



Photophysical and photochemical properties of a zinc phthalocyanine with four diphenylborinic ester moieties



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ABSTRACT

A novel zinc(II) phthalocyanine substituted with four diphenylborinic ester units was synthesized by the reaction of 2,9,16,23-tetra (salicylaldimino)-phthalocyaninatozinc(II) and triphenylborane in THF at reflux condition. The novel zinc phthalocyanine was characterized by using elemental analysis, IR, ¹H and ¹¹B-NMR and UV–Vis spectral data. ¹¹B-NMR data demonstrated that the boron atom is in tetraordinated state and diphenylborinate substituents have a cyclic structure with a coordinative N–B bond enhancing the stability of this borinated phthalocyanine derivative. Moreover, the consequences of the presence of diphenylborinic ester groups on the spectral, photophysical and photochemical properties of the new zinc phthalocyanine are investigated in detail.

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Introduction

Phthalocyanines, the synthetic porphyrin analogues, are macroheterocyclic compounds which comprise four isoindole units linked by nitrogen atoms at the meso position [1]. Each pyrrolic group is fused to a benzene ring resulting in the red-shift of their final absorption band [2]. These tetrapyrrolic macrocycles with two-dimensional 18 π -electron aromatic systems can form coordination complexes with most elements of the periodic table [1]. Phthalocyanines have found a number of important industrial applications as dyes and pigments due to their bright blue or green colours. Nearly a quarter of all pigments of organic origin are related to this class of compounds [3]. During the past decades phthalocyanines and their derivatives have been extensively studied and numerous applications have been developed in widely different areas due to their distinct properties like high thermal stability, chemical resistance, high colouring property, semi-conductivity, photoconductivity, catalytic activity, etc [4,5]. Their extended 18 π -electron aromatic systems and the lattice-packing in the solid state are responsible for their extraordinary physical

properties [6]. Another appealing feature of phthalocyanines is their versatile chemical system enabling one to modify the phthalocyanine core for a broad range of applications in order to meet specific qualities suitable for their applications. Changing the central atom, its axial coordination or peripheral functionalities has been the major ways of modifying the phthalocyanine molecules [1,7].

Phthalocyanines are traditional industrial dyes but recently they have been investigated for their potential use in many other fields, including catalysis, chemical sensors, non-linear optical materials, ink-jet printing, electrophotography, dye sensitized solar cells, semiconductors, electrochromic devices, functional polymers, liquid crystals and also in nanotechnology [4,8–13]. Apart from their important contributions in materials science, this class of functional dyes also has potential applications in the treatment of a range of cancers [14]. Owing to their strong absorptions in the region of biological optical window (600–800 nm), high efficiency at generating reactive oxygen species (ROS), lack of dark toxicity, flexibility in structural modifications including the central transition metal ions and photostability [15], phthalocyanines have emerged as a promising class of second-generation photosensitizers for photodynamic therapy (PDT) [8]. This technology is based on the light excitation of a photosensitizer which induces a localized oxidative damage within the cells by formation of highly

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reactive oxygen species, the most important of which is singlet oxygen [16]. Over the last decade, a substantial number of phthalocyanine-based photosensitizers have been prepared and evaluated for their photodynamic activity, with the focus on silicon, zinc and aluminum analogues with both high triplet yields and long lifetimes of the excited triplet state. Thus, these complexes are expected to exhibit strong photochemical and photodynamic activities due to a higher efficiency in generating reactive oxygen species than porphyrins [4,17].

Salicylaldehyde groups are accepted as efficient ligands to bind transition metal ions via nitrogen atom of C=N– double bond and an ortho-position oxygen (O) atom which have a lonely pair of electrons [18]. The acyclic and cyclic Schiff bases have been prepared by the self-condensation of formyl- or keto-groups and primary amine precursors, appropriately designed and peripherally decorated by incorporating certain steric or electronic recognition features in order to address the synthesis toward the desired product, avoiding byproducts difficult to be separated, or side reactions (hydrolysis, exchange, metathesis, etc.) [19]. Salicylaldehyde moieties have been extensively employed in understanding the molecular processes occurring in biochemistry, material science, catalysis, encapsulation, activation, transport and separation phenomena, hydrometallurgy, etc [20,21]. Therefore, remarkable efforts are currently aimed at the preparation, characterization and application of new salicylaldehyde ligands and related complexes [19]. Recently, we have reported the phthalocyanines with unsaturated cinnamaldimine moieties attached to the inner core through phenoxy-bridges [22], a new water-soluble tetracationic zinc phthalocyanine which contains four conjugated Schiff's base groups on peripheral positions in the phthalocyanine framework [23] and a novel pentanuclear metallo phthalocyanine (M = Zn) containing four additional salicylaldehyde complexes of Zn(II) at the peripheral positions [24].

In the past decade, rapid research progress and many important discoveries have been achieved in π -conjugated four-coordinate boron chemistry due to its many applications, such as fluorescent sensors, nonlinear optics and emitting and electron-transport materials in organic light-emitting devices (OLEDs) [25–29]. In these systems, incorporation of boryl groups into the π -conjugated skeleton allows intramolecular coordination from the Lewis base N atom to the boron atom [30]. The strength of this coordinative or dative N–B bond depends greatly on the substituents on both atoms; electron-withdrawing groups increase the Lewis acidity of boron, whilst electron-donating groups increase the Lewis basicity of nitrogen [31]. Among the four-coordinated boron compounds, organoboron quinolates such as 8-hydroxyquinolate diphenylboron turned out to be attractive as an alternative to tris(8-hydroxyquinolate)aluminum for organic light-emitting diodes (OLEDs) because of their good thermal stabilities as well as the high emission quantum yields [32]. The key advantage of boron compounds versus aluminum compounds is the much greater covalent nature of B–O, B–N, and B–C bonds than the corresponding Al–O, Al–N, and Al–C bonds, which could lead to a greater stability of the boron compounds [25]. In a recent review, it has been also reported that one or two diphenylborinic ester containing molecules on conjugated skeletons are intensely luminescent [33].

In continuation to our previous work on preparation of boronated tetrapyrrole derivatives and their precursors [34–37], herein the synthesis and characterization of a novel zinc phthalocyanine carrying four diphenylborinic ester groups on its peripheral positions is reported. Moreover, the effects of these diphenylborinic ester substituents on the spectral, photophysical and photochemical properties of the novel zinc phthalocyanine (**2**) are discussed in detail.

Experimental

Instruments and chemicals

All reagents and solvents were of reagent grade quality, obtained from commercial suppliers. The solvents were stored over molecular sieves (4 Å). 2,9,16,23-tetra-(salicylaldehyde)phthalocyaninatozinc(II) (**1**) was synthesized as reported in the literature [24]. Triphenylborane was used as supplied commercially. The progress of the reactions was monitored by TLC (SiO₂). IR spectra were recorded on a Perkin Elmer Spectrum One FTIR (ATR sampling accessory) spectrophotometer, electronic spectra in the UV–Vis region were recorded with an Scinco S-3100 single beam UV/Vis PDA spectrophotometer. ¹H NMR and ¹¹B NMR spectra were recorded on an Agilent VNMR5 500 MHz spectrophotometer using TMS as internal reference in ¹H NMR and boron trifluoride diethyl etherate was used as an external standard in ¹¹B NMR spectra. Elemental analyses were performed on a Thermo Flash EA 1112. Fluorescence excitation and emission spectra were recorded on a Varian Eclipse spectrofluorometer using 1 cm pathlength cuvettes at room temperature. Photo-irradiations were done using a General Electric quartz line lamp (300 W). 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, 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.

Synthesis

Synthesis of Diphenylborinic Acid Ester of 2,9,16,23-tetra-(salicylaldehyde)-phthalocyaninatozinc(II) (**2**)

184 mg (0.76 mmol) triphenylborane was added to 50 mL of THF solution containing 200 mg (0.19 mmol) of 2,9,16,23-tetra-(salicylaldehyde)phthalocyaninatozinc(II) (**1**). The reaction mixture was refluxed with vigorous stirring for 5 h under N₂. After the mixture was cooled to room temperature, it was filtered and concentrated under vacuum. The resulting green coloured solid product was washed with hexane and diethyl ether and then dried *in vacuo* [38,39]. Yield: 252 mg (77.6%). m.p. > 200 °C. FTIR (ν max/cm⁻¹): 3066–3040 (Ar–H), 1606 (HC=N), 1548, 1489 (B–N), 1454 (C=C), 1395, 1333, 1305 (B–O), 1264, 1238 (Ar–O–Ar), 1192, 1138, 1086, 1045, 943, 890, 819, 743, 701; ¹H NMR (DMSO- d₆) δ (ppm): 9.02–8.91 (d, 2H, Ar–H), 8.63–8.41 (m, 2H, Ar–H), 8.00 (s, 4H, N=CH), 7.78–6.78 (m, 64H, Ar–H); ¹¹B NMR (d₆-DMSO, ppm): 2.9 (s, tetracoordinated B); UV–Vis (THF): λ_{max} /nm (10⁻⁵ log ϵ , L mol⁻¹ cm⁻¹): 699 (5.20), 357 (4.99). Anal. Calc. for C₁₀₈H₇₂B₄N₁₂O₄Zn (1708.55 g/mol): C, 75.84; H, 4.24; N, 9.83; Found: C, 75.91; H, 4.15; N, 9.87%.

Photophysical parameters

Fluorescence quantum yields and lifetimes

Fluorescence quantum yields (Φ_F) were determined by the comparative method using Eq. (1) [40],

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

where F and F_{Std} are the areas under the fluorescence emission curves of the samples (**1**, and **2**) and the standard, respectively. A and A_{Std} are the respective absorbances of the samples and standard at the excitation wavelengths, respectively. n² and n_{Std}² are the

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