ChemPubSoc Europe

DOI: 10.1002/ejic.201900766

EurJIC European Journal of Inorganic Chemistry

Full Paper

Phthalocyanines

Preparation and Electrochemical and Optical Properties of α-Alkoxyphthalocyanines with β-Pyridylthio Groups

Takeshi Kimura*,[a] Chiko Kudo,[a] and Shiduko Nakajo[a]

Abstract: Phthalocyanines (Pcs) **5a-Mg**, **5b-Mg**, **6a-Mg**, and **6b-Mg** with eight alkoxy groups at α-positions and 2- or 4-pyridylthio groups at the β-positions, were prepared from 3,6-dialkoxy-4,5-dipyridylthiophthalonitriles. Magnesium complexes **5a-Mg**, **5b-Mg**, and **6a-Mg** were treated with trifluoroacetic acid to produce free-base compounds **5a-2H**, **5b-2H**, and **6a-2H**. In the UV/Vis spectra, Q-band absorption of Mg and free-base Pcs appeared near 760 nm and 780 nm, respectively, in chloroform and 745 nm and 760 nm, respectively, in methanol. Emission spectra of these Pcs showed small Stokes shifts in chloroform and methanol. Reactions of **5a-Mg**, **5b-Mg**, and **5b-2H** with methyl iodide produced the corresponding Pcs **7a-Mg**, **7b-Mg**, and **7b-2H** with methyl pyridinium groups, respectively. After methylation of the pyridine nitrogen, the Pcs were moderately soluble in water but had little solubility in chloroform. The UV/Vis and emission spectra of methylated Pcs **7a-Mg**, **7b-Mg**, and **7b-2H** were obtained in methanol and water. Photobleaching of diphenylisobenzofuran (DPBF) was examined in methanol in the presence of Pcs **7b-Mg** and **7b-2H**, and was monitored by UV/Vis spectroscopy.

Introduction

Phthalocyanines (Pcs) and related compounds have actual or potential ability as catalysts, optoelectronic devices, and sensitizers for photodynamic therapy of cancer.[1,2] The most attractive properties of Pcs for application to new functional materials include: possession of a multi-step redox system from the expanded π-conjugation system; a strong Q-band absorption and related emission in the near-infrared region; and efficacy to generate a singlet oxygen upon irradiation. However, many Pcs have the disadvantage of low solubility in common solvents. Although Pcs have been used as photosensitizers, their effect may be disabled by self-quenching upon aggregation in solution.[1b,1c,2b] Substituents, such as alkyl groups and heteroatoms at the α or β positions of the Pc core and axial ligands on the central metal atoms, can improve the solubility of Pcs in organic solvents, preventing aggregation in solution and promoting easy purification by chromatography, recrystallization, and reprecipitation.[3,4] In addition, α-substituents of Pcs can shift the Q-band absorption to lower energy [near-infrared] field compared to β-substituents.[3] On the other hand, the ability of ammonium,[5] methylpyridinium,[6] sulfonic,[7] cyclodextrin,[8] and peptide groups[9] to increase the solubility of Pcs in water, have led to their application as photo-sensitizers for photodynamic therapy. The results depended on the efficacy of the Pc to generate singlet oxygen.[1c,2b] Although many reports exist about Pcs with pyridyl,[10] pyridyloxy,[11] and pyridylthio groups at the β-positions as water soluble compounds,[12] reports about Pcs containing both α-alkoxy and β-pyridylthio substituents are rare. Through previous studies about tetraazaporphyrins and Pcs,[13] we were interested in Pcs soluble in both organic solvent and water. To construct Pcs with pyridylthio and alkoxy groups, 3,6-dialkoxy-4,5-dipyridylthiophthalonitrile was prepared from dichlorodicyano-*p*-benzoquinone via two-step reactions. This paper describes the preparation and structure determination of Pcs with eight alkoxy groups at α-positions and 2- or 4-pyridylthio groups at β-positions along with their optical and electrochemical properties. In addition, cationic species were prepared by treatment of pyridylthio groups of Pcs with methyl iodide to solubilize Pcs in water and the photobleaching of diphenylisobenzofuran (DPBF) with ambient light was examined in methanol in the presence of Pcs **7b-Mg** and **7b-2H**.

Results and Discussion

Preparation of 3,6-Dialkoxy-4,5-dipyridylthiophthalonitrile

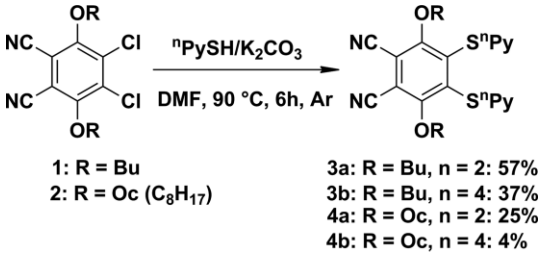
β-Octa(4-pyridylthio)phthalocyanine has been studied as a reagent for photodynamic therapy. However, this compound is insoluble in organic solvents such as chloroform, and the λ_{max} absorption in the UV/Vis spectrum is observed near 650 nm.[12]

To improve the solubility of this compound in organic solvents and shift the Q band absorption to lower energy field, substituents such as alkyl, alkoxy, and alkylthio groups could be introduced at the α-positions.[3] Therefore, we tried to prepare 3,6-dialkoxy-4,5-dipyridylthiophthalonitrile (Scheme 1). According to a method reported previously, 3,6-dibutoxy-4,5-dichlorophthalonitrile (**1**) and 3,6-dioctyloxy-4,5-dichlorophthalonitrile (**2**) were prepared by reduction of DDQ with sodium hydrogen

[a] *Center for Instrumental Analysis, Iwate University, 4–3-5 Ueda, Morioka, Iwate 020–8551, Japan*
E-mail: kimura@iwate-u.ac.jp
http://www.ccrd.iwate-u.ac.jp/kimura/index.html

Supporting information and ORCID(s) from the author(s) for this article are available on the WWW under https://doi.org/10.1002/ejic.201900766.

sulfite followed by butylation and octylation of the 3,6-dihydroxy-4,5-dichlorophthalonitrile produced.[14]

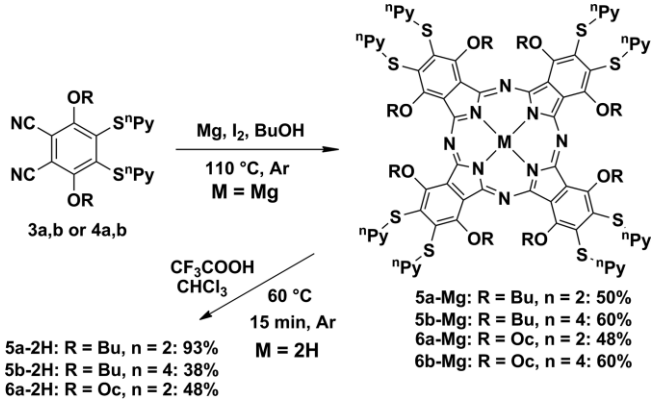


Scheme 1. Preparation of phthalonitriles **3** and **4**.

It is expected that the two chlorine atoms of compounds **1**and **2** can be substituted with nucleophiles, because reaction of mercaptopyridine and 4,5-dichlorophthalonitrile was reported.[6,11,12,15] Therefore, a slightly modified procedure was used to construct the starting phthalonitriles. Compounds **1** and **2** were treated with 2-mercaptopyridine or 4-mercaptopyridine in the presence of potassium carbonate in DMF at 90 °C for 6 h under Ar. The reaction gave the desired products, 3,6-dialkoxy-4,5-dipyridylthiophthalonitriles **3a** (57 %), **3b** (25 %), **4a** (37 %), and **4b** (4 %).

Preparation of Phthalocyanines

Several methods are available for preparing free base or metalated Pcs. Typically, compound **3a** was treated with magnesium butoxide in 1-butanol at 110 °C for 18 h (Scheme 2). The resulting green solid was purified by column chromatography to give α-octa(butoxy)-β-octa(2-pyridylthio)Pc (**5a-Mg**) in 50 % yield. In this reaction, the compound whose 2-pyridylthio groups were substituted with butoxy groups was not obtained under the reaction conditions. Treatment of **3b**, **4a**, and **4b** with a similar procedure produced Pcs **5b-Mg**, **6a-Mg**, and **6b-Mg** in 60 %, 48 %, and 60 % yields, respectively. The central magnesium atom of the products was eliminated easily by reaction with strong acid. Pc **5a-Mg** was treated with trifluoroacetic acid (TFA) in chloroform at 60 °C for 15 min to produce demetallated Pc **5a-2H** in 93 % yield after purification with column chromatography. Using a similar treatment, **5b-2H** and **6a-2H** were obtained in 38 % and 48 % yields, respectively. Since the products



Scheme 2. Preparation of phthalocyanines **5** and **6**.

have alkoxy groups at α-positions, they showed high solubility in organic solvents. The structures of all Pcs obtained were determined by ^{1}H NMR spectra and high-resolution fast atom bombardment mass spectrometry (HR-FAB-MS); the corresponding molecular ion peaks were observed as M^+ or MH^+; **5a-Mg**: m/z =1984.5805 [M^+]; **5b-Mg**: m/z =1984.5927 [M^+]; **6a-Mg**: m/z = 2434.0935 [MH^+]; **6b-Mg**: m/z = 2434.0834 [MH^+]; **5a-2H**: m/z = 1963.6171 [MH^+]; **5b-2H**: m/z = 1963.6171 [MH^+]; **6a-2H**: m/z = 2411.1214 [M^+].

UV/Vis Absorption and Emission Spectra of Phthalocyanines

The UV/Vis spectra of Pcs obtained in chloroform showed strong Q-band absorption at λ_{max} =764.5 nm for **5a-Mg**, 761.0 nm for **5b-Mg**, 762.0 nm for **6a-Mg**, 762.0 nm for **6b-Mg**, 787.0 nm for **5a-2H**, 782.0 nm for **5b-2H**, and 785.5 nm for **6a-2H** (Figure 1a and Table 1). The Q band absorption of these Pcs appear at the lower energy field than that of β-octa(4-pyridylthio)phthalocyanine, suggesting that the effect of α-alkoxy groups amounts to more than 110 nm (ca. 2200 cm^{-1}) in these Pcs. Since the magnesium complexes are D_{4h} symmetry, the Q-band absorption in chloroform was sharp compared with those of metal-free Pcs. The Q-band absorption of free-base Pcs appeared at a lower energy field than those of magnesium Pcs. The weak absorption of **5a-Mg** and **5b-Mg** near 830 nm may be originated from partial aggregation of the molecules.

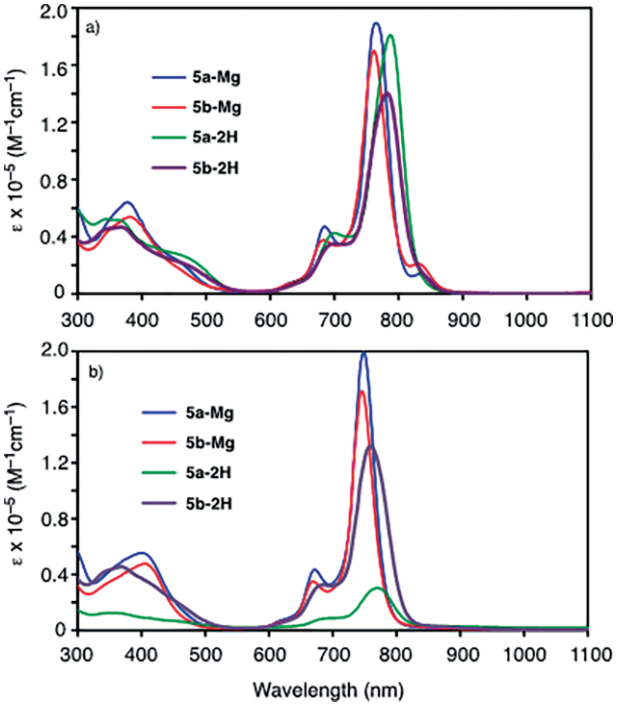


Figure 1. UV/Vis spectra of **5a-Mg**, **5b-Mg**, **5a-2H**, and **5b-2H**, obtained in (a) chloroform and (b) methanol (1.0×10^{-5} M).

In methanol solution, the Q-band absorption of Pcs was observed at λ_{max} =745.0 nm for **5a-Mg**, 748.5 nm for **5b-Mg**, 749.5 nm for **6a-Mg**, 746.0 nm for **6b-Mg**, 769.5 nm for **5a-2H**, 758.5 nm for **5b-2H**, and 770.0 nm for **6a-2H** (Figure 1b and

Table 1. UV/Vis [λ_{max} (nm)] and emission [λ_e (nm)] spectra of phthalocyanines.[a]

	Solvent	λ_{max} [nm], (ε)	$\Delta\lambda_{max}$ [nm]	λ_e [nm]	$\Delta\lambda_e$ [nm]	Stokes shift [nm]
5a-Mg	$CHCl_3$	764.5 (189000)	19.5	804	22	40
	MeOH	745.0 (199000)	–	782	–	37
5b-Mg	$CHCl_3$	761.0 (170000)	12.5	792	12	31
	MeOH	748.5 (171000)	–	777	–	29
5a-2H	$CHCl_3$	787.0 (181000)	17.5	822	34	35
	MeOH	769.5 (30700)	–	798	–	29
5b-2H	$CHCl_3$	782.0 (140000)	23.5	817	13	35
	MeOH	758.5 (132000)	–	804	–	46
6a-Mg	$CHCl_3$	762.0 (177000)	13.0	789	13	27
	MeOH	749.5 (168000)	–	776	–	27
6b-Mg	$CHCl_3$	762.0 (204000)	16.0	781	16	19
	MeOH	746.0 (198000)	–	765	–	19
6a-2H	$CHCl_3$	785.5 (191000)	36.0	814	14	29
	MeOH	749.5 (156000)	–	800	–	51

[a] $\Delta\lambda_{max} = \lambda_{max}$ ($CHCl_3$) – λ_{max} (MeOH); $\Delta\lambda_e = \lambda_e$ ($CHCl_3$) – λ_e (MeOH).

Table 1). The Q-band absorption of magnesium Pcs obtained in methanol also was sharp compared with free-base Pcs for which Q-band absorption appeared at lower energy field than those of magnesium Pcs. The solubility of **5a-2H** in methanol was lower than that of the other compounds and the absorption also was weaker.

The emission spectra of Pcs were measured in chloroform; the molecules were excited with 350 nm light (Figure 2a and Table 1). The spectra showed strong emission at λ_e = 804 nm for **5a-Mg**, 792 nm for **5b-Mg**, 822 nm for **5a-2H**, and 817 nm for **5b-2H**, together with a moderate emission peak near 900 nm. In the methanol solution, the emission spectra were obtained using 400 nm light as excitation, which produced a maximum peak at λ_e = 782 nm for **5a-Mg**, 777 nm for **5b-Mg**, 798 nm for **5a-2H**, and 804 nm for **5b-2H** (Figure 2b and Table 1). Since **5a-2H** was insoluble in methanol, only weak emission could be observed in this solvent. Apparently, Pcs showed solvatochromism in the UV/Vis and emission spectra between chloroform and methanol, and a small Stokes shift was observed in the spectra. As mentioned above, magnesium atoms were eliminated easily from Mg complexes. In the UV/Vis spectra obtained in methanol, the Q-band absorption of **5b-Mg** (748.5 nm) was different than that of free base Pc, **5b-2H** (758.5 nm). Thus, the stability of Mg-Pcs can be assessed using aqueous acetic acid and aqueous hydrochloric acid. The aqueous acetic acid solution of **5b-Mg** at pH 2.5 showed the Q band at 749 nm, suggesting that demetallation of **5b-Mg** did not proceed. In contrast, when **5b-Mg** was dissolved in aqueous hydrochloric acid at pH 3.2, the Q band was observed at 761 nm. Apparently, the magnesium atom was eliminated from **5b-Mg** in solution; therefore, elimination of magnesium atom from **5b-Mg** proceed more easily in aqueous hydrochloric acid than in aqueous acetic acid.

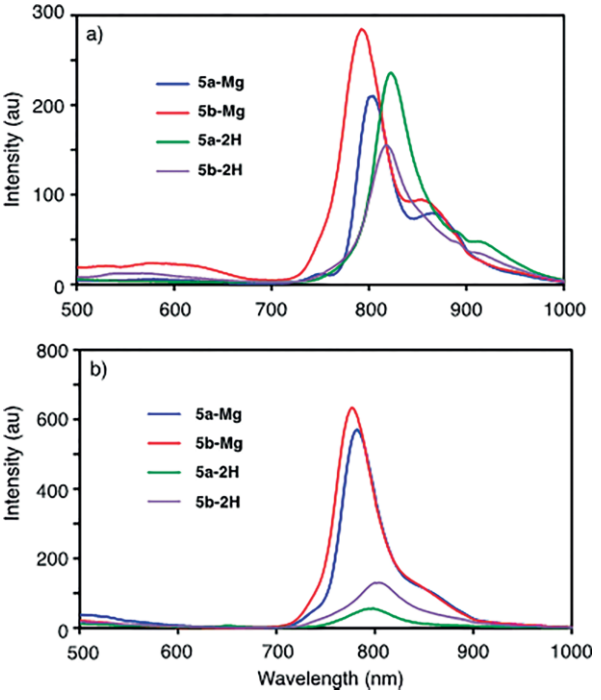


Figure 2. Emission spectra of **5a-Mg**, **5b-Mg**, **5a-2H**, and **5b-2H**, obtained in (a) chloroform and (b) methanol (1.0×10^{-5} M).

Oxidation and Reduction Potentials of Phthalocyanines

The electrochemical properties were determined using cyclic voltammetry with $Ag/AgNO_3$ as a reference electrode (Figure 3 and Table 2). It is known that the charge of Mg (II) does not change during the CV measurement of the magnesium Pc derivatives.[16] Although the oxidation potentials of **5a-Mg** were a quasi-reversible couple at $E_{1/2}$ = 0.48 V and irreversible peaks at E_p = 0.83 V and 1.30 V, the reduction potentials are two quasi-reversible couples at $E_{1/2}$ = –0.44 and –1.12 V. Compound **5b-Mg** showed a quasi-reversible couple and an irreversible peak during oxidation at $E_{1/2}$ = 0.56 V and E_p= 1.06 V, and two quasi-reversible couples during reduction at $E_{1/2}$ = –0.45 and –1.02 V. While the oxidation potentials of **6a-Mg** were a reversible couple and an irreversible peak at $E_{1/2}$ = 0.45 V and E_p= 1.20 V, the reduction potentials were two quasi-reversible couples at $E_{1/2}$ = –0.49 and –1.06 V. Although the oxidation potentials of free-base derivatives **5a-2H**, **5b-2H**, and **6a-2H** were irreversible, they showed quasi-reversible reduction potentials. The first oxidation and first reduction potentials of magnesium complexes showed the cathode shift compared to free-base Pcs, except for the first reduction potential of **5a-2H**.

Table 2. Oxidation and reduction potentials of phthalocyanines.[a]

	^{4th}Red	^{3rd}Red	^{2nd}Red	^{1st}Red	^{1st}Oxid	^{2nd}Oxid	^{3rd}Oxid	ΔE^1	ΔE^2[e]
5a-Mg			–1.12[b]	–0.44[b]	0.48[b]	0.83[c]	1.30[c]	0.92	1.62
5b-Mg			–1.02[b]	–0.45[b]	0.56[b]	1.06[c]		1.01	1.62
5a-2H			–0.78[b]	–0.37[b]	0.89[c]			1.26	1.57
5b-2H		–1.87[b]	–1.13[b]	–0.72[b]	0.82[c]			1.54	1.59
6a-Mg			–1.06[b]	–0.49[b]	0.45[d]	1.20[c]		0.94	1.62
6a-2H	–1.87[b]	–1.37[b]	–1.10[b]	–0.73[b]	1.00[c]			1.73	1.58

[a] Electrolyte, 0.1 M nBu$_4$N$^+$ClO$_4^-$/CH$_2$Cl$_2$; Reference electrode, Ag/AgNO$_3$; Counter electrode, Pt; Working electrode, glassy-carbon; Scan rate, 200 mV/s. [b] Quasi-reversible ($E_{1/2}$/V). [c] Irreversible (E_p/V); ΔE^1 = [^{1st}Oxid – ^{1st}Red], and. [d] Reversible ($E_{1/2}$/V). [e] ΔE^2 was calculated using λ_{max} (nm) in UV/Vis spectra.

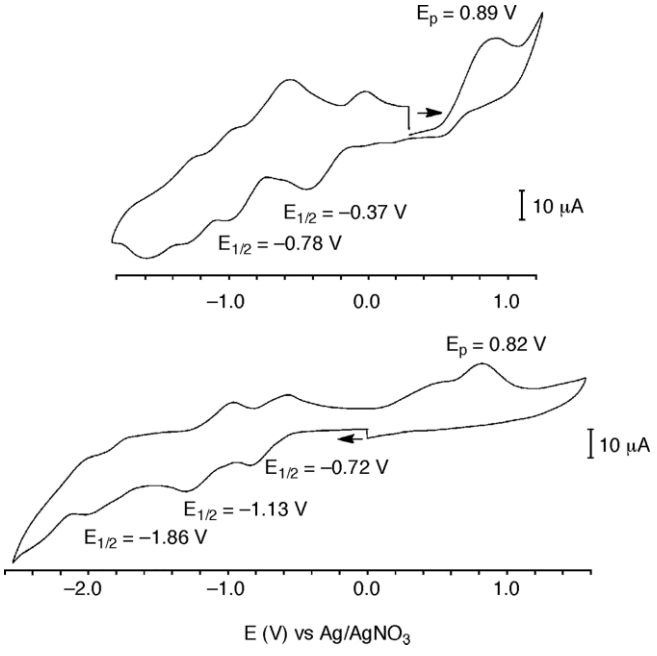
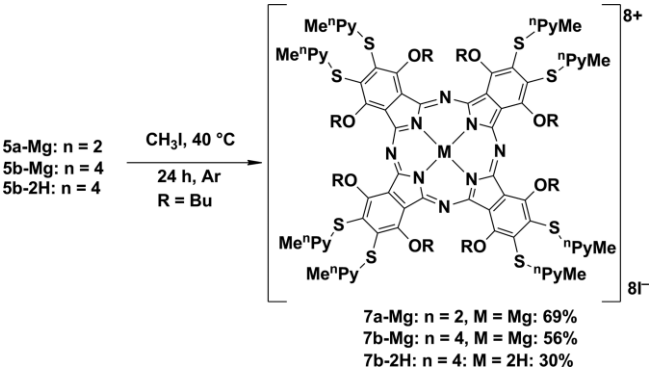


Figure 3. Cyclic voltammogram of **5a-2H** and **5b-2H**; 0.1 M nBu$_4$N$^+$ClO$_4^-$/CH$_2$Cl$_2$; reference electrode, Ag/AgNO$_3$; counter electrode, Pt; working electrode, glassy-carbon; scan rate, 200 mV/s.

Methylation of the Pyridine Nitrogen

Although Pcs obtained showed good solubility in organic solvent, polar and hydrophilic substituents were introduced to promote solubility in polar solvents such as water. Pyridinium salts can promote solubility of Pcs soluble in water. To introduce methyl groups on the pyridine nitrogen atoms substituted on Pcs, Li et al. and Pereira et al. used methyl iodide, while Nyokong et al. used dimethyl sulfate.[6,12] Based on these procedures, **5a-Mg** was treated with methyl iodide at reflux temperature for 24 h, producing the corresponding quaternized product **7a-Mg** in 69 % yield. The Pcs **5b-Mg** and **5b-2H** also were treated with methyl iodide to produce **7b-Mg** and **7b-2H** in 56 % and 30 % yields, respectively (Scheme 3). Reaction of **5a-2H** with methyl iodide produced an insoluble solid. The structures of Pcs **7a-Mg**, **7b-Mg**, and **7b-2H** obtained were determined by NMR spectra and matrix-assisted laser desorption ionization time-of-flight mass spectrometry (MALDI-TOF-MS); **7a-Mg**: m/z = 2022.4405 [M–7CH$_3$–8I + Na]$^+$; **7b-Mg**: m/z = 2022.4849 [M–7CH$_3$–8I + Na]$^+$; **7b-2H**: m/z = 2024.5093 [M–7CH$_3$–8I + 2Na]$^+$. It was reported that Pcs with methylpyridinium groups on the core ring showed fragment peaks of lost methyl groups and iodide ions as molecular ion peaks.[11a,12b]



Scheme 3. Methylation of phthalocyanines.

UV/Vis Absorption and Emission Spectra for 7a-Mg, 7b-Mg, 7b-2H

The UV/Vis and emission spectra of methylated Pcs **7a-Mg**, **7b-Mg**, and **7b-2H** were obtained in methanol and water. The 2-methylpyridinium derivative had lower solubility in water than 4-methylpyridinium derivatives; therefore, the results for **7b-Mg**, and **7b-2H** are shown in Figure 4. The UV/Vis spectra of **7b-Mg** measured in methanol, tap water, and ion-exchanged water (IEW) showed Q-band absorption around λ_{max} = 745 nm. Similarly, the UV/Vis spectra of **7b-2H** obtained in methanol, tap water, and ion-exchanged water showed Q-band absorption near λ_{max} = 750 nm.

The emission spectra of **7a-Mg**, **7b-Mg**, and **7b-2H** were obtained in methanol and water. Since the 2-methylpyridinium derivative showed lower solubility in water than 4-methylpyridinium derivatives, the results of **7b-Mg** and **7b-2H** are shown in Figure 5. The emission spectra of **7b-Mg** obtained in methanol, tap water, and ion-exchanged water showed Q-band absorption near λ_{max} = 766 nm.

1,3-Diphenylisobenzofuran (DPBF) readily reacts with singlet oxygen via 1,4-cycloaddition to produce the cyclic peroxide. However, the product then immediately decomposes to 1,2-dibenzoylbenzene.[17] Although DPBF shows a strong absorption at 412 nm in the UV/Vis spectrum, 2-dibenzoylbenzene has no absorption in that area. The presence of singlet oxygen can be determined by monitoring the absorbance of DPBF.[12a,18] The photobleaching of the absorbance of DPBF was investi-

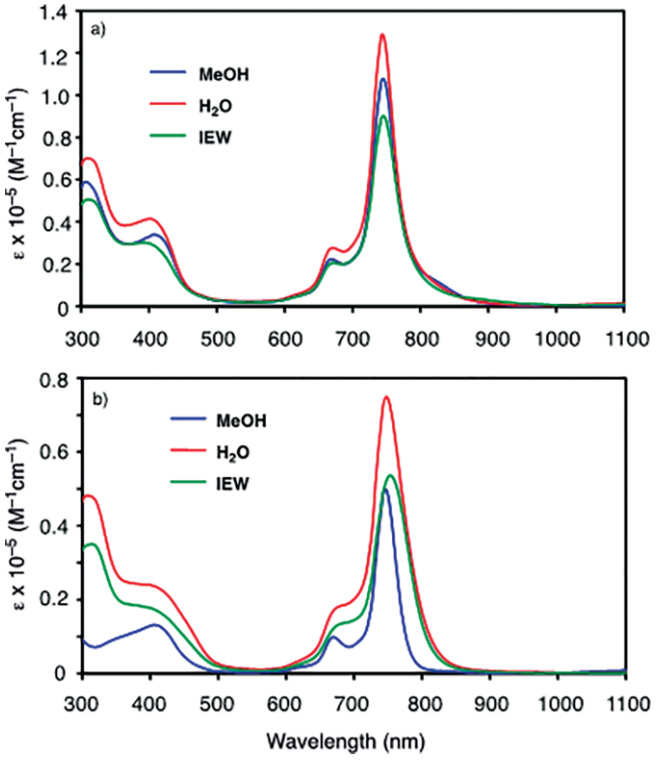


Figure 4. UV/Vis spectra of (a) **7b-Mg** and (b) **7b-2H** obtained in methanol, water, and ion-exchanged water (IEW) (1.0×10^{-5} M).

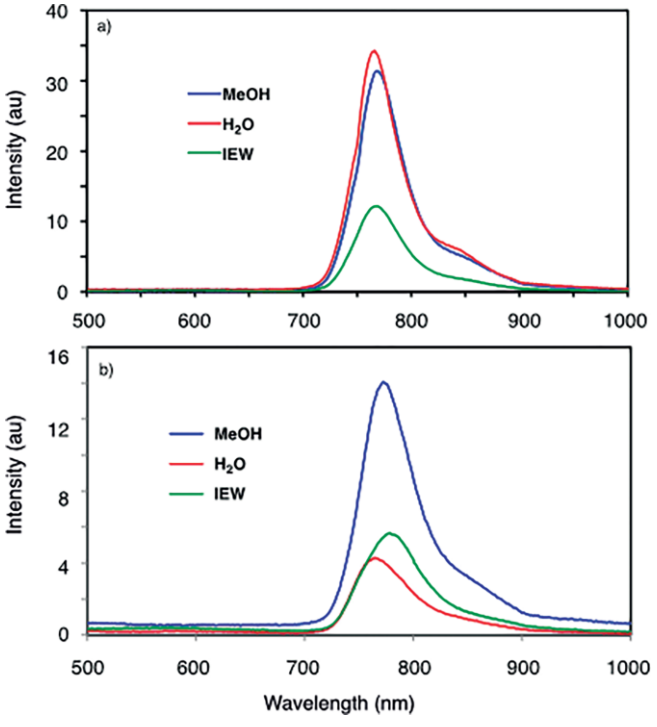


Figure 5. Emission spectra of (a) **7b-Mg** and (b) **7b-2H** obtained in methanol, water, and ion-exchanged water (IEW) (1.0×10^{-5} M).

gated with ambient light in methanol in the presence of Pcs **7b-Mg** and **7b-2H** for 120 min (Figure 6). The spectra were obtained at intervals of 15 min or 30 min, except for first 15 min. After 60 min, a decrease in the absorption of DPBF became small. The concentration of Pcs in the solution was based on the molar extinction coefficient; **7b-Mg**: 3.5×10^{-6} M, **7b-2H**: 1.8×10^{-6} M. As shown in Figure 6a, the absorption of DPBF at 410 nm decreased over time.

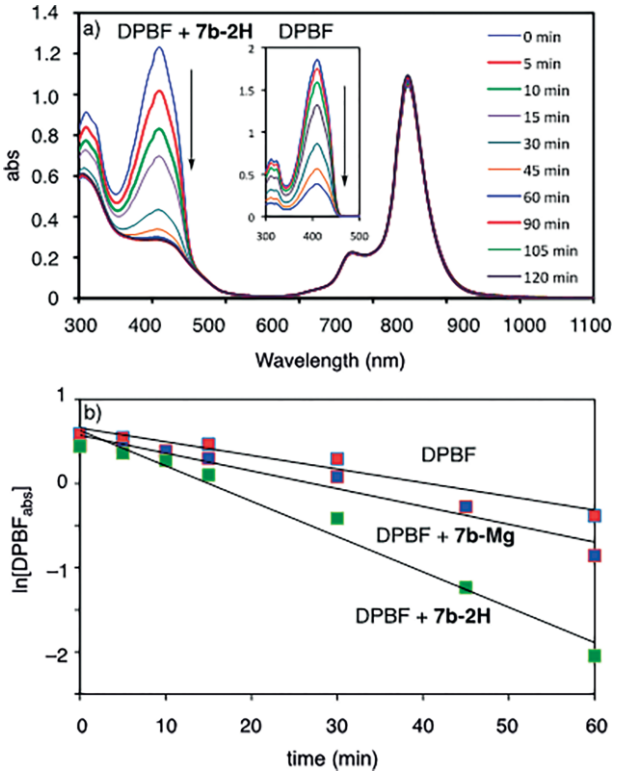


Figure 6. (a) Photobleaching of DPBF absorbance upon ambient light in methanol in the absence of Pc and in the presence of Pc **7b-2H**; (b) Plot of ln [$DPBF_{Abs}$] vs. reaction time.

Although the oxidation of DPBF is a two-molecule reaction, the concentration of oxygen was expected to be larger than that of DPBF.[19] Therefore, the oxidation reaction was treated as a pseudo-first-order reaction with respect to DPBF concentration. Figure 6b shows the plot of ln [$DPBF_{Abs}$] vs. reaction time. The absorption value of [$DPBF_{Abs}$] was calculated as [$DPBF_{Abs(t)}$ – $DPBF_{Abs(120)}$]; $DPBF_{Abs(t)}$ is absorption of DPBF at each time (t = 0–105) and $DPBF_{Abs\ (120)}$ is final absorption. The slope on the linear graph of ln [$DPBF_{Abs}$] was greater in the presence of **7b-Mg** and **7b-2H** than in the absence of Pcs. Furthermore, the results showed **7b-2H** was more effective at generating singlet oxygen than **7b-Mg** was.

Conclusions

Phthalocyanine derivatives with eight alkoxy groups at α-positions and 2- or 4-pyridylthio groups at β-positions were prepared, and the products showed good solubility in organic solvents and good to moderate solubility in methanol and water after methylation of the pyridine nitrogen. The structure of

the product was determined by ^{1}H NMR, FABMS, and MALDI-TOF-MS. The UV/Vis spectra of Pcs obtained in chloroform and methanol, showed Q-band absorption in the near-infrared region. These compounds produced emissions in chloroform and methanol. The electrochemical properties were determined by cyclic voltammetry using $Ag/AgNO_3$ as a reference electrode. Compounds **5a-Mg**, **5b-Mg**, **5a-2H**, and **5b-2H** reacted with methyl iodide to produce the corresponding methyl pyridinium iodides. The UV/Vis and emission spectra of methylated Pcs **7a-Mg**, **7b-Mg**, and **7b-2H** were obtained in methanol and water. The photobleaching of the absorbance of diphenylisobenzofuran (DPBF) with ambient light was examined in methanol in the presence and in the absence of Pcs **7b-Mg** and **7b-2H** for 120 min. The plot of ln [$DPBF_{Abs}$] vs. the reaction time showed that **7b-2H** generated singlet oxygen more effectively than **7b-Mg**.

Experimental Section

General. NMR spectra were obtained using Bruker AVANCE-500 and DRX-400 spectrometers and a JEOL JNM-ECA 500 spectrometer. Mass spectra were obtained using a JEOL JMS-700 mass spectrometer and a Shimadzu Biotech Axima Confidence mass spectrometer. UV/Vis spectra were recorded with a Jasco Ubest V-570 spectrometer. The IR spectra were obtained using a Jasco FT/IR-4200 spectrometer. Emission spectra were obtained with a Jasco FP8600 spectrofluorometer. A Hokuto Denko Co. Model HAB-151 apparatus was used to obtain measurements of redox potentials.

Oxidation and reduction potential. All measurements of redox potentials were performed by cyclic voltammetry, using $Ag/AgNO_3$ (0.01 mol/L) as a reference electrode, glassy carbon as a working electrode, and Pt wire as a counter electrode (scan rate: 200 mV/s). A solution of *n*-Bu_4NClO_4 in CH_2Cl_2 (0.1 mol/L) was used as an electrolyte. The oxidation potential of ferrocene was observed at $E_{1/2}$ = 0.09 V using the apparatus without any correction.

Materials. 3,6-Dibutoxy-4,5-dichlorophthalonitrile (**1**) and 3,6-dioctyloxy-4,5-dichlorophthalonitrile (**2**) were prepared using a method described previously.[14]

3,6-Dibutoxy-4,5-di(2-pyridylthio)phthalonitrile (3a). Compound **1** (685 g, 2.01 mmol), K_2CO_3 (835 mg, 6.04 mmol), and 2-mercaptopyridine (493 mg, 4.43 mmol) were placed in a glass reactor under Ar. The DMF (14 mL) was added to the reactor and the solution stirred at 90 °C for 6 h, then cooled to room temperature. Water was added to the solution and the product extracted using ethyl acetate. The extract was washed with brine and then with water. The organic layer was dried with $MgSO_4$ and the solvent evaporated. The product was purified by column chromatography [Wakogel C-300HG, $CHCl_3$ to $CHCl_3$/MeOH (50:1)] and 3,6-dibutoxy-4,5-di(2-pyridylthio)phthalonitrile (**3a**) was obtained in 53 % yield (520 mg); brown oil; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS) δ = 0.86 (t, *J* = 7.6 Hz, 6H, CH_3), 1.33 (sext, *J* = 7.6 Hz, 4H, CH_2), 1.61 (quint, *J* = 6.4 Hz, 4H, CH_2), 4.16 (t, *J* = 6.4 Hz, 4H, CH_2), 7.04 (ddd, *J* = 7.7, 4.8, 0.8Hz, 2H, Py-H), 7.12 (ddd, *J* = 7.7, 0.8, 0.8 Hz, 2H, Py-H), 7.52 (ddd, *J* = 7.7, 7.7, 1.8 Hz, 2H, Py-H), 8.29 (ddd, *J* = 4.8, 1.8, 0.8 Hz, 2H, Py-H); ^{13}C NMR (101 MHz, $CDCl_3$, 25 °C, TMS) δ = 14.1, 19.1, 32.2, 76.2, 110.7, 113.5, 121.3, 123.6, 137.2, 141.0, 150.0, 157.7, 159.7; HR-FAB-MS (m/z) 491.1574 [MH^+]; calcd. for $C_{26}H_{27}N_4O_2S_2$ = 490.1497.

3,6-Dibutoxy-4,5-di(4-pyridylthio)phthalonitrile (3b). 37 %; yellow crystal; mp: 98–101.5 °C; H NMR (500 MHz, $CDCl_3$, 25 °C, TMS) δ = 0.87 (t, *J* = 7.5 Hz, 6H, CH_3), 1.33 (sext, *J* = 7.5 Hz, 4H, CH_2), 1.61 (quint, *J* = 6.5 Hz, 4H, CH_2), 4.16 (t, *J* = 6.5 Hz, 4H, CH_2), 6.87(dd, *J* = 4.7, 1.5 Hz, 4H, Py-H), 8.40(dd, *J* = 4.7, 1.5 Hz, 4H, Py-H); ^{13}C NMR (126 MHz, $CDCl_3$, 25 °C, TMS) δ = 13.5, 18.6, 31.7, 76.3, 111.2, 112.4, 121.1, 138.9, 145.6, 149.8, 159.2; HR-FAB-MS (m/z) 490.1502 [M^+]; calcd. for $C_{26}H_{26}N_4O_2S_2$ = 490.1497.

3,6-Dioctyloxy-4,5-di(2-pyridylthio)phthalonitrile (4a). 25 %; red brown oil; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS) δ = 0.87 (t, *J* = 6.8 Hz, 6H, CH_3), 1.16–1.34 (m,), 1.63 (quint, *J* = 6.8 Hz, 4H, CH_2), 4.15 (t, *J* = 6.8 Hz, 6H, CH_2), 7.03 (ddd, *J* = 7.7, 4.8, 0.8 Hz, 2H, Py-H), 7.11 (7.7, 0.8 Hz, 2H, Py-H), 7.51 (ddd, *J* = 7.7, 7.7, 1.6 Hz, 2H, Py-H), 8.29 (ddd, *J* = 4.8, 1.6, 0.8 Hz, 2H, Py-H); ^{13}C NMR (101 MHz, $CDCl_3$, 25 °C, TMS) δ = 14.3, 22.9, 25.7, 29.36, 29.43, 30.1, 32.0, 76.4, 110.6, 113.4, 121.1, 122.5, 137.0, 140.8 149.9, 157.60, 159.63; HR-FAB-MS (m/z) 603.2830 [MH^+]; calcd. for $C_{34}H_{43}N_4O_2S_2$ = 603.2827.

3,6-Dioctyloxy-4,5-di(4-pyridylthio)phthalonitrile (4b). 4 %; yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C, TMS) δ = 0.87 (t, *J* = 7.0 Hz, 6H, CH_3), 115–1.29 (m, 20H, CH_2), 1.62 (quint, *J* = 6.8 Hz, 4H, CH_2), 4.14 (t, *J* = 6.8 Hz, 4H, CH_2), 6.87 (dd, *J* = 4.8, 1.4 Hz, 4H, Py-H), 8.40 (dd, *J* = 4.8, 1.4 Hz, 4H, Py-H); ^{13}C NMR (126 MHz, $CDCl_3$, 25 °C, TMS) δ = 14.1, 22.6, 25.5, 29.07, 29.12, 29.8, 31.7, 76.8, 111.3, 112.5, 121.1, 138.9, 145.7, 150.0, 159.3; HR-FAB-MS (m/z) 603.2830 [MH^+]; calcd. for $C_{34}H_{43}N_4O_2S_2$ = 603.2827.

1,4,8,11,15,18,22,25-Octabutoxy-2,3,9,10,17,17,23,24-octa(2-pyridylthio)phthalocyaninato magnesium (II) (5a-Mg). Magnesium (90 mg, 3.7 mmol) and iodine (30 mg, 0.12 mmol) were placed in a glass reactor and 1-butanol (3 mL) added under Ar, then the solution was stirred at 110 °C until the magnesium dissolved. The solution was poured into compound **3a** (235 mg, 0.52 mmol) under Ar, and stirred at 110 °C for 18 h. After cooling, MeOH was added to the reaction mixture and the resulting green precipitate removed by filtration. The residue was purified by column chromatography (Wakogel C-300HG, $CHCl_3$ and $CHCl_3$/MeOH = 50:1) to produce **5a-Mg** in 50 % yield (130 mg); green powder; m.p. 98–101.5 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS) δ = 0.62 (br, 24H, CH_3), 1.20 (br, 16H, CH_2), 1.65 (br, 16H, CH_2), 4.72 (br, 16H, CH_2), 6.87 (br, 8H, Py-H), 7.21 (br, 8H, Py-H), 7.43(br, 8H, Py-H), 8.16 (br, 8H, Py-H); HR-FAB-MS (m/z) 1984.5805 [M^+]; calcd. for $C_{104}H_{104}N_{16}O_8S_8{}^{24}Mg$ = 1984.5839.

1,4,8,11,15,18,22,25-Octabutoxy-2,3,9,10,17,17,23,24-octa-(4-pyrodylthio)phthalocyaninato Magnesium (II) 5b-Mg. 60 %; green solid; mp: 189–190 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS) δ = 0.54 (br, 24H, CH_3), 1.14 (br, 16H, CH_2), 1.67 (br, 16H, CH_2), 4.76 (br, 16H, CH_2), 6.94 (br, 16H, Py-H), 7.92 (br, 16H, Py-H); HR-FAB-MS (m/z) 1984.5927 [M^+]; calcd. for $C_{104}H_{104}N_{16}O_8S_8{}^{24}Mg$ = 1984.5839.

1,4,8,11,15,18,22,25-Octaoctyloxy-2,3,9,10,17,17,23,24-octa-(2-pyrodylthio)phthalo-cyaninato Magnesium (II) 6a-Mg. 48 %; green solid; mp: 79–80 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS) δ = 0.86 (t, *J* = 7.0 Hz, 24H, CH_3),1.02–1.36 (m, 80H, CH_2), 1.72–1.85 (m, 16H, CH_2), 4.85 (br, 16H, CH_2), 6.90 (br, 8H, Py-H), 7.22 (br, 8H, Py-H), 7.40 (br, 8H, Py-H), 8.27 (br, 8H, Py-H); HR-FAB-MS (m/z) 2434.0935 [MH^+]; calcd. for $C_{136}H_{169}N_{16}O_8S_8Mg$ = 2434.0926.

1,4,8,11,15,18,22,25-Octaoctyloxy-2,3,9,10,17,17,23,24-octa-(4-pyrodylthio)phthalocyaninato Magnesium (II) 6b-Mg. 60 %; green oil; ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C, TMS) δ = 0.80 (br, 24H, CH_3), 1.03–1.39 (s, 80H, CH_2), 1.69 (br, 16H, CH_2), 4.77 (br, 16H, CH_2), 6.95 (br, 16H, Py-H), 8.28 (br, 16H, Py-H); HR-FAB-MS (m/z) 2434.0834 [MH^+]; calcd. for $C_{136}H_{169}N_{16}O_8S_8Mg$ = 2434.0926.

1,4,8,11,15,18,22,25-Octabutoxy-2,3,9,10,17,17,23,24-octa-(2-pyrodylthio)phthalocyanine (5a-2H). To a solution of **5a-Mg** (50 mg, 0.025 mmol) in $CHCl_3$ (20 mL), CF_3COOH (1.0 mL) was added slowly and the solution stirred for 15 min under reflux. The solution was cooled to room temperature and K_2CO_3 was added followed by extraction with $CHCl_3$. After evaporation of the solvent, the residue was purified by column chromatography (Wakogel C-300HG, $CHCl_3$ and $CHCl_3$/MeOH = 50:1) to produce **5a-2H** in 93 % yield (46 mg); dark green solid; mp: 109–110 °C; ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C, TMS) δ = 0.75 (s, J = 7.2 Hz, 24H, CH_3), 1.30 (sext, J = 7.2 Hz, 16H, CH_2), 1.78 (quint, J = 6.8 Hz, 2H, CH_2), 4.77 (br, 16H, CH_2), 6.94 (dd, J = 6.4, 5.2 Hz, 8H, Py-H), 7.25 (br, 8H, Py-H), 7.44 (dd, J = 7.2, 1.4 Hz, 8H, Py-H), 8.35 (d, J = 3.6 Hz, 8H, Py-H); HR-FAB-MS (m/z) 1963.6171 [MH$^+$]; calcd. for $C_{104}H_{107}N_{16}O_8S_8$ = 1963.6224.

1,4,8,11,15,18,22,25-Octabutoxy-2,3,9,10,17,17,23,24-octa-(4-pyridylthio)phthalocyanine (5b-2H). 38 %; dark green crystal; mp: 209–210 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS) δ = 0.83 (t, J = 7.2 Hz, 24H, CH_3), 1.31(sext, J = 7.2 Hz, 16H, CH_2), 1.80 (quint, J = 6.4 Hz, 16H, CH_2), 4.78 (t, J = 6.4 Hz, 16H, CH_2), 7.10 (dd, J = 4.8, 1.6 Hz, 16H, Py-H), 8.34 (dd, J = 4.8, 1.6 Hz, 16H, Py-H); HR-FAB-MS (m/z) 1963.6171 [MH$^+$]; calcd. for $C_{104}H_{107}N_{16}O_8S_8$ = 1963.6224.

1,4,8,11,15,18,22,25-Octaoctyloxy-2,3,9,10,17,17,23,24-octa-(2-pyrodylthio)phthalocyanine (6a-2H). 64 %; green solid; m.p. > 300 °C; ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C, TMS) δ = 0.86 (t, J = 7.1 Hz, 24H, CH_3), 1.05–1.33 (m, 80H, CH_2), 1.80 (quint, J = 7.3 Hz, 16H, CH_2), 4.77 (br, 16H, CH_2), 6.92 (ddd J = 5.1 Hz, 8H, Py-H), 7.25 (d, J = 5.1 Hz, 8H, Py-H), 7.43 (ddd, J = Hz, 8H,Py-H), 8.31 (dd, J = 4.6 Hz, 8H, Py-H); HR-FAB-MS (m/z) 2411.1214 [M$^+$]; calcd. for $C_{136}H_{170}N_{16}O_8S_8$ = 2411.1153.

1,4,8,11,15,18,22,25-Octabutoxy-2,3,9,10,17,17,23,24-octa-(2-methylpyridiniumthio)phthalo-cyaninato magnesium (II) iodide (7a-Mg). Compound **7a-Mg** (49 mg, 0.025 mmol) was placed in a glass reactor and methyl iodide (6.0 mL) was added under Ar, then the solution was stirred at 40 °C for 24 h. After evaporation, the residue was washed with acetone and then chloroform. The product was dissolved in methanol and filtered. After evaporation, the product was recrystallized from DMF and $CHCl_3$ to produce 7a-Mg in 69 % yield (53 mg); green crystal; m.p. > 300 °C; ^{1}H NMR (500 MHz, CD_3OD,, 25 °C, TMS) δ = 0.76 (t, J = 7.0 Hz, 24H, CH_3), 1.23–1.38 (m, 16H, CH_2), 1.78–1.96 (m, 16H, CH_2), 4.54 (s, 24H, CH_3), 5.16 (br, 16H, CH_2), 7.74 (t, J = 6.9 Hz, 8H, Py-H), 7.96 (s, 8H, Py-H), 8.12–8.29 (m, 8H, Py-H), 8.92 (t, J = 6.9 Hz, 8H, Py-H); MALDI-TOF MS (m/z) 2022.4405 [M–7CH_3–8I + Na]$^+$; calcd. for $C_{105}H_{107}N_{16}O_8S_8Na$ = m/z 2022.5972.

1,4,8,11,15,18,22,25-Octabutoxy-2,3,9,10,17,17,23,24-octa-(4-methylpyridiniumthio)phthalo-cyaninato magnesium (II) iodide (7b-Mg). 56 %; green solid; m.p. > 300 °C; ^{1}H NMR (500 MHz, CD_3OD, 25 °C, TMS) δ = 0.77 (t, J = 7.4 Hz, 24H, CH_3), 1.41 (sext, J = 7.4 Hz, 16H, CH_2), 1.92 (br, 16H), 4.24 (brs, 24H, CH_3), 5.08 (br, 16H CH_2), 8.05 (d, J = 6.9 Hz, 16H, Py-H), 8.60 (d, J = 6.9 Hz, 16HPy-H), MALDI-TOF MS (m/z) 2022.4849 [M–7CH_3–8I + Na]$^+$; calcd. for $C_{105}H_{107}N_{16}O_8S_8Na$ = 2022.5972.

1,4,8,11,15,18,22,25-Octabutoxy-2,3,9,10,17,17,23,24-octa-(2-methylpyridiniumthio)phthalo-cyanine iodide (7b-2H). 30 %; green solid; m.p. > 300 °C; ^{1}H NMR (500 MHz, CD_3OD, 25 °C, TMS) δ = 0.68 (t, J = 7.4 Hz, 24H, CH_3), 1.39 (sext, J = 7.4 Hz, 16H, CH_2), 1.82 (br, 16H, CH_2), 4.15 (s, 24H, CH_3), 4.80–5.05 (m, 16H, CH_2), 8.12 (br, 16H, Py-H), 8.64 (d, J = 7.2 Hz, 16H, Py-H); MALDI-TOF MS (m/z) 2024.5093 [M–7CH_3–8I + 2Na]$^+$; calcd. for $C_{105}H_{109}N_{16}O_8S_8Na_2$ = 2023.6175.

Keywords: Phthalocyanines · Pyridylthio groups · Magnesium · Photochemistry · Isobenzofuran

[1] a) A. Jana, M. Ishida, J. P. Park, S. Bähring, J. O. Jeppesen, J. L. Sessler, *Chem. Rev.* **2017**, *117*, 2642–2710; b) S. Singh, A. Aggarwal, N. V. S. D. K. Bhupathiraju, G. Arianna, K. Tiwari, D. M. Drain, *Chem. Rev.* **2015**, *115*, 10261–10306; c) M. Urbani, M. Grätzel, M. Nazeeruddin, T. Torres, *Chem. Rev.* **2014**, *114*, 12330–12396.

[2] a) J. Mack, N. Kobayashi, *Chem. Rev.* **2011**, *111*, 281–321; b) F. Dumoulin, M. Durmuş, V. Ahsen, T. Nyokong, *Coord. Chem. Rev.* **2010**, *254*, 2792–2847.

[3] N. Kobayashi, H. Ogata, N. Nonaka, E. A. Luk'yanets, *Chem. Eur. J.* **2003**, *9*, 5123–5134; P. M. Burnham, M. J. Cook, L. A. Gerrard, M. J. Heenet, D. L. Hughes, *Chem. Commun.* **2003**, 2064–2065; K. Hatsusaka, M. Kimura, K. Ohta, *Bull. Chem. Soc. Jpn.* **2003**, *76*, 781–787; M. N. Yarasir, M. Kandaz, B. F. Senkal, A. Koca, B. Salih, *Polyhedron* **2007**, *26*, 5235–5242; T. B. Ogunbayo, T. Nyokong, *Polyhedron* **2009**, *28*, 2710–2718; T. Rawling, A. McDonagh, *Coord. Chem. Rev.* **2007**, *251*, 1128–1157.

[4] T. Furuyama, T. Sato, N. Kobayashi, *J. Am. Chem. Soc.* **2015**, *137*, 13788–13791; T. Furuyama, N. Kobayashi, *Phys. Chem. Chem. Phys.* **2017**, *19*, 15596–15612.

[5] P. Zimcik, V. Novakova, K. Kopecky, M. Miletin, R. Zeynep, U. Kobak, E. Svandrlikova, L. Váchová, K. Lang, *Inorg. Chem.* **2012**, *51*, 4215–4223; M. Machacek, A. Cidlina, V. Novakova, J. Svec, E. Rudolf, M. Miletin, R. Kučera, T. Simunek, P. Zimcik, *J. Med. Chem.* **2015**, *58*, 1736–1749.

[6] A. Erdoğmuş, T. Nyokong, *J. Mol. Struct.* **2010**, *977*, 26–38; A. Sindelo, O. L. Osifenko, T. Nyokong, *Inorg. Chim. Acta* **2018**, *476*, 68–76; S. Makhseed, M. Machacek, W. Alfady, A. Tuhl, M. Vinodh, T. Simunek, V. Novakova, P. Kubat, E. Rudolf, P. Zimcik, *Chem. Commun.* **2013**, *49*, 11149–11151; J. Mikkilä, E. Anaya-Plaza, V. Liljeström, J. Caston, T. Torres, A. de la Escosura, M. A. Kostiainen, *ACS Nano* **2016**, *10*, 1565–1571.

[7] T. Ikeuchi, J. Mack, T. Nyokong, N. Kobayashi, M. Kimura, *Langmuir* **2016**, *32*, 11980–11985.

[8] L. M. O. Lourenço, P. M. R. Pereira, E. Maciel, M. Válega, F. M. Domingues, M. R. M. Domingues, M. G. P. M. S. Neves, J. A. S. Cavaleiro, R. Fernandes, J. P. C. Tomé, *Chem. Commun.* **2014**, *50*, 8363–8366.

[9] E. Ranyuk, N. Cauchon, K. Klarskov, B. Guérin, J. E. van Lier, *J. Med. Chem.* **2013**, *56*, 1520–1534; H. He, P.-C. Lo, D. K. P. Ng, *Chem. Eur. J.* **2014**, *20*, 6241–6245.

[10] a) M. P. Donzello, E. Viola, X. Cai, L. Mannina, C. Rizzoli, G. Ricciardi, C. Ercolani, K. M. Kadish, A. Rosa, *Inorg. Chem.* **2008**, *47*, 3903–3919; b) I. Manet, F. Manoli, M. P. Donzello, C. Ercolani, D. Vittori, L. Cellai, A. Masi, S. Monti, *Inorg. Chem.* **2011**, *50*, 7403–7411; c) I. Manet, F. Manoli, M. P. Donzello, E. Viola, A. Masi, G. Andreano, G. Ricciardi, A. Rosa, L. Cellai, C. Ercolani, S. Monti, *Inorg. Chem.* **2013**, *52*, 321–328; d) M. P. Donzello, G. De Mori, E. Viola, C. Ercolani, G. Ricciardi, A. Rosa, *Inorg. Chem.* **2014**, *53*, 8009–8019.

[11] a) H. Li, J. Jensen, F. R. Fronczek, A. G. H. Vicente, *J. Med. Chem.* **2008**, *51*, 502–511; b) X. Jia, F.-F. Yang, J. Li, J.-Y. Liu, J.-P. Xue, *J. Med. Chem.* **2013**, *56*, 5797–5805; T. T. Tasso, T. Furuyama, N. Kobayashi, *Inorg. Chem.* **2013**, *52*, 9206–9215.

[12] a) M. Durmuş, H. Yaman, C. Göl, V. Ashen, T. Nyokong, *Dyes Pigm.* **2011**, *91*, 153–156; b) J. B. Pereira, E. F. A. Carvalho, M. A. F. Faustino, R. Fernandes, M. G. P. M. S. Neves, J. A. S. Cavaleiro, N. C. M. Gomes, Å. Cunha, A. Almeida, J. P. C. Tomé, *Photochem. Photobiol.* **2012**, *88*, 537–547.

[13] a) T. Kimura, A. Yomogita, T. Matsutani, T. Suzuki, I. Tanaka, Y. Kawai, Y. Takaguchi, T. Wakahara, T. J. Akasaka, *Org. Chem.* **2004**, *69*, 4716–4723; b) T. Kimura, N. Kanota, K. Matsui, I. Tanaka, T. Tsuboi, Y. Takaguchi, A. Yomogita, T. Wakahara, S. Kuwahara, F. Nagatsugi, T. Akasaka, *Inorg. Chem.* **2008**, *47*, 3577–3583; c) T. Kimura, N. Murakami, E. Suzuki, T. Furuyama, T. Nakahodo, H. Fujihara, N. Kobayashi, *J. Inorg. Biochem.* **2016**, *158*, 35–44; d) T. Kimura, H. Muraoka, S. Nakajo, S. Ogawa, S. Yamamoto, N. Kobayash, *Eur. J. Org. Chem.* **2018**, *2018*, 1255–1264.

[14] a) E. A. Safonova, A. G. Martynov, S. E. Nafedov, G. A. Kirakosyan, Y. G. Gobunova, A. Y. Tsivadze, *Inorg. Chem.* **2016**, *55*, 2450–2459; b) M. Matsutani, A. Takaki, H. Maekawa, I. Nishiguchi, *Sci. Technol. Adv. Mater.* **2005**, *6*, 172–180; c) S. Y. Al-Raqa, *Dyes Pigm.* **2007**, *77*, 259–265; d) D. S. Reddy, Y. E. Ovchinnikov, O. V. Shichkin, Y. T. Struchkov, G. R. Desiraju, *J. Am. Chem. Soc.* **1996**, *118*, 4085–4089.

[15] D. Wöhrle, M. Eskes, K. Shigehara, A. Yamada, *Synthesis* **1993**, 194–196.
[16] T. Nyokong, Z. Gasyna, M. J. Stillman, *Inorg. Chem.* **1987**, *26*, 548–553.
[17] S. J. Chadwick, D. Salah, P. M. Livesey, M. Brust, M. Volk, *J. Phys. Chem. A* **2016**, *120*, 10647–10657.
[18] T. Furuyama, Y. Miyaji, K. Maeda, H. Maeda, M. Segi, *Chem. Eur. J.* **2019**, *25*, 1678–1682.
[19] A. Kuesner, *J. Phys. E. Sci. Instrum.* **1987**, *20*, 224–230; M. G. Levi, *Gazz. Chim. Ital.* **1901**, *31*, 513–541.

Received: July 11, 2019