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A novel soluble phthalocyanine capable of binding four boronic esters

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A novel Zn phthalocyanine bearing 4 salicylideniminophenyloxy substituents on peripheral positions was synthesized from the reaction of 4-aminophenoxy substituted phthalocyanine and salicylaldehyde. The condensation reaction of salicylidene Schiff base groups and benzeneboronic acid produced a new phthalocyanine carrying benzeneboronic acid ester derivatives as substituents. Ethoxy groups were bound to boronic acid as a second ligand. The presence of B-N bond interactions enhanced the stability of this boronated phthalocyanine derivative, which exhibited sufficient air stability during the purification and characterization processes. The novel compounds were characterized by using elemental analysis, IR, ^{1}H-NMR, ^{11}B-NMR, ^{13}C-NMR, UV-Vis and MALDI-TOF MS spectral data.

Key Words: Phthalocyanine Schiff base, zinc, boronate complex, benzeneboronic acid, ^{11}B-NMR

Introduction

Phthalocyanines have a conjugated 2-dimensional 18 π-electron system thereby allowing the incorporation of more than 70 different metal or non-metal ions into their inner core.[1] Since their first synthesis at the beginning of the last century, phthalocyanines, the most important artificial structural analogous of porphyrins, have found widespread industrial applications as photosensitizers, catalysts, electrocatalysts, sensors, and nonlinear optical devices in addition to their traditional applications as dyes and pigments.[1,2]

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Boron chemistry has emerged as an interesting area of research due to its interesting applications in several areas of material sciences.[3,4] medicinal sciences,[5] and supramolecular chemistry.[6,7] The advantage of boron chemistry is the possibility of obtaining stable 3- and 4-coordinated boron compounds, which have been extensively employed in the preparation of supramolecular structures.[8,9]

Esters of boronic acids are notoriously unstable to hydrolysis.[10] However, organoboran compounds with a boroxazolidine ring in their structure exhibited high hydrolytic stability. This notable increase in hydrolytic stability is ascribed to the formation of a B-N coordinative bond.[11] Furthermore, compounds containing BN bonds have been shown to possess biological activity. In this respect, the formation of complexes containing a dative N–B bond has been studied intensively;[12,13] some examples include the condensation of boronic acids with ethanolamine,[14] amino acids,[15,16] or Schiff bases.[17]

Some success in the use of boron-containing compounds has been achieved in boron neutron capture therapy (BNCT).[18] Several porphyrins and derivatives containing borane moieties have been synthesized and evaluated as boron delivery agents for BNCT due to their high selectivity for tumor tissue over most normal tissues.[19] Furthermore, these tetrapyrroles are accumulated by a variety of malignant lesions in necessary amounts.[20] The molecular structure of phthalocyanines remains stable in response to irradiation with thermal neutrons. In this regard, phthalocyanines appear to be preferable for BNCT over porphyrins.[21] However, a limited number of boronated phthalocyanines have been reported to date,[19] probably as a consequence of their poor solubility in most solvents, causing problems in their synthesis and purification.[22]

Our interests lie in the preparation of novel tetrapyrrole derivatives in which control over the structure of the bulk material is achieved by the attachment of suitable substituents to the tetrapyrrole core.[23–26] Recently, we have reported boronic esters of octakis(2-hydroxyethylsulfanyl)porphyrazine and its precursor unsaturated dinitrile derivative.[27] In the present study, as part of our ongoing project on tetrapyrrole derivatives with boron-containing substituents, our aim was to prepare a novel phthalocyanine with 4 salicylideniminophenyloxy-substituents on peripheral positions and then prepare its complexes with benzeneboronic acid.

Experimental

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-(4-[4-aminophenoxy])-phthtalocyaninatozinc(II)] (**1**) was synthesized as reported in the literature.[28] Salicylaldehyde and benzeneboronic acid were used as supplied commercially. The progress of the reactions was monitored by TLC (SiO_2). IR spectra were recorded on a Perkin Elmer Spectrum One FTIR (ATR sampling accessory) spectrophotometer; electronic spectra in the UVVis region were recorded with a Scinco S-3100 single beam UV/Vis PDA spectrophotometer. ^{1}H-NMR spectra were recorded on a Varian UNITY INOVA 500 MHz spectrophotometer using TMS as internal reference. ^{13}C- and ^{11}B-NMR spectra were recorded on a Bruker Ultra Shield Plus 400 MHz spectrometer. Boron trifluoride diethyl etherate was used as an external standard in the ^{11}B-NMR spectra. Mass spectra were recorded on a Bruker microflex LT MALDI-TOF MS with 2,5-dihydroxybenzoic acid (DHB) as the matrix. Elemental analyses were performed on a Thermo Flash EA 1112.

Synthesis of 2,9,16,23-Tetra-(4-[4-salicylideneiminophenoxy])-phthtalocyaninato zinc(II) (3)
A solution of 2,9,16,23-tetra-(4-[4-aminophenoxy])-phthtalocyaninato zinc(II)[28] (140 mg, 0.139 mmol) in 20 mL

of dry THF was added dropwise to a solution of 2-hydroxybenzaldehyde (**2**) (0.06 mL, 0.556 mmol) in 15 mL of dry THF and the mixture was refluxed under argon for 15 h. The solvent was evaporated to 1/10 of the initial volume and the reaction mixture was precipitated by adding methanol at room temperature. The crude product was separated by filtration as a green solid, which was dissolved in chloroform (5 mL), and **3** was precipitated by the dropwise addition of methanol. The precipitate was filtered; washed several times successively with cold water, methanol, and ethanol; and dried in vacuo. (Yield: 73 mg, 37%); mp > 200 °C; FTIR (ν max/cm^1): 3058 (ArH), 2920, 1610 (-HC=N), 1574, 1485, 1469, 1393, 1278, 1230 (ArOAr), 1184, 1115, 1088, 1043, 945, 828, 745; ^{1}H-NMR (DMSO-d$_6$)δ (ppm): 13.20 (s, O-H), 9.05-8.99 (dd, 2H, Ar-H), 8.89-8.85 (dd, 2H, Ar-H), 8.74-8.69 (m, 4H, Ar-H), 8.37 (s, 4H, N=CH), 7.74-7.49 (m, 22H Ar-H), 7.42-7.38 (m, 6H, Ar-H), 6.99-6.93 (m, 8H, Ar-H); UVVis (THF): λ max/nm (log ε, L mol^{-1} cm^{-1}): 676 (4.91), 612 (4.18), 353 (4.72), 277 (4.50); Anal. ($C_{84}H_{52}N_{12}O_8Zn$): C, H, N calc. 70.91, 3.68, 11.81 found 70.67, 3.91, 11.70; MS (MALDI-TOF): m/z (%) 1422.676 ([M+1]$^+$, 100).

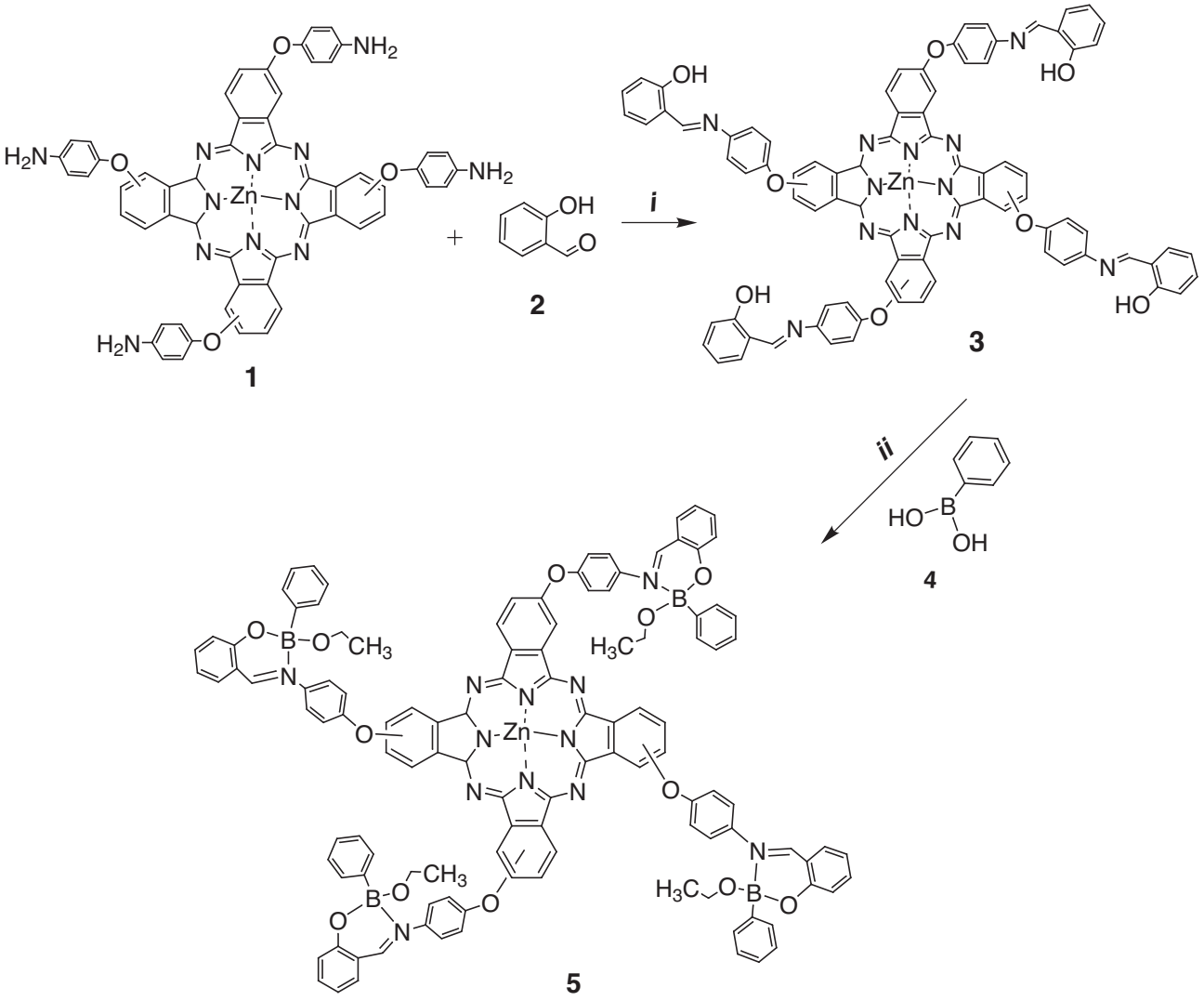
Synthesis of compound 5: In 90 mL of ethanol/toluene (1:8) mixture were dissolved 150 mg (0.105 mmol) of compound 2,9,16,23-tetra-(4-[4-salicylideneiminophenoxy])-phthtalocyaninatozinc(II) **(3)** and 52 mg (0.42 mmol) of benzeneboronic acid. The reaction mixture was refluxed for 12 h under stirring. The water generated in the reaction and part of the solvent were removed using a Dean-Stark trap. Removal of the solvent under reduced pressure left a green solid, which was then washed with a small amount of cold ethanol and dried in vacuo (Yield: 170 mg, 82.75%); mp = 177 °C; FTIR (νmax/cm^1): 3043 (Ar CH), 2956-2845 (alkyl CH), 1603 (C=NH), 1441 (C=C), 1366-1307 (B-O), 1232 (C-O-C), 1086, 1044, 944, 829, 745, 698 (B-Ar); ^{1}H-NMR ($CDCl_3$) δ (ppm): 8.15 (4H, N=CH), 7.84 (m, 8H, Ar-H)), 7.62-7.20 (m, 44 H, Ar-H), 7.11-6.92 (m, 12 H, Ar-H), 3.64 (q, 8H, O-CH2-C), 1.18 (t, 12H, O-C-CH3); ^{13}C-NMR ($CDCl_3$)δ (ppm): 172.55 (Ar C), 169.85 (Ar C), 163.42 (C=N), 160.56 (Ar C), 159.30 (Ar C), 158.10 (Ar C), 157.43 (Ar C), 155.69 (Ar C), 154.63 (Ar C), 143.87 (Ar C), 139.59 (Ar C), 137.31 (Ar C), 136.18 (Ar C), 135.51 (B-Ar CH), 134.59 (N-Ar CH), 133.56 (Ar CH), 132.45 (B-Ar C), 131.99 (Ar C), 131.17 (Ar C), 130.40 (Ar C), 130.08 (Ar C), 128.26 (Ar CH), 127.98 (B-Ar CH), 127.48 (Ar CH), 126.00 (Ar CH), 125.21 (Ar CH), 122.94 (Ar CH), 120.74 (Ar CH), 120.59 (Ar CH), 120.35 (Ar CH), 120.15 (Ar CH), 119.93 (Ar CH), 119.13 (Ar CH), 117.32 (Ar CH), 116.59 (Ar CH), 114.96 (Ar CH), 110.05 (Ar CH), 76.43 (Ar CH), 75.73 (Ar CH), 58.17 (O-Aliphatic CH), 23.21 (O-Aliphatic CH); ^{11}B-NMR (DMSO-d$_6$)δ (ppm): 2.3 (tetracoordinated B); UV-Vis (THF): λmax/nm (log ε, L mol^{-1} cm^{-1}): 677 (4.92), 613 (4.20), 353 (4.74), 279 (4.60); Anal. ($C_{116}H_{88}B_4N_{12}O_{12}Zn$): C, H, N calc. 71.42, 4.55, 8.62 found 71.24, 4.78, 8.83; MS (MALDI-TOF): m/z 1950.364 ([M+1]$^+$).

Results and discussion

To the best of our knowledge, this is the first report of the synthesis of zinc phthalocyanine substituted with boronic acid ester of Schiff base groups. As the first step, Schiff base product **3** was obtained from the reaction of salicylaldehyde with 2,9,16,23-tetra-(4-[4-aminophenoxy])-phthtalocyaninatozinc(II) (**1**)[28] in THF under argon atmosphere. Salicylidenimino groups on the peripheral positions were especially preferred due to the presence of -OH and azomethine donor sites capable of binding to benzeneboronic acid. The Schiff base structure obtained from the reaction of salicylaldehyde with amine groups of compound **1** presents 2 active sides to boron reagent: the OH group, which can form boron esters, and the nitrogen, which can give N-B coordination compounds.[29]

Hydrolytic stability of the weaker O-B bond in the boron complexes can be enhanced by the formation of a strong coordinative N-B bond.[14,16]

Treatment of compound **3** with benzeneboronic acid in ethanol/toluene mixture at reflux temperature for 12 h using a Dean-Stark apparatus in order to remove water generated through the esterification reaction afforded the phthalocyanine **5** substituted peripherally with 4 benzeneboronic acid esters of Schiff base groups (Scheme). The reaction was completed to give a green solid product in a relatively high yield (82.75%).



Scheme. Synthetic route for compound **3** and **5** (i) THF, reflux; (ii) Toluene: Ethanol (8/1, v/v), reflux, Dean-Stark.

In the esterification reaction, benzeneboronic acid was used rather than diphenylborinic acid because it was aimed to enhance the solubility of the Schiff base esters by introducing an ethoxy group obtained from the condensation reaction of ethanol with the second -OH group of the benzeneboronic acid into the structure. It is well reported in the literature that the solubility of the aryl esters of diphenylborinic acid is lower than that

of the alkyl aryl esters of benzeneboronic acid.[30,31] In the present case, enhancement in the solubility of the compound **5** is a consequence of these ethoxy groups attached to boronic ester. While compound **3** is soluble in chloroform, toluene, DMF, and DMSO, due to the presence of ethoxy groups in its structure, compound **5** is also soluble in methanol and ethanol and slightly soluble in diethyl ether in addition to the above solvents.

Both of the new compounds obtained in this study have been characterized as far as possible by spectroscopic techniques (IR and ^{1}H-, ^{13}C-, ^{11}B-NMR) and mass spectrometry.

The IR spectrum of the phthalocyanine derivative **3** showed a strong band at 1610 cm^{-1} attributed to the stretching frequency of the C=N bond. Aromatic C-H peaks were observed around 3058 cm^{-1} and aromatic C-O-C stretching was observed at 1230 cm^{-1} as a strong band. In the ^{1}H-NMR spectrum of **3** taken in DMSO-d$_6$ a signal for CH=N proton was observed at 8.37 ppm. The aromatic protons appeared as multiplets at 9.05-8.69 ppm and 7.74-6.93 ppm. The presence of the characteristic molecular ion peak at m/z = 1422 [M]$^{+}$ in the mass spectrum also confirmed the proposed structure.

Spectroscopic data allowed full characterization of the new phthalocyanine derivative **5**. The IR spectrum of **5** exhibited a strong adsorption band at 1603 cm^{-1}, attributable to the stretching band for the HC=N group. This band is shifted to lower wavenumbers compared to the same band in compound **3** (1610 cm^{-1}) due to the coordination of the nitrogen atom to boron.[32] Aliphatic CH stretching vibrations at 2956-2845 cm^{-1} confirm the alcoholysis of the B-OH groups to B-OR. The appearance of a new band in the region 1366-1307 cm^{-1} indicates the formation of a B–O bond.[33] Furthermore, the stretching vibrations of C-O-C (1232 cm^{-1}) and monosubstituted benzene (698 cm^{-1}) appeared at expected frequencies.

The ^{1}H-NMR and ^{13}C-NMR spectra of compound **5** were obtained in CDCl$_3$ In the ^{1}H-NMR spectrum of compound **3**, the OH proton was observed as a singlet at δ 13.20 ppm but it did not appear in the spectrum of compound **5**. This indicates the condensation of B–OH groups with Ar-OH units. Moreover the protons of OCH$_2$ and CH$_3$ appeared as a quartet and triplet at 3.64 and 1.18 ppm, respectively The aromatic protons were observed around 7.84-6.92 ppm as multiplets The ^{1}H-NMR spectrum of compound **5** also shows a singlet signal at 8.15 ppm for the imine proton.

The ^{13}C-NMR data of **5** confirm the results of the ^{1}H-NMR spectrum. The carbon atoms of the phenyl group attached to the boron atom appeared at 135.51, 132.45, and 127.98 ppm. Furthermore, as additional evidence of ester formation, the carbon signals of the ethoxy group were observed at 58.17 and 23.21 ppm. Moreover, the MALDI-TOF mass spectrum showed the molecular ion peak at m/z = 1950.

The ^{11}B spectrum of compound **5** in DMSO-d$_6$ at room temperature showed a broad signal at 2.3 ppm. This signal at 2.3 ppm was attributed to benzeneboronic esters coordinated with the nitrogen atom.[11,34] Therefore, for compound **5**, the intramolecular N$\rightarrow$B coordinated system should be present according to these data.[35,36]

In substituted metallo and metal-free phthalocyanines, strong absorption is detected in the visible region between 650 and 690 nm, termed the Q band, and in UV between 320 and 370, called the Soret band.[37] The Soret band arises from the deeper π-levels/LUMO transition and the Q band is attributed to the $\pi - \pi^*$ transition from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO) of the phthalocyanine ring.[37]

The UV-Vis spectra of **3** and **5** recorded in THF are presented in the Figure. The absorption spectrum of phthalocyanine **3** exhibiting a strong Q band at 676 nm due to a single $\pi\pi^*$ transition with shoulders at 612

nm is similar to that previously reported for 2,9,16,23-tetra-(4-[4-aminophenoxy])-phthtalocyaninatozinc(II).[28] However, the Soret (B) band of compound **3** is shifted to a longer wavelength in comparison to that of compound **1**.

The Q-band absorption peak of phthalocyanine **5** appeared at 677 nm, suggesting that introduction of boronated substituents into peripheral substituents has no significant effect on the position of Q band in UV-Vis spectrum of compound **5** compared to phthalocyanine **3**. Furthermore, the boronated phthalocyanine **5** exhibited a band at 279 nm with a higher absorbance value than that of phthalocyanine **3** at 277 nm. This increase in the absorbance value can be attributed to the presence of the benzene groups of boronated substituents attached to the structure of phthalocyanine **5** by the condensation reaction of benzeneboronic acid and phthalocyanine **3**.

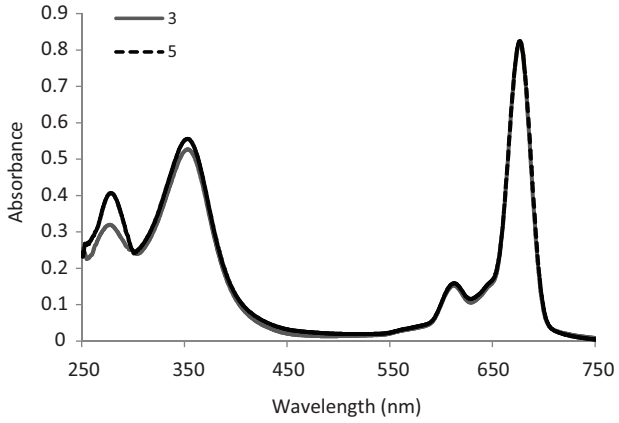


Figure. Absorption spectra of compound **3** and **5** in THF.

The identical position of the Q bands in non-boronated and boronated phthalocyanine derivatives is in accordance with expectations. First of all, boronated groups are isolated from the phthalocyanine core by phenoxy bridges. Secondly, the Lewis acidity of the boron atom in phthalocyanine **5** is diminished as a result of the presence of oxygen atoms adjacent to them; the lone pair of oxygen atoms can delocalize on the vacant p orbital of the boron atom to reduce the Lewis acidity of the boron leading a weaker B-N interaction.[38] The latter also weakens the B-N interaction in phthalocyanine **5**.

In this work, we demonstrated the synthesis of a novel Zn phthalocyanine substituted with salicylideniminophenyloxy substituents on peripheral position from the reaction of 4-aminophenoxy substituted phthalocyanine and salicylaldehyde. Subsequent condensation of salicylidene Schiff base functionalities with benzeneboronic acid in ethanol/toluene solvent mixture at reflux temperature produced a new Zn phthalocyanine carrying benzeneboronic acid ester groups. Spectrophotometric data indicated that the boron atom in the boronate groups is in tetracoordinated state with formation of a coordinative N-B bond. This newly synthesized boronated phthalocyanine exhibited sufficient air stability during the purification and characterization processes due to the presence of a B-N interaction in the compound.

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