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The influence of the various central metals on photophysical and photochemical properties of benzothiazole-substituted phthalocyanines

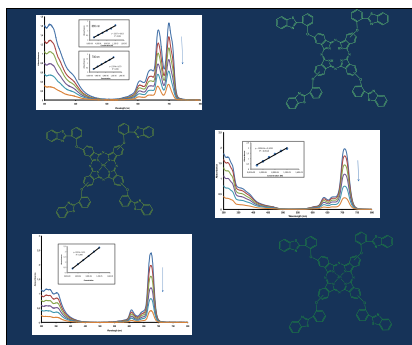
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HIGHLIGHTS

- The fluorescence quantum yields and lifetimes of phthalocyanines.
- The fluorescence quenching studies of phthalocyanines.
- The singlet oxygen quantum yields and photodegradation studies of phthalocyanines.
- The influence of the metal ions on the photophysical and photochemical parameters.

GRAPHICAL ABSTRACT

The fluorescence quantum yields and lifetimes, fluorescence quenching studies and singlet oxygen quantum yields and photodegradation studies of tetra-benzothiazole substituted metal-free (H_2Pc , **1**), lead(II) (PbPc, **2**) and zinc(II) (ZnPc, **3**) phthalocyanine compounds were investigated in tetrahydrofuran (THF) solution. The influence of the various central metal ions (zinc, lead or without metal) on the photophysical and photochemical parameters was also investigated and compared.



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ABSTRACT

The photophysical (fluorescence quantum yields and lifetimes, fluorescence quenching studies by 1,4-benzoquinone (BQ)) and photochemical (singlet oxygen quantum yields and photodegradation studies under light irradiation) properties of tetra-benzothiazole substituted metal-free (H_2Pc , **1**), lead (II) (PbPc, **2**) and zinc(II) (ZnPc, **3**) phthalocyanine compounds were investigated in tetrahydrofuran (THF) solution. All of these compounds did not show any aggregation and they produced good singlet oxygen (especially ZnPc). The influence of the various central metal ions (zinc, lead or without metal) on the photophysical and photochemical parameters was also investigated and compared.

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Introduction

Phthalocyanines (Pcs) are synthetic macrocyclic compounds containing four π -fused isoindole units which were synthesized

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accidentally in 1928 during the preparation of phthalimide from phthalic anhydride and ammonia [1]. Because these compounds have a large 18 π -electron conjugated system, they absorb strongly in the near-IR region, giving a characteristic blue–green color [2]. They are generally stable against to acids, bases, moisture, heat, light and solvents [1,3].

Phthalocyanine compounds, the synthetic analogs of the naturally occurring porphyrins, are functional materials in many different fields. Metallophthalocyanines (MPcs) have been shown to behave as semiconductors [4,5], catalysts [6,7], liquid crystals [8,9], chemical sensors [10,11] and especially in photodynamic therapy [12–14]. Photodynamic therapy (PDT) is a medical treatment of cancer tissues which employs the combination of light and photosensitizing agent like porphyrins, phthalocyanines, etc. [15,16]. A major objective for this cancer treatment is the selective destruction of tumor cells without damage to normal healthy tissues [17,18]. Phthalocyanines are porphyrin-like second generation sensitizers for photodynamic therapy of cancer [19]. In order to be used for PDT, a phthalocyanine derivative (photosensitizer) must have a long wavelength absorption in the red region [20]. The intense absorptions of the phthalocyanine derivatives in the red region of the visible spectrum make them suitable for PDT.

Another important circumstance is that the phthalocyanines have low solubility in aqueous media or common organic solvents, whereas water-soluble phthalocyanines are considered as the new generation of photosensitizers [20]. Adding some substituents to peripheral positions [21] leads to phthalocyanine derivatives soluble in several organic solvents. Also adding sulfo or quaternized ammonium groups increase the solubility of phthalocyanines in aqueous media [17]. With the increasing solubility of phthalocyanines, their usage as the new generation of photosensitizers also increases in photodynamic therapy.

The heterocycles, which are important not only due to their abundance but also because of their chemical, biological and technical significance, are the largest group of organic compounds. Thiazoles, which are heterocyclic compounds that contain both sulfur and nitrogen, are members of the heterocycles that include imidazoles and oxazoles [22].

Thiazoles, which are consisting of a 5-membered 1,3-thiazole ring fused to a benzene ring, are so-called benzothiazoles. Many benzothiazole derivatives are found to possess a number of biological activities such as antifungal, antidiabetic, antiviral, antitubercular and anti-inflammatory activities [23]. In recent years, there are number of paper dealing with thiazoles, which have both sulfur and nitrogen atom [24,25], but there are very few articles about photophysical and photochemical properties of the thiazole substituted phthalocyanines [26,27]. Whereas as a substituent the sulfur atom behaves as electron donating atom, which can influence the electronic spectra of complexes [28]. As a substituent group, benzothiazoles were used because they enhance the photosensitizer activities of complexes because of synergistic effect [26].

The PDT properties of the phthalocyanine molecules are vigorously influenced by the presence and nature of central metal ion and substitute group [28]. It is known that diamagnetic ions with a closed shell such as Zn^{2+} , Al^{3+} , Si^{4+} result in both high triplet quantum yields and relatively long triplet lifetimes [29]. While $ZnPc$ complexes are especially well known for their high photosensitizing abilities, unmetallated phthalocyanines show very little PDT effect [30].

In this study, the photophysical (fluorescence lifetime and quantum yields, fluorescence quenching studies by BQ and photochemical (singlet oxygen and photodegradation quantum yields) properties of metal-free (H_2Pc , **1**), lead(II) ($PbPc$, **2**) and zinc(II) ($ZnPc$, **3**) phthalocyanines (Fig. 1) were investigated in THF for the first time. In addition, the influence of the various central metal

ions (zinc, lead or without metal) on the photophysical and photochemical parameters was also investigated and compared.

Experimental

Materials

4-(2-(Benzo[d]thiazol-2-yl)phenoxy) substituted phthalocyanine derivatives (H_2Pc (**1**), $PbPc$ (**2**) and $ZnPc$ (**3**)) were prepared according to procedure in the relevant literature [31]. Unsubstituted zinc(II) phthalocyanine ($ZnPc$) were purchased from Sigma Aldrich. All other solvents and reagents were of reagent grade and used as received.

Results and discussion

Synthesis and characterization

The general synthetic route for the synthesis of the phthalocyanine compounds (H_2Pc (**1**), $PbPc$ (**2**) and $ZnPc$ (**3**)) is given in related literature [31]. Briefly, 4-(2-(benzo[d]thiazol-2-yl)phenoxy)-substituted H_2Pc (**1**) was prepared by cyclotetramerization of 4-(2-(benzo[d]thiazol-2-yl)phenoxy)phthalonitrile in the presence of 1,8-diazabicyclo[5.4.0] undec-7-ene in dry *n*-pentanol at 160°C for 24 h. Tetra-substituted $PbPc$ (**2**) and $ZnPc$ (**3**) compounds were also obtained by cyclotetramerization of 4-(2-(benzo[d]thiazol-2-yl)phenoxy)phthalonitrile in the presence of related metal salts (PbO) or ($Zn(ac)_2$) and two drops of 1,8-diazabicyclo[5.4.0] undec-7-ene in dry *n*-pentanol 160 °C for 24 h, respectively. All phthalocyanines were purified by column chromatography on silica gel using chloroform: methanol solvent system (93:7, 91:9, 93:7, respectively for compounds **1–3**) as eluent.

UV–Vis absorption spectra

As mentioned in our previous paper, the absorption spectrum of H_2Pc (**1**) includes a splitting intense Q-band at λ_{max} : 700 and 665 nm with shoulders at λ_{max} : 638 and 605 nm and the B-band at λ_{max} : 383 nm [31]. For compounds **2** and **3** the Q-bands were observed at λ_{max} : 707 and 673 nm, respectively. In the absorption spectra, $PbPc$ (**2**) was red shifted compared to H_2Pc (**1**) and $ZnPc$ (**3**). For compound **2**, the large red shift was attributed to highly deformed phthalocyanine skeleton because of the central metal ion (Pb^{2+}) which was not fitting into the cavity of phthalocyanine molecule due to large atomic size of lead atom. Namely, phthalocyanine ligand deformation causes in the red shifting of the Q-band [32]. In this study, the aggregation behavior of the studied phthalocyanine compounds (**1–3**) was investigated at different concentrations in THF, as the concentration was increased, the intensity of absorption of the Q band also increased and there were no new bands due to the aggregated species for the studied phthalocyanine compounds (**1–3**). Beer–Lambert law was obeyed in these compounds in the concentrations ranging from 2×10^{-6} to 12×10^{-6} M in THF.

Fluorescence spectra

The fluorescence emission and excitation wavelength maxima values were given in Table 1. The obtained Stokes shifts were 4 nm for H_2Pc (**1**) and $PbPc$ (**2**) compounds and 6 nm for $ZnPc$ (**3**) compound. For the H_2Pc (**1**) and $ZnPc$ (**3**) compounds, the excitation spectra were similar in the absorption spectra in THF. This attributes that the nuclear configuration of the ground state and the excited state are similar and not affect by the excitation. Fig. 2a–c show absorption, fluorescence emission and excitation spectra of compounds **1–3** in THF.

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