Preparation and Properties of Tetra- and Octa-substituted Phthalocyanines with Cationic Trimethylaniliniumyl Groups

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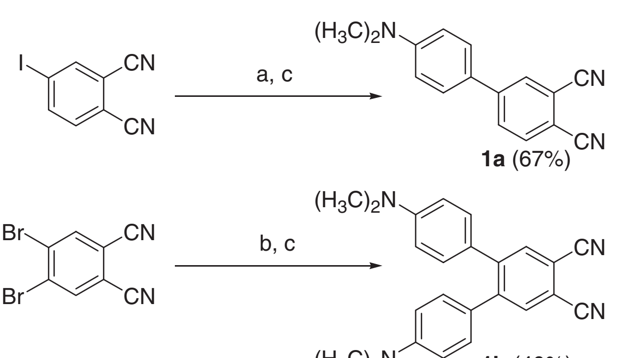
(Received May 24, 2004; CL-040590)

Substituted magnesium(II) phthalocyanines modified with dimethylaminophenyl and trimethylaniliniumyl groups were prepared and characterized. The tetra- and octa-substituted phthalocyanines with the cationic trimethylaniliniumyl groups were soluble in water, and the octa-substituted one existed as a photoactive monomer in water.

Phthalocyanines (pcs) have been extensively investigated and applied in widely different areas.[1] Recently, water-soluble pcs have been much interested because of their potential use for photodynamic therapy (PDT).[2] When using the pcs for PDT as well as homogenous photocatalysts in water, one of the most serious problems of pcs is their aggregating nature in water, which prevents them from their photocatalytic uses.[3] Although many water-soluble pcs with anionic or cationic substituents are known,[4] there have been only a few pc complexes that exist predominantly as a photoactive monomer even in water.[5] We have reported on the application of Suzuki-coupling reaction for the preparation of pcs substituted with four or eight phenyl-derivative groups.[6] This synthetic procedure has enabled the peripheral introduction of several kind of phenyl derivatives on the pc ring. Here, we introduce a synthetic way for tetra- and octa-substituted Mg(II)pcs with cationic phenyl derivatives through the mono- or di-substituted phthalonitriles with dimethylaminophenyl groups, which were prepared by Suzuki-coupling reaction.

4-*N*,*N*-dimethylaminophenyl boronic acid (dmapB(OH)$_2$) was prepared from 4-bromo-*N*,*N*-dimethylaniline via the Grignard reagents. The coupling reaction of 4-iodo- or 4,5-dibromophthalonitrile[7] with the dmapB(OH)$_2$ was carried out by similar procedures as described in a previous report (Scheme 1; **1a**, **b**).[6] The completion of the reaction was checked by GC–MS analysis. After the reaction mixture was filtered, followed by evaporation of the solvent, the crude product was purified by silica-gel column chromatography using benzene as eluent and recrystallized from ethanol.[8] The Mg(II)pcs substituted with dmap were prepared by the reaction of the corresponding phthalonitriles and magnesium propoxide (Figure 1; **2a**, **b**).[9] The obtained Mg(II)pcs were subsequently treated with iodomethane in chloroform for the methylation of dimethylamino groups. The charged pcs(**3a**, **b**) were obtained as the iodide salts, and characterized by ESI-MS.[10] As shown in Figure 2, a signal ($m/z = 201.2$) corresponding to $[C_{104}H_{112}N_{16}Mg]^{8+}$ was found for **3b**. This is the first evidence for the formation of an eight-positively charged species of the pc derivatives.[11]



Scheme 1. Reagents and conditions: a) dmapB(OH)$_2$ (1.4 equiv.), K$_3$PO$_4$ (1.4 equiv.), b) dmapB(OH)$_2$ (2.3 equiv.), K$_3$PO$_4$ (2.3 equiv.), c) Pd(PPh$_3$)$_4$ (3 mol %)/1,4-dioxane, at 90 °C.

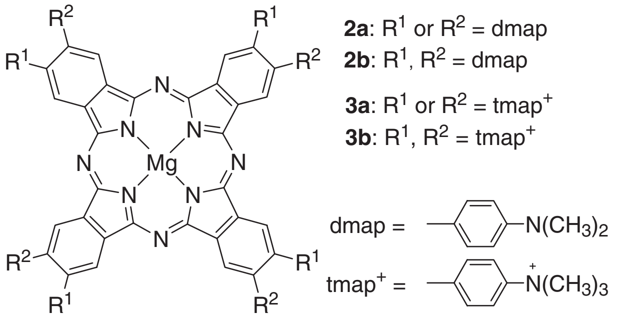


Figure 1. Tetra- and octa-substituted MgPcs.

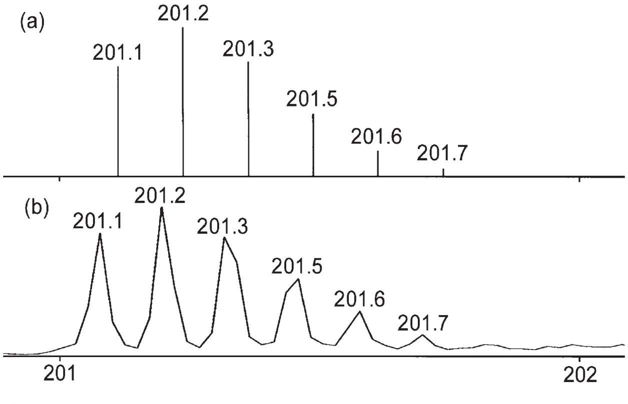


Figure 2. Selected area of the ESI mass spectrum for **3b**. (a) Predicted isotopic pattern for $[C_{104}H_{112}N_{16}Mg]^{8+}$. (b) Observed isotopic pattern.

The dmap-substituted pcs, **2a** and **2b**, were soluble in common organic solvents such as chloroform and benzene. The ab-

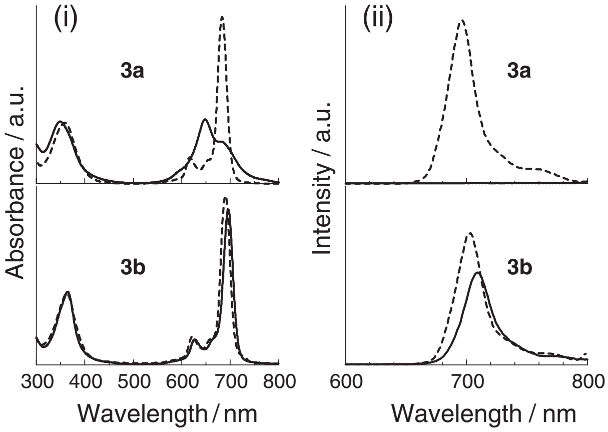


Figure 3. Absorption (i) and fluorescence (ii) ($\lambda_{ex} = 400$ nm) spectra of **3a** and **3b** in water (solid line) and in methanol (dashed line).

sorption spectra of the dmap-substituted pcs showed a Q-band peak at 711 nm (**2a**) and 718 nm (**2b**) in chloroform. The methylated pcs, **3a** and **3b**, were insoluble in those organic solvents, but highly soluble in water and in methanol. Absorption spectra of **3a** and **3b** in water and in methanol are shown in Figure 3(i). Both complexes showed a sharp Q-band, coming from their monomeric species in methanol. However, in water, their spectral features were different from each other. Although **3b** showed a sharp intensive Q-band at 697 nm, **3a** showed a broadened band at 649 nm with a shoulder band at 684 nm. The broadened band is considered to originate from the aggregated species. As shown in Figure 3(ii), the fluorescence spectra were observed for **3a** and **3b** in methanol and for **3b** in water, but not for **3a** in water because of the aggregation, where the measured solutions were set at the same absorbance at the excitation wavelength of 400 nm. That is, **3b** predominantly exists as a monomer in water, which could be due to the fact that there are strong electric repulsions among the cationic molecules with the eight positive charges on the pc ring themselves.

In this study, new octa- and tetra-substituted pcs with trimethylaniliniumyl groups were prepared and investigated for their spectral properties. It was found that the octa-substituted one was monomeric even in water and promising as a photocatalyst and a photosensitizer for PDT.

The authors gratefully acknowledge Kawaken Fine Chemicals Co., LTD. for supplying $Pd(PPh_3)_4$. This work was partially supported by Grant-in-Aid for Scientific Research No. 14740364 from the Ministry of Education, Culture, Sports, Science and Technology.

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8 Analytical data: **1a**: ^{1}H NMR ($CDCl_3$) δ: 3.05 (6H, s), 6.82–6.77 (1H, d), 7.54–7.48 (2H, d), 7.77–7.74 (2H, d), 7.87–7.83 (1H, d), 7.94 (1H, s); Anal. Found: C, 77.56; H, 5.35; N, 16.90%. Calcd. for $C_{16}H_{13}N_3$: C, 77.71; H, 5.30; N, 16.99%. **1b**: ^{1}H NMR ($CDCl_3$) δ: 2.97 (12H, s), 6.63–6.59 (4H, d), 7.05–7.00 (4H, d), 7.72–7.26 (2H, s); Anal.Found: C, 78.69; H, 6.19; N, 15.25%. Calcd. for $C_{24}H_{22}N_4$: C, 78.66; H, 6.05; N, 15.29%.

9 Analytical data: **2a**: Anal.Found: C, 75.42; H, 5.50; N, 16.12%. Calcd. for $C_{64}H_{52}N_{12}Mg$: C, 75.85; H, 5.17; N, 16.58%.

10 **3a**: ESI-MS: m/z calcd. for $[C_{68}H_{64}N_{12}Mg]^{4+}$ 268.13; found 268.2 **3b**: ESI-MS: m/z calcd. for $[C_{104}H_{112}N_{16}Mg]^{8+}$ 201.11; found 201.2

11 A tetra-substituted octa-cationic pc has been reported in Ref. 5b. However, its MS data shown there was only that for the fragments of the cationic pc.

Published on the web (Advance View) July 12, 2004; DOI 10.1246/cl.2004.1014