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Investigation of zinc bis(1,4-didecylbenzo)-bis(2,3-pyrido) porphyrazine as an efficient photosensitizer by cyclic voltammetry

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Abstract

The phthalocyanine analogue containing non-peripheral, long alkyl-substituted benzenoid rings and pyridine rings, zinc bis(1,4-didecylbenzo)-bis(2,3-pyrido)porphyrazine was synthesized. The synthesized product is an interesting compound because quaternization of the pyridine nitrogen is expected to impart cationic amphiphilic character. Zinc bis(1,4-didecylbenzo)-bis(2,3-pyrido)porphyrazine was reacted with dimethyl sulfate and monochloroacetic acid to produce the quaternized products and with diethyl sulfate to produce the sulfo-substituted product; all such compounds displayed amphiphilic character. Identical peaks in cyclic voltammograms were obtained for the products before and after quaternization. Zinc bis(1,4-didecylbenzo)-bis(2,3-pyrido)porphyrazine had no changes in its reduction or oxidation properties compared to phthalocyanine analogues.

Keywords: Amphiphilic; Phthalocyanine derivatives; Quaternization; Photosensitizer; Photodynamic therapy; Zinc bis(1,4-didecylbenzo)-bis(2,3-pyrido) porphyrazine

1. Introduction

Phthalocyanine derivatives have attracted attention as functional chromophores for various applications including organic charge carriers in photocopiers, laser light absorbers in data storage systems, photoconductors in photovoltaic cells and electrochromic displays [1–3].

Furthermore, phthalocyanine derivatives are known to have potential as second-generation photosensitizers for photodynamic therapy (PDT) because they show strong absorption in the far infrared region (between 600 and 850 nm) [3–7]. A good sensitizer for PDT requires high photostability, high selectivity to tumors, should not display cytotoxity when unirradiated, and long triplet state lifetime as well as strong absorption in the 600 and 800 nm region of the far infrared spectrum where light penetration of tissue is good [8]. Because phthalocyanine derivatives satisfy these requirements, they are good sensitizers for PDT.

Previously, we synthesized the non-peripherally substituted phthalocyanine, zinc alkylbenzopyridoporphyrazine, which possesses didecylbenzenoid and pyridinoid moieties [9]. We also described separation of an alkylbenzopyridoporphyrazine [9]. We reported a fundamental study on PDT technology by measuring the triplet state lifetime of the alkylbenzopyridoporphyrazines and regio isomers [10,11]. As alkylbenzopyridoporphyrazine exhibited solubility in organic solvents and was expected to have a higher tumor affinity, quaternization of the pyridine nitrogen in the alkylbenzopyridoporphyrazine was done to give solubility, bioavailability in an aqueous

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media and to have *in vivo* distribution [12]. Subsequently, Nyokong and her co-workers reported that phthalocyanine analogues, tetra-2,3-pyridoporphyrazine, and its quaternized compounds exhibited more excellent properties in comparison with un-substituted phthalocyanines [13]. They concluded that amphiphilic phthalocyanine derivatives were the best compounds for a new generation of photosensitizers for PDT [12]. In our previous papers [9–12], the reported zinc bis(1,4-didecylbenzo)-bis(3,4-pyrido)porphyrazine and its regio isomers were prepared by mixture of 3,6-didecylphthalonitrile and pyridine 3,4-dicarbonitrile.

In the present study, another type of novel non-peripheral substituted phthalocyanine derivative, zinc bis(1,4-didecylbenzo)-bis(2,3-pyrido)porphyrazine, was synthesized.

Related compounds such as 2,3-pyridoporphyrazines have been known to not absorb longer wavelengths but do possess stronger absorption intensity than corresponding phthalocyanines and 3,4-pyridoporphyrazines [14]. In accordance with the literature [14], zinc bis(1,4-didecylbenzo)-bis(2,3-pyrido)-porphyrazine and its quaternized derivatives have stronger absorption intensities than that of previously reported zinc bis(1,4-didecylbenzo)-bis(3,4-pyrido)porphyrazines [9–12]. Therefore, zinc bis(1,4-didecylbenzo)-bis(2,3-pyrido)porphyrazine and its quaternized derivatives are expected to serve as excellent photosensitizers for PDT. Substantiating these reports are measurements of electron transfer ability of zinc bis(1,4-didecylbenzo)-bis(2,3-pyrido)porphyrazine and its quaternized derivatives as estimated by cyclic voltammetry (CV) technique.

2. Experimental

2.1. Methods

Fourier transformation infrared (IR) spectra were recorded on a Shimadzu FT-IR 8100A spectrometer using potassium bromide (KBr) pellets. Ultraviolet–visible (UV–vis) spectra were measured on a Shimadzu UV-2400PC spectrometer; each sample was prepared at 5.0×10^{-5} mol dm^{-3} in toluene, pyridine and water. Fluorescence spectra were recorded in pyridine and water using either a Hitachi F-4500 fluorescence spectrometer or a Jasco (Nihon Bunko) FP-6600 spectrofluorometer. Proton nuclear magnetic resonance (^{1}H NMR) spectra were measured at 400 MHz on a Bruker Avance 400S and at 90 MHz using a Nihon Denshi Joel EX-90 in benzene-d_6 (C_6H_6-d_6) or chloroform-d ($CHCl_3$-d) using tetramethylsilane (TMS) as internal standard. Elemental analyses were carried out using a Perkin–Elmer 2400CHN instrument. Samples for elemental analysis were purified by repeated sublimation; the instrument was calibrated with copper phthalocyanine. Cyclic voltammograms (CVs) were recorded on a BAS CV-50W voltammetric analyzer at room temperature in acetonitrile containing a 0.01 mol dm^{-3} 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/silver chloride (Ag/AgCl) saturated sodium chloride electrode. The area of the working electrode was 2.0×10^{-2} cm^2.

2.2. Materials

Thin layer chromatography (TLC) was performed using Merck 60 F_{254} silica gel on aluminium sheets. Merck Silica gel 60, particle size 0.063–0.200 nm 7734 grade, was used in chromatographic separations.

Reagents were purchased from Aldrich Chemicals and were used as received without further purification.

3,6-Didecylphthalonitrile was synthesized from thiophene via 2,5-didecylthiophene and 2,5-didecylthiophene-1,1-dioxide, in accordance with our previous reports [9–12]. ^{1}H NMR (δ 90 MHz, $CHCl_3$-d/ppm) 0.88 (t, 6H), 1.26 (m,

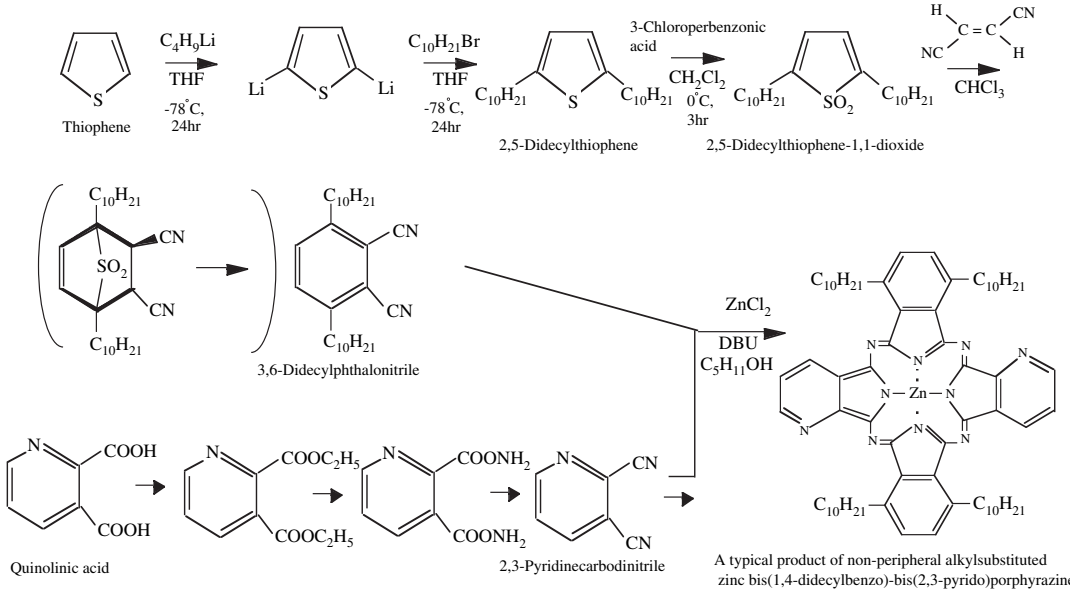


Fig. 1. Synthetic pathway of zinc bis(1,4-didecylbenzo)-bis(2,3-pyrido)porphyrazine.

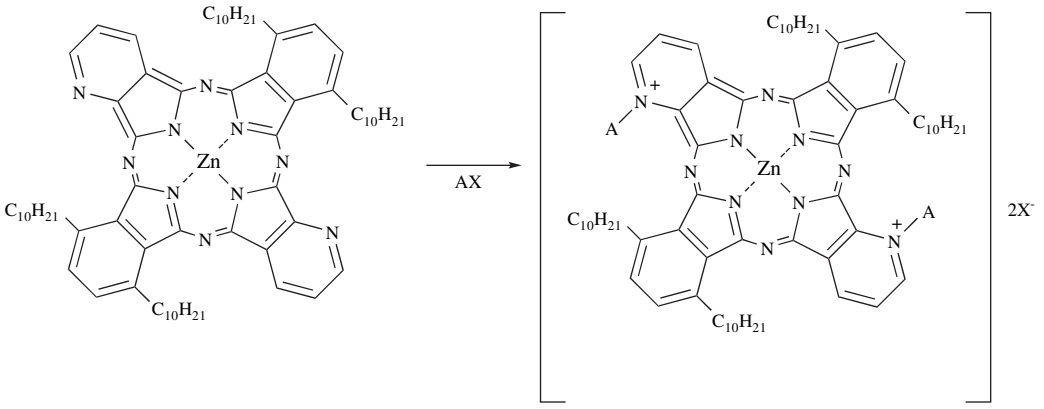


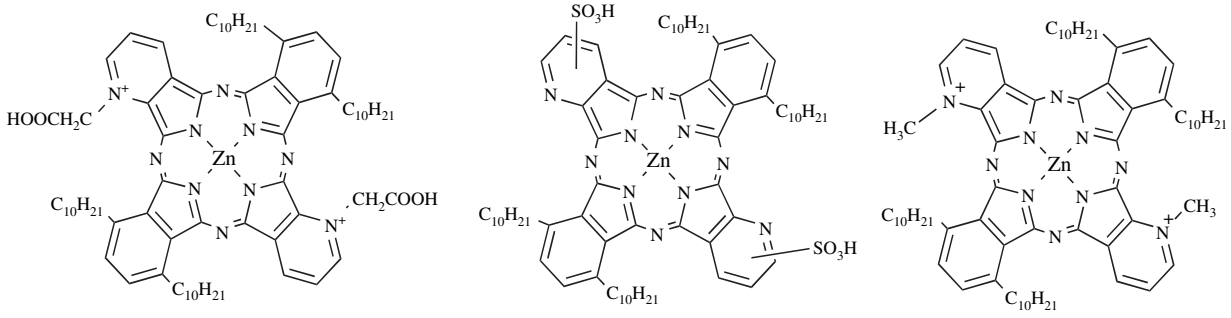
Fig. 2. Quaternization of zinc bis(1,4-didecylbenzo)-bis(2,3-pyrido)porphyrazine; AX: dimethyl sulfate (DMS), diethyl sulfate (DES), monochloroacetic acid (MCAA), and DMF, 140 °C, 2-h reflux.

32H), 2.85 (t, 4H), 7.46 (s, 2H); IR (ν KBr/cm^{-1}) 2960 (ν_{C-H}), 2240 (ν_{C-N}), 1560 (ν_{C-C}), 1460 (ν_{C-C}), 1410 (ν_{C-C}), 1230 (δ_{C-H}), 730 (δ_{C-H}); Anal Calcd. for $C_{28}H_4N_2$: C, 82.69; H, 10.85; N, 6.86. Found: C, 82.26; H, 10.84; N, 6.84.

Pyridine-2,3-dicarbonitrile was synthesized from pyridine-2,3-dicarboxylic acid. Pyridine-2,3-dicarboxylic acid (15 g, 0.09 mol) in 200 g of ethanol was refluxed in 7.5 cm^3 of concentrated sulfonic acid for 48 h. After the solvent was removed and neutralized with 3 M NaOH solution, the organic layer was extracted with three times of 75 cm^3 of diethyl ether. The extract was dried on calcium chloride, filtered and the solvent evaporated. The residue was distilled to afford pyridine-2,3-dicarboxy ethyl ester. The ester was dissolved in concentrated aqueous ammonia and the solution was stirred for 48 h to afford a white colored precipitate. The precipitate was filtered off and the corresponding diamide was obtained as m.p. 179–181 °C. Trifluoroacetic anhydride (12 cm^3, 0.11 mol) was added dropwise to the diamide (5.8 g, 0.04 mmol) in 14 cm^3 of dry pyridine and 46 cm^3 of 1,4-dioxane at 0 °C. After reaction the mixture was poured into water and extracted with ethyl acetate (2×50 cm^3). The organic layer was washed with water, 2%-hydrochloric acid and saturated brine. After that, solvent was removed to obtain crude product. The crude product was recrystallized with benzene–petroleum ether, colorless solid (1.97 g, 17%), m.p. 265 °C. ^{1}H NMR (δ 400 MHz, $CHCl_3$-*d*/ppm) 7.26 (s, 1H), 7.75 (s, 1H), 9.09 (s, 1H,); IR (ν KBr/cm^{-1}) 3090 (ν_{C-H}), 2240 (ν_{C-N}),1600 (ν_{C-C}), 1550 (ν_{C-C}), 1470 (ν_{C-C}), 1220 (δ_{C-H}), 750 (δ_{C-H}); Anal Calcd. for $C_7H_3N_3$: C, 65.11; H, 2.34; N, 32.55. Found: C, 65.12; H, 2.34; N, 32.56.

2.3. Zinc bis(1,4-didecylbenzo)-bis(2,3-pyrido) porphyrazine

3,6-Didecylphthalonitrile (0.12 g, 0.29 mmol) and pyridine-2,3-dicarbonitrile (0.04 g, 0.29 mmol) (Fig. 1) were dissolved in pentanol (7 cm^3) and zinc chloride (0.05 g) was added; the ensuing mixture was heated for 4 h in the presence of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) as catalyst. After cooling, the reaction mixture was dissolved in toluene (50 cm^3) and filtered; the solvent was removed by evaporation. The product was purified by TLC (eluent:toluene) yielding a blue solid (0.13 g; yield 80%). ^{1}H NMR (δ 400 MHz, C_6H_6-d_6/ppm) 0.9 (m, 12H, CH_3), 1.61–2.61 (m, 64H, CH_2), 4.18–4.36 (m, 8H, α-CH_2), 7.45 (m, 4H, arom), 8.26 (m, 6H, Py); IR (ν KBr/cm^{-1}) 2960 (ν_{C-H}), 1600 (ν_{C-C}), 1500 (ν_{C-C}), 1420 (ν_{C-C}), 1200 (δ_{C-H}), 1100 (δ_{C-H}), 750 (δ_{C-H}); UV–vis [λ_{max} toluene/nm (log ε_{max})] 665 (5.494); Anal Calcd. for $C_{70}H_{94}N_{10}Zn$: C, 73.68; H, 8.30; N, 12.28. Found: C, 73.67; H, 8.30; N, 12.28.



After reaction with MCAA | After reaction with DES | After reaction with DMS

Fig. 3. Typical structure of quaternized zinc bis(1,4-didecylbenzo)-bis(2,3-pyrido)porphyrazines.

Table 1
Analytical data of quaternized zinc bis(1,4-didecylbenzo)-bis(2,3-pyrido)porphyrazines

Quaternizing agent	Yield/%	ν_{max} (KBr)/cm^{-1}	Found (calcd)/%	δ[a] (^{1}H 400 MHz)/ppm
DMS	25	3070, 2980 (ν_{C-H}), 1500, 1400 ($\nu_{C=C}$), 1250, 1100, 950, 810, 660 (δ_{C-H})	C: 49.03 (49.03); H: 3.05 (3.09); N: 21.39 (21.43)	0.90 (m, 12H, CH_3), 0.95–1.45 (m, 56H, γ-CH_2), 1.60–2.41(m, 8H, β-CH_2), 4.05 (s, 6H, CH_3), 4.25–4.42 (m, 4H, α-CH_2), 7.45 (m, 4H, arom), 8.02 (m, 6H, Py)
DES	21	3480(ν_{O-H}), 3050, 2960(ν_{C-H}), 1600, 1460, 1400($\nu_{C=C}$), 1350, 1150($\nu_{S=O}$), 1250, 920, 770(δ_{C-H}), 580(δ_{C-S})	C: 37.14(37.11); H: 1.77(1.78); N: 18.54(18.54)	0.86 (m, 12H, CH_3), 1.02–1.63 (m, 56H, γ-CH_2), 1.88–2.61 (m, 8H, β-CH_2), 4.26–4.50 (m, 4H, α-CH_2), 7.37 (m, 4H, arom), 8.22 (m, 4H, Py)
MCAA	24	3480 (ν_{O-H}), 3050, 2970 (ν_{C-H}), 1740 ($\nu_{C=O}$), 1600, 1500, 1400 ($\nu_{C=C}$), 1210, 1100, 940, 790, 690 (δ_{C-H})	C: 45.02 (45.05); H: 2.53 (2.52); N: 17.48 (17.50)	0.87 (m, 12H, CH_3), 1.13–1.70 (m, 56H, γ-CH_2), 1.82–2.61 (m, 8H, β-CH_2), 4.11–4.38 (m, 4H, α-CH_2), 6.20 (s, 2H, CH_2), 7.14–7.27 (m, 4H, arom), 8.73–9.16 (m, 6H, Py)

[a] Dimethyl sulfoxide-d_6.

2.4. Quaternization of zinc bis(1,4-didecylbenzo)-bis(2,3-pyrido)porphyrazine

Zinc bis(1,4-didecylbenzo)-bis(2,3-pyrido)porphyrazine (0.17 g, 0.15 mmol) was reacted with monochloroacetic acid (MCAA) (0.57 g, 6 mmol), diethyl sulfate (DES) (0.1 g, 0.6 mmol) and dimethyl sulfate (DMS) (0.2 g, 1.5 mmol), respectively, in *N*,*N*-dimethylformamide (DMF) 140 °C for 2 h (Figs. 2 and 3). The reaction mixture was dissolved in acetone (20 cm^3), cooled to room temperature and the resulting solution was filtered. The solvent was removed and the product was purified by TLC (eluent:THF-toluene, 8:2); the product was recovered from the TLC plate, via dissolution in pyridine followed by filtration and solvent removal.

3. Results and discussion

3.1. Synthesis and quaternization of phthalocyanine derivative

The synthetic procedure used to prepare the novel non-peripheral substituted phthalocyanine derivative, zinc bis(1,4-didecylbenzo)-bis(2,3-pyrido)porphyrazine, was the same as that used for the preparation of zinc bis(1,4-didecylbenzo)-bis(3,4-pyrido)porphyrazine [9–12]. Zinc bis(1,4-didecylbenzo)-bis(2,3-pyrido)porphyrazine was synthesized in 80% yield using equimolar amounts of 3,6-didecylphthalodinitrile and pyridine-2,3-dicarbonitrile in the presence of DBU as catalyst (Fig. 1). The target compound, zinc bis(1,4-didecylbenzo)-bis(2,3-pyrido)porphyrazine, and its intermediates were studied using IR, ^{1}H NMR and UV–vis spectroscopy and elemental analysis. The analytical data of the compound were in good agreement with the proposed structure. The UV–vis spectrum of zinc bis(1,4-didecylbenzo)-bis(2,3-pyrido)porphyrazine around 700 nm is characteristic of phthalocyanine analogues, with the Q band attributable to the difference between the highest occupied molecular orbital (HOMO) energy level and the lowest unoccupied molecular orbital (LUMO) energy, i.e., the π–π* transition of the phthalocyanine ring.

The synthesized zinc bis(1,4-didecylbenzo)-bis(2,3-pyrido) porphyrazine was anticipated to be a mixture of products, with different numbers of pyridine rings in the molecule. However, the target compound comprised only the proposed constituent as confirmed by TLC. As the target compound had been purified by TLC using benzene as eluent, only one blue-colored constituent was obtained. It is thought that the desired compound was obtained in accordance with the mole ratio of the raw materials used. The same phenomenon has been observed in the case of synthesis of zinc bis(1,4-didecylbenzo)-bis(3,4-pyrido)porphyrazine [9–12].

Zinc bis(1,4-didecylbenzo)-bis(2,3-pyrido)porphyrazine has two alkylbenzenoid and two pyridinoid rings in different locations; thus, it has five regio isomers, three of which have rings adjacent to the pyridinoid rings while the other two have opposed pyridinoid rings. Although we previously reported the separation of regio isomers in alkylbenzopyridoporphyrazine [9–12], no attempt was made in this work to isolate the isomers of zinc bis(1,4-didecylbenzo)-bis(2,3-pyrido)porphyrazine.

Table 2
UV–vis and fluorescence spectral data of quaternized zinc bis(1,4-didecylbenzo)-bis(2,3-pyrido)porphyrazines

Quaternizing agent	Q-band		Fluorescence	
	λ_{max} pyridine/nm	λ_{max}water/nm	F_{max} pyridine/nm	F_{max} water/nm
DMS	746, *673*, 649, 606, 738[a], *668*[a], 641[a], 600[a]	723, *676*, 646	683	681
DES	*693*, 658, 628, 597, *673*[a], 645[a], 605[a]	708, *687*, 652	698	691
MCAA	*679*, 650, *677*[a], 620[a]	*687*, 647	692	688

Main peak (absorption maxima) values are italicized.
[a] In toluene.

Table 3
Potentials of quaternized zinc bis(1,4-didecylbenzo)-bis(2,3-pyrido)porphyrazines in DMF with tetrabutylammonium perchlorate

Quaternizing agent	Potential (V vs Ag/AgCl)	
	Reduction	Oxidation
Before quaternation	−0.94,[a] −0.62,[a] −0.29,[a] −0.03[a]	0.32,[a] 0.48,[a] 0.97[a]
DMS, ΔE[b]	−1.15,[a] −0.77, −0.14,[a] −0.05,[a] 0.11[b]	0.50[a]
DES, ΔE[b]	−0.83, −0.51,[a] −0.05,[a] 0.14[b]	0.25,[a] 1.05[a]
MCAA	−0.75,[a] −0.52,[a] −0.12[a]	0.96,[a] 1.28[a]

Potentials of reversible wave are midpoint potential of anodic and cathodic peaks for each couple.
[a] Irreversible peak.
[b] The anodic peak to cathodic peak separation for reversible couple.

The zinc bis(1,4-didecylbenzo)-bis(2,3-pyrido)porphyrazine was reacted with quaternizing agents such as MCAA, DES and DMS in DMF as a solvent at 140 °C for 2 h (Fig. 2). The respective products obtained were greenish-blue-colored powders. Zinc bis(1,4-didecylbenzo)-bis(2,3-pyrido)porphyrazine was dissolved in toluene, chloroform, pyridine and methanol but not in water. After reacted with quaternizing agents, the products were also dissoluble in water.

The yields of the respective products were 24, 21 and 25% for MCAA, DES and DMS (Fig. 3). In the cases of MCAA and DMS, analysis revealed that the structures of the products were in good agreement with those having N-CH_2COOH and N-CH_3 groups, respectively (Table 1). Whereas when DES was used as quaternizing agent, no N-CH_2CH_3 singlet peak was present in the ^1H NMR spectrum, S=O stretching in the IR spectrum was observed (Table 1). Therefore, sulfonation but not quaternization was achieved [12,15].

After reaction with the quaternizing agents, all compounds possessed amphiphilic properties.

3.2. Spectroscopic and reduction and oxidation properties

The quarternized derivatives of zinc bis(1,4-didecylbenzo)-bis(2,3-pyrido)porphyrazine showed strongest absorption at 676 and 687 nm in water after reaction with DMS, DES and MCAA, respectively (Table 2); these Q bands were bathochromic compared to the non-quaternized parent compound. As the UV–vis spectra of the quaternized compounds in water showed very broad peaks, the amphiphilic compounds had excellent molecular association tendency.

Zinc bis(1,4-didecylbenzo)-bis(2,3-pyrido)porphyrazine and its quaternized compounds fluoresced on exposure to ultraviolet light. Although fluorescence spectra generally were known to be mirror images of UV–vis spectra at the longer wavelengths, the Q bands nearly overlapped with the wavelengths at which fluorescence occurs in the case of zinc bis(1,4-didecylbenzo)-bis(2,3-pyrido)porphyrazine and its quaternized compounds, thus, the differences between λ_{max} of UV–vis and the F_{max} of fluorescence spectra, called the Storks shift, were very small. These observations are similar to that seen with the phthalocyanines zinc bis(1,4-didecylbenzo)-bis(2,3-pyrido)porphyrazine and its quaternized derivatives. These compounds are molecules with high planarity which cannot change their configuration after quaternization.

The important parameters of a CV are the reduction and oxidation potentials of the irreversible peaks and the mid-point potential for the reversible couple, E_{mid} (Table 3). The reduction and oxidation potentials of zinc bis(1,4-didecylbenzo)-bis(2,3-pyrido)porphyrazine comprise seven irreversible peaks which consist of three anodic and four cathodic peaks. In the case of metal phthalocyanine having zinc as central metal, the reduction and oxidation only occur at phthalocyanine ring because zinc has no reactivity [2].

The shapes of the CVs were changed as a result of quaternization. The redox potentials of the quaternized compounds were shown to be different as the CVs of the compounds changed in the number of anodic and cathodic peaks; quaternization with MCAA produced CVs with two anodic peaks and three cathodic peaks; quaternization with DMS produced CVs with two anodic peaks and four cathodic peaks; and quaternization with DES produced CVs with four anodic peaks and two cathodic peaks (Fig. 4).

The shapes of CVs of quaternized products appeared distinguishable from that of zinc bis(1,4-didecylbenzo)-bis(2,3-pyrido)porphyrazine (Fig. 5). Electron transfer ability of quaternized compounds has been increased remarkably by the possession of cation groups.

The potential difference in CVs between the reduction and the oxidation corresponds to the HOMO–LUMO energy gaps of the compound [16–18]. Just as chemical reactions occur during the electron transfer between HOMO and LUMO

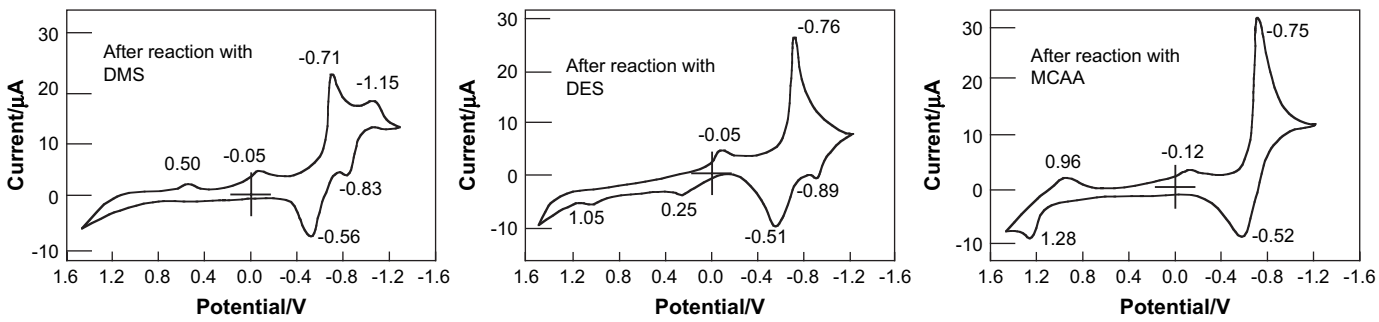


Fig. 4. Cyclic voltammograms of quaternized zinc bis(1,4-didecylbenzo)-bis(2,3-pyrido)porphyrazine derivatives in DMF with tetrabutylammonium perchlorate.

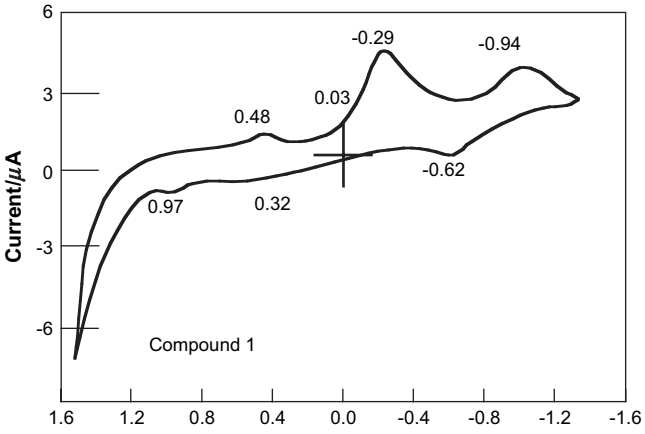


Fig. 5. Cyclic voltammogram of zinc bis(1,4-didecylbenzo)-bis(2,3-pyrido)-porphyrazine before quaternization in DMF with tetrabutylammonium perchlorate.

energy levels, photochemical reactions are also based on similar phenomena of energy transfer. Before and after the quaternization, the HOMO–LUMO energy gap of zinc bis(1,4-didecylbenzo)-bis(2,3-pyrido)porphyrazine was unchanged. The shapes of CVs clearly showed that quaternized zinc bis(1,4-didecylbenzo)-bis(2,3-pyrido)porphyrazines had increased electron transfer ability.

Thus, for the above-mentioned reasons, the quaternization of zinc bis(1,4-didecylbenzo)-bis(2,3-pyrido)porphyrazine is predicted to be an effective means for producing efficient PDT photosensitizers.

4. Conclusions

Zinc bis(1,4-didecylbenzo)-bis(2,3-pyrido)porphyrazines having two pyridine and two alkyl-substituted benzene rings were reacted with DMS, DES and MCAA as quaternizing agents.

When MCAA and DMS were employed as quaternizing agents, zinc bis(1,4-didecylbenzo)-bis(2,3-pyrido)porphyrazines were changed to their quaternized derivatives. However, when DES was employed, we showed that sulfonation but not quaternization was achieved.

Identical peaks in CVs appeared for the products before and after quaternization.

After reacting with quaternizing agents, the shapes of CVs indicated the acquisition of cationic groups. Thus, it can be presumed that the quaternized zinc bis(1,4-didecylbenzo)-bis(2,3-pyrido)porphyrazines had increased electron transfer ability and PDT photosensitizer efficiency.

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