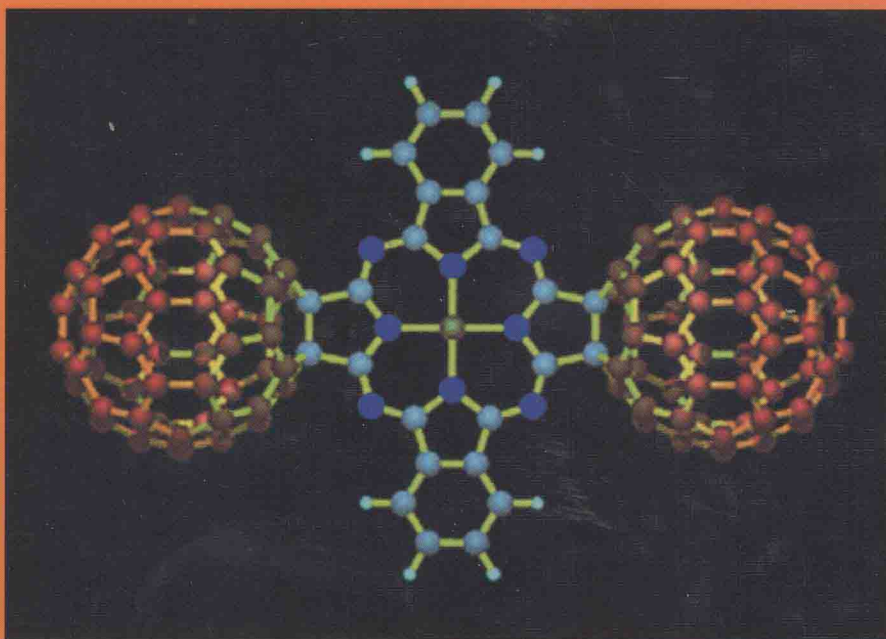# Functional Dyes

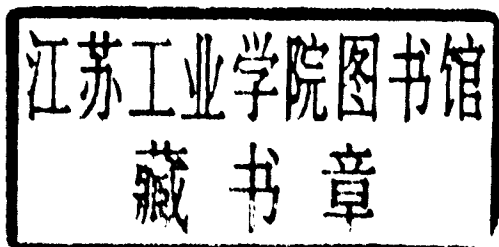## Editor: Sung-Hoon Kim

Functional Dyes

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Functional Dyes

Preface

For a long time, organic dyes from our surroundings have been used to impart coloration effects to textiles and polymer substrates. These colored materials greatly influence our emotions and aesthetic satisfactions. Traditionally, organic dyes have been used for coloration, especially of textiles, by means of dyeing technology. However, nowadays, organic colorants have become increasingly important for high-technology applications in new fields such as electronic materials, devices, reprographics, and so on. These organic materials are called functional dyes.

There are a great number of books concerning dyes and pigments and they deal with a variety of subjects such as its synthesis, property, application, and analysis. However, few books have been written on functional dyes with respect to recent interesting research trends. For that reason, this book is considered to be necessary for the readers engaged in university, research institute, and industry so as to improve their fundamental knowledge and have wider appreciation for functional dyes. In addition, this book is to provide information on the latest developments and future directions in the functional dye chemistry.

In general, dyes showing brilliant and beautiful colors with higher fastness properties are of great demand because of their suitability for various end-uses. Various numbers of chromophore have been investigated to achieve satisfactory characteristics in terms of functional applications and specialized uses. In this context, the special effects of organic colorants have been reevaluated and employed in the new areas of information-recording materials, information-display media, or optoelectronic devices. These dyes can also be applied to organic photoconductors, solar-energy utilizations, sensitizers, biomedical probe, photocatalysts, and so on. These new trends of dye chemistry have been recently developed and these classes of dyes are of significant importance in high-technology industries.

This book addresses various knowledge and information about functional dyes. It reviews recent advances on synthesis and characteristics of the functional dyes and their applications in high-technology uses. Furthermore, it provides a broad and interesting introduction to the science and technology of the applications of functional dyes. It will be a valuable information source for readers in that this book was peer-reviewed and written by special dye chemists around the world. The first chapter of the book deals with the recent progress in phthalocyanine chemistry. The second chapter covers the structure and properties of cyanine dyes for solar cells and optical data storage. The third chapter presents the synthesis and characterization of photochromic naphthopyrans, and Chapter 4

deals with the synthesis and application of cyanine dyes as fluorescent non-cova-
lent labels for nucleic acid research. Chapter 5 covers the surface plasmon reso-
nance-based sensing system using functional dyes. In Chapter 6, the synthesis
and application of squarylium dyes is described. The structures and physical
properties of fluorine-containing dye are included in Chapter 7.

Thus, the main intention in preparing this book is to provide a fundamental
understanding and an overview of the theories of dye chemistry for color
chemists, organic chemists, and material scientists. It is hoped that it will also be
useful for postgraduate students in chemistry and material science.

It is a pleasure to gratefully acknowledge the contributors of each chapter
and their great enthusiasm in spite of their very busy schedules.

S.H. Kim

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TABLE OF CONTENTS

Preface   v
Contributors   vii

1   Recent progress in phthalocyanine chemistry:
    Synthesis and characterization
    Nagao Kobayashi and Takamitsu Fukuda   1

2   Cyanine dyes for solar cells and optical data storage
    He Tian and Fanshun Meng   47

3   Photochromic naphthopyrans
    John D. Hepworth and B. Mark Heron   85

4   Cyanine dyes as fluorescent non-covalent
    labels for nucleic acid research
    Todor Deligeorgiev and Aleksey Vasilev   137

5   Functional dyes for surface plasmon resonance-based
    sensing system
    Sung-Hoon Kim and Kwangnak Koh   185

6   Syntheses and application of squarylium dyes
    Shigeyuki Yagi and Hiroyuki Nakazumi   215

7   Fluorine-containing dyes
    Masaki Matsui   257

Index   267

Chapter 1

Recent progress in phthalocyanine chemistry: Synthesis and characterization

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1. INTRODUCTION

Phthalocyanine (Pc) was first synthesized [1] in 1907, so the first centenary of Pc research is fast approaching. Since the heteroaromatic Pc ligand has a strong blue color and is chemically stable, Pc complexes have been used extensively in pigments and dyestuffs for more than 70 years [2]. Pcs have also been used as catalysts for the removal of sulfur from crude oil, as charge-generation materials in xerography, in optical read/write discs, as photodynamic reagents for cancer therapy, in deodorants, germicides and anti-bacterial reagents, and as growth promoting and retarding agents of plants [3]. Other active fields of Pc-related research include applications in or as chemical sensors, electrochromism, conductors, semiconductors, photovoltaic elements for electricity generation, one-dimensional metals, non-linear optics, electrocatalysis, liquid crystals, Langmuir–Blodgett films, and electrophotography [4]. Although most research results have been published as patents, academic research has become very intensive over the last 20 years. The fact that over the last decade, more than 1,000 papers have been published annually on Pc-related research, including both academic papers and industrial patents, indicates that the Pc ligand remains of interest to many researchers. The *Society of Porphyrins and Phthalocyanines* was established in the year 2000 by leading researchers within the field to help foster future collaborative research. In this chapter, representative synthetic methods and spectroscopic characterizations are summarized.

2. PROGRESS IN Pc SYNTHESIS

Pcs (Fig. 1) can be prepared using phthalic acid, phthalic anhydride, phthalic imide, phthalamide, phthalonitrile, and isoindolediimine (isoindoline) in the presence and
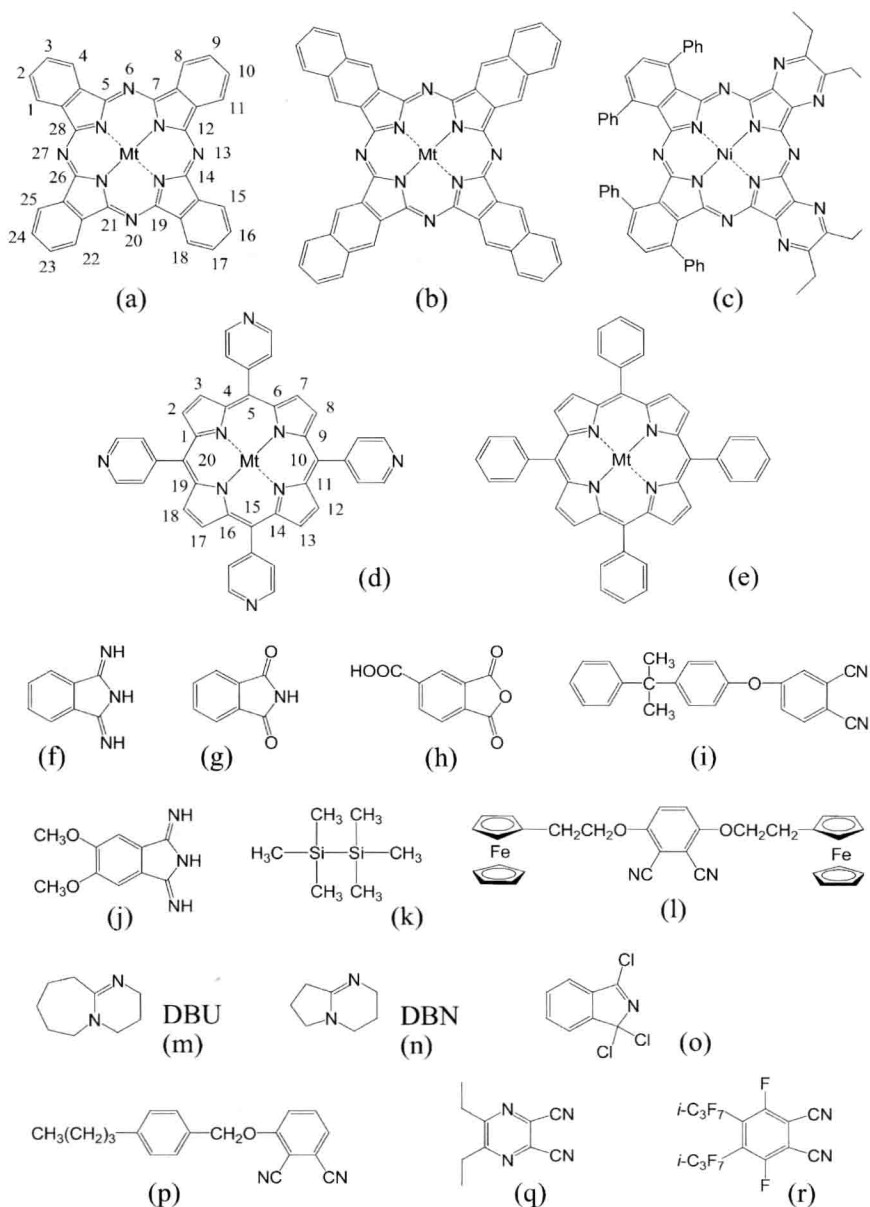
Fig. 1. Structures of some compounds appearing in this chapter: (a) Pc with numbering system, (b) Nc, (c) a C_{2v}-type NiPc derivative from Section 2.3.2(b), (d) 5,10,15,20-tetrapyridyl-porphyrin, (e) 5,10,15,20-tetraphenylporphyrin, (f) 1,3-diiminoisoinndoline, (g) phthalimide, (h) trimellitic anhydride, (i) 4–(cumylphenoxy)-4-phthalonitrile, (j) 5,6-dimethoxy-1, 3-diiminoisoinndoline, (k) HMDS, (l) 3,6-*bis*(2-ferrocenylethoxy)phthalonitrile, (m) DBU, (n) DBN, (o) trichloroisoindolenine, (p) 3-(*p-n*-butylbenzyloxy)phthalonitrile, (q) 2,3-dicyano-5,6-diethyl-1,4-pyrazine, and (r) perfluoro-(4,5-di-isopropyl)phthalonitrile.

absence of metal templates. Typical experimental procedures that have been developed for the synthesis of a wide range of different Pcs are presented below.

2.1. Water-soluble Pcs

2.1.1. Metal-free species

    (a) Pc-2,9(or 10),16(or 17),23(or 24)-tetrasulfonic acid [5]. No Pc product can be obtained by simply heating triammonium 4-sulfophthalate (10 g) and urea (50–75 g) to 230 °C. When, boric acid (0.5–1.5 g) and ammonium molybdate (1.0–2.5 g) are added as catalysts and the mixture is heated at 170–250 °C for 0.5~1.5 h, however, ammonium Pc-2,9(or 10),16(or 17),23(or 24)-tetrasulfonate can be synthesized in fairly good yields (8–18%). The reaction mixture is powdered and then extracted with water. The extract is then evaporated to dryness. The water extraction and evaporation steps are repeated approximately 10 times. The residue is then thoroughly washed with 70% ethanol and added into a saturated solution of ammonium carbonate, which is then warmed. The macrocycle is salted out to give ammonium sulfonate. The crude ammonium salt is thoroughly washed with 70% ethanol and then boiled in 95% ethanol. The tetraammonium sulfonate is converted into the corresponding tetrasulfonic acid through treatment with 6 N (or higher) hydrochloric acid. The blue crystalline product formed is collected by filtration, washed with 6 N hydrochloric acid and dissolved in a small amount of ethanol. The ethanol solution is then evaporated to dryness. The sulfonic acid is recrystallized from 8 N hydrochloric acid to give long thread-like crystals (final yield not reported).

    (b) 2,3,9,10,16,17,23,24-octacarboxy*phthalocyanine* [6]. Diluted lithium propanoate ($CH_3CH_2CH_2OLi$) (0.45 mol) is added stepwise to a refluxing propanol solution containing tetracyanobenzene (1 mol). The reaction is continued for *ca.* 30 min after addition of the last portion of $CH_3CH_2CH_2OLi$. After the removal of the solvent with an evaporator, the residue is extracted using CCl_4 in a Soxhlet apparatus. The yield of 2,3,9,10,16,17,23,24-octacyanophthalocyanine dilithium is quantitative. The hydrolysis of cyano groups of this Pc is performed in triethylene glycol/KOH to give the target compound (yield and further details are not described).

    (c) 2,3,9,10,16,17,23,24-octahydroxy*phthalocyanine* [7]. The corresponding 2,3,9,10,16,17,23,24-octamethoxyphthalocyanine (150 mg) is heated under reflux in 4.0 g of pyridine hydrochloride on a metal bath for 30 min. The reaction mixture is diluted with 40 mL of 10% aqueous hydrochloric acid and stirred for 1 h. The solution is filtered and the residue is washed with water and acetone under a nitrogen atmosphere. The product is then dried *in vacuo*. The yield is 99% of a black powder.

2.1.2. Metallated species

    (a) The tetrasodium salt of cobalt(II) 2,9(or 10),16(or 17),23(or 24)-tetra-sulfophthalocyanine 2-hydrate [8]. The monosodium salt of 4-sulfophthalic acid

(43.2 g, 0.162 mol), ammonium chloride (4.7 g, 0.09 mol), urea (58 g, 0.97 mol), ammonium molybdate (0.68 g, 0.6 mmol), and cobalt(II) sulfate 7-hydrate (13.6 g, 48 mmol) are thoroughly ground together. Nitrobenzene (40 mL) is added to a 500 mL three-necked flask fitted with a thermometer, a condenser, and a cork. The nitrobenzene is heated to 180 °C. The solid mixture is then added slowly, with stirring, while keeping the temperature between 160 and 190 °C. The heterogeneous mixture is heated for 6 h at 180 °C. The crude product, a solid cake, is ground and washed with methanol until the odor of nitrobenzene can no longer be detected. The remaining solid is added to 1,100 mL of 1 N hydrochloric acid saturated with sodium chloride. This step is crucial for the removal of excess cobalt(II) from the product. The solution with the accompanying undissolved material is briefly heated to boiling, cooled to room temperature, and filtered. The resulting solid is dissolved in 700 mL of 0.1 N sodium hydroxide. The solution is heated to 80 °C and the insoluble impurities are immediately separated by filtration. Sodium chloride (270 g) is added to the solution. At this point, some of the solid product precipitates. The slurry is heated and stirred at 80 °C until the evolution of ammonia stops. The product is then obtained by filtration and the initial reprecipitation process is repeated twice more. The solid is separated and washed with 80% aqueous ethanol until the filtrate is chloride-free. This product is refluxed for 4 h. in 200 mL of absolute ethanol. The blue, pure product is filtered and dried overnight *in vacuo* over P_2O_5 with a yield of 80%.

     (b) (2,3,9,10,16,17,23,24-octahydroxyphthalocyaninato)nickel(II), $Ni(OH)_8Pc$ [9]. $Ni(OMe)_8Pc$ (5.15 g, 6.4 mmol) is suspended in 100 mL of dichloromethane, and BBr_3 (24 mL, 254 mmol) is added under a nitrogen atmosphere. The mixture is stirred for 15 days, and 100 mL of methanol is added to the residue, and this procedure is repeated three additional times. $Ni(OH)_8Pc$ is separated from the solvent by filtration, to give a dark green precipitate in 47% yield (2.1 g). The complex can be recrystallized from pyridine, giving dark green solvated crystals of $Ni(OH)_8Pc \cdot 2NC_5H_5$.

     (c) Fe(III) and Co(II) Pc-2,9(or 10),16(or 17),23(or 24)-tetracarboxylic acid ($[(COOH)_4Fe^{III}Pc]^-$ or $(COOH)_4Co^{II}Pc$) [10]. 10 g (0.05 mol) of trimellitic anhydride (Fig. 1), 30 g (0.5 mol) of urea, 0.03 mol of metal salts ($FeCl_3$ or $CoCl_2$), 1 g (1 mmol) of ammonium molybdate and 150 mL of nitrobenzene, which is used as a solvent, are mixed in a mortar, and then placed in a 200 mL round-bottomed flask equipped with a reflux condenser. The reaction mixture is heated to 150–170 °C for 3 h. A blue–green black solid is obtained, which is removed from the flask with 200 mL of methanol and collected by filtration. The filtrate is fully washed with methanol until no nitrobenzene can be detected, and dried for 24 h at 60°C *in vacuo*. The yield of $(CONH_2)_4Fe^{III}Pc$ is 85% and that of $(CONH_2)_4Co^{II}Pc$ is 90%. The hydrolysis of these amides is carried out in NaOH-saturated boiling water for 12 h. After cooling, the solution is cautiously acidified by adding 6 N HCl to *ca.* pH 6. The blue solution is separated from the

precipitated NaCl by decantation. This procedure is repeated several times. Finally, the precipitate of the target carboxylic acid is obtained once the pH of the solution is below pH 4. The yield of tetraacids is *ca.* 80%.

2.2. Water-insoluble Pcs
2.2.1. Metal-free species

(a) H_2Pc via Li_2Pc [11]. 60 g of phthalonitrile are added to a solution of lithium (4 g) in amyl alcohol (300 mL). A green color appears, and when the mixture is warmed, a vigorous exothermic reaction takes place, and the color changes to deep blue with the precipitation of some dilithium Pc (Li_2Pc). The mixture is boiled for 30 min, cooled, diluted to 1,000 mL with benzene, and left aside for 3 h. After filtration, the dull blue residue of Li_2Pc (36 g) is extracted by Soxhlet extraction with acetone and dried over sodium sulfate. The basic lithium compounds are left in the extractor. Evaporation under reduced pressure yields Li_2Pc as a crystalline deposit with a purple lustre (30 g; 50%). Water (2 mL) is added to a solution of Li_2Pc (3 g) in absolute alcohol (25 mL). A blue precipitate of H_2Pc is formed immediately is collected after 3 h and recrystallized from 1-chloronaphthalene. Li_2Pc can be hydrolyzed similarly by dilute acid. The yield is almost quantitative.

(b) Substituted H_2Pc using hydroquinone as a catalyst *Tetrakis*(cumylphenoxy)-Pc [12]. A mixture of 1.00 g (2.96 mmol) of 4-(cumylphenoxy)-4-phthalonitrile (Fig. 1) and 81 mg (0.74 mmol) of hydroquinone (purified by sublimation) is fused by gentle heating to melting point, cooled, sealed under vacuum, and then reacted at 180 °C for 16 h and the yield is 0.49 g (49%).

(c) H_2Pc using DBU or DBN as a catalyst [13]. A mixture of phthalonitrile (2.56 g, 20 mmol) and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) (or 1,5-diazabicyclo[4.3.0]non-5-ene (DBN)) (20 mmol) in ethanol or propanol (50 mL) is heated to reflux. As the reaction proceeds, H_2Pc is gradually deposited as a blue precipitate, which is collected by filtration, washed with ethanol, and purified by extraction with ethanol. The yield is time dependent. Based on the conditions outlined above, the yield is *ca.* 20% or 45% after 24 h, in the presence of DBU or DBN, respectively.

(d) $H_2(CN)_8Pc$ by solid phase, room temperature synthesis [14]. 90 mg (1.66 mmol) of sodium methoxide is added to a solution of 100 mg (0.526 mmol) of 1,2,4,5-tetracyanobenzene in 5 mL of dry THF. The resulting suspension is stirred for 5 days at room temperature, and the solution is then acidified with acetic acid to neutral pH. The residue of the target compound is filtered, washed with 2-propanol, and precipitated from DMF solution by the addition of water. The yield is 51 mg (50%).

(e) H_2Pc via isoindoline [15]. *Method A*: A mixture of phthalonitrile (m.p. 140.5–141.0 °C, 25 g, 195 mmol) and 1-dimethylamino-2-propanol (b.p. 127–128 °C, 100 mL) is placed in a four-neck, 500 mL round-bottomed flask,

equipped with a mechanical stirrer, reflux condenser, thermometer, and gas inlet tube. The suspension is heated to 100 °C and the phthalonitrile is dissolved. A steady stream of ammonia gas is passed into the solution as the temperature is first raised to reflux (127–128 °C), which is then maintained for 7 h. A bluish-purple precipitate is collected by filtration from the hot solvent and washed thoroughly first with water or ethanol and then with acetone. The product is then air dried, with a yield of 22.5 g (90%). *Method B*: A mixture of 1,3-diiminoisoindo-line (20.0 g, 138 mmol) and 2-dimethylaminoethanol (b.p. 130–135 °C, 100 mL) is refluxed with stirring for 7 h, during which time ammonia is evolved. The mixture is filtered hot and the purple crystals of Pc are washed thoroughly with ethanol and then with acetone. The product is dried *in vacuo* at 80 °C for 3 h, with a yield of 15.1 g (85.5%).

(f) H_2Pc from phthalimide using hexamethyldisilazane (HMDS) as a cata-lyst [16]. A glass tube is filled with phthalimide (100 mg, 0.68 mmol), *p*-TsOH·H_2O (13 mg, 0.07 mmol), HMDS (560 μl, 438 mg, 2.7 mmol, Fig. 1) and DMF (50 μl, 0.68 mmol) under an argon atmosphere and then sealed. Upon heat-ing the mixture to 150 °C, a dark purple solid immediately appears. After heat-ing for 10 h, the mixture is cooled and filtered. The solid is washed with methanol and then dissolved in concentrated H_2SO_4 (5.0 mL). The resulting solu-tion is poured into H_2O (100 mL) and the blue precipitate is filtered and washed with H_2O. The solid is further purified by Soxhlet extraction with methanol to give 62 mg (58%) of H_2Pc as a blue solid.

(g) H_2Pc from phthalonitrile using oxime as a catalyst [17]. When 4 equiv. of oxime ($R^1R^2C = NOH$, where $R^1 = H$, $R^2 = Me$ or Et) are heated at 100 °C with 4 equiv. of phthalonitrile for 8 h, H_2Pc is obtained in *ca.* 60–65% yield (other details are not described).

(h) H_2Pc by electrosynthesis [18]. A 100 mL solution of either absolute ethanol or a mixture of ethanol and dimethyl acetamide, containing LiCl (3 g, 0.07 mol) is introduced into an electrolysis cell and deaerated at a fixed temperature (typically 75 °C). Phthalonitrile is added to the cathode compartment and a poten-tial of $-1.6 - -1.9$ V is applied. With ethanol as the solvent, the initial uncolored solution becomes yellow, then blue–green after the passage of 20–40 C and finally turns into a viscous blue suspension. Electrolysis is stopped after a fixed amount of charge has been passed, typically $Q/Q_{theo} = 1–1.5$, where $Q_{theo} = (N \times F)/2$, and N is the initial mole number of phthalonitrile in the catholyte. Then the catholyte is poured into 100 mL of a 0.2 M H_2SO_4 solution. The resulting sus-pension is stirred for 30 min and then filtered. The blue solid is washed with water and acetone and then treated with warm acetone in a Soxhlet apparatus. The resulting blue solid is H_2Pc (α-form). The yield depends on the Q/Q_{theo} value and on the initial concentration of phthalonitrile in the catholyte. When the initial con-centration of phthalonitrile is 50 mmol and electrolysis is stopped at $Q/Q_{theo} = 1$, the yield exceeds 70%.

2.2.2. Metallated species

(a) *Tert*-butylated CoPc by the anhydride method [19]. 4-*tert*-butylphthalic anhydride (13 g, 64 mmol), 13.5 g (225 mmol) of urea (water free), and 2.4 g (19 mmol) of cobalt(II) chloride are suspended in 50 mL of trichlorobenzene, treated with 0.5 g of ammonium molybdate, and heated at 190 °C for 4 h. After the mixture is cooled, 50 mL of petroleum ether (60–90 °C) is added and the mixture is vacuum filtered. The residue on the filter is discarded, and the filtrate is concentrated. The precipitate is purified as described above with 1 N HCl and 1 N NaOH solutions to give a yield of 4 g (31%).

(b) CuPc from phthalimide using HMDS as a catalyst [20]. A glass tube is filled with phthalimide (100 mg, 0.68 mmol), $CuCl_2$ (23 mg, 0.25 mmol), *p*-toluenesulfonic acid monohydrate (13 mg, 0.07 mmol), and HMDS (560 µl, 438 mg, 2.7 mmol) and the mixture is stirred at 100 °C for 1 h under an argon atmosphere. The mixture is cooled and then DMF (50 µl, 0.68 mmol) is added. The tube is then sealed and the mixture is heated at 150 °C. A dark purple solid immediately appears and the tube is heated for a further 10 h. The mixture is cooled and filtered. The solid is washed with methanol and then dissolved in concentrated H_2SO_4 (5 mL). The solution is poured into 100 mL of water. The resulting blue precipitate is filtered and washed successively with dilute H_2SO_4, water, and methanol. The solid is further purified by Soxhlet extraction with methanol to give 62 mg of CuPc (63%) as a blue solid.

(c) ZnPc from substituted phthalonitrile using DBU in alcohol. [1,4,8,11,15,18,22,25-*Octakis*(2-ferrocenylethoxy)phthalocyaninato]zinc(II) [21]. A mixture of 3,6-*bis*(2-ferrocenylethoxy)phthalonitrile (100 mg, 0.17 mmol, Fig. 1) and $Zn(OAc)_2 \cdot 2H_2O$ ((22 mg, 0.10 mmol), Ac = anthracocyanine) in *n*-pentanol (3 mL) is heated to 90 °C. DBU (0.01 mL, 0.07 mmol) is then added. The mixture is stirred at 150 °C overnight and then poured into a mixture of methanol and water (1:1, 50 mL). The precipitate formed is filtered off and chromatographed on a basic alumina column using $CHCl_3$/THF (5:1) as the eluent to give ZnPc as a green powder (54 mg, 53%).

(d) NiPc from phthalonitrile using hydroquinone in quinoline [22]. A 2.00 g (15.6 mmol) sample of phthalonitrile is reacted with 0.76 g (4.3 mmol) of 99.999% pure anhydrous $Ni(OCOCH_3)_2$ and 0.48 g (4.4 mmol) of hydroquinone in 6 mL of quinoline. The solution is refluxed under nitrogen for 5 h and then cooled. The resulting precipitate is collected and washed with hot water and acetone. Purification by sublimation yields 0.47 g (21%) of NiPc.

(e) ZnPc from substituted phthalonitrile and zinc dust [*Tetrakis*(cumylphenoxy)Pc]zinc [12]. A mixture of 676 mg (2.00 mmol) of 4-(cumylphenoxy-4-phthalonitrile (Fig. 1) and 262 mg (4.00 mmol) of Zn powder (HCl etched, washed, and dried) is reacted at 280 °C for 70 h resulting in a yield of 397 mg (56%).

(f) MgPc from substituted phthalonitrile and magnesium powder [*Tetrakis*(cumylphenoxy)Pc]magnesium [12]. A mixture of 0.50 g (1.48 mmol) of

4- (cumylphenoxy)-4-phthalonitrile (Fig. 1) and 0.14 g (5.92 mmol) of Mg powder (lightly etched with dilute HCl) is reacted at 280 °C for 70 h to yield 72 mg (14%).

(g) PbPc from substituted phthalonitrile and PbO [*Tetrakis*(cumylphenoxy)Pc]lead [12]. A mixture of 500 mg (1.48 mmol) of 4-(cumylphenoxy)-4-phthalonitrile (Fig. 1) and 250 mg (1.12 mmol) of PbO is reacted at 210 °C for 14 h resulting in a yield of 280 mg (49%).

(h) O=TiPc from phthalonitrile and Ti(OBu)$_4$ [23]. *Method A*: A mixture of phthalonitrile (5.0 g, 39 mmol), Ti(OBu)$_4$ (3.65 g, 10.7 mmol), urea (1.17 g, 19.5 mmol), and 1-octanol (6.0 g, 46.1 mmol) is heated at 150 °C under nitrogen for 6 h. After addition of methanol (30 mL) to the reaction mixture followed by refluxing for 30 min, the fine blue crystals are collected by filtration, washed with toluene, methanol, and water, and then dried at 100 °C and at a pressure of 1 Torr for 3 h to give 4.92 g of O=TiPc (87.6%). *Method B*: A mixture of phthalonitrile (64.07 g, 0.5 mol), Ti(OBu)$_4$ (46.75 g, 138 mmol), urea (15.15 g, 0.25 mol), and 1-octanol (76.8 g, 0.59 mol) is heated at 150 °C under stirring for 6 h. After addition of methanol (100 mL) followed by refluxing for 30 min, the suspension is filtered. The collected solid is washed with toluene (3×250 mL), methanol (3×100 mL), and water (500 mL) and dried at 100 °C and a pressure of 1 Torr for 6 h to give 62.1 g of O=TiPc (86.2%). Although TiCl$_4$ had long been used for this procedure, the use of Ti(OBu)$_4$ makes the synthesis much easier, since Ti(OBu)$_4$ is much more stable against moisture.

(i) AlPc from phthalonitrile and Al(OBu)$_3$ [23]. A mixture of phthalonitrile (1.0 g, 7.8 mmol), Al(OBu)$_3$ (0.58 g, 2.3 mmol), urea (0.47 g, 7.8 mmol), and 1-butanol (1.5 g, 20 mmol) is heated at 140 °C for 6 h. 25 mL of dilute H$_2$SO$_4$ (3 M) is added to the reaction mixture, and the suspension is then stirred at 100 °C for 2 h. The blue solid is collected by filtration, successively washed with water, 28% ammonia solution, water, and methanol, and then dried to give 0.73 g (65%) of (OH)AlPc·H$_2$O.

(j) FePc from phthalonitrile and Fe(CO)$_5$. 1,2,3,4,8,9,10,11,15,16,17,18,22, 23,24,25-hexadecamethyl-phthalocyaninato iron(II) [24]. A solution of Fe(CO)$_5$ (0.2 g, 1 mmol) dissolved in 1-chloronaphthalene (2 mL) is added dropwise over 5 min to a solution of tetramethylphthalonitrile (0.73 g, 4 mmol) in 1-chloronaphthalene (6 mL) under reflux in a nitrogen atmosphere. The black suspension is held at 270 °C for a further 3 h and then cooled, after which the precipitate is suction filtered, and then washed with chloroform, toluene, and acetone. The product is first boiled in dilute HCl followed by water, placed in the thimble of a Soxhlet extractor, washed overnight with acetone, and then the following night with chloroform. After drying *in vacuo*, a blue–black powder of the target compound is obtained (0.13 g, 17%). The use of metallocarbonyl compounds is the preferred method when the reactivity of phthalonitrile derivatives is not high. CoNc [25] (Nc = naphthalocyanine, Fig. 1) and FeNc [26] have been synthesized by this metal-carbonyl method.

(k) Cl_2SiPc from isoindoline [27]. In a flask equipped with a water condenser, a mechanically stirred mixture of 36.5 g (0.25 mol) of 1,3-diiminoisoindoline, 41.5 mL (0.36 mol) of silicon tetrachloride, and 415 mL of quinoline is slowly brought to reflux (219 °C). It is maintained at this temperature for 30 min and then cooled to 184 °C and filtered. The purple crystalline product is washed with quinoline, benzene, methanol, and acetone and then dried at 110 °C to yield 27.4 g (71% based on 1,3-diiminoisoindoline). This Cl_2SiPc can be recrystallized from 1-chloronaphthalene (*ca.* 60–70%) and can be hydrolyzed in H_2O/MeOH containing NaOH, pyridine/aqueous ammonia, or dilute H_2SO_4 to produce $(OH)_2SiPc$.

2.3. Phthalocyanines with specific symmetry

2.3.1. Metal-free species

(a) A D_{2h} symmetry H_2Pc from trichloroisoindolenine and isoindoline 2,16(or 17)-*bis*(4-*tert*-butylphenoxy)-9(or 10),23(or 24)-dinitroPc [28]. 100 mg (0.34 mmol) of 6-(4-*tert*-butylphenoxy)diiminoisoindoline and 69 mg (0.068 mmol, 1.5 equiv.) of triethylamine are placed in a dried 100-mL round-bottomed flask equipped with a magnetic stirrer and sealed with a septum. Dry nitrogen is swept through the flask by the two-needle method; and 30 mL of freshly dried THF is added with a syringe, and the mixture is stirred to dissolve the diiminoisoindoline. The mixture is then cooled to approximately 0 °C in a salt and ice bath. A solution of 90 mg (0.34 mmol) of 6/7-nitro-1,3,3-trichloroisoindolenine (Fig. 1) in 10 mL of dry THF is gradually added by means of a syringe over a 15-min period. The reaction mixture is then stirred for 1 h at approximately 0 °C and allowed to slowly warm to room temperature with stirring over a 6-h period. During this time, the solution turns from yellow to a yellow–green color. The reaction mixture is then filtered to remove the triethylamine hydrochloride and is then returned to the reaction flask. 37 mg (0.34 mmol) of hydroquinone and 54 mg (1 mmol) of sodium methoxide are added to the reaction vessel, which is equipped with a reflux condenser and is refluxed under nitrogen for 6 h. The solution is cooled to room temperature and filtered, leaving a dark blue–black residue. The residue is washed by boiling in water and filtering until the filtrate is clear; this procedure is then repeated with ethanol. The yield of the target compound is 48%.

(b) D_{2h} and C_{2v} symmetry H_2Pc from *bis*-phthalonitrile (Fig. 2, [29]). *Bis*-phthalonitriles ((*S*)-**1** and (*R*)-**1**) prepared from (*S*)-(-)-dihydroxy-1,1'-binaphthyl and (*R*)-(+)-dihydroxy-1,1'-binaphthyl and 3-nitrophthalonitrile are converted into the isoindoline derivatives by bubbling ammonia gas in dry methanol followed by reaction with 2 equiv. of 5,6-dimethoxyisoindoline [19] in refluxing *N*, *N*-dimethylaminoethanol for 3 h. After evaporation of the solvent, the residue is separated on a basic alumina column (Act III) using CH_2Cl_2/methanol (9:1 v/v) and then CH_2Cl_2/pyridine (1:1 v/v). The blue–green fraction is collected and separation is first attempted by gel-permeation chromatography using Bio-beads SX-2 (Bio-rad)