

# Synthesis of highly soluble phthalocyanine from a new phthalonitrile under mild conditions

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## ABSTRACT

Novel syntheses of zinc phthalocyanine (ZnPc) are achieved by exploring our hexamethyldisilazane (HMDS) method. Reactions are clean and efficient by replacing harmful and strongly smelling triethylamine with HMDS. The compound is highly soluble in organic solvents and can be used as a donor material for organic thin film photovoltaic solar cells. Copyright © 2010 VBRI press.

**Keywords:** Phtalocyanine, phtalonitrile, hexamethyldisilazane, photovoltaics.



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## Introduction

Phthalocyanines (Pc's) are a very versatile class of heteroaromatic compound, and are well-known as one of the most important classes of industrial dye and pigment materials [1]. Recent advances in synthetic methods and chromatographic separation techniques have made possible a wide range of new Pc derivatives with different skeletons and substituents. Consequently, a variety of functionalized Pc derivatives have now become available, and their spectroscopic and electrochemical properties have been studied extensively in order to develop these for a wide variety of applications such as organic conductors, chemical sensors, photodynamic therapy, catalysts, liquid crystal displays and information storage devices [1-3]. Recent academic developments of Pc analogues have also been reviewed in several papers and books [1-8]. Related aromatic macrocycles of phthalocyanines are also intensively studied due to their unique structural and photo physical properties that make them attractive compounds for technological applications [9-13].

Hexamethyldisilazane (HMDS) is a cheap and commercially available reagent. Its handling does not need special precaution and the work up of the reaction mixture is not time consuming. This reagent has been used for silylation of various alcohols in the presence of trimethylchlorosilane [14], sulfonic acids [15], amines, and trimethylsilylated amides such as saccharin [16]. Moreover, HMDS is very useful in synthesis of phtalocyanines as demonstrated in previous studies [17,18].

Here we reexamined the conventional reaction conditions of phthalocyanines with triethylamine and contemplated important changes to make the reaction clean

and efficient by replacing harmful and strongly smelling triethylamine with HMDS. In continuation of our efforts to develop new synthetic methods for widely used compounds, our group has recently reported that HMDS [19-23] is an excellent reagent for the construction of the phthalocyanine framework from phthalimides, phthalic anhydrides, and phthalonitriles [17,18]. Moreover, various metallophthalocyanines can be prepared by heating HMDS under mild conditions. HMDS is a nitrogen source and it also accelerates dehydration in the formation of the phthalocyanine framework [24].

yielded colorless oil (82%) [25].  $^1\text{H NMR}$  ( $\text{CDCl}_3$ , 200MHz):  $\delta$  6.86 (s, 4H), 3.97 (t, 4H,  $J=5.6\text{Hz}$ ), 1.87-1.73 (m, 4H) 1.47-1.28 (m, 20H), 0.90 (t, 6H,  $J=6.2\text{Hz}$ ).

**Compound 2.** 5-Bromopentanoyl chloride (1.8 mL, 13.45 mmol) was dissolved in  $\text{CH}_2\text{Cl}_2$  (7.5 mL). Aluminium trichloride (1.99 g, 14.95 mmol) was added in portions at  $0^\circ\text{C}$ . Subsequently, 1, 2-bis-octyloxy benzene **1** (5 g, 14.95 mmol) in  $\text{CH}_2\text{Cl}_2$  (7.5 mL) was added. The reaction was allowed to stir until the end of visible gas evolution ( $\pm 45$  min.). Subsequently, the reaction mixture was stirred for another 20 min. at  $40^\circ\text{C}$ . The reaction mixture turned

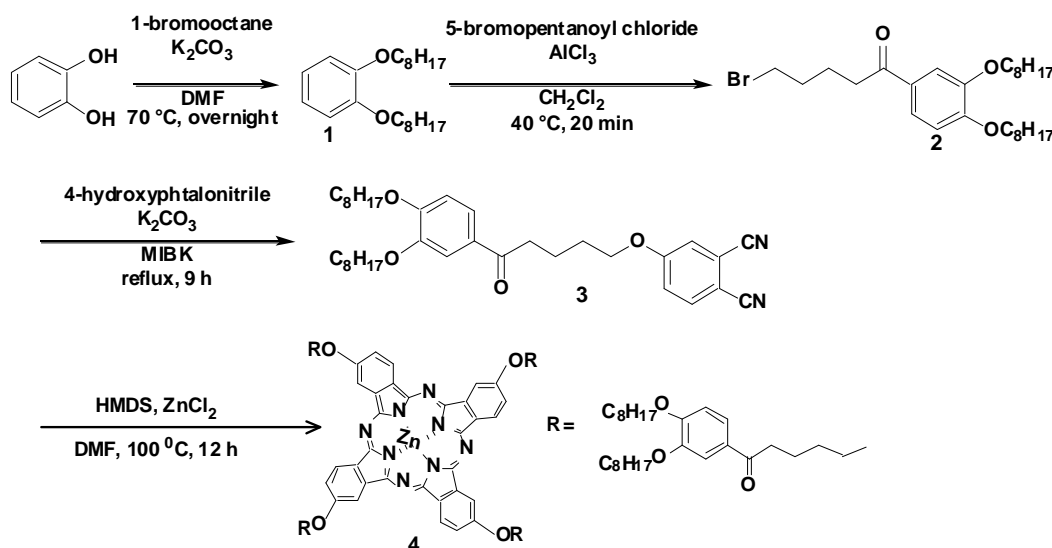


Fig. 1. Reaction scheme.

## Experimental

### General

All solvents were dried and distilled according to standard procedures. All of the reactions were monitored by thin-layer chromatography (TLC) carried out on 0.25 mm Merck silica-gel plate (60F-254). Column chromatography was carried out on a column packed with silica gel 60N spherical neutral size 63–210  $\mu\text{m}$ .  $^1\text{H NMR}$  (200 MHz) and  $^{13}\text{C}$  (50.3 MHz) spectra were taken on a Varian Gemini-200 spectrometer. Chemical shifts are expressed in ppm downfield from tetramethylsilane. Infrared (IR), UV-vis spectra were recorded on a JASCO FT/IR-200 Spectrometer, V-530 spectrometer. Mass spectra of MALDI-TOF were taken on a SHIMADZU Axima CFR plus.

### Synthesis

**Compound 1.** A mixture of  $\text{K}_2\text{CO}_3$  (50.2 g, 363.2 mmol), catechol (10.0 g, 90.8 mmol) and 1-bromooctane (32.94 mL, 190.68 mmol) in DMF (150 mL) was heated at  $70^\circ\text{C}$  for 14 h, then cooled to room temperature. After filtration through celite ( $\text{CH}_2\text{Cl}_2$ ) and evaporation, the residue was taken up in  $\text{CH}_2\text{Cl}_2$ . The organic layer was washed with a saturated aqueous NaCl solution, dried ( $\text{Na}_2\text{SO}_4$ ), filtered and evaporated. Purification enforced by column chromatography ( $\text{SiO}_2$ , Ethyl acetate-hexane 10: 90)

reddish brown. Cooling to room temperature was followed by removal of the solvent. The product was purified by column chromatography (silica gel; ethyl acetate: hexane = 10: 90) yielded (86%) pure product [25].  $^1\text{H NMR}$  ( $\text{CDCl}_3$ , 200 MHz):  $\delta$  7.55 – 7.50 (m, 2H), 6.87 (d,  $J = 7.8$ , 1H), 4.08 – 4.04 (m, 4H), 3.47 (t,  $J = 12$ , 2H), 2.98 (t,  $J = 13.6$ , 2H), 2.02 – 1.75 (m, 8H), 1.56–1.28(m, 20H), 0.88 (t,  $J = 7.0$ , 6H);  $^{13}\text{C}$  ( $\text{CDCl}_3$ , 200MHz):  $\delta$  197.74, 153.17, 156.7, 148.56, 129.57, 122.34, 112.21, 111.41, 69.22, 37.00, 33.48, 32.40, 31.92, 29.48, 29.37, 29.14, 26.14, 23.28, 22.81, 14.27. EI- MS:  $m/z$  497, Anal. Calcd for  $\text{C}_{27}\text{H}_{45}\text{BrO}_3$ : C, 65.19, H, 9.05 Found C, 65.09, H, 9.02.

**Compound 3.** 1-(3, 4-Bis-octyloxy-phenyl)-5-bromopentan-1-one **2** (3.0 g, 6.04 mmol) and 4-hydroxy phthalonitrile (792.00 mg, 5.49 mmol) were dissolved in methyl-iso-butylketone (10 mL), and potassium carbonate (2.3 g, 16.48 mmol) was added. The solution was heated under reflux for 9 h. Subsequently, the solvent was evaporated in vacuum. The aqueous phase was extracted with dichloromethane. Purification is achieved by column chromatography (Silica gel; ethyl acetate: hexane= 4: 6) that yielded pure product (83%) [26]. IR (KBr): 3082, 2952, 2231, 1670, 1592, 1520, 1465, 1380, 1346, 1270, 1188, 1129, 1098, 1018, 969, 879, 837, 818;  $^1\text{H NMR}$  ( $\text{CDCl}_3$ , 200 MHz):  $\delta$  7.69 (d,  $J=8.6$ , 1H), 7.54 (d,  $J = 9.8$ , 2H), 7.24–7.11 (m, 2H), 6.87(d,  $J=8.2$ , 1H), 4.08 (m, 6H), 3.0 (br, 2H), 1.91 – 1.75 (m, 8H), 1.59–1.28(m, 20H), 0.90 (t,  $J = 10.8$ , 6H);  $^{13}\text{C}$ ( $\text{CDCl}_3$ , 200MHz):  $\delta$  197.63, 161.67,

153.27, 148.56, 134.86, 129.52, 122.34, 119.33, 119.04, 117.11, 115.48, 115.05, 112.25, 111.43, 106.84, 69.26, 37.31, 31.88, 29.43, 29.41, 29.34, 29.28, 29.15, 28.47, 26.10, 22.76, 20.89, 14.22; EI-MS:  $m/z$  560; Anal. Calcd for  $C_{35}H_{48}N_2O_4$ : C, 74.96; H, 8.63; N, 5.00; Found: C, 74.56; H, 9.03; N, 4.90.

**Compound 4.** A mixture of phthalonitrile **3** (100 mg, 0.178 mmol) HMDS (0.74 mL, 0.356 mmol),  $ZnCl_2$  (7.28 mg, 0.053 mmol) and DMF (cat.) was heated at 100 °C for overnight under  $N_2$  atmosphere. The solvent was evaporated under reduce pressure and the crude product was washed successively with  $CHCl_3$  (50 mL) and with water (50 mL). The obtained crude product was filtered through a short plug of silica (THF) followed by precipitation in methanol yielded dark green solid of **4** (67 %): IR (KBr): 2923, 2853, 1741, 1671, 1606, 1512, 1489, 1466, 1387, 1337, 1264, 1170, 1121, 1091, 1049, 800, 747; MALDI-TOF MASS: 2305 (M-2); UV-VIS ( $CHCl_3$ ,  $2.16 \times 10^{-6}$  M)  $\lambda_{max} = 683, 615$  nm.

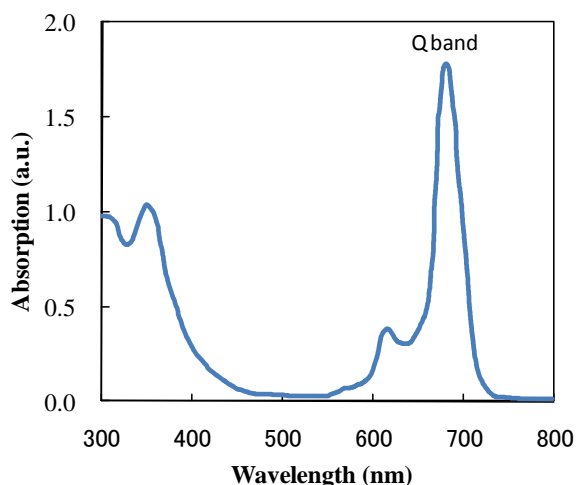


Fig. 2. UV-visible spectra of compound **4** ( $2.16 \times 10^{-6}$  M) in  $CHCl_3$ .

## Result and discussion

We herein further explored our HMDS method for a convenient synthesis of phthalocyanine on treatment of a new phthalonitrile with metal salt and HMDS under mild conditions [23]. To overcome the solubility problem, phthalocyanine framework was covered by long alkyl chains, which allow high solubility in  $CHCl_3$  that could be used in spin-coating of thin film organic solar cells. The convergent synthetic route towards phthalocyanine **4** is shown in **Scheme 1**. Commercially available catechol was bis-alkylated with 1-bromooctane yielding **1** (76%). Subsequently, Friedel-Craft acylation with 5-bromopentanoyl chloride afforded **2** in (86%). Synthesis of 4-[5-(3,4-bis-octyloxy-phenyl)-5-oxo-pentyloxy] phthalonitrile **3**, started from **2** and 4-hydroxy phthalonitrile in the presence of potassium carbonate in methyl-isobutylketone under reflux yielded (73%) as a white solid. ZnPc **4** was readily synthesized starting from 4-(5-(3, 4-bis (octyloxy) phenyl)-5-oxopentyloxy) benzene-1, 2-dinitrile **3**, with metal salt in presence of HMDS in DMF at 100 °C for 12 h, final purification was done by precipitation in methanol, affording pure **4** (ZnPc) as a greenish powder in

67 % **Scheme 1**. All compounds **1**, **2** and **3** were fully characterized by  $^1H$ -NMR,  $^{13}C$ -NMR, IR, EI mass spectrometry and elemental analysis. The ZnPc **4** was fully characterized by UV/vis, IR spectroscopies and MALDI-TOF mass spectrometry. The absorption spectrum of compound **4** is presented in **fig. 2**. Compound **4** in  $CHCl_3$  solution exhibit well-resolved absorption spectrum with a weak band located at 615 nm and an intense Q band located at 683 nm.

## Conclusion

In summary, we have synthesized new ZnPc **4** under mild conditions by exploring our HMDS method. Due to its high solubility ZnPc could be used in organic thin film solar cells. Photovoltaic performances of compound **4** are currently underway.

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