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Synthesis and optoelectronic properties of hexachloro- and hexaiodosubnaphthalocyanines as organic electronic materials

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ABSTRACT

Chloroboron(III) hexachloro- and hexaiodosubnaphthalocyanines were prepared, and their solubility, electronic absorption spectroscopy, fluorescence emission spectroscopy and HOMO/LUMO energy levels were evaluated. These subnaphthalocyanines showed lower HOMO/LUMO energies than the parent subnaphthalocyanine by 0.13–0.39 eV. The optical band gap decreased in the order: hexafluoro->hexachloro->unsubstituted>hexaiodo-subnaphthalocyanine. Fluorescence quantum yield of hexaiodosubnaphthalocyanine was 0.05, significantly lower than those of the parent, hexafluoro- and hexachloro-subnaphthalocyanines whose quantum yields ranged from 0.2 to 0.22, indicating that the heavy atom effects of iodine work effectively.

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1. Introduction

Organic semiconducting materials[1] attract interest for various applications such as photovoltaic cells, light emitting diodes and organic thin film transistors. Subphthalocyanines and subnaphthalocyanines have a dipolar bowl-shaped molecular structure with attractive properties as electronic materials such as red light absorption and emission, and semiconductive charge transport.[2] Chloroboron(III) subnaphthalocyanine has a dipole moment owing to a polar B–Cl bond with a negative charge on the Cl atom, and dipolar interactions would be important to control optoelectrical properties particularly in a condensed phase. Introduction of halogens on the naphthalene moieties can produce additional dipoles canceling the original dipole moment, giving rise to less polar properties. Application of these dyes to photovoltaic cells has been reported with improved energy conversion efficiency compared with phthalocyanines because chloroboron(III) subphthalocyanine has a lower HOMO energy level than phthalocyanine by ca. 0.4 eV, thus the open circuit voltage generated by the photovoltaic cell was improved by ca. 0.5 V when combined with C_{60} as an acceptor.[3] One of the disadvantage of subphthalocyanine is that the absorption maximum wavelength (λ_{max}) is 565 nm and the red light cannot be absorbed by the dye. Although subnaphthalocyanine absorbs light in the longer wavelength region with λ_{max} of 660 nm, the HOMO energy level of subnaphthalocyanine is higher than subphthalocyanine, reducing the open circuit voltage when combined with C_{60}.[4]

Although subnaphthalocyanines with substituents are rarely known, electronic tuning, molecular packing,[5] and p–n semiconductor interface can be improved by introducing appropriate substituents.[6] Halogenation of subphthalocyanine has been studied systematically to tune the HOMO/LUMO energy levels for organic photovoltaics applications.[7] We previously reported preparation of fluorinated subnaphthalocyanine and demonstrated that fluorination at the peripheral naphthalene rings efficiently tuned the HOMO/LUMO energy levels.[8] Halogenated organic semiconductive materials attracted much interest recently, where the energy levels, crystal packing, and intermolecular charge transport can be controlled by introduction of halogen atoms at the π-conjugated core.[9] For pentacenes, a tetrachloro derivative has a similar HOMO energy level to that of a tetrafluoro derivative, while the LUMO energy level

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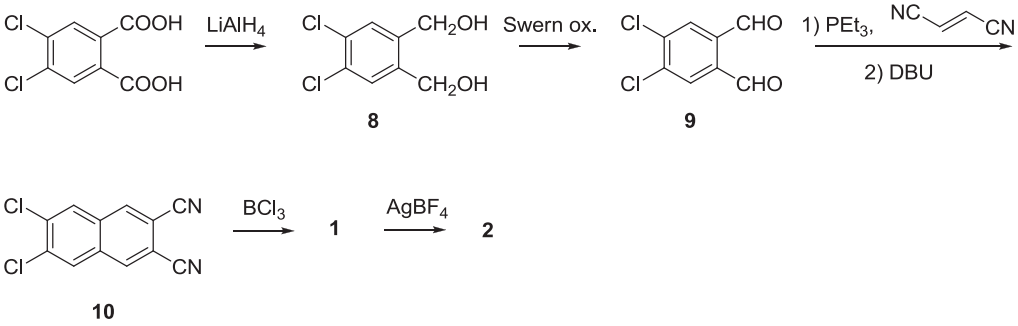
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of the tetrachloro derivative was lower than that of the tetrafluoro derivative, leading to smaller HOMO–LUMO band gap for the chlorinated pentacene.[10] We performed comparative studies on halogenated subnaphthalocyanines with several objectives such as (1) elucidation of electronic effects of halogen atoms introduced on the subnaphthalocyanine core on HOMO/LUMO energy levels and electric dipole moment, (2) roles of halogen atoms in intermolecular interactions such as molecular packing and solubility, (3) formation of triplet excited states by halogenation on the nucleus for possible application to triplet materials,[11] and (4) halogenated subnaphthalocyanines as a possible intermediate for further functionalization of subnaphthalocyanines via cross-coupling reactions.[12] We report in this paper preparation of chloroboron(III) hexachloro- and hexaiodosubnaphthalocyanines and their chemical and optical properties as well as electronic structures.

2. Results and discussion

2.1. Synthesis of halogenated chloroboron(III) subnaphthalocyanines

Chloroboron(III) subnaphthalocyanines having halogen atoms at the β-positions of naphthalene were synthesized by cyclotrimerization of the corresponding dihalonaphthalenedicarbonitrile. We report here the synthesis of hexachloro- and hexaiodo-derivatives. Hexachlorosubnaphthalocyanines **1** and **2** were prepared as shown in Scheme 1. Dicarbonitrile **10** was prepared according to the literature.[13] Conversion to subnaphthalocyanine **1** was carried out in a yield of 22%. Cyclotrimerization of unsubstituted naphthalenedicarbonitrile with BCl_3 suffers from chlorination of the naphthalene ring to give chlorinated by-products, while such chlorination was suppressed for the cyclotrimerization of **10**. Therefore, the isolation of the product was facilitated. In all steps in the synthesis of **3**, column chromatographic separation was avoided, rendering the synthetic route suitable for large scale preparation. We also attempted to cyclotrimerize 6,7-dibromonaphthalene-2,3-dicarbonitrile. It yielded, however, various unidentified by-products, and isolation of the desired hexabromosubnaphthalocyanine was failed. Axial ligand exchange was performed according to the Torres's method[14] to obtain fluoroboron derivative **2** in 89% yield.



Scheme 1. Synthesis of hexachlorosubnaphthalocyanines **1** and **2**.

Hexaiodosubnaphthalocyanines **3** and **4** were prepared similarly according to Scheme 2. Cyclotrimerization of **16** afforded hexaiodosubnaphthalocyanine **3** in 73% yield. In all steps of the preparation of **3**, column chromatographic separation was not used, and the synthetic route is suitable for a large scale preparation. These halogenated subnaphthalocyanines were characterized by ^1H NMR, high resolution mass spectrometry and UV–visible spectroscopy.

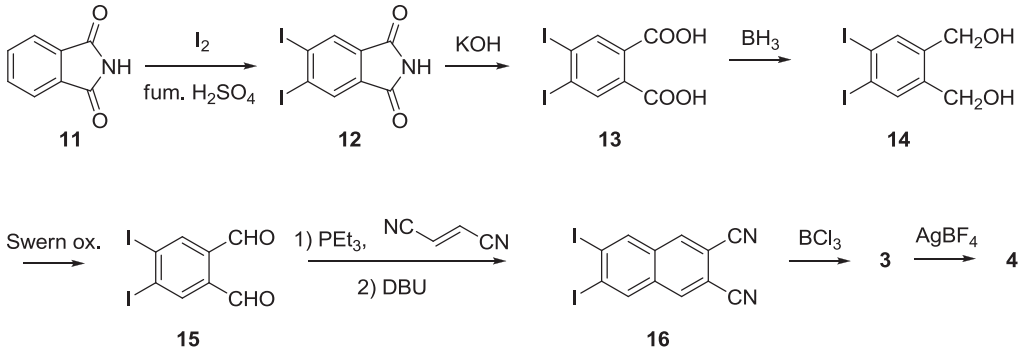
2.2. Solubilities and dipolar properties of halogenated chloroboron(III) subnaphthalocyanines

Solubilities of **1**–**7** in *o*-dichlorobenzene are listed in Table 1. Generally, low solubility of these semiconductive molecules causes problems in purification and device fabrication. Hexachlorosubnaphthalocyanines **1** and **2** were less soluble than the parent chloroboron(III) subnaphthalocyanine **7**, while hexaiodosubnaphthalocyanine **3** showed better solubility. The solubility of chloroboron(III) subphthalocyanine was reported to be improved by changing the axial chlorine to phenoxy groups.[15] Fluoroboron derivative **2** showed lower solubility than chloroboron derivative **1**. This is in contrast to the fact that fluoroboron(III) subphthalocyanine was approximately one order of magnitude more soluble than chloroboron(III) or bromoboron(III) subphthalocyanine in most organic solvents.[16] It is interesting to note that hexafluorosubnaphthalocyanine and hexachlorosubnaphthalocyanine showed similar HOMO/LUMO levels, while the solubility of the former was much higher than the latter.

Electric dipole moments of **1**–**7** calculated with DFT molecular orbital theory are also listed in Table 1. Electric dipole moment of the parent subnaphthalocyanine **7** was parallel to the B–Cl bond, with a negative charge directing toward Cl. Substitution with halogen atoms partially cancel the dipole moment originated from the B–Cl bond to reduce the magnitude of the dipole moment. Electric dipoles of C-halogen bonds decrease in the order: Cl>F>I, resulting in the least dipolar moment in the chloro derivatives **1** or **2**. Electronic effects of halogen on the dipole moments of halobenzene are not straight forward as discussed in the literature.[17] Owing to the empty 3d orbital of Cl,[10] and the back donation of 2p electrons of F to the π-electron system,[18] Cl can accept more π-electron from the aromatic π-system than F. These mechanisms can account for peculiar electronic effects of F and Cl on the dipolar properties of subnaphthalocyanines. Substitution of the axial Cl with F also reduced the dipole moments. Inspection of Mulliken changes (see Table S9) indicates that, although the B–F bond is more polar than the B–Cl bond, the atomic changes of N bonding to B and those of α-C of pyrrole of the chloroboron derivative **1** are more positive than those of the fluoroboron derivative **2**. Therefore, larger charge transfer from the aromatic π-electrons to the B–Cl bond can account for the larger dipole moment in the chloroboron derivative **1**.

2.3. Effects of halogenation on the HOMO and LUMO energy levels

To evaluate the electronic effects of halogen substituents on the energy levels of the frontier orbitals, HOMO and LUMO energy levels were determined: photoelectron spectroscopy in air was recorded for the thin film with a few 10 nm thickness of **1**–**7** on ITO glass substrate, and ionization potential was obtained (see Table 2).



Scheme 2. Synthesis of hexaiodosubnaphthalocyanines **3** and **4**.

Table 1
Solubilities of chloroboron(III) subnaphthalocyanines **1**–**5** and **7** in *o*-dichlorobenzene at 25 °C and dipole moments calculated with DFT MO theory

	Solubility (g/L)	Dipole moment (D)[a]
1	3.50	1.51
2	3.09	1.14
3	16.17	3.78
4	—[b]	2.76
5	34.56	2.39
7	9.04	5.24

[a] Dipole moments were calculated with B3LYP/LAN2DZ.
[b] Not determined.

Table 2
HOMO and LUMO energy levels of chloroboron(III) subnaphthalocyanines **1**–**7** in solid state determined by photoelectron spectroscopy and optical band gap

	HOMO (eV)	LUMO (eV)
1	−5.69	−3.96
2	−5.59	−3.86
3	−5.52	−3.82
4	−5.43	—[b]
5[a]	−5.69	−3.92
6[a]	−5.67	−3.90
7	−5.30	−3.58

[a] Taken from literature.[8]
[b] Not determined. Compound **4** showed a very low solubility in halogenated aromatic solvents.

The HOMO energy levels were estimated from the ionization potential, and the LUMO energy levels were estimated from the ionization potential and the optical band gap obtained from the UV–visible spectra of the thin film of **1**–**7**. As shown in Table 2, chlorine and iodine substituents stabilized the HOMO energy levels by 0.13–0.39 eV and the LUMO energy levels by 0.24–0.38 eV, compared to the parent subnaphthalocyanine **7**. It is interesting to note that hexachloro derivatives **1** and **2** showed similar HOMO and LUMO levels to those of hexafluoro derivatives **5** and **6**. The ionization potentials of **1** and **5** calculated by DFT molecular orbital theory using the B3LYP/6-31G(D) as the difference between the radical cation and the neutral molecule were 6.26 and 6.15 eV, respectively. Therefore, molecular orbital theory predicted that chlorine substituents stabilized the HOMO level than fluorine substituents in vacuo. Similar HOMO and LUMO levels in the solid state shown in Table 2 indicate that intermolecular interactions such as dipolar forces would perturb the frontier orbital levels. Substitution of the axial Cl with F resulted in destabilization of both HOMO and LUMO energy levels by 0.1 eV.

2.4. Optical properties of halogenated subnaphthalocyanines

Fig. 1 shows UV–visible spectra of halogenated subnaphthalocyanines. The absorption maxima in the Q-band were red shifted in the order: **5** (F)<**1** (Cl)<**7** (H)<**3** (I). The molar absorption coefficients increased in the order: **7**∼**5**<**1**<**3**. This trend of halogen electronic effects was also reproduced by TD-DFT calculations listed in Table 3. The electronic absorption in the Q-band can be ascribed to the HOMO-LUMO transition and the HOMO-next LUMO transition. According to the TD-DFT calculations, the absorption maxima were red-shifted and the oscillator strengths were increased in the order: **5**<**7**<**1**<**3**. Absorption of the longer wavelength region with enhanced absorptivity by **3** is advantageous for the use as the active element of photovoltaic cells. HOMO and LUMO orbitals of **3** are shown in Fig. 2. There is contribution of the atomic orbital of carbon atoms carrying iodo substituents to the HOMO, indicating that the halogen substituents in the β-positions of the naphthalene ring can perturb the frontier molecular orbital, leading to variations in the peak maxima and molar extinction coefficients. Kobayashi et al. reported the importance of frontier orbital perturbation for manipulating optical properties of phthalocyanines.[19] Bao and co-workers[10] reported that tetrafluorination of pentacene caused no change in the absorption maximum relative to that of the parent compound, while tetrachlorination caused a red shift of 14 nm. Loo et al. reported that chlorination of hexabenzocoronene lowers the LUMO energy level more effectively compared to fluorination, resulting in a narrowing of the optical band gap.[9d] These effects were attributed to the stronger electron withdrawing property of chlorine directly attached to a π-conjugated system, although the electronegativity of fluorine was higher than chlorine. In line with these observations, for halogenation of subnaphthalocyanines, the optical band gap decreased in the order: hexafluoro>hexachloro>unsubstituted>hexaiodo derivatives (see Table 4).

2.5. Fluorescence emission of halogenated subnaphthalocyanines

Fluorescence spectra are compared for these subnaphthalocyanines in Fig. 3. Absorption and emission data are summarized in Table 4. Hexachlorosubnaphthalocyanine **1** showed a similar fluorescence quantum yield to that of the parent subnaphthalocyanine **7**, while hexaiodosubnaphthalocyanine **3** showed a much lower fluorescence quantum yield. The fluorescence life time of hexaiodo derivative **3** was much shorter than other derivatives. The reduced fluorescence quantum yield and shorter fluorescence life-time of **3** can be ascribed to the heavy atom effects. Fluorescence quantum yields were determined by using subnaphthalocyanine **7** as a reference compound, whose fluorescence quantum yield was reported to be 0.22.[20] Bonnett's et al. reported systematic investigation on the effects of halogenation on the porphyrin nucleus on triplet quantum yield. While halogenation at the *meso* positions effectively caused spin-orbit coupling to results in almost unity quantum yield of intersystem

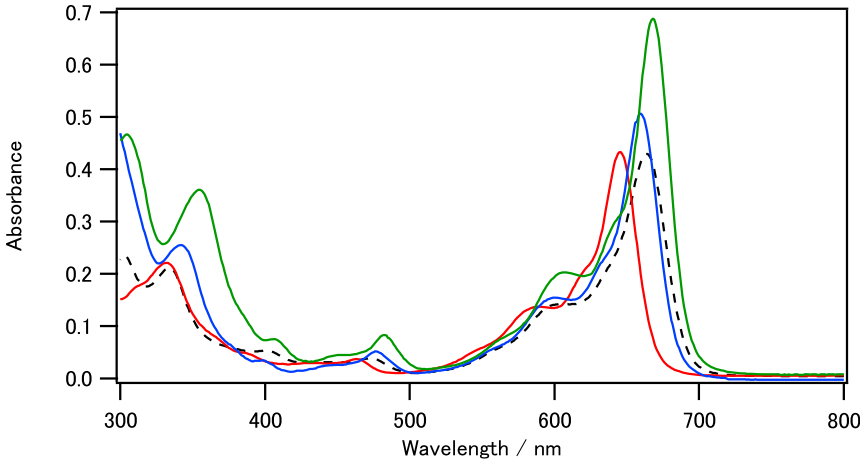


Fig. 1. UV–visible spectra of **1** (blue), **3** (dark green), and **5** (red) and the parent chloroboron(III) subnaphthalocyanine **7** (dotted line). The concentration was 5×10^{-6} M in *o*-dichlorobenzene.

Table 3
B3LYP/LanL2DZ calculations of UV–visible absorption maxima and oscillator strengths *f*

Compound	HOMO–LUMO		HOMO–next LUMO	
	λ_{max}/nm	*f*	λ_{max}/nm	*f*
1	582.4	0.4622	582.2	0.4623
3	594.2	0.5214	593.9	0.5228
5	572.0	0.4143	571.8	0.4145
7	580.9	0.4185	580.8	0.4185

Table 4
Absorption and emission maxima, fluorescence quantum yields, and fluorescence life times of **1**–**3**, **5**–**6** and parent chloroboron(III) subnaphthalocyanine **7**

	λ_{abs}/nm	λ_{em}/nm	Stokes shift (nm)	Fluorescence quantum yield	Fluorescence life time (ns)
1	660	668	8	0.20	3.23
2	655	664	9	0.20	—[a]
3	668	676	8	0.05	0.75
5	645	655	10	0.22	3.43
6	641	649	8	0.21	—[a]
7	664	674	10	0.22	3.11

[a] Not determined.

crossing, halogenation at pyrrole and at the alkyl group on pyrrole of octaethylporphyrin was less efficient to produce the triplet state.[21] Bonnett's study suggests that fluorescence quantum yield may vary when iodine was introduced at different positions (Chart 1).

3. Conclusion

Chloroboron(III) hexachloro- (**1**) and hexaiodosubnaphthalocyanine (**3**) were prepared and their optical properties were compared with those of chloroboron(III) hexafluoro- (**5**) and unsubstituted subnaphthalocyanines **7**. Chloroboron(III) hexachlorosubnaphthalocyanine **1** had the least dipole moment with the lowest solubility in *o*-dichlorobenzene. Chloroboron(III) hexaiodo-subnaphthalocyanine **3** exhibited both moderate dipole moment and solubility, and its molar absorptivity was the largest. The fluorescence quantum yield of the hexaiodo derivative was much smaller than other derivatives, suggesting that it can be used as a triplet material. The hexachloro derivative showed similar frontier orbital levels with those of hexafluoro derivatives: HOMO and LUMO energy levels were stabilized in the order: **5** (F) ~**1** (Cl)> **3** (I)>**7** (H). The optical band gap decreased in the order: **5** (F)>**1** (Cl)>**7** (H)>**3** (I). Halogenation of subnaphthalocyanine resulted in tuning of the frontier orbital energy levels, and these derivatives are promising for the active layer of organic electronic devices.

4. Experimental

4.1. Instrumentation

^{1}H NMR spectra were recorded with a JEOL JNM-ECA500 spectrometer. Tetramethylsilane was used as an internal standard. Matrix-assisted laser desorption–ionization time-of-flight mass (MALDI-TOF MS) spectra were recorded on a Bruker Daltonics Autoflex Speed spectrometer. High resolution mass spectra were obtained with a double focusing, magnetic sector, high-resolution

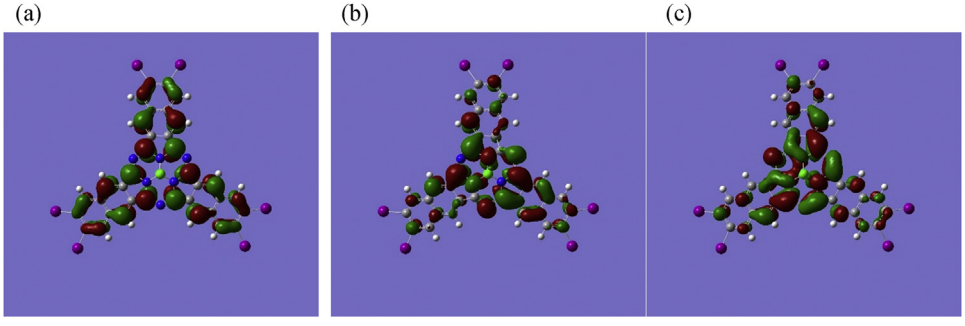


Fig. 2. HOMO (a) and two degenerated LUMOs (b, c) of **3**. B3LYP/LanL2DZ calculations.

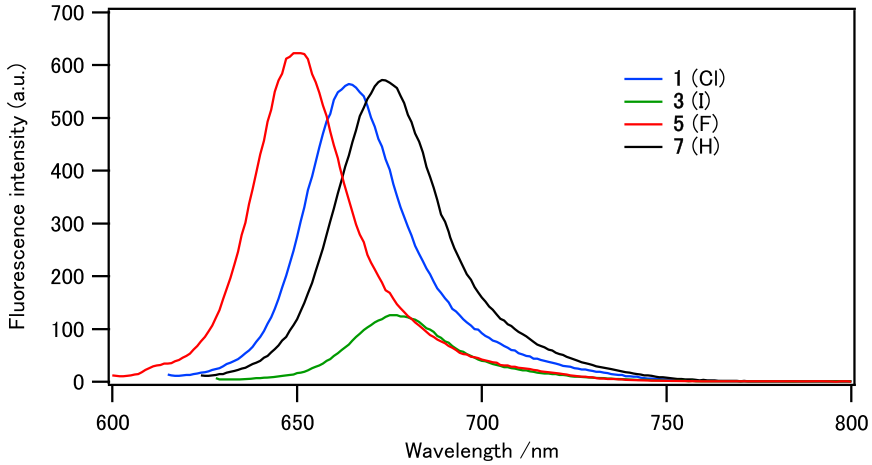


Fig. 3. Fluorescence spectra of **1**, **3**, **5**, and **7** at 298 K in *o*-dichlorobenzene where the samples were excited at ($\lambda_{max\ abs}$—50) nm. Each sample has absorbance of 0.02 at the excitation wavelength.

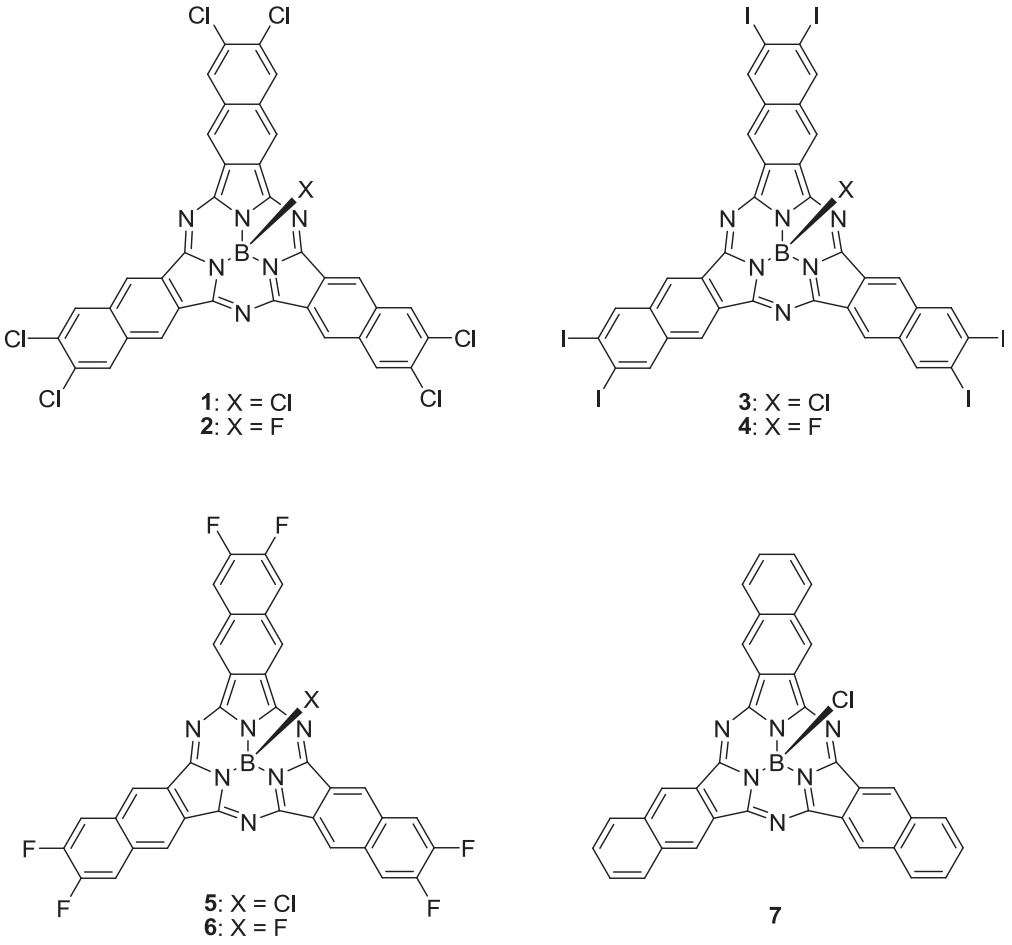


Chart 1. Structures of subnaphthalocyanines.

mass spectrometer, JEOL JMS-700 with FAB ionization. UV–visible spectra were recorded on an Agilent 8453 UV–visible spectrometer. Fluorescence spectra were recorded on a Shimadzu RF-5300PC spectrofluorophotometer. Photoelectron spectroscopy was recorded on a surface analyzer AC-2 of Riken Keiki. Fluorescence lifetimes in toluene were measured by a streak camera (Hamamatsu C4330) using the output from optical parametric amplifier (600 nm) operated by the amplified output from Ti:Sapphire laser (Spectra Physics Spitfire XP) as the excitation pulse.

4.2. 4,5-Dichlorobenzene-1,2-dimethanol (8)

Compounds **8** and **9** were prepared according to the reported procedure.[22]

In a 1-L three-necked flask were placed $LiAlH_4$ (12.3 g, 0.33 mol) and dry THF (700 mL). A solution of 4,5-dichlorobenzene-1,2-dicarboxylic acid (38.87 g, 0.165 mol) in dry THF (120 mL) was slowly added dropwise at −78 °C under Ar. The reaction mixture was warmed up to room temperature, and refluxed overnight. An

aqueous solution of NaOH (10%, 100 mL) was added, followed by the addition of water (150 mL) and THF (300 mL). The organic layer was separated. The aqueous layer was extracted with THF three times and the THF layer was combined with the organic layer. The combined organic layer was washed with saturated aqueous NaCl three times and the solvent was evaporated. The white solid was washed with hexane and dichloromethane: 28.8 g, 84% yield. Mp: 92–95 °C. ^{1}H NMR data matched published data.[22]

^{1}H NMR (acetone-d_6, 500 MHz): δ (ppm)=7.64 (s, 2H), 4.67 (d, 4H, J=5.8 Hz), 4.46 (br, 2H).

4.3. 4,5-Dichlorobenzene-1,2-dicarbaldehyde (9)

In a 500-mL three-necked flask were placed dry dichloromethane (100 mL) and oxalyl chloride (10 mL, 0.116 mol). A mixture of dry dichloromethane (25 mL) and dry DMSO (13.6 mL) was slowly added at −78 °C under Ar with stirring. After the mixture was stirred for 5 min, a solution of **8** (12.4 g, 59.8 mmol) in dry DMSO (15 mL) and dry dichloromethane (15 mL) was slowly added and the mixture was stirred for 30 min. Dry triethylamine (125 mL) was then added slowly and stirring was continued for 10 min. The mixture was then warmed up to room temperature and stirred overnight. The reaction was quenched by adding water, and the organic layer was collected. The aqueous layer was washed with dichloromethane three times, and the dichloromethane solution was combined with the organic layer. The organic solvents were evaporated and the residue was subjected to silica gel chromatography using ethyl acetate:hexane (30:70) as eluant: 6.1 g, 50% yield. White powder, mp: 134–135 °C. ^{1}H NMR data matched published data.[22]

^{1}H NMR ($CDCl_3$, 500 MHz): δ (ppm)=10.49 (s, 2H), 8.11 (s, 2H).

4.4. 6,7-Dichloronaphthalene-2,3-dicarbonitrile (10)

Compound **10** was prepared according to the reported procedure.[13] In a 200-mL three-necked flask were placed fumaronitrile (0.435 g, 5.41 mmol), **9** (1.00 g, 4.92 mmol), and dry dichloromethane (35 mL). A solution of 1 M triethylphosphine in THF (5.90 mL, 5.9 mmol) diluted with dry dichloromethane (5.90 mL) was added slowly at −78 °C under Ar. DBU (74.9 mg, 0.492 mmol) was then added and the mixture was stirred overnight. The reaction was quenched by the addition of water and the organic layer was separated. The aqueous layer was washed with dichloromethane three times and the dichloromethane solution was combined with the organic layer. The organic solvent was evaporated and the residue was washed with hexane, dichloromethane, acetone, and methanol, to obtain **10**: 1.05 g, 87% yield. White powder, dec at 289–290 °C. ^{1}H NMR data matched published data.[13]

^{1}H NMR (acetone-d_6, 500 MHz): δ (ppm)=8.75 (s, 2H), 8.52 (s, 2H).

4.5. Chloroboron(III) 3,4,12,13,21,22-hexachlorosubnaphthalocyanine (1)

In a 1-L three-necked flask were placed **10** (1.00 g, 4.06 mmol), dry *p*-xylene (80 mL), dry *o*-dichlorobenzene (80 mL). A solution of 1 M BCl_3 in heptane (10 mL, 10 mmol) was then added under Ar. The reaction mixture was warmed to 160 °C at the rate of 2 °C/min and heated at 160 °C for 2 h. After cooled to room temperature, the reaction mixture was filtered. The filtrate was evaporated in vacuo, and the residue was washed with methanol and hexane. The solid was subjected to silica gel column chromatography using $CHCl_3$:hexane (6:4) as eluant. The product was washed with diethyl ether and recrystallized from toluene to obtain 230 mg (22%) of **1**. Blue powder, mp: >375 °C.

^{1}H NMR ($CDCl_3$, 500 MHz): δ (ppm)=9.31 (s, 6H), 8.45 (s, 6H). MALDI-TOF MASS: m/z=784.2 [M^+], calcd for $C_{36}H_{12}BN_6Cl_7$ m/z=785.9. HRMS (FAB): m/z=785.9000, calcd for $^{12}C_{36}{}^1H_{12}{}^{14}N_6{}^{35}Cl_6{}^{37}Cl^{11}B$ m/z=785.9007. UV–visible (*o*-dichlorobenzene) λ_{max}/nm (log ε): 660 (5.01), 342 (4.71).

4.6. Fluoroboron(III) 3,4,12,13,21,22-hexachlorosubnaphthalocyanine (2)

In a 200-mL three-necked flask were placed **1** (95 mg, 0.12 mmol), silver tetrafluoroborate (66 mg, 0.24 mmol) and dry *p*-xylene (50 mL), and the mixture was stirred at room temperature for 30 min under Ar. After the reaction was quenched by adding water, the solvent was evaporated in vacuo. The obtained solid was washed with hexane, methanol, acetone, dichloromethane, chloroform, ethyl acetate, 28% aqueous ammonia, and diethyl ether to obtain **2**: 83 mg, 89% yield. Blue powder, mp: >375 °C.

^{1}H NMR (toluene-d_8, 500 MHz): δ (ppm)=8.91 (s, 6H), 7.85 (s, 6H). MALDI-TOF MASS: m/z=768.1[M^+], calcd for $C_{36}H_{12}BN_6FCl_6$ m/z=767.9. HRMS (FAB): m/z=769.9331, calcd for $^{12}C_{36}{}^1H_{12}{}^{14}N_6{}^{35}Cl_5{}^{37}Cl^{11}B$ m/z=769.9302. UV–visible (*o*-dichlorobenzene) λ_{max}/nm (log ε): 655 (5.06), 339 (4.77).

4.7. 4,5-Diiodophthalimide (12)

Compounds **12**–**15** were prepared according to the reported procedure.23 In a 500-mL three-necked flask were placed 30% fuming sulfuric acid (90 mL), phthalimide (22 g, 0.15 mol) and iodine (38 g, 0.15 mol) and the mixture was heated at 85 °C for 40 h. The mixture was added to crushed ice (600 g). A white solid was collected by filtration and washed with 2% aqueous K_2CO_3, saturated $NaNO_2$, and water to obtain **12**: 43.4 g, 90% yield. White powder, mp: >375 °C.

4.8. 4,5-Diiodobenzene-1,2-dicarboxylic acid (13)

In a 2-L three-necked flask were placed **12** (56.5 g, 0.142 mmol) and 10% aqueous KOH (1.45 L) and the mixture was heated at 100 °C for 20 h. The reaction mixture was neutralized by adding 6 M HCl until pH was below 2. The white solid was collected by suction filtration: 43.4 g, 73% yield. White powder, mp: >375 °C. ^{1}H NMR data matched published data.[23]

^{1}H NMR (DMSO-d_6, 500 MHz): δ (ppm)=8.59 (s, 2H).

4.9. 4,5-Diiodobenzene-1,2-dimethanol (14)

In a 3-L three-necked flask were placed dry THF (1750 mL) and **13** (62.3 g, 149 mmol). A solution of 1 M BH_3 in THF (350 mL, 350 mmol) was added at 0 °C under Ar over 1 h. After the addition, the mixture was stirred at 0 °C for 1 h, and then refluxed at 66 °C for 40 h. After the mixture was cooled, saturated aqueous K_2CO_3 (1050 mL) was slowly added and stirring was continued for 12 h at 50 °C. The organic layer was separated and the aqueous layer was extracted with THF three times. The organic layers were combined and washed with saturated aqueous NaCl three times. The organic solvent was evaporated in vacuo. The solid was washed successively with hexane, dichloromethane, and water. The product was dried in vacuo to obtain 53.5 g, 91% of **14**. White solid, mp: 163–165 °C. ^{1}H NMR data matched published data.[23]

^{1}H NMR (acetone-d_6, 500 MHz): δ (ppm)=7.98 (s, 2H), 4.61 (d, 4H), 4.47 (t, 2H).

4.10. 4,5-Diiodobenzene-1,2-dicarbaldehyde (15)

In a 500-mL three-necked flask were placed dry dichloromethane (116 mL) and oxalyl chloride (6.2 mL, 71.6 mmol). A

mixture of dry dichloromethane (24 mL) and dry DMSO (11.6 mL) was slowly added at −78 °C under Ar with stirring. After the mixture was stirred for 10 min, a solution of **14** (9.0 g, 22.8 mmol) in dry DMSO (20 mL) and dry dichloromethane (40 mL) was slowly added and the mixture was stirred for 8 h. Dry triethylamine (34 mL) was then added slowly and stirring was continued for 1 h. The mixture was then warmed up to room temperature and stirred overnight. The reaction was quenched by adding water, and the organic layer was separated. The aqueous layer was washed with dichloromethane three times, and the dichloromethane solution was combined with the organic layer. The organic solvent was evaporated and the residue was washed with dichloromethane and hexane, to yield 8.67 g of **15** in 97% yield. White powder, mp: 131–133 °C. ^{1}H NMR data matched published data.[23]

^{1}H NMR ($CDCl_3$, 500 MHz): δ (ppm)=10.41 (s, 2H), 8.37 (s, 2H).

4.11. 6,7-Diiodonaphthalene-2,3-dicarbonitrile (16)

In a 500-mL three-necked flask were placed fumaronitrile (2.60 g, 33.3 mmol), **15** (10.0 g, 25.9 mmol), and dry dichloromethane (175 mL). A solution of 1 M triethylphosphine in THF (31.1 mL, 31.1 mmol) diluted with dry dichloromethane (31.1 mL) was added slowly at −78 °C under Ar. DBU (393.5 mg, 2.59 mmol) was then added and the mixture was stirred overnight. The reaction was quenched by the addition of water and the organic layer was separated. The aqueous layer was washed with dichloromethane three times and the dichloromethane solution was combined with the organic layer. The organic solvent was evaporated and the residue was washed with hexane and methanol to obtain **16**: 9.41 g, 84% yield. White needle, mp: 284–285 °C.

^{1}H NMR (acetone-d_6, 500 MHz): δ (ppm)=8.87 (s, 2H), 8.67 (s, 2H). GC-MASS: m/z=430 [M^+], calcd for $C_{12}H_4I_2N_2$ m/z 429.8.

4.12. Chloroboron(III) 3,4,12,13,21,22-hexaiodosubnaphthalocyanine (3)

In a 200-mL three-necked flask were placed **16** (5.00 g, 16.7 mmol), dry *p*-xylene (200 mL), dry *o*-dichlorobenzene (200 mL). A solution of 1 M BCl_3 in heptane (23 mL, 23 mmol) was then added under Ar. The reaction mixture was warmed to 180 °C at the rate of 2 °C/min and heated at 180 °C for 1.5 h. After the reaction mixture was cooled in an ice-water bath for 30 min, blue crystals were collected by suction filtration, and washed successively with hexane, toluene, and acetone. The solid was dissolved in 2 L of $CHCl_3$, and insoluble impurities were filtered. The filtrate was evaporated to obtain 3.80 g (73%) of **3**. Blue powder, mp: >375 °C.

^{1}H NMR ($CDCl_3$, 500 MHz): δ (ppm)=9.23 (s, 6H), 8.91 (s, 6H). MALDI-TOF MASS: m/z=1335.6 [M^+], calcd for $C_{36}H_{12}BN_6ClI_6$ m/z=1335.5. HRMS (FAB): m/z=1335.5162, calcd for $^{12}C_{36}{}^1H_{12}{}^{14}N_6{}^{35}Cl$ ^{11}B I_6 m/z=1335.5173. UV–visible (*o*-dichlorobenzene) λ_{max}/nm (log ε): 668 (5.14), 355 (4.86).

4.13. Fluoroboron(III) 3,4,12,13,21,22-hexaiodosubnaphthalocyanine (4)

In a 200-mL three-necked flask were placed **3** (100 mg, 0.075 mmol), silver tetrafluoroborate (33 mg, 0.12 mmol) and dry *p*-xylene (10 mL), and the mixture was stirred at room temperature for 30 min under Ar. After the reaction was quenched by adding water, the solvent was evaporated in vacuo. The obtained solid was washed with hexane, methanol, acetone, dichloromethane, chloroform, ethyl acetate, 28% aqueous ammonia, and diethyl ether to obtain **4**: 70 mg, 71% yield. Blue powder, mp: >375 °C.

^{1}H NMR (pyridine-d_5, 500 MHz): δ (ppm)=9.42 (s, 6H), 9.07 (s, 6H). MALDI-TOF MASS: m/z=1319.7 [M^+], calcd for $C_{36}H_{12}BN_6FI_6$ m/z=1319.6. HRMS (FAB): m/z=1319.5453, calcd for $^{12}C_{36}{}^1H_{12}{}^{14}N_6{}^{19}F$ ^{11}B I_6 m/z=1319.5469.

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Supplementary data

Supplementary data (These data include ^{1}H NMR, ^{13}C NMR, and MALDI-TOF MS spectra and photoelectron spectra and UV–visible spectra of thin film of subnaphthalocyanines) associated with this article can be found in the online version, at http://dx.doi.org/10.1016/j.tet.2016.06.064.

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