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Novel metal free, zinc 1,2,3,4,15,16,17,18-octaphenyl-9,10,23,24-tetradodecyloxyphthalocyanines were synthesized by condensation of excess 1,3-diimino-4,5,6,7-tetraphenylisoindoline with 1,3-diimino-5,6-bis(dodecyloxy)isoindoline. The compound was separated by gel permeation chromatography. The structure was confirmed by elemental analysis, ^1H nmr, ^{13}C nmr, uv-vis and ir spectroscopy.

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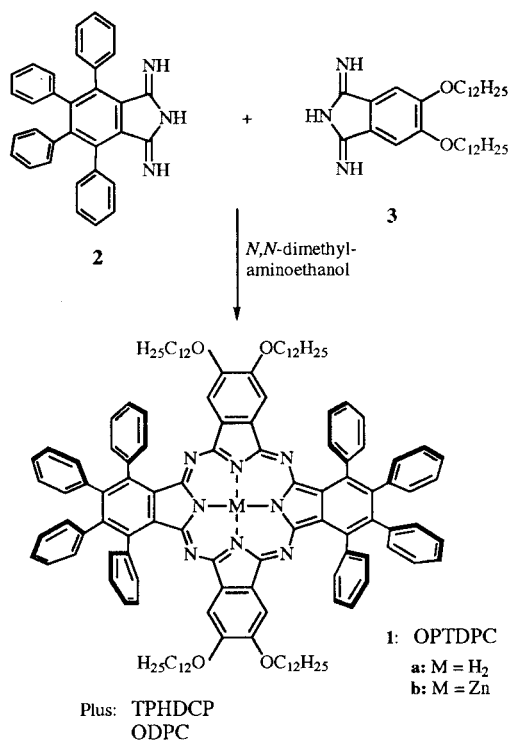
Introduction.

Phthalocyanines are important blue and green colorants both as dyes and pigments [1]. Their structural analogy to the natural pigments such as the porphyrins is of great interest in academic research. Solvent soluble phthalocyanine dyes have attracted special interest, because of their conducting [2], catalytic [3,4], photovoltaic [5,6], liquid-crystalline [7,8], Langmuir-Blodgett (LB) film [9,10] and electrochromic [11] properties. Unsymmetrical substituted phthalocyanines have outstanding electronic and optical properties, and are valuable in fabricating thin film by the LB technique. Therefore, these compounds are very important in understanding the nature and applications of phthalocyanines.

Phthalocyanines are cyclic tetramers, AAAA, usually formed from a single phthalato monomer, A, with the first being connected to the fourth mer. When cophthalates are used, mixed phthalocyanines are possible AAAA, BBBB, AAAB, BBBA, AABB ("adjacent" type) and ABAB ("opposite" type). Mono-substituted type phthalocyanines have been obtained by the mixed condensation method [12], a polymer support method [13], or via the so called subphthalocyanines [14]. Direct synthesis of "opposite" disubstituted ABAB type phthalocyanines have been reported using the cross condensation of substituted 1,3-diiminoisoindoles with 6/7-nitro-1,3,3-trichloroisoindolenine [15] or using steric hindrance 3,6-diphenylphthalonitrile as one of starting dinitrile to minimize the "adjacent" type phthalocyanine formation [16].

Molecular design using the SYBYL program illustrates that the tetraphenyl phthalate could not self condense to form hexadecylphenyl phthalocyanine due to the severe steric hindrance of the phenyl groups, and our early experiment verified the above conclusion [17] by condensation of tetraphenyl phthalate and only getting a brown colored instead of the green or blue colored phthalocyanine. Therefore, only monosubstituted AAAB and dual "opposite" ABAB incorporation of the tetraphenyl seg-

Scheme I



ment were possible. No two tetraphenyl units can be adjacent and coplanar due to steric hindrance.

We have reported unsymmetrical AAAB type 1,2,3,4-tetraphenyl-9,10,16,17,23,24-hexadodecyloxyphthalocyanine in our previous communication [18]. Recently, we have succeeded in the synthesis of the disubstituted "opposite" ABAB system incorporation of two didodecyloxyphthalato units and two tetraphenylphthalato units with minimal formation of the other cophthalates by using the excess molar ratio of 1,3-diimino-4,5,6,7-tetraphenylisoindoline, and report hereby. In view of technical importance of phthalocyanine's aggregation behavior [19] for

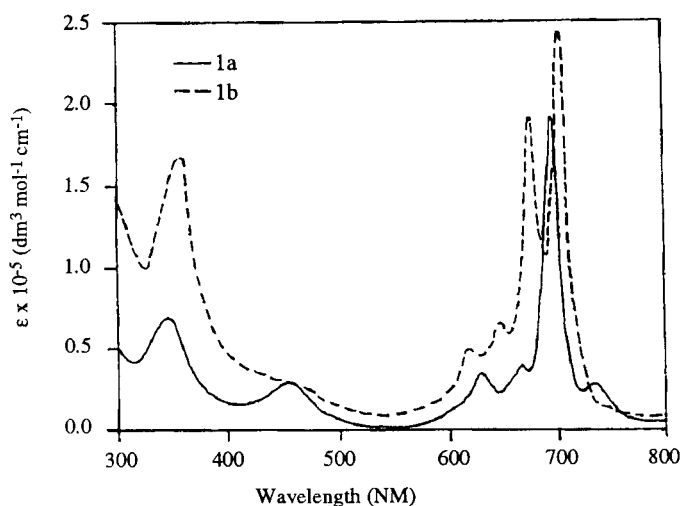


Figure 1. Ultraviolet-visible-near infrared absorption spectra of 1,2,3,4,15,16,17,18-octaphenyl-9,10,23,24-tetradodecyloxyphthalocyanine metal free **1a** and metallo-zinc **1b** at $4.01 \times 10^{-6} M$ in chloroform at room temperature.

deuteriochloroform. The uv/visible spectra were recorded on a Hitachi 2000 spectrometer. Elemental analyses were performed by Galbraith Laboratories, Inc, Knoxville, TN. Flash chromatography was performed using silica gel of particle size 40-60 μm . All solvents were freshly distilled before use.

1,2,3,4,15,16,17,18-Octaphenyl-9,10,23,24-tetradodecyloxyphthalocyanine (**1a**).

1,3-Diimino-4,5,6,7-tetraphenylisoindoline (**2**) (1.72 g 3.8 mmoles) and 0.51 g (1.0 mmole) of 1,3-diimino-5,6-bis(dodecyloxy)isoindoline (**3**) in 8 ml of 2-*N,N*-dimethylaminoethanol was heated at 150° (oil bath) under an argon atmosphere for 70 hours. The mixture was then cooled to room temperature, diluted with acetone, filtered, and washed thoroughly with methanol until the filtrate was almost clear. The crude product was extracted with methanol in a soxhlet apparatus for 48 hours to remove yellow impurities. The product was further purified by flash chromatography using 2-methoxyethanol/toluene (3/40, v/v) as the eluent. The crude product was then passed through a gel permeation column using Bio-beads SX1 (Bio-rad) with toluene as the eluent, the first two fast running fractions gave, after evaporation of solvent, 0.025 g (5%) of 2,3,9,10,16,17,23,24-octakis(dodecyloxy)-

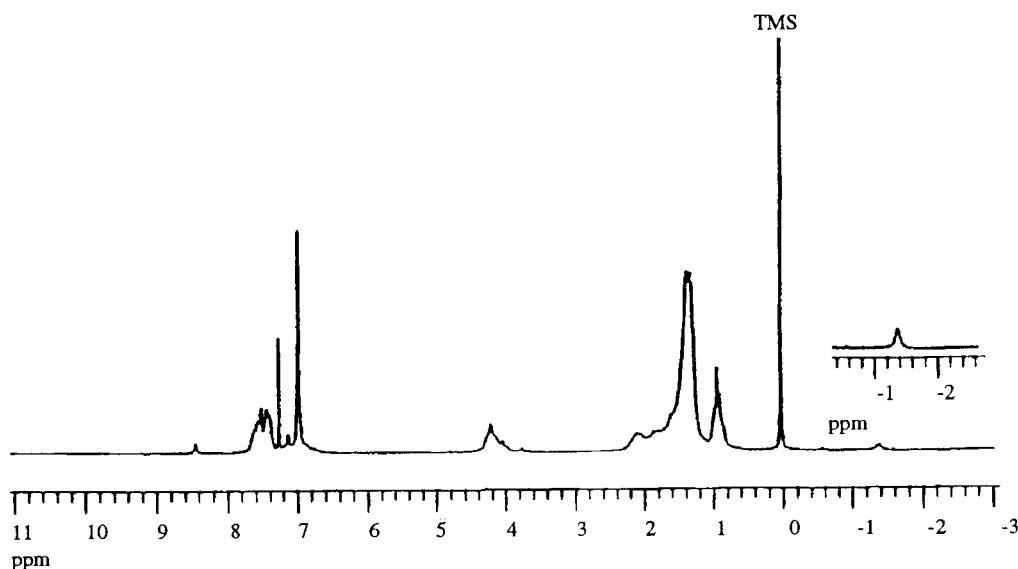


Figure 2. The proton nuclear magnetic resonance spectrum of metal free phthalocyanine **1a** in deuteriochloroform.

pigments, dyes and photosensitizer, this highly steric bulky octaphenyl on both sides of phthalocyanine ring have some unique properties in respect of its aggregation behavior, and we will report its physical chemical properties in detail later.

EXPERIMENTAL

The ir spectra were recorded on a Perkin-Elmer 1750 FTIR spectrophotometer in potassium bromide pellets. The nmr spectra were recorded on a JEOL FX-100 multinuclear magnetic resonance spectrometer using TMS as the internal standard in

phthalocyanine and 0.090 g (14%) of 1,2,3,4-tetraphenyl-9,10,16,17,23,24-hexadodecyloxyphthalocyanine respectively. While the third fraction yielded, after evaporation of solvent, 0.10 g (11%) product **1a** as a green solid with a yellow shade.

Compound **1a** had ir: 3316 (w), 2853/2922 (s), 1606 (m), 1105 (s), 1024 (m) cm^{-1} ; 1H nmr (4.5%, w/w): δ -1.40 (br, 2H), 0.92-2.30 (br, 92H), 4.21 (s, 8H), 6.97-8.66 (m, 44H) ppm; ^{13}C nmr: δ 13.9, 22.6, 29.5, 31.8, 69.9, 103.9, 104.7, 104.9, 115.4, 118.4, 120.3, 125.6, 126.1, 126.8, 127.2, 128.0, 131.2, 131.8, 135.6, 137.7, 140.4, 141.5, 143.4, 151.9, 152.3, 152.8, 157.0 ppm; uv/visible (chloroform): λ_{max}/nm [$\log \epsilon/dm^3 mol^{-1} cm^{-1}$] 730 (4.43, sh), 696 (5.27), 665 (4.56, sh), 626 (4.52).

Anal. Calcd. for $C_{128}H_{146}N_8O_4$: C, 82.63; H, 7.91; N, 6.02. Found: C, 82.77; H, 8.17; N, 6.09.

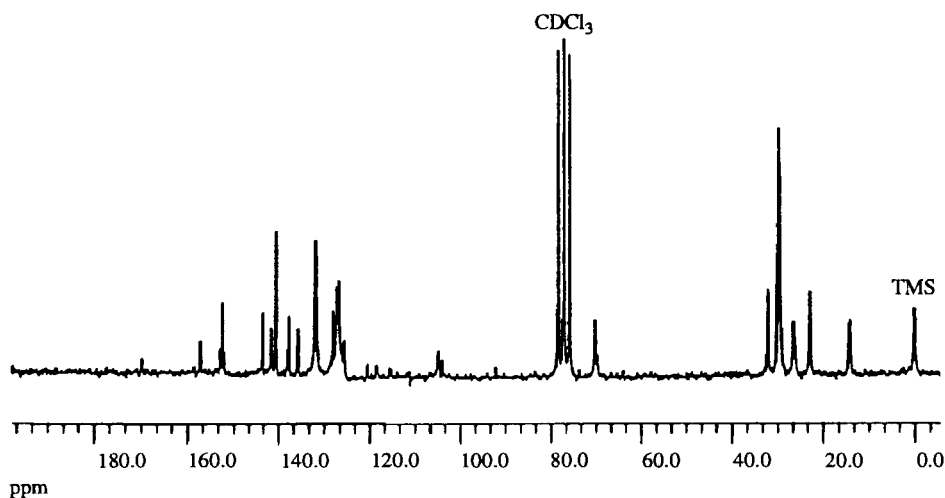


Figure 3. The carbon thirteen nuclear magnetic resonance spectrum of metal free 1,2,3,4,15,16,17,18-octaphenyl-9,10,23,24-tetradodecyloxyphthalocyanine **1a** in deuteriochloroform.

2,3,9,10,16,17,23,24-Octakis(didodecyloxy)phthalocyanine and 1,2,3,4-tetraphenyl-9,10,16,17,23,24-hexadodecyloxyphthalocyanine obtained in the above reaction exhibited ir and nmr spectra consistent with the values reported in the literature [20,18] except that the nmr spectra were measured at the same concentration in order to compare its corresponding cavity proton's chemical shift.

1,2,3,4,15,16,17,18-Octaphenyl-9,10,23,24-tetradodecyloxyphthalocyanine-zinc(II) (**1b**).

A mixture of metal free octaphenyl di-disubstituted phthalocyanine **1a** (50 mg, 0.027 mmole), anhydrous zinc acetate dihydrate (50 mg, 0.27 mmole) and 10 ml of 2-methoxyethanol/toluene (1/2, v/v) were heated at 120° for 20 hours under an argon atmosphere. The solution was then cooled and the product was purified by passing through an alumina column, and eluted with chloroform/methanol (4/1, v/v) gave, after solvent evaporation, 45 mg (87%) of the zinc phthalocyanine **1b** as a blue-green solid; ir: 2853/2922 (s), 1605 (m), 1105 (s), cm^{-1} ; ^1H nmr (deuteriochloroform): δ 0.90-2.10 (br, 92H), 4.18 (s, 8H), 7.03-7.72 (m, 44H) ppm; uv/visible (chloroform): $\lambda_{\text{max}}/\text{nm}$ [$\log \epsilon/\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$] 707 (5.40), 676 (5.28), 644 (4.82, sh), 614 (4.68), 356 (5.22).

Anal. Calcd. for $\text{C}_{128}\text{H}_{144}\text{N}_8\text{O}_4\text{Zn}$: C, 79.91; H, 7.54; N, 5.82. Found: C, 80.20; H, 7.24; N, 6.05.

Results and Discussion.

The synthetic route to produce compound **1** is summarized in Scheme I. The 1,3-diimino-4,5,6,7-tetraphenylisoindoline (**2**) and 1,3-diimino-5,6-bis(dodecyloxy)isoindoline (**3**) were prepared by the method described in our previous papers [18]. The mixed condensation of a 3.8:1 molar ratio of **2** and **3** in 2-*N,N*-dimethylaminoethanol gave ABAB type 1,2,3,4,15,16,17,18-octaphenyl-9,10,23,24-tetra-dodecyloxyphthalocyanine, **1a**, (OPTDPC) in 11% yield, AAAB type 1,2,3,4-tetraphenyl-9,10,16,17,23,24-hexadodecyloxyphthalocyanine (TPHDPC) in 14% and AAAA type 2,3,9,10,16,17,23,24-octakis(dodecyloxy)phthalocyanine (ODPC) in 5% yield. The development of the green color for the reaction between compounds **2** and **3** was much slower than that for the self condensation of **3** only. The steric hindrance of the tetraphenyl group directs and retards the

rate of reaction to incorporate the tetraphenyl unit into the phthalocyanine. Obviously, the excess of 1,3-diimino-4,5,6,7-tetraphenylisoindoline is decisive in formation of 1,2,3,4,15,16,17,18-octaphenyl-9,10,23,24-tetradodecyloxyphthalocyanine (**1a**). The Compounds **2** and **3** reacted in a 1:1 molar ratio resulted in no detectable amount of **1a** [18].

The R_f values of these compounds on thin layer chromatography (tlc) (silica gel/toluene/2-methoxyethanol, 40/3, v/v) were in order of OPTDPC (green with a yellow shade) > TPHDPC (green) > ODPC (blue green). This different R_f value on tlc was due to the steric hindrance of tetraphenyl substitution, and hence make it less effective in interaction with the silica gel from ODPC, TPHDPC and OPTDPC. However, it was difficult to separate these three compounds cleanly on the usual chromatographic column. The compounds can be readily separated as three separate green bands by gel-permeation column which utilizes the different steric shape of the molecules.

The metallo zinc-phthalocyanine derivative **1b** can be readily formed by refluxing the metal free phthalocyanine with the metal salt, zinc acetate, in toluene/2-methoxyethanol (2/1, v/v) under an inert atmosphere. However, the Zinc-phthalocyanine **1b** was not very stable and decomposed with a color change from blue green to yellow upon standing a few days in a dilute chloroform solution. The instability of the metallo phthalocyanine derivative was probably due to the high steric strain on the phthalocyanine ring with an octaphenyl moiety substituted on both sides, or may distort the planarity of the phthalocyanine aromatic core.

We have also tried to synthesize the target compound **1a** by mixed condensation between tetraphenyl-*o*-phthalonitrile and 1,2-dicyano-4,5-bis(dodecyloxy)benzene, but no desired compound **1a** was obtained under the above condition.

Compound **1a** was very soluble in chloroform, tetrahydrofuran and toluene, but insoluble in methanol and acetone. The solubility of metallo phthalocyanine derivative **1b** was found to be slightly lower than their metal free phthalocyanine counterpart, which was in part due to the increased symmetry of metalated phthalocyanine.

The infrared spectrum of compound **1a** showed the characteristic NH absorption of phthalocyanine at 3316 and 1606 cm^{-1} .

The visible/ultraviolet spectrum of the metal free OPTDPC, **1a**, showed only one Q band at 696 nm (Figure 1), while the metal free ODPC with D_{2h} symmetry showed a 38 nm splitting of the Q band at 665 and 703 nm [20]. The lack of the double Q band in **1a** was due to a change in the symmetry by incorporation of a tetraphenyl group in **1a**, and thus a change in their ground and excited states. The spectrum of zinc-phthalocyanine **1b** showed a 31 nm splitting of the Q band at 707 and 676 nm (Figure 1). This splitting was opposite to the spectra of the normal symmetrical metallo "AAAA" type phthalocyanine which had no splitting in this band. The difference can be attributed to the loss of symmetry from the D_{4h} of the normal metallo phthalocyanine to D_{2h} in the "opposite" type zinc-phthalocyanine **1b**. These results were consistent with Kobayashi's similar compounds with diphenyl substitution [16]. However, the results were contradictory to Subbotin's report [21]. Subbotin used one of the precursors, tetraphenylphthalonitrile (B), which reacted with phthalonitrile (A) in 1:1 molar ratio. Subbotin reported that there were significant amounts of AABB and ABBB besides ABAB type phthalocyanine formation. However, the spectra given were inconsistent with the symmetry of molecular structure, for instance, both metallo phthalocyanine ABAB (D_{2h} symmetry) and AABB (C_s symmetry) have the same uv-visible spectra with no splitting of the Q band. We found no such compounds as AABB and ABBB type formation in our experiments as evidenced for the spectra discussed above.

The proton nmr (Figure 2) and carbon-13 nmr (Figure 3) of **1a** was as expected, the multiple peaks at 6.79-7.64 δ region in 1H nmr and 100-150 δ region in ^{13}C nmr indicate the presence of several different aromatic hydrogens and carbons in the compound, and **1a** shows the exact expected number of aromatic hydrogen atoms (44 H) by integration in 1H nmr. An unusually strong down field shift of the cavity hydrogens (-1.4 δ) in the 1H nmr due to shielding of the phthalocyanine ring was observed in **1a** relative to TPHDPC (-2.1 δ) and ODPC (-2.7 δ). From compound ODPC, tetraphenyl substituted TPHDPC, to the "opposite" octaphenyl substituted OPTDPC, **1a**, the chemical shifts of the cavity hydrogen atoms shift to lower field for each tetraphenyl group incorporated at the same concentration ($1.6 \times 10^{-2} M$). This shifting of the NH position was obviously due to the deshielding effect of multiphenyl substitution on the phthalocyanine ring. The orthogonality of the aromatic rings produces this profound shift in the core hydrogens. It should be noted that the shift of the core hydrogen was concentration dependent [22].

In conclusion, the novel "opposite" octaphenyl substituted solvent soluble phthalocyanine was synthesized and characterized. The Q band of metallo phthalocyanine was split due to its D_{2h} symmetry. Due to its octaphenyl group set at a 45° dihedral angle to the phthalocyanine ring, a highly steric bulky phthalocyanine resulted. The compound was expected to have unique aggregation behavior and other properties due to its molecular shape.

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