Inorganic Chemistry
Article
pubs.acs.org/IC

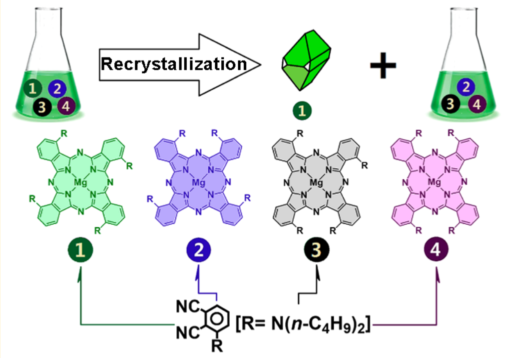
Nonperipheral Tetrakis(dibutylamino)phthalocyanines. New Types of 1,8,15,22-Tetrakis(substituted)phthalocyanine Isomers

Yuxiang Chen,[†] Wenjuan Fang,[‡] Kang Wang,*[,†] Wei Liu,[‡] and Jianzhuang Jiang*[,†]

[†]Beijing Key Laboratory for Science and Application of Functional Molecular and Crystalline Materials, Department of Chemistry, University of Science and Technology Beijing, Beijing 100083, People's Republic of China

[‡]State Key Laboratory of Crystal Materials, Shandong University, Jinan 250012, People's Republic of China

Ⓢ *Supporting Information*



ABSTRACT: Cyclic tetramerization of 3-(dibutylamino)phthalonitrile in refluxing *n*-pentanol in the presence of magnesium pentanoate afforded the four regioisomer-containing nonperipheral 1,8-/11,15-/18,22-/25-tetrakis(dibutylamino)phthalocyaninato magnesium complexes with the 1,8,15,22-tetrakis(dibutylamino)phthalocyanine isomer $\mathrm{Mg\{Pc[\alpha\text{-}N(C_4H_9)_2]_4\text{-}C_4\}}$ (**2**). This, in combination with its much superior crystallinity over the remaining three isomers, renders the easy isolation of **2** only through two simple recrystallizations from THF and methanol. Treatment of **2** with trifluoroacetic acid induced the isolation of metal-free 1,8,15,22-tetrakis(dibutylamino)phthalocyanine, $\mathrm{H_2\{Pc[\alpha\text{-}N(C_4H_9)_2]_4\text{-}C_4\}}$ (**1**), which further reacted with $\mathrm{M(OAc)_2{\cdot}}n\mathrm{H_2O}$ (M = Ni, Zn) in refluxing *n*-pentanol, giving the 1,8,15,22-tetrakis(dibutylamino)phthalocyaninato metal complexes $\mathrm{M\{Pc[\alpha\text{-}N(C_4H_9)_2]_4\text{-}C_4\}}$ (M = Ni (**3**), Zn (**4**)). The full series of four 1,8,15,22-tetrakis(dibutylamino)phthalocyanine isomeric compounds have been characterized by a series of spectroscopic methods and single-crystal X-ray diffraction analyses. Obviously, the present result provides a simple and effective pathway for the synthesis and isolation of novel 1,8,15,22-tetrakis(dibutylamino)phthalocyanine isomeric derivatives, providing one step forward toward completing bis(alkyl)amino-incorporated phthalocyanine species.

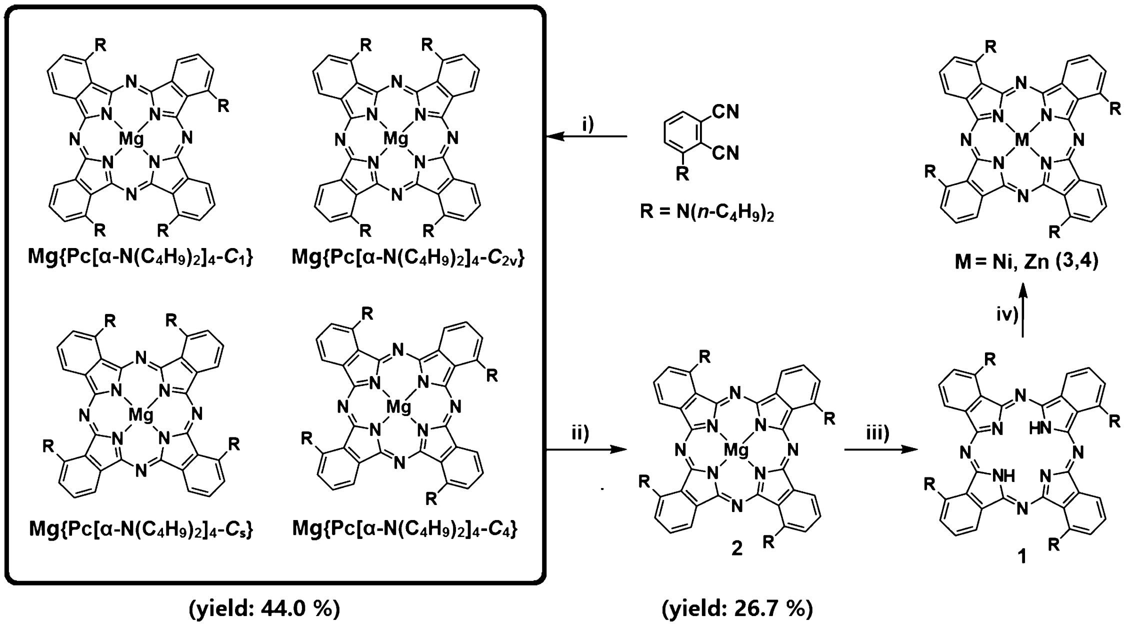
■ INTRODUCTION

Due to the different disturbing effects on the electronic and even molecular structure of the central conjugated chromophore, introduction of even the same number of functional groups onto the peripheral positions of phthalocyanine has been revealed to lead to optical, electrochemical, and functional properties of the resulting phthalocyanine derivatives different from those with nonperipherally substituted analogues.[1] This has aroused a long-term effort in trying to isolate the four regioisomers of both 2,9-/10,16-/17,23-/24- and 1,8-/11,15-/18,22-/25-tetrakis(substituted)phthalocyanine compounds for the purpose of unraveling the structure−property relationship and in particular detailing the positional effect of the substituents on the phthalocyanines.[2] In 1988, Leznoff et al. claimed the formation and isolation of pure 2,9,16,23-tetrakis(neopentyloxy)phthalocyanine isomer, with a fraction of the ^{1}H NMR spectrum as the sole evidence, from the cyclic tetramerization of methylthioisoindolenine at the low temperature of −20 °C in the presence of zinc acetate.[3] By means of a similar method through lowering of the reaction temperature, 1,8,15,22-tetrakis(*p*-*n*-butylbenzyloxy)phthalocyanine was also formed and isolated as the sole isomeric product according to the same group.[4] This was followed by the isolation of 2,9,16,23-tetrakis(*p*-*n*-butylbenzyloxy)phthalocyanine isomer from the four regioisomer-containing products resulting from the cyclic tetramerization of 4-(*p*-*n*-butylbenzyloxy)phthalonitrile, using silica gel column chromatography. Interestingly, the combination of employing the bulky 3-pentoxy substituent and controlling the reaction temperature to below 120 °C in *n*-pentanol rendered the successful isolation of 1,8,15,22-tetrakis(3′-pentoxy)phthalocyanine as the main isomer also from the four-regioisomer-containing product afforded from the cyclic tetramerization of 3-(3′-pentoxy)phthalonitrile precursor, using silica gel column chromatography according to Kasuga and co-workers.[5] This actually represents the sole well-studied 1,8,15,22-tetrakis(substituted)phthalocyanine species. As expected, HPLC is also able to isolate the tetrakis(substituted)phthalocyanine regioisomers, affording all four isomers of 2,9,16,23-tetrakis(2-ethylhexyloxyl)phthalocyaninato nickel complex and two of the four isomers of 2,9,16,23-tetrakis(*tert*-butyl)phthalocyaninato nickel complex.[6] Obviously, for the purpose of developing new molecular advanced materials, a more reliable, simple, and effective method toward the preparation and isolation of new types of tetrakis(substituted)phthalocyanine isomeric derivatives is highly desired in this field.

Received: June 8, 2016

DOI: 10.1021/acs.inorgchem.6b01371
Inorg. Chem. XXXX, XXX, XXX−XXX

Scheme 1. Synthesis and Schematic Molecular Structures of Nonperipheral 1,8,15,22-Tetrakis(dibutylamino)phthalocyanine Compounds M{Pc[α-N(C_4H_9)$_2$]$_4$-C_4} (1–4; M = 2H, Mg, Ni, Zn)[a]



[a]Legend: (i) Mg, I_2, n-$C_5H_{11}OH$, reflux; (ii) recrystallization in THF and methanol (two times); (iii) CF_3COOH, room temperature; (iv) M(OAc)$_2$·nH$_2$O, DBU, n-$C_5H_{11}OH$, reflux.

In the present paper, we describe the first synthesis and in particular easy isolation of new types of nonperipheral 1,8,15,22-tetrakis(substituted)phthalocyanine isomers, i.e. 1,8,15,22-tetrakis(dibutylamino)phthalocyanines M{Pc[α-N(C_4H_9)$_2$]$_4$-C_4} (**1**–**4**; M = 2H, Mg, Ni, Zn), also as part of our continuous effort toward completing bis(alkyl)amino-incorporated phthalocyanine species.[7,8] In addition, it is worth noting that, due to the special molecular symmetry associated with the special substituent arrangement, nonperipheral 1,8,15,22-tetrakis(substituted)phthalocyanine has been an effective building block in constructing chiral molecular systems.[9] As a consequence, 1,8,15,22-tetrakis(dibutylamino)-phthalocyanines developed in the present work provide new building blocks for the design and synthesis of novel chiral phthalocyanine systems with both fundamental importance and application potentials.

■ RESULTS AND DISCUSSION

Synthesis and Spectroscopic Characterization. 3-(Dibutylamino)phthalonitrile was prepared in three steps with 3-nitrophthalonitrile as the starting material in an overall yield of 18.6%.[7,10] It is worth noting that 3-(dibutylamino)-phthalonitrile could be synthesized directly from 3-nitrophthalonitrile in one step. However, the significantly decreased yield relative to that employing the method as detailed in the Experimental Section led us not to choose the direct one-step method. As expected, cyclic tetramerization of 3-(dibutylamino)phthalonitrile in refluxing n-pentanol in the presence of magnesium pentanoate afforded the nonperipheral 1,8-/11,15-/18,22-/25-tetrakis(dibutylamino)phthalocyaninato magnesium complex as a mixture of four regioisomers in a yield of 44.0% (Scheme 1). However, unexpectedly, only two simple recrystallizations of the four-regioisomer-containing product from THF and methanol rendered the successful isolation of the pure 1,8,15,22-tetrakis(dibutylamino)phthalocyaninato magnesium isomer Mg{Pc[α-N(C_4H_9)$_2$]$_4$-C_4} (**2**) as dark green microcrystals in a yield of 26.7% in terms of the initial starting material, 3-(dibutylamino)phthalonitrile, revealing the main product nature of **2** due to the bulky dibutylamino substituent effect during the cyclic tetramerization procedure of the precursor and much superior crystallinity of this isomer over the remaining three. Treatment of Mg{Pc[α-N(C_4H_9)$_2$]$_4$-C_4} (**2**) with trifluoroacetic acid then induced the isolation of metal-free 1,8,15,22-tetrakis(dibutylamino)phthalocyanine, H_2{Pc[α-N(C_4H_9)$_2$]$_4$-C_4} (**1**), in a yield of 66.9%. This metal-free phthalocyanine further reacted with M(OAc)$_2$·nH$_2$O (M = Ni, Zn) in refluxing n-pentanol in the presence of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU), inducing the formation and isolation of the corresponding 1,8,15,22-tetrakis(dibutylamino)phthalocyaninato metal complexes M{Pc[N(C_4H_9)$_2$]$_4$} (M = Ni (**3**), Zn (**4**)) in yields of 74.5 and 67.8%, respectively. Obviously, the present work provided a simple and effective pathway toward the preparation and isolation of pure nonperipheral 1,8,15,22-tetrakis(substituted)-phthalocyanine isomeric compounds with quite good yield that were hard to obtain previously by means of lengthy and time-consuming separation procedures.[3−6] At this point, it is worth noting that trials toward increasing the yield of the target isomer Mg{Pc[α-N(C_4H_9)$_2$]$_4$-C_4} (**2**) through lowering the reaction temperature completely failed, due probably to the decreased reaction activity of 3-(dibutylamino)phthalonitrile along with a decrease in reaction temperature, which actually led to the isolation of a decreased yield of the four-regioisomer-containing sample and also the isomer Mg{Pc[α-N(C_4H_9)$_2$]$_4$-C_4} (**2**).

Satisfactory elemental analysis results were obtained for all of the newly prepared phthalocyanine derivatives **1**–**4**. Their MALDI-TOF mass spectra clearly showed intense signals for the molecular ion $[M + H]^+$, which closely resemble the simulated signals given in Figure S1 in the Supporting Information. These newly prepared 1,8,15,22-tetrakis-

DOI: 10.1021/acs.inorgchem.6b01371

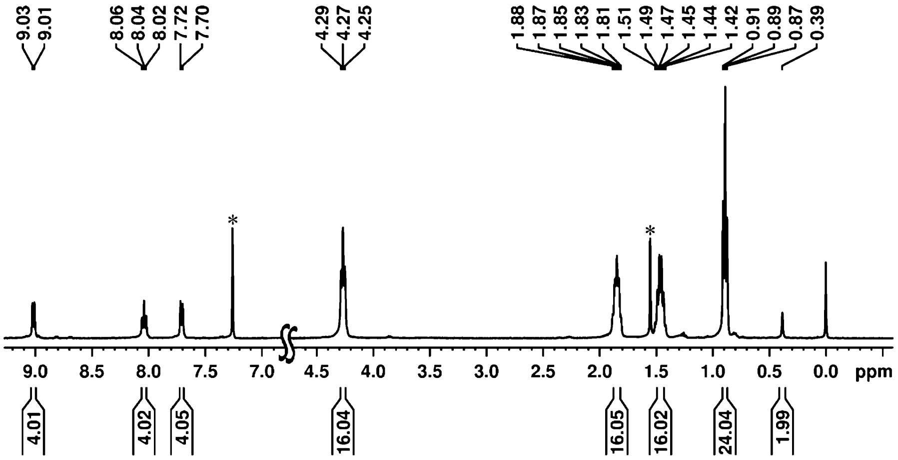


Figure 1. ^{1}H NMR spectrum of $H_2\{Pc[\alpha\text{-}N(C_4H_9)_2]_4\text{-}C_4\}$ (**1**) recorded in $CDCl_3$ at 25 °C. The signals due to residue $CHCl_3$ and H_2O are denoted with asterisks.

(dibutylamino)phthalocyanine isomers have also been characterized by other spectroscopic methods including NMR and electronic absorption spectroscopy.

Satisfactory ^{1}H NMR spectra were recorded for **1** and **3** in $CDCl_3$. However, reasonably good spectra for **2** and **4** in $CDCl_3$ could be recorded only in the presence of ca. 1% (v/v) hydrazine hydrate, which was used to reduce a small (or even trace) fraction of paramagnetic oxidized species to the neutral species (Figures S2–S4 and Table S2 in the Supporting Information). As shown in Figure 1, the aromatic protons due to the four α protons and eight β protons of the Pc ring in $H_2\{Pc[\alpha\text{-}N(C_4H_9)_2]_4\text{-}C_4\}$ (**1**) give three sets of doublet, triplet, and doublet signals at δ 9.02, 8.04, and 7.71 ppm, respectively, with an integral ratio of 1:1:1. However, 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 4.27, 1.85, 1.46, and 0.89 ppm, respectively, with an integral ratio of 2:2:2:3. This is also true for the metal complexes $M\{Pc[\alpha\text{-}N(C_4H_9)_2]_4\text{-}C_4\}$ (M = Mg (**2**), Ni (**3**), Zn (**4**)) (Table S2), except for the lack of a signal due to the inner isoindole protons. Due to the phthalocyanine ring current effect, the two inner isoindole protons in metal-free phthalocyanine **1** appear at δ 0.39 ppm.

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

compound	λ_{max}/nm (log ε)			
1	340 (4.79)	514 (3.88)	690 (4.54)	770 (5.07)
2	347 (4.77)	488 (3.82)	672 (4.51)	745 (5.11)
3	331 (4.66)	498 (3.82)	670 (4.45)	745 (5.02)
4	343 (4.74)	489 (3.81)	674 (4.48)	746 (5.07)

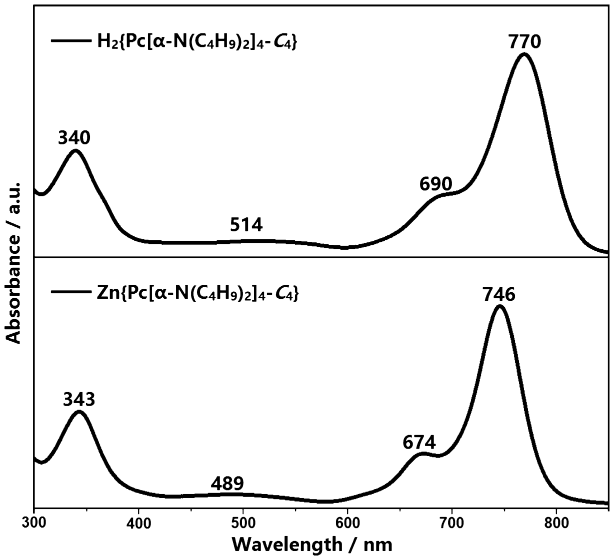


Figure 2. Electronic absorption spectra of $H_2\{Pc[\alpha\text{-}N(C_4H_9)_2]_4\text{-}C_4\}$ (**1**) and $Zn\{Pc[\alpha\text{-}N(C_4H_9)_2]_4\text{-}C_4\}$ (**4**) in $CHCl_3$.

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, $H_2\{Pc[\alpha\text{-}N(C_4H_9)_2]_4\text{-}C_4\}$ (**1**) shows a Soret band at 340 nm and a broad Q-band at 770 nm. Similarly to the peripherally substituted analogue $H_2\{Pc[\beta\text{-}N(C_4H_9)_2]_4\}$,[7] the Q-band for **1** does become split because of the p−π conjugation between the nonperipheral nitrogen atoms and the central phthalocyanine chromophore, which expands the conjugated system of the molecule of **1**. It is worth noting that the weak band at 514 nm is due to the n → π^* transitions arising from the nitrogen lone pair of electrons. Insertion of the metal ion into the phthalocyanine central core induces an increase in the molecular symmetry from D_{2h} for **1** to D_{4h} for $M\{Pc[\alpha\text{-}N(C_4H_9)_2]_4\text{-}C_4\}$ (M = Mg (**2**), Ni (**3**), Zn (**4**)), resulting in a significantly narrowed Q band in the range of 745−746 nm for the three metal complexes **2**−**4** (Figure 2, Figure S5 in the Supporting Information, and Table 1). In line with our previous result for both the 2,3,9,10,16,17,23,24-octakis(dibutylamino)phthalocyanine and 2,9(10),16(17),23(24)-tetrakis(dibutylamino)phthalocyanine analogues,[7] the Q band of $M\{Pc[\alpha\text{-}N(C_4H_9)_2]_4\text{-}C_4\}$ (M = 2H (**1**), Mg (**2**), Ni (**3**), Zn (**4**)) also has an obvious red shift in comparison with those of other 1,8,15,22-tetrakis(substituted)-phthalocyanine counterparts containing either alkoxy or alkylthio groups[1e] due to the stronger electron-donating nature of the dibutylamino groups in combination with the effective p−π conjugation between the N atom and the central phthalocyanine chromophore. It is, however, noteworthy that the absorption in the region of 400−600 nm due to the n → π^* transitions for $M\{Pc[\alpha\text{-}N(C_4H_9)_2]_4\text{-}C_4\}$ (M = 2H, Mg, Ni, Zn) is much weaker than that for $M\{Pc[\beta\text{-}N(C_4H_9)_2]_4\}$ (M = 2H, Mg, Ni, Zn), as revealed by the significantly smaller absorption

DOI: 10.1021/acs.inorgchem.6b01371
Inorg. Chem. XXXX, XXX, XXX−XXX

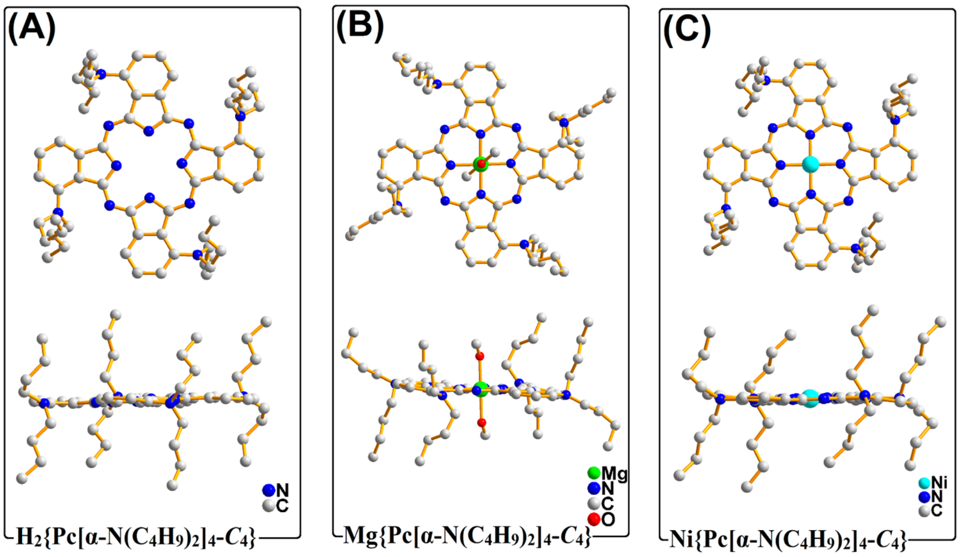


Figure 3. Molecular structures of (A) **1**, (B) **2**, and (C) **3** in top (top) and side (bottom) views with all H atoms and solvent molecules omitted for clarity.

coefficients of **1**−**4** in this range in comparison to those for their β-tetrakis(substituted) analogues by roughly one-fourth, due to the much stronger interaction between the dibutylamino group and phthalocyanine chromophore in the latter species.[7] The fluorescence emission spectra of **1**, **2**, and **4** were recorded in CH_2Cl_2. As shown in Figure S16 in the Supporting Information and summarized in Table S4 in the Supporting Information, the three compounds in CH_2Cl_2 solution display single emission peaks appearing at 772, 746, and 752 nm, respectively. However, their fluorescence quantum yields are very low ($\Phi_F < 0.01$) (Table S4), due to the increased nonradiative decay rate associated with the p−π conjugation between the N atom and the central phthalocyanine chromophore.

Structural Studies. Single crystals of the whole series of four newly isolated 1,8,15,22-tetrakis(dibutylamino)-phthalocyanine isomeric species M{Pc[α-N(C_4H_9)$_2$]$_4$-C_4} (**1**−**4**) suitable for X-ray diffraction analysis were obtained by slow diffusion of methanol into CH_2Cl_2 and THF solution mixtures of the respective compounds. Interestingly, all four compounds crystallize in the same monoclinic system with space group, $P2_1/c$ (Table S3 in the Supproting Information), and the unit cell of each compound contains two phthalocyanine molecules despite the different central metal ions. However, in the unit cells of **2** and **4**, in addition to two solvated methanol molecules, either Mg or Zn is actually hexacoordinated due to the two axially coordinated methanol molecules (Figure 3B), with an Mg−O bond length of 2.203 Å and Zn−O bond length of 2.390 Å, respectively. This is in contrast to the tetracoordinated Ni ion in the counterpart **3** (Figure 3C). Figure 3A shows the molecular structure of H_2\{Pc[α-N(C_4H_9)$_2$]$_4$-C_4\} (**1**). As can be seen, the two *n*-butyl moieties of the dibutylamino groups attached onto the nonperiphery of the Pc ring locate on the two sides of the Pc plane. In addition, the length of the C−N bond connecting the central Pc chromophore and the dibutylamino groups amounts to 1.387/1.395 Å, indicating the p−π conjugation between the nonperipheral N atoms and the phthalocyanine chromophore.[7] This is surely also true for the remaining three members **2**−**4** in this series (Table 2).

Table 2. Length of the C−N Bond Connecting the Central Pc Chromophore and the Dibutylamino Groups for 1−4

compound	bond length/Å	
H_2\{*Pc*[α-N(C_4H_9)$_2$]$_4$-C_4\} (**1**)	1.387	1.395
Mg\{*Pc*[α-N(C_4H_9)$_2$]$_4$-C_4\} (**2**)	1.391	1.413
Ni\{*Pc*[α-N(C_4H_9)$_2$]$_4$-C_4\} (**3**)	1.386	1.394
Zn\{*Pc*[α-N(C_4H_9)$_2$]$_4$-C_4\} (**4**)	1.387	1.422

The crystal packing diagrams of the complexes **1**−**4** are shown in Figures S7−S14 in the Supporting Information). As shown in Figures S7 and S11, adjacent molecules of **1** are packed into a one-dimensional supramolecular structure with the neighboring phthalocyanine molecules being connected in a staircase manner depending on the C−H···π interaction between the C−H bonds of dibutylamino groups and the π system of the neighboring phthalocyanine chromophore, leading to a relatively large distance between the neighboring metal-free phthalocyanine rings, 7.717 Å. However, in the single crystal of **2**, the solvated methanol molecules connect neighboring phthalocyaninato magnesium molecules into a face-to-face stacking supramolecular structure depending on the O−H···N (between the O−H bonds of one solvated methanol molecule and the N atom of the dibutylamino group of the neighboring phthalocyanine molecule) and O−H···O (between the O−H bonds of one coordinated methanol molecule and the O atom of the solvated methanol molecule) hydrogen bonds with distances of 2.251 and 2.022 Å, respectively, leading to a relatively shorter distance between the neighboring phthalocyaninato magnesium rings, 7.050 Å (Figures S8 and S12). This is also true for Zn\{Pc[α-N(C_4H_9)$_2$]$_4$-C_4\} (**4**) (Figures S10 and S14). However, adjacent molecules of **3** are packed into a one-dimensional supramolecular structure depending on the C−H···π interaction between the C−H bonds of dibutylamino groups and the π system of the neighboring phthalocyanine chromophore (Figures S9 and S13).

Electrochemical Properties. The electrochemical behavior of **1**−**4** was investigated by cyclic voltammetry (CV) in CH_2Cl_2 containing 0.1 mol dm^{-3} [NBu_4][ClO_4], (Figure S6 in the Supporting Information). The half-wave potentials are summarized in Table 3. The cyclic voltammogram of $H_2\{Pc[\alpha\text{-}N(C_4H_9)_2]_4\text{-}C_4\}$ (**1**) is displayed in Figure 4 as a typical representative. As can be seen, $H_2\{Pc[\alpha\text{-}N(C_4H_9)_2]_4\text{-}C_4\}$ (**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 four dibutylamino groups onto the nonperipheral positions of the phthalocyanine chromophore of **1** induces significant shifts in both the first oxidation and the first reduction potentials to the negative direction, relative to those of H_2Pc, revealing the strong electron-donating nature of the dibutylamino groups and the p−π conjugation between the nonperipheral nitrogen atoms and the central phthalocyanine chromophore.[7] This is also true for the remaining members **2**−**4**.

Table 3. Electrochemical Data (V) for 1−4

compound	Oxd_1	Red_1	Red_2	$\Delta E°_{1/2}$[a]
$H_2\{Pc[\alpha\text{-}N(C_4H_9)_2]_4\text{-}C_4\}$ (**1**)	+0.52	−0.83	−1.23	1.35
$Mg\{Pc[\alpha\text{-}N(C_4H_9)_2]_4\text{-}C_4\}$ (**2**)	+0.24	−1.13		1.37
$Ni\{Pc[\alpha\text{-}N(C_4H_9)_2]_4\text{-}C_4\}$ (**3**)	+0.51	−0.94	−1.43	1.45
$Zn\{Pc[\alpha\text{-}N(C_4H_9)_2]_4\text{-}C_4\}$ (**4**)	+0.36	−0.95		1.31

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

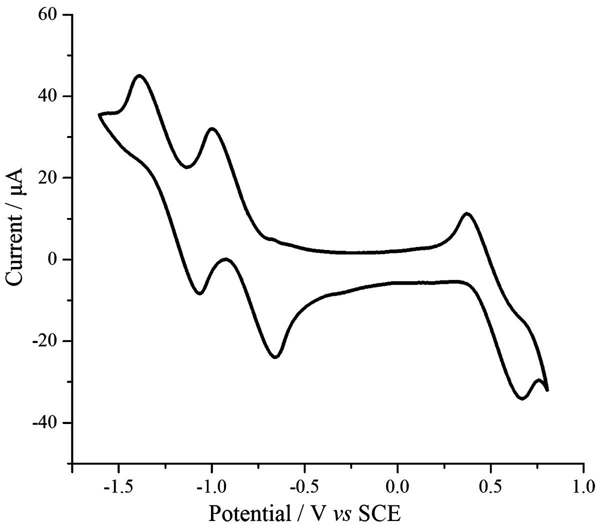


Figure 4. Cyclic voltammogram of $H_2\{Pc[\alpha\text{-}N(C_4H_9)_2]_4\text{-}C_4\}$ (**1**) in CH_2Cl_2 containing 0.1 M $[NBu_4][ClO_4]$ at scan rates of 30 mV/s.

Singlet Oxygen Quantum Yield. For the purpose of revealing the application potential of this new series of 1,8,15,22-tetrakis(dibutylamino)phthalocyanine isomers for photodynamic therapy (PDT), the singlet oxygen quantum yields of **1**, **2**, and **4** (Φ_Δ) were measured by steady-state methods using 3-diphenylisobenzofuran (DPBF) as the scavenger.[11] The solutions of **1**, **2**, and **4** (2 μM) and DPBF (40 μM) dissolved in DMF were respectively irradiated with red light (λ >610 nm, fluence rate 0.2 mW/cm^2) and the concentrations of DPBF monitored by absorption spectroscopy at 415 nm during the irradiation, resulting in singlet oxygen quantum yields of 0.021, 0.25, and 0.67 with the unsubstituted ZnPc in DMF as reference, $\Phi_\Delta = 0.56$[12] (Figure S15 in the Supporting Information). Obviously, $Zn\{Pc[\alpha\text{-}N(C_4H_9)_2]_4\text{-}C_4\}$ (**4**) presents the best result among this series of compounds in terms of the singlet oxygen quantum yield, since phthalocyaninato zinc compounds usually possesses high triplet yield and can in turn generate highly singlet oxygen because of the d^{10} configuration of the Zn(II) ion;[13] however this value is still slightly lower in comparison with those for other nonperipherally substituted phthalocyaninato zinc(II) counterparts reported thus far, such as 1,4,15,18-tetrakis(3-thienyl)-8,11,22,25-tetrakis(decyl)phthalocyaninato zinc(II)[14a] (Φ_Δ = 0.92), 1,8-/11,15-/18,22-/25-tetrakis(propoxy)-phthalocyaninato zinc(II)[14b] (Φ_Δ = 0.88), and 1,4-bis(glucosylated)phthalocyaninato zinc(II)[14c] (Φ_Δ = 0.86).

■ CONCLUSION

In summary, a simple and effective pathway has been developed for the synthesis, isolation, and spectroscopic and structural characterization of novel nonperipheral 1,8,15,22-tetrakis(dibutylamino)phthalocyanine isomeric derivatives, providing one step forward toward completing bis(alkyl)amino-incorporated phthalocyanine species. Nevertheless, the present result is helpful toward clarifying the chemistry of 1,8,15,22-tetrakis(substituted)phthalocyanine isomeric derivatives.

■ EXPERIMENTAL SECTION

General Procedures. 3-Nitrophthalonitrile was purchased from J&K SCIENTIFIC Ltd. *n*-Pentanol was freshly distilled from sodium. *N*,*N*-dimethylformamide (DMF) and CH_2Cl_2 were freshly distilled from CaH_2. Column chromatography was carried out on silica gel (200−300 mesh) or alkaline alumina (200−300 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 without further notification.

^{1}H NMR spectra were recorded on a Bruker DPX 400 spectrometer in $CDCl_3$ or $CDCl_3$/80% hydrazine hydrate (100/1 v/v). Spectra were referenced internally using the residual solvent resonance (δ 7.26 ppm in $CDCl_3$ for ^{1}H NMR) relative to $SiMe_4$. Electronic absorption spectra were recorded on a Hitachi U-2910 spectrophotometer. MALDI-TOF mass spectra were taken on a Bruker BIFLEX III ultrahigh-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 instrument. 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 in diameter and a silver-wire 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. The measurements were 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.

Crystal data for $H_2\{Pc[\alpha\text{-}N(C_4H_9)_2]_4\text{-}C_4\}$ (**1**), $Mg\{Pc[\alpha\text{-}N(C_4H_9)_2]_4\text{-}C_4\}$ (**2**), $Ni\{Pc[\alpha\text{-}N(C_4H_9)_2]_4\text{-}C_4\}$ (**3**), and $Zn\{Pc[\alpha\text{-}N(C_4H_9)_2]_4\text{-}C_4\}$ (**4**) were all 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 S3 in the Supporting Information. CCDC file numbers 1479950, 1479951, 1479952, and 1479953 containing 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.

The singlet oxygen quantum yields (Φ_Δ) of **1**, **2**, and **4** were measured in DMF following the published method,[11] on the basis of photoinduced decomposition of the chemical scavenger 1,3-diphenylisobenzofuran (DPBF) that reacts readily with $^1O_2$. Unsubstituted ZnPc was used as the reference compound (Φ_Δ = 0.56 in DMF). Steady-state fluorescence spectroscopic measurements were carried out on an F4500 (Hitachi) instrument. The fluorescence quantum yields (Φ_F) were calculated following the published method with $H_2Pc(t\text{-Bu})_4$ as reference compound (Φ_F = 0.77).[15]

Synthesis of 3-Aminophthalonitrile. 3-Nitrophthalonitrile (13.0 g, 75.1 mmol) was added to a mixture of methanol (230 mL) and concentrated HCl (66.6 mL), and the suspension was heated to reflux. To this mixture was added iron powder (12.7 g, 227 mmol) in small portions over 2 h, and then the mixture was stirred vigorously for further 1 h at the same temperature. The resulting mixture was then poured into cold water and filtered through a Büchner funnel. The precipitate was washed with water, giving the target compound as a yellow solid: yield 9.21 g, 85.7%. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.40 (t, *J* = 3.38 Hz, 1H), 7.09 (d, *J* = 6.12 Hz, 1 H), 6.97 (d, *J* = 7.80 Hz, 1 H), 4.71 (s, 2 H). Mp: 195−197 °C. Anal. Calcd for $C_8H_5N_3$: C, 67.12; H, 3.52; N, 29.35. Found: C, 67.19; H, 3.61; N, 29.33. IR (KBr): ν_{max} (cm^{-1}) 3468, 3367, 1718, 1631, 1593, 1477, 1313, 1055, 798, 743, 417.

Synthesis of 3-Chlorophthalonitrile. 3-Aminophthalonitrile (8.50 g, 59.4 mmol) was added to concentrated HCl maintained below −5 °C. A solution of sodium nitrite (8.19 g, 87.0 mmol) in water (18 mL) was added dropwise over 30 min, and then the mixture was stirred for a further 30 min. To this mixture was added a solution of CuCl (14.7 g, 148 mmol) in concentrated HCl (50 mL) dropwise over 1 h. After toluene (200 mL) was added, the mixture was stirred at 80 °C for 1 h. After the mixture was cooled to room temperature, the two layers were separated and the aqueous layer was extracted with toluene, dried over Na_2SO_4, and filtered. After the solvent was removed by evaporation under reduced pressure, the crude product was chromatographed on a silica gel column using CH_2Cl_2 as eluent, providing the target compound as a white solid: yield 4.03 g, 41.8%. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.79 (d, *J* = 8.04 Hz, 1H), 7.74 (d, *J* = 7.36 Hz, 1 H), 7.69 (t, *J* = 7.90 Hz, 1 H). Mp: 108−111 °C. Anal. Calcd for $C_8H_3N_2Cl$: C, 59.10; H, 1.86; N, 17.23. Found: C, 59.15; H, 1.73; N, 17.20. IR (KBr): ν_{max} (cm^{-1}) 3087, 1733, 1577, 1452, 1178, 1030, 942, 862, 800, 727, 549, 437.

Synthesis of 3-(Dibutylamino)phthalonitrile. To a mixture of 3-chlorophthalonitrile (3.32 g, 20.4 mmol) and K_2CO_3 (5.65 g, 40.9 mmol) in DMF (30 mL) at 150 °C was added dibutylamine (7.95 g, 62.0 mmol). The resulting system was heated at the same temperature for 6 h. After it was cooled to room temperature, the reaction mixture was poured into water (100 mL) and extracted with petroleum ether, dried over Na_2SO_4, and filtered. After the solvent was removed by evaporation under reduced pressure, the crude product was chromatographed on a silica gel column using dichloromethane/petroleum ether (3/1) as eluent, giving the target compound as a yellow oil: yield 2.70 g, 51.8%. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.41 (m, 1 H), 7.11 (d, *J* = 7.36 Hz, 1 H), 7.07 (d, *J* = 8.88 Hz, 1 H), 3.42 (t, *J* = 7.66 Hz, 4 H), 1.59 (m, *J* = 7.20 Hz, 4 H), 1.34 (m, *J* = 7.43 Hz, 4 H), 0.97 (t, *J* = 7.36 Hz, 6 H). Anal. Calcd for $C_{16}H_{21}N_3$: C, 75.26; H, 8.29; N, 16.46. Found: C, 75.30; H, 8.20; N, 16.33. IR (KBr): ν_{max} (cm^{-1}) 2959, 2872, 2206, 1585, 1468, 1369, 1288, 1227, 1072, 945, 785, 554.

Synthesis of 1,8,15,22-Tetrakis(dibutylamino)phthalocyaninato Magnesium, Mg{Pc[α-N(C_4H_9)$_2$]$_4$-C_4} (2). A mixture of magnesium turnings (16.1 mg, 0.662 mmol) and a small amount of iodine in anhydrous *n*-pentanol (3 mL) was refluxed for 1 h under a slow steam of nitrogen. Then 3-(dibutylamino)phthalonitrile (150 mg, 0.587 mmol) was added. The resulting mixture was refluxed for another 11 h. After the mixture was cooled, the solvent was evaporated. The crude product was chromatographed on an alkaline alumina column with dichloromethane/methanol (200/1) as eluent, affording the sample containing the four regioisomers of 1,8-/11,15-/18,22-/25-tetrakis(dibutylamino)phthalocyaninato magnesium complex as a green powder: yield 67.6 mg, 44.0%. This sample was then recrystallized twice from tetrahydrofuran and methanol, giving dark green microcrystals of pure 1,8,15,22-tetrakis(dibutylamino)phthalocyaninato magnesium isomer Mg{Pc[α-N(C_4H_9)$_2$]$_4$-C_4} (**2**): yield 41.0 mg, 26.7%. Anal. Calcd for $C_{64}H_{84}N_{12}Mg$: C, 73.50; H, 8.10; N, 16.07. Found: C, 73.27; H, 7.91; N, 16.00. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 9.02 (d, *J* = 7.24 Hz, 4 H), 7.98 (t, *J* = 7.48 Hz, 4 H), 7.65 (d, *J* = 7.72 Hz, 4 H), 4.30 (t, *J* = 7.26 Hz, 16 H), 1.83 (m, *J* = 7.31 Hz, 16 H), 1.44 (m, *J* = 7.39 Hz, 16 H), 0.88 (t, *J* = 7.34 Hz, 24 H). MS (MALDI-TOF): *m*/*z* 1045.9 [M + H]$^+$, 989.5 [M − C_4H_8]$^+$. UV−vis ($CHCl_3$): λ/nm (10^{-5} M^{-1} cm^{-1}) 745 (1.31), 670 (0.285), 489 (0.0648), 343 (0.549), 284 (0.349).

Synthesis of Metal-Free 1,8,15,22-Tetrakis(dibutylamino)phthalocyanine, H_2 {Pc[α-N(C_4H_9)$_2$]$_4$-C_4} (1). Compound **2** (51.5 mg, 0.0492 mmol) was dissolved in CF_3COOH (2 mL) and the mixture stirred under a slow steam of nitrogen for 20 min. The reaction mixture was then poured into cold water and neutralized with ammonia solution. The precipitate was collected and washed several times with CH_3OH and then applied on an alkaline alumina column with dichloromethane/petroleum ether (4/1) as eluent. Further recrystallization from tetrahydrofuran and methanol afforded dark green microcrystals of H_2{Pc[α-N(C_4H_9)$_2$]$_4$-C_4} (**1**): yield 33.7 mg, 66.9%. Anal. Calcd for $C_{64}H_{86}N_{12}$: C, 75.11; H, 8.47; N, 16.42. Found: C, 75.28; H, 8.26; N, 16.44. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 9.02 (d, *J* = 7.28 Hz, 4 H), 8.04 (t, *J* = 7.54 Hz, 4 H), 7.71 (d, *J* = 7.80 Hz, 4 H), 4.27 (t, *J* = 7.12 Hz, 16 H), 1.85 (m, *J* = 7.16 Hz, 16 H), 1.46 (m, *J* = 7.29 Hz, 16 H), 0.89 (t, *J* = 7.34 Hz, 24 H), 0.39 (s, 2H). MS (MALDI-TOF): *m*/*z* 1023.9 [M + H]$^+$, 966.8 [M − C_4H_8]$^+$. UV−vis ($CHCl_3$): λ/nm (10^{-5} M^{-1} cm^{-1}) 770 (1.19), 690 (0.346), 514 (0.0751), 340 (0.613), 285 (0.462).

Synthesis of 1,8,15,22-Tetrakis(dibutylamino)phthalocyaninato Nickel, Ni{Pc[α-N(C_4H_9)$_2$]$_4$-C_4} (3). A mixture of metal-free phthalocyanine **1** (40.5 mg, 0.0396 mmol), Ni(OAc)$_2$·4H_2O (25.0 mg, 0.100 mmol), and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU, 0.3 mL) in anhydrous *n*-pentanol (2 mL) was heated to reflux for 6 h under nitrogen. After it was cooled to room temperature, the mixture was evaporated to dryness under reduced pressure and the residue was chromatographed on an alkaline alumina column using dichloromethane as the eluent. The product was then further purified by recrystallization from tetrahydrofuran and methanol, affording dark green microcrystals of Ni{Pc[α-N(C_4H_9)$_2$]$_4$-C_4} (**3**): yield 31.8 mg, 74.5%. Anal. Calcd for $C_{64}H_{84}N_{12}Ni\cdot 0.5CH_2Cl_2$: C, 69.01; H, 7.63; N, 14.97. Found: C, 69.08; H, 7.55; N, 15.09. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.93 (d, *J* = 7.16 Hz, 4 H), 7.97 (t, *J* = 7.60 Hz, 4 H), 7.63 (d, *J* = 7.72 Hz, 4 H), 4.16 (t, *J* = 7.08 Hz, 16 H), 1.81 (m, *J* = 7.27 Hz, 16 H), 1.44 (m, *J* = 7.34 Hz, 16 H), 0.88 (t, *J* = 7.34 Hz, 24 H). MS (MALDI-TOF); *m*/*z* 1079.1 [M + H]$^+$, 1022.9 [M − C_4H_8]$^+$. UV−vis ($CHCl_3$): λ/nm (10^{-5} M^{-1} cm^{-1}) 745 (1.05), 670 (0.285), 498 (0.0660), 331 (0.453), 289 (0.514).

Synthesis of 1,8,15,22-Tetrakis(dibutylamino)phthalocyaninato Zinc, Zn{Pc[α-N(C_4H_9)$_2$]$_4$-C_4} (4). By employing the procedure described above to prepare Ni{Pc[α-N(C_4H_9)$_2$]$_4$-C_4} (**3**) with Zn(OAc)$_2$·2H_2O (22.0 mg, 0.100 mmol) instead of Ni(OAc)$_2$·4H_2O as starting material, pure Zn{Pc[N(C_4H_9)$_2$]$_4$-C_4} (**4**) was isolated as dark green microcrystals: yield 29.2 mg, 67.9%. Anal. Calcd for $C_{64}H_{84}N_{12}Zn$: C, 70.24; H, 7.86; N, 15.24. Found: C, 70.67; H, 7.59; N, 15.45. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 9.03 (d, *J* = 7.24 Hz, 4 H), 7.99 (t, *J* = 7.44 Hz, 4 H), 7.66 (d, *J* = 7.68 Hz, 4 H), 4.31 (t, *J* = 7.16 Hz, 16 H), 1.83 (m, *J* = 5.32 Hz, 16 H), 1.44 (m, *J* = 5.90 Hz, 16 H), 0.88 (t, *J* = 7.26 Hz, 24 H). MS (MALDI-TOF): *m*/*z* 1085.3 [M + H]$^+$, 1029.0 [M − C_4H_8]$^+$. UV−vis ($CHCl_3$): λ/nm (10^{-5} M^{-1} cm^{-1}) 746 (1.17), 674 (0.303), 489 (0.0648), 343 (0.549), 284 (0.349).

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorgchem.6b01371.

Synthesis of 3-(dibutylamino)phthalonitrile, experimental and simulated isotopic patterns for **1**−**4**, ^{1}H NMR spectra of **2**−**4**, electronic absorption spectra of **1**−**4**, cyclic voltammograms of **1**−**4**, absorption changes of **1**,

2, and **4** and DPBF in DMF, fluorescence emission spectra of **1**, **2**, and **4**, analytical and mass spectrometric data for **1**−**4**, ^{1}H NMR data (δ) for **1**−**4**, molecular packing diagrams of single crystals of **1**−**4**, crystal data and structure refinement details for **1**−**4**, and fluorescence emission data of **1**, **2**, and **4** (PDF)

Crystal data for **1** (CIF)

Crystal data for **2** (CIF)

Crystal data for **3** (CIF)

Crystal data for **4** (CIF)

AUTHOR INFORMATION

Corresponding Authors

*E-mail for K.W.: kangwang@ustb.edu.cn.
*E-mail for J.J.: jianzhuang@ustb.edu.cn.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

Financial support from the National Key Basic Research Program of China (Grant No. 2013CB933402), Natural Science Foundation of China (Nos. 21290174 and 21401009), Beijing Municipal Commission of Education, and University of Science and Technology Beijing is gratefully acknowledged.

REFERENCES

(1) (a) *Handbook of Porphyrin Science With Applications to Chemistry, Physics, Materials Science, Engineering, Biology and Medicine: Electronic Absorption Spectra− Phthalocyanines*; Kadish, K. M., Smith, K. M., Guilard, R., Eds.; World Scientific Publishing: Singapore, 2010; Vol. *9*. (b) McKeown, N. B. *Phthalocyanines Materials: Synthesis, Structure and Function*; Cambridge University Press: New York, 1998. (c) *Functional Phthalocyanine Molecular Materials, Structure and Bonding*; Jiang, J., Vol. Ed.; Mingos, D. M. P., Series Ed.; Springer: Heidelberg, Germany, 2010. (d) Li, R.; Zhang, X.; Zhu, P.; Ng, D. K. P.; Kobayashi, N.; Jiang, J. Electron−Donating or − Withdrawing Nature of Substituents Revealed by the Electrochemistry of Metal−Free Phthalocyanines. *Inorg. Chem.* **2006**, *45*, 2327−2334. (e) Kobayashi, N.; Ogata, H.; Nonaka, N.; Luk'yanets, E. A. Effect of peripheral substitution on the electronic absorption and fluorescence spectra of metal−free and zinc phthalocyanines. *Chem. - Eur. J.* **2003**, *9*, 5123−5134. (f) Kobayashi, N.; Sasaki, N.; Higashi, Y.; Osa, T. Regiospecific and Nonlinear Substituent Effects on the Electronic and Fluorescence Spectra of Phthalocyanines. *Inorg. Chem.* **1995**, *34*, 1636−1637.

(2) (a) *The Porphyrin Handbook: Phthalocyanines: Properties and Materials*; Kadish, K. M., Smith, K. M., Guilard, R., Eds.; Academic Press: San Diego, CA, 2000 and 2003; Vol. *17*. (b) Sommerauer, M.; Rager, C.; Hanack, M. Separation of 2(3),9(10),16(17),23(24)−Tetrasubstituted Phthalocyanines with Newly Developed HPLC Phases. *J. Am. Chem. Soc.* **1996**, *118*, 10085−10093. (c) Rager, C.; Schmid, G.; Hanack, M. Influence of substituents, reaction conditions and central metals on the isomer distributions of 1(4)−tetrasubstituted phthalocyanines. *Chem. - Eur. J.* **1999**, *5*, 280−288. (d) Durmus, M.; Yesilot, S.; Ahsen, V. Separation and mesogenic properties of tetraalkoxy−substituted phthalocyanine isomers. *New J. Chem.* **2006**, *30*, 675−678. (e) Mack, J.; Kobayashi, N. Low symmetry phthalocyanines and their analogues. *Chem. Rev.* **2011**, *111*, 281−321. (f) Ayhan, M. M.; Altinbas Oezpinar, G.; Durmus, M.; Guerek, A. G. Effects of position (α or β) and linker heteroatom (O or S) of substituent on the photophysicochemical behavior of poly(oxyethylene) substituted ZnPcs and assessment of J−aggregation or protonation using TD−DFT computations. *Dalton Trans.* **2013**, *42*, 14892−14904.

(3) Greenberg, S.; Lever, A. B. P.; Leznoff, C. C. Approaches towards the synthesis of a 2,9,16,23−tetrasubstituted phthalocyanine as a pure isomer. *Can. J. Chem.* **1988**, *66*, 1059−1064.

(4) Leznoff, C. C.; Hu, M.; McArthur, C. R.; Qin, Y.; van Lier, J. E. The syntheses of 2,9,16,23− and 1,8,15,22−tetrahydroxyphthalocyanines. *Can. J. Chem.* **1994**, *72*, 1990−1998.

(5) Kasuga, K.; Kawashima, M.; Asano, K.; Sugimori, T.; Kikkawa, T.; Fujiwara, T. Preparation of one structural isomer of tetra−substituted phthalocyanine, 1,8,15,22−tetra(3′−pentoxy)phthalocyanine, and a crystal structure of its nickel(II) complex. *Chem. Lett.* **1996**, *25*, 867−868.

(6) (a) Hanack, M.; Meng, D.; Beck, A.; Sommerauer, M.; Subramanian, L. R. Separation of structural isomers of tetra−tert−butylphthalocyaninatonickel(II). *J. Chem. Soc., Chem. Commun.* **1993**, 58−60. (b) Hanack, M.; Schmid, G.; Sommerauer, M. Chromatographic separation of the four possible constitutional isomers of a tetrasubstituted phthalocyanine: tetrakis[(2−ethylhexyl)oxy]phthalocyaninatonickel(II). *Angew. Chem.* **1993**, *105*, 1540−1542.

(7) (a) Chen, Y.; Cao, W.; Wang, K.; Jiang, J. Unprecedented Phthalocyanines Bearing Eight Di−butylamino Peripheral Substituents: Synthesis, Spectroscopy, and Structure. *Inorg. Chem.* **2015**, *54*, 9962−9967. (b) Chen, Y.; Cao, W.; Wang, C.; Qi, D.; Wang, K.; Jiang, J. Four Dibutylamino Substituents Are Better Than Eight in Modulating the Electronic Structure and Third−Order Nonlinear−Optical Properties of Phthalocyanines. *Inorg. Chem.* **2016**, *55*, 3151−3160.

(8) (a) Mikhalenko, S. A.; Luk'yanets, E. A. Dimethylamino−substituted phthalocyanines. *Zh. Obshch. Khim.* **1976**, *46*, 2156. (b) Mikhalenko, S. A.; Derkacheva, V. M.; Luk'yanets, E. A. Phthalocyanines and related compounds. XIX. Tetra- and octaamino-substituted phthalocyanines. *Zh. Obshch. Khim.* **1981**, *51*, 1650−1657. (c) Vachova, L.; Machacek, M.; Kucera, R.; Demuth, J.; Cermak, P.; Kopecky, K.; Miletin, M.; Jedlickova, A.; Simunek, T.; Novakova, V.; Zimcik, P. Heteroatom−substituted tetra(3,4−pyrido)-porphyrazines: a stride toward near−infrared−absorbing macrocycles. *Org. Biomol. Chem.* **2015**, *13*, 5608−5612.

(9) (a) Bian, Y.; Wang, R.; Jiang, J.; Lee, C. H.; Wang, J.; Ng, D. K. P. Synthesis, spectroscopic characterisation and structure of the first chiral heteroleptic bis(phthalocyaninato) rare earth complexes. *Chem. Commun.* **2003**, 1194−1195. (b) Zhou, Y.; Zhang, Y.; Wang, H.; Jiang, J.; Bian, Y.; Muranaka, A.; Kobayashi, N. Mixed (Phthalocyaninato) (Porphyrinato) Rare Earth Double−Decker Complexes with C_4 Chirality: Synthesis, Resolution, and Absolute Configuration Assignment. *Inorg. Chem.* **2009**, *48*, 8925−8933. (c) Wang, R.; Li, R.; Li, Y.; Zhang, X.; Zhu, P.; Lo, P. C.; Ng, D. K. P.; Pan, N.; Ma, C.; Kobayashi, N.; Jiang, J. Controlling the nature of mixed (phthalocyaninato) (porphyrinato) rare−earth(III) double−decker complexes: the effects of non−peripheral alkoxy substitution of the phthalocyanine ligand. *Chem. - Eur. J.* **2006**, *12*, 1475−1485. (d) Wang, R.; Li, R.; Bian, Y.; Choi, C. F.; Ng, D. K. P.; Dou, J.; Wang, D.; Zhu, P.; Ma, C.; Hartnell, R. D.; Arnold, D. P.; Jiang, J. Studies of "Pinwheel−Like" Bis[1,8,15,22−tetrakis(3−pentyloxy)phthalocyaninato] Rare Earth(III) Double−Decker Complexes. *Chem. - Eur. J.* **2005**, *11*, 7351−7357. (e) Bian, Y.; Li, L.; Wang, D.; Choi, C. F.; Cheng, D. Y. Y.; Zhu, P.; Li, R.; Dou, J.; Wang, R.; Pan, N.; Ng, D. K. P.; Kobayashi, N.; Jiang, J. Synthetic, structural, spectroscopic, and electrochemical studies of heteroleptic tris(phthalocyaninato) rare earth complexes. *Eur. J. Inorg. Chem.* **2005**, *2005*, 2612−2618. (f) Wang, R.; Li, Y.; Li, R.; Cheng, D. Y. Y.; Zhu, P.; Ng, D. K. P.; Bao, M.; Cui, X.; Kobayashi, N.; Jiang, J. Heteroleptic Rare Earth Double−Decker Complexes with Naphthalocyaninato and Phthalocyaninato Ligands. General Synthesis, Spectroscopic, and Electrochemical Characteristics. *Inorg. Chem.* **2005**, *44*, 2114−2120. (g) Bian, Y.; Li, L.; Dou, J.; Cheng, D. Y. Y.; Li, R.; Ma, C.; Ng, D. K. P.; Kobayashi, N.; Jiang, J. Synthesis, Structure, Spectroscopic Properties, and Electrochemistry of (1,8,15,22−Tetrasubstituted phthalocyaninato)lead Complexes. *Inorg. Chem.* **2004**, *43*, 7539−7544. (h) Bian, Y.; Wang, R.; Wang, D.; Zhu, P.; Li, R.; Dou, J.; Liu, W.; Choi, C. F.; Chan, H. S.; Ma, C.; Ng, D. K. P.; Jiang, J. Synthesis, structure, and spectroscopic and electrochemical

properties of heteroleptic bis(phthalocyaninato) rare earth complexes with a C_4 symmetry. *Helv. Chim. Acta* **2004**, *87*, 2581−2596. (i) Liu, W.; Lee, C. H.; Chan, H. S.; Mak, T. C. W.; Ng, D. K. P. Synthesis, spectroscopic properties, and structure of [tetrakis(2,4−dimethyl−3−pentyloxy)phthalocyaninato]metal complexes. *Eur. J. Inorg. Chem.* **2004**, *2004*, 286−292.

(10) (a) Moynihan, H. A.; Claudon, G. Direction of copper phthalocyanine crystallization using in situ generated tethered phthalocyanines. *CrystEngComm* **2010**, *12*, 2695−2696. (b) Lee, C. C.; Zhang, C. H.; Abd-El-Aziz, A. S.; Piorko, A.; Sutherland, R. G. Studies on some mono− and disubstitution reactions with cyclopentadienyliron complexes of *o*−, *m*− and *p*−dichlorobenzenes. *J. Organomet. Chem.* **1989**, *364*, 217−229.

(11) (a) DeRosa, M. C.; Crutchley, R. J. Photosensitized singlet oxygen and its applications. *Coord. Chem. Rev.* **2002**, *233-234*, 351−371. (b) Kucinska, M.; Skupin-Mrugalska, P.; Szczolko, W.; Sobotta, L.; Sciepura, M.; Tykarska, E.; Wierzchowski, M.; Teubert, A.; Fedoruk-Wyszomirska, A.; Wyszko, E.; Gdaniec, M.; Kaczmarek, M.; Goslinski, T.; Mielcarek, J.; Murias, M. Phthalocyanine Derivatives Possessing 2−(Morpholin−4−yl)ethoxy Groups As Potential Agents for Photodynamic Therapy. *J. Med. Chem.* **2015**, *58*, 2240−2255. (c) Maree, M. D.; Kuznetsova, N.; Nyokong, T. Silicon octaphenoxyphthalocyanines: photostability and singlet oxygen quantum yields. *J. Photochem. Photobiol., A* **2001**, *140*, 117−125.

(12) Spiller, W.; Kliesch, H.; Wohrle, D.; Hackbarth, S.; Roder, B.; Schnurpfeil, G. Singlet oxygen quantum yields of different photosensitizers in polar solvents and micellar solutions. *J. Porphyrins Phthalocyanines* **1998**, *02*, 145−158.

(13) (a) Vummidi, B. R.; Noreen, F.; Alzeer, J.; Moelling, K.; Luedtke, N. W. Photodynamic Agents with Anti−metastatic Activities. *ACS Chem. Biol.* **2013**, *8*, 1737−1746. (b) Al-Sohaimi, B. R.; Piskin, M.; Ghanem, B. S.; Al-Raqa, S. Y.; Durmus, M. Efficient singlet oxygen generation by triptycene substituted A_3B type zinc(II) phthalocyanine photosensitizers. *Tetrahedron Lett.* **2016**, *57*, 300−304.

(14) (a) Al-Raqa, S. Y. Synthesis, photochemical and photophysical properties of novel unsymmetrically substituted zinc(II) phthalocyanines. *J. Porphyrins Phthalocyanines* **2006**, *10*, 55−62. (b) Guerol, I.; Durmus, M.; Ahsen, V. Photophysical and photochemical properties of fluorinated and nonfluorinated *n*−propanol−substituted zinc phthalocyanines. *Eur. J. Inorg. Chem.* **2010**, *2010*, 1220−1230. (c) Liu, J. Y.; Lo, P. C.; Fong, W. P.; Ng, D. K. P. Effects of the number and position of the substituents on the *in vitro* photodynamic activities of glucosylated zinc(II) phthalocyanines. *Org. Biomol. Chem.* **2009**, *7*, 1583−1591. (d) *Photosensitizers in Medicine, Environment, and Security*; Nyokong, T., Ahsen, V., Eds.; Springer: New York, 2012; pp 149−246.

(15) (a) Cui, A.; Peng, X.; Fan, J.; Chen, X.; Wu, Y.; Guo, B. Synthesis, spectral properties and photostability of novel boron−dipyrromethene dyes. *J. Photochem. Photobiol., A* **2007**, *186*, 85−92. (b) Teuchner, K.; Pfarrherr, A.; Stiel, H.; Freyer, W.; Leupold, D. Spectroscopic properties of potential sensitizers for new photodynamic therapy start mechanisms *via* two−step excited electronic states. *Photochem. Photobiol.* **1993**, *57*, 465−471.

DOI: 10.1021/acs.inorgchem.6b01371
Inorg. Chem. XXXX, XXX, XXX−XXX