Inorg. Chem. **2007**, *46*, 7136–7141

Inorganic Chemistry

Article

2,3,9,10,16,17,24,25-Octakis(octyloxycarbonyl)phthalocyanines. Synthesis, Spectroscopic, and Electrochemical Characteristics

Xueying Wang, Yuexing Zhang, Xuan Sun, Yongzhong Bian, Changqin Ma, and Jianzhuang Jiang*

Key Lab for Colloid and Interface Chemistry of Education Ministry, Department of Chemistry, Shandong University, Jinan 250100

Received March 16, 2007

A series of three novel 2,3,9,10,16,17,24,25-octakis(octyloxycarbonyl)phthalocyanine compounds M[Pc(COOC$_8$H$_{17}$)$_8$] (M = 2H, Cu, Zn) (**1**–**3**) have been synthesized via the cyclic tetramerization of 4,5-di(octyloxycarbonyl)phthalonitrile, which was obtained by a newly developed procedure with *o*-xylene as starting material, promoted with organic base 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) in the absence and presence of metal salt like M(acac)$_2$•H$_2$O (M = Cu, Zn) in *n*-octanol at 120 °C. In addition to elemental analysis, these novel octakis(octyloxycarbonyl)-substituted phthalocyanine compounds have been characterized by a series of spectroscopic methods. The electrochemistry of these compounds was also studied by cyclic voltammetry (CV) and differential pulse voltammetry (DPV) methods. A significant shift to the positive direction for both the first oxidation and the first reduction of compound **1**, relative to H$_2$Pc, reveals the electron-withdrawing nature of octyloxycarbonyl groups attached to the peripheral positions of phthalocyanine. The effect of peripheral octyloxycarbonyl substitution on the electrochemistry of the series of phthalocyanines **1**–**3** has been reasonably explained by theoretical calculation results using the density functional theory (DFT) method.

Introduction

Ever since their early synthesis at the beginning of the last century, phthalocyanines have been an important class of dyes and pigments.[1] Closely related to their unique spectroscopic and electrochemical properties,[2,3] these macromolecules have been found to be important in applications in materials science,[4] medicine,[5] optical storage,[6] and photocatalysis.[7] Because of their large conjugated molecular structure, together with strong $\pi-\pi$ interactions between aromatic rings, phthalocyanine derivatives have also been used as staple building blocks for ordered molecular systems.[8]

It is well-known that incorporating substituents onto the phthalocyanine ring is the most important method used to tune the physichemical, electrochemical, and spectroscopic properties of phthalocyanine derivatives. Thus far, various kinds of different substituents such as alkyl, alkoxy, and thioalkyl groups have been introduced onto the peripheral and/or nonperipheral positions of the phthalocyanine ligand.[9,10] However, except for the few cases of well-characterized 2(3),9(10),16(17),24(25)-tetrakis(alkoxycarbonyl)phthalo-

---

* To whom correspondence should be addressed. E-mail: jzjiang@sdu.edu.cn (J.J.).

(1) (a) Lever, A. B. P.; Leznoff, C. C. *Phthalocyanine: Properties and Applications*; VCH Publishers: 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. (d) Berezin, B. D. *Coordination Compounds of Porphyrins and Phthalocyanines*; Wiley & Sons: New York, 1981.

(2) de la Torre, G.; Vaquez, P.; Agullo-Lopez, F.; Torres, T. *Chem. Rev.* **2004**, *104*, 3723.

(3) (a) Ou, Z.; Shen, J.; Kadish, K. M. *Inorg. Chem.* **2006**, *23*, 9570.(b) Zhu, P.; Lu, F.; Pan, N.; Arnold, D. P.; Zhang, S.; Jiang, J. *Eur. J. Inorg. Chem.* **2004**, 510.

(4) Hanack, M.; Lang, M. *Adv. Mater.* **1994**, *6*, 819.

(5) (a) Rosenthal, I.; Ben-Hur, E. *Int. J. Radiat. Biol.* **1995**, *67*, 85. (b) Bonnett, R. *Chem. Soc. Rev.* **1995**, 19.

(6) (a) Gregory, P. *High-Technology Applications of Organic Colorants*; Plenum Publishing: New York, 1991. (b) Ao, R.; Kilmmert, L.; Haarer, D. *Adv. Mater.* **1995**, *7*, 495. (c) Birkett, D. *Chem. Ind.* **2000**, 178.

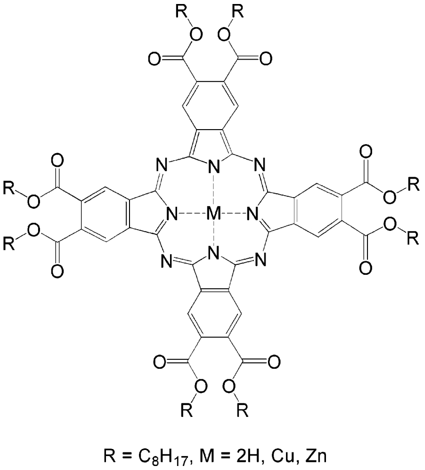
(7) Wöhrle, D.; Schlettwein, D.; Schnurpfeil, G.; Schneider, G.; Karmann, E.; Yoshida, T.; Kaneko, M. *Polym. Adv. Technol.* **1995**, *6*, 118.

(8) (a) Yoshimoto, S.; Higa, N.; Itaya, K. *J. Am. Chem. Soc.* **2004**, *27*, 8544. (b) Johannes, A. A.; Elemans, W.; van Hameren, R.; Nolte, R. J. M.; Rowan, A. E. *Adv. Mater.* **2006**, *18*, 1251. (c) Wang, X.; Chen, Y.; Liu, H.; Jiang, J. *Thin Solid Films* **2006**, *496*, 619. (d) Zangmeister, R. A. P.; Smolenyak, P. E.; Drager, A. S.; O'Brien, D. F.; Armstrong, N. R. *Langmuir* **2001**, *17*, 7071.

(9) (a) Nazeeruddin, Md. K.; Humphry-Baker, R.; Gratzel, M.; Murrer, B. *Chem. Commun.* **1998**, *6*, 719. (b) Piechocki, C.; Simon, J.; Skoulios, A.; Guillon, D.; Weber, P. *J. Am. Chem. Soc.* **1982**, *104*, 5245.

10.1021/ic700517e CCC: $37.00

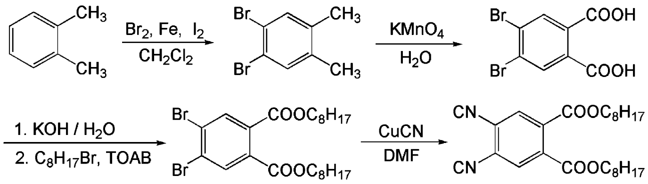
Scheme 1. Schematic Molecular Structure of 2,3,9,10,16,17,24,25-Octakis(octyloxycarbonyl)phthalocyanines **1**−**3**



cyanine derivatives,[11,12] there a reliable report on octakis(alkoxycarbonyl)phthalocyanine derivatives still does not exist, despite their potential application in photodynamic therapy (PDT). In 1972, Boston and Bailar claimed to have synthesize octakis(octacarboxylated)phthalocyanine by the tetramerization of 1,2,4,5-tetracyanobenzene or pyromellitic dianhydride without the use of a mass spectrum,[13] the only evidence being the elemental analysis and an IR spectrum. With this octakis(octacarboxylated)phthalocyanine as a starting material, further reaction with alcohol through acyl chlorination led to octakis(alkoxycarbonyl)phthalocyanines accordingly, again without mass spectroscopic evidence and elemental analysis.[14]

As part of our continuous effort to develop new phthalocyanine molecular materials, we have developed an efficient synthetic pathway for preparing 4,5-di(octyloxycarbonyl)phthalonitrile with *o*-xylene as the starting material. Using this as the starting material, corresponding octakis(octyloxycarbonyl)phthalocyanines have been easily prepared and isolated in good yield. In the present article, we describe the synthesis, spectroscopic characteristics, and electrochemistryof2,3,9,10,16,17,24,25-octakis(octyloxycarbonyl)phthalocyanine compounds $\mathrm{M[Pc(COOC_8H_{17})_8]}$ (M = 2H, Cu, Zn) (**1**−**3**), Scheme 1, together with those of the novel 4,5-di(octyloxycarbonyl)phthalonitrile precursor for the first time.

Scheme 2. Preparation of 4,5-Di(octyloxycarbonyl)phthalonitrile with *o*-Xylene as the Starting Material



Results and Discussion

Synthesis of 2,3,9,10,16,17,24,25-Octakis(octyloxycarbonyl)phthalocyanines. Despite the huge number of various kinds of substituted phthalocyanine compounds reported thus far, attempts at making octakis(alkoxycarbonyl)phthalocyanines rarely appear. As mentioned above, Boston and Bailar claimed the synthesis of 2,3,9,10,16,17,24,25-octakis(octacarboxylated)phthalocyanine via the corresponding 2,3,9,10,16,17,24,25-octakis(cyano)phthalocyanine.[13] However, except for the elemental analysis and IR spectrum, the authors did not give any other spectroscopic evidence.[13] Because of the difficulty in separating and purifying the low yield of 2,3,9,10,16,17,24,25-octakis(cyano)phthalocyanine from the main oligomeric and polymeric byproducts even at the first step,[15] in turn the preparation of octakis(alkoxycarbonyl)phthalocyanines via octakis(octacarboxylated)phthalocyanines is not practically applicable. Nevertheless, the only evidence for 2,3,9,10,16,17,24,25-octakis(dodecyloxycarbonyl)phthalocyaninato copper prepared according to the above-mentioned procedure is a strong absorption band at 630 nm, together with a relatively weak absorption at 684 nm in the electronic absorption spectrum in $CHCl_3$.[14] This clearly conflicts with the result of the present work that one intense Q band at 684 nm with a very weak vibronic band at 615 nm was found for 2,3,9,10,16,17,24,25-octakis(octyloxycarbonyl)phthalocyaninato copper (**2**) in the same $CHCl_3$ solution.

It is well-known that the most common way to prepare phthalocyanines is the organic-base-promoted tetramerization of phthalonitriles. With this in mind, we developed an effective pathway to prepared 4,5-di(alkoxycarbonyl)phthalonitrile with *o*-xylene as the starting material, after a series of reactions involving substitution, oxidation, bromination, and phase transfer catalysis esterification, Scheme 2. As expected, cyclic tetramerization of the obtained 4,5-di(octyloxycarbonyl)phthalonitrile in the presence of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) in *n*-octanol at 120 °C leads to the formation of metal-free 2,3,9,10,16,17,24,25-octakis(octyloxycarbonyl)phthalocyanine $\mathrm{H_2[Pc(COOC_8H_{17})_8]}$ (**1**) in relatively good yield. A similar reaction in the presence of a metal−salt such as $\mathrm{M(acac)_2 \cdot H_2O}$ (M = Cu, Zn) induces the isolation of the corresponding metal complexes $\mathrm{M[Pc(COOC_8H_{17})_8]}$ (M = Cu, Zn) (**2**, **3**), also in good yields. To the best of our knowledge, these compounds represent the first examples of octakis(alkoxycarbonyl)phthalocyanine derivatives that have been unambiguously characterized by a wide range of spectroscopic techniques.

---

(10) (a) Jiang, J.; Liu, R. C. W.; Mak, T. C. W.; Chan, T. W. D.; Ng, D. K. P. *Polyhedron.* **1997**, *16*, 515. (b) Jiang, J.; Liu, W.; Law, W. F.; Lin, J.; Ng, D. K. P. *Inorg. Chim. Acta.* **1998**, *268*, 141. (c) Jiang, J.; Xie, J.; Choi, M. T. M.; Yan, Y.; Sun, S.; Ng, D. K. P. *J. Porphyrins Phthalocyanines.* **1999**, *3*, 322. (d) Liu, W.; Jiang, J.; Du, D.; Arnold, D. P. *Aust. J. Chem.* **2000**, *53*, 131. (e) Winter, G.; Heckmann, H.; Haisch, P.; Eberhardt, W.; Hanack, M.; Lüer, L.; Egelhaaf, H.-J.; Oelkrug, D. *J. Am. Chem. Soc.* **1998**, *120*, 11663.

(11) (a) Mo, X.; Chen, H.; Wang, Y.; Shi, M.; Wang, M. *J. Phys. Chem. B* **2005**, 109, 7659. (b) He, J.; Hagfeldt, A.; Lindquist, S. *Langmuir* **2001**, *17*, 2747. (c) Pasimeni, L.; Meneghetti, M.; Rella, R.; Valli, L.; Granito, C.; Troisi, L. *Thin Solid Films* **1995**, *265*, 58.

(12) (a) Shirai, H.; Yagi, S.; Suzuki, A.; Hojo, N. *Makromol. Chem.* **1977**, *178*, l889. (b) Shirai, H.; Maruyama, A.; Kobayashi, K.; Hojo, N. *Makromol. Chem.* **1980**, *181*, 575.

(13) Boston, D. R.; Bailar, J. C. *Inorg. Chem.* **1972**, *12*, 1579.

(14) (a) Osburn, E. J.; Chau, L.-K.; Chen, S.-Y.; Collins, N.; O'Brien, D. F.; Armstrong, N. R. *Langmuir* **1996**, *12*, 4785. (b) Ogawa, K.; Kinoshita, S.; Yonehara, H.; Nakahara, H.; Fukuda, K. *J. Chem. Soc., Chem. Commun.* **1989**, 477.

(15) Achar, B. N. *J. Mater. Chem.* **2000**, *10*, 1979.

Table 1. Analytical and Mass Spectroscopic Data for the Three 2,3,9,10,16,17,24,25-octakis(octyloxycarbonyl)phthalocyanine Compounds **1**−**3**[a]

			M^+/MH^+	analysis (%)		
compound	molecular formula	yield (%)	(*m/z*)	C	H	N
1	$C_{104}H_{146}N_8O_{16}$	52	1765.0	69.75	8.24	6.36
			(1765.3)[b]	(69.79)	(8.22)	(6.25)[d]
2	$CuC_{104}H_{144}N_8O_{16}$	82	1826.8	68.58	8.07	6.21
			(1826.8)[b]	(68.41)	(7.95)	(6.14)
3	$ZnC_{104}H_{144}N_8O_{16}$	59	1827.5	67.10	7.92	6.24
			(1827.7)[c]	(67.41)	(7.83)	(6.03)[d]

[a] Calculated values given in parentheses. [b] The value corresponds to the most abundant isotopic peak of the protonated molecular ion [(HM)$^+$]. [c] The value corresponds to the most abundant isotopic peak of the molecular ion (M$^+$). [d] Contains 0.25 equivs of solvated $CHCl_3$.

Table 2. Electronic Absorption Data for Compounds **1**−**3** in CH_2Cl_2

compound	λ_{max}/nm (log ϵ)				
1	349 (2.75)	607 (2.28)	646 (2.47)	668 (2.95)	705 (3.04)
2	350 (2.82)	615 (2.49)		684 (3.22)	
3	356 (2.78)	618 (2.52)		685 (3.31)	

Satisfactory elemental analysis results have been obtained for each of these three newly prepared octyloxycarbonyl-substituted phthalocyanine compounds, after repeated column chromatography and recrystallization (Table 1).

Spectroscopic Characterization. Each of these three novel octakis(octyloxycarbonyl)phthalocyanine compounds were well characterized by a series of spectroscopic methods including MALDI-TOF mass, ^{1}H NMR, ^{13}C NMR, UV−vis, and IR spectroscopy. The MALDI-TOF mass spectra of these compounds clearly showed intense signals for the molecular ion (M)$^+$ or the protonated molecular ion (MH)$^+$ (Table 1). The isotopic pattern closely resembled the simulated one, as exemplified by the spectrum of **3** given in Figure S1 (Supporting Information).

The electronic absorption spectra of the series of octakis(octyloxycarbonyl)phthalocyanine compounds **1**−**3** were recorded in both $CHCl_3$ and CH_2Cl_2, and the data are summarized in Tables 2 and S1 (Supporting Information). Figure 1 shows the UV−vis spectra of metal-free compound **1** and copper complex **2**. Both the metal-free and metal compounds display typical features of unsubstituted phthalocyanine counterparts.[1,16] As shown in Figure 1, the absorption spectra show a typical Soret band at 349−356 nm. The Q band for octakis(octyloxycarbonyl)phthalocyaninato copper complex **2** is observed at 684 nm, with a very weak vibronic band at 615 nm. In contrast, compound **1** gives typical, split Q bands of metal-free phthalocyanine at 705 and 668 nm, with concomitant weak vibronic bands at 646 and 607 nm, respectively, due to the lowering in molecular symmetry from C_4 for metal complex **2** to C_2 for metal-free compound **1**. In comparison with the unsubstituted counterparts, the Q absorption bands for both the metal-free and metal complexes take a significant red shift,[1,16] revealing the relatively smaller HOMO−LUMO gap of octakis(octyloxycarbonyl)phthalocyanines. This result is in line with the electrochemical studies and reasonably explained by considering the energy levels of the frontier molecular orbitals of corresponding compounds, which were obtained by calculations using the density functional theory (DFT) method, vide infra.

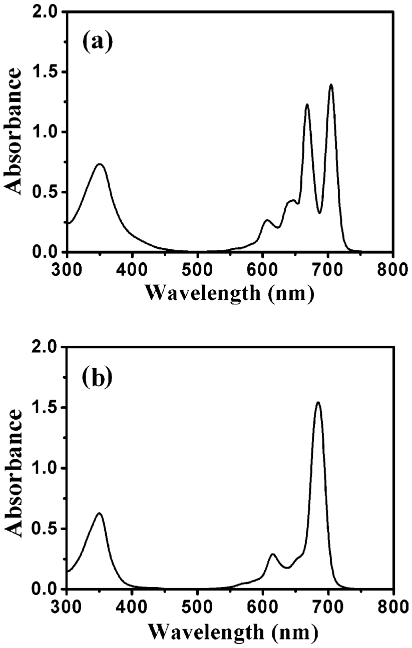


Figure 1. Electronic absorption spectra of (a) $H_2[Pc(COOC_8H_{17})_8]$ (**1**) and (b) $Cu[Pc(COOC_8H_{17})_8]$ (**2**) in CH_2Cl_2.

It has been proven that vibrational spectroscopy is a versatile technique for studying the intrinsic properties of phthalocyanine compounds.[17] In the IR spectra of **1**−**3**, in addition to the absorption bands contributed from the central aromatic Pc macrocycle including the wagging and torsion vibrations of C−H groups, isoindole ring stretching vibrations, and the C=N aza group stretching vibrations,[17] the newly observed absorptions at 2955−2956, 2920−2927, 2871−2872, 2852, 1725−1731, 1274−1278, and 1085−1092 cm^{-1} are attributed to the asymmetiric and symmetric C−H stretching vibrations, C=O stretching vibrations, and the asymmetric and symmetric C−O−C stretching vibrations of the octyloxycarbonyl groups, respectively. It is worth noting that the predicted asymmetrical N−H stretching vibration mode located at 3000 cm^{-1} for the metal-free compound **1** cannot be distinguished from the very strong water absorption in the same region, according to our previous calculations.[18]

To assist the assignments of the IR absorption bands, an infrared spectrum for simplified mode $ZnPc(COOCH_3)_8$ has been calculated using the density functional theory (DFT) method. The calculated vibrational frequencies were scaled by a factor of 0.96.[19] According to the calculation results,

---

(16) Li, R.; Zhang, X.; Zhu, P.; Ng, D. K. P.; Kobayashi, N.; Jiang, J. *Inorg. Chem.* **2006**, *45*, 2330.

(17) (a) Jiang, J.; Bao, M.; Rintoul, L.; Arnold, D. P. *Coord. Chem. Rev.* **2006**, *250*, 424. (b) Bao, M.; Wang, R.; Rintoul, L.; Arnold, D. P.; Jiang, J. *Vib. Spectrosc.* **2006**, *40*, 47. (c) Su, W.; Bao, M.; Jiang, J. *Vib. Spectrosc.* **2005**, *39*, 186. (d) Bao, M.; Bian, Y.; Rintoul, L.; Wang, R.; Arnold, D. P.; Ma, C.; Jiang, J. *Vib. Spectrosc.* **2004**, *34*, 283. (e) Bao, M.; Pan, N.; Ma, C.; Arnold, D. P.; Jiang, J. *Vib. Spectrosc.* **2003**, *32*, 175. (f) Lu, F.; Bao, M.; Ma, C.; Zhang, X.; Arnold, D. P.; Jiang, J. *Spectrochimica Acta Part A.* **2003**, *59*, 3273. (g) Jiang, J.; Arnold, D. P.; Yu, H. *Polyhedron.* **1999**, *18*, 2129.

(18) Zhang, X.; Zhang, Y.; Jiang, J. *Vib. Spectrosc.* **2003**, *33*, 153.

Table 3. Half-Wave Redox Potentials of Octakis(octyloxycarbonyl)phthalocyanines (V versus Fe/Fe$^+$) in CH_2Cl_2 Containing 0.1 M TBAP

compound	**Oxd$_2$**	**Oxd$_1$**	**Red$_1$**	**Red$_2$**	**Red$_3$**^{a}	$\Delta E°_{1/2}$^{b}
1	+1.04	+0.77	−0.88	−1.18	−1.92	1.65
2	+1.10	+0.64	−0.99	−1.31	−2.00	1.63
3	+1.10	+0.48	−1.10	−1.36	−1.96	1.58
H_2Pc^{c}	+0.64	+0.43	−1.28	−1.80	−2.40	1.71

[a] Recorded by DPV. [b] $\Delta E°_{1/2}$ is the potential difference between the first oxidation and first reduction processes. [c] Cited from ref 16.

the C−H stretching vibrations of methyloxycarbonyl groups should appear at 2958 cm^{-1}, whereas the C═O stretching vibrations should appear at 1738 cm^{-1} and asymmetiric and symmetric C−O−C stretching vibrations should appear at 1260 and 1092 cm^{-1}, respectively. All of these results are in good accordance with the experimental observations, as detailed above.

Because of the paramagnetic nature of the divalent copper in $Cu[Pc(COOC_8H_{17})_8]$ (**2**), ^{1}H NMR and ^{13}C NMR spectra only for $H_2[Pc(COOC_8H_{17})_8]$ (**1**) and $Zn[Pc(COOC_8H_{17})_8]$ (**3**) were recorded in $CDCl_3$, which provided strong support for the identity of these compounds. In ^{1}H NMR spectra, both metal-free and zinc phthalocyanine compounds **1** and **3** simply display a singlet at ca. 9.65 δ for the eight phthalocyanine α ring protons, whereas all of the aliphatic protons in the peripheral octyloxycarbonyl groups give signals in the range of 0.89−4.65 δ, with correct integrations. The isoindole protons in metal-free compound **1** show a singlet in high field at −1.24 δ (Figure S2, Supporting Information). In the ^{13}C NMR spectra, the carbonyl carbon atoms of the side chains display signal at ca. 168 δ for both **1** and **3**, whereas the aromatic carbon atoms in the phthalocyanine ring show signals at ca. 155, 138, 133, and 124 δ, respectively. For both compounds, the signals for the eight carbon atoms in the aliphatic octyl groups appear in the range of 14−67 δ, (Figure S3, Supporting Information).

Electrochemical Properties. The redox behavior of the octakis(octyloxycarbonyl)phthalocyanines **1**−**3** was studied by cyclic voltammetry (CV) and differential pulse voltammetry (DPV) in CH_2Cl_2. These compounds exhibited two quasireversible or irreversible one-electron oxidations and three quasireversible or irreversible one-electron reductions, all of which can be attributed to ligand-based redox processes. The half-wave potentials are summarized in Table 3. Representative cyclic voltammograms and differential pulse voltammograms for $Zn[Pc(COOC_8H_{17})_8]$ (**2**) are displayed in Figure 2.

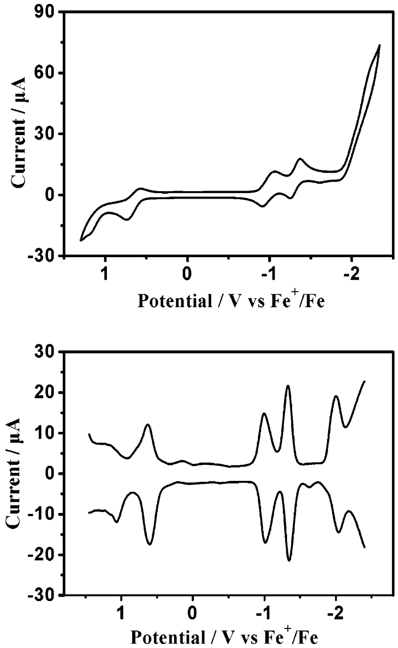


Figure 2. Cyclic voltammetry (CV) and differential pulse voltammetry (DPV) of $Cu[Pc(COOC_8H_{17})_8]$ (**2**) in CH_2Cl_2 containing 0.1 M $[NBu_4][ClO_4]$ at scan rates of 20 and 10 mV s^{-1}, respectively.

The effect of peripheral octyloxycarbonyl substitution at the phthalcoyanine ring is clearly reflected by the shift in the half-wave potentials, in particular of the first oxidation and first reduction together with their difference, of metal-free phthalocyanine **1**. As can be seen in Table 3, the substitution of eight octyloxycarbonyl groups at the peripheral positions of the phthalocyanine ring induces a significant shift to the positive direction for both the first oxidation and the first reduction and a slight decrease in the difference between these two redox processes, relative to H_2Pc, revealing the electron-withdrawing nature of octyloxycarbonyl groups attached onto the peripheral positions of the phthalocyanine ring. It is worth noting that the slightly smaller potential difference between the first oxidation and first reduction of metal-free octakis(octyloxycarbonyl)phthalocyanine **1** in comparison with unsubstituted H_2Pc is in good agreement with the red-shift of the Q absorption band of the former species relative to the later one. In line with previous results,[20,21] substitution of the stronger Lewis acid Cu^{2+} in compound **2** by the weaker Lewis acid Zn^{2+} in **3** induces an obvious shift to the *negative* direction for both the first oxidation and the first reduction (Table 3).

To understand the effect of octyloxycarbonyl substituents on the electrochemistry of phthalocyanine derivatives **1**−**3**, we carried out molecular orbital (MO) calculations on $ZnPc(COOCH_3)_8$ using the DFT method. According to the calculations, the introduction of eight octyloxycarbonyl groups onto the peripheral positions of the phthalocyanine skeleton induces a significant negative shift in the energy level of both the HOMO and the LUMO. The calculated energy of the HOMO and the LUMO is −5.49 and −3.36 eV respectively for $ZnPc(COOCH_3)_8$ and −4.94 and −2.75 eV for ZnPc,[22] respectively, with a HOMO−LUMO gap of 2.13 and 2.19 eV. All of these results are in line with the electrochemical experimental findings, as detailed above.

The HOMO and LUMO maps of $ZnPc(COOCH_3)_8$ are shown in Figure S4 (Supporting Information). As can be seen, in addition to the main contribution from the *p* orbitals

---

(19) NIST Computational Chemistry Comparison and Benchmark Database, NIST Standard Reference Database Number 101, Release 12, Aug 2005, Editor: Russell D. Johnson III, http://srdata.nist.gov/cccbdb.

(20) Mazur, U.; Hipps, K. W. *J. Phys. Chem. B* **1999**, *103*, 9721.

(21) Contakes, S. M.; Beatty, S. T.; Dailey, K. K.; Rauchfuss, T. B.; Fenske, D. *Organometallics* **2000**, *19*, 4767.

(22) Liu, Z.; Zhang, X.; Zhang, Y.; Jiang, J. *Spectrochim. Acta Part A* Doi: 10.1016/j.saa.200610.013 web released.

of the carbon and nitrogen atoms of the central Pc ring, oxygen atoms from the electron-withdrawing C═O groups attached onto the peripheral positions of the phthalocyanine ring also contribute to the HOMO of $ZnPc(COOCH_3)_8$. As a result, the energy level of the HOMO for $ZnPc(COOCH_3)_8$ is lower than that of ZnPc. This is also true for the LUMO of $ZnPc(COOCH_3)_8$ as a result of the additional contribution from both the carbon and oxygen atoms of the peripheral C═O groups. As described above, extension of the phthalocyanine π system as a result of the contribution from the peripheral C═O groups results in a decrease in the HOMO−LUMO gap of $ZnPc(COOCH_3)_8$, relative to ZnPc. This is also in good agreement with the experimental observations (Table 3).

Conclusion

Briefly summarizing the above, a series of three novel 2,3,9,10,16,17,24,25-octakis(octyloxycarbonyl)phthalocyanine compounds have been prepared and fully characterized with a wide range of spectroscopic methods for the first time. Both electrochemical and theoretical calculation results reveal the electron-withdrawing nature of the octyloxycarbonyl groups attached onto the peripheral positions of phthalocyanine ring.

Experimental Section

General Remarks. *n*-Octanol was distilled from sodium. Dimethylformamide (DMF) was distilled from anhydrous $MgSO_4$. Hexane used for chromatography was distilled from anhydrous $CaCl_2$. Column chromatography was carried out on a silica gel column (Merck, Kieselgel 60, 70−230 mesh) with the indicated eluents. The electrolyte $[Bu_4N][ClO_4]$ was recrystallized twice from tetrahydrofuran. Dichloromethane for voltammetric studies was freshly distilled from CaH_2 under nitrogen. All of the other reagents and solvents such as *o*-xylene, $Cu(acac)_2 \cdot H_2O$, and $Zn(acac)_2 \cdot H_2O$ were used as received.

^1H NMR and ^{13}C NMR spectra were recorded on a Bruker DPX 300 spectrometer in $CDCl_3$. Spectra were referenced internally using the residual solvent resonances ($\delta = 7.26$ for ^1H NMR) relative to $SiMe_4$. Electronic absorption spectra were recorded on a Hitachi U-4100 spectrophotometer. IR spectra were recorded as KBr pellets using a Bio-Rad FTS-165 spectrometer with 2 cm^{-1} resolution. MALDI-TOF mass spectra were taken on a Bruker BIFLEX III ultrahigh resolution Fourier transform ion cyclotron resonance mass spectrometer with R-cyano-4-hydroxycinnamic acid as a matrix. Elemental analyses were performed by the Institute of Chemistry, Chinese Academy of Sciences.

Electrochemical measurements were carried out with a BAS CV-50W voltammetric analyzer. The cell comprised inlets for a glassy carbon disk working electrode of 2.0 mm in diameter and a silverwire counter electrode. The reference electrode was Ag/Ag^+ (a solution of 0.01M $AgNO_3$ and 0.1M 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 Fe^+/Fe couple. Typically, a 0.1 M solution of $[NBu_4][ClO_4]$ in CH_2Cl_2 containing 0.5 M of sample was purged with nitrogen for 10 min, and then the voltammograms were recorded at ambient temperature. The scan rates were 20 and 10 mV s^{-1} for CV and DPV, respectively.

Computational Details. The primal input structure of $Zn[Pc(COOCH_3)_8]$ was obtained by putting eight methyloxycarbonyl groups onto the peripheral positions of ZnPc. The hybrid density functional B3LYP (Becke−Lee−Young−Parr composite of the exchange-correlation functional) method was used for both geometry optimizations and property calculations.[23] In all of the cases, the 6-31G(d) basis set was used.[24] The Berny algorithm using redundant internal coordinates was employed in energy minimization, and the default cutoffs were used throughout.[25] C_4 symmetry for this compound in the input structure was detected and then enforced by the program. Using the energy-minimized structure generated in the previous step, normal coordinate analyses were carried out. The primarily calculated vibrational frequencies were scaled by a factor of 0.96.[19] All of the calculations were carried out using the *Gaussian 03* program[26] in the IBM P690 system at the Shandong Province High Performance Computing Centre.

Preparation of 1,2-Dimethyl-4,5-dibromobenzene. To an ice-cold suspension of *o*-xylene (24 mL, 0.2 mol), iodine (2.5 g, 10 mmol), and iron powder (0.6 g, 10 mmol) in dichloromethane (30 mL), a solution of bromine (20.5 mL, 0.4 mol) in dichloromethane (10 mL) was added dropwise over 6 h. The mixture was stirred for 38 h at 0 °C and another 6 h at room temperature. After washing and adjusting the pH value to 7 using a NaOH solution (5%) followed by a $NaHSO_3$ solution (5%), the reaction mixture was dried over anhydrous Na_2SO_4. Evaporation of the solvent followed by recrystallization in methanol gave the pure target compound as white crystals (32.7 g, 62%). ^1H NMR ($CDCl_3$, 300 MHz) δ: 7.37 (s, 2 H, benzene ring), 2.18 (s, 6 H, CH_3); MS: an isotopic cluster peaking at *m*/*z* 264.0, calcd for $C_8H_8Br_2$, $[M]^+$ 264.0; Anal. Calcd for $C_8H_8Br_2$: C, 36.40; H, 3.05. Found: C, 36.36; H, 2.92.

Preparation of 4,5-Dibromo-*o*-phthalic acid. A mixture of 1,2-dimethyl-4,5-dibromobenzene (6.5 g, 0.025 mol) and $KMnO_4$ (15.8 g, 0.1 mol) in water (200 mL) was heated to reflux for 6 h and then cooled to room temperature. After reducing the unreacted $KMnO_4$ with $NaHSO_3$, the pH of the mixture was adjusted to greater than 12 using KOH. The mixture was then filtered through a sintered glass funnel, and the filtrate was slowly acidified to a pH value of 2 using HC1 (18 M). Then white precipitate was obtained by filtration and washed with dilute HCl solution (0.1M, 7.3 g, 90%). It is worth noting that a satisfactory ^1H NMR spectrum for this compound could not be recorded because of its limited solubility in common organic solvents, which also makes it very hard to further purify this compound by either column chromatography or recrystallization. As detailed below, few elemental analysis results were obtained for this compound. MS: an isotopic cluster

---

[23] (a) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785. (b) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648.

[24] (a) Hay, P. J.; Wadt, W. R. *J. Chem. Phys.* **1985**, *82*, 299. (b) Jr. Dunning, T. H.; Hay, P. J. In *Modern Theoretical Chemistry*; Schaefer, H. F., III, Ed.; Plenum Publishing: New York, 1976; Vol. 3.

[25] Peng, C.; Ayala, P. Y.; Schlegel, H. B.; Frisch, M. J. *J. Comput. Chem.* **1996**, *17*, 49.

[26] Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J. A., Jr.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A. *Gaussian 03*, revision C.02; Gaussian, Inc.: Wallingford, CT, 2004.

peaking at *m*/*z* 323.2, calcd for $C_8H_4O_4Br_2$, $[M]^+$ 323.9; Anal. Calcd for $C_8H_4O_4Br_2$: C, 29.66; H, 1.24. Found: C, 27.73; H, 1.20.

Preparation of 4,5-Dibromo-di-*n*-octylphthalate. A mixture of 4,5-dibromo-*o*-phthalic acid (3.24 g, 0.01 mol) and KOH (1.12 g, 0.02 mol) completely dissolved in water (100 mL) was treated with 1-bromooctane (3.86 g, 0.02 mol). The resulting solution was then heated to reflux for 4 h in the presence of tetraoctyl ammonium bromide (TOAB, 2 g) as a phase transfer catalyst.[27] The reaction mixture was extracted with toluene, and the combined extracts were washed with water, dried over anhydrous $MgSO_4$, and evaporated. The residue was purified by silica gel column chromatography with chloroform as the eluent to give 4,5-dibromo-di-*n*-octylphthalate as a pale-yellow oil, 4.22 g, 77%. ^1H NMR ($CDCl_3$, 300 MHz) δ: 7.94 (s, 2 H, benzene ring), 4.29 (t, $J = 5.1$, 4 H, CH_2), 1.72 (p, $J = 5.4$, 4 H, CH_2), 1.40−1.28 (br m, 20 H, $CH_2CH_2CH_2CH_2CH_2$), 0.88 (t, $J = 5.4$, 6 H, CH_3); MS: an isotopic cluster peaking at *m*/*z* 441.7, calcd for $C_{24}H_{36}O_4Br_2$, $[MH]^+$ 441.6; Anal. Calcd for $C_{24}H_{36}O_4Br_2$: C, 52.57; H, 6.62. Found: C, 51.56; H, 6.38.

Preparation of 4,5-Di(octyloxycarbonyl)phthalonitrile. A mixture of 4,5-dibromo-di-*n*-octylphthalate (5.48 g, 0.01 mol) and CuCN (1.79 g, 0.02 mol) in DMF (100 mL) was heated to reflux for 2 h under nitrogen. After being cooled to room temperature, the mixture was poured into water (200 mL) and then extracted with toluene (3 × 35 mL). The combined extracts were washed with water, dried over anhydrous $MgSO_4$, and evaporated. The crude product was chromatographed over a silica gel column with hexane/chloroform (1:1) as the eluent, giving white crystals after recrystallization in methanol (1.19 g, 27%). ^1H NMR ($CDCl_3$, 300 MHz) δ: 7.94 (s, 2 H, benzene ring), 4.29 (t, $J = 5.1$, 4 H, CH_2), 1.72 (p, $J = 5.4$, 4 H, CH_2), 1.40−1.28 (br m, 20 H, $CH_2CH_2CH_2CH_2CH_2$), 0.88 (t, $J = 5.4$, 6 H, CH_3); MS: an isotopic cluster peaking at *m*/*z* 549.5, calcd for $C_{26}H_{36}N_2O_4$, $[MH]^+$ 549.4; Anal. Calcd for $C_{26}H_{36}O_4N_2$: C, 70.88; H, 8.24; N, 6.36. Found: C, 70.87; H, 8.22; N, 6.32.

Preparation of 2,3,9,10,16,17,24,25-Octakis(octyloxycarbonyl)phthalocyanine $H_2[Pc(COOC_8H_{17})_8]$ (1). 4,5-Di(octyloxycarbonyl)phthalonitrile (0.44 g, 1 mmol) was dissolved in *n*-octanol (5 mL), which was heated at 120 °C for 3 h under nitrogen in the presence of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU, 1 mL). After being cooled to room temperature, the mixture was evaporated under reduced pressure, and the residue was chromatographed on a silica gel column using $CHCl_3$/hexane (1:3) as the eluent. A green band was developed, which was collected and rotary evaporated. Repeated chromatography followed by recrystallization from $CHCl_3$ and MeOH gave pure $H_2[Pc(COOC_8H_{17})_8]$ as a green powder (230 mg, 52% yield). ^1H NMR ($CDCl_3$, 300 MHz) δ: 9.67 (s, 8 H, Pc H_α), 4.65 (t, $J = 7.2$, 16 H, OCH_2), 2.03 (p, $J = 7.2$, 16 H, CH_2), 1.62−1.35 (br m, 80 H, $CH_2CH_2CH_2CH_2CH_2$), 0.91 (t, $J = 6.9$, 24 H, CH_3), −1.24 (s, 2 H). ^{13}C NMR ($CDCl_3$, 75 MHz) δ: 167.67, 155.76, 137.70, 134.64, 124.59, 66.75, 31.90, 29.42, 29.32, 28.83, 26.13, 22.70, 14.11.

Preparation of 2,3,9,10,16,17,24,25-Octakis(octyloxycarbonyl)phthalocyaninato Copper Complex $Cu[Pc(COOC_8H_{17})_8]$ (2). A mixture of 4,5-di(octyloxycarbonyl)phthalonitrile (0.44 g, 1 mmol), $Cu(acac)_2{\cdot}H_2O$ (0.14 g, 0.5 mmol), and 1,8-diazabicyclo-[5.4.0]undec-7-ene (DBU, 1 mL) in *n*-octanol (5 mL) was heated at 120 °C for 3 h under nitrogen. After being cooled to room temperature, the mixture was evaporated under reduced pressure, and the residue was chromatographed on a silica gel column using $CHCl_3$/hexane (1:2) as the eluent. After a small, green band containing the metal-free phthalocyanine appeared, the second green band containing the target 2,3,9,10,16,17,24,25-octakis(octyloxycarbonyl)phthalocyaninato copper complex $Cu[Pc(COOC_8H_{17})_8]$ was developed. Repeated chromatography followed by recrystallization from $CHCl_3$ and MeOH gave blue powder (374 mg, 82% yield).

Preparation of 2,3,9,10,16,17,24,25-Octakis(octyloxycarbonyl)phthalocyaninato Zinc Complex $Zn[Pc(COOC_8H_{17})_8]$ (3). By employing the procedure described above using $Zn(acac)_2{\cdot}H_2O$ instead of $Cu(acac)_2{\cdot}H_2O$ as the starting material, compound **3** was obtained after repeated chromatography with $CHCl_3$/hexane (1:2) as the eluent, followed by recrystallization from $CHCl_3$ and MeOH as a green powder (270 mg, 59% yield). ^1H NMR ($CDCl_3$, 300 MHz) δ: 9.64 (s, 8 H, Pc H_α), 4.37 (t, $J = 6.9$, 16 H, OCH_2), 1.83 (p, $J = 7.2$, 16 H, CH_2), 1.59−1.34 (br m, 80 H, $CH_2CH_2CH_2CH_2CH_2$), 0.89 (t, $J = 6.9$, 24 H, CH_3). ^{13}C NMR ($CDCl_3$, 75 MHz) δ: 168.13, 153.79, 139.80, 132.58, 123.82, 66.70, 31.87, 29.35, 29.27, 28.60, 26.00, 22.68, 14.10.

Acknowledgment. Financial support from the Natural Science Foundation of China (Grants 20325105, 20431010, 20601017, and 50673051), the Ministry of Education of China, and Shandong University are gratefully acknowledged. We are also grateful to the Shandong Province High Performance Computing Centre for a grant of computer time.

Supporting Information Available: Experimental and simulated isotopic pattern for the molecular ion of $Zn[Pc(COOC_8H_{17})_8]$ (**3**) shown in the MALDI-TOF mass spectrum; ^1H NMR spectrum for $H_2[Pc(COOC_8H_{17})_8]$ (**1**) in $CDCl_3$; ^{13}C NMR spectrum for $Zn[Pc(COOC_8H_{17})_8]$ (**3**) in $CDCl_3$; molecular orbital maps of the HOMO and the LUMO for $Zn[Pc(COOCH_3)_8]$ in two perspective views; electronic absorption data for compounds **1**−**3** in $CHCl_3$. This material is available free of charge via the Internet at http://pubs.acs.org.

IC700517E

---

[27] Makosza, M. *Pure Appl. Chem.* **2000**, *72*, 1399.