from Merck. All reactions were carried out under dry and oxygen free nitrogen atmosphere using Schlenk system. DMF (dimethylformamide) was dried and purified as described by Perrin and Armarego [19], 4-[2-(4-methoxyphenyl)ethyl]-5-propyl-2,4-dihydro-3H-pyrazol-3-one (**1**) [20] and 4-nitrophthalonitrile (**2**) [21] were prepared as described in the literature.

2.2. Equipments

¹H NMR and ¹³C NMR (for phthalonitrile compound) spectra were recorded on a Varian XL-200 NMR spectrometer CDCl₃, and chemical shifts were reported (δ) relative to Me₄Si (tetramethylsilane) as internal standard. FT-IR spectra were recorded on a Perkin-Elmer Spectrum One FT-IR spectrometer with ATR technique. The MS spectra were measured with a Thermo Quantum Access Mass spectrometer with H-ESI probe. Methanol and chloroform were used as solvents in mass analysis and all mass analysis were conducted in positive ion mode. Melting points were measured by an Electrothermal apparatus. The elemental analyses were performed on a Costech ECS 4010 instrument. Optical spectra in the UV–vis region were recorded by a Perkin Elmer Lambda 25 and a 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 cuvette at room temperature. Fluorescence lifetimes were measured using a time correlated single photon counting setup (TCSPC) (Horiba Fluorolog 3 equipment). 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 or 700 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) [22,23].

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

where F and F_{Std} are the areas under the fluorescence emission curves of the samples (**4–6**) and the standard, respectively. A

and A_{Std} are the relative absorbance of the samples (**4–6**) and standard at the excitation wavelength, respectively. n² and n_{Std}² are the refractive indices of solvents for the sample and standard, respectively. Unsubstituted ZnPc (Φ_F = 0.12 in DMF) [24] was employed as the standard. Both the sample and standard were excited at the same wavelength. The absorbance of the solutions was ranged between 0.04 and 0.05 at the excitation wavelength.

The fluorescence lifetime (τ_F) values were directly determined by time correlated single photon counting (TCSPC) method. The k_F value is the rate constant for fluorescence and this value was calculated using k_F = Φ_F/t_F. The τ₀ is the natural radiative life time and this value was calculated using τ₀ = t_F/Φ_F.

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 literature [25]. Typically, a 3 mL portion of the respective 3-(2H-benzo[d][1,2,3]triazol-2-yl)-4-hydroxyphenethyl methacrylate substituted phthalocyanines (**4–6**) (concentration = 1 × 10⁻⁵ M) containing the singlet oxygen quencher was irradiated in the Q band region with the photo-irradiation set-up described in the reference [25]. The Φ_Δ values were determined in air using the relative method with unsubstituted zinc(II) phthalocyanine as a standard. DPBF was used as chemical quencher for singlet oxygen in DMF. The Φ_Δ values of the studied phthalocyanines (**4–6**) were calculated using Eq. (2):

$$\Phi_{\Delta} = \Phi_{\Delta}^{\text{Std}} \frac{R \cdot I_{\text{Abs}}^{\text{Std}}}{R_{\text{Std}} \cdot I_{\text{Abs}}} \quad (2)$$

where Φ_Δ^{Std} is the singlet oxygen quantum yield for the standard. Unsubstituted zinc(II) phthalocyanine (Φ_Δ^{Std} = 0.56 in DMF) [26] was used as standard. R and R_{Std} are the DPBF photobleaching rates in the presence of the respective samples (**4–6**) and standard, respectively. I_{abs} and I_{abs}^{Std} are the rates of light absorption by the samples and standards, respectively. I_{abs} was determined by using Eq. (3).

$$I_{\text{abs}} = \frac{\alpha \cdot S \cdot I}{N_A} \quad (3)$$

To avoid chain reactions induced by DPBF in the presence of singlet oxygen [27], the concentration of quenchers (DPBF) was lowered to ~3 × 10⁻⁵ M. Solutions of sensitizer (concentration = 1 × 10⁻⁵ M) containing DPBF were prepared in the dark and irradiated in the Q band region using the setup described in literature [26]. DPBF degradation at 417 nm was monitored. The light intensity used for Φ_Δ determinations was found to be 6.60 × 10¹⁵ photons s⁻¹ cm⁻².

2.4.2. Photodegradation quantum yields

Photodegradation quantum yield (Φ_d) determinations were carried out using the experimental set-up described in literature [26]. 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 C₀ and C_t are the samples (**4–6**) concentrations before and after irradiation respectively, V is the reaction volume, N_A is the 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 (**4–6**). A light intensity

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