

Synthesis of Novel Asymmetrical Tri-tert-butyl Naphthalocyanine Using Structurally Distorted Subnaphthalocyanine

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Abstract: A novel asymmetrical tri-tert-butyl naphthalocyanine was prepared for the first time by the condensation method and by the use of structurally distorted subnaphthalocyanine, respectively. The advantages of the latter method were more convenient purification and relatively higher yield.

Keywords: Subnaphthalocyanine; asymmetrical; naphthalocyanine; condensation.

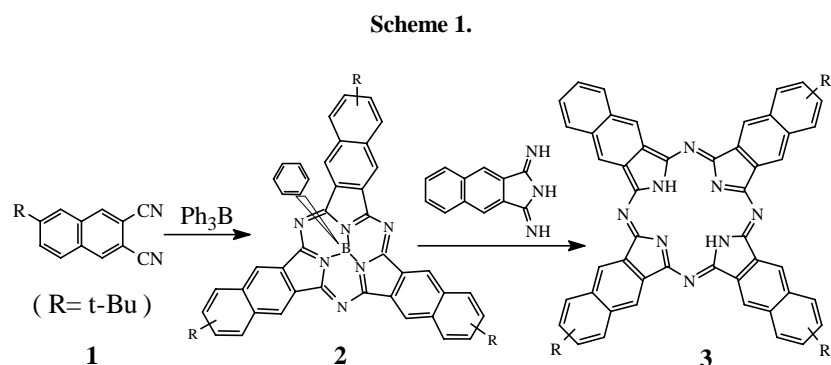
Phthalocyanines (Pcs) often show high thermal and chemical stability and interesting optical and electrical properties. In addition to traditional uses, Pcs are considered to be candidates in many fields as functional materials such as semiconductors, gas sensors, photocatalysts, and non-linear optical devices¹.

Recently much attention has been focused on the synthesis of novel asymmetrical phthalocyanine derivatives with various functional groups. Our interest in the synthesis of novel asymmetrical tri-tert-butyl naphthalocyanine results from its potential optical application as SHG (second-order harmonic generation), in which non-centro-symmetry is an indispensable character².

Until now many symmetrical substituted Pcs were well documented, but few reports on asymmetrical Pcs were presented because of their synthetic difficulties. Traditional strategies for preparing an asymmetrical phthalocyanine, mostly involved the condensation of two differently substituted phthalonitrile-precursors in appropriate stoichiometric ratios to yield the desired product³. There are twofold difficulties encountered in the condensation method. First, condensation of two different precursors can give a statistical distribution of mono-, di-, tri-, and tetra- substituted phthalocyanines, which offers a very low yield of the desired product. Secondly, their similar properties preclude the purification of products by column chromatography.

A new route was recently reported by the use of subphthalocyanine to prepare asymmetrical Pcs⁴. However, there is no report on the synthesis of asymmetrical naphthalocyanines by this method. Our group has prepared a novel asymmetrical naphthalocyanine by the traditional method and the new method, respectively, and demonstrated that the new method was also feasible for the synthesis of asymmetrical naphthalocyanine.

First, asymmetrical tri-tert-butyl naphthalocyanine was prepared according to the synthetic route shown below (**Scheme 1**).



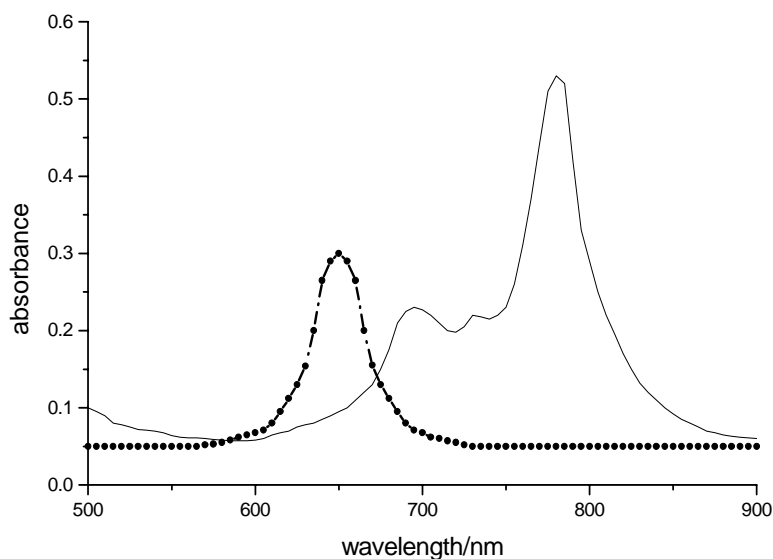
Compound **2**, (μ -phenyl)-tri-tert-butyl subnaphthalocyninatoboron, was prepared under reflux for 20min by reaction of 6-tert-butyl-2,3-naphthalenedinitrile (compound **1**)⁵ with triphenylboron⁶ in α -bromonaphthalene as solvent. The product was purified by column chromatography using n-hexane as eluent. It was found to be unstable to light⁷. The yield was about 5%. Compound **3** was then synthesized by reaction of resulting compound **2** with 1,3-diiminobenzoindole⁸ in a mixing solvent of DMSO and trichlorobenzene at 90–100°C. After removal of the solvents at reduced pressure, the resulting dark-blue mixture was separated by column chromatography using a mixing solvent of chloroform and cyclohexane as eluent. Two colored bands were collected respectively. The first greenish band was the starting material (compound **2**), the latter blue band was the desired product and repurified by the same procedure. The yield was about 10%. Compounds **2** and **3** were identified by FAB (fast atom bombardment technique), Elemental analysis, IR spectra⁹.

Also the condensation method was used to prepare the desired product. The precursor **1** reacted with 2,3-dicyanonaphthalene in a 3:1 molar ratio to obtain compound **3**. The appropriate stoichiometry of two precursors was efficient to afford the desired product as major product. Though the desired product can be prepared as major product by the appropriate stoichiometry, other four byproducts were still obtained at the same time, which greatly increased the difficulties of the purification. In the separation, unsubstituted and mono-tert-butyl substituted naphthalocyanines were easily separated due to their poor solubility. The difficulties encountered come from the similarity of di- and tetra-tert-butyl substituted naphthalocyanines to the desired product. Compound **3** was carefully separated from the mixture in several steps by alumina column chromatography. The resultant mixture was first separated using CHCl_3 as eluent, and a blue band was collected. Then the blue component was purified using a mixing solvent of CH_2Cl_2 and cyclohexane (2:3) as eluent, and two bands were obtained. The latter band was then repurified using pure cyclohexane as eluent, also two bands were collected, respectively, of which the first band was further treated with ether, and the pure compound **3** was obtained. The yield was so low that it was difficult to be determined.

Compared to the condensation method, the method by the use of subnaphthalo-cyanine has two marking advantages: (i) Only the desired product can be obtained so that the yield of target compound is relatively higher; (ii) Purification by column chromatography is easier because of less byproducts and observably different color of each band. The distorted structure of compound **2** is proved to be suitable for ring-expansion reaction to prepare asymmetrical naphthalocyanines.

In addition, the electronic absorption spectra of compounds **2** and **3** were shown in **Figure 1**. Compound **2** has a Q-band at the wavelength of 650 nm with a low extinction coefficient ($\epsilon = 9 \times 10^2$). Compound **3** has maximum absorption peaks at 780 nm and 696 nm, where the peak at 696 nm was demonstrated to be its aggregation. The Q-band of compound **3** appears red-shifted 130 nm compared with that of compound **2** because its 18π -electron conjugated system is much larger than 14π -electron conjugated unit in compound **2**.

Figure 1 The electronic absorption spectra of compounds **2** (...) and **3** (—)



The Q-band of compound **3** suits the wavelength of solid semiconductor lasers very well and its non-centro-symmetry is a significant property for SHG. Accordingly, the compound was expected to be a potential candidate for nonlinear optical material and optical recording media. Further work is in progress in our laboratory.

Acknowledgments

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References and notes

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9. Satisfactory elemental analysis data were obtained for compounds **2** and **3**. ¹H-NMR indicated pure products, and the aromatic protons were difficult to discern because of the wide range absorption at upfield. FAB: compound **2**, 792 (M⁺+H), 715 (M⁺+H-Ph), compound **3**, 884 (M⁺+H). IR (selected absorption peaks, cm⁻¹): compound **2**, 2955, 1620, 1586, 1488, 1379, 1365, 761, 699, compound **3**, 2955, 1610, 1475, 1361, 1259, 1094, 1021.

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