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Synthesis and characterization of novel 2-{{2-(dimethylamino)ethyl}(methyl)amino} ethoxy-substituted metallophthalocyanines

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Abstract: The synthesis of novel, symmetrical, tetrasubstituted metallophthalocyanines (cobalt, zinc, and copper) bearing four 2-{{2-(dimethylamino)ethyl}(methyl)amino} ethoxy units was reported. The dinitrile derivative was converted into the water-soluble quaternized product by its reaction with methyl iodide. The quaternized zinc phthalocyanine was obtained from the reaction of the water-soluble dinitrile derivative with zinc acetate. The structures of the newly synthesized molecules were proposed according to elemental analysis, ¹H NMR, FT-IR, and UV-Vis spectral data.

Key words: Phthalocyanine, 2-{{2-(dimethylamino)ethyl}-methylamino} ethanol, water-soluble

1. Introduction

Phthalocyanines (Pcs) constitute an important class of tetrapyrrolic macrocycles. Pcs have attracted major research attention for many years due to their π -electron conjugation, chemical and high thermal stability, and catalytic properties.^{1–3} Pc derivatives as photosensitizers can be used in photodynamic therapy.^{4,5} Skin diseases and cancer are generally the target illnesses in the treatment. Pc derivatives have favorable photophysical and chemical properties, which include strong absorbance at long wavelengths, a high singlet oxygen quantum yield, and chemical versatility.⁶ Therefore, substituents are added on the periphery of the macrocycle or as the axial ligands. However, like with most photosensitizing agents, Pcs have poor solubility in water. Tailoring the properties of these compounds by either addition of various groups on the periphery of the macrocycle or of the axial ligands enables the reaching of the desired goal.^{7,8} Amino, sulfo, or carboxyl substituents have often been added on the peripheral or nonperipheral positions of Pcs to improve solubility in water and polar solvents.^{9–11}

In general, chemical synthesis is mainly performed by heating with the use of traditional heat equipment such as oil baths, heating jackets, and sand baths. These heating techniques are of slow nature. Furthermore, a temperature gradient can develop within the sample, which causes local overheating and leads to the decomposition of the products or reagents. Microwave technology has recently been a fast procedure for chemical synthesis.¹² Microwave-assisted synthesis reinforces the polarization of the reactants to accelerate the reactions. Microwave irradiation has recently attracted interest because it is selective, internal, rapid, and controllable.^{13–15}

In this study, the synthesis, characterization, and structural investigation of Co(II), Zn(II), and Mn(II)

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Pcs containing 2-{{2-(dimethylamino)ethyl}(methyl)amino} ethoxy groups are described. The phthalonitrile and the resulting zinc Pc were converted into the water-soluble quaternized product by reaction with methyl iodide. The new compounds were characterized by elemental analysis, IR, ^1H NMR, and electronic spectra.

2. Results and discussion

The preparation of metallophthalocyanines was attempted by the standard method of cyclotetramerization of the dinitrile derivatives in the presence of metal salts in a high-boiling solvent at reflux temperature. Thus, first the synthesis of 4-(2-{{2-(dimethylamino)ethyl}(methyl)amino} ethoxy) phthalonitrile (**3**) was accomplished in 74% yield through base-catalyzed aromatic displacement of 4-nitrophthalonitrile (**1**) with 2-{{2-(dimethylamino)ethyl}-methylamino} ethanol using K_2CO_3 as the base in dry DMSO. The reaction was carried out at 35°C under N_2 atmosphere for 6 days (Figure 1). Quaternization of the phthalonitrile precursor was performed with iodomethane in chloroform, by reacting in a dark medium for 12 h (Figure 2).

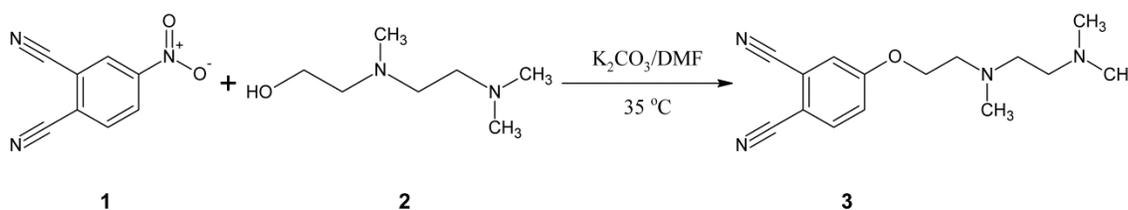


Figure 1. Synthesis of 4-(2-{{2-(dimethylamino)ethyl}(methyl)amino} ethoxy)phthalonitrile.

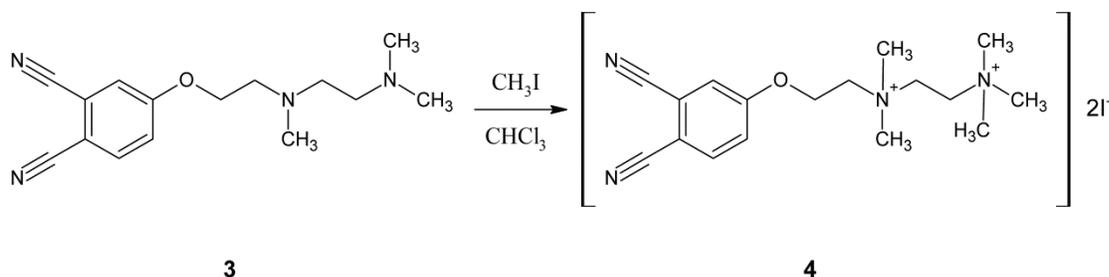


Figure 2. Synthesis of 4-(2-{{2-(trimethylammonium)ethyl}(dimethyl)ammonium} ethoxy)phthalonitrile diiodide.

The metallophthalocyanines (**5–8**) were synthesized using microwave irradiation from the corresponding phthalonitrile compounds (**3** or **4**) and metal salts (CoCl_2 , $\text{Zn}(\text{CH}_3\text{COO})_2$, and MnCl_2) in 2-dimethylaminoethanol for 3 min (Figure 3).^{16,17} After the reaction mixture was evaporated to dryness, the solid was dissolved in a solution of acetic acid (5.7×10^{-6} M). The solution was extracted with acetone, ethyl acetate, dichloromethane, and chloroform.¹⁸ The water solution was neutralized with potassium carbonate and then the precipitated Pc derivatives (**5–7**) were obtained. All compounds were characterized by spectral data (IR, elemental analyses, and UV-Vis spectra). The data are consistent with the assigned structures.

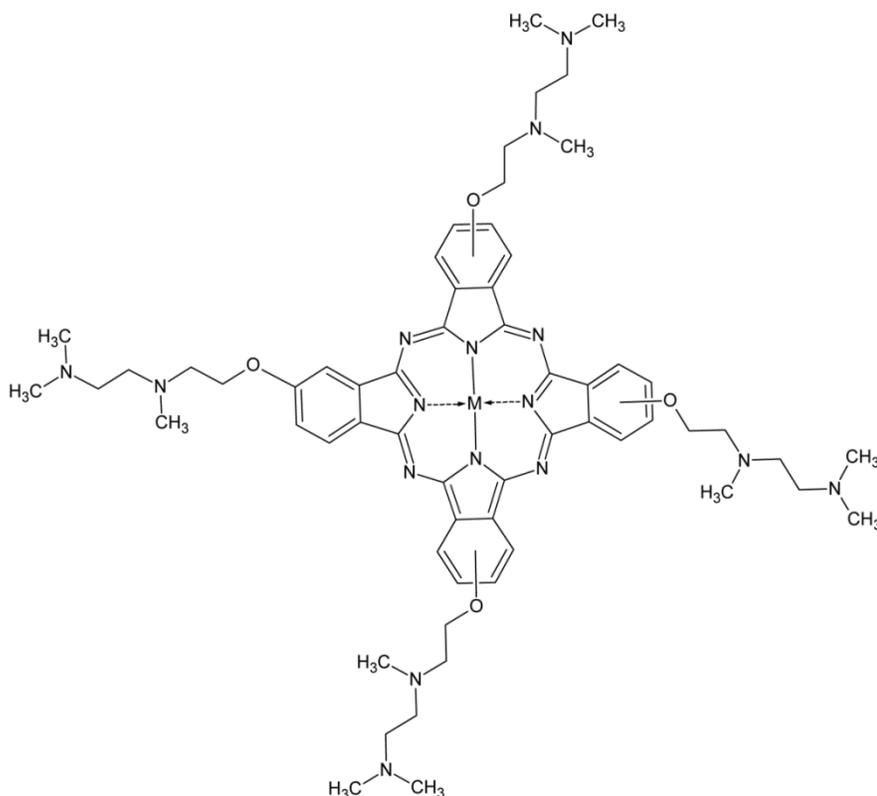


Figure 3. Molecular structure of the synthesized phthalocyanines.

In the IR spectrum of compound **3**, the absorption bands at 2230 and 2945–2770 cm^{-1} were assigned to the $\text{C}\equiv\text{N}$ stretching and to the C-H stretching of the aromatic rings. In addition, the appearance of new stretching modes at 1258 cm^{-1} belonging to aliph-O-Ar groups confirmed the proposed structure of compound **3**. In the ^1H NMR spectrum of compound **3**, the signals of the aromatic protons were at 7.17–7.19, 7.25, and 7.66–7.68 ppm as doublet, singlet, and doublet, respectively. Aliphatic CH_3 protons of amino groups were observed as a singlet at 2.20 ppm (3H) and a singlet at 2.31 ppm (6H). The $\text{CH}_2\text{-O}$ protons were at 4.12 ppm as a triplet. Aliphatic CH_2 protons of amino groups were observed as triplets at 2.38 ppm (2H), 2.55 ppm (2H), and 2.83 ppm (2H).

The IR spectra of all Pcs are very similar to each other. The sharp $\text{C}\equiv\text{N}$ vibration at 2230 cm^{-1} disappears after formation of the Pcs.^{19,20} The characteristic vibrations corresponding to the ether groups at about 1260–1255 cm^{-1} were observed for all Pc derivatives (**5–7**). In the IR spectra of novel symmetrically substituted Pcs (**5–7**), aromatic CH and aliphatic CH were observed at about 3065–3055 and 2938–2857, respectively.

In the ^1H NMR spectrum of zinc Pc **5** in CDCl_3 , the aromatic protons resonated between 7.55 and 6.91 ppm, integrating for 12 protons for the complex. Aliphatic CH_3 protons of amino groups were observed as a singlet at 2.21 ppm (12H) and a singlet at 2.33 ppm (24H). The $\text{CH}_2\text{-O}$ protons were at 4.12 ppm. Aliphatic CH_2 protons of amino groups were observed at 2.55 ppm (8H) and 3.49 ppm (16H). The ^1H NMR spectra of the compounds are somewhat broader than the corresponding signals for dinitrile derivative **3**.

The UV-vis spectra of the Pc core is dominated by 2 intense bands, the Q band around 680 nm and the B band in the near-UV region around 330 nm, both correlating to $\pi\text{-}\pi^*$ transitions.^{21–23} Electronic spectra

are especially useful to establish the structure of all the Pcs. UV-Vis spectra of metallophthalocyanines (**5** and **6** in CHCl_3) exhibited intense single Q band absorption of the $\pi-\pi^*$ transitions at 682 and 677 nm and B bands in the UV region at 357 and 331, respectively (Figure 4). The UV-Vis spectrum of **7** in CHCl_3 exhibited the B band at 366 nm and the intense Q band at 734 nm with a weak band at 498 nm. For the water-soluble quaternized zinc phthalocyanine **8**, Q bands appeared at 684 nm and a B band at 299 nm.

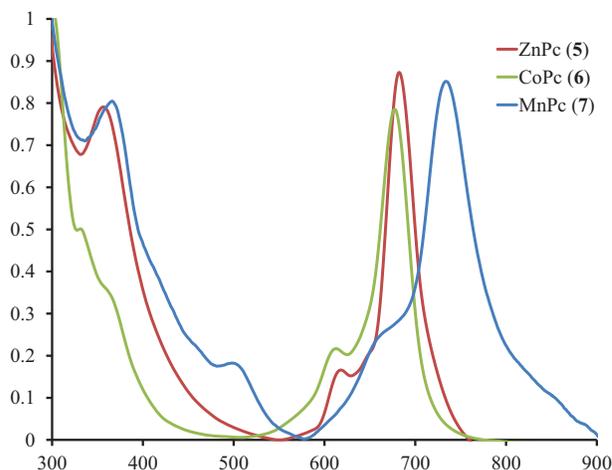


Figure 4. Electronic absorption spectra of **5–7** (in CHCl_3).

The wavelengths of the absorption of the Q band of **5–7** follow the order $\text{Mn} > \text{Zn} \sim \text{Co}$.²⁴ The order shows that manganese Pc **7** has the largest red shift compared to the other metallophthalocyanines. The UV-Vis spectrum of manganese Pc **7** is clearly different from the spectra of the other metal complexes. The oxidation state of Mn in the complex with Pc is 3^+ , whereas the other metals Zn and Co are in oxidation state 2^+ .

The quaternarization of the Pc precursor ligand including 4-(2-{[2-(dimethylamino)ethyl](methylamino)ethoxy}phthalonitrile (**3**) and methyl iodide were dissolved in CHCl_3 . This mixture was stirred at room temperature in dark for 12 h. The yellow precipitate was filtered off and washed with chloroform and ethyl acetate to remove any organic impurities. Finally, water-soluble quaternized phthalonitrile derivative was dried in vacuo.

In the ^1H NMR spectrum of compound **4**, the terminal CH_3 protons were observed at 3.19 ppm as a singlet while N-CH_2 and O-CH_2 protons were at 3.88–3.99 ppm and at 5.37–5.39 ppm, respectively. The aromatic protons resonated at 7.54–7.56, 7.86, and 8.14–8.15 ppm, respectively. In the IR spectrum of **4**, C–O–C groups, $\text{C}\equiv\text{N}$ groups, aliphatic groups, and aromatic groups gave characteristic peaks at 1260 cm^{-1} , 2234 cm^{-1} , 2900 cm^{-1} , and 3085 cm^{-1} , respectively. In the mass spectrum of **4**, the peak for $[\text{M-2I}]^+$ was found at $m/z = 302.72$.

Cyclotetramerization of compound **4** to yield the tetra-substituted zinc Pc **8** was accomplished in 2-dimethylaminoethanol at 140°C under nitrogen atmosphere (Figure 5). The quaternized zinc Pc compound (**8**) is soluble in water, DMF, DMSO, and ethanol. In the IR spectra of novel symmetrically substituted quaternized zinc phthalocyanines, aromatic CH, aliphatic CH, and C–O–C groups were observed at 3059, 2953–2860, and 1255 , respectively.

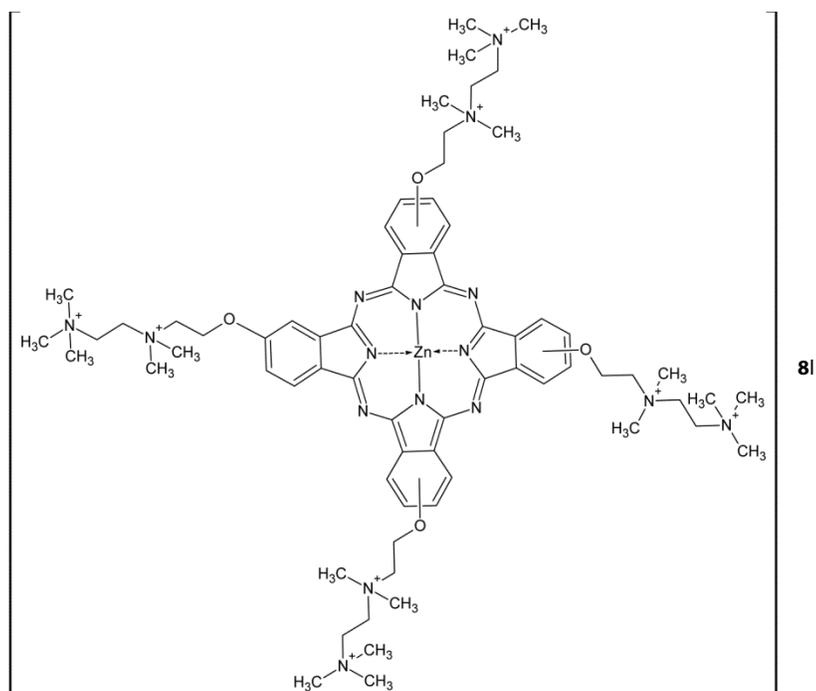


Figure 5. Quaternized zinc phthalocyanine **8**.

In the ^1H NMR spectrum of zinc Pc **8** in DMSO-d_6 , the aromatic protons resonated between 7.46 and 8.04 ppm, integrating for 12 protons for the complex. Aliphatic CH_3 protons of amino groups were observed as a singlet at 2.21 ppm (24H) and a singlet at 3.17 ppm (36H). The $\text{CH}_2\text{-O}$ protons were at 5.23 ppm. Aliphatic CH_2 protons of amino groups were observed at 3.26 ppm (8H), 3.41 ppm (8H), and 3.82 ppm (8H).

3. Experimental

IR spectra were recorded on a PerkinElmer Spectrum One FT-IR spectrometer with ATR capability; electronic spectra were recorded on a Scinco d-1000 spectrophotometer. ^1H NMR spectra were recorded on Agilent VNMRS 500 MHz using TMS as the internal reference. Mass spectra were measured on a PerkinElmer Clarus 500 mass spectrometer. A single-mode microwave reactor (CEM Discover SP) was used for carrying out the synthesis of metallophthalocyanines. All reagents and solvents were of reagent-grade quality and obtained from commercial suppliers. The homogeneity of the products was tested in each step by TLC. All solvents were dried and purified as described by Perrin and Armarego.²⁵ The solvents were stored over molecular sieves. 4-Nitrophthalonitrile was synthesized according to published methods.²⁶

3.1. 4-(2-{{2-(Dimethylamino)ethyl}(methyl)amino} ethoxy)phthalonitrile (**3**)

4-Nitrophthalonitrile (**1**) (0.5 g, 2.89 mmol) was dissolved in 7 mL of dry DMF under N_2 atmosphere, and 2-{{2(dimethylamino)ethyl}-methylamino} ethanol (**2**) (1.4 mL, 8.67 mmol) was added and heated at 35°C . After stirring for 15 min, anhydrous K_2CO_3 (8 g, 57.8 mmol) was added portion-wise during 2 h with efficient stirring. The reaction mixture was stirred under nitrogen for 6 days. The reaction content was then poured into 50 g of ice-water mixture and extracted with chloroform. After drying over Na_2SO_4 , the pure product was evaporated to dryness. Yield: 0.58 g (74%). IR $\nu_{\text{max}}/\text{cm}^{-1}$: 3060 (C-H, aromatic), 2945–2770 (C-H,

aliphatic), 2230 (C≡N), 1258 (C-O-C). ¹H NMR (500 MHz; CDCl₃): δ 2.20 (3H, s, CH₃), 2.31 (6H, s, CH₃), 2.38–2.40 (2H, t, *J* = 6.7 Hz, CH₂-N), 2.56–2.58 (2H, t, *J* = 7.1 Hz, CH₂-N), 2.82–2.84 (2H, t, *J* = 5.6 Hz, CH₂-N), 4.11–4.13 (2H, t, *J* = 5.6 Hz, CH₂-O), 7.17–7.19 (1H, d, *J* = 8.6 Hz, Ar), 7.25 (1H, s, Ar), 7.66–7.68 (1H, d, *J* = 8.3 Hz, Ar). Analysis of C₁₅H₂₀N₄O (272.35) (% calcd./found): C: 66.15/65.01, H: 7.40/7.43, N: 20.57/20.59.

3.2. 4-(2-{[2-(Trimethylammonium)ethyl] (dimethyl)ammonium} ethoxy) phthalonitrile diiodide (4)

Compound **3** (0.1 g, 0.37 mmol) was dissolved in 4 mL of chloroform and 1 mL of iodomethane was added to this solution. The mixture was kept in the dark for 12 h. The resulting precipitate was filtered off and then washed with chloroform and ethyl acetate to remove any organic impurities and subsequently dried under vacuum. The solid was obtained with a yield of 90% (0.1 g). IR $\nu_{\max}/\text{cm}^{-1}$: 3085 (C-H, aromatic), 2900 (C-H, aliphatic), 2234 (C≡N), 1260 (C-O-C). ¹H NMR (500 MHz; CDCl₃): δ 3.19 (15H, s, CH₃), 3.88–3.99 (6H, m, CH₂-N), 5.37–5.39 (2H, t, *J* = 4.7 Hz, CH₂-O), 7.54–7.56 (1H, d, *J* = 8.8 Hz, Ar), 7.86 (1H, s, Ar), 8.14–8.15 (1H, d, *J* = 8.8 Hz, Ar). MS (ESI): *m/z* 302.72 [M-2I]⁺. MS (ESI): *m/z* 302.72 [M-2I]⁺. Analysis of C₁₇H₂₆I₂N₄O (556.22) (% calcd./found): C: 36.71/36.51, H: 4.71/4.69, N: 10.07/10.01.

3.3. 2, 9(10), 16(17), 23(24)-Tetrakis-(2-{[2-(dimethylamino)ethyl] (methyl)amino} ethoxy) phthalocyaninatozinc(II) (5)

Compound **3** (0.1 g, 0.37 mmol), anhydrous Zn(CH₃COO)₂ (0.018 g, 0.10 mmol), and 2-dimethylaminoethanol (0.5 mL) were irradiated in a quartz vessel of 10 mL in a microwave oven at 140 °C and 200 W for 3 min. The reaction mixture was evaporated to dryness. The product was dissolved in a solution of acetic acid (pH 5). The solution was extracted with acetone, ethyl acetate, dichloromethane, and chloroform. After the solution was neutralized with potassium carbonate, a green product precipitated. The solid was collected by filtration and washed with water until the filtrate was neutral. Yield: 0.020 g (18%). UV-Vis (CHCl₃): λ, nm (log ε) 357 (5.12), 682 (5.16). IR $\nu_{\max}/\text{cm}^{-1}$: 3060 (C-H, aromatic), 2930–2857 (C-H, aliphatic), 1257 (C-O-C). ¹H NMR (500 MHz; CDCl₃): δ 2.21 (12H, s, CH₃), 2.33 (24H, s, CH₃), 2.55 (8H, br, CH₂-N), 3.49 (16H, br, CH₂-N), 4.12 (8H, br, CH₂-O), 6.91–7.55 (12H, m, Ar). Analysis of C₆₀H₈₀N₁₆O₄Zn (1154.79) (% calcd./found): C: 62.40/63.01, H: 6.98/6.69, N: 19.41/19.41.

3.4. 2, 9(10), 16(17), 23(24)-Tetrakis-(2-{[2-(dimethylamino)ethyl](methyl)amino} ethoxy) phthalocyaninatocobalt(II) (6)

Compound **3** (0.1 g, 0.37 mmol) was dissolved in 0.5 mL of 2-dimethylaminoethanol and anhydrous CoCl₂ (0.013 g, 0.10 mmol) was added to this solution. The solution was irradiated in a microwave oven at 140 °C and 200 W for 3 min. After cooling, the reaction mixture was evaporated to dryness. The product was then isolated from the impurities through protonation of the amino groups by treatment with aqueous acetic acid. The solution was extracted with acetone, ethyl acetate, dichloromethane, and chloroform. After the solution was neutralized with potassium carbonate, a greenish blue product precipitated. The solid was collected by filtration and washed with water until the washings were neutral. Yield: 0.015 g (15%). UV-Vis (CHCl₃): λ, nm (log ε) 331 (4.97), 677 (5.18). IR $\nu_{\max}/\text{cm}^{-1}$: 3065 (C-H, aromatic), 2931–2866 (C-H, aliphatic), 1260 (C-O-C). Analysis of C₆₀H₈₀CoN₁₆O₄ (1148.32) (% calcd./found): C 62.76/62.70, H: 7.02/6.78, N: 19.52/19.55.

3.5. 2, 9(10), 16(17), 23(24)-Tetrakis-(2-{[2-(dimethylamino)ethyl](methyl amino) ethoxy} phthalocyaninato(chloro) - manganese (II) (7)

Compound **3** (0.1 g, 0.37 mmol), anhydrous MnCl_2 (0.013 g, 0.10 mmol), and 2-dimethylaminoethanol (0.5 mL) were irradiated in a microwave oven at 140 °C and 200 W for 3 min. After being cooled, the reaction mixture was evaporated to dryness. The product was dissolved in a solution of acetic acid (pH 5). The solution was extracted with acetone, ethyl acetate, dichloromethane, and chloroform. After the solution was neutralized with potassium carbonate, a greenish blue product precipitated. The solid was collected by filtration and washed with water until the washings were neutral. Yield: 0.018 g (17%). UV-Vis (DMSO): λ , nm (log ϵ) 366 (5.10), 498 (4.47), 734 (5.12). IR $\nu_{\text{max}}/\text{cm}^{-1}$: 3055 (C-H, aromatic), 2938–2876 (C-H, aliphatic), 1259 (C-O-C). Analysis of $\text{C}_{60}\text{H}_{80}\text{ClMnN}_{16}\text{O}_4$ (1179.77) (% calcd./found): C: 61.08/61.70, H: 6.83/6.78, N: 19.00/18.95.

3.6. 2, 9(10), 16(17), 23(24)-Tetrakis-(2-{[2-(trimethylamino)ethyl] (dimethyl)amino} ethoxy} phthalocyaninatozinc(II) octaiodide (8)

Compound **4** (0.206 g, 0.37 mmol), anhydrous $\text{Zn}(\text{CH}_3\text{COO})_2$ (0.018 g, 0.10 mmol), and 2-dimethylaminoethanol (0.5 mL) were irradiated in a quartz vessel of 10 mL capacity by a microwave oven at 140 °C and 200 W for 3 min. The resulting dark green solid was filtered off, washed several times with diethyl ether, and dried in vacuo. UV-Vis (DMSO): λ , nm (log ϵ) 299 (4.32), 684 (4.25). IR $\nu_{\text{max}}/\text{cm}^{-1}$: 3059 (C-H, aromatic), 2953–2860 (C-H, aliphatic), 1255 (C-O-C). ^1H NMR (500 MHz; CDCl_3): δ 2.21 (24H, s, CH_3), 3.17 (36H, s, CH_3), 3.26 (8H, br, $\text{CH}_2\text{-N}$), 3.41 (8H, br, $\text{CH}_2\text{-N}$), 3.82 (8H, br, $\text{CH}_2\text{-N}$), 5.23 (8H, br, $\text{CH}_2\text{-O}$), 7.46–8.04 (12H, m, Ar). Analysis of $\text{C}_{68}\text{H}_{104}\text{I}_8\text{N}_{16}\text{O}_4\text{Zn}$ (2290.30) (% calcd./found): C 35.66/ 35.70, H: 4.58/ 4.78, N: 9.78/ 9.95.

4. Conclusion

The synthesis and the characterization of Pcs with 4 amino-based substituents have been reported and these new complexes were characterized by elemental analysis, FT-IR, ^1H NMR spectroscopy, and electronic spectroscopy. The synthesized Pcs are highly soluble in common organic solvents such as THF, chloroform, and dichloromethane. The quaternized products are soluble in water. For this reason, these compounds deserve further research for their properties as photosensors.

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