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Synthesis and self-assembly of phthalocyanines bearing sulfur-containing substituents



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ABSTRACT

Asymmetrically substituted phthalocyanines with sulfur-containing substituents for fabrication of self-assembled monolayers were synthesized. Phthalocyanine **7**, bearing a disulfide group, was synthesized from phthalocyanine with a hydroxyl group, which was prepared *via* mixed condensation of the corresponding substituted phthalonitriles. Phthalocyanine **10**, bearing an acetyl protected thiol group, was synthesized through the Pd-catalyzed coupling reaction of an iodophthalocyanine. Their self-assembling behavior on gold substrates was further studied by UV–vis spectroscopy.

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1. Introduction

With their outstanding electronic and optical properties, phthalocyanines and their metallic derivatives have become a promising family of materials in recent years having already been used in laser printers, photo-copiers, light-emitting diodes (LEDs), data storage systems and photovoltaic cells. Their potential applications in optical limiting, gas sensors, field-effect transistors (FETs) and photodynamic therapy have attracted even more research interests. In the above research, phthalocyanine thin films have always required fabrication. Consequently, there are several ways to fabricate the thin films [1]: Langmuir–Blodgett technique, solvent evaporation, thermal evaporation, electrochemical deposition, stamping and self-assembly method. Among them, the self-assembly method seems to become even more attractive with the growth of the research field in molecular electronics. This method has already been used in fabricating organic electronic devices [2]. Compared with thin films prepared by other methods, the self-assembled monolayers (SAMs) are simple to fabricate, very thermally and mechanically stable and can be grown on substrates of all sizes. The self-assembling behavior of small molecules bearing sulfur-containing substituents, such as disulfide, *S*-acetyl and mercapto-groups, has been studied extensively [3]. They have been shown to form self-assembled monolayers on gold, silver and copper substrates. Compared to these small molecules, the self-assembly of phthalocyanines with excellent optical and electrical properties may be of more importance. As is well known, a variety

of substituents can be introduced onto the periphery of the phthalocyanine rings and their properties can be finely tuned as such. Many substituted phthalocyanines have been synthesized, but only limited work has been done on the synthesis and the self-assembly of phthalocyanines bearing sulfur-containing substituents [4–6]. We report here on the synthesis and self-assembly of two phthalocyanines bearing sulfur-containing substituents including disulfide and *S*-acetyl groups.

2. Experimental

The precursors, 4-nitrophthalonitrile and 4-*tert*-butylphthalonitrile, were purchased from Tokyo Kasei Kogyo Co., Ltd. and used as received without further purification. Phthalocyanines **8**, **9** and *S*-(4-iodophenyl)ethanethioate were prepared according to literature methods. Tetrahydrofuran (THF) was distilled from *N*-benzophenone under nitrogen. Other solvents were dried over 4 Å molecular sieve and distilled prior to use. The ¹H NMR spectra were obtained on a Varian Unity 200 NMR Spectrometer, or Bruker DMX 300 NMR Spectrometer. UV–vis spectra were measured using a Hitachi Model U-3010 Spectrophotometer. MS spectra (MALDI-TOF-MS) were obtained on a Bruker BIFLEX III Mass Spectrometer.

2.1. Synthesis of 1,6-hexanediol monotetrahydropyranyl ether (**2**)

To an ice-cooled solution of 1,6-hexanediol (59 g, 500 mmol), *p*-toluene sulfuric acid monohydrate (1.6 g, 8.4 mmol) and dihydropyran (4.2 g, 50 mmol) were added with stirring. The mixture was then allowed to warm to room temperature and stirred for 24 h. The resulting mixture was diluted with ether, washed with

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saturated aqueous potassium carbonate solution and dried with anhydrous potassium carbonate. After solvent evaporation, the remaining white solid was extracted with petroleum ether (60–90 °C). Upon removal of the solvent, 6.4 g (63% yield) of **2** was obtained as colorless oil. Data for **2**: $^1\text{H NMR}$ (200 MHz, CDCl_3): δ 1.41 (m, 4H, CH_2), 1.55 (m, 8H, CH_2), 1.87 (m, 2H, CH_2), 3.31–3.57 (m, 2H, OCH_2), 3.64 (t, 2H, $J = 7.1$ Hz, OCH_2), 3.70–3.95 (m, 2H, OCH_2), 4.58 (t, 1H, $J = 7.3$ Hz, OCHO).

2.1.1. Synthesis of 4-[6-(tetrahydro-pyran-2-yloxy)hexyloxy]phthalonitrile (**3**)

A mixture of 4-nitrophthalonitrile (5.0 g, 29 mmol), 1,6-hexanediol monotetrahydropyranyl ether **2** (5.8 g, 29 mmol) and anhydrous potassium carbonate (12 g, 87 mmol) in DMF (150 mL) was stirred overnight at 60 °C. The solvent was removed under reduced pressure. The residue was dissolved with dichloromethane, filtered and purified by column chromatography (silica gel) using dichloromethane as eluant. The product **3** was obtained as yellow oil (7.5 g, 79% yield). Data for **3**: $^1\text{H NMR}$ (200 MHz, acetone- d_6): δ 1.48 (m, 12H, CH_2), 1.80 (m, 2H, CH_2), 3.40 (m, 2H, OCH_2), 3.75 (m, 2H, OCH_2), 4.23 (t, 2H, $J = 7.1$ Hz, OCH_2), 4.54 (m, 1H, OCHO), 7.45 (dd, 1H, *phenyl*), 7.60 (d, 1H, *phenyl*), 7.94 (d, 1H, *phenyl*).

2.2. Synthesis of 4-(6-hydroxyhexyloxy)phthalonitrile (**4**)

Phthalonitrile **3** (7.5 g, 23 mmol) and *p*-toluenesulfonic acid (PTSA) (0.43 g, 2.3 mmol) were dissolved in ethanol (150 mL). The resulting solution was stirred at 50 °C for 10 h at 50 °C. After removal of the solvent, the residue was purified by column chromatography (silica gel) using dichloromethane as eluant. Phthalonitrile **4** (3.5 g, 63% yield) was obtained as a light yellow solid. Data for **4**: $^1\text{H NMR}$ (300 MHz, acetone- d_6): δ 1.84 (m, 4H, CH_2), 1.50 (m, 4H, CH_2), 3.65 (t, 2H, $J = 7.1$ Hz, OCH_2), 4.05 (t, 2H, $J = 7.1$ Hz, OCH_2), 4.58 (br, 1H, OH), 7.18 (dd, 1H, *phenyl*), 7.25 (d, 1H, *phenyl*), 7.71 (d, 1H, *phenyl*).

2.2.1. Synthesis of 2,9,16-tri(tert-butyl)-23-(6-hydroxyhexyloxy)phthalocyanine (**5**)

To *n*-pentanol (70 mL), 4-*tert*-butylphthalonitrile (6.1 g, 33 mmol) and phthalonitrile **4** (2.7 g, 11 mmol) were added. The mixture was brought to reflux. Then lithium metal (1.0 g, 0.14 mmol) was added in small portions. The reaction was continued for 6 h. The solvent was removed under reduced pressure. The black residue was washed with methanol and further purified by column chromatography (silica gel) using chloroform as eluant. The first band proved to be tetra-*tert*-butylphthalocyanine. Then the second band was collected. Upon removal of the solvents, the desired product was obtained as a shining purple solid (1.7 g, 19% yield). Data for **6**: $^1\text{H NMR}$ (300 MHz, C_6D_6): δ 2.34 (br, 1H, NH), –2.79 (br, 1H, NH), 1.71 (m, 2H), 1.86 (m, 31H), 2.16 (m, 2H), 3.84 (m, 2H, OCH_2), 4.46 (m, 2H, OCH_2), 7.20–9.20 (m, 12H, *aryl*). MALDI-TOF-MS: m/z calcd. for $\text{C}_{50}\text{H}_{54}\text{N}_8\text{O}_2$: 798.44, found: 798.3 (M^+). UV-vis (in chloroform): λ_{max} (log ϵ) 701 (0.49), 665 (0.41), 648 (0.17), 603 (0.09), 343 (0.25).

2.2.2. Synthesis of 2,9,16-tri(tert-butyl)-23-(6-methanesulfonyloxyhexyloxy)phthalocyanine (**6**)

To an ice-cooled solution of **5** (120 mg, 150 μmol) in dichloromethane (20 mL), triethylamine (60 drops) and methane sulfonyl chloride (30 drops) were added with stirring. The mixture was allowed to warm to room temperature and stirring continued for 30 min. Then the resulting solution was washed with water and dried with anhydrous magnesium sulfate. The product was purified by column chromatography (silica gel) using chloroform as eluant to yield **6** as a black blue solid (90 mg, 68% yield).

2.3. Synthesis of phthalocyanine disulfide (**7**)

A solution of phthalocyanine **6** (90 mg, 103 μmol) in THF (20 mL) and ethanol (6 mL) was brought to reflux. Then thiourea (60 mg, 0.79 mmol) was added. The reaction was monitored by TLC. After all of the starting material was consumed, aqueous sodium hydroxide solution (20%, 12 mL) was added. When the reaction monitored by TLC was complete, the resulting mixture was poured into a mixture of dilute hydrochloric acid and ice and extracted with dichloromethane. The organic phase was separated and dried with anhydrous magnesium sulfate. After removal of the solvent, the residue was purified by column chromatography using dichloromethane as eluant. Phthalocyanine disulfide **7** was obtained as a purple solid (36 mg, 43% yield). Data for **7**: $^1\text{H NMR}$ (300 MHz, C_6D_6): δ 3.64 (br, 2H, NH), –3.33 (br, 2H, NH), 0.54–1.95 (m, 70H), 2.98 (m, 4H, SCH_2), 4.35 (m, 4H, OCH_2), 7.00–9.40 (m, 24H, *aryl*). MALDI-TOF-MS: m/z calcd. for $\text{C}_{100}\text{H}_{106}\text{N}_{16}\text{O}_2\text{S}_2$: 1626.81, found: 1627.1 (M^+). UV-vis (in chloroform): λ_{max} (log ϵ) 701 (0.37), 664 (0.54), 641 (0.52), 338 (0.60).

2.4. Synthesis of phthalocyanine (**10**)

To a solution of phthalocyanine **9** (0.2 g, 0.26 mmol) and *S*-(4-iodophenyl) ethanethioate (72 mg, 0.26 mmol) in triethylamine (10 mL), dichlorobis(triphenylphosphine)palladium(II) (9 mg, 13 μmol) and copper (I) iodide (5 mg, 26 μmol) were added. The mixture was stirred at room temperature for 23 h. The solvent was evaporated under reduced pressure. The residue was purified by column chromatography using dichloromethane/methanol (50:1) as eluent. The product was obtained as a black solid (83 mg, 35% yield). Data for **10**: $^1\text{H NMR}$ (300 MHz, C_6D_6): δ 1.67 (m, 27H, *t-butyl*), 2.42 (s, 3H, COCH_3), 6.54–8.70 (m, 16H, *aryl*). MALDI-TOF-MS: m/z calcd. for $\text{C}_{54}\text{H}_{46}\text{N}_8\text{OSZn}$: 918.28, found: 918.4 (M^+). UV-vis (in chloroform): λ_{max} (log ϵ) 692 (1.6), 617 (0.38), 350 (0.93).

Quartz slides were washed with chloroform and immersed into a solution of potassium hydroxide in 100 mL of deionized water and 250 mL methanol for 12 h. Then the quartz slides were washed thoroughly with deionized water and dried in a stream of nitrogen. The gold substrates were prepared by thermal evaporation of a layer of gold onto freshly cleaned quartz slides that had been precoated with a chromium adhesion layer. For UV-vis characterization, 5 nm of chromium was deposited on cleaned quartz slides followed by an 8 nm gold layer. Phthalocyanine SAMs were prepared by immersing gold substrates into phthalocyanine solutions in chloroform (6.7×10^{-5} mol/L and 2.9×10^{-5} mol/L for **7** and **10**, respectively) for 24 h at room temperature. References for UV-vis measurements were prepared by immersing corresponding substrates into pure chloroform for 24 h. Then the substrates were washed thoroughly with chloroform and dried in a stream of nitrogen.

3. Results and discussion

Several methods have been developed to synthesize substituted phthalocyanines. Among these methods, condensation of the corresponding phthalonitriles is the method usually referenced and appears to be the most successful one. A variety of uniformly substituted phthalocyanines have been synthesized through this method. There are also several reports with details to synthesize non-uniformly substituted phthalocyanines [7,8], however, it seems that the above method is the most satisfactory one at present. Two kinds of phthalonitriles bearing different substituents were used in the condensation. The product is a mixture of substituted phthalocyanines. The desired substituted phthalocyanine is then obtained after following a careful separation procedure. 4-

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