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Unprecedented Phthalocyanines Bearing Eight Di-butylamino Peripheral Substituents: Synthesis, Spectroscopy, and Structure

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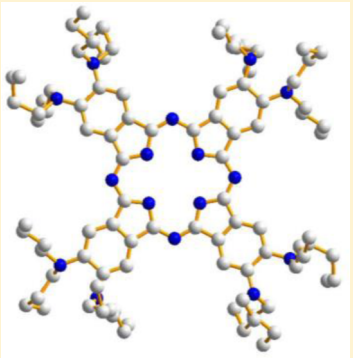
Supporting Information

ABSTRACT: Unprecedented 2,3,9,10,16,17,23,24-octakis(di-butylamino)phthalocyanine compounds M{Pc[N(C_4H_9)$_2$]$_8$} (M = 2H, Mg, Cu, Zn) (**1**−**4**) were prepared and structurally characterized on the basis of single-crystal X-ray diffraction analysis, representing the first structurally characterized alkylamino-substituted phthalocyanine examples. These novel phthalocyanine derivatives have also been characterized by a wide range of spectroscopic methods including MALDI-TOF mass spectra, NMR, electronic absorption, and IR spectroscopy in addition to elemental analysis. Their electrochemistry was also studied by cyclic voltammetry.

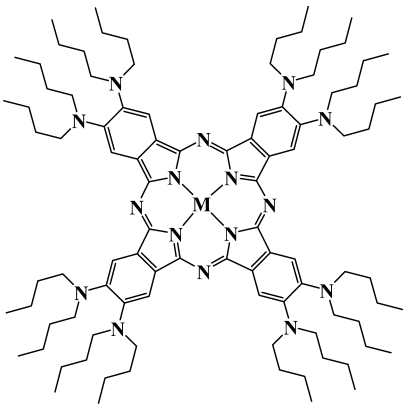


INTRODUCTION

Phthalocyanines have found a wide range of industrial applications ever since their first synthesis at the beginning of the last century.[1] Because of their unique spectroscopic and electrochemical properties together with extraordinary chemical and thermal stabilities, this series of tetraisoindole macrocyclic molecular materials have also attracted increasing research interests in organic semiconductors,[2] medicine,[3] optical storage,[4] memory devices,[5] and photocatalysis[6] in recent years. To enhance their application-related functionalities, various kinds of substituents including alkyl, alkoxyl, ether, and alkylthio groups have been introduced onto the peripheral and/or nonperipheral positions of phthalocyanine chromophores to tune their optical and electrochemical properties.[7] Because of the significant electron-donating properties, great efforts have been paid toward introducing the amino and/or alkylamino substituents onto the phthalocyanine peripheries. However, reliable reports with enough experimental supporting data, in particular, the mass and NMR spectroscopic information on the corresponding amino/alkylamino-substituted phthalocyanines, still remain extremely rare, limited to tetraaminometallophthylocyanines[8] and 2,3,9,10,16,17,23,24-octakis(amino)phthalocyaninato nickel complexes,[9] to the best of our knowledge. Nevertheless, structurally characterized amino-involved-substituted phthalocyanines on the basis of single-crystal X-ray diffraction analysis still remain unreported thus far.

In the present paper, we describe the synthesis, spectroscopic, and electrochemical properties of unprecedented 2,3,9,10,16,17,23,24-octakis(di-butylamino)phthalocyanine compounds M{Pc[N(C_4H_9)$_2$]$_8$} (M = 2H, Mg, Cu, Zn) (**1**−**4**) (Scheme 1). In particular, the molecular structures of **1** and **4** have been clearly revealed on the basis of single-crystal X-ray diffraction analysis, representing the first structurally characterized alkylamino-substituted phthalocyanine examples.

Scheme 1. Schematic Molecular Structures of Octakis(di-butylamino)phthalocyanine Compounds M{Pc[N(C_4H_9)$_2$]$_8$} (M = 2H, Mg, Cu, Zn) (1−4)



RESULTS AND DISCUSSION

Synthesis and Spectroscopic Characterization. The key precursor for the synthesis of octakis(di-butylamino)-phthalocyanine compounds, 1,2-dicyano-4,5-bis(di-butylamino)benzene, was prepared in three steps with *o*-phenylenediamine as starting material in an overall yield of 8.80%.[10,11] Cyclic tetramerization of 1,2-dicyano-4,5-bis(di-

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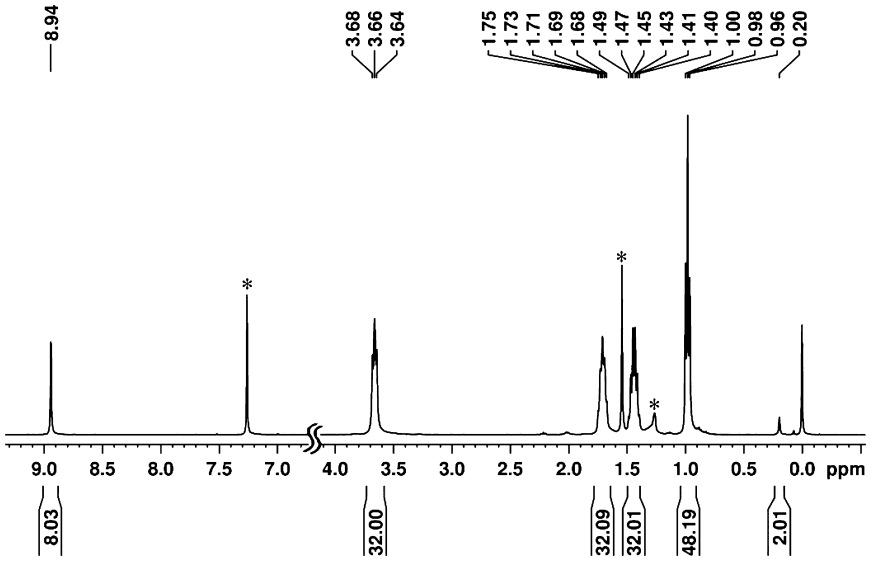

Figure 1. ^{1}H NMR spectrum of $H_2\{Pc[N(C_4H_9)_2]_8\}$ (**1**) recorded in $CDCl_3$ at 25 °C. The signals due to residual $CHCl_3$, H_2O, and petroleum ether are denoted as ∗.

Table 1. Electronic Absorption Data for the Compounds 1−4 in $CHCl_3$

compound	λ_{max}/nm (log ε)					
1	341 (4.94)		525 (4.64)		725 (5.08)	750 (5.17)
2	341 (5.00)	362 (4.95)	509 (4.48)	654 (4.62)		728 (5.39)
3	335 (5.13)		513 (4.58)	656 (4.60)		731 (5.36)
4	341 (5.00)		522 (4.56)	657 (4.59)		732 (5.37)

butylamino)benzene in refluxing *n*-pentanol in the presence of magnesium pentanoate led to the isolation of $Mg\{Pc[N(C_4H_9)_2]_8\}$ (**2**) in the yield of 34.8%. Further treatment of $Mg\{Pc[N(C_4H_9)_2]_8\}$ (**2**) yielded *in situ* with trifluoroacetate without the necessary isolation induced the isolation of the corresponding metal-free phthalocyanine $H_2\{Pc[N(C_4H_9)_2]_8\}$ (**1**) in the yield of 22.3%. Reaction of **1** with $M(OAc)_2{\cdot}H_2O$ (M = Cu, Zn) in refluxing DMAE afforded the corresponding phthalocyaninato metal complexes $M\{Pc[N(C_4H_9)_2]_8\}$ (M = Cu, Zn) (**3**, **4**) in the yields 65.7% and 87.5%, respectively. Alternatively, direct cyclic tetramerization of 1,2-dicyano-4,5-bis(di-butylamino)benzene in the presence of $M(OAc)_2{\cdot}H_2O$ (M = Cu, Zn) in refluxing DMAE also led to the isolation of **3** and **4** in the yields of 12.0% and 37.2%.

Satisfactory elemental analysis results were obtained for the whole series of four newly prepared phthalocyanine derivatives **1**−**4** after repeated column chromatography, followed by recrystallization. Their MALDI-TOF mass spectra clearly showed intense signals for the molecular ion $[M + H]^+$, which closely resemble the simulated ones given in Figure S1 (Supporting Information). These newly prepared phthalocyanine derivatives have also been characterized by other spectroscopic methods including NMR, electronic absorption, and IR spectroscopy.

Satisfactory ^{1}H NMR spectra were recorded for the phthalocyanine compounds **1**, **2**, and **4** containing a diamagnetic metal ion in $CDCl_3$ (Table S2, Supporting Information). This, however, is not true for the copper complex **3** due to the paramagnetic nature of the divalent copper ion. As shown in Figure 1, the α protons of the Pc ring in $H_2\{Pc[N(C_4H_9)_2]_8\}$ (**1**) resonate at δ 8.94 ppm as a singlet, while the methylene, methylene, methylene, and methyl protons of the peripheral *n*-butyl groups give four sets of triplet, multiplet, multiplet, and triplet signals at δ 3.66, 1.71, 1.44, and 0.98 ppm with the integral ratio of 2:2:2:3, respectively. This is also true for the metal complexes $M\{Pc[N(C_4H_9)_2]_8\}$ (M = Mg, Zn) (**2**, **4**) (Table S2, Supporting Information), except for the lack of signals due to the inner isoindole protons. Because of the p−π conjugation between the peripheral N atoms and the phthalocyanine chromophore, the ring current of $H_2\{Pc[N(C_4H_9)_2]_8\}$ (**1**) becomes smaller in comparison with that for other phthalocyanines substituted with alkyl or alkoxyl groups such as $H_2Pc(^tBu)_4$,[12] resulting in the appearance of the two inner isoindole protons' signal of the former compound at a relatively lower field of δ 0.20 ppm than that at δ −2.17 ppm for the latter species.

The electronic absorption spectra of **1**−**4** were recorded in $CHCl_3$, and the data are summarized in Table 1. As shown in Figure 2, $H_2\{Pc[N(C_4H_9)_2]_8\}$ (**1**) shows a typical non-aggregated molecular electronic absorption spectrum of metal-free phthalocyanines with the Soret band appearing at 341 nm and split Q bands at 725 and 750 nm. It is worth noting that the weak band at 525 nm is due to the n → π^* transitions arising from the nitrogen lone pair of electrons. Insertion of metal ion into the phthalocyanine central core induces an increase in the molecular symmetry from D_{2h} for $H_2\{Pc[N(C_4H_9)_2]_8\}$ (**1**) to D_{4h} for $M\{Pc[N(C_4H_9)_2]_8\}$ (M = Mg, Cu, Zn) (**2**−**4**), resulting in a unsplit Q band in the range of 728−732 nm for the latter three metal complexes (Figure S4, Supporting Information, and Table 1). This seems to represent the lowest energy of the Q band that has been revealed for the monomeric β-substituted phthalocyaninato metal complexes.[13]

Figure S5 (Supporting Information) displays the IR spectra of **1**−**4**. As can be seen, in addition to the absorption bands contributed from the central aromatic Pc macrocycle, including

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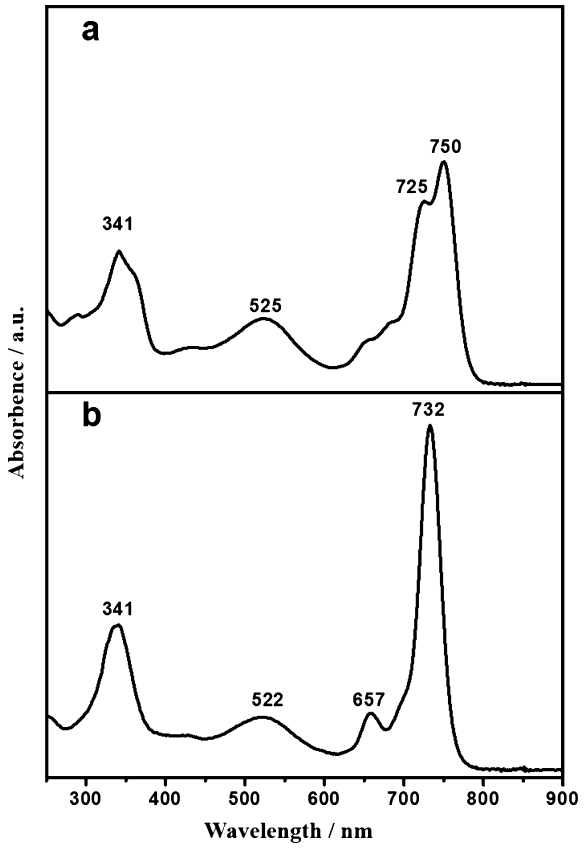

Figure 2. Electronic absorption spectra of $H_2\{Pc[N(C_4H_9)_2]_8\}$ (**1**) (a) and $Zn\{Pc[N(C_4H_9)_2]_8\}$ (**4**) (b) in $CHCl_3$.

the wagging and torsion vibrations of the C−H groups, isoindole ring stretching vibrations, and the C═N aza group stretching vibrations,[14] the absorptions observed at ca. 1103−1096 cm^{-1} are attributed to the C−N stretching vibrations of the $-N(n\text{-}C_4H_9)_2$ groups. The intense absorption bands observed at ca. 2955−2864 cm^{-1} in the IR spectra are the C−H stretching vibrations of the $-CH_2-$ and $-CH_3$ groups of the side chains. In the IR spectrum of **1**, a weak band at ca. 3298 cm^{-1} can be assigned to the N−H stretching vibrations of the isoindole moieties, which disappears in the IR spectra of the metal complexes $M\{Pc[N(C_4H_9)_2]_8\}$ (M = Mg, Cu, Zn) (**2**−**4**).

Structural Studies. Single crystals of $H_2\{Pc[N(C_4H_9)_2]_8\}$ (**1**) and $Zn\{Pc[N(C_4H_9)_2]_8\}$ (**4**) suitable for X-ray diffraction analysis were obtained by slow diffusion of methanol into the $CHCl_3$ and THF solution of the respective compound. Compound **1** crystallizes in the monoclinic system with the space group *C*2/*c* and the unit cell contains four metal-free phthalocyanines, whereas **4** crystallizes in the orthorhombic system with the space group *C*222(1) and the unit cell contains eight phthalocyaninato zinc molecules and eight THF molecules (Table S3, Supporting Information). Figure 3 shows the molecular structure of $H_2\{Pc[N(C_4H_9)_2]_8\}$ (**1**) in two different perspective views. As can be seen, the two *n*-butyl moieties of the di-butylamino groups attached onto the periphery of the Pc ring locate on the two sides of the Pc plane. In particular, the length of the C−N bond connecting the central Pc chromophore and the butylamino group ranges from 1.416 to 1.424 Å (Table S4, Supporting Information), just between the single C−N bond length (1.47 Å) and the double C═N bond length (1.29 Å),[15] indicating the p−π conjugation between the peripheral N atoms and the phthalocyanine chromophore. This is also true for $Zn\{Pc[N(C_4H_9)_2]_8\}$ (**4**) (Figure 4 and Table S5, Supporting Information). However, in the phthalocyaninato zinc complex, the central zinc(II) ion is five-coordinated by four isoindole N atoms and one tetrahydrofuran O atom. As a consequence, the phthalocyanine chromophore in $Zn\{Pc[N(C_4H_9)_2]_8\}$ (**4**) adopts a conformation that is slightly domed toward the zinc(II) ion with the distance of Zn from the N4 mean plane amounting to 0.313 Å.

In the single crystal of the metal-free phthalocyanine $H_2\{Pc[N(C_4H_9)_2]_8\}$ (**1**), the adjacent molecules of **1** are packed into a one-dimensional supramolecular structure with the neighboring phthalocyanine molecules connected in a perpendicular manner depending on the C−H···N hydrogen bonds formed between the two C−H(α) bonds of one phthalocyanine ring and the meso-N atom of the neighboring phthalocyanine molecules with the distances of 2.503 and 2.604 Å,[16] respectively (Figure S7, Supporting Information). This, as a basic building block, further packs into a three-dimensional structure depending on the intermolecular van der Waals interaction between the neighboring 1-D chains (Figure S8,

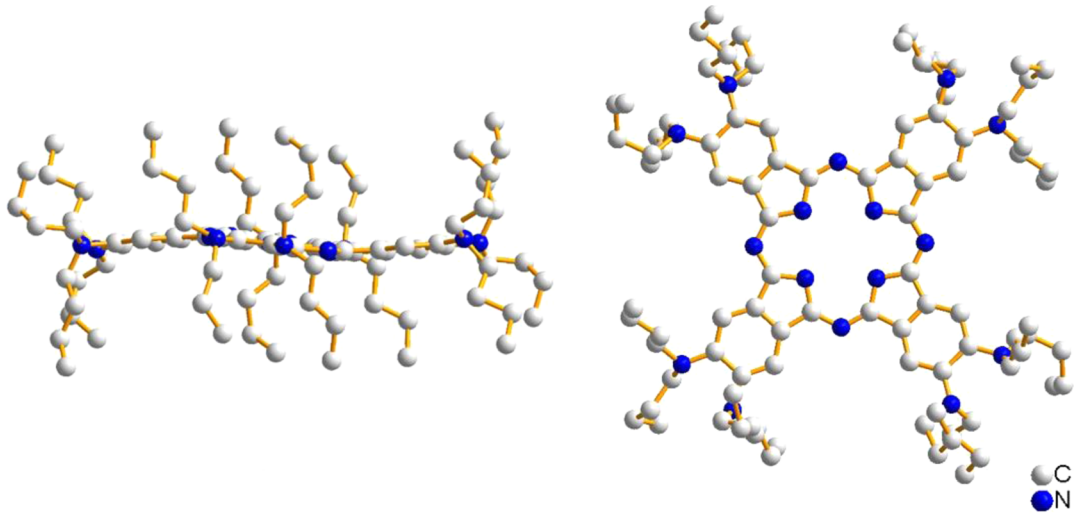

Figure 3. Structure diagrams of compound **1** in side (left) and top (right) views, respectively, with all H atoms omitted for clarity.

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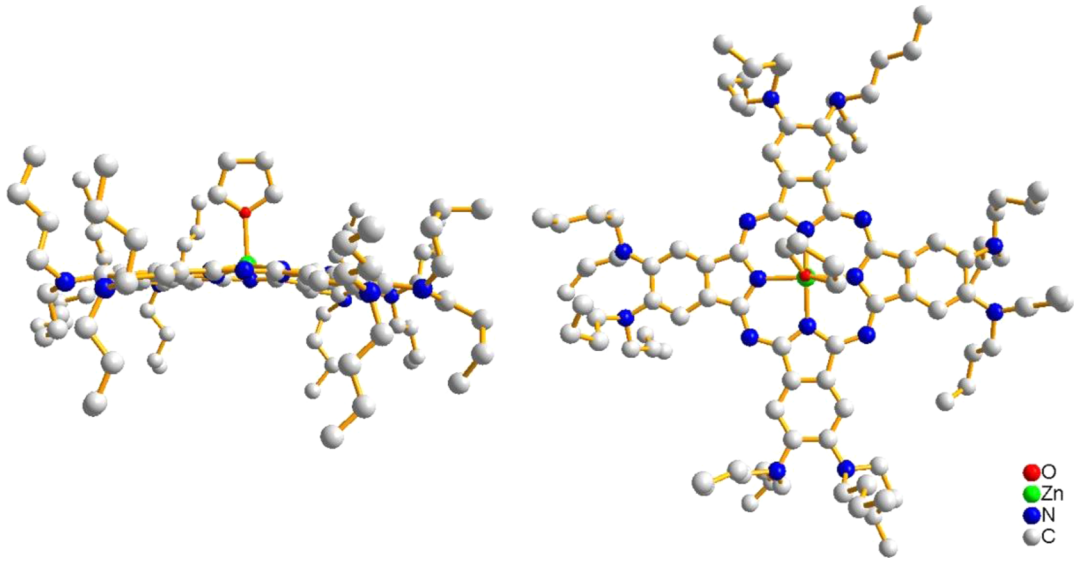

Figure 4. Structure diagrams of compound **4** in side (left) and top (right) views, respectively, with all H atoms omitted for clarity.

Supporting Information). This is also true for Zn{Pc[N-$(C_4H_9)_2]_8$} (**4**), except for the slightly increased C−H···N hydrogen bond distances of 2.662 and 2.780 Å, respectively, for the zinc complex (Figures S9 and S10, Supporting Information). Interestingly, because of the steric hindrance effect from the eight bulky di-butylamino groups attached at the peripheral position of the phthalocyanine ring, there seems to be lacking a direct face-to-face $\pi\cdots\pi$ stacking interaction between the neighboring phthalocyanine molecules in the single crystals of both **1** and **4**.

Electrochemical Properties. The electrochemical behavior of **1**−**4** was investigated by cyclic voltammetry (CV) in CH_2Cl_2/pyridine (v/v = 50:1) containing 0.1 mol·dm^{-3} $[NBu_4][ClO_4]$. The half-wave potentials are summarized in Table 2. The cyclic voltammogram of $H_2\{Pc[N(C_4H_9)_2]_8\}$ (**1**) is displayed in Figure 5 as a typical representative. As can be seen, $H_2\{Pc[N(C_4H_9)_2]_8\}$ (**1**) exhibited one quasi-reversible oxidation and up to two quasi-reversible one-electron reductions, all of which are due to the ligand-based redox processes. Obviously, introduction of eight di-butylamino groups with a strong electron-donating nature onto the peripheral positions of phthalocyanine chromophore of **1** induces significant shift in both the first oxidation and the first reduction potentials at +0.51 and −0.89 V, respectively, to the negative direction, relative to those of H_2Pc at +0.93 and −0.78 V, respectively[17] (Table 2). In addition, the potential difference between the first oxidation and the first reduction processes is lower than that of the unsubstituted metal-free phthalocyanine due to the p−π conjugation between the peripheral N atoms and the phthalocyanine chromophore, which expands the conjugated system of the whole molecule for **1**. As a result, the Q-band absorption for **1** also takes a significant red shift in comparison with that of the unsubstituted metal-free phthalocyanine.[13] This is also true for the remaining members **2**−**4** (Table 2).

Table 2. Electrochemical Data for the Compounds 1−4 in CH_2Cl_2/Pyridine (v/v = 50:1) Containing 0.1 M $[NBu_4][ClO_4]$ and the Unsubstituted Metal-Free Phthalocyanine in DMF Containing 0.1 M $[NBu_4][ClO_4]$

compound	Oxd_1	Red_1	Red_2	$\Delta E^0_{1/2}$[a]
H_2Pc[b]	+0.93	−0.78	−1.30	1.71
$H_2\{Pc[N(C_4H_9)_2]_8\}$ (**1**)	+0.51	−0.89	−1.27	1.40
$Mg\{Pc[N(C_4H_9)_2]_8\}$ (**2**)	+0.088	−1.36		1.45
$Cu\{Pc[N(C_4H_9)_2]_8\}$ (**3**)	+0.29	−1.16		1.45
$Zn\{Pc[N(C_4H_9)_2]_8\}$ (**4**)	+0.10	−1.26		1.36

[a] $\Delta E^0_{1/2}$ is the potential difference between the first oxidation and the first reduction processes, i.e., the HOMO−LUMO gap of the compounds: $\Delta E^0_{1/2} = Oxd_1 - Red_1$. [b] Cited from ref 17.

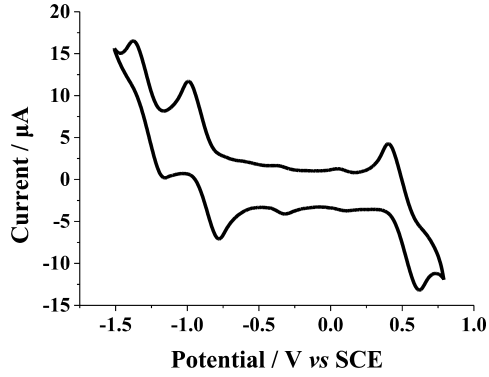

Figure 5. Cyclic voltammogram of $H_2\{Pc[N(C_4H_9)_2]_8\}$ (**1**) in CH_2Cl_2/pyridine (v/v = 50:1) containing 0.1 M $[NBu_4][ClO_4]$ at scan rates of 30 mV s^{-1}.

CONCLUSION

In summary, novel 2,3,9,10,16,17,23,24-octakis(di-butylamino)-phthalocyanine derivatives $M\{Pc[N(C_4H_9)_2]_8\}$ (M = 2H, Mg, Cu, Zn) (**1**−**4**) have been prepared and spectroscopically characterized, and the molecular structures of the metal-free and zinc compounds were revealed on the basis of the single-crystal X-ray diffraction, representing the first structurally characterized alkylamino-substituted phthalocyanine examples. Electrochemical and electronic absorption measurements reveal a significant decrease by 0.26−0.35 V for the HOMO−LUMO gap in comparison with the unsubstituted phthalocyanine due to the effective p−π conjugation between the peripheral N atoms and the phthalocyanine chromophore. This, in

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combination with their good solubility in common organic solvents, ensures their good application potentials in chemical sensors, photodynamic therapy, and light harvesting.

EXPERIMENTAL SECTION

General. *o*-Phenylenediamine was purchased from J&K Scientific Ltd. *n*-Pentanol and *N*,*N*-dimethylethanolamine (DMAE) were freshly distilled from Na. *N*,*N*-Dimethylformamide (DMF) and dichloromethane were freshly distilled from CaH_2. Column chromatography was carried out on silica gel (Merck, Kieselgel 60, 70−230 mesh) with the indicated eluents. The electrolyte $[NBu_4][ClO_4]$ was recrystallized twice from tetrahydrofuran. All other reagents and solvents were used as received.

Measurements. ^{1}H NMR spectra were recorded on a Bruker DPX 400 spectrometer in $CDCl_3$ or $CDCl_3/[D_5]$ pyridine (v/v = 150/1). Spectra were referenced internally using the residual solvent resonance (δ = 7.26 ppm for ^{1}H NMR) relative to $SiMe_4$. Electronic absorption spectra were recorded on a Hitachi U-2910 spectrophotometer. IR spectra were recorded as KBr pellets using a Bruker Tensor 37 spectrometer with 2 cm^{-1} resolution. MALDI-TOF mass spectra were taken on a Bruker BIFLEX III ultra-high-resolution Fourier transform ion cyclotron resonance (FT-ICR) mass spectrometer with α-cyano-4-hydroxycinnamic acid as the matrix. Elemental analyses were performed on an Elementar Vavio El III. Electrochemical measurements were carried out with a BAS CV-50W voltammetric analyzer. The cell comprised inlets for a glassy-carbon-disk working electrode with a diameter of 2.0 mm and a silver-ware counter electrode. The reference electrode was Ag^+/Ag (a solution of 0.01 M $AgNO_3$ and 0.1 M TBAP in acetonitrile), which was connected to the solution by a Luggin capillary whose tip was placed close to the working electrode. It was corrected for junction potentials by being referenced internally to the ferrocenium/ferrocene (Fc^+/Fc) couple [$E_{1/2}(Fc^+/Fc)$ = 0.501 V vs SCE]. Typically, a 0.1 M solution of $[NBu_4][ClO_4]$ in CH_2Cl_2 containing 1 mM of sample was purged with nitrogen for 10 min, and then the voltammograms were recorded at ambient temperature. The scan rate was 50 mV/s for the CV measurement. Crystal data for $H_2\{Pc[N(C_4H_9)_2]_8\}$ (**1**) and $Zn\{Pc[N(C_4H_9)_2]_8\}$ (**4**) were determined by X-ray diffraction analysis at 150 K using an Oxford Diffraction Gemini E system with Cu Kα radiation, λ = 1.5418 Å, and details of the structure refinement are given in Table S4 (Supporting Information). CCDC 1412942 and 1412943 containing the supplementary crystallographic data for this paper can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Synthesis of 1,2-Bis(di-butylamino)benzene. To the mixture of *o*-phenylenediamine (10.8 g, 0.100 mol) and K_2CO_3 (70.0 g, 0.507 mol) in DMF (200 mL) at 130 °C was added butyl iodide (92.2 g, 0.501 mol). The resulting system was heated at the same temperature for 24 h. After being cooled to room temperature, the reaction mixture was poured into water (200 mL) and extracted with petroleum ether, dried over Na_2SO_4, and filtered. After removing the solvent by evaporation under reduced pressure, the crude product was chromatographed on a silica gel column using petroleum ether as eluent, providing the target compound as colorless oil with the yield of 19.0 g, 57.2%. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 6.89 (s, 2 H), 6.88 (s, 2 H), 3.14 (t, J = 7.46 Hz, 8 H),1.40 (m, J = 7.40 Hz, 8 H),1.25 (m, J = 7.29 Hz, 8 H), 0.87 (t, J = 7.28 Hz, 12 H).

Synthesis of 1,2-Dibromo-4,5-bis(di-butylamino)benzene. 1,2-Bis(di-butylamino)benzene (16.2 g, 0.049 mol) was dissolved in a mixed solvent of CH_2Cl_2 (100 mL) and acetate (200 mL). After being cooled to 0 °C, 6.7 mL (0.13 mol) of Br_2 was added in a dropwise manner over a period of 1 h, and the mixture was then stirred for 7 h at the same temperature. The mixture was poured into a saturated $NaHSO_3$ solution and extracted with CH_2Cl_2. The extract was washed with water, dried over Na_2SO_4, and then evaporated. Chromatography with petroleum ether as eluent gave the target compound as a colorless oil with the yield of 16.7 g, 69.9%. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.01 (s, 2H), 3.11 (t, J = 7.44 Hz, 8 H),1.36 (m, J = 7.35 Hz, 8 H), 1.23 (m, J = 7.24 Hz, 8 H), 0.87 (t, J = 7.24 Hz, 12 H).

Synthesis of 1,2-Dicyano-4,5-bis(di-butylamino)benzene. A mixture of 1,2-dibromo-4,5-bis(di-butylamino)benzene (24.6 g, 0.0502 mol) and CuCN (11.2 g, 0.13 mol) in dry DMF (150 mL) was heated at reflux for 8 h under a slow stream of nitrogen. After being cooled to room temperature, the mixture was poured into an aqueous ammonia solution (25%−28%, 1 L) and stirred under blowing air for 24 h. After filtration, the water phase was extracted with petroleum ether and then dried by Na_2SO_4 and concentrated. The crude product was purified by column chromatography over silica gel with petroleum ether/CH_2Cl_2 (3:1) as eluent, giving the target compound as a light yellow oil with the yield of 4.23 g, 22.0%, which becomes yellow crystals at a temperature below 0 °C. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.07 (s, 2 H), 3.22 (t, J = 7.38 Hz, 8 H), 1.34 (m, J = 7.28 Hz, 8 H), 1.22 (m, J = 7.23 Hz, 8 H), 0.86 (t, J = 7.22 Hz, 12 H).

Synthesis of 2,3,9,10,16,17,23,24-Octakis(di-butylamino)-phthalocyaninato Magnesium (2). A mixture of magnesium turnings (24 mg, 1.0 mmol) and a small amount of iodine in anhydrous *n*-pentanol (4 mL) was refluxed for 1 h under a slow stream of nitrogen. Then, 1,2-dicyano-4,5-bis(di-butylamino)benzene (232 mg, 0.606 mmol) was added. The resulting mixture was refluxed for another 14 h. After being cooled, the solvent was evaporated. The crude product was chromatographed on a silica gel column with dichloromethane/methanol (100:1) as eluent. Repeated column chromatography, followed by recrystallization from dichloromethane and methanol, gave dark-green microcrystals with the yield of 82.0 mg, 34.8%. Elemental analysis (%) calcd. for $C_{96}H_{152}N_{16}Mg\cdot H_2O\cdot 1.5CH_3OH$: C 72.25, H 9.95, N 13.82; found: C 72.29, H 9.95, N 13.89. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.96 (s, 8 H), 3.65 (t, J = 7.38 Hz, 32 H), 1.70 (m, J = 7.29 Hz, 32 H), 1.42 (m, J = 7.32 Hz, 32 H), 0.96 (t, J = 7.32 Hz, 48 H). MS (MALDI-TOF) m/z: 1555.4 $[M + H]^+$, 1499.3 $[M - C_4H_8]^+$. UV−vis ($CHCl_3$) λ/nm ($M^{-1}\cdot cm^{-1}\cdot 10^{-5}$): 728 (2.44), 654 (0.419), 509 (0.303), 362 (0.895), 341 (1.01).

Synthesis of 2,3,9,10,16,17,23,24-Octakis(di-butylamino)-phthalocyanine $H_2\{Pc[N(C_4H_9)_2]_8\}$ (1). Compound **2** (99.5 mg, 0.0640 mmol) was dissolved in CF_3COOH (3 mL), and the mixture was stirred for 10 min. The reaction mixture was then poured into cold water and neutralized with ammonia solution. The precipitate collected was washed several times with CH_3OH and then applied on a silica gel column with dichloromethane/methanol 100:1 as eluent. Repeated chromatography, followed by recrystallization from dichloromethane and methanol, afforded the target compound as dark-green microcrystals with the yield of 63.0 mg, 64.2%. Elemental analysis (%) calcd. for $C_{96}H_{154}N_{16}\cdot 0.125CHCl_3\cdot 0.25CH_3OH$: C 74.42, H 10.05, N 14.41; found: C 74.38, H 9.90, N 14.50. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.94 (s, 8 H), 3.66 (t, J = 6.96 Hz, 32 H), 1.71 (m, J = 7.30 Hz, 32 H), 1.44 (m, J = 7.23 Hz, 32 H), 0.98 (t, J = 7.28 Hz, 48 H), 0.20 (s, 2 H). MS (MALDI-TOF) m/z: 1533.4 $[M + H]^+$, 1476.3 $[M - C_4H_8]^+$. UV−vis ($CHCl_3$) λ/nm ($M^{-1}\cdot cm^{-1}\cdot 10^{-5}$): 750 (1.47), 725 (1.21), 525 (0.435), 341 (0.880).

Synthesis of 2,3,9,10,16,17,23,24-Octakis(di-butylamino)-phthalocyaninato Copper $Cu\{Pc[N(C_4H_9)_2]_8\}$ (3) by Insertion of Metal Ion into $H_2\{Pc[N(C_4H_9)_2]_8\}$. The mixture of copper acetate (36.3 mg, 0.20 mmol) and **1** (61.5 mg, 0.0401 mmol) in anhydrous DMAE (3 mL) was heated to reflux for 12 h under nitrogen. After being cooled to room temperature, the mixture was evaporated to dryness under reduced pressure and the residue was chromatographed on a silica gel column using dichloromethane/methanol 100:1 as the eluent. Repeated chromatography, followed by recrystallization from dichloromethane and methanol, gave a dark-brown sample with the yield of 42.0 mg, 65.7%. Elemental analysis (%) calcd. for $C_{96}H_{152}N_{16}Cu\cdot 0.25H_2O\cdot 0.5CH_3OH$: C 71.79, H 9.64, N 13.88; found: C 71.79, H 9.59, N 13.78. MS (MALDI-TOF) m/z: 1594.4 $[M + H]^+$, 1537.3 $[M - C_4H_8]^+$. UV−vis ($CHCl_3$) λ/nm ($M^{-1}\cdot cm^{-1}\cdot 10^{-5}$): 731 (2.27), 656 (0.400), 513 (0.376), 355 (1.35).

Synthesis of 2,3,9,10,16,17,23,24-Octakis(di-butylamino)-phthalocyaninato Copper $Cu\{Pc[N(C_4H_9)_2]_8\}$ (3) by Direct Cyclic Tetramerization of 1,2-Dicyano-4,5-bis(di-butylamino)-benzene. The mixture of $Cu(OAc)_2\cdot H_2O$ (38 mg, 0.19 mmol) and

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1,2-dicyano-4,5-bis(di-butylamino)benzene (152 mg, 0.397 mmol) in DMAE (2 mL) was refluxed for 15 h under a slow stream of nitrogen. After being cooled, the solvent was evaporated. The crude product was chromatographed on a silica gel column with dichloromethane/methanol (100:1) as eluent. Repeated column chromatography, followed by recrystallization from dichloromethane and methanol, gave a dark-brown sample with the yield of 19.0 mg, 12.0%.

Synthesis of 2,3,9,10,16,17,23,24-Octakis(di-butylamino)-phthalocyaninato Zinc Zn{Pc[N(C_4H_9)$_2$]$_8$} (4) by Insertion of Metal Ion into H_2{Pc[N(C_4H_9)$_2$]$_8$}. By employing the above-described procedure used to prepare Cu{Pc[N(C_4H_9)$_2$]$_8$} (**3**) with $Zn(OAc)_2{\cdot}2H_2O$ (36.7 mg, 0.20 mmol) instead of $Cu(OAc)_2{\cdot}H_2O$ as starting material, pure Zn{Pc[N(C_4H_9)$_2$]$_8$} (**4**) was isolated as dark-green microcrystals with the yield of 56.0 mg, 87.5%. Elemental analysis (%) calcd. for $C_{96}H_{152}N_{16}Zn{\cdot}0.5H_2O{\cdot}0.5CH_3OH$: C 71.51, H 9.64, N 13.83; found: C 71.52, H 9.87, N 13.95. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.96 (s, 8 H), 3.67 (t, J = 7.38 Hz, 32 H), 1.71 (m, J = 7.34 Hz, 32 H), 1.44 (m, J = 7.31 Hz, 32 H), 0.98 (t, J = 7.32 Hz, 48 H). MS (MALDI-TOF) m/z: 1596.6 $[M + H]^+$, 1539.6 $[M - C_4H_8]^+$. UV−vis ($CHCl_3$) λ/nm ($M^{-1}{\cdot}cm^{-1}{\cdot}10^{-5}$): 732 (2.37), 657 (0.393), 522 (0.366), 341 (1.00).

Synthesis of 2,3,9,10,16,17,23,24-Octakis(di-butylamino)-phthalocyaninato Zinc Zn{Pc[N(C_4H_9)$_2$]$_8$} (4) by Direct Cyclic Tetramerization of 1,2-Dicyano-4,5-bis(di-butylamino)-benzene. By using the procedure described above with $Zn(OAc)_2{\cdot}2H_2O$ (95 mg, 0.433 mmol) instead of $Cu(OAc)_2{\cdot}H_2O$ as starting material, pure Zn{Pc[N(C_4H_9)$_2$]$_8$} (**4**) was isolated as dark-green microcrystals with the yield of 59.0 mg, 37.2%.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorgchem.5b01734.

Synthesis of **1**−**4**. Experimental and simulated isotopic patterns for **1**−**4**. ^{1}H NMR spectrum of **2** and **4**. Electronic absorption spectra and IR spectra of **1**−**4**. Cyclic voltammograms of **1**−**4**. The two adjacent molecules and 1-D supramolecular structure of **1** and **4**, respectively. The three-dimensional structures of **1** and **4**. Analytical and mass spectrometric data for **1**−**4**. ^{1}H NMR data (δ) for **1**, **2**, and **4**. Crystal data and structure refinements for **1** and **4**. Selected bond lengths of **1**. Selected bond lengths of **4** (PDF)

Crystallographic data for **1** (CIF)

Crystallographic data for **4** (CIF)

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Notes

The authors declare no competing financial interest.

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