

Synthesis of New Soluble Subphthalocyanine Substituted with Crown Ethers

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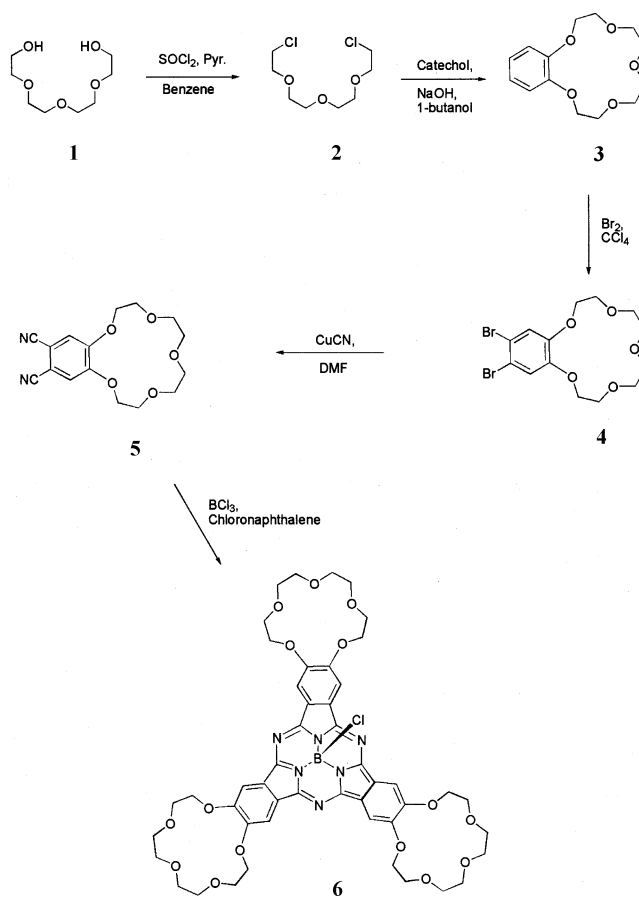
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Recently, metallophthalocyanines have evoked much interest due to their electroconductivity, photoconductivity, electrochromic property, and catalytic activity.¹ A variety of technological applications of phthalocyanines have been actively investigated depending on the nature of the peripheral substituents and the central metal ion, such as photovoltaics, electrochromism, optical discs, laser dyes, liquid crystals, electrocatalysis, chemical sensors and photodynamic cancer therapy.² Phthalocyanines have also been studied as models of naturally occurring porphyrins.³ Another interesting group of compounds used as biological models are crown ethers, which form complexes with alkali and alkaline-earth metal ions as well as with primary ammonium salt of organic molecules.⁴ As analogues of phthalocyanine which consists of four isoindoline units, the so-called superphthalocyanine (five isoindoline units) and subphthalocyanine (three isoindoline units), [BX(subpc)] (X=F, Cl) have also been reported.⁵ [BX(subpc)] with a 14 π -electron system and a C_{3v} symmetry shows a Q band around 570 nm, and also changes to phthalocyanine by a reaction with 1,3-isoindolinediimine.⁶

The ring-expansion reaction of subphthalocyanines is an attractive method for the preparation of unsymmetrical phthalocyanine derivatives with wanted substituents at a particular position on the ring.⁷ It has been further reported that the subphthalocyanine derivatives presented very large second-order molecular polarizabilities, and were expected to serve as novel targets for second-order nonlinear optical applications; these second-order polarizabilities were mostly associated with the octupolar contribution, and were comparable to those found in the most efficient linear compounds, such as polyenes.⁸ Nevertheless, the very poor solubility of these metallomacrocycles in organic media often precludes the study of their properties.

Here we report the synthesis of new subphthalocyanine **6**, highly soluble in various organic solvents (14.3 mg/mL in CDCl₃), containing three 15-crown-5 subunits on the isoindole moieties. The addition of crown ether groups into the phthalocyanine has provided considerable opportunity to investigate the properties of the complexes by enhancing their solubility in various solvents and in water.⁹

The synthetic route of new 'crowned' subphthalocyanine **6** began with substitution reaction of hydroxy group of tetraethylene glycol **1** with thionyl chloride to provide 1,11-dichloride-3,6,9-trioxaundecane **2** in 89% yield. The resulting dichloride compound **2** was treated with catechol to give benzo-15-crown-5 **3** in 62% yield. Bromination of cyclic polyether **3** with bromine provided 4',5'-dibromobenzo-15-



Scheme 1

crown-5 **4** in 84% yield. The resulting compound 4',5'-dibromobenzo-15-crown-5 **4** was treated with CuCN in refluxing DMF to produce 4',5'-dicyanobenzo-15-crown-5 **5** in 38% yield. The desired final product, crowned subphthalocyanine **6**, was obtained by cyclotrimerization of the 4',5'-dicyanobenzo-15-crown-5 in chloronaphthalene in the presence of BCl₃ in 3.5% yield. Compound **6** can be purified by column chromatography on alumina and was characterized by ¹H NMR, ¹³C NMR, IR, and FAB-MS.¹⁰

The properties of the compound **6**, such as photo- and electroluminescence properties, and nonlinear optical properties, are under investigation. This new soluble subphthalocyanine **6** may also be utilized as a powerful and selective extracting reagent for metal cations.

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 10. **6**: Purple shining powder; mp >300 °C, MS (FAB, *m*-NBA) *m/z* 1001 (M+H⁺); IR (KBr, cm⁻¹) 1630, 1591, and 1520; ¹H NMR (200 MHz, CDCl₃) δ 7.22 (s, 3H, arom.), 7.18 (s, 3H, arom.); 4.18, 3.94, 3.73 (each br, 48H, CH₂O); ¹³C NMR (50 MHz, CDCl₃) δ 69.18, 70.77, 109.11, 115.41, 117.17, 152.37.
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