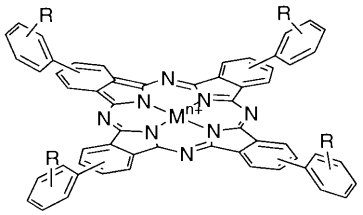
Phthalocyanines Obtained from Phthalonitriles with Phenyl Derivatives: A New Method for the Synthesis of the Phthalonitriles by Use of Suzuki-Coupling Reaction

Tamotsu Sugimori,* Satoru Okamoto, Naoko Kotoh, Makoto Handa, and Kuninobu Kasuga
Department of Material Science, Faculty of Science and Engineering, Shimane University, Matsue 690-8504.

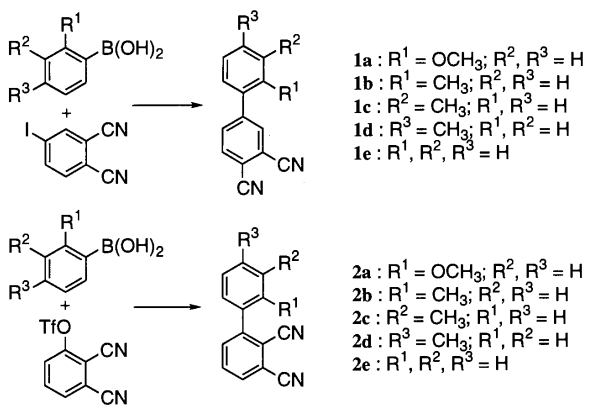
(Recieved August 14, 2000; CL-000777)

Phthalocyanines peripherally introduced with four phenyl derivatives have been prepared from the corresponding phthalonitriles, which were obtained in high yields with Suzuki-Miyaura coupling. It was found that the substituent groups on the pc ring significantly affect the spectral properties and solubilities in chloroform.

The phthalocyanines (pcs) soluble in organic solvents have been developed by peripheral introduction of substituents groups.[1] The variety of the substituent groups are still limited due to their synthetic problem of the phthalonitriles, precursors for pcs; most of them are alkoxy and alkylthio groups. The introduction of phenyl substituents onto the pc ring is considered promising because the space above the pc ring can be functionalized by further introduction of substituents to the phenyl groups.



However, only few studies for the phenyl introduced pcs have been reported.[2] We established a new facile preparation method of the phenyl-substituted phthalonitriles in the high yield based on a Suzuki–Miyaura cross-coupling reaction (Scheme 1), which have been employed for hetero aromatic ring coupling; the phenyl boronic acids used in this reaction are inert to water and oxygen, and hence handled with ease.[3] During the course of this study, the preparation of a pc substituted with 2,5-dimethoxyphenyl group by a Stille coupling reaction using organostannane was reported.[4] In the present study, we first performed a systematic investigation on the pcs with phenyl derivatives regarding the difference of the substituent groups and their positions on the pc-benzo ring.

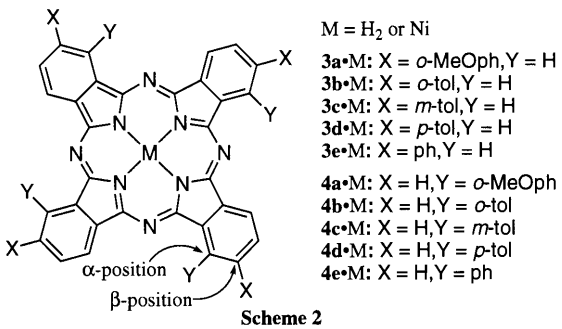


1a : R^1 = OCH_3; R^2, R^3 = H
1b : R^1 = CH_3; R^2, R^3 = H
1c : R^2 = CH_3; R^1, R^3 = H
1d : R^3 = CH_3; R^1, R^2 = H
1e : R^1, R^2, R^3 = H

2a : R^1 = OCH_3; R^2, R^3 = H
2b : R^1 = CH_3; R^2, R^3 = H
2c : R^2 = CH_3; R^1, R^3 = H
2d : R^3 = CH_3; R^1, R^2 = H
2e : R^1, R^2, R^3 = H

Scheme 1. Reagents and conditions: Na_2CO_3, $Pd(PPh_3)_4$ / DME, reflux 8h.

The phenyl boronic acids ($RPhB(OH)_2$) were prepared from bromobenzene derivatives via the Grignard reagent. The coupling reaction of $RPhB(OH)_2$ with 4-iodophthalonitirile[5] or 3-trifluoromethanesulfonyloxyphthalonitrile[6] was carried out by following procedures (Scheme 1, **1a–e**, **2a–e**)[7]; a flask was charged with $Pd(PPh_3)_4$ (30 μmol), 1,2-dimethoxyethane (10 mL), phthalonitriles (1.0 mmol), Na_2CO_3 (3.0 mmol) and $RPhB(OH)_2$ (1.0 mmol) under argon, and the mixture was stirred at 90°C. The completion of the reaction was confirmed by GC–MS analysis. After the reaction mixture was filtered and evaporated, the crude product was purified by silica-gel column chromatography using toluene–chloroform (1:1) as eluent and recrystallized from ethanol. The yields of phthalonitriles were about 80%. The phenyl substituted pcs were obtained from the corresponding phthalonitriles in a general method for the preparation of pcs (Scheme 2).



M = H_2 or Ni
3a•M: X = *o*-MeOph,Y = H
3b•M: X = *o*-tol,Y = H
3c•M: X = *m*-tol,Y = H
3d•M: X = *p*-tol,Y = H
3e•M: X = ph,Y = H
4a•M: X = H,Y = *o*-MeOph
4b•M: X = H,Y = *o*-tol
4c•M: X = H,Y = *m*-tol
4d•M: X = H,Y = *p*-tol
4e•M: X = H,Y = ph

Scheme 2

The pcs that have the ortho-substituted phenyl groups at β-position (**3a**•Ni, **3b**•Ni) and α-substituted pcs (**4a–e**•M) were very soluble in chloroform, while **3c**•Ni, **3d**•Ni and **3e**•Ni were less soluble in chloroform. The absorption spectrum of **3c**•Ni in chlo-

Table 1. Q-band positions (nm) of metal free and Ni(II) pcs in chloroform.

	H_2		Ni(II)	
	3 (β)	**4** (α)	**3** (β)	**4** (α)
a	708 673	703 669	679	—
b	704 668	703 669	674	675
c	711 676	721 689	688*	693
d	713, 678	725 693	690*	694
e	710, 675	713 681	688*	692
$MPc(t\text{-}Bu)_4$	701, 664	—	672	—

* data in 1-chloronaphthalene

roform shows a Q-band peak at 680 nm with a large broad band at a shorter wavelength as a result of its aggregation.[8] In the same conditions, the spectrum of **3b**·Ni shows a sharp Q-band at 674 nm with a small discernible shoulder. The Q-band positions of **3c**–**e**·M were shifted to a longer wavelength compared with those of tetra-*t*-butylphthalocyanine complexes (MPc(*t*-Bu)$_4$). The Q-band shift of the complexes **3c**–**e**·M may come from the extended π-systems when the introduced phenyl rings or their derivatives become coplanar to the pc ring in solution. The Q-band positions of the α-substituted pcs, **4c**·M, **4d**·M and **4e**·M, were shifted to a longer wavelength compared with those of the corresponding β-substituted pcs. This result is consistent with the report that the substituent effect at the α position is much larger than that at the β position.[9] In contrast, the Q-band positions of **4b**·Ni and **3b**·Ni were almost the same as that of NiPc(*t*-Bu)$_4$. This suggests that the substituent effect of the *o*-tolyl group is weak in **4b**·Ni and **3b**·Ni, because the methyl group at the ortho position of the *o*-tolyl group makes the dihedral angle between the pc core and the *o*-tolyl group nearly perpendicular, and the electronic interaction between the *o*-tolyl group and the pc core is weakened.

Generally, the tetra-substituted pcs have four structural isomers. In the case of **4a**–**e**·Ni, however, only one structural isomer can be obtained because of steric hindrance of the substituent phenyl groups. The single crystals of **4b**·Ni suitable for an X-ray diffraction measurement were obtained by the recrystallization from a chloroform–*n*-hexane solution. The molecular structure of **4b**·Ni is shown in Figure 1.[10] The introduced four sub-

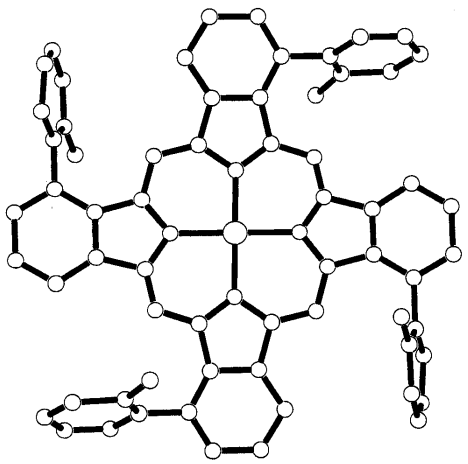


Figure 1. Molecular structure of **4b**•Ni.

stituents are placed to avoid contacting each other. The conformation of the substituents is the same as that previously reported for 1,8,15,22-tetrakis(pentan-3'-yloxy)phthalocyaninatonickel(II).[11] The Ni–N bond lengths are 1.93(2), 1.92(2), 1.93(2) and 1.94(2)Å, which are in the range of those for the other pc complexes of nickel(II).[12] The nickel(II) ion is placed in the plane formed by four coordinated nitrogen atoms. The dihedral angles between the phenyl rings of the substituents and the pc plane are 72°, 63°, 64° and 84°, which may cause the high solubility of the α-substituted pcs in organic solvents because the bulky phenyl groups perpendicular to the pc ring can prevent the aggregation of the pcs.

References and Notes

1 C. C. Leznoff, in "Phthalocyanines – Properties and Applications," ed. C. C. Leznoff and A. B. P. Lever, VCH, New York, 1989, p. 1.

2 S. A. Mikhalenko and E. A. Luk'yanets, *Zh. Obshch. Khim.*, **39**, 2129 (1969); S. A. Mikhalenko, S. A. Gladyr', and E. A. Luk'yanets, *Zh. Organ. Khim.*, **8**, 341 (1972).

3 N. Miyaura and A. Suzuki, *Chem. Rev.*, **95**, 2457 (1995).

4 V. Aranyos, A. M. Castaño, and H. Grennberg, *Acta Chem. Scand.*, **53**, 714 (1999).

5 S. M. Marcuccio, P. I. Svirskaya, S. Greenberg, A. B. P. Lever, and K. B. Tomer, *Can. J. Chem.*, **63**, 3057 (1985).

6 3-Trifluoromethanesulfonyloxyphthalonitrile was prepared by the reaction of 3-hydroxyphthalonitrile and trifluoromethanesulfonyl chloride. 3-Hydroxyphthalonitrile was prepared by similar manner with following literature: N. Kobayashi, R. Higashi, and T. Tomura, *Bull. Chem. Soc. Jpn.*, **70**, 2693 (1997).

7 Analytical data: **1a**: ^{1}H-NMR ($CDCl_3$) δ: 3.85 (3H, s), 7.02–7.12 (2H, m), 7.28–7.36 (1H, dd), 7.41–7.48 (1H, m), 7.80–7.90 (2H, m), 8.02 (1H, dd); Anal. Found: C, 77.13; H, 4.50; N, 11.63%. Calcd for $C_{15}H_{10}N_2O$: C, 76.91; H, 4.30; N, 11.96%. **1b**: ^{1}H-NMR ($CDCl_3$) δ: 2.23 (3H, s), 7.16–7.40 (4H, m), 7.78 (1H, d), 6.69–7.72 (1H, m), 7.87 (1H, d); Anal. Found: C, 82.42; H, 4.64; N, 12.67%. Calcd for $C_{15}H_{10}N_2$: C, 82.55; H, 4.62; N, 12.83%. **1c**: Anal. Found: C, 82.32; H, 4.66; N, 12.49%. Calcd for $C_{15}H_{10}N_2$: C, 82.55; H, 4.62; N, 12.83%. **1d**: ^{1}H-NMR ($CDCl_3$) δ: 2.43 (3H, s), 7.32–7.35 (2H, m), 7.47–7.50 (2H, dd), 7.83–8.02 (3H, m), 8.02 (1H, dd); Anal. Found: C, 82.62; H, 4.80; N, 12.75%. Calcd. for $C_{15}H_{10}N_2$: C, 82.55; H, 4.62; N, 12.83%. **1e**: Anal. Found: C, 82.62; H, 4.14; N, 13.42%. Calcd for $C_{14}H_8N_2$: C, 82.34; H, 3.95; N, 13.72%. **2a**: Anal. Found: C, 75.77; H, 4.71; N, 11.07%. Calcd for $C_{15}H_{10}N_2O{\cdot}0.3C_2H_5OH$: C, 75.53; H, 4.79; N, 11.29%. **2b**: Anal. Found: C, 82.30; H, 4.63; N, 12.82%. Calcd for $C_{15}H_{10}N_2$: C, 82.55; H, 4.62; N, 12.83%. **2c**: Anal. Found: C, 81.04; H, 4.76; N, 12.15%. Calcd for $C_{15}H_{10}N_2{\cdot}0.04CHCl_3$: C, 81.00; H, 4.54; N, 12.56%. **2d**: Anal. Found: C, 82.67; H, 4.81; N, 12.71%. Calcd. for $C_{15}H_{10}N_2$: C, 82.55; H, 4.62; N, 12.83%. **2e**: Anal. Found: C, 77.63; H, 3.98; N, 12.76%. Calcd for $C_{14}H_8N_2{\cdot}0.1CHCl_3$: C, 77.41; H, 3.74; N, 12.96%.

8 N. Kobayashi and A. B. P. Lever, *J. Am. Chem. Soc.*, **109**, 7433 (1987).

9 N. Kobayashi, N. Sasaki, Y. Higashi, and T. Osa, *Inorg. Chem.*, **34**, 1636 (1995).

10 The analysis is now under way; there is a problem to be solved concerning a disorder at a substituent *o*-tolyl group. Crystal data for **4b**·Ni: $C_{60}H_{40}N_8Ni$, M_r = 931.73, triclinic, $P\bar{1}$, a = 14.2704(2), b = 23.6456(4), c = 7.8483(1) Å, α = 90.572(1), β = 93.3680(6), γ = 80.487(1)° V = 2607.34(7) Å^3, Z = 2, D_c = 1.187 g cm^{-3}, Mo Kα, λ = 0.71069 Å, μ = 4.18 cm^{-1}, $F(000)$ = 968, 2857 observed with $I>3\sigma(I)$, 11040 collected at 25°C, refined to R (R_w) = 0.121 (0.093)

11 K. Kasuga, K. Asano, L. Lin, T. Sugimori, M. Handa, K. Abe, T. Kikkawa, and T. Fujiwara, *Bull. Chem. Soc. Jpn.*, **70**, 1859 (1997).

12 M. K. Engel, *Report of Kawamura Institute of Chemical Research*, **1997**, 11–54.