

Synthesis and X-Ray Single Crystal Study of 5-(4,4,5,5 – Tetramethyl – 1,3,2 – Dioxaborolane) – 10,20 – Diphenylporphyrin (Sintesis dan Kajian Sinar-X Hablur Tunggal 5-(4,4,5,5-tetrametil- 1,3,2-dioxaborolana)-10,20-difenilporfirin)

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ABSTRACT

Borylated porphyrin is one of building blocks in coupling reactions to obtain the multiporphyrin containing two, three or more subunits of porphyrins. In this study, one of borylated porphyrin derivatives, 5-(4,4,5,5 – tetramethyl – 1,3,2 – dioxaborolane) -10,20 – diphenylporphyrin (B-DPP) was synthesized through four steps of reactions. The building block of porphyrin, dipyrromethane was synthesized through a condensation reaction in the presence of trifluoroacetic acid as catalyst. Subsequently, A_2B_2 type of porphyrin was obtained by Lindsey condensation reaction followed by bromination reaction to produce porphyrin halide. Suzuki cross coupling reaction between porphyrin halide and pinacolborane with Pd (II) catalyst afforded 40% of borylated porphyrin. The product was successfully characterized by using nuclear magnetic resonance spectroscopy (NMR) and UV-Visible spectroscopy (UV-Vis). This compound crystallized from a mixture of dichloromethane/methanol to give violet needle-like crystal. Crystallographic studies showed this compound crystallized in monoclinic system with space group of $P2_1/c$.

Keywords: Borylated porphyrin; porphyrin; Suzuki cross coupling; X-ray structural study

ABSTRAK

Sebatian porfirin borilasi merupakan salah satu blok binaan dalam tindak balas penggandingan untuk mendapatkan sebatian multiporfirin yang terdiri daripada dua, tiga atau lebih unit porfirin. Melalui kajian ini, salah satu terbitan sebatian porfirin borilasi, 5-(4,4,5,5-tetrametil-1,3,2-dioxaborolana)-10,20-difenilporfirin (B-DPP) telah disintesis melalui empat langkah tindak balas. Blok binaan asas iaitu dipirometana disintesis melalui tindak balas penjejatan dengan kehadiran asid trifloroasetik, selaku mangkin. Porfirin jenis A_2B_2 diperolehi melalui tindak balas penjejatan Lindsey dan diikuti dengan tindak balas pembrominan untuk menghasilkan sebatian porfirin halida. Tindak balas penggandingan Suzuki antara sebatian porfirin halida dan pinakolborona menggunakan bahan pemangkin Pd (II) menghasilkan 40% sebatian porfirin borilasi. Sebatian ini telah berjaya dicirikan dengan menggunakan teknik resonans magnetik nuklear (RMN) dan spektroskopi ultra-lembayung boleh nampak (UL-BN). Sebatian ini menghablur daripada sistem campuran pelarut diklorometana/methanol dan menghasilkan kristal jejarum berwarna ungu. Kajian kristalografi menunjukkan sebatian ini terhablur dalam sistem monoklinik dengan kumpulan ruang $P2_1/c$.

Kata kunci: Kajian struktur sinar-X; porfirin; porfirin borilasi; tindak balas penggandingan Suzuki

INTRODUCTION

Borylated porphyrins or Suzuki porphyrins (Hyslop et al. 1998) have great importance in porphyrin synthesis because of their key role in coupling reactions especially Suzuki-Miyaura coupling reactions (Prakash & Sankar 2017). The boron centre in borylated porphyrins has capability to form coordinate bonds with different heteroatoms including oxygen, nitrogen, sulphur and phosphorus (Nishiyabu et al. 2011). Therefore, these porphyrins are not only useful building blocks for the synthesis of multiporphyrin assemblies (Yedukondalu & Ravikanth 2010) but also leads to the formation of other supramolecular assemblies as well. Numerous contributions have been carried out in the development of borylated porphyrins all over the world particularly in

the synthesis of porphyrin-based molecular assemblies (Hata et al. 2007).

The route to obtain borylated porphyrin start with the synthesis of dipyrromethane, which is the smaller building block in the world of porphyrin synthesis. Dipyrromethane occupy a central place in porphyrin chemistry (Joydev et al. 2003). There are many dipyrromethane synthesis route have been developed since 1994. One of the most fascinating methods involved the Kugelrohr distillation (Boyle et al. 1999) for dipyrromethane purification. The next synthetic route to obtain borylated porphyrin is the formation of 5,15- A_2B_2 porphyrin systems. A_2B_2 type porphyrins are easily prepared by a [2+2] condensation using dipyrromethane and the respective aldehyde with *meso*-substituent (Lindsey 2000). Bromination reaction

produced bromine-substituted porphyrin that can be used in cross-coupling reaction like Heck (Locos & Arnold 2006), Sonogashira (Aratani et al. 2003), Stille (Dimagno 1993) and also Suzuki (Aratani et al. 2003).

The final step of this synthetic route of reaction is the formation of borylated porphyrin from aryl halide porphyrin via Suzuki cross-coupling reaction. In this reaction, pinacolborane functions as *trans*-metalating reagent, enabling the conversion of bromine-substituted porphyrin into borylated porphyrin (Murata et al. 1997). Muntaz et al. (2011) reported the synthetic route of borylated porphyrin (Scheme 1). However, the X-ray single crystal study of this compound has not yet been reported. Therefore, a detailed discussion on the synthetic route and X-ray single crystal data of this compound were first described in this article.

MATERIALS AND METHODS

MATERIALS AND PHYSICAL MEASUREMENT

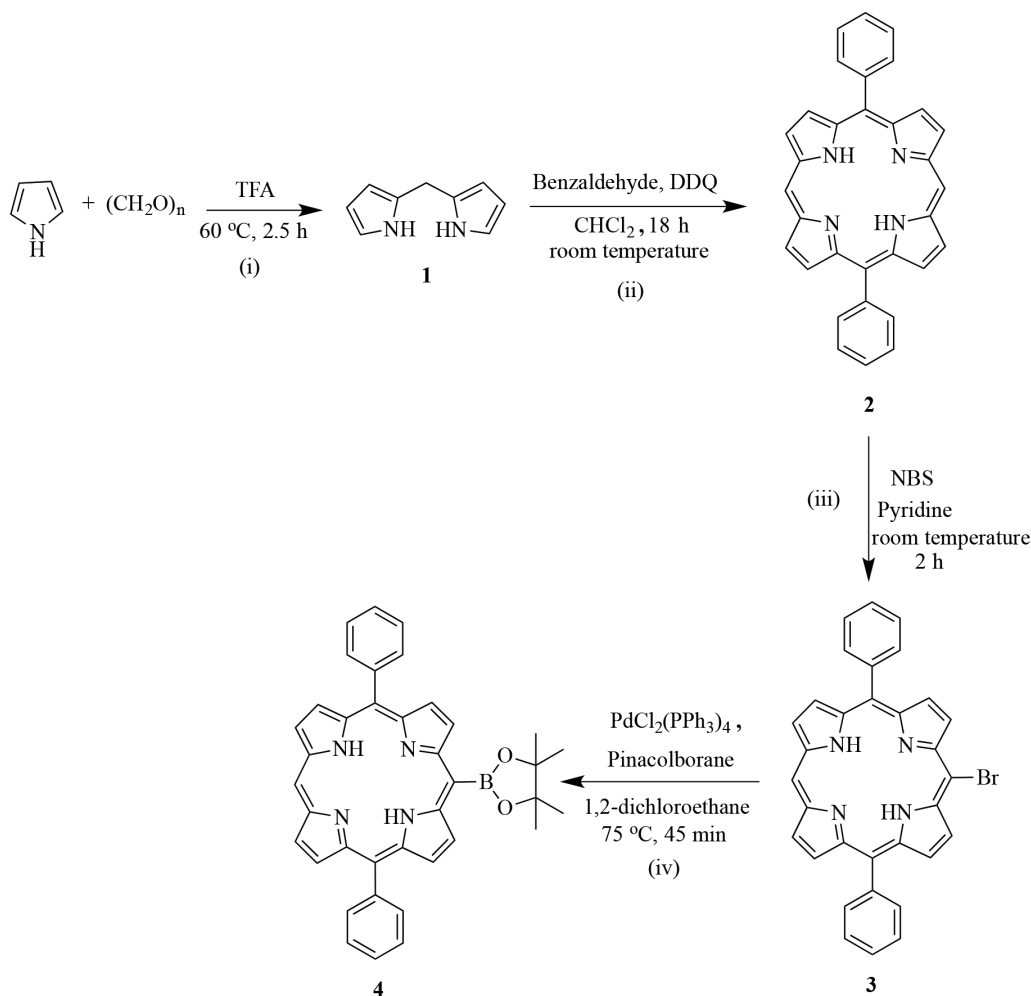
All the chemicals utilized in this work were commercially available from Sigma Aldrich and Friendschmidth and were

used without further purification. Dry dichloromethane and 1,2-dichloroethane were prepared by distillation over phosphorus pentoxide (P_2O_5) whereas dry triethylamine (TEA) was prepared by distillation without using drying agent.

Nuclear Magnetic Resonance (1H and ^{13}C) experiments were performed on a Bruker 400 MHz instrument using $CDCl_3$ as the solvent. UV-VIS spectra were recorded using UV-1800 Shimadzu Spectrophotometer using dichloromethane as the solvent. Single crystal X-ray experiments was performed on a Bruker D-QUEST diffractometer (Bruker, AXS Inc., Madison, WI, USA) using graphite - monochromated.

SYNTHESIS OF DIPYRRROMETHANE (1)

Paraformaldehyde (346 mg, 0.12 mol) and pyrrole (200 mL, 0.23 mmol) were stirred with the continuous flow of nitrogen gas by using Schlenk technique. The solution was heated to $60^\circ C$ and heat source was removed. Trifluoroacetic acid (TFA) (0.2 mL) was added immediately. A sharp increase in temperature ($8-10^\circ C$) was observed and the



SCHEME 1. Synthesis of borylated porphyrin (i) Synthesis of dipyrromethane catalyzed by trifluoroacetic acid (38%) (ii) Synthesis of 5,15-porphyrin (A_2B_2 type) by Lindsey condensation reaction (30%) (iii) Bromination reaction (67%) (iv) Borylation by Suzuki cross coupling reaction (40%)

solution became dark. The solution was heated not more than 90°C for half an hour. Sodium hydroxide (NaOH) (700 mg in 20 mL H₂O) was added and the reaction mixture was left to cool to room temperature. The mixture was filtered through silica gel and eluted with dichloromethane (DCM). The solvents were evaporated and the product was purified by Kugelrohr glass oven Buchi 585 at 180°C (start at 50°C and increased slowly by 10°C) to yield dipyrromethane **1** (DPM) as pale yellow crystal.

SYNTHESIS OF 5,15-DIPHENYLPORPHYRIN (2)

Dry dichloromethane (DCM) (700 mL) was placed in a three-neck round bottom flask equipped with magnetic stirrer and nitrogen inlet (Schlenk technique). The flask was covered with aluminium foil. Compound **1** (1.0 g, 6.84 mmol) was added followed by benzaldehyde (0.7 mL) and the resulting mixture was degassed with nitrogen gas for another 10 min. Trifluoroacetic acid (TFA) was added and the mixture was left to stir for 18 h at room temperature. After 18 h, 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) was added and the mixture was left to stir for another hour. Triethylamine (TEA) (5 mL) was added later to quench the reaction. The mixture was filtered through silica and eluted with dichloromethane. The solvent was removed followed by recrystallization of the crude product from dichloromethane/methanol. After 96 h, the product was washed with methanol to yield 5,15-diphenylporphyrin **2** as violet solid.

SYNTHESIS OF 5-BROMO-10,20-DIPHENYLPORPHYRIN (3)

A solution of compound **2** (300 mg, 0.65 mmol) in chloroform (CHCl₃) (150 mL) and pyridine (0.1 mL) was chilled at to 0°C. N-bromosuccinimide (NBS) (0.9 g, 0.52 mmol) was added and the progress of reaction was monitored at five min interval for 2 h by TLC using dichloromethane/hexane (1:1) as eluent. The reaction was quenched with acetone (2 mL). The solution was evaporated and the residue dissolved in chloroform (CHCl₃). Then, the solution was filtered through silica plug and solvent was removed under reduced pressure. The crude was purified by recrystallization from chloroform/methanol to yield 5-bromo 10,20-diphenylporphyrin **3** as violet solid.

SYNTHESIS OF OF 5-(4,4,5,5-TETRAMETHYL-1,3,2-DIOXABOROLANE)-10,20-DIPHENYLPORPHYRIN (4)

Porphyrin **3** (126 mg, 0.23 mmol) was dissolved in dry dichloroethane (10 mL) and dry TEA under nitrogen flow (Schlenk technique). This was followed by three cycle of freeze-pump and thaw before the addition of pinacolborane and PdCl₂(PPh₃). The mixture was stirred at 75°C for 45 min and the reaction monitored by TLC. The residue was filtered through silica to remove the catalyst and was purified by column chromatography (hexane/dichloromethane = 1:1). The crude was recrystallized from dichloromethane/methanol to yield compound **4** as violet colour crystal.

RESULTS AND DISCUSSION

DIPYRROMETHANE (1)

Yield 6 g (38%); ¹H NMR (400 MHz, CDCl₃) δ 7.70 (s, 2H), 6.64 (dd, *J* = 1.60 Hz, 2H) 6.21 (dd, *J* = 2.80 Hz, 2H), 6.10 (dd, 2H), 3.96 ppm (s, 2H) ppm. The NMR data were in accordance with the literature (Basic 2010).

5,15-DIPHENYLPORPHYRIN (2)

Yield 500 mg (30%) mp > 300°C; R_f 0.44 (hexane/DCM, 3:2 v/v); ¹H NMR (400 MHz, CDCl₃) δ -3.09 (s, 2H), 7.85 (m, 6H), 8.31 (m, 4H), 9.13 (d, *J* = 4.40 Hz, 4H), 9.43 (d, *J* = 4.40 Hz, 4H), 10.34 (s, 2H) ppm. ¹³C NMR (100.6 MHz, CDCl₃) δ 147.2, 145.2, 141.4, 134.9, 131.7, 131.1, 127.8, 127.0, 119.1, 105.3 ppm; UV-Vis (CH₂Cl₂): λ_{max} nm (log ε) = 403.6 (5.70), 505.2 (4.62), 540.8 (4.35), 575.6 (4.38), 631.2 (4.28). The NMR data were in agreement with the literature (Bruckner 1998).

5-BROMO-10,20-DIPHENYLPORPHYRIN (3)

Yield 188 mg (67%) ; mp = 340 - 351°C ; R_f 0.5 (hexane/DCM, 4:1 v/v); ¹H NMR (400 MHz, CDCl₃) δ -3.01 (s, 2H), 7.82 (m, 6H), 8.24 (d, 4H), 8.98 (d, *J* = 4.4 Hz, 4H), 9.28 (d, *J* = 4.40 Hz, 2H), 9.77 (d, *J* = 4.4 Hz, 2H), 10.16 (s, 1H) ppm; ¹³C NMR (100.6 MHz, CDCl₃) δ 141.4, 134.7, 132.6, 132.1, 131.8, 127.9, 126.9, 120.3, 105.6, 103.7; UV-Vis (CH₂Cl₂): λ_{max} nm (log ε) = 414.0 (5.56), 510.8 (4.55), 544.8 (4.38), 586.4 (4.37), 642.8 (4.31) (Kato et al. 2004).

5-(4,4,5,5-TETRAMETHYL-1,3,2-DIOXABOROLANE)-10,20-DIPHENYLPORPHYRIN (4)

Yield 50 mg (40%); mp = 347 - 351°C; R_f 0.3 (hexane/DCM, 1:1, v/v); ¹H NMR (400 MHz, CdCl₂) δ -3.11 (s, 2H), 1.89 (s, 12H) 7.84 (m, 6H), 8.29 (d, *J* = 5.2 Hz 4H), 9.04 (d, 2H), 9.10 (d, 2H), 9.37 (d, *J* = 4.4 Hz, 2H), 9.93 (d, *J* = 4.4 Hz, 2H), 10.31 (s, 1H) ppm; ¹³C NMR (100.6 MHz, CDCl₃) δ 142.0, 134.8, 132.2, 131.9, 131.3, 131.1, 127.7, 126.8, 119.5, 106.3, 85.4, 25.4 ppm; UV-Vis (CH₂Cl₂): λ_{max} nm (log ε) = 409.6 (5.73), 506.0 (4.69), 548.2 (4.40), 558.4 (4.47), 640.8 (4.35).

CHARACTERIZATION

NMR STUDIES

All of the desired peak signals with suitable integrations for compound **4** were displayed in Figure 1. The successful formation of compound **4** was proved by the presence of signal at chemical shift around 1.90 ppm (**H7**) that represent 12 protons of methyl group within the borone group. Besides, the presence of peak at 10.31 that represent one proton proved that there was one free *meso* position in compound **4**. The β-proton (**H1**, **H2**, **H3**, **H4**) showed peaks at 9.94, 9.39, 9.10 and 9.05 ppm with dublet multiplicity. Whereas, the chemical shift in range of 7.82 to 8.29 ppm belongs to the proton of phenyl group that attached to two

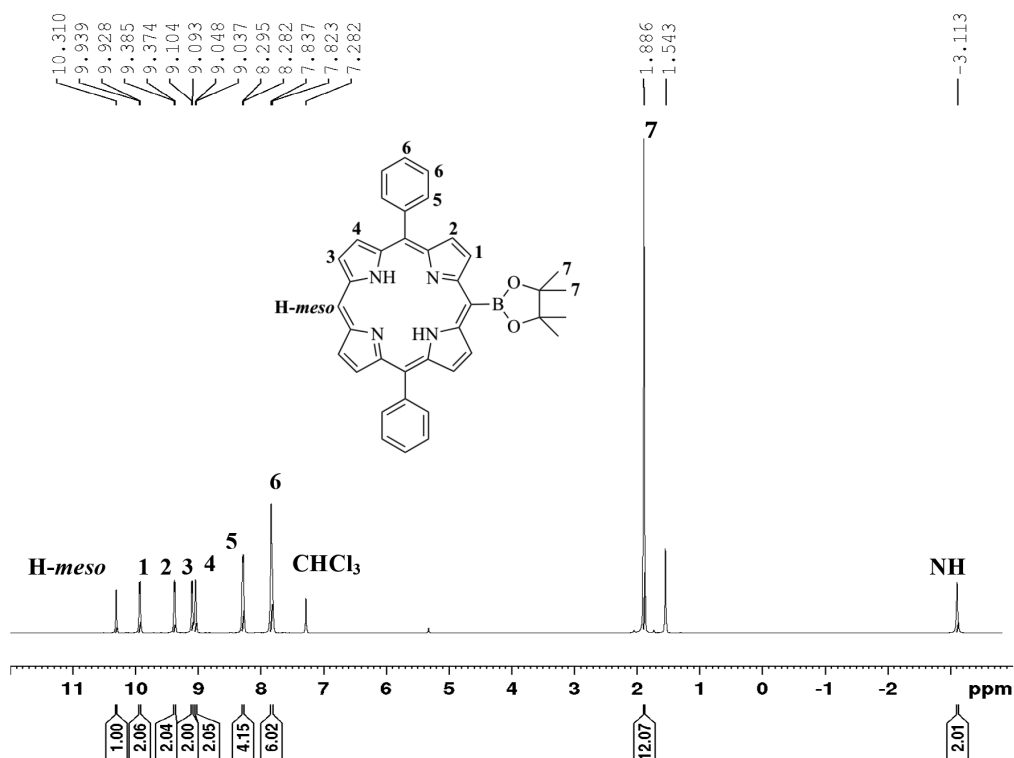


FIGURE 1. ¹H-NMR (400 MHz) spectrum of compound **4** in CDCl₃ at room temperature

meso-position of porphyrin ring. The signal at the most shielded region, which was negative region become an identity of free base porphyrin compound since this peak belongs to inner NH group of porphyrin ring. This chemical shift was highly shielded due to the anisotropy effect that occurred around the porphyrin ring.

Based on ¹³C NMR spectrum of compound **4** in Figure 2, there were 12 peaks of carbon signals that represent 12 carbons in this compound. Two signals at high field region

prove the presence of 2 types of carbons in borane group that attach to main porphyrin ring. Whereas all the signals that represent carbon of main porphyrin ring and two phenyl group at *meso* position showed peaks at 106.3, 119.5, 126.8, 127.7, 131.1, 131.3, 134.8 and 142.0. However, there were few signals did not appear since this compound is symmetry and overlaid of peaks might be occurred. All the chemical shift and data of ¹H-NMR and ¹³C NMR of compound **4** satisfied with literature data (Muntaz et al. 2011).

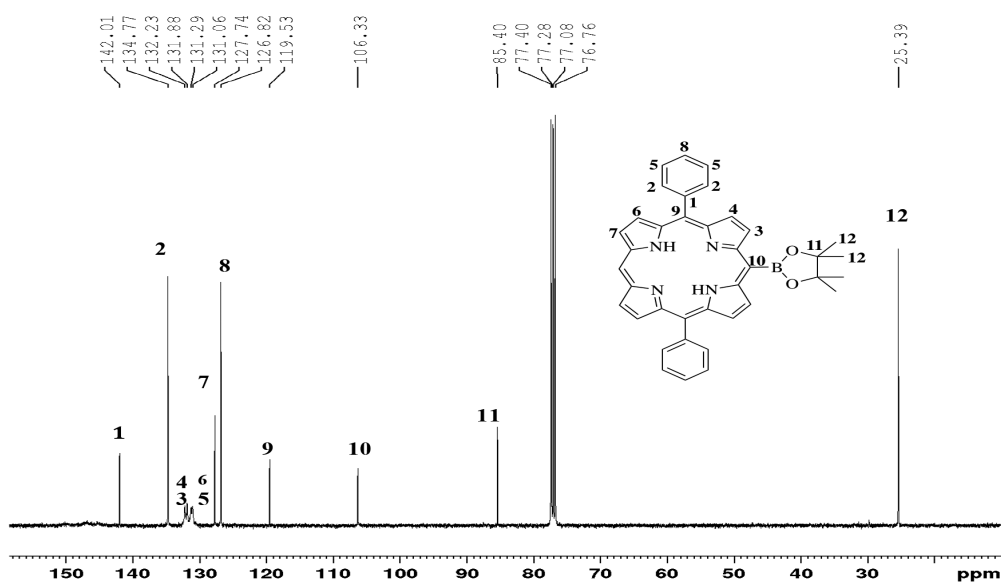


FIGURE 2. ¹³C NMR (100 MHz) spectrum of compound **4** in CDCl₃ at room temperature

UV-VIS STUDIES

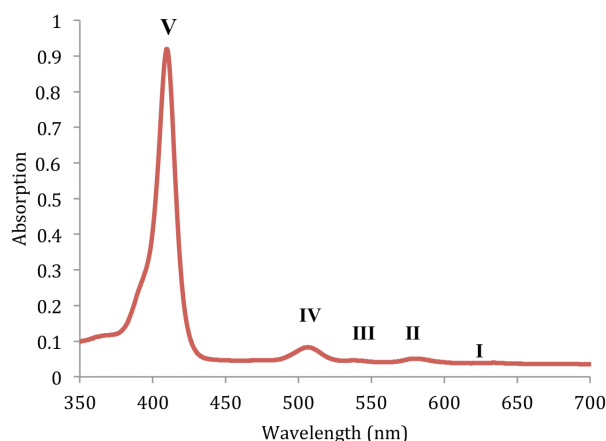
The intensity and colour of porphyrins are derived from the highly conjugated π -electron systems (Giovanetti 2012). The most fascinating feature of porphyrin is the UV-Visible spectra that consist of two distinct regions which are in the near ultraviolet and in the visible region. Based on the UV-Vis spectrum shown in Figure 3, the first band that appeared around 400 nm was called as Soret or B band that represent the transition from the ground state to the second excited state ($S_0 - S_2$). The low intensity bands that formed in range of 500 to 700 nm were Q bands and it showed the weak transition state from ground state to first excited state ($S_0 - S_1$).

X-RAY CRYSTALLOGRAPHIC STUDIES

The boronated porphyrin **4** is crystallized from dichloromethane/methanol and afforded needle-like and

violet coloured crystals. It is crystallized in crystal system of monoclinic with space group of $P2_1/c$. Figure 4 shows the structure molecular with labels of the porphyrin. The molecule does not have asymmetric unit since it is not centrosymmetric. The porphyrin body itself (N1-N4)/(C1-C5)/(C12-C32) possess a planar geometry with maximum deviation of 0.111(3) Å for atom C16. Both benzenes are perpendicular with the porphyrin at C23/C22/C21/C28 and C4/C5/C6/C7 with dihedral angle at 59.83 (12)° and 64.12 (12)°. The (borone group) is also slightly perpendicular at C33/O1/B1/C32 with dihedral angle 22.07 (13)°. The overall crystallographic data listed in Tables 1 and 2 show the simplified bond lengths and bond angles are in normal range. The full data was provided in supplementary data.

From the crystal structure, pair of the molecules is connected by carbon's hydrogen of benzene ring to the nitrogen of porphyrin **4** with intermolecular hydrogen



Concentration: 4.0×10^{-6} M. I-IV: Q bands, V: Soret band

FIGURE 3. UV-Vis spectrum of compound **4** in dichloromethane at room temperature

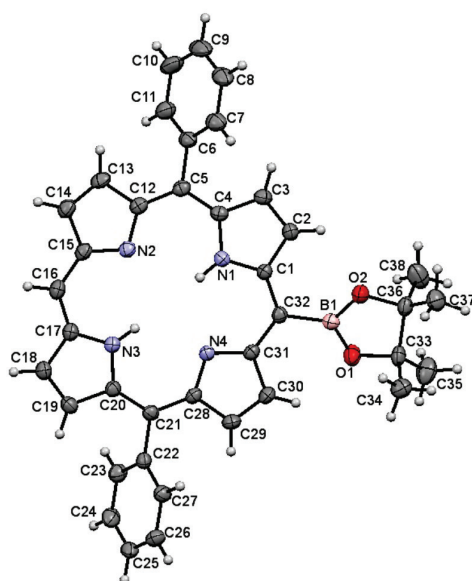


FIGURE 4. ORTEP diagrams of porphyrin drawn at 50% probability displacement ellipsoid

TABLE 1. Crystallographic data of compound 4

Crystal parameters	Porphyrin	
CCDC deposition number	1818771	
Empirical formula	C ₃₈ H ₃₃ B N ₄ O ₂	
Formula weight	588.49	
Temperature	293(2) K	
Wavelength	0.71076 Å	
Crystal system	Monoclinic	
Space group	P2 ₁ /c	
Unit cell dimensions	a = 8.495(6) Å b = 26.643(14) Å c = 13.995(7) Å	α = 90°. β = 105.51(2)°. γ = 90°.
Volume	3052(3) Å ³	
Z	4	
Density (calculated)	1.281 Mg/m ³	
Absorption coefficient	0.080 mm ⁻¹	
F(000)	1240	
Crystal size	0.320 × 0.190 × 0.060 mm ³	
Independent reflections	7604 [R(int) = 0.2788]	
Data / restraints / parameters	7604 / 0 / 418 ×	
Final R indices [I > 2σ(I)]	R1 = 0.0855, wR2 = 0.1672 ×	
R indices (all data)	R1 = 0.1679, wR2 = 0.1996 ×	

TABLE 2. Bond length and angle data for compound 4

Porphyrin			
Bond	Dist.	Bond	Dist.
N(1)-C(1)	1.370(4)	N(2)-C(12)	1.364(4)
N(1)-C(4)	1.380(4)	O(2)-C(36)	1.462(4)
B(1)-O(1)	1.367(4)	N(3)-C(17)	1.362(4)
B(1)-O(2)	1.372(4)	N(3)-C(20)	1.368(4)
B(1)-C(32)	1.567(4)	N(4)-C(31)	1.365(3)
O(1)-C(33)	1.469(3)	N(4)-C(28)	1.376(3)
N(2)-C(15)	1.362(4)	C(4)-C(5)	1.394(4)
Bond	Angle (°)	Bond	Angle (°)
C(1)-N(1)-C(4)	111.0(2)	N(2)-C(12)-C(13)	110.6(2)
O(1)-B(1)-O(2)	111.9(3)	N(2)-C(15)-C(16)	125.8(3)
O(1)-B(1)-C(32)	126.1(3)	N(2)-C(15)-C(14)	110.7(3)
O(2)-B(1)-C(32)	121.9(3)	N(3)-C(17)-C(16)	126.2(3)
B(1)-O(1)-C(33)	107.6(2)	N(3)-C(17)-C(18)	106.6(3)
N(1)-C(1)-C(32)	127.1(2)	N(3)-C(20)-C(21)	125.5(2)
N(1)-C(1)-C(2)	106.0(2)	N(3)-C(20)-C(19)	106.7(2)
B(1)-O(2)-C(36)	108.0(2)	C(1)-C(32)-B(1)	116.9(2)
C(31)-N(4)-C(28)	105.7(2)	C(31)-C(32)-B(1)	118.6(2)
N(1)-C(4)-C(5)	127.5(3)	O(1)-C(33)-C(34)	106.9(2)
N(1)-C(4)-C(3)	105.7(2)	O(1)-C(33)-C(35)	107.6(2)
N(4)-C(28)-C(21)	126.6(3)	O(1)-C(33)-C(36)	101.3(2)
N(4)-C(28)-C(29)	110.4(2)	O(2)-C(36)-C(38)	107.4(3)
N(4)-C(31)-C(32)	126.2(2)	O(2)-C(36)-C(37)	107.8(3)
N(4)-C(31)-C(30)	110.0(2)	O(2)-C(36)-C(33)	101.7(2)
N(2)-C(12)-C(5)	125.1(3)	C(38)-C(36)-C(33)	114.3(3)

bond of C24-H24...N4. Figure 5 shows the molecule with intermolecular hydrogen bond at a-axis and Table 3 listed the hydrogen bond length and bond angle for porphyrin.

CONCLUSION

The borylated porphyrin, 5-(4,4,5,5 – tetramethyl – 1,3,2 – dioxaborolane) – 10,20 – diphenylporphyrin **4**

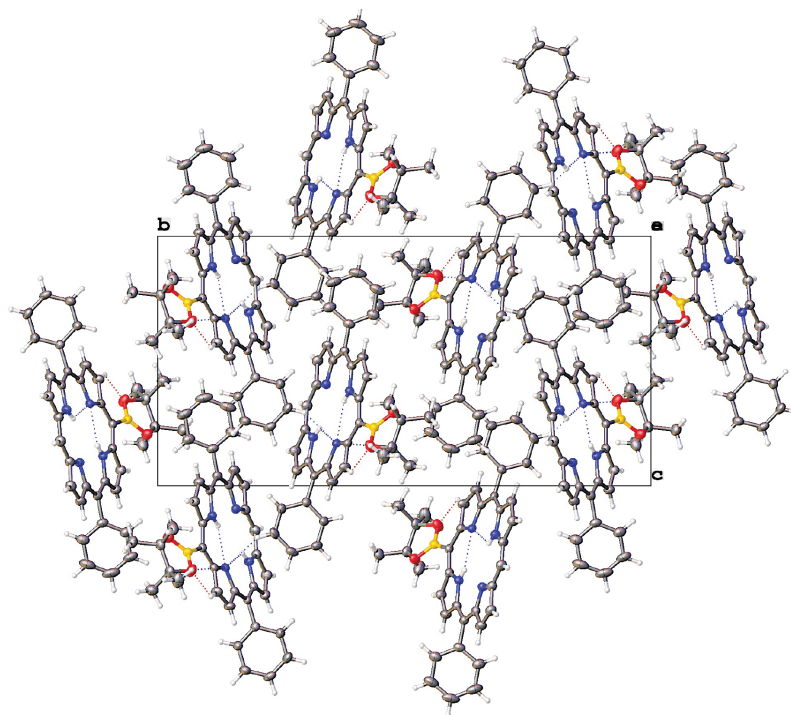


FIGURE 5. Molecule packing of porphyrin at a axis. The dashed lines indicate the C—H···N hydrogen bond

TABLE 3. Hydrogen bond lengths (Å) and bond angles for compound **4**

Compound	D—H···A	D—H	H···A	D···A	D—H···A	Symmetry code
Porphyrin	C24—H24···N4	0.93	2.47	3.295(4)	148	x, -y-1/2, z-3/2

was successfully synthesized through a series of step, starting with the synthesis of dipyrromethane followed by formation of 5,15-diphenylporphyrin *via* Lindsey condensation reaction. The bromination reaction takes place using *N*-bromosuccinimide to yield brominated porphyrin in 67% yield. Subsequently, the Suzuki cross-coupling reaction between brominated porphyrin and pinacolborane yielded 40% of borylated porphyrin. Borylated porphyrin **4** was further crystallized in the solvent mixture of dichloromethane and methanol and afforded violet colored needle-like crystal. Based on The Cambridge Crystallographic Data Centre (CCDC) database, the X-ray single crystal of this borylated porphyrin **4** has not yet been reported. This compound has monoclinic system with space group of $P2_1/c$.

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