Synthesis and characterization of a new soluble metal-free and metallophthalocyanines bearing biphenyl-4-yl methoxy groups

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ABSTRACT

The synthesis and characterization of peripherally tetra-biphenyl-4-yl-methoxy substituted metal-free (4), Ni(II) (5), Cu(II) (6), Zn(II) (7), Co(II) (8) and Pb(II) (9) phthalocyanine derivatives are reported. These new phthalocyanine derivatives show the enhanced solubility in organic solvents and they have been characterized by a combination of IR, ^{1}H NMR, ^{13}C NMR, UV—vis, mass spectral data, elemental analysis and thermal analysis methods (TG/DTA). The photophysical (fluorescence quantum yield and lifetime) and photochemical (singlet oxygen generation and photodegradation quantum yield) properties of tetra-biphenyl-4-yl-methoxy substituted zinc (II) phthalocyanine derivative (7) are also investigated. The fluorescence of this phthalocyanine derivative (7) is effectively quenched by addition of 1,4-benzoquinone (BQ).

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1. Introduction

Phthalocyanines (Pcs) have many considerable physical and chemical features. Therefore, they have attracted many investigators in the science world for decades [1]. Because of these properties, phthalocyanines have been utilized in many fields such as gas sensors [2], semiconductor materials [3], photovoltaic cells [4,5], liquid crystals [6,7], optical limiting devices [8—10], molecular electronics [11], non-linear optical applications [12], Langmuir—Blodgett films [13], fibrous assemblies [14] and photodynamic therapy [15—18].

Phthalocyanines can be synthesized using microwave irradiation as an alternative method, which has been used since 1980 [19,20]. Recently, microwave processing techniques have been received a great deal of attention due to its various advantages such as selectivity, rapid, direct, controllable and internal etc [21—23]. In the last years, much effort has been dedicated to the microwave assisted synthesis of metal-free and metallophthalocyanines [24,25].

The main disadvantage of phthalocyanines is their insolubility in organic solvents. Lower solubilitiy of phthalocyanines hinders the utilization in many fields including PDT and makes difficult to purify and characterize them. However, the solubility of Pcs is very important for investigating their chemical and physical characteristics [26]. In order to improve the solubility of phthalocyanines, several substituents such as long alkyl, alkoxy, phenoxy groups and crown ethers can be added from peripheral positions of the phthalocyanines [27,28]. Soluble phthalocyanines with enhanced optical, electronic, redox and magnetic properties are expected to increase their possible application fields [29].

In this paper, we describe the synthesis and characterization of a new type soluble metal-free phthalocyanine (4) and its Ni(II) (5), Cu(II) (6), Zn(II) (7), Co(II) (8) and Pb(II) (9) complexes substituted with biphenyl-4-yl methoxy groups by microwave irradiation. Photophysical and photochemical properties of phthalocyanine complexes are very useful for photocatalytic applications such as photodynamic therapy (PDT) of cancer. We also investigated the photophysical (fluorescence quantum yield and lifetime) and photochemical (singlet oxygen generation and photodegradation quantum yield) properties of zinc phthalocyanine derivative (7) in DMSO, because zinc phthalocyanines have been extensively used as photosensitizers for PDT application because of closed shell d^{10} configuration of zinc atom [30]. Zinc phthalocyanines have intensive long wavelength absorption and high singlet and triplet yields, which make them valuable photosensitizer for PDT applications. The fluorescence-quenching behavior of this zinc phthalocyanine (7) by 1,4-benzoquinone in DMSO is also reported.

2. Experimental

2.1. Materials

Biphenyl-4-yl-methanol (**1**) and 4-nitrophthalonitrile (**2**) were prepared by reported procedures [31,32]. All reactions were carried under a dry nitrogen atmosphere using standard Schlenk techniques. 1,3-diphenylisobenzofuran (DPBF) was purchased from Fluka. All chemicals, solvents, and reagents were of reagent grade quality and were used as purchased from commercial sources. All solvents were dried and purified as described by Perrin and Armarego [33].

2.2. Equipments

FTIR spectra were obtained on a Perkin Elmer 1600 FTIR spectrophotometer with the samples prepared as KBr pellets. ^1H and ^{13}C NMR spectra were recorded on a Varian Mercury 200 MHz spectrometer in $CDCl_3$, 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. Elemental analyses of the complexes were performed on a LECO Elemental Analyzer (CHNS O932) and Unicam 929 AA spectrophotometer. UV–vis spectra were recorded using a Unicam and Shimadzu 2001 UV–vis spectrometers operating in the range 200–900 nm with quartz cells. Melting points were measured on an electrothermal apparatus. Domestic microwave oven was used for all synthesis of phthalocyanines.

Photo-irradiations were done using a General Electric quartz line lamp (300 W) for zinc (II) phthalocyanine derivative (**7**). 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 by the comparative method (equation (1)) [34,35]

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

where F and F_{Std} are the areas under the fluorescence emission curves of the zinc phthalocyanine (**7**) and the standard, respectively. A and A_{Std} are the relative absorbance of the sample and standard at the excitation wavelength, respectively. n and n_{std} are the refractive indices of solvents for the sample and standard, respectively. Unsubstituted ZnPc (in DMSO) ($\Phi_F = 0.20$) [36] 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.

Natural radiative (τ_0) lifetimes were determined using Photochem CAD program which uses the Strickler–Berg equation [37]. The fluorescence lifetimes (τ_F) were evaluated using equation (2).

$$\Phi_F = \frac{\tau_F}{\tau_0} \tag{2}$$

2.4. Photochemical parameters

2.4.1. Singlet oxygen quantum yields

Singlet oxygen quantum yield (Φ_Δ) determination was carried out by using the experimental set-up described in literature [38–40]. Typically, 3 ml portion of the respective zinc (II) phthalocyanine (**7**) solution (absorbance $\sim$ 1 at the irradiation wavelength) containing the singlet oxygen quencher was irradiated in the Q band region with the photo-irradiation set-up described in references [38–40]. Φ_Δ was determined in air using the relative method with ZnPc (in DMSO) as a reference. DPBF was used as chemical quenchers for singlet oxygen in DMSO. Equation (3) was employed for the calculations of Φ_Δ:

$$\Phi_\Delta = \Phi_\Delta^{Std} \frac{R \cdot I_{abs}^{Std}}{R^{Std} \cdot I_{abs}} \tag{3}$$

where Φ_Δ^{Std} is the singlet oxygen quantum yield for the standard ZnPc ($\Phi_\Delta^{Std} = 0.67$ in DMSO) [41] R and R_{Std} are the DPBF photobleaching rates in the presence of the respective sample (**7**) and standard, respectively. I_{abs} and I_{abs}^{Std} are the rates of light absorption by the sample (**7**) and standard, respectively. To avoid chain reactions induced by DPBF in the presence of singlet oxygen [42], the concentration of quencher was lowered to $\sim 3 \times 10^{-5}$ mol dm^{-3}. Solutions of sensitizer containing DPBF was prepared in the dark and irradiated in the Q band region using the above set-up. DPBF degradation at 417 nm was monitored. The light intensity was 6.57×10^{15} photons s^{-1} cm^{-2} for Φ_Δ determinations.

2.4.2. Photodegradation quantum yields

Determination of photodegradation quantum yield (Φ_d) was carried out previously described in the literature [38–40]. Φ_d was determined using equation (4),

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

where C_0 and C_t are the sample (**7**) concentrations before and after irradiation respectively, V, N_A, S, t and I_{abs} are reaction volume, the Avogadro's constant, irradiated cell area, irradiation time and the overlap integral of the radiation source light intensity, respectively. A light intensity of 2.19×10^{16} photons s^{-1} cm^{-2} was employed for Φ_d determinations.

2.4.3. Fluorescence quenching by 1,4-benzoquinone (BQ)

Fluorescence quenching experiments on the substituted ZnPc derivative (**7**) was carried out by the addition of different concentrations of BQ to a fixed concentration of the sample, 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 substituted ZnPc derivative (**7**) at each BQ concentration were recorded, and the changes in fluorescence intensity related to BQ concentration by the Stern–Volmer (S–V) equation [43] was shown in equation (5):

$$\frac{I_0}{I} = 1 + K_{SV}[BQ] \tag{5}$$

where I_0 and I are the fluorescence intensities of fluorophore in the absence and presence of quencher, respectively. [BQ] is the concentration of the quencher and K_{SV} is the Stern–Volmer constant which is the product of the bimolecular quenching constant (k_q) and the τ_F and is expressed in equation (6).

$$K_{SV} = k_q \cdot \tau_F \tag{6}$$