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PREPARATION AND ELECTROCHEMICAL PROPERTY OF OCTABUTYLPHTHALOCYANINE FUSED WITH FOUR TTF UNITS

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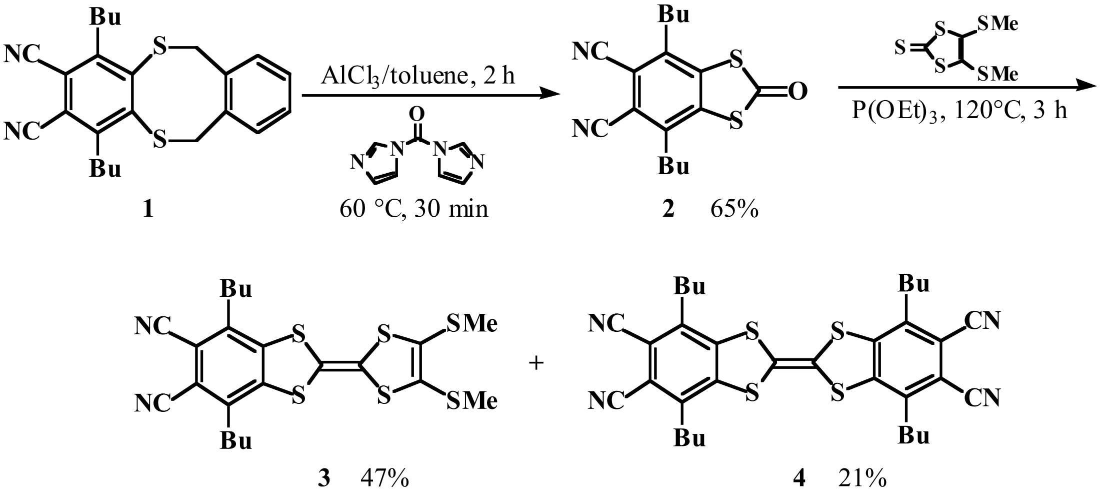
Dedicated to Professor Ryoji Noyori on the occasion of his 70th birthday.

Abstract – 3,6-Dibutylphthalonitrile (**3**) fused with a TTF unit was prepared and treated with lithium in *n*-pentanol to produce octabutyltetrakis(tetrathiafulvaleno)phthalocyanine (**5**). The structure of the product was determined by ^{1}H NMR and FAB MS. Electrochemical and optical properties of compound (**5**) were estimated by cyclic voltammetry and UV-vis spectroscopy.

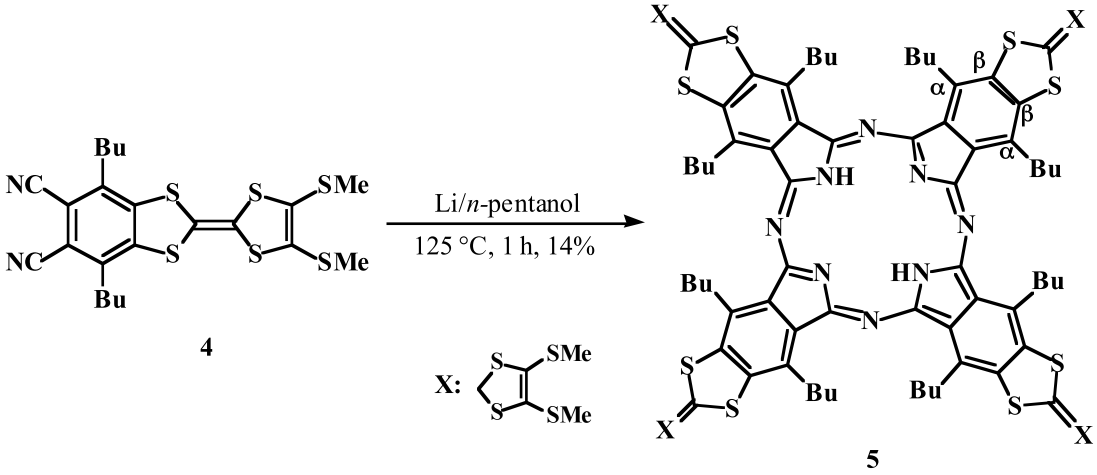
Phthalocyanines and related compounds have attracted considerable attention for their actual and potential applications in many fields, for example, catalysis, optical disks, charge-generating materials, and sensitizers for photodynamic therapy.[1] It is significant that Q-band absorption lies in the near infrared region for the application of phthalocyanines to new functional materials. A redshift of the wavelength of the Q-band can be accomplished by attaching electron-donating substituents at the α-positions of the macrocycle.[2] Introducing heteroatoms as substituents at the peripheral positions or in fused ring systems can also be an efficient method.[3,4] As a related study, we recently reported the preparation of tetrakis(*o*-xylylenedithio)phthalocyanine [**PcSXyl**], octakis(benzylthio)phthalocyanine, and their related compounds.[5,6] On the other hand, it is well known that tetrathiafulvalene (TTF) is an excellent electron donor.[7] If the TTF unit fuses to tetraazaporphyrin or phthalocyanine, the molecules are expected to have unique electrochemical, optochemical, and physicochemical characteristics. There are several reports that TTF and phthalocyanine are connected with some linkers.[8] In contrast, Becher reported porphyrin derivatives bearing a TTF unit,[9a,b] while Decurtins prepared phthalocyanines with four TTF scaffolds,[9c] in which the TTF is covalently and directly fused to the macrocycles. The phthalocyanines reported by Decurtins seem to have a high aggregative property in solution even at low concentration. To prepare phthalocyanine bearing eight long alkyl groups at the α-positions and four

TTF units at the β-positions, 3,6-dibutylphthalonitrile (**3**) connected with one TTF unit at the 4,5-positions was prepared and treated with lithium in *n*-pentanol. This paper reports the preparation, structure determination, and optical and electrochemical properties of tetrakis(tetrathiafulvaleno)-phthalocyanine with eight butyl groups at the α-positions.



Scheme 1

As a starting compound, 4,5-(*o*-xylylenedithio)-3,6-dibutylphthalonitrile (**1**) was prepared from 1,4-dichlorobenzene *via* five reaction steps by using a method described previously.[5] To construct the TTF unit, compound (**1**) was initially treated with AlCl3 in toluene under N_2 for 2 h to remove the *o*-xylylene group, and then carbonyldiimidazole was added to the reaction mixture (Scheme 1). The solution was stirred at 60 °C for 30 min. After purification, 3,6-dibutylphthalonitrile (**2**) fused with a 1,3-dithiole-2-one ring was obtained in 65% yield. If the reaction were carried out at room temperature, the corresponding dimercaptobenzene was obtained together with compound (**2**) while the mixture could not be easily separated. The product (**2**) was condensed with commercially available 4,5-bis(methylthio)-1,3-dithiole-2-thione in triethyl phosphite at 120 °C for 3 h to produce 3,6-dibutylphthalonitrile (**3**) with one TTF unit in 47% yield.[10] In this reaction, dibenzotetrathiafulvalene derivative (**4**) was produced together with compound (**3**) in 21% yield. For the tetramerization of phthalonitrile, compound (**3**) (104 mg, 0.2 mmol) was added to a solution of lithium *n*-pentoxide in *n*-pentanol, which was prepared from lithium (15.0 mg, 2.0 mmol) and the solvent (1 mL) under Ar (Scheme 2). The solution was stirred at 125 °C for 1 h. The reaction finally produced a blue-green suspension and the product was poured into methanol containing a small amount of hydrochloric acid. The solid that precipitated into the solution was filtered, dried, and purified by silica gel column chromatography, which gave octabutyltetrakis(tetrathiafulvaleno)phthalocyanine (**5**) in 14% yield (14.2 mg). Compound (**5**) was soluble in the usual organic solvents except for methanol, acetonitrile, and DMF. When the ^{1}H NMR of **5** was measured in chloroform-*d* at 25 °C, broadened signals were observed in the spectrum. In contrast, compound (**5**) showed clear signals for the butyl and methylthio groups when the spectrum was measured at 50 °C.[11] However, the protons on the nitrogen atoms could not be observed in the spectrum. The UV-vis spectrum of **5** shows one slightly broadened Q-band (λ_{max} = 769 nm, log ε = 5.20),[12] which is similar to that of **PcSXyl**, suggesting that an aggregative property of **5** is obstructed by the butyl groups at the α-positions. A FAB MS experiment was performed for **5.** The molecular ion peak observed at m/z = 2034.12 [MH^+] is consistent with the presence of the four TTF units on the central phthalocyanine core.



Scheme 2

To determine the electrochemical property of **5**, the redox potential was measured by cyclic voltammetry using Ag/$AgNO_3$ as a reference electrode (solvent: CH_2Cl_2). The voltammogram showed one quasi-reversible couple ($E_{1/2}$ = 0.43 V) and one reversible couple ($E_{1/2}$ = 0.73) for oxidation potentials; scan rate: 20 mV/s, while one reversible couple and one irreversible peak ($E_{1/2}$ = –0.78 and Ep = –1.04 V) were observed for reduction potentials; scan rate: 200 mV/s.

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10. **3**: red crystals; mp 159 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.98 (t, J = 7.5 Hz, 6H, CH_3), 1.41-1.51 (m, 4H, CH_2), 1.61-1.67 (m, 4H, CH_2), 2.45 (s, 6H, SCH_3), 2.77 (t, J = 8.1 Hz, 4H, $ArCH_2$); ^{13}C NMR (101 MHz, $CDCl_3$) δ 13.7, 19.2, 22.6, 30.3, 35.2, 105.8, 113.5, 114.7, 115.1, 127.6, 138.4, 143.7; HRMS (EI) Calcd for $C_{22}H_{24}N_2S_6$: 508.0264. Found: 508.0247 (M^+).
11. **5**: dark blue powder; mp >300 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.89 (t, J = 7.5 Hz, 24H, CH_3), 1.48-1.57 (m, 16H, CH_2), 1.90-1.94 (m, 16H, CH_2), 2.51 (s, 24H, SCH_3), 4.32-4.36 (m, 16H, $ArCH_2$); FABMS 2034.12 (MH^+).
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