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Electron-Donating or -Withdrawing Nature of Substituents Revealed by the Electrochemistry of Metal-Free Phthalocyanines

Renjie Li,[†] Xianxi Zhang,[†] Peihua Zhu,[†] Dennis K. P. Ng,[‡] Nagao Kobayashi,[§] and Jianzhuang Jiang*,[†]

Department of Chemistry, Shandong University, Jinan 250100, China,
Department of Chemistry, The Chinese University of Hong Kong, Shatin, N.T.,
Hong Kong, China, and Department of Chemistry, Graduate School of Science,
Tohoku University, Sendai 980-8578, Japan

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The effect of substituents on the electrochemistry of metal-free phthalocyanines was examined for 17 phthalocyanine compounds. This work also provides new information about the electron-donating or -withdrawing nature of various substituents, namely, alkoxy, alkylthio, alkyl, alkynyl, phenyloxy, and phenylthio groups attached to the phthalocyanine system, from the viewpoint of electrochemistry. Most of the effects of peripheral and nonperipheral substitution and changes in the ring (π-conjugated system) size on the electrochemistry of metal-free phthalocyanines can be reasonably explained by considering the energy levels of frontier molecular orbitals of the corresponding compounds, which were obtained by calculations using the semiempirical PM3 method.

Introduction

Phthalocyanines have been an important class of dyes and pigments since their first synthesis early last century.[1] They have also found use as catalysts for desulfurization processes in the oil industry. Quite recently, these macromolecules have been applied as photoconducting agents in photocopiers, laser printers, and optical read/write disks. They are expected to play a more important role in material chemistry because of their potential applications in molecular electronics and photonics,[2] electrochromic displays,[3] nonlinear optics,[4] and electrocatalytic reagents.[5] All of these applications of phthalocyanines are related to their high chemical and thermal stability, which, in turn, is closely related to the electrochemical properties of phthalocyanine compounds. It is well-known that the electrochemical and spectroscopic properties of phthalocyanine derivatives can be tuned by either varying the central metal atom; changing the size of the π-conjugated system of phthalocyanines; or alternating the type, number, and positions of the substituents on the macrocycle ligands. However, except for the recent work of Kobayashi and coworkers systematically studying the effect of a number of substituents on the electronic absorption of a series of metal-free phthalocyanine compounds,[6] there has been no report in which the influence on the electrochemistry of incorporating a number of substituents on the phthalocyanine ligands has been systematically studied. In the present article, we describe regiospecific effects of various kinds of substituents and ring-size changes on the electrochemistry of a series of metal-free phthalocyanines. Molecular-orbital calculations within the framework of PM3 approximations have been carried out to support the experimental results.

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* To whom correspondence should be addressed. E-mail: jzjiang@sdu.edu.cn.
[†] Shandong University.
[‡] The Chinese University of Hong Kong.
[§] Tohoku University.

(1) (a) Lever, A. B. P.; Leznoff, C. C. *Phthalocyanine: Properties and Applications*; VCH: New York, 1989−1996; Vols. 1−4. (b) McKeown, N. B. *Phthalocyanines Materials: Synthesis, Structure and Function*; Cambridge University Press: New York, 1998. (c) Kadish, K. M.; Smith, K. M.; Guilard, R. *The Porphyrin Handbook*; Academic Press: San Diego, CA, 2000−2003; Vols. 1−20.

(2) (a) Turek, P.; Petit, P.; Andre, J.-J.; Simon, J.; Even, R.; Boudjema, B.; Guillaud, G.; Maitrot, M. *J. Am. Chem. Soc.* **1987**, *109*, 5119−5122. (b) Madru, R.; Guillaud, G.; Al Sadoun, M.; Maitrot, M.; Andre, J.-J.; Simon, J.; Even, R. *Chem. Phys. Lett.* **1988**, *145*, 343−346. (c) Jiang, J.; Kasuga, K.; Arnold, D. P. In *Supramolecular Photosensitive and Electroactive Materials*; Nalwa, H. S., Ed.; Academic Press: New York, 2001; Chapter 2, pp 113−210. (d) Ng, D. K. P.; Jiang, J. *Chem. Soc. Rev.* **1997**, *26*, 433−442. (e) Jiang, J.; Liu, W.; Arnold, D. P. *J. Porphyrins Phthalocyanines* **2003**, *7*, 459−473. (f) Chen, Y.; Su, W.; Bai, M.; Jiang, J.; Li, X.; Liu, Y.; Wang, L.; Wang, S. *J. Am. Chem. Soc.* **2005**, *127*, 15700−15701.

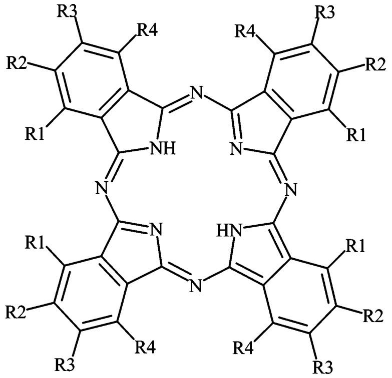
(3) Nicholson, M. M. In *Phthalocyanine: Properties and Applications*; Lever, A. B. P., Leznoff, C. C., Eds.; VCH: New York, 1993; Vol. 3, Chapter 2, pp 71−117.

(4) de la Torre, G.; Torres, T.; Agullo-Lopz, F. *Adv. Mater.* **1997**, *9*, 265−269.

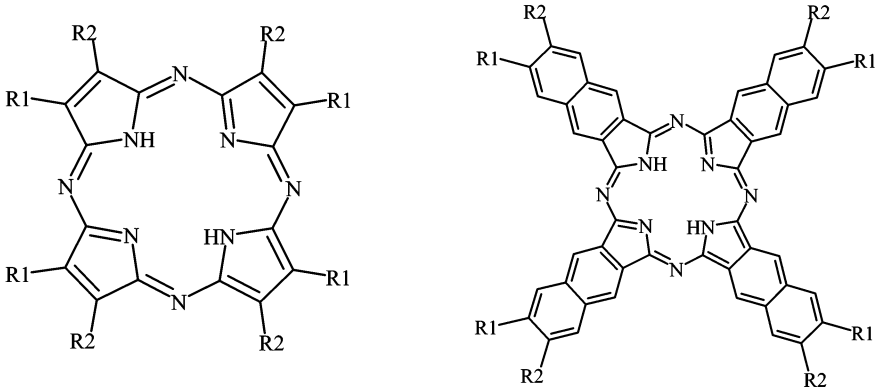
(5) Lever, A. B. P.; Hempstead, M. R.; Leznoff, C. C.; Liu, W.; Melnik, M.; Nevin, W. A.; Seymour, P. *Pure Appl. Chem.* **1986**, *58*, 1467−1476.

(6) (a) Kobayashi, N.; Sasaki, N.; Higashi, Y.; Osa, T. *Inorg. Chem.* **1995**, *34*, 1636−1637. (b) Kobayashi, N.; Ogata, H.; Nonaka, N.; Luk'yanets, E. A. *Chem. Eur. J.* **2003**, *9*, 5123−5134.

10.1021/ic051931k CCC: $33.50



H_2Pc	$R_1 = R_2 = R_3 = R_4 = H$
$H_2Pc(tBu)_4$	$R_1 = R_4 = H$; $R_2 \neq R_3 = H$, *tert*-C_4H_9
$H_2Pc(C_5H_{11})_8$	$R_1 = R_4 = H$; $R_2 = R_3 = C_5H_{11}$
$H_2Pc(OC_5H_{11})_4$	$R_1 = R_4 = H$; $R_2 \neq R_3 = H$, OC_5H_{11}
$H_2Pc(OC_5H_{11})_8$	$R_1 = R_4 = H$; $R_2 = R_3 = OC_5H_{11}$
$H_2Pc(OPh)_4$	$R_1 = R_4 = H$; $R_2 \neq R_3 = H$, OPh
$H_2Pc[O(4\text{-}OCH_3\text{-}Ph)]_8$	$R_1 = R_4 = H$; $R_2 = R_3 = O(4\text{-}OCH_3\text{-}Ph)$
$H_2Pc(C{\equiv}C\text{-}tBu)_4$	$R_1 = R_4 = H$; $R_2 \neq R_3 = H$, $C{\equiv}C\text{-}tBu$
$H_2Pc(\alpha\text{-}OC_5H_{11})_4$	$R_1 \neq R_4 = H$, OC_5H_{11} ; $R_2 = R_3 = H$
$H_2Pc(\alpha\text{-}OC_7H_{15})_4$	$R_1 \neq R_4 = H$, OC_7H_{15} ; $R_2 = R_3 = H$
$H_2Pc(\alpha\text{-}OC_5H_{11})_8$	$R_1 = R_4 = OC_5H_{11}$; $R_2 = R_3 = H$
$H_2Pc(SC_{12}H_{25})_4$	$R_1 = R_4 = H$; $R_2 \neq R_3 = H$, $SC_{12}H_{25}$
$H_2Pc(SC_8H_{17})_8$	$R_1 = R_4 = H$; $R_2 = R_3 = SC_8H_{17}$
$H_2Pc(SPh)_4$	$R_1 = R_4 = H$; $R_2 \neq R_3 = H$, SPh
$H_2Pc(SPh)_8$	$R_1 = R_4 = H$; $R_2 = R_3 = SPh$



$H_2TAP(tBu)_4$	$R_1 \neq R_2 = H$, *tert*-C_4H_9
$H_2Nc(tBu)_4$	$R_1 \neq R_2 = H$, *tert*-C_4H_9

Figure 1. Structure and abbreviations for the metal-free phthalocyanines in this work.

It is also worth pointing out that a huge number of phthalocyanine derivatives have been prepared and found applications in various disciplines since their first synthesis. Their electrochemistry has also attracted research interest in association with their application in areas such as sensors, molecular electronics, and electrochromism and in understanding the nature of their electronic absorption spectral properties. However, very little work has been conducted on metal-free phthalocyanines. To date, only scattered reports with incomplete reduction or oxidation data exist on the electrochemical characteristics of several kinds of metal-free phthalocyanines such as $H_2Pc(^tBu)_4$ and $H_2Pc(\alpha\text{-}OC_4H_9)_8$, some of which are obviously strange.[7] The present work, focusing on the intrinsic electrochemical properties of metal-free phthalocyanines (Figure 1 and Table 1) is therefore of common interest for scientists in different fields.

It is also noteworthy that the electronic effects of various substituents were intensively studied around 1970.[8] As a result, it was found that alkoxy groups act as typical electron-donating substituents.[9] Alkylthio substituents have been revealed to be more likely to function as electron-withdraw-

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(7) L'Her, M.; Pondaven, A. In *The Porphyrin Handbook*; Kadish, K. M., Smith, K. M., Guilard, R., Eds; Academic Press: San Diego, CA, 2003; Vol. 16, pp 117−170.

Table 1. List of Abbreviations for (na)Phthalocyanine Ligands

abbreviation	ligand
H_2Pc	unsubstituted phthalocyanine
$H_2Pc(^tBu)_4$	2(3),9(10),16(17),24(25)-tetrakis(*tert*-butyl)phthalocyanine
$H_2Pc(C_5H_{11})_8$	2,3,9,10,16,17,24,25-octakis(pentyl)phthalocyanine
$H_2Pc(OC_5H_{11})_4$	2(3),9(10),16(17),24(25)-tetrakis(3-pentyloxy)phthalocyanine
$H_2Pc(OC_5H_{11})_8$	2,3,9,10,16,17,24,25-octakis(pentyloxy)phthalocyanine
$H_2Pc(OPh)_4$	2(3),9(10),16(17),24(25)-tetrakis(phenyloxy)phthalocyanine
$H_2Pc(OPh)_8$	2,3,9,10,16,17,24,25-octakis(phenyloxy)phthalocyanine
$H_2Pc[O(4\text{-}OCH_3\text{-}Ph)]_8$	2,3,9,10,16,17,24,25-octakis[(4-methyloxy)phenyloxy]phthalocyanine
$H_2Pc(C\equiv C\text{-}^tBu)_4$	2(3),9(10),16(17),24(25)-tetrakis(*tert*-butylalkynyl)phthalocyanine
$H_2Pc(\alpha\text{-}OC_5H_{11})_4$	1,8,15,22-tetrakis(3-pentyloxy)phthalocyanine
$H_2Pc(\alpha\text{-}OC_7H_{15})_4$	1,8,15,22-tetrakis[di(2,4-methyl)-3-pentyloxy]phthalocyanine
$H_2Pc(\alpha\text{-}OC_5H_{11})_8$	1,4,8,11,15,18,22,25-octakis(pentyloxy)phthalocyanine
$H_2Pc(SC_{12}H_{25})_4$	2(3),9(10),16(17),24(25)-tetrakis(dodecylthio)phthalocyanine
$H_2Pc(SC_8H_{17})_8$	2,3,9,10,16,17,24,25-octakis(octylthio)phthalocyanine
$H_2Pc(SPh)_4$	2(3),9(10),16(17),24(25)-tetrakis(phenylthio)phthalocyanine
$H_2Pc(SPh)_8$	2,3,9,10,16,17,24,25-octakis(phenylthio)phthalocyanine
$H_2TAP(^tBu)_4$	2(3),7(8),12(13),17(18)-tetrakis(*tert*-butyl)tetraazaporphyrizine
$H_2Nc(^tBu)_4$	3(4),12(13),21(22),30(31)-tetrakis(*tert*-butyl)-2,3-naphthalocyaninate

Table 2. Half-Wave Redox Potentials of Metal Free (na)Phthalocyanines (V vs SCE) in CH_2Cl_2 Containing 0.1 M TBAP

	Oxd_2	Oxd_1	Red_1	Red_2	Red_3	Red_4	$\Delta E°_{1/2}{}^a$
H_2Pc (**1**)	+1.14	+0.93	−0.78	−1.30	−1.90		1.71
$H_2Pc(^tBu)_4$ (**2**)	+1.27	+0.95	−0.80	−1.23	-1.47^b		1.75
$H_2Pc(C_5H_{11})_8$ (**3**)	+1.29	+0.94	−0.77	−1.24			1.71
$H_2Pc(OC_5H_{11})_4$ (**4**)	+1.22	+0.85	−0.86	−1.31	−1.58		1.71
$H_2Pc(OC_5H_{11})_8$ (**5**)	+1.19	+0.72	−0.97	−1.25	-1.52^b		1.69
$H_2Pc(OPh)_4$ (**6**)	+1.31	+1.13	−1.04	−1.22			2.17
$H_2Pc[O(4\text{-}OCH_3\text{-}Ph)]_8$ (**7**)	+1.56	+1.12	−1.06	−1.31			2.18
$H_2Pc(C\equiv C\text{-}^tBu)_4$ (**8**)	+1.36	+1.22	−0.69	−1.01	−1.83		1.91
$H_2Pc(\alpha\text{-}OC_5H_{11})_4$ (**9**)	+1.11	+0.67	−0.82	−1.26	-1.51^b	-1.78^b	1.49
$H_2Pc(\alpha\text{-}OC_7H_{15})_4$ (**10**)	+1.09	+0.66	−0.82	−1.24	-1.55^b	-1.76^b	1.48
$H_2Pc(\alpha\text{-}OC_5H_{11})_8$ (**11**)	+0.72	+0.46	−0.90	−1.24	-1.51^b	-1.78^b	1.36
$H_2Pc(SC_{12}H_{25})_4$ (**12**)	+1.35	+0.97	−0.73	−1.05	−1.81		1.70
$H_2Pc(SC_8H_{17})_8$ (**13**)	+1.31	+0.94	−0.76	−0.99	−1.79		1.70
$H_2Pc(SPh)_4$ (**14**)	+1.33	+0.99	−0.70	−0.94	−1.76		1.69
$H_2Pc(SPh)_8$ (**15**)	$+1.33^b$	+1.10	−0.61	−0.86	-1.81^b		1.71
$H_2TAP(^tBu)_4$ (**16**)	+1.61	+1.31	−0.74	−1.18	−1.52	−1.84	2.05
$H_2Nc(^tBu)_4$ (**17**)	+1.03	+0.65	−0.89	−1.17	−1.44		1.55

[a] $\Delta E°_{1/2}$ is the potential difference between the first oxidation and first reduction processes, i.e., the HOMO−LUMO gap of corresponding molecules. [b] Recorded by DPV.

ing groups than the corresponding alkoxy groups.[10] However, in contrast to the generally accepted view that alkyl groups are typical electron-donating substituents, gas-phase rate studies of alcohols and amines have indicated that small alkyl groups such as methyl, ethyl, and propyl groups appear to act as electron-donating substituents, whereas bulky alkyl groups, especially the *tert*-butyl group, act as electron-withdrawing substituents.[11] The present article is therefore also helpful in providing new information on the electronic effects of various substituents, namely, alkoxy, alkylthio, alkyl, alkynyl, phenyloxy, and phenylthio groups, attached to the phthalocyanine system, from the viewpoint of electrochemistry.

Results and Discussion

Electrochemical Characteristics. The electrochemical behavior of all of the metal-free phthalocyanines was investigated by cyclic voltammetry (CV) and differential pulse voltammetry (DPV) in CH_2Cl_2. The half-wave redox potential values vs SCE are summarized in Table 2. Figure 2 shows the cyclic voltammograms and differential pulse voltammograms of $H_2Pc(\alpha\text{-}OC_5H_{11})_4$ (9) and $H_2Pc(\alpha\text{-}OC_5H_{11})_8$ (**11**) as typical representatives of the series of compounds. Within the electrochemical window of CH_2Cl_2, all of the metal-free phthalocyanine compounds undergo two quasireversible one-electron oxidations and up to four quasireversible one-electron reductions as the separation of the reduction and oxidation peak potentials for each process is 60−95 mV. All of these processes are attributed to successive removal of electrons from, or addition of electrons to, the macrocycle orbitals. The oxidations and reductions are labeled as Oxd_n and Red_n, respectively.

Our observations of the electrochemistry of these metal-free phthalocyanines in CH_2Cl_2 differ from those reported previously. For instance, only one oxidation curve and one reduction curve were observed for unsubstituted H_2Pc (1) in DMF.[7] However, as mentioned above, under our experi-

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(8) (a) Brauman, J. I.; Blair, L. K. *J. Am. Chem. Soc.* **1968**, *90*, 5036−5037. (b) Baker, F. W.; Parish, R. C.; Stock, L. M. *J. Am. Chem. Soc.* **1967**, *89*, 5677−5685.

(9) (a) Brauman, J. I.; Blair, L. K. *J. Am. Chem. Soc.* **1970**, *92*, 5986−599. (b) Naka, K.; Uemura, T.; Chujo, Y. *Macromolecules.* **2002**, *35*, 3539−3543.

(10) (a) McMahon, T. B.; Kebarle, P. *J. Am. Chem. Soc.* **1977**, *99*, 9, 2222−2230. (b). Karty, J. M; Wu, Y.; Brauman, J. I. *J. Am. Chem. Soc.* **2001**, *123*, 9800−9805.

(11) (a) Brauman, J. I.; Blair, L. K. *J. Am. Chem. Soc.* **1968**, *90*, 6561−6562. (b) Brauman, J. I.; Blair, L. K. *J. Am. Chem. Soc.* **1969**, *91*, 2126−2127.

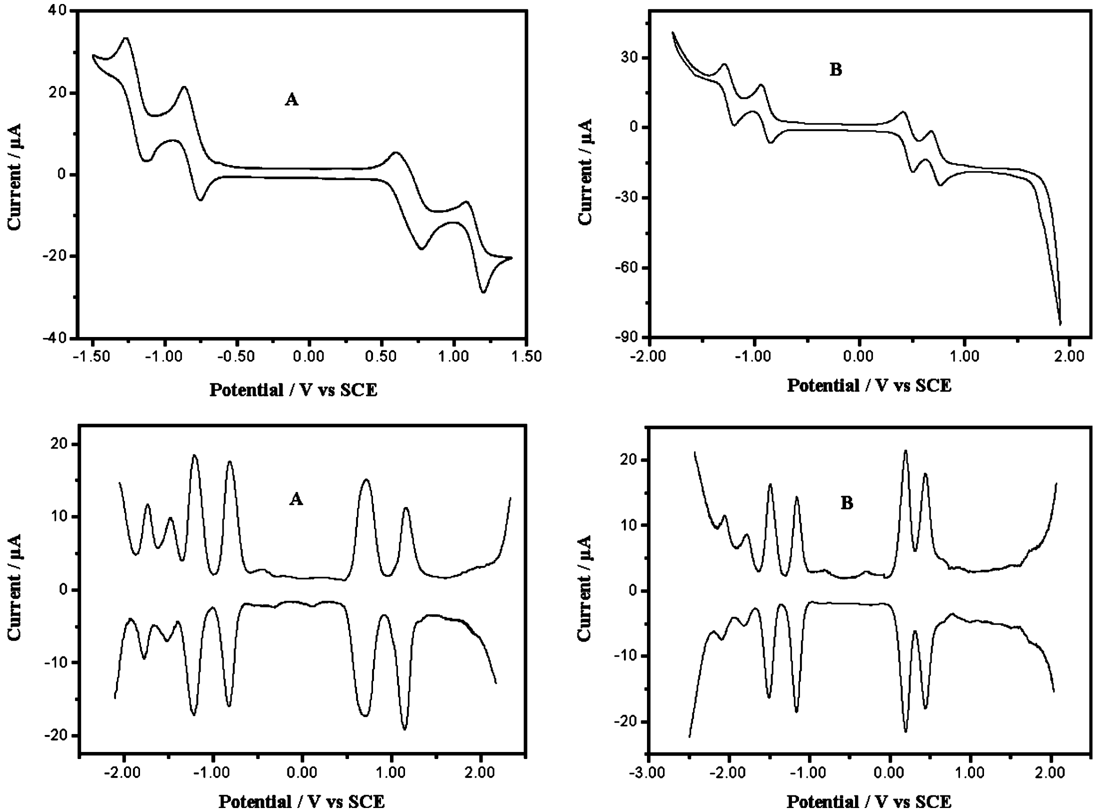

Figure 2. Cyclic voltammetry and differential pulse voltammetry of (A) $H_2Pc(\alpha\text{-}OC_5H_{11})_4$ (9) and (B) $H_2Pc(\alpha\text{-}OC_5H_{11})_8$ (**11**) in CH_2Cl_2 containing 0.1 M $[NBu_4][ClO_4]$ at scan rates of 20 and 10 mV s^{-1}, respectively.

mental conditions, this compound has been revealed to undergo two one-electron oxidations and three one-electron reductions according in the CV and, more clearly, the DPV results. It is worth noting that the redox data recorded for H_2Pc might not be as accurate as for the other metal-free phthalocyanine analogues because of its limited solubility in CH_2Cl_2. Nevertheless, the result reported here was justified by the systematic and comparative studies over a number of metal-free phthalocyanines with different substituents on different positions of the macrocycle ring, which is further rationalized by the theoretical calculations of their molecular orbitals using the semiempirical PM3 method.

The effects of substituent species and positions as well as the ring-size changes are clearly reflected by the shift in the half-wave potentials of the first oxidation and first reduction, together with their difference, of metal-free phthalocyanine derivatives. As can be seen in Table 2, substitution of four alkoxy groups at the peripheral positions of phthalocyanine (4) induces a slight shift in the negative direction for both the first oxidation and the first reduction, without changing the difference between these two redox processes, relative to H_2Pc (**1**), revealing the electron-donating nature of the alkoxy groups attached to the peripheral positions of phthalocyanine. An increase in the number of alkoxy groups from four in **4** to eight at the same peripheral positions of **5** results in a further shift of the two redox processes in the negative direction, again with the potential difference between the first oxidation and first reduction remaining unchanged. The extent of the shift induced by the substitution of the four alkoxy groups at the remaining peripheral positions approximately parallels the first-step alkoxy tetrasubstitution at the same peripheral positions from the experimental point of view.

The effects of alkyl groups at the peripheral positions of phthalocyanine skeleton on the electrochemistry of metal-free phthalocyanine were also examined. Incorporating four *tert*-butyl groups at the peripheral positions of phthalocyanine induces a very slight positive shift for the first oxidation and also a very slight negative shift for the first reduction, thus slightly enlarging the potential difference between these two redox processes, actually the HOMO−LUMO gap of $H_2Pc(^tBu)_4$ (2). In contrast, both the first oxidation and the first reduction of $H_2Pc(C_5H_{11})_8$ (**3**) remain almost unchanged relative to those of H_2Pc, with the HOMO−LUMO gap also remaining unchanged (Table 2).

As also reported in Table 2, for metal-free phthalocyanines with the same numbers of electron-donating alkoxy groups, substitution at the nonperipheral positions affords a much more significant effect on the electrochemistry of the corresponding compounds. Introduction of four alkoxy groups at the nonperipheral positions of the phthalocyanine ring (**9**, **10**) also shifts the first oxidation and first reduction in the negative direction. However, the degree of the shift for the first oxidation is larger than that induced by peripheral alkoxy substitutions, whereas for the first reduction, it is smaller. This results in a significant decrease in the potential difference between the first oxidation and first reduction of $H_2Pc(\alpha\text{-}OR)_4$ [R = C_5H_{11} (**9**), C_7H_{15} (**10**)]. As in the case of peripherally substituted phthalocyanines, introduction of four alkoxy groups at the remaining four nonperipheral positions

Table 3. Electronic Absorption Data for the Metal-Free (na)Phthalocyanines (1−17) in $CHCl_3$

compd	λ_{max} (nm^{-1}) (log ϵ)					
1[a]	347	387 (sh)	603 (sh)	632 (sh)	656	692
2	341 (4.96)	367 (sh)	602 (4.50)	645 (4.75)	664 (5.17)	701 (5.23)
3	347 (4.90)	377 (sh)	617 (4.46)	647 (4.76)	677 (5.14)	701 (5.28)
4	344 (4.85)	392 (4.55)	610 (4.41)	645 (4.62)	671 (5.04)	707 (5.11)
5	349 (4.99)	427 (4.64)	604 (4.48)	639 (4.77)	664 (5.16)	700 (5.23)
6	344 (4.86)	393 (sh)	607 (4.46)	639 (4.75)	666 (5.15)	701 (5.22)
7	341 (4.76)	422 (sh)	602 (sh)	623 (4.78)	650 (sh)	701 (5.20)
8	349 (4.91)	399 (4.60)	615 (4.57)	645 (4.78)	674 (5.25)	712 (5.28)
9	353 (4.52)	387 (4.62)	631 (4.58)	663 (4.68)	696 (5.12)	727 (5.29)
10	353 (4.53)	389 (4.62)	634 (4.49)	666 (4.60)	700 (5.10)	730 (5.18)
11	331 (4.88)	406 (sh)	676 (4.60)	705 (4.65)	753 (5.14)	774 (5.19)
12	346 (4.89)	422 (4.56)	621 (sh)	655 (4.58)	682 (5.12)	716 (5.12)
13	362 (4.86)	451 (sh)	660 (4.53)	679 (4.72)	699 (5.13)	730 (5.30)
14	342 (4.90)	423 (sh)	618 (4.56)	651 (4.78)	681 (5.11)	714 (5.26)
15	348 (4.91)	435 (4.60)	643 (4.50)	672 (4.76)	709 (5.12)	735 (5.20)
16	336 (5.28)	520 (4.48)	553 (5.11)	622 (5.23)		
17	324 (5.23)	360 (4.93)	412 (4.62)	699 (4.82)	737 (4.94)	782 (5.28)

[a] Because of the low solubility in chloroform, no extinction coefficient was obtained.

of $H_2Pc(\alpha\text{-OR})_4$ leads to a further shift of the first oxidation and first reduction processes of **11** in the negative direction, again with a further diminished potential gap between these two redox processes. However, the effect of the shift induced by introducing alkoxy groups at the remaining nonperipheral positions is smaller than that of initially incorporating four alkoxy groups at the nonperipheral positions. According to the data reported in Table 2, incorporation of the first four alkoxy groups at the nonperipheral positions produces a decrease of 0.22 eV in the potential difference between the first oxidation and first reduction processes, i.e., the HOMO−LUMO gap, whereas the substitution of the second four alkoxy groups at the nonperipheral positions leads to a decrease of 0.13 eV. These results reveal that the effect of decreasing the HOMO−LUMO gap due to the first four substituents is about 1.7 times that due to the second four substituents. The calculation data give 1.3, as drawn from the results in Table 3.

The effect of substituent species was examined by comparing the electrochemistry of alkoxy, alkylthio, phenyloxy, and phenylthio peripherally substituted phthalocyanines. In contrast to alkoxy groups, introducing four alkylthio groups at the peripheral positions induces a very slight shift of the first oxidation and first reduction processes of **12** in the positive direction without changing the potential difference, with respect to H_2Pc (Table 2). However, the introduction of alkylthio groups at the remaining peripheral positions of $H_2Pc(SR)_4$ seems to afford an effect on the electrochemistry that is the reverse of that induced by the initial substitution of four alkylthio groups at the peripheral positions of the phthalocyanine ring. In any event, as shown in Table 2, the shift induced by incorporating the alkylthio groups at the peripheral positions of the phthalocyanine ligand is smaller than that observed upon alkoxy substitution. However, this is not the case for the phenyloxy pheriperally substituted phthalocyanines. Examination of the data in Table 2 indicates that the introduction of four and eight phenyloxy groups at the peripheral positions of phthalocyanine ligand (**6**, **7**) seems to afford quite similar effects on the first oxidation and first reduction. In good contrast to the various kinds of above-mentioned phthalocyanine examples, the incorporation of phenyloxy groups leads to a positive shift for the first oxidation and a negative shift for the first reduction, resulting in a significantly increased potential difference between these two redox processes, i.e., increased HOMO−LUMO gap of the compounds. Unlike the effect of phenyloxy groups, introducing four phenylthio groups at the peripheral positions also induces a positive shift for the first oxidation but a positive shift for the first reduction to almost the same degree, and therefore, does not alter the potential difference between these two redox processes for **14**. Increasing the number of phenylthio substituents at the peripheral positions of phthalocyanine from four to eight causes a further shift in the *positive* direction for both the first oxidation and the first reduction processes of **15**, again with the potential difference between these two redox processes remaining unchanged. These results clearly reveal the electron-withdrawing nature of phenylthio groups at the peripheral positions of phthalocyanine.

To learn more about the electrochemistry of metal-free phthalocyanines, the species with four alkynyl groups at peripheral positions of phthalocyanine was also electrochemically studied. As shown in Table 2, substitution of four alkynyl groups at the peripheral positions of phthalocyanine induces an obvious shift in the positive direction for both the first oxidation and first reduction and slightly enlarges the difference between these two redox processes for 8 relative to that of H_2Pc (**1**), revealing the electron-withdrawing nature of alkynyl groups attached at the peripheral positions of phthalocyanine.

Furthermore, the availability of electrochemical data for $H_2TAP(^tBu)_4$ (16), $H_2Pc(^tBu)_4$ (**2**), and $H_2Nc(^tBu)_4$ (**17**) renders it possible to compare the effect of a ring-size change, actually a π-network change, on the electrochemistry of phthalocyanine derivatives. Comparison of the value of the difference between the first oxidation and first reduction, actually the HOMO−LUMO gap, for $H_2TAP(^tBu)_4$ (**16**), 2.05 V; $H_2Pc(^tBu)_4$ (**2**), 1.75 V; and $H_2Nc(^tBu)_4$ (**17**), 1.55 V, makes it clear that the extension of the π-network has an obvious effect on the MO levels. The increase in ring size induces significant modifications in the orbital systems of these compounds, manifested in the decrease in the HOMO−

Table 4. Energy Levels (in eV) of the HOMO and LUMO for the Metal-Free Phthalocyanines Obtained by PM3 Calculations

	E_{HOMO}	E_{LUMO}	ΔE^{a}
H_2Pc	−7.122	−2.565	4.557
$H_2Pc(CH_3)_4$	−7.044	−2.498	4.546
$H_2Pc(CH_3)_8$	−6.952	−2.430	4.522
$H_2Pc(OCH_3)_4$	−7.083	−2.536	4.547
$H_2Pc(OCH_3)_8$	−6.948	−2.428	4.520
$H_2Pc(OPh)_4$	−7.671	−1.993	5.678
$H_2Pc(OPh)_8$	−7.879	−2.193	5.686
$H_2Pc(C{\equiv}C\text{-}{}^{t}Bu)_4$	−7.612	−1.998	5.614
$H_2Pc(\alpha\text{-}OCH_3)_4$	−7.009	−2.631	4.378
$H_2Pc(\alpha\text{-}OCH_3)_8$	−6.695	−2.434	4.261
$H_2Pc(SCH_3)_4$	−7.265	−2.744	4.521
$H_2Pc(SCH_3)_8$	−7.182	−2.753	4.429
$H_2Pc(SPh)_4$	−7.184	−2.667	4.517
$H_2Pc(SPh)_8$	−7.049	−2.628	4.421
$H_2TAP(CH_3)_4$	−7.795	−2.651	5.144
$H_2Pc(CH_3)_4$	−7.044	−2.498	4.546
$H_2Nc(CH_3)_4$	−6.705	−2.470	4.235

[a] ΔE is the energy difference between the HOMO and LUMO of the corresponding phthalocyanine, $\Delta E = |E_{\mathrm{HOMO}} - E_{\mathrm{LUMO}}|$.

LUMO gap shown in Table 2. Further extension of the π-network is therefore predicted to lead to corresponding molecular materials with progressively narrower HOMO−LUMO gaps. It is worth pointing out that the effect of the ring-size change is more significant on the first oxidation than on the first reduction (Table 2).

It is noteworthy that the values of the potential difference between the first oxidation and first reduction, actually the HOMO−LUMO gap, for phthalocyanines are very important for obtaining information on their electronic absorptions. As the first oxidation step and first reduction step involve the HOMO and the LUMO, respectively, of the molecule, the energy difference between these two redox processes for H_2-Pc corresponds to its electrochemical molecular band gap. The value $\Delta E°_{1/2}$ thus should reflect the energy necessary for the transition of an electron from the HOMO to the LUMO of the corresponding metal-free phthalocyanine and therefore should correlate with the lowest-energy optical transition in the electronic absorption spectrum of H_2Pc. For example, the decreasing trend observed for the $\Delta E°_{1/2}$ value of metal-free phthalocyanines in the order H_2Pc (1) > $H_2Pc(\alpha\text{-}OC_5H_{11})_4$ (**9**) > $H_2Pc(\alpha\text{-}OC_5H_{11})_8$ (**11**) is in good agreement with the red-shift of the Q absorption band of these compounds (Table 3), where the Q-band position is determined as $(Q_x + Q_y)/2$, giving 674 nm for 1, 712 nm for **9**, and 769 nm for **11**. Further support comes from the gradual decrease in the HOMO−LUMO gap from $H_2TAP({}^{t}Bu)_4$ (**16**), to $H_2Pc({}^{t}Bu)_4$ (**2**), to $H_2Nc({}^{t}Bu)_4$ (**17**), and the gradual red-shift in the Q-band position from 588, to 682, and to 782 nm, in the same order.

Molecular-Orbital Calculations. To enhance the understanding of the effect of substituents on the electrochemistry of metal-free phthalocyanine derivatives, we carried out molecular-orbital (MO) calculations on these metal-free phthalocyanine species within the framework of the PM3 approximations.[12] This method has been well evaluated and widely used in calculations of conjugated compounds for qualitative simulations of experimental results.[13,14] The calculated molecular-orbital (HOMO and LUMO) energy data are summarized in Table 4. Most of the trends found by experimental measurements in the potentials of the first oxidation and first reduction processes according to different types of substituents on the phthalocyanine ring are reproduced by the calculation. This is also true for the variation in the HOMO−LUMO gap of various kinds of metal-free phthalocyanine compounds.

For instance, as can be easily clarified in Table 4, enlargement of the π-conjugated system from $H_2TAP(CH_3)_4$, to $H_2Pc(CH_3)_4$, and to $H_2Nc(CH_3)_4$ gradually increases the energy level of the LUMO to a small degree but increases the energy level of the HOMO to a significant extent, leading to a significant decrease in the HOMO−LUMO gap in the same order. All of these results agree well with those obtained by electrochemical techniques. It is worth noting that, by subtracting the HOMO−LUMO gap of $H_2TAP(CH_3)_4$, the effect of enlargement in the π-conjugated system can be calculated quantitatively. The first linear benzoannulation yields a decrease of 0.61 eV in the HOMO−LUMO gap, while the second linear benzoannulation induces a decrease of 0.30 eV. These values indicate that the effect of the first linear benzoannulation is about 2.0 times that of the second linear benzoannulation. The experimental data amount to 1.5 (Table 2).

Conclusion

Two one-electron oxidations and up to four quasireversible one-electron reductions were observed within the electrochemical window of CH_2Cl_2 for metal-free phthalocyanine derivatives substituted with various kinds of groups at peripheral or nonperipheral positions. Experimental results reveal that alkyl groups at the peripheral positions of phthalocyanine act similarly to protons in terms of electrochemistry. This also appears true for alkylthio substituents at the same positions of phthalocyanine. However, alkoxy groups at either the peripheral or nonperipheral positions of phthalocyanine function as typical electron-donating substituents. In good contrast, phenylthio groups at the peripheral positions of phthalocyanine act as typical electron-withdrawing substituents. The effect of phenyloxy groups at the same peripheral positions is a bit complicated, shifting the first oxidation process in the positive direction but the first reduction process in the negative direction. To enhance our understanding of the effect of substituents on the electrochemistry of these metal-free phthalocyanines, molecular-orbital (MO) calculations within the framework of the PM3 approximations were carried out. The experimental findings in the change of potentials of the first oxidation and first reduction processes and their difference due to various

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(12) (a) Stewart, J. J. P. *J. Comput. Chem.* **1989**, *10*, 209−220. (b) Stewart, J. J. P. *J. Comput. Chem.* **1989**, *10*, 221−264.

(13) (a) Morpurgo, S.; Bossa, M.; Morpurgo, G. O. *J. Mol. Struct. (THEOCHEM)* **1998**, *429*, 71−80. (b) Bräuer, M.; Kunert, M.; Dinjus, E.; Klussmann, M.; Döring, M.; Gorls, H.; Anders, E. *J. Mol. Struct. (THEOCHEM)* **2000**, *505*, 289−301.

(14) (a) Türker, L. *J. Mol. Struct. (THEOCHEM)* **1999**, *492*, 159−163. (b) Buam, D. M. L.; Lyngdoh, R. H. D. *J. Mol. Struct. (THEOCHEM)* **2000**, *505*, 149−159.

different types of substituents on the phthalocyanine ring appear in line with the results obtained by calculation.

Experimental Section

Measurements. MALDI-TOF mass spectra were recorded on a Bruker APEX47e ultrahigh-resolution Fourier transform ion cyclotron resonance (FT-ICR) mass spectrometer with α-cyano-4-hydroxycinnamic acid as a matrix. Elemental analyses were performed by the Institute of Chemistry, Chinese Academy of Sciences. CV and DPV measurements were carried out with a BAS CV-50W voltammetric analyzer with a resolution of ±0.0025 V. The cell contained inlets for a glassy carbon disk working electrode of 3.0-mm diameter and a silver-wire counter electrode. The reference electrode was Ag/Ag$^+$ connected to the solution by a Luggin capillary whose tip was placed close to the working electrode. Results were corrected for junction potentials by being referenced internally to the ferrocenium/ferrocene (Fe$^+$/Fe) couple [$E_{1/2}$(Fe$^+$/Fe) = +0.50 V vs SCE]. Potentials in this article are referenced to the SCE. Typically, a 0.1 M solution of [NBu_4][ClO_4] in CH_2Cl_2 containing 0.5 mM sample was purged with nitrogen for 10 min, and then voltammograms were recorded at ambient temperature. The scan rates were 20 and 10 mV/s for CV and DPV, respectively. It is worth noting that, to increase the solubility of unsubstituted metal-free phthalocyanine in CH_2Cl_2, the solution of [NBu_4][ClO_4] in CH_2Cl_2 containing sample was sonicated for ca. 20 min until a dark green solution was obtained before electrochemical measurements.

Method of Calculation. The frontier molecular-orbital calculations for metal-free phthalocyanine derivatives were carried out using the semiempirical MP3 method. The input structures were derived from the optimized geometries of H_2Pc for respective compounds and then optimized again. All calculations were carried out using the Gaussian 98W program.[15]

Chemicals. *n*-Pentanol was distilled from sodium. Dichloromethane (CH_2Cl_2) for voltammetric studies was freshly distilled from CaH_2 under nitrogen. All other reagents and solvents were used as received. The phthalonitriles, namely, 4,5-(pentyl)phthalonitrile,[16] 4,5-(pentyloxy)phthalonitrile,[16] 4-(3-pentyloxy)phthalonitrile,[17] 3-(3-pentyloxy)phthalonitrile,[17] 1,4-(pentyloxy)phthalonitrile,[18] and 4-(*tert*-butylalkynyl)phthalonitrile[19] were synthesized according to the literature procedures. Phthalonitriles and corresponding metal-free phthalocyanine derivatives that are not listed below were reported in early work.[20−25] Column chromatography was carried out on silica gel columns (Merck, Kieselgel 60, 70−230 mesh) with the indicated eluents.

$H_2Pc(^tBu)_4$ (2). A mixture of 4-(*tert*-butyl)phthalonitrile (85 mg, 0.35 mmol) and lithium (5 mg, 0.72 mmol) in 1-pentanol (3 mL) was heated to reflux under nitrogen for 4 h. After being cooled to room temperature, the resulting green solution was poured into methanol (100 mL) containing a few drops of concentrated HCl. The precipitate was collected by filtration and chromatographed on a silica gel column using CH_2Cl_2/hexane (1:1) as the eluent. A green band was developed that was collected and rotary evaporated. Repeated chromatography followed by recrystallization from CH_2Cl_2 and MeOH gave pure $H_2Pc(^tBu)_4$ as a green powder (40 mg, 47%). MS: calcd for $C_{48}H_{50}N_8$ (M$^+$), 738.4; found for $H_2Pc(^tBu)_4$, 738.7. Elemental analysis (%): calcd for $C_{48}H_{50}N_8$ (FW = 738.98) C 78.02, H 6.82, N 15.16; found for $H_2Pc(^tBu)_4$ C 77.44, H 7.05, N 14.92.

$H_2Pc(C_5H_{11})_8$ (3). A mixture of 4,5-(pentyl)phthalonitrile (94 mg, 0.35 mmol) and lithium (5 mg, 0.72 mmol) in 1-pentanol (3 mL) was heated to reflux under nitrogen for 4 h. After being cooled to room temperature, the resulting green solution was poured into methanol (100 mL) containing a few drops of concentrated HCl. The precipitate was collected by filtration and chromatographed on a silica gel column using CH_2Cl_2/hexane (1:1) as the eluent. A green band was developed that was collected and rotary evaporated. Repeated chromatography followed by recrystallization from $CHCl_3$ and MeOH gave pure $H_2Pc(C_5H_{11})_8$ as a green powder (34 mg, 36%). MS: calcd for $C_{72}H_{98}N_8$ (MH$^+$), 1075.8; found for $H_2Pc(C_5H_{11})_8$, 1075.6.

$H_2Pc(OC_5H_{11})_4$ (4). Using the procedure described above with 4-(3-pentyloxy)phthalonitrile (75 mg, 0.35 mmol) instead of 4,5-(pentyl)phthalonitrile as the starting material, $H_2Pc(OC_5H_{11})_4$ (40 mg, 53%) was obtained. MS: calcd for $C_{52}H_{58}N_8O_4$ (M$^+$), 859.5; found for $H_2Pc(OC_5H_{11})_4$, 859.2. Elemental analysis (%): calcd for $C_{52}H_{58}N_8O_4$ (FW = 859.08) C 72.70, H 6.81, N 13.04; found for $H_2Pc(OC_5H_{11})_4$ C 72.28, H 6.91, N 12.77.

$H_2Pc(OC_5H_{11})_8$ (5). Employing the above-described procedure with 4,5-(pentyloxy)phthalonitrile (105 mg, 0.35 mmol) as the starting material, $H_2Pc(OC_5H_{11})_8$ (58 mg, 55%) was obtained. MS: calcd for $C_{72}H_{98}N_8O_8$ (MH$^+$): 1203.8; found for $H_2Pc(OC_5H_{11})_8$: 1203.3. Elemental analysis (%): calcd for $C_{72}H_{98}N_8O_8 \cdot 0.5CHCl_3 \cdot 0.5CH_3OH$ (FW = 1279.32) C 68.54, H 7.92, N 8.76; found for $H_2Pc(OC_5H_{11})_8$ C 68.36, H 8.02, N 8.10.

$H_2Pc(C{\equiv}C\text{-}^tBu)_4$ (8). A mixture of 4-(*tert*-butylalkynyl)phthalonitrile (73 mg, 0.35 mmol) and lithium (5 mg, 0.72 mmol) in 1-pentanol (3 mL) was heated to reflux under nitrogen for 2 h.

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(15) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A., Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B. G.; Chen, W.; Wong, M. W.; Andres, J. L.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian 98*, revision A.9; Gaussian, Inc.: Pittsburgh, PA, 1998.

(16) Nishi, H.; Azuma, N.; Kitahara, K. *J. Heterocyclic Chem.* **1992**, *29*, 475−477.

(17) Siegl, W. O. *J. Heterocyclic Chem.* **1981**, *18*, 1613−1618.

(18) Cook, M. J.; Dunn, A. J.; Howe, S. D.; Thomson, A. J. *J. Chem. Soc., Perkin Trans. 1* **1988**, 2453−2458.

(19) Maya, E.; Haisch, P.; Vazquez, P.; Torres, T. *Tetrahedron* **1998**, *54*, 4379−4404.

(20) Zhu, P.; Lu, F.; Pan, N.; Arnold, D. P.; Zhang, S.; Jiang, J. *Eur. J. Inorg. Chem.* **2004**, 510−517.

(21) (a) Jiang, J.; Liu, R. C. W.; Mak, T. C. W.; Ng, D. K. P.; Chan, T. W. D. *Polyhedron* **1997**, *16*, 515−520. (b) Jiang, J.; Liu, W.; Lin, J.; Law, W. F.; Ng, D. K. P. *Inorg. Chim. Acta* **1998**, *268*, 49−52. (c) Jiang, J.; Xie, J.; Choi, M. T. M.;. Ng, D. K. P *J. Porphyrins Phthalocyanines* **1999**, *3*, 322−328. (d) Bian, Y.; Jiang, J.; Tao, Y.; Choi, M. T. M.; Li, R.; Ng, A. C. H.; Zhu, P.; Pan, N.; Sun, X.; Arnold, D. P.; Zhou, Z.; Li, H.-W.; Mak, T. C. W.; Ng, D. K. P. *J. Am. Chem. Soc.* **2003**, *125*, 12257−12267.

(22) (a) Bian, Y.; Wang, R.; Jiang, J.; Lee, C.-H.; Wang, J.; Ng, D. K. P. *Chem. Commun.* **2003**, 1194. (b) 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. *Helv. Chim. Acta* **2004**, *87*, 2581−2596. (c) Bian, Y.; Li, L.; Wang, D.; Choi, C.-F.; Cheng, D. F. F.; Zhu, P.; Li, R.; Dou, J.; Wang, R.; Pan, N.; Ma, C.; Ng, D. K. P.; Kobayashi, N.; Jiang, J. *Inorg. Chem.* **2004**, *43*, 7539−7544.

(23) Zhang, H.; Wang, R.; Zhu, P.; Han, J.; Lu, F.; Lee, C.-H.; Ng, D. K. P.; Cui, X.; Ma, C.; Jiang, J. *Inorg. Chem.* **2004**, *43*, 4740−4742.

(24) (a) Kobayashi, N.; Nakajima, S.; Osa, T. *Chem. Lett.* **1992**, 2415−2418. (b) Kobayashi, N.; Nakajima, S.; Ogata, H.; Fukuda, T. *Chem. Eur. J.* **2004**, *10*, 62940−6312.

(25) (a) Jiang, J.; Liu, W.; Poon, K. W.; Du, D.; Arnold, D. P.; Ng, D. K. P. *Eur. J. Inorg. Chem.* **2000**, 205−209. (b) Nyokong, T.; Furuya, F.; Kobayashi, N.; Du, D.; Liu, W.; Jiang, J. *Inorg. Chem.* **2000**, *39*, 128−135.

After being cooled to room temperature, the resulting green solution was poured into methanol (100 mL) containing a few drops of concentrated HCl. The precipitate was collected by filtration and chromatographed on a silica gel column using CH_2Cl_2 as the eluent. A green band was developed that was collected and rotary evaporated. Repeated chromatography followed by recrystallization from CH_2Cl_2 and MeOH gave pure $H_2Pc(C{\equiv}C\text{-}^tBu)_4$ as a green powder (20 mg, 27%). MS: calcd for $C_{56}H_{50}N_8$ (M^+), 834.4; found for $H_2Pc(^tBu)_4$, 834.6. Elemental analysis (%): calcd for $C_{56}H_{50}N_8$ (FW = 835.08) C 80.55, H 6.04, N 13.42; found for $H_2Pc(C{\equiv}C\text{-}^tBu)_4$ C 80.21, H 6.06, N 13.16.

$H_2Pc(\alpha\text{-}OC_5H_{11})_4$ (9). A mixture of 3-(3-pentyloxy)phthalonitrile (80 mg, 0.33 mmol) and lithium (5 mg, 0.72 mmol) in 1-pentanol (3 mL) was heated to 100 °C under nitrogen for 3 h. After being cooled to room temperature, the resulting green solution was poured into methanol (100 mL) containing a few drops of concentrated HCl. The precipitate was collected by filtration and chromatographed on a silica gel column using $CHCl_3$/MeOH (100:1) as the eluent. A green band was developed that was collected and rotary evaporated. Repeated chromatography followed by recrystallization from $CHCl_3$ and MeOH gave pure $H_2Pc(\alpha\text{-}OC_5H_{11})_4$ as a green powder (30 mg, 42% yield). MS: calcd for $C_{52}H_{58}N_8O_4$ (M^+), 859.5; found for $H_2Pc(\alpha\text{-}OC_5H_{11})_4$, 859.9. Elemental analysis (%): calcd for $C_{52}H_{58}N_8O_4$ (FW = 859.08) C 72.70, H 6.81, N 13.04; found for $H_2Pc(\alpha\text{-}OC_5H_{11})_4$ C 72.64, H 6.93, N 12.99.

$H_2Pc(\alpha\text{-}OC_5H_{11})_8$ (11). Lithium (5 mg, 0.72 mmol) was dissolved in 1-pentanol (5 mL). Then, 1,4-(pentyloxy)phthalonitrile (90 mg, 0.3 mmol) was added, and the resulting mixture was refluxed for 2 h. The green solution was cooled to room temperature and poured into methanol (100 mL) containing a few drops of concentrated HCl. The precipitate was collected by filtration and chromatographed on a silica gel column using $CHCl_3$/MeOH (100:1) as the eluent. A green band was developed that was collected and rotary evaporated. Repeated chromatography followed by recrystallization from $CHCl_3$ and MeOH gave pure $H_2Pc(\alpha\text{-}OC_5H_{11})_8$ as a green powder (39 mg, 43% yield). MS: calcd for $C_{72}H_{98}N_8O_8$ (MH^+), 1203.8; found for $H_2Pc(\alpha\text{-}OC_5H_{11})_8$, 1203.3. Elemental analysis (%): calcd for $C_{72}H_{98}N_8O_8$ (FW =1203.61) C 71.85, H 8.21, N 9.31; found for $H_2Pc(\alpha\text{-}OC_5H_{11})_8$ C 70.91, H 8.35, N 9.10.

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