Synthesis of phthalocyanines having thio-alkyl substituents at non-peripheral positions and their photochemical and photophysical properties

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ABSTRACT

Phthalocyanines possess similar structure of natural chromophore porphyrins. The phthalocyanines are known to utilize in important functional colorants for many fields. The phthalocyanines are especially expected to use photosensitizers for both dye-sensitized solar cells and photodynamic therapy of cancer. In the present study, novel non-peripheral substituted thio-alkyl zinc phthalocyanines were synthesized in order to develop second-generation photosensitizer for photodynamic therapy of cancer. In order to evaluate the influence of heteroatom existence and chain length, synthesized non-peripheral substituted thio-alkyl phthalocyanines were reported photoexcited triplet lifetime using laser-flash photolysisand singlet oxygen quantum yields by 1,3-diphenylbenzofuranemethod. Of synthesized non-peripheral substituted phthalocyanines, ultraviolet-visible spectra showed around 780 nm, photoexcited triplet lifetimes were estimated around 1 as and singlet oxygen quantum yields. It is thought that synthesized non-peripheral hetero-alkyl substituted phthalocyaines had enough ability for photodynamic therapy of cancer.

GRAPHICAL ABSTRACT
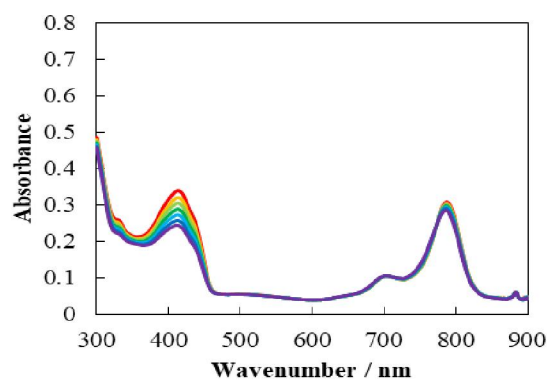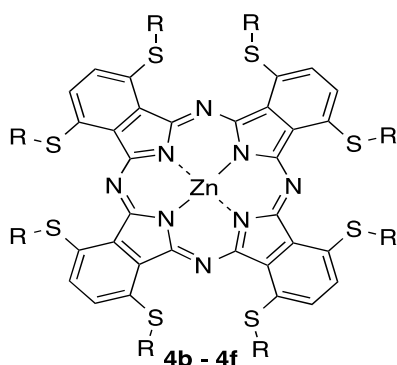
1. Introduction

Molecular structure of phthalocyanines is closely related to the naturally occurring porphyrins. Phthalocyanines are used as important colorants from their discovery in 1928. In this century, phthalocyanines are anticipated as functional materials for various applications especially photosensitizers for both dye-sensitized solar cells and photodynamic therapy of cancer (PDT).[1-4] PDT photosensitizers accumulate in cancer cells. Then, phthalocyanines attack and eventually destroy cancer cells that receive sufficient light to produce lethal amount of singlet oxygen. Precisely, the method of PDT selectively becomes extinct cancer cells in the presence of photosensitizers using around 650 nm laser radiation giving rise to photochemical reactions with oxygen. At present time, porphyrins such as hematoporphyrins, Photofrin[TM] and Laserphyrin[TM] have been practically used as a photosensitizer for PDT at medical institutions, but they are known to have the main absorption ability around 400 nm at which wavelength tissue penetration is low with absorption of near infrared laser radiation. Further, they have some weak points for cytotoxity: a slow metabolism rate and accumulation. On the other hand, phthalocyanines exhibit suitable properties for use as a photosensitizer for PDT as will be mentioned below.

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Phthalocyanines are known to have a potential to utilize as second-generation photosensitizer for PDT. Utilization for PDT, phthalocyanines are required to possess a high photostability, high selectivity to tumours, a long lifetime of photoexcited triplet state and show strong absorption maxima called Q band between 600 and 800 nm where penetration of tissue is good, and no cytotoxity when no light is irradiated.[5] However, non-substituted phthalocyanines are known to be insoluble or to have lower solubility in common organic solvents. The drawback of phthalocyanines has been improved to introduce substituents such as alkyl groups onto the ring system of phthalocyanine.

Phthalocyanines exhibit aromaticity owing their 18-electron conjugation by Hückel's theory. The introduction of substituents on benzenoid rings of phthalocyanines provides solubility either aqueous or organic solvents. Substituted phthalocyanines at peripheral (2, 3, 9, 10, 16, 17, 23, 24) positions have solubility, but the Q bands of them are not moved to longer wavelength. While on the other hand, phthalocyanines having substituents at non-peripheral (1, 4, 8, 11, 15, 18, 22, 25) positions become soluble in common organic solvents, result in the longer wavelength shift of Q band and decrease of aggregation.[6] The authors previously reported that non-peripheral substituted alkylbenzopyridoporphyrazines were measured the lifetime of photoexcited

triplet state using laser-flash photolysis. The non-peripheral substituted alkylbenzopyridoporphyrazines showed intense absorption and photoexcited longer triplet lifetime.[7] Cook and his co-workers reported that non-peripheral octa-alkyl zinc phthalocyanines function as potential photosensitizer for PDT.[8] Phthalocyanines having thio-alkyl substituents at non-peripheral positions show Q band around 700 nm, and high ionization potential approximately 5 eV.[9] The central metal of phthalocyanines for PDT is suitable to closed d shell or diamagnetic metal ions such as zinc (II), aluminium (III) and gallium which produce high triplet yield with long lifetimes.[10] Especially, non-transition metal phtha-locyanines were known to be excellent photosensitizers for PDT.The authors have reported the synthesis of non-peripheral thio-substituted phthalocyanines of which Q band appeared at around 800 nm.[9]

In this study, in order to evaluate the influence for existence of heteroatom and chain length, non-peripheral substituted thio-alkyl zinc phthalocyanines are synthesized. Alkyl and thio-alkyl groups are chosen substituents of synthesized non-peripheral thio-alkyl zinc phthalocyanines. Furthermore, we also report their photochemical properties obtained from photoexcited triplet lifetime using laser-flash photolysis and single oxygen quantum yields by 1,3-diphenylisobenzofurane (DPBF) method.

Scheme 1. Synthetic pathways of non-peripheral (1, 4, 8, 11, 15, 18, 22, 25) substituted zinc phthalocyanines **4**.
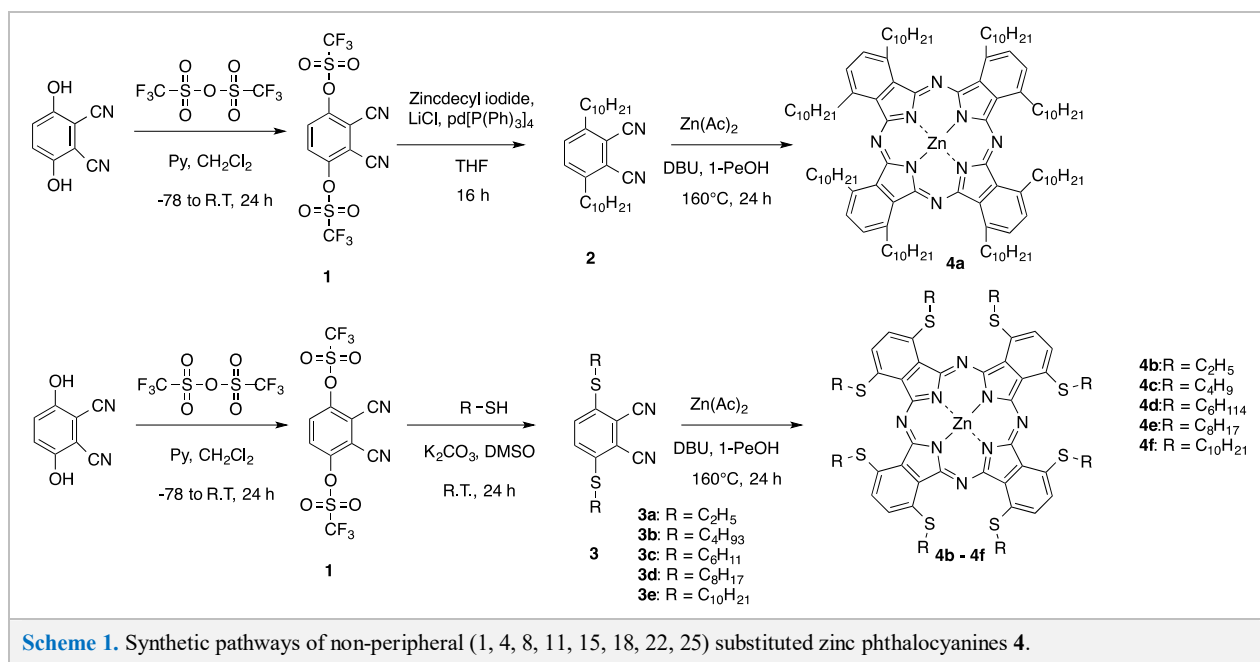
2. Results and Discussion

2.1. Synthetic chemistry

Non-peripheral (1, 4, 8, 11, 15, 18, 22, 25) thio-alkyl substituted zinc phthalocyanine (**4**) were synthesized in three steps corresponding phthalonitriles (**2** or **3**). The synthetic pathway was shown in **Scheme 1**.

In the concrete, zinc 1, 4, 8, 11, 15, 18, 22, 25-octadecylphthalocynine (**4a**) was synthesized from 3,6-didecylphthalo-

nitrile (**2**), zinc 1, 4, 8, 11, 15, 18, 22, 25-octakis(ethylthio)-phthalocyanine (**4b**), zinc 1, 4, 8, 11, 15, 18, 22, 15-octakis-(butylthio)phthalocyanine (**4c**), zinc 1, 4, 8, 11, 15, 18, 22, 25-octakis(hexylthio)phthalocyanine (hexylthio)phthalocyanine (**4d**), zinc 1, 4, 8, 11, 15, 18, 22, 25-octakis(octylthio)phthalo-cyanine (**4e**) and zinc 1, 4, 8, 11, 15, 18, 22, 15-octakis(decylthio)phthalocyanine (**4f**) were synthesized respectively, corresponding phthalonitriles, 3,6-bis(ethylthio)-phthalonitrile (**3a**), 3,6-bis(butylthio)phthalonitrile (**3b**), 3,6-bis(hexylthio)phthalonitrile (**3c**), 3,6-

bis(octylthio)phthalonitrile (**3e**), 3,6-bis(decylthio)phthalo-nitrile (**3f**) and zinc acetate (Zn(Ac)$_2$) in the presence of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) or 1,5-diazabicyclo-[4.3.0]non-5-ene (DBN) as a catalyst and 1-pentanol (1-PeOH) for 24 h. Intermediates, **2** and **3** were synthesized from phthalonitrile-3,6-ditrifluoromethanesulfate (**1**) and decylzinc iodide or alkylthiols such as ethanethiol, butanethiol, hexane-thiol, octanethiol and decanethiol at room temperature for 12 h, respectively. All synthesized phthalocyanines **4** were isolat-ed using column chromatography on silica gel with toluene as eluent. Further, intermediate **1** was synthesized from 2,3-dicyanohydroquinone and trifluoromethansulfonic anhydride for 24 h in accordance with a description from literatures. [1,5] Intermediates **1**- **3** and phthalocyanines **4** were analysed using elemental analysis, infrared (IR), ultraviolet-visible (UV-Vis),

proton magnetic resonance (^{1}HNMR) and mass (MS) spectro-scopy. The analytical data showed good agreement with the proposed structure.

2.2. Photochemistry

The UV-Vis spectra of phthalocyanines **4b**–**4f** were shown in **Fig 1**. The strongest absorption peaks are assigned as Q band, which is attributed to the highest occupied molecular orbital (HOMO)–lowest unoccupied molecular orbital (LUMO), π–π* transition in the same manner as phthalo-cyanines. A typical value for the extinction coefficient (ε) of the Q band is around 10^5 L. mol^{-1} cm^{-1}. The Q band of **4b** – **4f** showed around 780 nm of which wavelength shifted by 112 nm to longer in comparison with unsubstituted phthaloc-yanine.
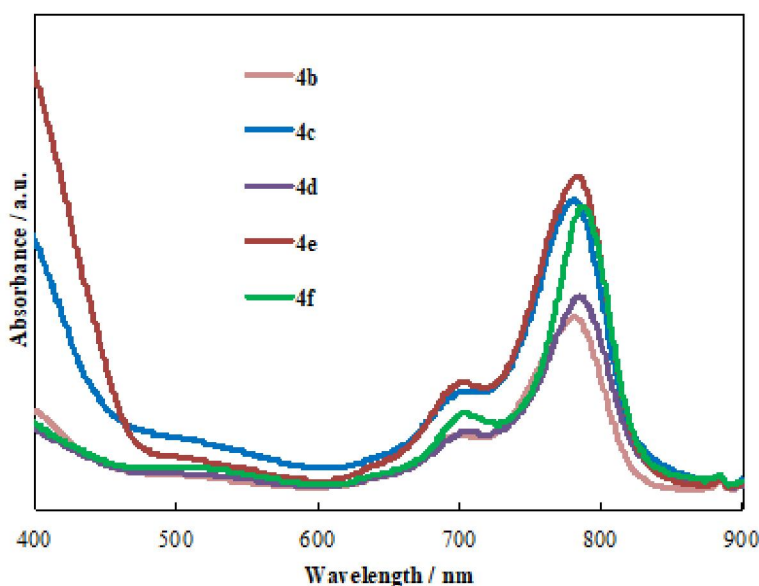

Fig 2. UV-Vis spectra of **4b-4f**.

Table 1. The spectral data of Q band in UV-Vis and fluorescence for phthalocyanines **4**.

Entry	Compound	Q band in UV-Vis spectrum		Fluorescence spectrum (F_{max}/ nm)	Stokes shift / nm
		λ_{max} / nm	log ε		
1	**4a**	703	5.01	715	11
2	**4b**	785	5.00	812	27
3	**4c**	785	4.93	806	21
4	**4d**	786	4.74	803	16
5	**4e**	773	4.77	792	19
6	**4f**	778	5.12	800	22

The Q band of compound **4** depends upon the change in the electron distribution in the phthalocyanine ring caused by substituents of which bathochromic increase in order of decyl, and alkylthio groups.

The Q band and fluorescence spectral data of **4** were shown in **Table 1**. Fluorescence spectra of **4** showed the right of Q band in UV-Vis spectra around 790 nm and the excitation

spectra have almost same of UV-Vis spectra. In general, the fluorescence spectra appeared as a mirror image of their excitation or UV-Vis spectra.

The excitation spectra have almost same of UV-Vis spectra, of course the values of wavelength of excitation maxima (λ_{ex}) equalize to wavelength of absorption maxima (λ_{max}). The difference between wavelength of fluorescence maxima (F_{max})

and excitation λ_{ex} or UV-Vis spectra λ_{max} is called Stokes shift. The value of Stokes shift is relatively small in a few nanometers in the case of phthalocyanines. These phenomena mean that phthalocyanines constitute rigid molecules between grand and excited electronic states. In the case of compound **4**, their value of Stokes shifts showed partially large. The molecules of compound **4** transform their structure between electron transitions under light irradiation, since the constitution of **4** exhibit different conformation and steric hindrance as a result of their substituents at non-peripheral positions.
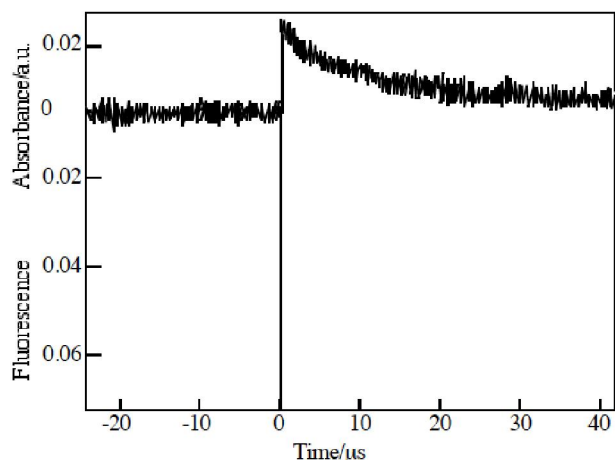

Fig 2. The triplet decay trace of phthalocyanine **4a**.

2.3. Photophysicochemistry

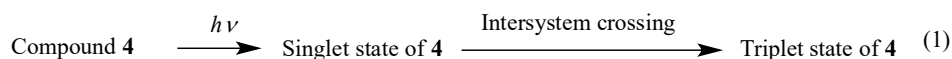Fluorescence and transient decay curves were observed upon pulsed excitation of 355 nm in $1.5 \cdot 10^5$ mol L^{-1} chloroform (CHCl$_3$) solutions. The transition absorption was reasonably assigned to the photoexcited triplet state. The strongest fluorescence was quenched by oxygen for laser flash excitation of 560 nm. The time profile of the photoexcited triplet state for one of compound **4a** was observed using laser-flash photolysis (**Fig 2**).

Similar decay curves were obtained for the other phthalocyanines **4b**–**4f**. For laser-flash excitation of 560 nm, the strongest fluorescence was quenched by oxygen. The photoexcited triplet state lifetime of phthalocyanines **4** was estimated to be around 1 μs except for **4a**. Phthalocyanines **4** have relatively longer triplet lifetime. The value of the photoexcited triplet lifetime for phthalocyanines **4** is not dependent upon the individual molecular structure, particularly their length of substituents. The photoexcited triplet lifetime of phthalocyanines **4** except **4a** increased with not only the number of carbon atoms but also existence of heteroatom in the substituents.

The photoexcited triplet lifetime of phthalocyanines **4** was summarized in **Table 2**. In the presence of phthalocyanines **4** as a photosensitizer, photooxidation progresses *via* singlet state oxygen ($^1O_2$).[11] Phthalocyanines **4** in the photoexcited triplet state react with ground triplet state oxygen ($^3O_2$). The $^3O_2$ generated $^1O_2$.

Non-transition metal phthalocyanines, especially those containing aluminum and zinc, are recognized to be excellent photosensitizer for the Type II process, since they exhibit long photoexcited triplet lifetime and give high quantum yields for $^1O_2$ formation.[1-2, 11-13] The photochemistry of phthalocyanines **4** results in the same process of above mentioned Type II mechanism. The Type II mechanism is shown in **Equations 1–3**.

Entry	Compound	Triplet lifetime /μs	Φ_Δ
	Table 2. Photophysical parameters of phthalocyanines **4**.		
1	Zinc phthalocyanine	0.4	0.64
2	**4a**	2.6	0.66
3	**4b**	1.2	0.67
4	**4c**	1.2	0.72
5	**4d**	1.2	0.57
6	**4e**	1.2	0.77
7	**4f**	1.2	0.68

$$\text{Compound } \mathbf{4} \xrightarrow{h\nu} \text{Singlet state of } \mathbf{4} \xrightarrow{\text{Intersystem crossing}} \text{Triplet state of } \mathbf{4} \quad (1)$$

$$\text{Triplet state of } \mathbf{4} + {}^3O_2 \longrightarrow \text{Compound } \mathbf{4} + {}^1O_2 \quad (2)$$

$$^1O_2 + \text{substrate} \longrightarrow \text{substrate oxide} \quad (3)$$

Singlet oxygen quantum yield (Φ_Δ) indicates the potential of photosensitizer in application in which singlet oxygen is required in Type II mechanism. The Φ_Δ was determined in air with zinc phthalocyanine as a standard chemical and DPBF was used as a chemical quencher for singlet oxygen.[2, 11-13] The chemical quencher DPBF reacts with singlet oxygen to produce cyclohexa-3,5-diene-1,2-diylbis(phenylmethanone).

An efficacy of singlet oxygen quenching is monitored of DPBF peak intensity at 417 nm on UV-Vis spectra. The Φ_Δ was estimated using **Equation 4**.

$$\Phi_\Delta = \Phi_\Delta^{Std} \frac{R I_{abs}^{Std}}{R^{Std} I_{abs}} \quad (4)$$

where Φ_Δ^{Std} is the singlet oxygen quantum yields for zinc phthalocyanine as a standard $\Phi_\Delta^{Std} = 0.61$ in pyridine (Py), R and R^{Std} are DPBFphotobleaching rate in the presence of phthalocyanines **4** and zinc phthalocyanine as a standard, respectively. Symbols I_{abs} and I_{abs}^{Std} are intensity of light for phthalocyanines **4** and zinc phthalocyanine, respectively. The change of UV-Vis spectra for determination of Φ_Δ of phthalocyanines **4** using DPBF is shown in **Fig 3**.

Absorption bands in UV-Vis spectra appeared at 417 and 786 nm for DPBF and phthalocyanine **4c**, respectively. The intensity of DPBF peaks at 417 nm was decreased with increasing elapsed time, whereas no change was shown on Q band of **4c** at 786nm during Φ_Δ measurements. The DPBF absorbance at 417 was decreased in proportion to elapsed time. The relationship between Φ_Δ and elapsed time was inset in the figure. Similar shapes of absorption bands and tendencies of spectral change were observed for the other phthalocyanines **4** during Φ_Δ measurements. It seems that the Φ_Δ of non-peripheral thio-alkyl substituted phthalocyanines **4b**–**4f** is not dependent upon length of substituents (**Table 2**). The Φ_Δ values of phthalocyanines **4** are considered to be enough ability to utilize photosensitizer for PDT.[6, 13]
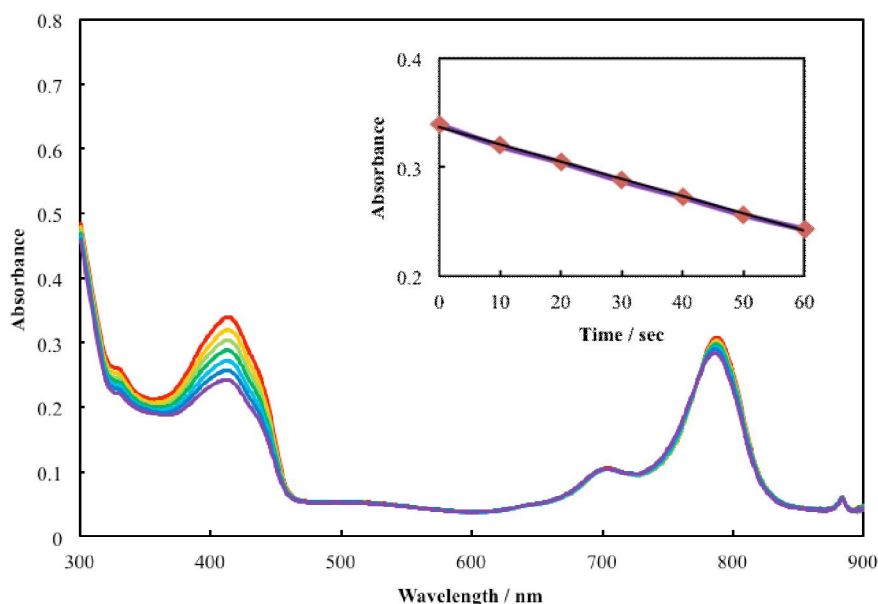

Fig 3. A typical absorption spectral change for determination of singlet oxygen quantum yield of phthalocyanine **4c** in DMFisingDPBF as a singlet oxygen quencher.

3. Conclusions

Non-peripheral thio-alkyl substituted zinc phthalocyanines **4a**–**4f** were synthesized in order to develop next-generation PDT photosensitizer. The UV-Vis spectra of **4** showed around 780 nm. The Q band is suitable for PDT photosensitizer. The photoexcited triplet lifetime of **4** was estimated around 1 μs. The Φ_Δ of **4** estimated around 0.6.The PDT efficiency is not dependent upon length of substituents. It is concluded that these phthalocyanines **4** have suitable Q band absorption, photoexcited triplet lifetime and singlet oxygen quantum yields to photosensitizer for PDT.

4. Experimental

4.1. Materials

All Chemicals were purchased from Aldrich, Tokyo Chemical Industry, Kanto Chemical or Wako Pure 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). Thin layer chromategraphy was performed using Merck 60 F_{254} silica gel.

4.2. Method

The IR spectra were recorded on a Perkin-Elmer Spectram 65 FT-IR spectrometer by attenuated total reflection (ATR) method. The UV-Vis spectra were measured on a Shimadzu UV-2400PC spectrometer. Each sample was prepared at $1.0 \cdot 10^{-5}$ mol L^{-1} in $CHCl_3$ or N,N-dimethylformamide (DMF). Fluorescent spectra were recorded at $1.0 \cdot 10^{-5}$ mol L^{-1} in $CHCl_3$ on a Nihon Bunko Jasco FP-6600 spectrofluorometer. The ^{1}HNMR spectra were measured on a Bruker advance III in dimethyl sulfoxide (DMSO)-d_6 or $CHCl_3$-d using tetramethylsilane as the internal standard. The MS spectra were taken with a Nihon Denshi Joel JMS-AX500 mass spectrometer. Melting points were measured with a Stanford research system MPA 100 optimelt automated system. Photoexcited triplet lifetime was observed using Laser-flash photolysis (Tokyo Instruments) at $1.5 \cdot 10^{-5}$ mol L^{-1} in $CHCl_3$. An excitation light pulse (29 ms, 355 nm and 10 mJ / pulse) from a YAG laser was exposed over the sample. A monitoring light from a xenon lamp passed through the multireflection cell, which was connected to the head of an optical fiber attached to monochrometer equipped with photomultiplier or to a spectral multichannel analyzer system.

The Φ_Δ was estimated by DPBF method using zinc phthalo-cyanine as a standard material for $\Phi_\Delta{}^{Std} = 0.67$.[2, 11-13] Synthesized non-peripheral thio-alkyl zinc phthalocyanines containing DPBF as a singlet oxygen quencher in 1.7 mL of $3 \cdot 10^{-5}$ mol L^{-1}DMF solutions was irradiated at 635 nm Laser (2 mW) for 10 s, 6 times.

4.3. Synthesis of non-pripheralthio-alkyl zinc phthalocyanines and preparation of their intermediates

4.3.1. Phthalonitrile-3,6-ditrifluoromethanesulfate (1)

2,3-Dicyanohydroquinone (4.85 g, 30 mmol) in dichloromethane (CH_2Cl_2) (100 mL) and Py (5.93 g, 75 mmol) was treated with trifluoromethanesulfonic anhydride (21.16 g, 75 mmol) under argon (Ar) at -78°C. After 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) and the organic layer was extracted using CH_2Cl_2 (5 · 100 mL). The extract was washed in tern with water, 2%-hydrochloric acid, water, brine and water, dried on magnesium sulfate ($MgSO_4$). The filtrate and the solvent evaporated. The crude product was recrystallized from CH_2Cl_2 to affore**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 (ATR); ν cm^{-1} 3115 (ν_{C-H}), 2550 (ν_{C-N}), 1601 (ν_{C-C}), 1472 (ν_{C-C}), 1439 (ν_{C-C}), 1134 ($\nu_{S=O}$).^{1}HNMR (500 MHz, DMSO-d_6): δ ppm 8.44 (s, 2H), MS (FAB): *m/z* found 396, calcd. 396.26.

4.3.2. 3,6-Didecylphthalonitrile (2)

A mixture of **1** (0.55 g, 1.30 mmol), lithium chloride (0.17 g, 3.00 mmol), tetrakis(triphenylphosphine)palladium (68 mg) and dry tetrahydrofuran (THF) (10mL) was stirred for 10 min at room temperature. After that, decylzinc iodide was added into the mixture and the solution was refluxed for 16 h. After the reaction, THF was evaporated. The crude product was purified by column chromatography to afford **2** (0.51 g, 26%). **Found:** C, 82.26%; H, 10.84%; N, 6.84%. Calcd. for$C_{28}H_{44}N_2$: C, 82.29%; H, 10.87%; N, 6.85%. IR (ATR): ν cm^{-1} 3119 (ν_{C-H}), 2970 (ν_{C-H}), 2256 (ν_{C-N}), 1603 ($\nu_{C=C}$), 1443 (δ_{C-H}), 955 ($\delta_{C=C}$). ^{1}HNMR (500 MHz, DMSO-d_6): δ ppm 7.66 8s, 2H), 2.63 (t, 4H), 1.59 (m, 4H), 1.26 (m, 28H), 0.88 (t, 6H). MS (FAB): *m/z* found 409, calcd. 408.74.

4.3.3. 3,6-Bis(alkylthio)phthalonitrile (3)

In a mixture of **1** (2.00 g, 4.71 mmol), potassium carbonate (4.00 g), DMF (15 mL) and thiols (12.0 mmol) for instance ethanethiol, butanethiol, hexanethiol, octanethiol and decanethiol was added; the mixture was reacted at room temperature for 12 h under Ar atmosphere. The reaction products were poured into water (50 mL), and the organic layer extracting using $CHCl_3$ (5×20 mL), and dried on $MgSO_4$. The crude products were recrystallized from methanol to afford **3** as yellow solid.

3,6-Bis(ethylthio)phthalonitrile (3a) (0.54 g, 46%). **Found:** C, 60.14%; H, 5.16%; N, 11.66%. Calcd. for$C_{12}H_{12}N_2S_2$: C, 58.02%; 4.88%; N, 11.28%; S, 25.82%. IR (ATR): ν cm^{-1} 2973 (ν_{C-H}), 2969 (ν_{C-H}), 2911 (ν_{C-H}), 2227 (ν_{C-N}), 1655 ($\nu_{C=C}$), 1595 ($\nu_{C=C}$), 864 (δ_{C-H}), 755 (δ_{C-H}), 610 (ν_{C-S}). ^{1}HNMR (500 MHz, CHCl_3-d): δ, ppm 7.22 (s, 2H), 2.86 (m, 4H), 1.31 (t, 6H). MS (FAB): *m/z* found 249, calcd. 248.40.

3,6-Bis(butylthio)phthalonitrile (3b) (0.62 g, 43%). **Found:** C, 63.07%; H, 6.46%; N, 9.23%. Calcd. for$C_{16}H_{20}N_2S_2$: C, 63.10%; H, 6.63%; N, 9.20%; S, 21.06%. IR (ATR): ν cm^{-1}3087 (ν_{C-H}), 2962 (ν_{C-H}), 2856 (ν_{C-H}), 2223 (ν_{C-N}), 1424 (δ_{C-H}), 824 (δ_{C-H}), 738 (ν_{C-S}). ^{1}HNMR (500 MHz, CHCl_3-d): δ ppm 7.26 (s, 2H), 2.89 (t, 4H), 1.60 (m, 4H), 1.44 (m, 4H), 0.92 (t, 6H). MS (FAB): *m/z* found 305, calcd. 304.52.

3,6-Bis(hexylthio)phthalonitrile (3c) (0.84 g, 49%). **Found:** C, 63.47%; H, 6.93%; N, 8.93%. Calcd. for$C_{20}H_{28}N_2S_2$: C, 66.60%; H, 7.84%; N, 7.77%; S, 17.79%. IR (ATR): ν cm^{-1} 3084 (ν_{C-H}), 2927 (ν_{C-H}), 2850 (ν_{C-H}), 2227 (ν_{C-N}), 1450 (δ_{C-H}), 835 (δ_{C-H}), 727 (ν_{C-S}). ^{1}HNMR (500 MHz, CHCl_3-d): δ ppm 7.72 (s, 2H), 3.01 (t, 4H), 1.64 (m, 4H), 1.42 (m, 4H), 1.31 (m, 8H), 0.88 (t, 6H). MS (FAB): *m/z* found 361, calcd. 360.64.

3,6-Bis(octylthio)phthalonitrile (3d) (1.09 g, 56%). Found: C, 64.16%; H, 9.55%; N, 7.85%. Calcd. for$C_{24}H_{36}N_2S_2$: C, 69.16%; H, 8.72%; N, 6.72%; S, 15.39%. IR (ATR) ν cm^{-1} 3082 (ν_{C-H}), 2915 (ν_{C-H}), 2850 (ν_{C-H}), 2227 (ν_{C-N}),1450 (δ_{C-H}), 835 (δ_{C-H}), 725 (ν_{C-S}). ^{1}HNMR (500 MHz, CHCl_3-d): δ ppm 7.72 (s, 2H), 2.89 (t, 4H), 1.64 (m, 4H), 1.31 (m, 20H), 0.88 (t, 6H). MS (FAB): *m/z* found 417, calcd. 416.76.

3,6-Bis(decylthio)phthalonitrile (3e) (0.87 g, 35%). Found: C, 71.31%; H, 9.66%; N, 6.03%. Calcd. for$C_{28}H_{44}N_2S_2$: C, 71.11%; H, 9.40%; N, 5.93%; S, 13.56%. IR (ATR) ν cm^{-1} 3085(ν_{C-H}), 2918 (ν_{C-H}), 2849 (ν_{C-H}), 2227 (ν_{C-N}), 1450 (δ_{C-H}), 834 (δ_{C-H}), 722 (ν_{C-N}). ^{1}HNMR (500 MHz, CHCl_3-d): δ ppm 7.72 (s, 2H), 2.89 (t, 4H), 1.64 (m, 4H), 1.40 (m, 4H), 1.26 (m, 24H), 0.88 (t, 6H). MS (FAB): *m/z* found 473, calcd. 472.88.

4.3.4. Non-peripheral (1,4,8,11,15,18,22,25) substituted zinc phthalocyanines (4)

Non-peripheral (1, 4, 8, 11, 15, 18, 22, 15) substituted zinc phthalocyanines (**4**) were synthesized from corresponding phthalonitriles **2** or **3** (0.25 mmol), zinc acetate, DBU or DBN as a catalyst and 1-PeOH for 24 h reflux. After cooling, the reaction products were poured into methanol to form a precipitate, which was washed with water and methanol, and column-chromatographed on silica gel with toluene as eluent.

Zinc 1, 4, 8, 11, 15, 18, 22, 15-octadecylphthalocyanine (4a) (0.94 g, 96%). **Found:** C, 79.12%; H, 10.41%; N, 6.61%. Calcd. for$C_{112}H_{176}N_8Zn$: C, 79.12%; H, 10.45%; N, 6.59%; Zn, 3.85%. IR(ATR): ν cm^{-1} 2960 (ν_{C-H}), 2240 (ν_{C-N}), 1600 ($\nu_{C=C}$), 1500 ($\nu_{C=C}$), 1460 ($\nu_{C=C}$), 1210 (δ_{C-H}), 1100 (δ_{C-H}), 730 (δ_{C-H}). UV-Vis (toluene): λ_{max} nm (log ε) 703 (5.01). ^{1}HNMR (500 MHz, CHCl_3-d): δ ppm 7.40 (s, 8H), 2.80 (m,16H), 1.30 (m, 128H), 0.90 (t, 24H). MS (FAB): *m/z* found 1700, calcd.1700.27.

Zinc 1, 4, 8, 11, 15, 18, 22, 25-octakis(ethylthio)phthalocyanine (4b) (1.08 g, 80%). **Found:** C, 54.45%; H, 4.57%; N, 10.58%. Calcd. for$C_{48}H_{48}N_8S_8Zn$: C, 54.44%; H, 4.58%; N,

10.58%; S, 24.22%; Zn, 6.18%. IR (ATR): ν cm^{-1} 2973 (ν_{C-H}), 2962 (ν_{C-H}), 2911 (ν_{C-H}),1655 ($\nu_{C=C}$), 1595 ($\nu_{C=C}$), 1286 (ν_{C-N}), 864 (δ_{C-H}), 610 (ν_{C-S}). UV-Vis (CHCl$_3$): λ_{max} nm (log ε) 773 (4.02).^{1}HNMR (500 MHz, CHCl$_3$-d): δ ppm 7.20 (s, 8H), 2.10 (s, 16H), 1.30 (t, 24H). MS (FAB): m/z 1060, calcd. 1059.01.

Zinc 1, 4, 8, 11, 15, 18, 22, 25-octakis(butylthio)phthalocyanine (4c) (1.31 g, 77%). **Found:** C, 59.90%; H, 6.28%; N, 8.73%. Calcd. For C$_{64}$H$_{80}$N$_8$S$_8$Zn: C, 59.89%; H, 6.30%; N, 8.73%; S, 19.99%; Zn, 5.10%. IR (ATR): ν cm^{-1} 2970 (ν_{C-H}), 2933 (ν_{C-H}), 1654 ($\nu_{C=C}$), 1587 ($\nu_{C=C}$), 1286 (ν_{C-N}), 861 (δ_{C-H}), 746 (δ_{C-H}), 609 (ν_{C-S}). UV-Vis (CHCl$_3$): λ_{max} nm (log ε) 778 (4.27).^{1}HNMR (500 MHz, CHCl$_3$-d): δ ppm 7.30 (s, 8H), 1.60 (m, 48H), 0.90 (t, 24H). MS (FAB): m/z 1284, calcd. 1283.49.

Zinc 1, 4, 8, 11, 15, 18, 22, 25-octakis(hexylthio)phthalocyanine (4d) (1.61 g, 79%). **Found:** C, 63.73%; H, 7.49%; N, 7.43%. Calcd. For C$_{80}$H$_{112}$N$_8$S$_8$Zn: C, 63.71%; H, 7.50%; N, 7.43%; S, 17.01%; Zn, 4.34%. IR (ATR): ν cm^{-1} 2929 (ν_{C-H}), 2855 (ν_{C-H}), 1653 ($\nu_{C=C}$), 1588 ($\nu_{C=C}$), 1287 (ν_{C-N}), 865 (δ_{C-H}), 749 (δ_{C-H}), 608 (ν_{C-S}). UV-Vis (CHCl$_3$): λ_{max} nm (log ε) 785 (4.63). ^{1}HNMR (500 MHz, CHCl$_3$-d): δ ppm 7.20 (s, 8H), 2.10 (m, 16H), 1.50 (m, 32H), 1.30 (m, 32H), 0.80 (t, 24H). MS (FAB): m/z1508, calcd. 1507.97.

Zinc 1, 4, 8, 11, 15, 18, 22, 25-octakis(octylthio)phthalocyanine (4e) (1.68 g, 70%). **Found:** C, 66.57%; H, 8.38%; N, 6.47%. Calcd. For C$_{96}$H$_{144}$N$_8$S$_8$Zn: C, 66.55%; H, 8.40%; N, 6.50%; S, 14.81%; Zn, 3.78%. IR (ATR): ν cm^{-1} 2928 (ν_{C-H}), 2857 (ν_{C-H}), 1654 ($\nu_{C=C}$), 1604 ($\nu_{C=C}$), 1285 (ν_{C-N}), 866 ($\delta_{C=C}$),772 ($\delta_{C=C}$), 610 (ν_{C-S}).UV-Vis (CHCl$_3$): λ_{max} nm (log ε) 783 (4.15). ^{1}HNMR (500 MHz, CHCl$_3$-d): δ ppm 7.20 (s, 8H), 2.90 (m, 48H), 1.70 (m, 24H), 1.30 (m, 40H), 0.80 (t, 24H). MS (FAB): m/z 1733, calcd. 1732.45.

Zinc 1, 4, 8, 11, 15, 18, 22, 25-octakis(decylyhio)phthalocyanine (4f) (1.94 g, 71%). **Found:** C, 68.76%; H, 9.07%; N, 5.73%. Calcd. For C$_{112}$H$_{176}$N$_8$S$_8$Zn: C, 68,74%; H, 9.08%; N, 5.73%; S, 12.80%; Zn, 3.34%. IR (ATR): ν cm^{-1} 2922 (ν_{C-H}), 2852 (ν_{C-H}),1657 ($\nu_{C=C}$), 1608 ($\nu_{C=C}$), 1318 (ν_{C-N}), 865 (δ_{C-H}), 791 (δ_{C-H}), 618 (ν_{C-S}). UV-Vis (CHCl$_3$): λ_{max} nm (log ε) 787 (5.79). ^{1}HNMR (500 MHz, CHCl$_3$-d): δ ppm 7.30 (s, 8H), 3.80 (m, 16H), 3.50 (m, 64H), 2.10 (t, 24H). MS (FAB): m/z 1957, calcd. 1956.93.

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