



# Synthesis and photophysical properties of zinc phthalocyanine derivatized with benzothiazole or carbazole photosensitizers



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## ABSTRACT

The synthesis of new zinc phthalocyanine complexes containing 3-(2-benzothiazol-2-yloxy) (complex **3**) and 3-(carbazol-2-yloxy) (complex **4**) substituents at the non-peripheral positions are reported. The new compounds were characterized by elemental analysis, FT-IR, <sup>1</sup>H NMR, mass spectrometry and UV-Vis spectroscopy. The effects of carbazole and benzothiazole substituents on the photophysical and photochemical parameters of ZnPc are reported. These new phthalocyanines are non-aggregated in common solvents and show improved photophysical properties. The 3-(2-benzothiazol-2-yloxy) substituted complex showed the longest triplet lifetime ever reported for a zinc phthalocyanine (1.7 ms).

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## 1. Introduction

Phthalocyanines (Pcs) continue to receive attention for applications in a variety of scientific fields due to the unique physicochemical properties that arise from their aromatic structure [1,2]. Phthalocyanine derivatives have gained popularity as photosensitizers in photodynamic therapy (PDT) of cancer [3–7]. The photodynamic activity of Pcs is not only limited to cancer treatment [3], it has also been applied to the inactivation of bacteria [8], viruses [9] and yeasts [10] and in the phototransformation of pollutants [11]. Pcs are highly efficient in generating reactive oxygen species (ROS), which are the reactive in the application of these molecules as photosensitizers [12]. High triplet yields and lifetimes as well as high singlet oxygen quantum yields are required for the use of Pcs as photosensitizers [11]. The development of Pcs with these properties continues to be of interest.

The phthalocyanine ring substituents (benzothiazole or carbazole) used in this work were chosen since they are also known to be photosensitizers [13,14]. Thus the combination of a benzothiazole or carbazole skeletons with phthalocyanines is aimed at enhancing the photosensitizer activity due to a synergistic effect. Other than the recent work reported by Aktas et al. [15], who studied benzothiazole substituted phthalocyanines in the presence of a linker, no work has been reported on photophysical and photochemical behavior of benzothiazole derivatized ZnPc complexes, where the benzothiazole substituent is directly linked to the Pc ring. To the best of our knowledge, carbazole derivatized

phthalocyanines have not been reported. The complexes are substituted at the non-peripheral positions which will result in the red-shifting of the Q band and effect a decrease in aggregation [16]. These two properties are important requirements in PDT applications. We report herein on the photophysical and photochemical properties of benzothiazole and carbazole substituted zinc phthalocyanines. Organic chromophores with long-lived triplet excited states at room temperature are useful for designing new photosensitizers. Benzothiazole chromophores are known [17] for their long triplet lifetimes, hence their additional importance of this work.

## 2. Experimental

### 2.1. Materials

Zinc acetate dihydrate (99%), 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU), 3-nitrophthalonitrile, 2-hydroxybenzothiazole, 2-hydroxycarbazole, zinc phthalocyanine (used as a standard) and 1,3-diphenylisobenzofuran (DPBF) were purchased from Sigma Aldrich. Dimethylformamide (DMF), potassium carbonate, methanol, ethanol, 1-pentanol, acetone, diethyl ether and tetrahydrofuran (THF) were from SAARCHEM.

### 2.2. Equipment

Ground state absorption spectra were recorded on a Shimadzu UV-2550 spectrophotometer. Fluorescence excitation and emission spectra were recorded on a Varian Cary Eclipse Fluorescence

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spectrophotometer. Infrared spectra were recorded on a Perkin Elmer Spectrum 100 FT-IR (with Universal ATR Sampling Accessory) spectrometer, while  $^1\text{H}$  nuclear magnetic resonance signals were recorded on a Bruker AMX 400 MHz NMR spectrometer or a Bruker Advance II+ 600 MHz NMR spectrometer.

Fluorescence lifetimes were measured using a time correlated single photon counting (TCSPC) setup (FluoTime 200, Picoquant GmbH). The excitation source was a diode laser (LDH-P-670 driven by PDL 800-B, 670 nm, 20 MHz repetition rate, 44 ps pulse width, Picoquant GmbH), as described in detail before [18].

Mass spectral data were collected with a Bruker AutoFLEX III Smart beam TOF/TOF Mass spectrometer. The spectra were acquired using  $\alpha$ -cyano-4-hydroxycinnamic acid as the MALDI matrix, and a 355 nm Nd:YAG laser as the ionizing source. Elemental analyses were carried out on a Vario EL III MicroCube CHNS Analyzer.

A laser flash photolysis system was used for the determination of triplet decay kinetics. The excitation pulses were produced by a tunable laser system consisting of Nd:YAG laser (355 nm, 135 mJ/4–6 ns), pumping an optical parametric oscillator (OPO, 30 mJ/3–5 ns) with a wavelength ranges from 420 to 2300 nm (NT-342B, Ekspla). The details have been provided previously [18]. Triplet lifetimes were determined by the exponential fitting of the kinetic curves using the ORIGIN 6 Professional software. The absorbance used for triplet state studies was kept at 1.5 and degassed by bubbling argon for 30 min prior to measurements.

Photo-irradiation for singlet oxygen determinations 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 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 and were found to  $2.97 \times 10^{16}$  photons  $\text{s}^{-1} \text{cm}^{-2}$ . For singlet oxygen studies, the absorbance of the DPBF and Q band was kept at 1 and 0.5 respectively.

### 2.3. Synthesis

#### 2.3.1. 3-(2-Benzothiazol-2-yloxy)-phthalonitrile (**1**)

A mixture of 2-hydroxybenzothiazole (1.00 g, 6.6 mmol) and 3-nitrophthalonitrile (1.14 g, 6.6 mmol) in DMF (10 ml) was stirred under an argon atmosphere at room temperature.  $\text{K}_2\text{CO}_3$  (10.07 g, 72.4 mmol) was added portion-wise to the reaction mixture which was then stirred at room temperature for 48 h. The reaction mixture was subsequently poured into ice water, and the precipitate filtered off, washed with water and methanol and dried. The crude product was recrystallized from an ethanol:water (1:1) and dried *in vacuo*.

Yield: 0.95 g (52%). FT-IR ( $\nu_{\text{max}}/\text{cm}^{-1}$ ): 3020 (Ar-CH), 2961, 2834 (CH), 2230 (CN), 1560 (C=N), 1579 (C-C), 1475, 1456, 1442, 1383, 1325, 1277 (C-O-C), 740 (C-S-C). *Anal. Calc.* for  $\text{C}_{15}\text{H}_7\text{N}_3\text{O}_3$ : C, 64.97; H, 2.54; N, 15.15; S, 11.56. Found: C, 64.66; H, 2.75; N, 15.61; S, 11.32%.  $^1\text{H}$  NMR (DMF- $d_7$ ): 9.12 (1H, d,  $J = 8.40$  Hz, Ar-H), 8.97 (1H, d,  $J = 8.40$  Hz, Ar-H), 8.81 (1H, m, Ar-H), 8.67–8.57 (2H, m, Ar-H), 8.29 (1H, m, Ar-H), 7.76 (1H, m, Ar-H).

#### 2.3.2. 3-(Carbazol-2-yloxy)phthalonitrile (**2**)

The synthesis of **2** was the same as for **1**, except 2-hydroxycarbazole (1.21 g, 6.6 mmol) was employed instead of 2-hydroxybenzothiazole. The amounts of the reagents as well as reaction conditions were kept the same.

Yield: 1.2 g (59%). FT-IR ( $\nu_{\text{max}}/\text{cm}^{-1}$ ): 3300 (NH), 3078 (Ar-CH), 2941, 2855 (C-H), 2240 (CN), 1645 (NH), 1579 (C-C), 1575, 1356, 1342, 1283 (C-O-C). *Anal. Calc.* for  $\text{C}_{20}\text{H}_{11}\text{N}_3\text{O}$ : C, 77.66; H, 3.58;

N, 13.58. Found: C, 77.87; H, 4.21; N, 13.07%.  $^1\text{H}$  NMR (DMSO- $d_6$ ): 11.46 (1H, s, NH), 8.24–8.22 (1H, d,  $J = 8.48$  Hz, Ar-H), 8.16–8.14 (1H, d,  $J = 7.63$  Hz, Ar-H), 7.85–7.78 (2H, m, Ar-H), 7.53 (1H, d,  $J = 7.63$  Hz, Ar-H), 7.43 (1H, t,  $J = 7.63$  Hz, Ar-H), 7.29 (1H, s, Ar-H), 7.28 (1H, d,  $J = 7.63$  Hz, Ar-H), 7.20 (1H, t,  $J = 7.63$  Hz, Ar-H), 7.03 (1H, m, Ar-H).

#### 2.3.3. 1,(4)-Tetra-(2-benzothiazol-2-yloxy) phthalocyaninato zinc (II) ( $\alpha\text{ZnTBTPc}$ ) (**3**)

A mixture of zinc (II) acetate dehydrate (0.25 g, 1.1 mmol), 3-(2-benzothiazol-2-yloxy)-phthalonitrile (**1**, 0.5 g, 1.8 mmol), DBU (3 drops) and 1-pentanol (10 mL) was stirred at 160 °C for 5 h under a nitrogen atmosphere. After cooling, the solution was mixed with methanol. The green solid product was precipitated and collected by filtration and washed with methanol. The crude product was re-dissolved in DMF. After concentrating, the green product was precipitated with hot ethanol, filtered, and then washed with ethanol, acetone, *n*-hexane and diethyl ether. The green product was further purified by passing through silica gel using THF as the eluent.

Yield: 0.215 g (10%). UV-Vis (DMSO):  $\lambda_{\text{max}}$  nm ( $\log \epsilon$ ): 672 (5.29), 606 (4.59), 337 (4.79), FT-IR: ( $\nu_{\text{max}}/\text{cm}^{-1}$ ): 3018 (Ar-H), 1598 (C=C), C=N (1560), 1288, 1120 (C-O-C), 940 (C-S-C), 730, 714, 760, 830 (C-H).  $^1\text{H}$  NMR (DMF- $d_7$ ): 10.00–9.75 (4H, m, Ar-H), 9.70–9.45 (4H, m, Ar-H), 8.85–8.70 (8H, m, Ar-H), 8.68–8.60 (6H, m, Ar-H), 8.55–8.40 (6H, m, Ar-H). MALDI TOF-MS: Calculated: 1174. Found: 1181 [M+7H] $^+$ . *Anal. Calc.* for  $\text{C}_{60}\text{H}_{28}\text{N}_{12}\text{S}_4\text{O}_4\text{Zn}$ : C, 61.35; H, 2.39; N, 14.32; S, 10.91. Found: C, 61.50; H, 2.09; N, 13.96; S, 10.34%.

#### 2.3.4. 1,(4)-Tetra-(carbazol-2-yloxy)phthalocyaninato zinc (II) ( $\text{ZnTCPC}$ ) (**4**)

The synthesis was the same as for complex **3**, except compound **2** was employed instead of **1**. The purification procedure was the same as that of **3**.

Yield: 0.86 g (53%). UV-Vis (DMSO):  $\lambda_{\text{max}}$  nm ( $\log \epsilon$ ): 700 (5.12), 630 (4.59), FT-IR: ( $\nu_{\text{max}}/\text{cm}^{-1}$ ): 3200 (NH), 3161 (Ar-H), 1576, 1077, 1110 (C-O-C), 1559 (C=N), 1412 (C=C).  $^1\text{H}$  NMR (DMSO- $d_6$ ): 11.46 (4H, s, NH), 8.00–7.99 (4H, d,  $J = 8.4$  Hz, Ar-H), 7.93–7.92 (4H, d,  $J = 7.7$  Hz, Ar-H), 7.56–7.54 (4H, t,  $J = 7.8$  Hz, Ar-H), 7.34–7.31 (8H, m Ar-H), 7.18–7.15 (4H, t,  $J = 7.6$  Hz, Ar-H), 7.10 (4H, s, Ar-H), 7.00–6.96 (8H, m, Ar-H), 6.79–6.78 (4H, dd, Ar-H). MALDI TOF-MS ( $m/z$ ): Calculated 1301. Found: 1302 [M+H] $^+$ . *Anal. Calc.* for  $\text{C}_{80}\text{H}_{44}\text{N}_{12}\text{O}_4\text{Zn}$ : C, 73.76; H, 3.40; N, 12.90. Found: C, 73.06; H, 3.79; N, 12.88%.

### 2.4. Photophysical and photochemical parameters

Triplet ( $\Phi_{\text{T}}$ ), fluorescence ( $\Phi_{\text{F}}$ ) and singlet oxygen ( $\Phi_{\Delta}$ ) quantum yields were determined using the comparative methods as described before [19–22], and using ZnPc as a standard in DMSO. Values of the ZnPc standards used were as follows:  $\Phi_{\text{T}} = 0.65$  [19],  $\Phi_{\text{F}} = 0.20$  [21] and  $\Phi_{\Delta} = 0.67$  [11]. The samples and the standard were both excited at the same relevant wavelength in each case. For singlet oxygen quantum yields, DPBF was employed as a chemical quencher and, to avoid chain reactions, the concentration of the DPBF solution was lowered to  $\sim 3 \times 10^{-5}$  mol  $\text{dm}^{-3}$  [22]. Solutions of the sensitizer containing DPBF were prepared in the dark and irradiated at the Q band using the setup described above. DPBF degradation at 417 nm was monitored in DMSO.

The quantum yields of internal conversion ( $\Phi_{\text{IC}}$ ) were obtained from Eq. (1), which assumes that only three processes (fluorescence, intersystem crossing and internal conversion) jointly deactivate the excited states of complexes **3** and **4**

$$\Phi_{\text{IC}} = 1 - (\Phi_{\text{F}} + \Phi_{\text{T}}) \quad (1)$$

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