

Selected Papers

μ-Oxo-Bridged Subphthalocyanine Dimers: Preparation and Characterization by X-ray Structure Analysis

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In connection with our previous research on μ-oxo-bridged metal phthalocyanine dimers, we have synthesized μ-oxo-bridged subphthalocyanine dimers (μ-oxo subpc dimers) with various peripheral substituents and studied their properties. Compared to the corresponding subpc monomer, the Q-band absorption of subpc dimers broadens, the wavelength undergoes a blue shift by approximately 30–35 nm, and the molar absorptivity is enhanced almost 1.5–2.0 times. Additionally, its solubility in various organic solvents is much improved. We carried out an X-ray crystal structure analysis of [{B(subpc)}$_2$O] and provided a direct observation of its asymmetric structure for the first time.

Phthalocyanines are well-known, two-dimensional, 18π-electron systems with unusual electrical and optical properties that lead to interesting potential technological applications owing to their light and/or heat resistance, large absorptivity, narrow Q-band, feasibility for mass-production, and, in particular, their durability for industrial use as compared to common NIR dyes such as cyanine and metal-chelated azo dyes. Their lowest homologs, subphthalocyanines (subpcs), are composed of three diiminoisoindole rings capable of coordinating with a core boron atom and warped 14π-electron aromatic systems. Subpcs are also attracting considerable attention for their applications as functional optical dyes for recording media and neon-cutting filters in plasma displays because their chemical and/or physical properties differ from those of phthalocyanines.

During our ongoing research on the chemistry of μ-oxo-bridged dimers of a chromophore, we have already reported the synthesis and the properties of μ-oxo-bridged homometal phthalocyanine dimers[1,2] and μ-oxo-bridged heterometal phthalocyanine dimers.[3] We discovered that some derivatives with a specific polymorph have intriguing characteristics amenable for a charge generating material of an organic photoconductor.

Recently, there has been an increase in the number of reports regarding derivatives of subphthalocyanine[4] and subpc dimer derivatives such as fused-,[5–7] μ-oxo-bridged-,[8] and some spacer-linked-types.[9] In addition, dimers of subpc with pc are known.[10] A peripheral nonsubstituted μ-oxo-bridged subpc dimer was isolated and characterized by Geyer et al. in 1996;[11] the corresponding analog with a *tert*-butyl group as its peripheral substituent has only been discussed.[12] Therefore, the synthetic methodology and the characterization of μ-oxo subpc dimers with various peripheral substituents are not sufficiently developed for applications as industrial dyestuffs.[13] Notably, an X-ray crystal structure of a neutral μ-oxo subpc dimer has not yet been reported.[14]

As the wavelength of the light sources employed in optical devices has shortened recently due to the discovery of a blue-ray diode, purple dyestuffs like subpcs are becoming more attractive for several optical applications such as dyes for printing, electrolithography, photodynamic therapy (PDT), recording media, and composites of color filters. For such practical applications, some characteristics, such as solubility, light-resistance, and heat-resistance, will be required, however these characteristics of subpc monomers with a required wavelength are still insufficient.[15] We report here the synthesis and properties of μ-oxo subpc dimers with various peripheral substituents. We found that these derivatives improved some of the required properties. Further, we show the asymmetric crystal structure of [{B(subpc)}$_2$O] determined by X-ray structure analysis for the first time. The asymmetric structure may lead to an improvement of the solubility compared to the corresponding monomeric derivative.

Results and Discussion

Synthesis. According to the previous work,[16,17] we followed the methodology for the synthesis of peripherally nonsubstituted chlorido(subphthalocyaninato)boron(III) [BCl(subpc)] with minor modifications.[1–3] This method enabled the general preparation of peripherally substituted [BCl(subpc)] ([BCl(R_3subpc)]). However, the success of the subsequent hydrolysis reaction of [BCl(R_3subpc)] to [B(R_3subpc)(OH)] depended on the peripheral substituent. Once [B(R_3subpc)(OH)] was obtained, it was simple to synthesize the corresponding μ-oxo R_3subpc dimer in moderate yields by a dehydration reaction of [B(R_3subpc)(OH)]. The serial reaction scheme is illustrated in Figure 1, and we report and discuss here the results of the individual synthetic processes in detail.

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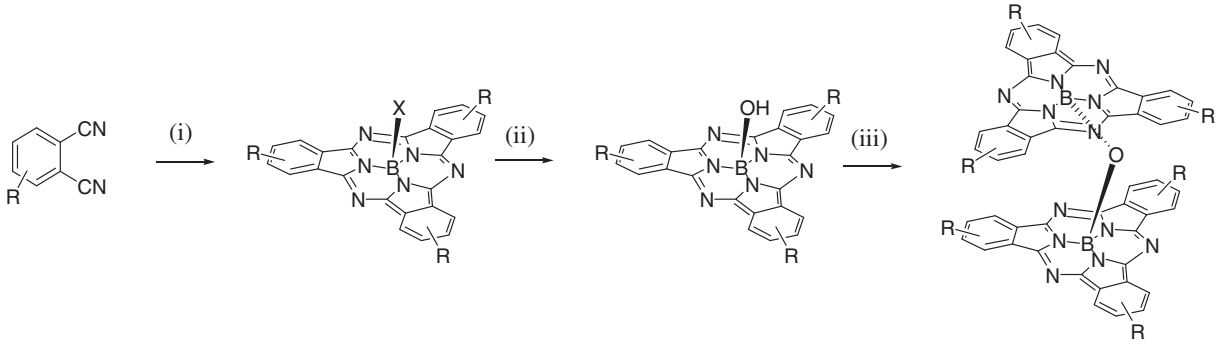

Figure 1. The synthesis of μ-oxo-bridged R_3subpc dimers via [BX(R_3subpc)] and [B(R_3subpc)(OH)]: (i) BCl_3 xylene solution, xylene, reflux; (ii) see the conditions in Table 2; (iii) *o*-dichlorobenzene, reflux, $-H_2O$.

Table 1. The Reaction Yields of the Condensation Process Affording [BCl(R_3subpc)]

Entry	R	[BCl(R_3subpc)] Yield/%
1	H–	34.0
2	*t*-Bu–	27.9
3	*n*-Oct–O–	37.7
4	*n*-Oct–S–	66.0
5	isopentyl–S–	44.0
6	Ph–S–	34.2
7	NO_2–	45.2
8	3,4,5,6-F_4–	32.9
9	4,5-Cl_2–	26.9

Table 2. The Reaction Yields and Conditions of the Hydrolysis Process Affording [B(R_3subpc)(OH)]

Entry	R	[B(R_3subpc)(OH)] Yield/%	Reaction conditions
1	H–	65.9	Acid-pasting method[a)]
2	*t*-Bu–	58.2	CH_3CN/H_2O/reflux[b)]
3	*n*-Oct–O–	80.5	NaOH/DMF/rt
4	*n*-Oct–S–	87.0	NaOH/DMF/rt
5	isopentyl–S–	75.0	CH_3CN/H_2O/reflux[b)]
6	Ph–S–	68.4	CH_3CN/H_2O/reflux[b)]
7	NO_2–	—	deteriorated
8	3,4,5,6-F_4–	—	deteriorated
9	4,5-Cl_2–	—	deteriorated

a) Acid-pasting: Treated in concd H_2SO_4 at 0 to -5 °C, then the reaction mixture was poured onto ice/water. After filtration, the obtained solid was subjected to the hydroxylation reaction in aqueous NH_4OH. b) Reference 11.

The typical procedure for the synthesis of [BCl(R_3subpc)] is as follows: phthalonitrile with a substituent (R) was dissolved in xylene and a 1.0 M xylene solution of boron trichloride was gradually added to the mixture in an ice/water bath. The mixture was then subjected to heating and refluxing with stirring for 1 h. The precipitate was filtrated from the reaction mixture and washed with appropriate organic solvents to afford the corresponding peripherally substituted chlorido(subphthalocyaninato)boron(III) [BCl(R_3subpc)] with sufficient purity for the hydrolysis. The conditions of this condensation enabled the general synthesis of [BCl(R_3subpc)] with any peripheral substituent in moderate yields. The reaction yields for this step are summarized in Table 1.

The reaction conditions of the subsequent hydrolysis of [BCl(R_3subpc)] to [B(R_3subpc)(OH)] strongly depended on the substituent. As shown in Table 2, when the peripheral substituent is an electron-withdrawing group such as a halogen or a nitro group, the expected hydrolysis of B–Cl bond did not occur under a variety of conditions but rather resulted in deterioration to give an undefined blue composite. In contrast, [BCl(R_3subpc)] with an electron-donating substituent or without a substituent (R = H) could be easily hydrolyzed to afford the corresponding [B(R_3subpc)(OH)] in fairly good yields. The results are summarized in Table 2 with the reaction conditions that afforded the best results for the respective substrate.

Thus-obtained [B(R_3subpc)(OH)] could easily be converted to the desired target, i.e., μ-oxo subpc dimers [{B(R_3subpc)}$_2$O], in low to moderate yields except when *n*-Oct–O– was the peripheral substituent. The dehydration reaction of [B{(*n*-Oct–O)$_3$subpc}OH] resulted in deterioration to give a complex mixture. The results are summarized in Table 3 together with the λ_{max} of the Q-band absorption and the molar absorptivity from the UV–vis spectroscopic analyses. The UV–vis spectra are depicted in Figure 2.

As shown in Table 3, it can be seen that, as the general tendency, the change of the axial substituent of subpc monomers from Cl to OH shifted the λ_{max} of the Q-band toward the short wavelength region by several nanometers and slightly decreased the molar absorptivity (ε [$dm^3\,cm^{-1}\,mol^{-1}$]); however, the λ_{max} of the Q-band absorption of the corresponding μ-oxo subpc dimers (Entries 1, 2, 5, and 6) were blue-shifted by approximately 30–34 and 27–32 nm compared to [BCl(subpc)] (Refs. 1–4) and [B(subpc)(OH)] (Refs. 5–8), respectively, depending on the substituent, and the molar absorptivity (ε [$dm^3\,cm^{-1}\,mol^{-1}$], Entries 1, 2, 5, and 6) was enhanced by almost 1.45–2.16 times compared with the monomeric subpcs ([BCl(R_3subpc)]; Refs. 1–4, [B(R_3subpc)-(OH)]; Refs. 5–8). It can be also seen that the Q-band absorptions of the μ-oxo subpc dimers were broadened, which is due to the π–π aggregation of two macrocycles; this fact may be explained on the basis of an excitation interaction.[12]

In the ultraviolet region around 300 nm, the characteristic Soret and/or B bands were also observed. The peripheral substitution of subpcs by a sulfanyl group gave a bathochromic

Table 3. The Reaction Yields of the Dimerizing Process Affording [{B(R_3subpc)}$_2$O] with the λ_{max}, the Molar Absorptivity (ε), and the Solubility

Entry	R	[{B(R_3subpc)}$_2$O] Yield/%	λ_{max} /nm	$\varepsilon \times 10^{-5}$ /dm^3 mol^{-1} cm^{-1}	Solubility/g L^{-1}	
					MEK[a)]	TL[b)]
1	H–	34.3	532.0	1.06	1.14	>10.0
2	*t*-Bu–	25.2	536.0	1.12	>10.0	—[c)]
3	*n*-Oct–O–	deteriorated				
4	*n*-Oct–S–	2.3	554.0	0.91	>10.0	—[c)]
5	isopentyl–S–	28.4	554.0	1.30	>10.0	—[c)]
6	Ph–S–	10.7	552.0	1.10	>10.0	—[c)]
Ref. 1	H–	[BCl(R_3subpc)]	565.0	0.56	<0.03	<0.2
Ref. 2	*t*-Bu–	[BCl(R_3subpc)]	570.0	0.57	>10.0	—[c)]
Ref. 3	isopentyl–S–	[BCl(R_3subpc)]	587.5	0.68	>10.0	—[c)]
Ref. 4	Ph–S–	[BCl(R_3subpc)]	586.0	0.76	>10.0	—[c)]
Ref. 5	H–	[B(R_3subpc)(OH)]	561.0	0.49	<0.03	<0.2
Ref. 6	*t*-Bu–	[B(R_3subpc)(OH)]	568.0	0.52	>10.0	—[c)]
Ref. 7	isopentyl–S–	[B(R_3subpc)(OH)]	581.5	0.66	>10.0	—[c)]
Ref. 8	Ph–S–	[B(R_3subpc)(OH)]	580.5	0.73	>10.0	—[c)]

a) MEK: butan-2-one. b) TL: toluene. c) —: not investigated.

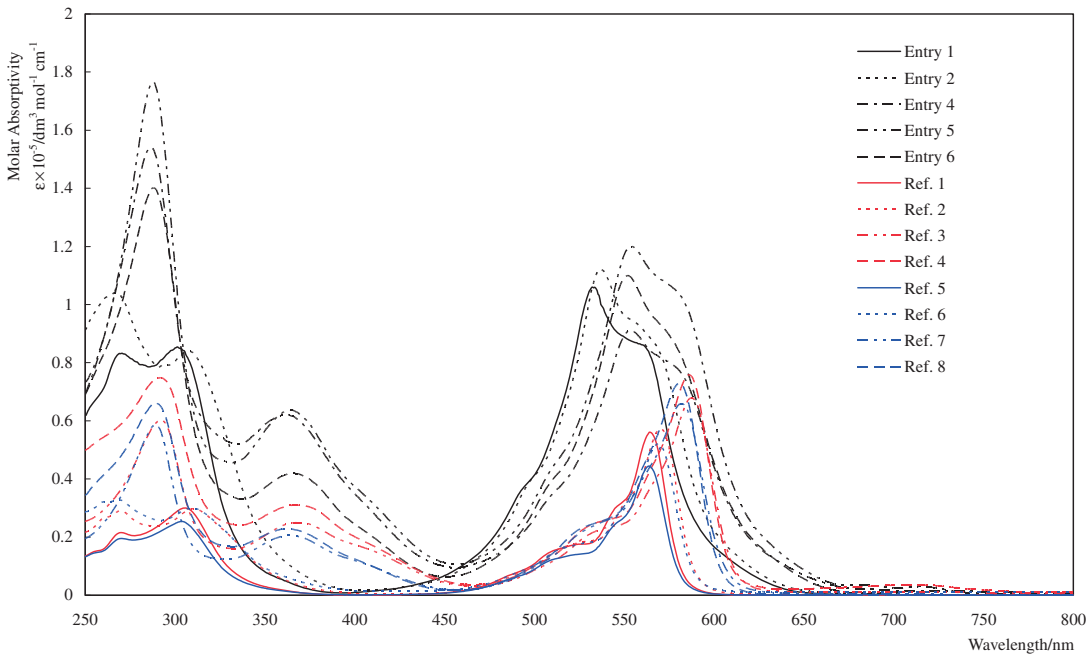

Figure 2. The UV–vis spectra of μ-oxo-bridged subpc dimers compared with those of chlorido- and hydroxido(subpc)boron monomers. All measurements were carried out in $CHCl_3$.

shift of both the Q band and Soret band regardless of whether the derivatives were monomeric or dimeric. Interestingly, the absorption of the derivatives with peripheral sulfanyl groups was extremely enhanced and was more than double those of the corresponding monomers in the region of around 280–290 nm. The absorption was broadened regardless of whether the derivatives were dimers or monomers, although the derivatives without sulfanyl groups (Refs. 1, 2, 5, and 6) have a small Soret band in the 300–320 nm region. This fact is likely due to an n–π transition in the sulfanyl sulfur atom.

Table 3 also shows the solubility of the derivatives in butan-2-one (MEK) and toluene. We can see that the peripheral substituent generally enhances the solubility of subpcs. Apparently, the solubility of μ-oxo subpc dimers improved compared to that of the corresponding monomer. In particular, even for the derivative without a peripheral substituent (Entry 1; R = H), the solubility of above 10% in toluene should enable its practical application for making thin-filmed devices. The enhancement of the molar absorptivity and solubility enables a reduction in the required volume of the solution containing a functional dyestuff for making a thin film; this would lead to a reduction in the cost of production for industrial applications.

X-ray Structure Analysis. An X-ray crystal structure of a neutral μ-oxo-bridged subpc dimer derivative has not been hitherto reported, except for a di-*meso*-*N*-protonated μ-oxo

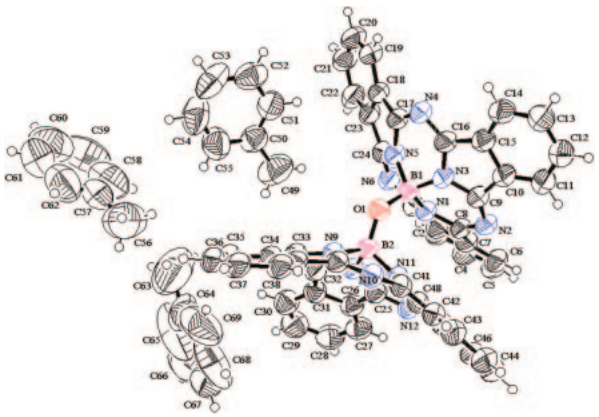

Figure 3. ORTEP representation of the X-ray crystal structure of [{B(subpc)}$_2$O] showing the asymmetric structure with three solvated molecules of toluene.

subpc dimer,[14] an optically active binuclear subpc,[18] and a fused bicyclic subpc dimer.[19] The X-ray crystal structure of [BCl(subpc)] showed strain deformation, but still maintained C_3 symmetry.[20] As discussed in the previous section, the solubility of μ-oxo subpc dimers is considerably improved compared to that of the corresponding monomer. In order to obtain the basic crystal data for μ-oxo subpc dimer derivatives, we obtained single crystals of the derivative without peripheral substituents, i.e., [{B(subpc)}$_2$O], and succeeded in analyzing them via crystallography.

The ORTEP representation plot of [{B(subpc)}$_2$O] is depicted in Figure 3. The subpc macrocycles display their familiar bowl shape and the two core boron atoms in the both macrocycles are linked to the oxygen atom with a bond length of 1.409 Å. The B–O–B bond angle is 134.77(16)°. Each macrocycle still displays the bowl shape and the geometry of each macrocycle seems to be C_3 symmetric, however the two macrocycles are twisted to avoid steric interactions. Accordingly, as the entire molecule of the μ-oxo subpc dimer is warped and is solvated by three molecules of toluene upon recrystallization, it is not able to maintain C_3 symmetry. This may be the reason why the μ-oxo-bridged subpc dimers have improved solubility in various organic solvents compared to the monomeric subpcs. According to the previous work using MNDO-calculation,[8] a bent structure, not a linear structure, was suggested as the geometry of the μ-oxo subpc dimer; we provided a direct observation of this for the first time.

Single crystals of [{B(subpc)}$_2$O] were grown in toluene, and thus, were solvated by toluene. Data collection was carried out on a Rigaku R-AXIS Rapid diffractometer that was equipped with an optical microscope (SMZ-U) manufactured by Olympus, and analyzed by the software CrystalStructure (Ver. 3.7.0). Crystal data. $C_{48}H_{24}N_{12}B_2O\cdot3(C_7H_8)$, FW: 1082.84, triclinic, $a = 13.4098(9)$, $b = 13.7773(9)$, $c = 16.7064(11)$ Å, $\alpha = 98.338(5)$, $\beta = 113.182(4)$, $\gamma = 91.118(4)°$, $V = 2797.4(3)$ Å^3, $T = 20 \pm 1$ °C, space group $P\bar{1}$(#2), $Z = 2$, μ(Cu Kα) = 6.222 cm^{-1}, 53213 reflections measured, and 10069 unique ($R_{int} = 0.085$), which were used in all calculations. The final $wR2$ (all reflections) was 0.1684. The crystallographic data have been deposited with the Cambridge Crystallographic Data Centre: deposition number CCDC-792081 for compound [{B(subpc)}$_2$O]$\cdot$3(C_6H_5–CH_3). Copies of the data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge, CB2 1EZ, U.K.; Fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk) for crystallographic data in .cif or other electronic formats.

Experimental

Materials and Analysis. All chemicals, which were purchased from commercial sources, were of analytical grade. The reaction solvents were purified by distillation and the other reagents were used without further purification. The ^{1}H NMR and the ^{13}C NMR spectra were measured at 300.4 and 75.45 MHz, respectively, using a JEOL JNM-AL 300 instrument. The UV–vis spectra were obtained using a Hitachi U-3410 spectrophotometer and the infrared (IR) spectra were measured by KBr pellet using a JEOL JIR-SPX-60S instrument. The field desorption mass spectrometry (FD-MS) spectra were measured by the positive and direct-induced mode using a JEOL JMS 600 instrument. The measurements of the melting points of the phthalonitrile derivatives were carried out using a micro melting point apparatus (MP-500D, YANACO Instrument Co., Ltd.).

Synthetic Procedure for the Preparation of the Intermediates and μ-Oxo-Bridged Subphthalocyanine Dimers, and the Spectroscopic Data. In this section we describe the detailed synthetic procedures for the preparation of the intermediates and μ-oxo subpc dimers. The compounds that are not described here can be prepared by the same method as those described, as shown in the Tables, and, otherwise, are commercially available. We did not take the solvated molecules into consideration for the calculated data of elemental analyses because the subpc derivatives are supposed to have a few solvated molecules derived from the solvent in the synthetic process.

Synthesis of 4-Isopentylsulfanylphthalonitrile. 4-Nitro-1,2-dicyanobenzene (138 g, 800 mmol), dry K_2CO_3 (165 g, 1.20 mol), and 800 mL of dried dimethylformamide (DMF) were placed in a 3 L round-bottom flask equipped with an overhead stirrer and rubber seal. After a stream of nitrogen was passed through the slurry to remove the oxygen, 100 mL of 3-methylbutanethiol (800 mmol) was added and the resulting mixture was stirred at room temperature for 5 h. Additional dry K_2CO_3 (55 g, 0.4 mol) was then added, and the mixture was stirred for an additional 19 h. The resulting mixture was filtered and the obtained solid was washed with 100 mL of DMF. 500 mL of water was poured into the combined filtrate over 1 h with stirring and the resulting slurry was filtered. The obtained solid was washed with ethanol and water and then dried to yield 144.7 g (yield 78.6%) of 4-isopentylsulfanylphthalonitrile. ^{1}H NMR (300.4 MHz, $CDCl_3$): δ 7.62 (d, $J_{ortho\text{-Ar–H}} = 8.4$ Hz, 1H), 7.52 (d, $J_{meta\text{-Ar–H}} = 2.1$ Hz, 1H), 7.45 (dd, $J_{ortho\text{-Ar–H}} = 8.7$ Hz, $J_{meta\text{-Ar–H}} = 2.1$ Hz, 1H), 2.98 (t, $J_{H–H} = 7.8$ Hz, 2H), 1.73 (m, 1H), 1.56 (m, 2H), 0.94 (s, 3H), 0.92 (s, 3H); ^{13}C NMR (75.45 MHz, $CDCl_3$): δ 147.5, 133.1, 129.8, 129.7, 116.0, 115.5, 115.1, 110.4, 36.8, 29.8, 27.4, 22.0; IR (KBr/cm^{-1}): ν 2227 ($\nu_{C\equiv N}$), 1579 ($\nu_{S–C}$), 1070, 831, 524; Anal. Calcd for $C_{13}H_{14}N_2S$: C, 67.79; H, 6.13; N, 12.16;

S, 13.92%. Found: C, 67.83; H, 6.32; N, 12.11; S, 14.05%. Mp 62.9–64.0 °C.

Synthesis of 4-Phenylsulfanylphthalonitrile. 4-Nitro-1,2-dicyanobenzene (337 g, 2.0 mmol), dry K_2CO_3 (200 g, 1.48 mol), and 1400 mL of dried DMF were placed in a 5 L round-bottom flask equipped with an overhead stirrer and rubber seal. After a stream of nitrogen was passed through the slurry to remove the oxygen, 200 mL of phenylthiol (2.0 mol) was added and the resulting mixture was stirred at room temperature for 5 h. Additional dry K_2CO_3 (97 g, 0.72 mol) was then added and the mixture was stirred for an additional 19 h. The resulting mixture was filtered and the obtained solid was washed with 500 mL of DMF. 1 L of water was poured into the combined filtrate over 1.5 h with stirring and the obtained slurry was filtered. The resultant solid was washed with ethanol and water then dried to yield 450.5 g (yield 97.9%) of 4-phenylsulfanylphthalonitrile. ^{1}H NMR (300.4 MHz, $CDCl_3$): δ 7.52–7.38 (m, 6H), 7.27–7.12 (m, 2H); ^{13}C NMR (75.45 MHz, $CDCl_3$): δ 148.2, 135.1, 133.2, 130.5, 130.4, 130.0, 129.9, 128.3, 116.2, 115.4, 115.0, 111.1; IR (KBr/cm^{-1}): ν 2233 ($\nu_{C\equiv N}$), 1585, 1066, 831, 763, 694, 521; Anal. Calcd for $C_{14}H_8N_2S$: C, 71.16; H, 3.41; N, 11.86; S, 13.57%. Found: C, 71.14; H, 3.24; N, 11.98; S, 13.48%. Mp 172.4–174.0 °C.

Synthesis of Chlorido(subphthalocyaninato)boron(III). Boron trichloride (300 mL, 300 mmol, 1 M in *p*-xylene) was added over 30 min to a suspension of phthalonitrile (76.8 g, 600 mmol) in 300 mL of *p*-xylene under a nitrogen atmosphere in a 1 L round-bottom flask. The mixture was heated with stirring under reflux for 1 h. After cooling, 300 mL of hexane was added to the mixture to afford a slurry. After filtration, the obtained solid was washed thoroughly with 6 L of 1.0 M aqueous sodium hydroxide solution, 8 L of water, and 4 L of methanol. The obtained purple solid was dried to yield 29.3 g (yield 34.0%) of chlorido(subphthalocyaninato)boron(III), and employed for the next step without further purification. ^{1}H NMR (300.4 MHz, $CDCl_3$): δ 8.92–8.89 (dd, $J_{ortho\text{-Ar–H}} =$ 6.3 Hz, $J_{meta\text{-Ar–H}} = 3.0$ Hz, 6H), 7.96–7.94 (dd, $J_{ortho\text{-Ar–H}} =$ 6.3 Hz, $J_{meta\text{-Ar–H}} = 3.0$ Hz, 6H); ^{13}C NMR (75.45 MHz, $CDCl_3$): unable to be measured because of low solubility; IR (KBr/cm^{-1}): ν 3061, 1612, 1454, 1441, 1280, 1196, 1130, 960, 951, 750, 696, 630 ($\nu_{B–Cl}$), 569; Anal. Calcd for $C_{24}H_{12}N_6BCl$ (MW: 430.7): C, 66.93; H, 2.81; N, 19.51; Cl, 8.23%. Found: C, 66.65; H, 2.64; N, 18.94; Cl, 8.84%.

Synthesis of Chlorido[tris(isopentylsulfanyl)subphthalocyaninato]boron(III). Boron trichloride (304 mL, 310 mmol, 1 M in *p*-xylene) was added over 30 min to a suspension of 4-isopentylsulfanylphthalonitrile (140 g, 610 mmol) in 304 mL of *p*-xylene under a nitrogen atmosphere in a 1 L round-bottom flask. The mixture was heated with stirring under reflux for 3 h. After cooling, the mixture was condensed with a rotary evaporator. The obtained solid was dissolved in 400 mL of toluene, and 800 mL of hexane was slowly added to the mixture over 1 h to precipitate the impurities. After removing the precipitate by filtration, the filtrate was condensed by a rotary evaporator to give a dark-purple solid, which was washed with 500 mL of an aqueous solution of 80% acetonitrile. This process was repeated three times and the obtained solid was then dispersed in 500 mL of water for a few hours under vigorous stirring. After filtration and drying, 65.4 g (yield 44.0%) of chlorido[tris(isopentylsulfanyl)subphthalocyaninato]boron(III) was obtained. ^{1}H NMR (300.4 MHz, $CDCl_3$): δ 8.75 (d, $J_{H–H} = 8.1$ Hz, 3H), 8.70–8.68 (m, 6H), 3.19 (m, 6H), 1.83 (m, 3H), 1.70 (m, 6H), 0.99–0.97 (m, 18H); ^{13}C NMR (75.45 MHz, $CDCl_3$): δ 150.3–148.4, 141.9–141.6, 131.8–131.5, 129.3, 127.9–127.7, 122.2–122.1, 119.8–119.7, 37.5, 31.1, 31.06, 31.03, 27.5, 22.2; IR (KBr/cm^{-1}): ν 2954–2868, 1605, 1466, 1443, 1188, 1070, 970, 789, 779, 704 ($\nu_{B–Cl}$); Anal. Calcd for $C_{39}H_{42}N_6BS_3Cl$ (MW: 737.25): C, 63.54; H, 5.74; N, 11.40; S, 13.05; Cl, 4.81%. Found: C, 62.68; H, 5.74; N, 10.37; S, 12.39; Cl, 6.42%.

Synthesis of Chlorido[tris(phenylsulfanyl)subphthalocyaninato]boron(III). Boron trichloride (943 mL, 940 mmol, 1 M in *p*-xylene) was added over 30 min to a suspension of 4-phenylsulfanylphthalonitrile (445 g, 1.89 mol) in 943 mL of *p*-xylene under a nitrogen atmosphere in a 3 L round-bottom flask. The mixture was heated with stirring under reflux for 2 h, and then ≈1.5 L of xylene was removed from the mixture by distillation. After cooling, the mixture was condensed with a rotary evaporator. The obtained solid was washed twice with 500 mL of acetonitrile and four times with 1 L of methanol. After being dried, the obtained dark-purple solid was dissolved in 800 mL of toluene, then 800 mL of hexane was slowly added to the mixture over 1 h with stirring to precipitate the impurities. After removing the precipitate by filtration, the filtrate was condensed to afford a dark-purple solid. This solid was dissolved again in toluene, and the latter processes were repeated twice, after which the obtained solid was dried to yield 162.3 g (215.0 mmol, yield 34.2%) of chlorido[tris(phenylsulfanyl)subphthalocyaninato]boron(III). ^{1}H NMR (300.4 MHz, $CDCl_3$): δ 8.60–8.54 (m, 6H), 7.65–7.59 (m, 3H), 7.40–7.23 (m, 15H); ^{13}C NMR (75.45 MHz, $CDCl_3$): δ 150.5–149.4, 139.5–139.2, 134.34–134.27, 132.3–132.2, 131.4–131.2, 130.6–129.5, 129.0–128.6, 128.2–128.0, 125.2, 122.7–122.1; IR (KBr/cm^{-1}): ν 3055, 1605, 1581, 1439, 1186, 788, 746, 704, 690 ($\nu_{B–Cl}$); Anal. Calcd for $C_{42}H_{24}N_6BS_3Cl$ (MW: 755.1): C, 66.80; H, 3.20; N, 11.13; S, 12.74; Cl, 4.69%. Found: C, 67.19; H, 3.52; N, 9.97; S, 11.33; Cl, 4.89%.

Synthesis of Hydroxido(subphthalocyaninato)boron(III). 20 g (46.4 mmol) of chlorido(subphthalocyaninato)boron(III) was gradually added to 600 mL of concentrated sulfuric acid in a 1 L beaker below 5 °C. The mixture was stirred for 5 h at this temperature then poured into 3 L of ice/water maintained below 5 °C to afford precipitation. After filtration, the obtained purple solid was dispersed in 3 L of water then filtered again. The resultant solid was washed thoroughly with 3 L of water and dried to give 12.6 g (30.6 mmol, yield 65.9%) of hydroxido(subphthalocyaninato)boron(III). ^{1}H NMR (300.4 MHz, $CDCl_3$): δ 8.78–8.73 (dd, $J_{ortho\text{-Ar–H}} = 6.0$ Hz, $J_{meta\text{-Ar–H}} =$ 2.7 Hz, 6H), 7.89–7.83 (dd, $J_{ortho\text{-Ar–H}} = 6.0$ Hz, $J_{meta\text{-Ar–H}} =$ 2.7 Hz, 6H); ^{13}C NMR (75.45 MHz, $CDCl_3$): unable to be measured because of low solubility; IR (KBr/cm^{-1}): ν 3415 ($\nu_{O–H}$), 1582, 1456, 1431, 1288, 1130, 1095, 762, 739, 571; Anal. Calcd for $C_{24}H_{13}N_6BO$ (MW: 412.2): C, 69.93; H, 3.18; N, 20.39%. Found: C, 69.20; H, 3.13; N, 19.50%.

Synthesis of Hydroxido[tris(isopentylsulfanyl)subphthalocyaninato]boron(III). A mixture of 55.0 g of chlorido-[tris(isopentylsulfanyl)subphthalocyaninato]boron(III) (74.6 mmol), 2.4 L of acetonitrile, and 600 mL of water was re-

fluxed at 77 °C for 24 h. After removing 1.2 L of acetonitrile then cooling, the precipitated solid was removed via filtration. The solid was washed thoroughly with water and dried to yield 40.2 g of hydroxido[tris(isopentylsulfanyl)subphthalocyaninato]boron(III) (55.6 mmol, yield 75.0%) as a brown solid. ^{1}H NMR (300.4 MHz, $CDCl_3$): δ 8.36–8.28 (m, 6H), 7.62–7.57 (m, 3H), 3.19–3.08 (m, 6H), 1.86–1.77 (m, 3H), 1.69–1.61 (m, 6H), 0.98 (s, 9H), 0.96 (s, 9H); ^{13}C NMR (75.45 MHz, $CDCl_3$): δ 150.2–148.7, 140.8–140.5, 130.6–130.5, 128.1, 126.6–126.5, 121.1, 118.6–118.5, 37.5, 31.0–30.9, 27.6, 22.4–22.3; IR (KBr/cm^{-1}): ν 3390 (ν_{-OH}), 2954–2867, 1604, 1550, 1466–1429, 1184, 1101–1047, 764, 708; Anal. Calcd for $C_{39}H_{43}N_6OBS_3$ (MW: 718.8): C, 65.17; H, 6.03; N, 11.69; S, 13.38%. Found: C, 64.49; H, 5.99; N, 11.29; S, 13.26%.

Synthesis of Hydroxido[tris(octylsulfanyl)subphthalocyaninato]boron(III). A suspension of 5.5 g of chlorido[tris(octylsulfanyl)subphthalocyaninato]boron(III) (6.4 mmol) in 50 mL of DMF was gradually added to 100 mL of a 1.0 M sodium hydroxide aqueous solution and stirred for 30 min below 10 °C. Then, the temperature was elevated to ambient temperature and the mixture was stirred for an additional 2 h. After cooling, 200 mL of toluene was added to the mixture and the organic layer was extracted and washed three times with 200 mL of water using a separating funnel. The combined organic layer was dried over magnesium sulfate and condensed by a rotary evaporator. The obtained solid was dispersed in 50 mL of water with vigorous stirring and the subsequent filtration afforded 4.7 g of hydroxido[tris(octylsulfanyl)subphthalocyaninato]boron(III) (5.57 mmol, yield 87.0%) as a dark-purple solid. ^{1}H NMR (300.4 MHz, $CDCl_3$): δ 8.31–8.22 (m, 6H), 7.61–7.26 (m, 3H), 3.21–3.11 (m, 6H), 1.80–1.75 (m, 6H), 1.53 (brs, 6H), 1.27 (brs, 24H), 0.85 (t, $J_{H-H} = 6.3$ Hz, 9H); ^{13}C NMR (75.45 MHz, $CDCl_3$): δ 147.8, 133.5–131.5, 128.4, 123.6, 120.5, 32.2, 31.8–31.7, 29.2, 29.1–29.0, 28.9–28.8, 28.5, 22.6, 14.1; IR (KBr/cm^{-1}): ν 3361 (ν_{-OH}), 2956–2852, 1605, 1464, 1431, 1186, 1101, 816, 763, 706; Anal. Calcd for $C_{48}H_{61}N_6OBS_3$ (MW: 845.04): C, 68.22; H, 7.28; N, 9.95; S, 11.38%. Found: C, 64.15; H, 7.12; N, 8.86; S, 11.46%.

Synthesis of Hydroxido[tris(phenylsulfanyl)subphthalocyaninato]boron(III). A mixture of 10.0 g of chlorido[tris(phenylsulfanyl)subphthalocyaninato]boron(III) (13.3 mmol), 400 mL of acetonitrile, and 100 mL of water was refluxed at 77 °C for 24 h, then filtered after cooling. The obtained solid was washed thoroughly with water and dried to yield 6.7 g of hydroxido[tris(phenylsulfanyl)subphthalocyaninato]boron(III) (9.10 mmol, yield 68.4%) as a brown solid. ^{1}H NMR (300.4 MHz, $CDCl_3$): δ 8.32–8.17 (m, 6H), 7.66–7.34 (m, 18H); ^{13}C NMR (75.45 MHz, $CDCl_3$): δ 150.2–149.2, 148.1, 140.1–139.8, 134.5, 133.8–133.4, 132.8–132.6, 131.8, 130.9–130.0, 129.6–129.5, 128.2–128.1, 127.9, 123.8, 121.9–121.4; IR (KBr/cm^{-1}): ν 3417 (ν_{O-H}), 1604, 1581, 1464, 1439, 1182, 1103, 1085, 764, 742, 706, 688; Anal. Calcd for $C_{42}H_{25}N_6OBS_3$ (MW: 736.7): C, 68.47; H, 3.42; N, 11.41; S, 13.06%. Found: C, 67.64; H, 3.28; N, 10.64; S, 12.37%.

Synthesis of Compound Entry 1, [{B(subpc)}$_2$O]. A mixture of hydroxido(subphthalocyaninato)boron(III) (13.4 g, 32.5 mmol) and 500 mL of *o*-dichlorobenzene was refluxed at about 180 °C under a nitrogen atmosphere while removing generated water. After completion of the reaction, the reaction mixture was cooled and filtered. The filtrate was condensed with a rotary evaporator and the obtained dark-purple solid was dispersed in 400 mL of DMF, filtered, and washed with 100 mL of DMF and 200 mL of water. The resultant wet cake was dried to yield 4.5 g (5.58 mmol, yield 3.43%) of [{B(subpc)}$_2$O]. ^{1}H NMR (300.4 MHz, $CDCl_3$): δ 8.62–8.59 (m, 12H, Ar–H), 7.86–7.75 (m, 12H, Ar–H); ^{13}C NMR (75.45 MHz, $CDCl_3$): δ 150.4, 130.5, 129.5, 121.9; IR (KBr/cm^{-1}): ν 3056, 1614, 1606, 1456, 1288, 1191, 1130, 740 (ν_{B-O-B}); Anal. Calcd for $C_{48}H_{24}N_{12}B_2O$ (MW: 806.41): C, 71.49; H, 3.00; N, 20.84%. Found: C, 69.37; H, 3.08; N, 19.95%. FD-MS m/z (=M$^+$) (%) 806.24 (100%).

Synthesis of Compound Entry 2, [{B(*t*-Bu$_3$subpc)}$_2$O]. The conditions of the dehydration reaction were followed according to the procedure for the synthesis of Entry 1 except for the use of hydroxido[(tris(*t*-butyl)subphthalocyaninato]-boron(III). After completion of the reaction, the reaction mixture was cooled and filtered. The filtrate was condensed with a rotary evaporator and the obtained dark-purple solid was subjected to column chromatography eluting with the mixed solvent of hexane and ethyl acetate (5:1) to afford [{B(*t*-Bu$_3$subpc)}$_2$O] (yield 25.2%). ^{1}H NMR (300.4 MHz, $CDCl_3$): δ 8.64–8.60 (m, 6H, Ar–H), 8.49–8.43 (m, 6H, Ar–H), 7.79–7.74 (m, 6H, Ar–H), 1.53–1.46 (a few singlets, 54H); ^{13}C NMR (75.45 MHz, $CDCl_3$): δ 157.6, 152.9–152.7, 150.7–150.0, 133.3, 130.8–130.3, 128.3–128.2, 127.1, 121.8–121.1, 118.0–117.9, 115.8–115.5, 35.61–35.33, 31.7–30.6; IR (KBr/cm^{-1}): ν 2962–2867, 1618, 1454–1431, 1182, 1140, 773 (ν_{B-O-B}); Anal. Calcd for $C_{72}H_{72}N_{12}B_2O$ (MW: 1143.0): C, 75.66; H, 6.35; N, 14.70%. Found: C, 74.88; H, 6.62; N, 12.58%. FD-MS m/z (=M$^+$) (%) 1142.61 (100%).

Synthesis of Compound Entry 4, [(B{(*n*-Oct–S)$_3$subpc})$_2$O]. The synthetic procedure was followed according to that for Entry 2 except for the use of hydroxido[tris(octylsulfanyl)subphthalocyaninato]boron(III) to yield [(B{(*n*-Oct–S)$_3$subpc})$_2$O] (yield 2.3%). ^{1}H NMR (300.4 MHz, $CDCl_3$): δ 8.76–8.58 (m, 12H, Ar–H), 7.70 (d, 6H, Ar–H, $J_{H-H} = 8.1$ Hz), 3.22 (m (broad), 12H, S–CH_2–), 1.80 (m (broad), 12H), 1.55 (m (broad), 12H), 1.28 (m (broad), 48H), 0.88 (m (broad), 18H, CH_3); ^{13}C NMR (75.45 MHz, $CDCl_3$): δ 150.9–150.3, 149.9–149.2, 140.7–140.4, 131.6–131.2, 128.9–128.8, 127.8–127.6, 121.8–121.7, 119.8, 33.4, 31.8, 29.2, 29.1, 29.0, 28.9, 22.6, 14.0; IR (KBr/cm^{-1}): ν 2953–2854, 1606, 1462, 1430, 1186, 767.5 (ν_{B-O-B}); Anal. Calcd for $C_{96}H_{120}N_{12}B_2S_6O$ (MW: 1672.1): C, 68.96; H, 7.23; N, 10.05; S, 11.51%. Found: C, 66.75; H, 7.13; N, 9.86; S, 10.36%. FD MS m/z (=M$^+$) (%) 1671.83 (100%).

Synthesis of Compound Entry 5, [(B{(Isopentyl–S)$_3$subpc})$_2$O]. The synthetic procedure was followed according to that of Entry 2 except for the use of hydroxido[tris(isopentylsulfanyl)subphthalocyaninato]boron(III) to yield [(B{(Isopentyl–S)$_3$subpc})$_2$O] (yield 28.4%). ^{1}H NMR (300.4 MHz, $CDCl_3$): δ 8.41 (m, 12H, Ar–H), 7.62 (d, 6H, Ar–H, $J_{H-H} = 8.7$ Hz), 3.14 (m, 12H, –CH_2–S), 1.80 (m, 6H, –CH–), 1.63 (m, 12H, –CH_2–), 0.96 (d, 36H, –CH_3); ^{13}C NMR (75.45 MHz, $CDCl_3$): δ 150.9–150.2, 149.8, 149.6, 149.1, 140.5–140.2, 131.4–131.1, 128.7, 127.7–127.4, 121.7–121.6, 119.6–119.5, 37.5, 31.3, 27.5, 22.3; IR (KBr/cm^{-1}): ν 2954–2868,

1606, 1462–1431, 1184, 768 (ν_{B-O-B}); Anal. Calcd for $C_{78}H_{84}N_{12}B_2S_6O$ (MW: 1419.6): C, 65.99; H, 6.96; N, 11.84; S, 13.55%. Found: C, 65.45; H, 5.64; N, 11.19; S, 13.42%. FD MS m/z (=M^+) (%) 1419.54 (100%).

Synthesis of Compound Entry 6, [{B(Ph–S)$_3$subpc}$_2$O]. The synthetic procedure was followed according to that of Entry 2 except for the use of hydroxido[tris(phenylsulfanyl)-subphthalocyaninato]boron(III) to yield [{B(Ph–S)$_3$subpc}$_2$O] (yield 10.7%). ^{1}H NMR (300.4 MHz, $CDCl_3$): δ 8.42–8.36 (m, 12H, Ar–H), 7.60–7.57 (m, 6H, Ar–H), 7.40–7.39 (m, 12H, Ar–H), 7.31–7.24 (m, 18H, Ar–H); ^{13}C NMR (75.45 MHz, $CDCl_3$): δ 150.5–149.4, 139.5–139.2, 134.34–134.27, 132.3–132.2, 131.4–131.2, 130.6–129.5, 129.0–128.6, 128.2–128.0, 125.2, 122.7–122.1; IR (KBr/cm^{-1}): ν 3054, 2958–2866, 1604, 1581, 1473–1425, 1180, 738 (ν_{B-O-B}); Anal. Calcd for $C_{84}H_{48}N_{12}B_2S_6O$ (MW: 1455.4): C, 69.32; H, 3.32; N, 11.55; S, 13.22%. Found: C, 69.25; H, 3.23; N, 11.07; S, 12.76%. FD MS m/z (=M^+) (%) 1455.26 (100%).

Conclusion

In summary, we reported the synthesis and properties of μ-oxo-bridged subphthalocyanine dimers with various peripheral substituents. We have shown that the wavelength of the Q-band absorption shifts approximately 30–35 nm toward the short wavelength region and that the molar absorptivity is about 1.5–2.0 times greater compared to that of the corresponding monomer. The asymmetric crystal structure of [{B(subpc)}$_2$O] as determined by X-ray crystallography was shown for the first time, and is suspected to lead to the improved solubility of the dimers as compared to the corresponding monomers. We can expect that μ-oxo subpc dimers should be useful for the recent thin film applications in optical devices. Further study focused on making thin-filmed devices consisting of the above μ-oxo subpc dimers is currently underway.

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Supporting Information

^{1}H and ^{13}C NMR spectra of the newly synthesized dimers, i.e., Entries 1, 2, 4, 5, and 6, shown in Table 3. This material is available free of charge on the web at http://www.csj.jp/journals/bcsj/.

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