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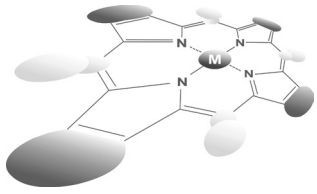

Synthesis of arylsulfanyl-subphthalocyanines and their ring expansion reaction

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Dedicated to Professor Nagao Kobayashi on the occasion of his 65th birthday

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ABSTRACT: For dye-sensitized solar cells, phthalocyanines require strong absorption of far-red light between 700 and 850 nm because of their high electron transfer efficiency. Nevertheless phthalocyanines lack of affinity to basal plats, they inhibit utilization as dye-sensitized solar cell photosensitizer. Then, subphthalocyanines are used as precursors to prepare asymmetric 3:1 type phthalocyanines using a ring-enlargement technique to give affinity to basal plates. As subphthalocyanines having arylsulfanyl substituents used as a precursor, asymmetric phthalocyanines are expected to have good affinity to basal plates. Spectroscopic properties and electron transfer abilities to synthesize non-peripheral arylsulfanyl-subphthalocyanines were estimated. In addition to prepare as trial, asymmetric 3:1 type phthalocyanine, hexakis[(4-methylphenyl)thio]phthalocyanine, was synthesized from corresponding subphthalocyanine.

KEYWORDS: arylsulfanyl substituents, subphthalocyanine, cyclic voltammetry.

INTRODUCTION

Phthalocyanines are known for use as dyes, pigments and important functional colorants for various applications such as catalysts, electron charge carriers, and photosensitizers [1–17].

The non-peripheral (1, 4, 8, 11, 15, 18, 22, 25) substituted phthalocyanines can show a bathochromic effect of the strongest absorption called Q-band in comparison with the peripheral (2, 3, 9, 10, 16, 17, 23, 24) positions [4, 18, 19].

Non-peripheral alkyl substituents linked through heteroatoms have the important effect of moving the Q-band from 780 nm to the near infrared region [20]. Although most metal phthalocyanines have a planar structure, the bathochromic effect of the Q-band observed for the octakis(*p*-methoxyphenyl)phthalocyanines was shifted beyond 800 nm, which arises from ligand deformation [21, 22]. Moreover, the Q-bands of non-peripheral substituted octakis(arylsulfanyl)phthalocyanines appeared at around 860 nm [5].

The non-peripheral substituted octakis(arylsulfanyl) phthalocyanines are assumed to have low affinity to basal plates such as titania (TiO_2). In orders to conquer the defect, few papers are reported many kinds of phthalocyanines having anchoring substituents and subphthalocyanines [2–29]. Asymmetric 3:1 type phthalocyanines containing six arylsulfanyl groups at non-peripheral positions have molecular-designed possessing anchoring functional groups, such as carboxy groups, at peripheral positions, which expect to show affinity to TiO_2 basal plates. Asymmetric phthalocyanines are known to be prepared with stoichometric mixture of raw materials [4]. The other method, asymmetric phthalocyanines are synthesized

◊ SPP full member in good standing

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from corresponding subphthalocyanine as a precursor and phthalic derivatives. In the later method, the ring-enlargement technique is very useful to synthesize asymmetric 3:1 type phthalocyanines. And then, corresponding subphthalocyanines act as precursors for phthalocyanine synthesis of ring-enlargement technique. Subphthalocyanines consist of three isoindole units with boron as the center of the molecule.

In this study, non-peripheral substituted hexakis(arylsulfanyl)subphthalocyanines are synthesized as precursor of hexakis(arylsulfanyl)phthalocyanines possessing anchoring functional groups. The non-peripheral substituted hexakis(arylsulfanyl)subphthalocyanines are estimated to have their own basic properties of spectroscopic tendency in comparison with the corresponding octakis(arylsulfanyl)phthalocyanines and electron transfer ability.

EXPERIMENTAL

Equipment

Infrared (IR) spectra were recorded on a Shimadzu IR-8400A spectrometer and a Perkin-Elmer Spectrum 65 FT-IR spectrometer. Ultraviolet-visible (UV-vis) spectra were measured on a Shimadzu UV-2400PC spectrometer, while fluorescence spectra were measured on a Nihon Bunko JASCO FP-6000 fluorescence spectrometer. Each sample was prepared in chloroform ($ChCl_3$) at a concentration of 5.0×10^{-5} M. The proton magnetic resonance (^{1}H NMR) spectra and carbon magnetic resonance (^{13}C NMR) spectra were measured on a Bruker Advance 400S and a Bruker AdvanceIII 500 in dimethylsulfoxide (DMSO)-d_6 or $CHCl_3$-*d* using tetramethylsilane as the internal standard. Elemental analysis was carried out using a Perkin-Elmer 2400CHN instrument. Mass (MS) spectra were taken with a Nihon Denshi Joel JMS-AX500 mass spectrometer. Cyclic voltammograms (CVs) were recorded on an ALS electrochemical analyzer 600D at room temperature in dichlorobenzene or $CHCl_3$ containing 0.1 M tetrabutylammonium perchlorate (TBAP). CVs were recorded by scanning the potential at a rate of 50 $mV.s^{-1}$. The working and counter electrodes were platinum wires, and the reference electrode was a silver (Ag)/silver chloride (AgCl) electrode. The area of the working electrode was 2.0×10^{-2} cm^2.

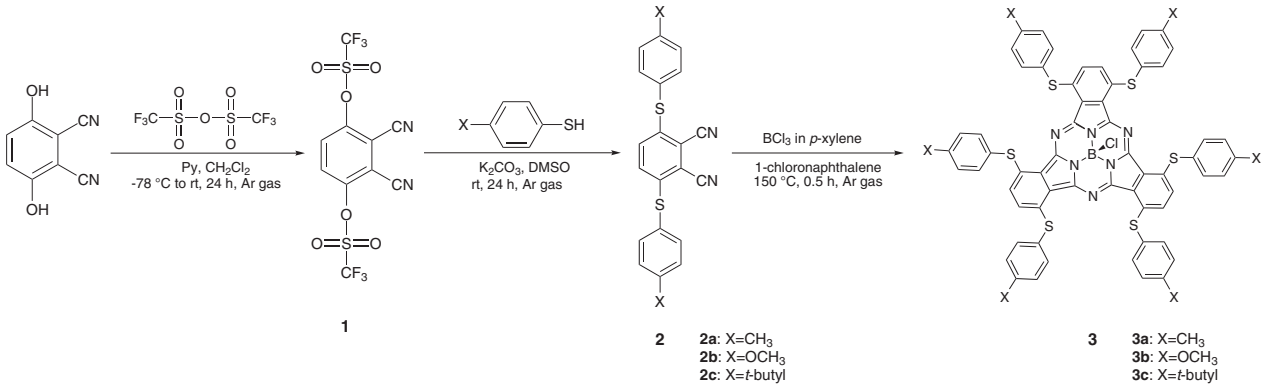
Synthesis

The synthetic route to the target hexakis(arylsulfanyl) subphthalocyanines (**3**) were shown in Scheme 1. Target compounds **3** were synthesized in three steps *via* intermediates, phthalonitrile-3,6-ditriflate (**1**) and 3,6-bis(arylsulfanyl)phthalonitriles (**2**).

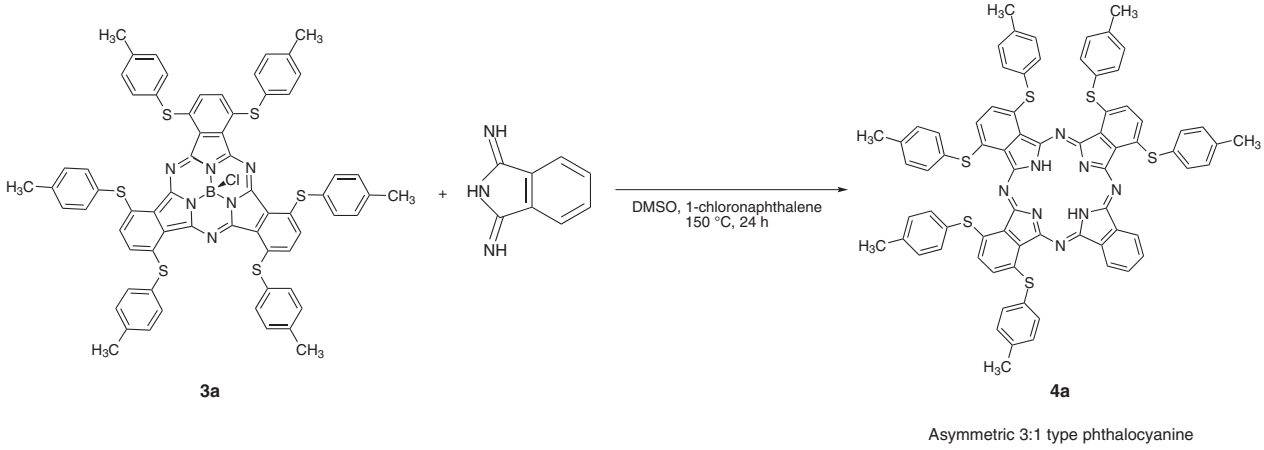
All chemicals were purchased from Aldrich or Tokyo Chemical Industry. They were used as received without further purification. For chromatographic separation, silica gel was used (60, particle size 0.063–0.200 nm, 7734-grade; Merck).

Phthalonitrile-3,6-ditrifluoromethanesulfate (1). 2,3-Dicyanohydroquinone (4.80 g, 30 mmol) in dichloromethane (100 mL) and pyridine (py) (5.93 g, 75 mmol) was treated with trifluoromethanesulfonic anhydride (21.16 g, 75 mmol) under argon at -78 °C. After the reaction, the mixture was allowed to warm slowly to room temperature; stirring was continued for 24 h. The mixture was poured into water (600 mL). Then the organic layer was extracted using dichloromethane (5×100 mL). The extract was washed in turn with water, 2%-hydrochloric acid, water, brine and water, and dried on magnesium sulfate ($MgSO_4$). The filtrate and the solvent evaporated. The crude product was recrystallized from dichloromethane to afford **1** (6.35 g, 50%) as colorless needles. Found C, 28.32%; H, 0.48%; N, 6.59%. Calcd. for $C_{10}H_2F_6N_2S_2O_6$: C, 28.31%; H, 0.48%; F, 26.87%; N, 6.60%; O, 22.63%; S, 15.12%. IR (KBr): ν cm^{-1} 3115 ($\nu_{C\text{-}H}$), 2550 ($\nu_{C\text{-}N}$), 1601 ($\nu_{C\text{-}C}$), 1472 ($\nu_{C\text{-}C}$), 1439 ($\nu_{C\text{-}C}$), 1134 ($\nu_{S=O}$). ^{1}H NMR (400 MHz, DMSO-d_6): δ, ppm 8.44 (s, 2H).

3,6-Bis(arylsulfanyl)phthalonitriles (2). In a mixture of **1** (0.85 g, 2 mmol), potassium carbonate (1.16 g) and DMSO (15 mL), thiophenols (4 mmol) for instance *p*-toluenethiol, 4-methoxybenzenethiol and *ter*t-butylthiophenol was added; the mixture was reacted at room temperature for 24 h in nitrogen atmosphere. The reaction products were poured into water (300 mL), and the organic layer extracted using dichloromethane (5×100 mL), and dried on $MgSO_4$. The filtrate and the solvent evaporated. The crude product was washed with methanol (3×50 mL) and recrystallized from toluene to afford **2** as a yellow solid. **3,6-Bis[(4-methylphenyl)thio] phthalonitrile (2a).** (0.43 g, 56%) Found C, 70.90%; H, 4.30%; N, 7.50%. Calcd. for $C_{22}H_{16}N_2S_2$: C, 70.93%; H, 4.33%; N, 7.52%; S, 17.22. IR (KBr): ν cm^{-1} 3050 ($\nu_{C\text{-}H}$), 2970 ($\nu_{C\text{-}H}$), 2218 ($\nu_{C\text{-}N}$), 1600 ($\nu_{C\text{-}C}$), 1535 ($\nu_{C\text{-}C}$), 1490 ($\nu_{C\text{-}C}$), 1435 ($\nu_{C\text{-}C}$), 1210, 809 ($\delta_{C\text{-}H}$). ^{1}H NMR (400 MHz, DMSO-d_6): δ, ppm 7.54 (d, 4H), 7.46 (d, 4H), 7.35 (s2H), 2.66 (tt, 6H). ^{13}C NMR (125 Hz, $CHCl_3$-*d*): δ, ppm 21.3, 76.7, 77.0, 77.2, 111.3, 130.9, 131.6, 134.9, 140.6, 143.2. **3,6-Bis[(4-methoxyphenyl)thio]phthalonitrile (2b).** (0.61 g, 75%) Found C, 65.30%; H, 4.00%; N, 6.93%. Calcd. for $C_{22}H_{16}N_2S_2O_2$: C, 65.32%; H, 3.99%; N, 6.93%; S, 15.82%; O, 7.91%. IR (KBr): ν cm^{-1} 3050 ($\nu_{C\text{-}H}$), 2970 ($\nu_{C\text{-}H}$), 2216 ($\nu_{C\text{-}N}$), 1600 ($\nu_{C\text{-}C}$), 1540 ($\nu_{C\text{-}C}$), 1487 ($\nu_{C\text{-}C}$), 1430 ($\nu_{C\text{-}C}$), 1210, 810 ($\delta_{C\text{-}H}$). ^{1}H NMR (400 MHz, DMSO-d_6): δ, ppm 7.49 (d, 4H), 7.06 (d, 4H), 7.04 (s2H), 3.79 (s, 6H). ^{13}C NMR (125 Hz, $CHCl_3$-*d*): δ, ppm 55.4, 76.8, 77.0, 77.2, 113.6, 113.7, 115.8, 119.3, 131.0, 137.1, 143.8, 161.3. **3,6-Bis[(4-*ter*t-butylphenyl)thio] phthalonitrile (2c).** (0.38 g, 42%) Found C, 73.65%; H, 6.18%; N, 6.11%. Calcd. for $C_{28}H_{28}N_2S_2$: C, 73.64%; H, 6.18%; N, 6.13%; S, 14.04%. IR (KBr): ν cm^{-1} 3040 ($\nu_{C\text{-}H}$), 2960 ($\nu_{C\text{-}H}$), 2210 ($\nu_{C\text{-}N}$), 1600 ($\nu_{C\text{-}C}$), 1500 ($\nu_{C\text{-}C}$), 1460



Scheme 1. Synthetic pathway of non-peripheral arylsulfanyl-subphthalocyanines (**3**)



Scheme 2. A typical synthesis pathway from non-peripheral arylsulfanyl-subphthalocyanines (**3**) to asymmetric 3:1 type phthalocyanine using ring enlargement technique

(ν_{C-C}), 1210, 808 (δ_{C-H}). ^{1}H NMR (400 MHz, DMSO-d_6): δ, ppm 7.50 (d, 4H), 7.46 (d, 4H), 7.26 (s, 2H), 1.28 (s, 18H). ^{13}C NMR (125 Hz, $CHCl_3$-d): δ, ppm 31.2, 34.8, 76.7, 77.0, 77.2, 113.7, 114.5, 125.8, 127.3, 131.8, 134.5, 143.1, 153.7.

Non-peripheral arylsulfanyl-subphthalocyanines (3). A mixture of **2** (10.0 mmol) and boron trichloride (6 mL, 1 M in *p*-xylene) in 1-chloronaphthalene (18 g) was refluxed at 150 °C for 30 min under argon atmosphere. The products were dissolved in toluene. Into the toluene solution, hexane was added to precipitate non-peripheral arylsulfanyl-substituted subphthalocyanines. The non-peripheral arylsulfanyl-substituted subphthalocyanines were column-chromatographed on silica gel with chloroform as eluent. **Hexakis[(4-methoxyphenyl) thio]subphthalocyanine (3a).** (2.00 g, 17%) Found C, 67.68%; H, 3.96%; N, 6.81%. Calcd. for $C_{66}H_{48}N_6S_6BCl$: C, 68.11%; H, 4.16%; N, 7.22%. IR (KBr): ν cm^{-1} 3020 (ν_{C-H}), 2920 (ν_{C-H}), 2864 (ν_{C-H}), 1586 (ν_{C-C}), 1546 (ν_{C-C}), 1490 (ν_{C-C}), 1449 (ν_{C-C}), 1415, 1380, 807 (δ_{C-H}). ^{1}H NMR (500 MHz, DMSO-d_6): δ, ppm 7.62 (d, 12H), 7.29 (d, 12H), 6.94 (d, 6H), 2.33 (s, 18H). ^{13}C NMR (125 Hz, $CHCl_3$-d): δ, ppm 21.3, 76.8, 77.0, 77.2, 77.6, 127.0, 127.1, 128.2, 129.8, 130.6, 131.0, 134.9, 135.9. MS (FAB): *m/z* found 1163, calcd. 1163.78. **Hexakis[(4-methoxyphenyl)thio])subphthalocyanine (3b).** (0.85 g, 7%) Found C, 62.91%; H, 3.78%; N, 6.40%. Calcd. for $C_{66}H_{48}N_6S_6O_6BCl$: C, 62.92%; H, 3.84%; N, 6.67%. IR (KBr): ν cm^{-1} 3056(ν_{C-H}), 2933 (ν_{C-H}), 2840 (ν_{C-H}), 1591 (ν_{C-C}), 1566 (ν_{C-C}), 1504 (ν_{C-C}), 1489 (ν_{C-C}), 968, 786, 758 (δ_{C-H}). ^{1}H NMR (500 MHz, DMSO-d_6): δ, ppm 7.68 (d, 12H), 7.00 (d, 12H), 6.87 (d, 6H), 3.82 (s, 18H). MS (FAB): *m/z* found 1259, calcd. 1259.28. **Hexakis[(4-*tert*-butylphenyl)thio] subphthalocyanine (3c).** (0.41 g, 7%) Found C, 71.27%; H, 5.63%; N, 5.97%. Calcd. for $C_{84}H_{84}N_6S_6BCl$: C, 71.24%; H, 5.98%; N, 5.93%. IR (KBr): ν cm^{-1} 3057 (ν_{C-H}), 2954 (ν_{C-H}), 1592 (ν_{C-H}), 1504 (ν_{C-C}), 1458 (ν_{C-C}), 835, 820 (δ_{C-H}). ^{1}H NMR (500 MHz, DMSO-d_6): δ, ppm 7.70 (d, 12H), 7.48 (d, 12H), 6.95 (d, 6H), 1.35 (d, 54H). ^{13}C NMR (125 Hz, $CHCl_3$-d): δ, ppm 31.2, 34.8, 76.8, 77.0, 77.2, 77.6, 124.4, 125.7, 126.1, 126.7, 126.8, 126.9, 127.0, 127.2, 128.2, 135.8. MS (FAB): *m/z* found 1415, calcd. 1416.26.

Hexakis(arylsulfanyl-phthalocyanine (4). Asymmetric 3:1 type phthalocyanines were obtained from **3** and isoindoline (Scheme 2). A typical synthetic procedure

is following: a mixture of compound **3a** (0.27 mmol) and 1,3-diiminoisoindoline (2.69 mmol) in DMSO — 1-chloronaphthalene (2:1 V/V, 18 g) was refluxed 90 °C for 24 h. Obtained material was washed with hexane and methanol. Hexakis[(4-methoxyphenyl)thio] phthalocyanine (**4a**) was column-chromatographed on silica gel with chloroform, and obtained 7% yield. IR (KBr): ν cm^{-1} 3289 (ν_{N-H}), 3025 (ν_{C-H}), 2918 (ν_{C-H}), 2885(ν_{C-H}), 1597 (ν_{C-C}), 1556 (ν_{C-C}), 1487 (ν_{C-C}), 1452 (ν_{C-C}), 1438, 1400, 805, 745 (δ_{C-H}). ^{1}H NMR (500 MHz, DMSO-d_6): δ, ppm 7.89 (d, 4H), 7.38 (d, 12H), 7.22 (d, 12H), 6.88 (d, 6H), 2.37 (d, 18H). -0.12 (s, 2H).

RESULTS AND DISCUSSION

Compounds **3** were synthesized *via* intermediates **1** and **2** (Scheme 1). Intermediate **1** was synthesized from 2,3-dicyanohydroquinone and trifluoromethanesulfonic anhydride. [4, 5]. Intermediates **2** were synthesized from **1**, and *p*-toluenethiol, 4-methoxybenzenethiol and *tert*-butylthiophenol, respectively to obtained **2a**, **2b** and **2c**. Intermediates **1** and **2** were analyzed using IR and ^{1}H NMR and ^{13}C NMR spectroscopy, and elemental analysis. Their analytical data showed good agreement with proposed structure.

The obtained target compounds non-peripheral arylsulfanylsubstituted subphthalocyanines, **3** were synthesized from corresponding intermediates **2**, respectively, and boron trichloride in 1-chlonaphthalene under argon atmosphere. The products of **3** were purified using column chromatography on silica gel with chloroform as eluent. The target compounds **3** were analyzed using IR, ^{1}H NMR, ^{13}C NMR and MS spectroscopy, and elemental analysis. The analytical data showed good agreement with the proposed structure.

To prepare asymmetric 3:1 type phthalocyanines, compounds **3** and isoindoline were reacted to obtain metal-free corresponding phthalocyanines **4** (Scheme 2). The analytical data of **4** showed good agreement with proposed structure.

The UV-vis spectra of compounds **3** were shown in Fig. 1. The strongest absorption peak assignee are the Q-band, which is attributed highest occupied molecular orbital (HOMO) — lowest unoccupied molecular orbital (LUMO) π–π* transition in the same manner as phthalocyanines. The Q-band of compounds **3** shows around 650 nm. The Q-band of compounds **3** moved to longer wavelength by 86 nm in comparison to subphthalocyanine which appeared around 560 nm. Absorption maxima of subphthalocyanine and thioalkyl-substituted fluorosubphthalocyanines appeared around 560 to 630 nm with increasing their molecular weight [23].

Subphthalocyanines have domed concave shape molecular arising from three isoindole units whereas phthalocyanines possess planer structure as the result of their porphyrazines rings consisting of four isoindole

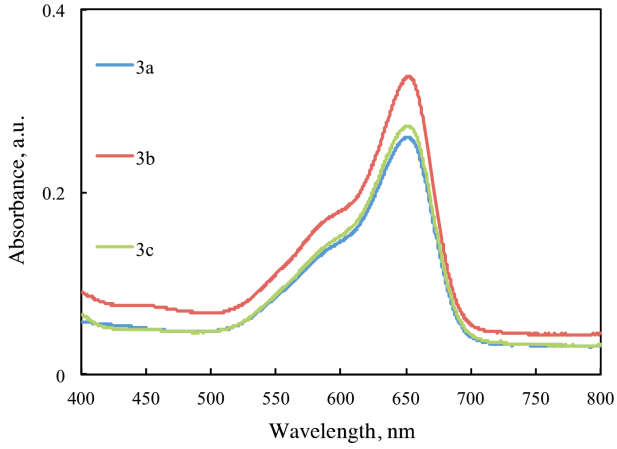


Fig. 1. UV-vis spectra of non-peripheral arylsulfanyl-subphthalocyanines (**3**)

Table 1. The Q-band absorption data of non-peripheral arylsulfanyl-subphthalocyanines (**3**)

	3a	**3b**	**3c**	**4a**
λ_{max}, nm	651.5	651.5	651.0	773
log ε	3.48	3.61	3.33	4.98

units. Since the compounds **3** have remarkably bulky substituents, the molecular distortion is increased. Selected terminal substituents, methyl, methoxy and *tert*-butyl, their absorption properties are significantly low. However in the present work, it is known that these substituents were selected to compare the size of terminal groups. The steric hindrance arises from substituted arylsulfanyl groups, which appear to be as significant [22]. The difference of Q-band absorption in **3** is however low between substituents, methyl, methoxy, and *tert*-butyl groups. The chromopher of subphthalocanines as same as phthalocyanines are π-conjugated macro rings, hence substituents only slightly affect the movement to bathochromic effect. The Q-band data of **3** are presented in Table 1.

Fluorescence and excitation spectra of **3** are shown in Fig. 2. Fluorescence spectra of **3** appeared around 681 nm, and the excitation spectra have almost same of absorption spectra. The fluorescence spectra of **3** appeared as a mirror image of their excitation spectra. The difference of maximum value of **3** between fluorescence and excitation spectra showed approximately 30 nm.

Fluorescence is reflected as aromatic and/or conjugation double-bonded with a high degree of resonance stability. The same as the fluorescence maxima of **3** signifies dependence on the π electron environment. The difference in maxima of spectra is called the Stokes shift. In the general case of phthalocyanines, including subphthalocyanines, the value of the Stokes shift is relatively small in a few nanometers. The phenomena mean that phthalocyanines form rigid molecules between

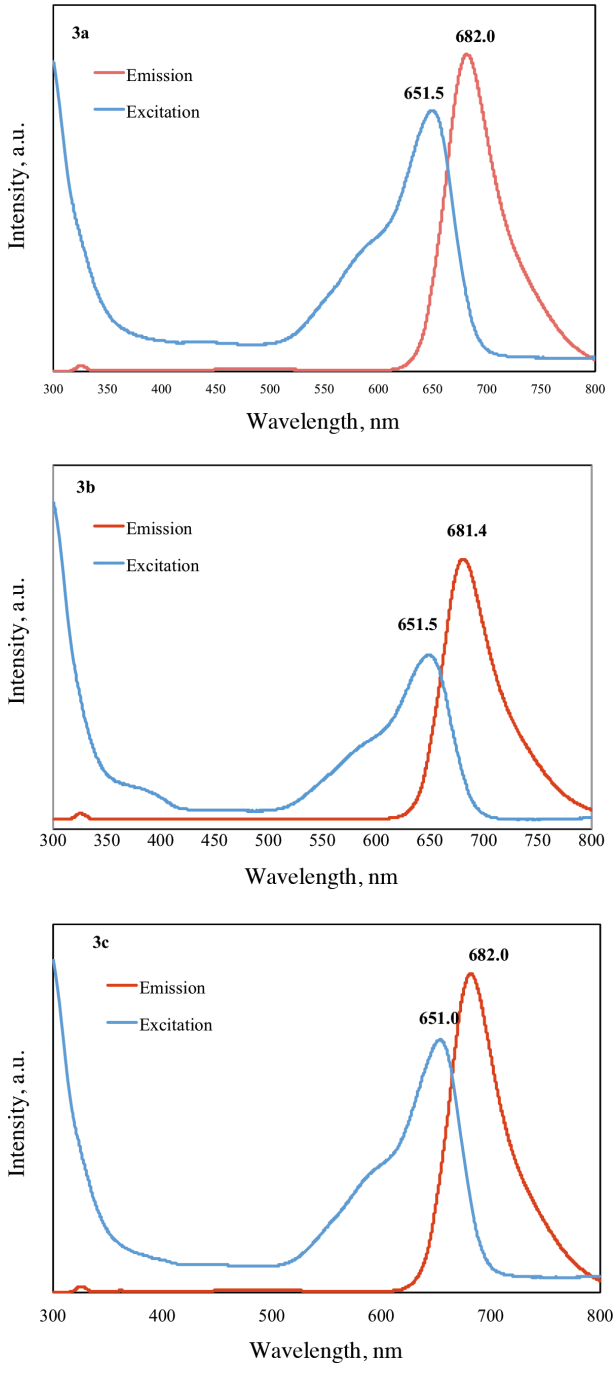


Fig. 2. Fluorescence and excitation spectra of non-peripheral arylsulfanyl-subphthalocyanines (**3**)

their ground and excited electronic states. In the case of **3**, the molecules transform their structures between electron transitions because the constitutions of **3** exhibit flexibility as a result of their remarkable bulky substituents.

Asymmetric 3:1 type phthalocyanine **4** appeared at 773 nm (log ε = 4.98) in Q-band, shifted by 122 nm to a longer wavelength than the corresponding compound **3**. The Q-bands of previous reported non-peripheral substituted octakis(arylsulfanyl)phthalocyanines appeared at around 800 nm, especially metal-free octakis(arylsulfanyl)phthalocyanines showed longer wavelength than corresponding metal phthalocyanines [5]. The Q-band of synthesized **4** is showed shorter wavelength by 42 nm in comparison with previous reported non-peripheral substituted octakis(thiophenyl methyl)phthalocyanine, which appeared at 815 nm [5]. It means that the Q-band depends upon the electron distribution caused by number of substitution. The ring enlargement technique is suitable for the synthesis of asymmetric 3:1 type phthalocyanine. Sinrh and his co-workers reported that asymmetric phthalocyanines prepared with stoichometric mixture of raw materials appeared at 750 nm [24], which means that the Q-band depends upon the electron distribution caused by number of substitution.

CVs were carried out with an ALS electrochemical analyzer 600D at room temperature in dichlorobenzene and/or chloroform containing 0.1 M TBAP. Important parameters of CVs are the reduction and oxidation potentials for irreversible peaks, and the mid-point potential for reversible couple (E_{mid}). The shapes of CVs are present as upward cathodic and downword anodic peaks.

A typical CV of **3** is shown in Fig. 3. The CVs of **3** show similar shapes except for subphthalocyanine. The shapes of **3c** showed cathodic and anodic peaks. These pair of peaks appeared around -1.69, -1.15. +0.62 and +0.88 V *vs.* Ag/AgCl. Oxidation and reduction potentials of **3** were summarized in Table 2.

In general, metal phthalocyanines having transition metal behave as electrochemically irreversible, and exhibit reduction and oxidation properties resulting from interaction between the phthalocyanine ring and their central metal. The oxidation potential is about 1.0 V *vs.* standard hydrogen electrode (SHE). The reduction potential occurs between -0.3 and -0.8 V *vs.* SHE. Electrons are added either to the molecular orbital of the

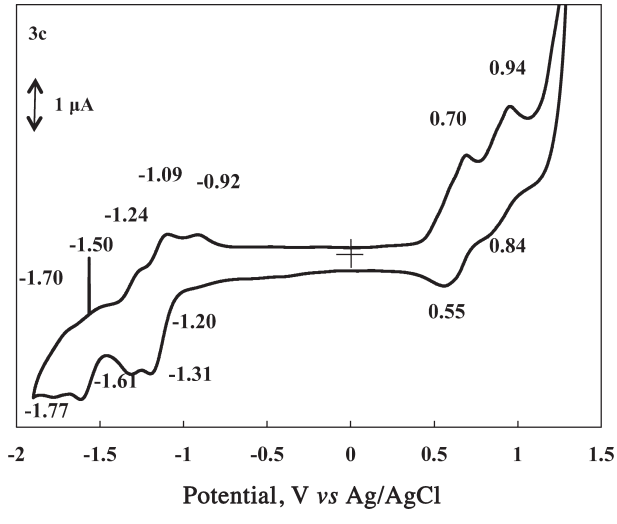


Fig. 3. A typical cyclic voltammogram of compound **3c**

Table 2. Reduction and oxidation potential of compounds **3a** and **3c** in *o*-dichlorobenzene or chloroform with tetrabutylammonium perchlorate

	Potential, V *vs.* Ag/AgCl dichloromethane solvent						
	Reduction					Oxidation	
3a	-1.74	-1.56	-1.28	-1.14	-0.92*	0.62	0.90
3c		-1.69	-1.15	-0.90*		0.62	0.88
4a		-1.25	-0.86	-0.46		0.38	
SubPC			-1.31			0.75	
	Potential, V *vs.* Ag/AgCl chloroform solvent						
	Reduction					Oxidation	
3a			-1.81	-1.43*		0.80*	
3c			-1.81			0.74*	
SubPC			-1.52*	-1.20*		0.81*	

Potentials of reversible wave are midpoint of anodic and cathodic peaks for each couple E1/2. *Irreversible peak.

phthalocyanine ring or the central metal, depending on the reduction-oxidation potential for reduction process. For subphthalocyanines, the authors have reported that an irreversible reduction potential appeared around -0.3 V *vs.* Ag/AgCl [23]. The irreversible peaks of subphthalocyanines are attributed to the deduction of the subphthalocyanine ring. The reduction and oxidation potentials of subphthalocyanines result from their substituents.

CVs of compounds **3** differ in terms of shape from subphthalocyanine, **3c** have many reduction and oxidation peaks. These phenomena mean that the substituents variedly act in accordance with their electro-donating property for methyl, methoxy and *tert*-butyl, although they do not demonstrate the effect as chromophores. The substituents of compounds **3** are affected more by subphthalocyanines than porphyrazines ring before reported corresponding octakis(arylsulfanyl)phthalocyanines [7]. Compounds **3** show many reduction potentials and are acceptable electrons in the subphthalocyanine ring compare with corresponding octakis(arylsulfanyl)phthalocyanines.

CV of asymmetric 3:1 type phthalocyanine, **4a** shows peaks at -1.25, -0.86, -0.46 and +0.38 V *vs.* Ag/AgCl. These data are similar to the previous reported octakis(arylsulfanylmethyl)subphthalocyanine [7].

CONCLUSION

The target compounds, hexakis(arylsulfanyl) subphthalocyanines **3**, were synthesized in three steps in order to prepare the precursor of 3:1 type asymmetric hexakis(arylsulfanyl)phthalocyanines. The Q-band of compounds **3** shows around 650 nm, which shifts to longer wavelength by 86 nm in comparison to subphthalocyanine. Compounds **3** show many reduction potentials. Compounds **3** are acceptable electrons in the subphthalocyanine ring, meaning that the compounds **3** have good electron transfer properties. Then, compound **4** has similar properties of previous reported phthalocyanines.

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