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Selective Ligation to Sterically Isolated Metallophthalocyanines

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A new class of sterically hindered phthalocyanine has been synthesized and characterized. Pentaphenylbenzene units were introduced at the periphery of each phthalocyanine to yield a sterically protected metal center. The attachment of the bulky oligophenylbenzene units resulted in the complete isolation of individual MPc molecules. The pockets around a cobalt center affect selectivity in the ligation of pyridines that have different sizes and shapes.

Phthalocyanines (Pc's) possess a large, flat π-conjugation system, which provides functional materials with interesting photophysical, catalytic, optoelectronic, conductometric, and liquid crystalline properties.[1] Nonsubstituted Pc's are difficult to dissolve in solvents due to their strong $\pi-\pi$ stacking interaction. To improve the solubility of Pc's, many substituents have been introduced at the peripheral positions of the Pc ring.[2] The introduced substituents also controlled the aggregation behavior among Pc's. When Pc's are aggregated, the intense absorption band attributed to their $\pi-\pi^*$ transition in the visible region is broadened and blue shifted.[1] Moreover, the catalytic activities of metalated Pc's are diminished by intermolecular aggregation.[3] While a wide range of sterically hindered metalloporphyrins have been synthesized[4] and employed in regioselective or shape-selective catalytic reactions[5] and ligations,[6] sterically hindered Pc compounds have not been as extensively explored.[7]

Polyphenylene-based nanostrutures have been intensely studied in recent years.[8] Rigid polyphenylenes create shape-persistent supramolecular structures, and the rigid structures of these molecules provide unique physical properties such as highly efficient electro- and photoconductivity[9] and the recognition of small guest molecules in the nanospaces within the polyphenylenes.[8,10] The bulky oligophenylene units have been attached at the periphery of the metallophthalocyanine core to prevent intermolecular aggregation. Walsh and Mandal reported the synthesis of pentaphenylbenzene-substituted Pc's and large enhancement of the third-order nonlinear optical absorptions.[11] The prevention of intermolecular aggregation among the planar Pc's leads to high solubility and single-site isolation in the respective physical environments. Furthermore, the construction of pockets around a Pc molecule may result in steric control of the ligation of substituted pyridines. In this paper, we report the synthesis and selective ligation of sterically isolated Pc's.

Phthalocyanine precursors were synthesized in an eight-synthetic-step process from 4,5-dibromotoluene by means of the methodology developed by Müllen et al. (Scheme 1).[12]

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(1) (a) *Phthalocyanines: Properties and Applications*; Leznoff, C. C., Lever, A. B. P., Eds.; VCH: New York, 1990−1996; Vols. 1−4. (b) McKeown, N. B. *Phthalocyanine Materials: Synthesis, Structure and Function*; Cambridge University Press: Cambridge, 1998. (c) *Phthalocyanines*−*Chemistry and Functions*−; Shirai, H., Kobayashi, N., Eds.; I. P. C.: Tokyo, 1997.

(2) Lezoff, C. C. *Phthalocyanines: Properties and Applications*; Leznoff, C. C., Lever, A. B. P., Eds.; VCH: New York, 1990; Vols. 1−4 and Vol. 1, p 1 and related references therein.

(3) (a) Shirai, H.; Tsuiki, H.; Masuda, E.; Koyama, T.; Hanabusa, K. *J. Phys. Chem.* **1991**, *95*, 417. (b) Kimura, M.; Yamaguchi, Y.; Koyama, T.; Hanabusa, K.; Shirai, H. *J. Porphyrins Phthalocyanines* **1997**, *1*, 309.

(4) (a) Cook, B. R.; Reinert, T. J.; Suslick, K. S. *J. Am. Chem. Soc.* **1986**, *108*, 7281. (b) Groves, J. T.; Nemo, T. E. *J. Am. Chem. Soc.* **1987**, *109*, 5045. (c) Ostovic, D.; Bruice, T. C. *J. Am. Chem. Soc.* **1989**, *111*, 6511. (d) Collman, J. P.; Brauman, J. I.; Fitzgerald, J. P.; Hampton, P. D.; Naruta, Y.; Michida, T. *Bull. Chem. Soc. Jpn.* **1988**, *61*, 47. (e) Collman, J. P.; Wang, Z.; Straumanis, A.; Quelquejeu, M.; Rose, E. *J. Am. Chem. Soc.* **1999**, *121*, 460.

(5) Bhyrappa, P.; Young, J. K.; Moore, J. S.; Suslick, K. S. *J. Am. Chem. Soc.* **1996**, *118*, 5708.

(6) (a) Tomoyose, Y.; Jiang, D.-L.; Jin, R.-H.; Aida, T.; Yamashita, T.; Horie, K.; Yashima, E.; Okamoto, Y. *Macromolecules* **1996**, *29*, 5236. (b) Bhyrappa, P.; Vaijayanthimala, G.; Suslick, K. S. *J. Am. Chem. Soc.* **1999**, *121*, 262.

(7) (a) Kingsborough, R.; Swager, T. M. *Angew. Chem., Int. Ed.* **2000**, *39*, 2897. (b) Bench, B. A.; Beveridge, A.; Sharman, W. M.; Diebold, G. J.; van Lier, J. E.; Gorum, S. M. *Angew. Chem., Int. Ed.* **2002**, *41*, 748. (c) Bench, B. A.; Brennessel, W. W.; Lee, H.-J.; Gorum, S. M. *Angew. Chem., Int. Ed.* **2002**, *41*, 750.

(8) Berresheim, A. J.; Müller, M.; Müllen, K. *Chem. Rev.* **1999**, *99*, 1747 and related references therein.

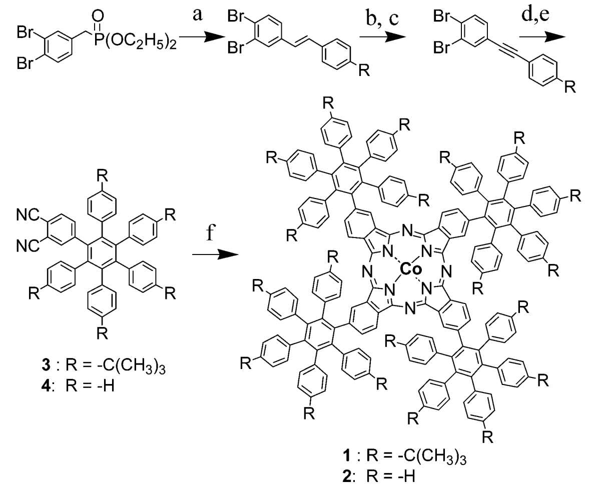
(9) van de Craats, A. M.; Warman, J. M.; Müllen, K.; Geerts, Y.; Brand, J. D. *Adv. Mater.* **1998**, *10*, 36.

(10) Kimura, M.; Shiba, T.; Yamazaki, M.; Hanabusa, K.; Shirai, H.; Kobayashi, N. *J. Am. Chem. Soc.* **2001**, *123*, 5636.

(11) Walsh, C. J.; Mandal, B. K. *Chem. Mater.* **2000**, *12*, 287.

10.1021/ic026149o CCC: $25.00

Scheme 1. Synthetic Approach to Sterically Hinderededed Phthalocyanines **1** and **2**[a–f]



[a] 4-(*t*-Butyl)benzaldehyde, *t*-BuOH. [b]Br$_2$, CH$_2$Cl$_2$. [c]*t*-BuOK, *t*-BuOH. [d]Tetra(4-*tert*-butylphenyl)cyclopentadienone or tetraphenylcyclopentadienone, diphenylether. [e]CuCN, NMP. [f]CoCl$_2$, DMAE. Compounds **1** and **2** are composed of a mixture of regioisomers.

The synthesis path commences with the bromination of 3,4-dibromotoluene by *N*-bromosuccinamide (NBS). The phosphonate compound was obtained from 1-bromomethyl-4,5-dibromobenzene by treatment with triethyl phosphate. Wittig–Horner coupling reactions between the phosphonate compound and aldehydes produced stilbenes. Bromination of the stilbene double bond, followed by treatment with potassium *tert*-butanolate, gave diphenylacetylenes. Unsymmetrical hexaphenylbenzenes were obtained by intermolecular Diels–Alder reactions of diphenylacetylenes with substituted or nonsubstituted 2,3,4,5-cyclopenta-2,4-dien-1-one. A Rosenmund–von Braun reaction of unsymmetrical hexaphenylbenzene with CuCN in *N*-methylpyrrolidone (NMP) yielded the phthalocyanine precursors **3** and **4**, which were converted into the corresponding metallophthalocyanines **1** and **2** by refluxing in 2-(dimethylamino)ethanol (DMAE). After purification by column chromatography, ca. 30% of pure products were isolated. All of the intermediate and final metallophthalocyanines were fully characterized by ^{1}H and ^{13}C NMR spectroscopy, matrix-assisted laser desorption/ionization time-of-flight (MALDI-TOF) mass spectroscopy, UV–vis spectroscopy, and HPLC (see Supporting Information). The obtained Pc's **1** and **2** are highly soluble in many organic solvents, including toluene, CH$_2$Cl$_2$, THF, *n*-hexane, CH$_3$CN, and EtOH. The MALDI-TOF mass spectrum of **1** shows the molecular ion peak at *m/z* 3519 (calcd 3518). The ^{1}H NMR spectrum in the aromatic region of **1** is complicated due to the presence of several regioisomers. The observation of proton resonances of the peripheral *tert*-butyl groups of **1** at $\delta = 1.41$, 1.29, -1.00, and -1.17 is remarkable and suggests that the chemical shifts of the peripheral *tert*-butyl protons near the large π-conjugated Pc core are affected by a ring-current effect. Corey–Pauling–Koltun (CPK) space-filling models indicate that the pentaphenylbenzene architecture creates nanometer-ordered pockets around the Pc and that eight *tert*-butyl groups are located within the pocket.

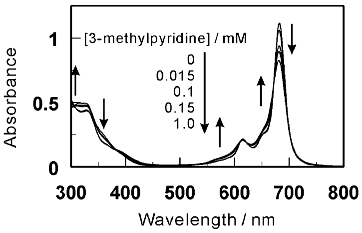


Figure 1. UV–vis spectral change of **1** (5.0 μM) in CH$_2$Cl$_2$ at 25 °C on titration with 3-methylpyridine (0, 0.015, 0.1, 0.15, 1.0mM).

The tetrakis(*tert*-butyl)phthalocyaninatocobalt(II) complex (CoPc(*t*-Bu)$_4$) in a mixture of EtOH and CH$_2$Cl$_2$ (1:1 v/v) gave a broad band at 620 nm, which can be attributed to the presence of dimeric and oligomeric Pc species.[13] In polar solvents, hydrophobic Pc rings are readily stacked because of their strong π–π interaction. In contrast, UV–vis spectra of **1** in EtOH exhibited a sharp Q-band at 694 nm and a Soret band at 350 nm which is characteristic of nonaggregated cobalt phthalocaynines.[13] Furthermore, the absorption maxima (λ_{max}) and molar absorption coefficient (ϵ) of **1** in EtOH remained virtually intact throughout the range of concentrations from 5.0 μM to 0.1 mM (Figure 1). These results suggest that the introduction of bulky pentaphenylbenzene units prevents molecular aggregation of the Pc's in polar solvents.

Steric control of the intermolecular interaction between a functional molecule and the target guest molecules has been widely explored.[14] The introduction of bulky substituents at the peripheral positions of a metalloporphyrin affects the selectivity of these guest molecules in terms of catalytic activities and ligation. Cobalt phthalocyanines are capable of binding ligands at their axial positions. The pockets around the CoPc within **1**, which is constructed with four bulky pentaphenylbenzene units, may affect the selectivity of the binding sites of the CoPc. The selectivities of **1** in the axial ligation of various pyridine derivatives with different substituents (XPy) were demonstrated. On the addition of pyridines, the absorption spectra of **1** changed, and the change showed clear isosbestic points. The equilibrium constants (K_{eq}'s) were evaluated from the spectral change in the Q-band for **1**, **2**, and CoPc(*t*-Bu)$_4$.[6] The plots of ln[$(A_{obs} - A_0)/(A_{max} - A_{obs})$] versus ln[XPy], where A_0 is the Q-band absorbance without XPy, A_{obs} is the absorbance at an individual concentration of XPy, and A_{max} is the absorbance in the presence of a large excess of XPy, were straight lines. The slopes of these straight lines are almost exactly 1.0, indicating the formation of 1:1 complexes of **1** and XPys. The K_{eq} values for **1** were sensitive to the sizes and shapes of XPys (Figure 2a). The K_{eq} value for the binding of linear

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(12) Ito, S.; Wehmeier, M.; Brand, J. D.; Kübel, C.; Epsch, R.; Rabe, J. P.; Müllen, K. *Chem. Eur. J.* **2000**, *6*, 4327.

(13) (a) Stillman, M. J.; Nyokong, T. *Phthalocyanines: Properties and Applications*; Leznoff, C. C., Lever, A. B. P., Eds.; VCH: New York, 1989, Vols. 1–4 and Vol. 1, p 135. (b) Kobayashi, N.; Lam, H.; Nevin, W. A.; Janda, P.; Leznoff, C. C.; Koyama, T.; Monden, A.; Shirai, H. *J. Am. Chem. Soc.* **1994**, *116*, 879.

(14) (a) Pugh, V. J.; Hu, Q.-S.; Pu, L. *Angew. Chem., Int. Ed.* **2000**, *39*, 3638. (b) Schlupp, M.; Weil, T.; Berresheim, A. J.; Wiesler, U. M.; Bargon, J.; Müllen, K. *Angew. Chem., Int. Ed.* **2001**, *40*, 4011.

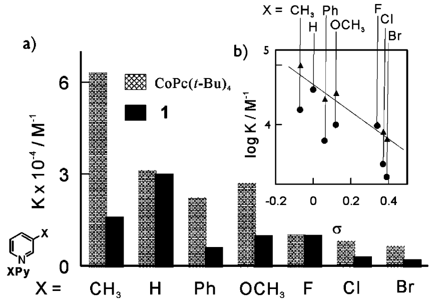

Figure 2. (a) Ligand binding constants (K_{eq}) for **1** relative to CoPc(t-Bu)$_4$. (b) Hammett plots of K_{eq} values for **1** (●) and CoPc(t-Bu)$_4$ (▲).

4-phenylpyridine with **1** ($K_{eq} = 1.2 \times 10^4$ M^{-1}) is comparable to that with CoPc(t-Bu)$_4$ ($K_{eq} = 1.5 \times 10^4$ M^{-1}). In contrast with this case, the observed K_{eq} for **1** with bended 3-phenylpyridine was ca. $^1/_4$ that of CoPc(t-Bu)$_4$. Pentaphenylbenzene-substituted CoPc **2** lacking the peripheral *tert*-butyl groups showed an intermediate K_{eq} value ($K_{eq} = 1.4 \times 10^4$ M^{-1}) between those for **1** ($K_{eq} = 8.1 \times 10^3$ M^{-1}) and CoPc(t-Bu)$_4$ ($K_{eq} = 2.2 \times 10^4$ M^{-1}). The *tert*-butyl groups within the pockets of **2** affect the sensitivity for the ligation. Figure 2b is the Hammett plot of K_{eq} toward *meta*-substituted pyridines. The result for the reference compound CoPc(t-Bu)$_4$ exhibits a good linear relationship between log K_{eq} and the Hammett constants, indicating that the electronic changes with variation of the substituents in a pyridine ring affected the binding affinity of XPy with CoPc(t-Bu)$_4$. On the other hand, the relationship for **1** is not linear, suggesting that a steric effect of the substituents in XPys operates along with the electronic effects. The steric repulsion around the CoPc reduced the accessibility of ligands bearing large substituents.

In summary, novel sterically protected MPc's have been synthesized and characterized. The attachment of bulky pentaphenylbenzene units to the periphery of the MPc resulted in the complete isolation of the MPc in polar solvents. The pentaphenylbenzene around the MPc's served to prevent direct interaction among the MPc's. Ligation studies demonstrated that pockets around CoPc provided the selective control of ligation through steric recognition within the pocket. On the basis of changes in their absorption and fluorescence spectra, these designed materials will be applicable as chemosensors.[15] The interaction between small molecules (target analytes) and MPc's induces the changes of absorption and fluorescence spectra as output signals. The design of pockets may affect the selectivity and sensitivity to target analytes. Studies to examine chemosensing for gaseous substrates by using sterically isolated MPc's are now in progress.

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Supporting Information Available: Synthetic procedures and their analytical data. This material is available free of charge via the Internet at http://pubs.acs.org.

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(15) (a) Yang, J.-S.; Swager, T. M. *J. Am. Chem. Soc.* **1998**, *120*, 5321. (b) Yang, J.-Y.; Swager, T. M. *J. Am. Chem. Soc.* **1998**, *120*, 11864. (c) McQuade, D. T.; Pullen, A. E.; Swager, T. M. *Chem. Rev.* **2000**, *100*, 237.