

<Research Paper>

Preparation of Novel Iron Phthalocyanine Containing Reactive Groups and its Deodorizing Property on Cellulose

Eun-Mi Kim and Jae-Hong Choi[†]

Department of Textile System Engineering, Kyungpook National University, Daegu, Korea

(Received: September 11, 2013 / Revised: October 22, 2013 / Accepted: December 10, 2013)

Abstract: The enzyme-like catalytic functions of metal complex phthalocyanine derivatives those containing carboxylic acid groups could be applied as odor-removing systems and antibacterial systems. Pyromellitic dianhydride and 4-nitrophthalimide were used as starting material for synthesizing dinitro-tetracarboxylic acid iron phthalocyanine(compound 1). Then diamino-tetracarboxylic phthalocyanine(compound 2) was obtained by reduction of compound 1. For the formation of covalent bond with cellulose fiber, cyanuric chloride was introduced to the amino group of compound 2 by condensation reaction compound 3. The exhaustion method was employed for adsorbing compound 3 on cotton fiber. K/S values of each fabrics were measured by a CCM system and deodorizing rates were tested by a detector tube method for ammonia gas. K/S values of treated cotton fiber with compound 3 were arranged from 2.1 to 4.2 at 90°C of exhaustion temperature. Deodorizing rates provided result of 81%, 84%, 88%, 91%, by passing time of 30 min, 60 min, 90 min, 120 min, respectively.

Keywords: *phthalocyanine, deodorizing, exhaustion, reactive dye, reduction*

1. Introduction

Metal phthalocyanine compounds(MPc) have received a great deal of attention due to similarity in structure between their molecules and chlorophyll or hemoglobin. They are hardly soluble in almost solvents except those of very acidic or very basic. Since highly insoluble character of phthalocyanines, their structural investigations or applications are difficult¹⁻³.

By *Bailar, Boston, Shirai*, and others, phthalocyanine was designed to study the preparation as well as the properties of some soluble metal phthalocyanine derivatives with functional groups⁴⁻⁸. Phthalocyanine derivatives, which have four or eight carboxyl acid groups, can afford water solubility and particularly deodorizing property, could be obtained by hydrolysis of the phthalocyanine tetracarboxamide or octacarboxamide.

By deodorizing mechanisms, deodorants could be roughly classified into five types⁹; 1. Sensory deodorization, 2. Chemical deodorization, 3. Physical or chemical adsorption, 4. Physical adsorption, 5. Bio-

logical deodorization.

Many studies investigated metal complex phthalocyanine(MPc) derivatives have catalase-like activity. The enzyme-like catalytic functions of MPc derivatives those containing carboxylic acid groups could be applied as odor-removing systems and antibacterial systems. In 1980s, it was found that the metal complex phthalocyanine derivatives containing carboxyl groups catalyzed the decomposition of H₂O₂ and some of oxidation reaction¹⁰⁻¹². Metallic phthalocyanine derivatives mainly employ a reaction resembling that of an oxidizing enzyme, which efficiently oxidizes mercaptan or hydrogen sulfide, thus making them into odorless substances¹¹.

In these days, there are several efforts to apply the functional metalphthalocyanine derivatives to textiles that can exhibit particular properties such as odor-removing and antibacterial effect^{13,14}. Various methods to manufacture deodorizing fiber are focused to anchor the deodorant to the fiber in the finishing stage, such as spraying, immersion, padding, coating, laminating and printing¹⁵. Most of them, the deodorants and fiber are physically attached rarely bonded chemically. Due to that, it is difficult to

[†]Corresponding author: Jae-Hong Choi (jaehong@knu.ac.kr)
Tel.: +82-53-950-5644 Fax.: +82-53-950-6617

©2013 KSDF 1229-0033/2013-12/247-253

obtain outstanding durability of odorant-removing effects.

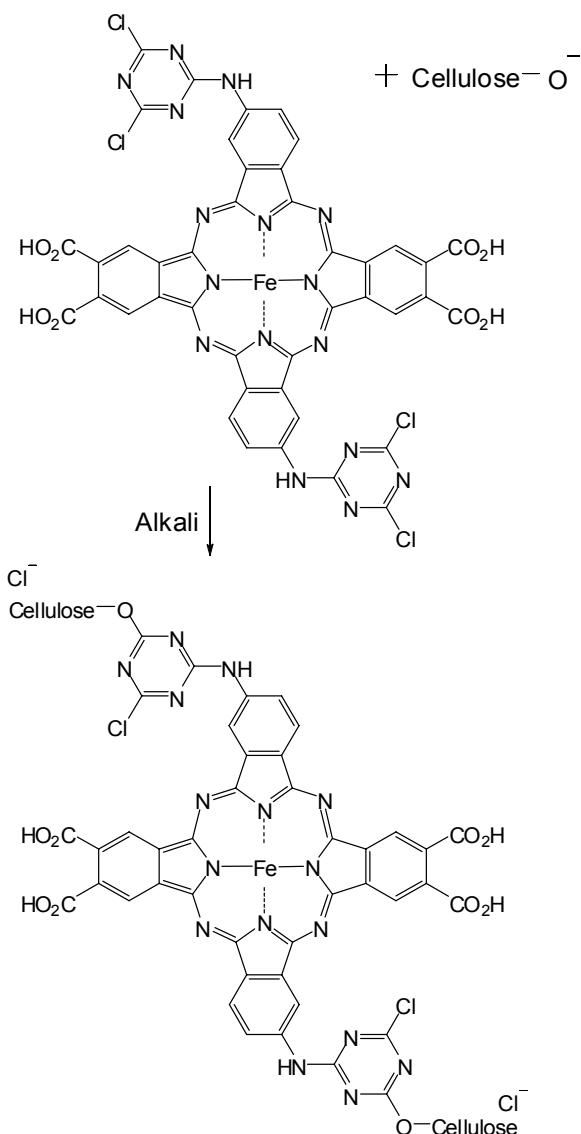
In general, reactive dyes with excellent durability to washing have certain reactive groups forming covalent bonds between cellulose and dye molecule^{16,17}. The principal reactive systems of Procion® dyes are based on a nucleophilic substitution mechanism by halogeno-substituted triazine, pyrimidine, pyrazine, thiazole and pyridazone groups in the presence of alkali¹⁸.

In this paper, novel type of reactive dye 3 based on Fe(III)-phthalocyanine derivative, which contain four carboxylic acid groups in the aromatic rings providing both the water solubility at basic conditions and the deodorization effect was synthesized and evaluated their properties. Chlorotriazine ring acts as a functional group forming covalent bond with the hydroxylic groups in the cellulose, as shown in Scheme 1.

2. Experimental

2.1 Synthesis of phthalocyanine derivatives

Dinitro tetracarboxylic iron phthalocyanine (Compound 1): Pyromellitic dianhydride(1.2g), 4-nitrophthalimide(1g), urea(4.8g), ferric chloride(0.5g), ammonium molybdate(0.05g) and 2-nitrotoluene(8g) as solvent was stirred uniformly at room temperature and heated up to 125~130°C for 4 hours. After then, the mixture heated up to between 190~195°C with heating rate of 0.5°C per minutes. It was maintained at 190~195°C for 5 hours. The color of reaction mixture gradually deepened and finally a greenish solid was obtained. From the reaction mixture, solvent was distilled off by a reduced pressure, then precipitates were filtered and washed with methyl alcohol. After filtration, the wet cake was added into 5% aqueous sodium hydroxide solution and hydrolyzed for 24 hours with a refluxing condition. After cooling to room temperature, c-HCl was added into the above solution until neutral pH condition(pH 6~7) within temperature of around 30°C, then further stirring was carried out for 1 hour at room temperature.



Scheme 1. Dyeing mechanism of phthalocyanine derivatives on cellulose fiber.

After filtration, the solid was subsequently washed with plenty of hot water until free from salt in the product. Filter cake was dried in a drying oven at 90°C for 16 hours.

Diamino tetracarboxylic iron phthalocyanine (Compound 2): Diamino tetracarboxylic phthalocyanine was prepared starting from dinitro tetracarboxylic phthalocyanine (Compound 1). Dinitro tetracarboxylic phthalocyanine 1(1g) was dispersed in water then sodium sulfide nonahydrate(1.8g) was gradually added. The reaction mixture was heated up to 70~75°C with stirring for 10 hours. After cooling to room temperature,

c-HCl was added and pH was controlled to between 1 and 2 then further stirring carried out for 1 hour without heating. After filtration, the solid was washed with plenty of hot water until free from salt in the product.

Compound 3: Diamino tetracarboxylic phthalocyanine 2(1g), cyanuric chloride(0.6g) and pyridine(0.3g) were dissolved in DMF(10g) and stirred for 6 hours at 75~80°C. When the reaction completed, cooled to room temperature, then filtered and washed with hot water. Filter cake was dried in a drying oven at 90°C for 16 hours.

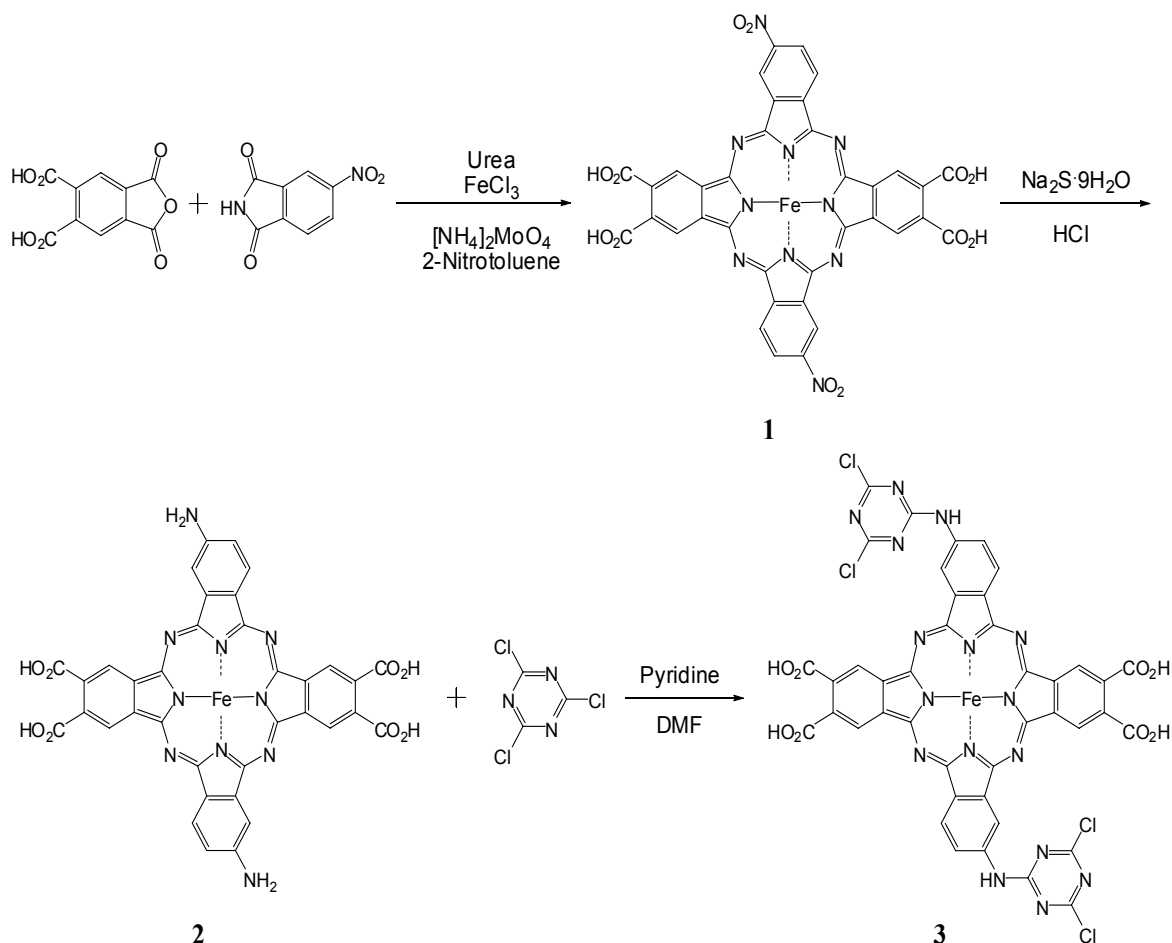
All of reagents and solvents used for this study was supplied by TCI(Japan) and Duksan Chem.(Korea).

2.2 Dyeing and determination of fixation yields

The compound 3 was dyed onto cotton fiber by an exhaust method which was carried out at 1, 2, 3% o.w.f.(on the weight of fiber), liquor ratio 1:100, 45g/l of NaCl, 25g/l of Na₂CO₃ and temperature of 60°C and 90°C for 60min. Then, the dyed fabrics were dried at room temperature and washed out under condition of liquor ratio 1:100, 90°C for 30min. All of dyeing process was carried out by means of a KS-W24 Inter Cooler IR dyeing machine(Korea Scientific Co.).

2.3 Wash fastness

Wash fastness was evaluated according to the Marks & Spencer C4A 60°C method.



Compound 1 : Yield: 64%; C₃₆H₁₄FeN₁₀O₁₂, MS(m/z) 834(M⁺).

Compound 2 : Yield: 87%; C₃₆H₁₈FeN₁₀O₈, MS(m/z) 774(M⁺).

Compound 3 : Yield: 89%; C₄₂H₁₆Cl₄FeN₁₆O₈, MS(m/z) 1067(M⁺).

Scheme 2. Synthetic route of compound 1-3 via cyclization, reduction and condensation reactions.

2.4 Determination of dye exhaustion yields, final dyeing yields and K/S values

The dye uptake was determined by using UV-VIS spectrophotometer (Evolution 300BB, Thermo Electron), measured the absorbance of diluted dye bath sample at the wavelength of maximum absorption (λ_{\max}) of the dye. The percentage of dye bath exhaustion (% E) was calculated using equation (1);

$$\%E = [(A_0 - A_1) / A_0] \times 100 \quad (1)$$

where A_0 and A_1 are the absorbance at λ_{\max} of the dye originally in the dye bath and of the residual dye after dyeing, respectively. For evaluation of final dyeing yield, amount of dyes extracted by water during wash out process were measured with UV-VIS spectrophotometer and calculated by equation (2);

$$\%D = [(A_0 - A_1 - A_2) / A_0] \times 100 \quad (2)$$

where A_0 and A_1 are the absorbance at λ_{\max} of the dye originally in the dye bath and of the residual dye after dyeing, respectively and A_2 is the absorbance at λ_{\max} of the dye extracted during wash out process.

K/S values of treated cotton fabrics were measured by a CCM system (X-Rite Color Premier 8200, X-Rite) and deodorizing rates were tested by a detector tube method for ammonia gas (GV-100, Gastec, Japan).

3. Results and Discussion

Molecular weight (MALDI-TOF, Voyager DE-STR, Applied biosystems, USA) and FT-IR spectra (by KBr method, Spectrum GX & AutoImage, PerkinElmer, USA) of synthesized phthalocyanine derivatives were investigated. Figure 1 compares the FT-IR spectra of synthesized phthalocyanine derivatives 1, 2 and 3 with those of Iron phthalocyanine which is unsubstituted in the aromatic rings. For all three compounds 1-3, the absorption peaks 1330cm^{-1} – 1250cm^{-1} are assigned to C-N of tertiary amine estimated phthalocyanine skeleton. Peaks at 3435cm^{-1} and 1653cm^{-1} indicate the presence of OH and C=O of the COOH group, respectively, as well as peak at 1321cm^{-1} is assigned to NO_2 , for

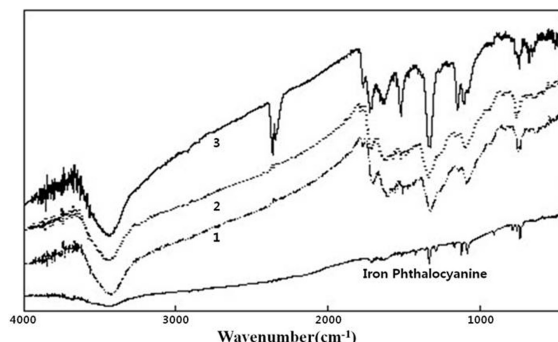


Figure 1. FT-IR spectra of Compound 1-3 and Iron Phthalocyanine.

Table 1. Analytical results of SEM-EDS for compounds 1-3

Compound number	Element(%)			
	C	O	Cl	Fe
1	64.84	20.88	0.32	13.96
2	67.20	20.89	0.30	11.30
3	68.77	17.52	14.17	9.54

compound 1. In the case of compound 2, C=O and OH of carboxyl groups were confirmed by peaks at 3430cm^{-1} and 1706cm^{-1} , and NH_2 was figured by peak at 1335cm^{-1} . For compound 3, the absorption peaks at 3434cm^{-1} and 1706cm^{-1} correspond to OH and C=O of the COOH group, and absorption peak at 1617cm^{-1} is due to the presence of N-H.

As shown in Table 1, existence of Cl atom on compound 3 was confirmed by SEM-EDS (Energy Dispersive spectroscopy).

In terms of dyeing temperature, higher exhaustion yields and K/S values were observed at 90°C , comparing to those of 60°C , as shown in Figure 2. The commercial reactive dyes containing a dichlorotriazinyl moiety as functional group are optimum to be dyed at 60°C on cellulose fiber. For compound 3 which also contains two dichloro-triazinyl moieties as functional group, a valid dyeing temperature was found to be 90°C rather than 60°C that can be explained by its bigger molecule size (molecular weight) compared to that of commercial reactive dyes as well as the increased solubility. A tendency of increase was found most in 3% o.w.f., the exhaustion yield was raised to

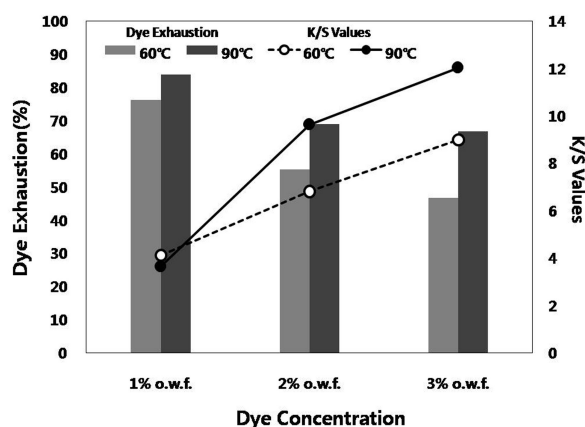


Figure 2. Percentage of exhaustion and K/S values of compound 3 on cotton fiber.

66.8% at 90°C from 46.7% at 60°C. K/S values were also increased as temperature goes up, thus dyeing on 3% o.w.f. the K/S value was increased around 30% at 90°C compared to that of 60°C dyeing.

The exhaustion and fixation yields at 90°C dyeing were compared between compound 1 and compound 3, as shown in Table 2. Results of exhaustion yields for two analogues clearly indicated their similar affinity onto cellulosic fiber, which ranged from 81.6% to 82.7%. By comparing with those of conventional reactive dyes, these figures seem to be slightly lower when their molecular size was considered. However, two analogues showed different values in the fixation yields, as it was expected. Much higher final dyeing yield was observed for compound 3, which was 74%, in comparison with that of compound 1, which was just 61%, therefore around 20% higher result was observed. This figure can be explained by the formation of covalent bonds between triazinyl groups of compound 3 and hydroxyl groups in the cellulosic fiber exerted by a nucleophilic aromatic substitution reaction. Wash fastness of compound 3 on cotton fiber exhibited ratings of 4-5

Table 2. Comparison of exhaustion and final dyeing yields between compound 1 and 3

Compound number	Exhaustion yield(%)	Final dyeing yield(%)
1	82	61
3	83	74

or 5 in gray scale onto the adjacent multifibers, as shown in Table 3. In particular, the ratings on PET and acrylic fibers to be better than other fibers.

Fe(III)-phthalocyanine derivatives are protohemin with a trivalent ion complex, a biological oxidizing enzyme, so these are also referred to as artificial enzymes. The mechanism relies first on movement of electrons due to replacement action with the foul smelling substance and the ligands of the metal complex. This oxidizes the foul smelling substance and renders it odorless. The metal complex is reduced, but it returns to its original status through air oxidation, so the reaction involves cyclic oxidation and reduction. With amines, neutralization and complex generation reaction also occur in addition to oxidizing enzyme like reaction¹⁹.

Deodorizing rates of cotton fiber dyed with compound 3 were gradually increased from 81%, 84%, 88% upto 91%, by passing time of 30 min, 60 min, 90 min, 120 min, respectively (Table 4). The high deodorizing rate at initial stage (30 min) can illustrate the efficient formation of acid-base complex between carboxylic acids of compound 3 and ammonia gas.

In textile segments, most of deodorants including TiO₂ photo-catalyst exhibit less than 80% of deodorizing rate, even it would be dramatically reduced after several times of washing due to their poor durability. Therefore the advanced deodorizing rate for compound 3 can be promising to be a novel reactive dye performing durable and effective deodorizing function.

Table 3. Wash fastness of compound 3

Compound number	Staining on multifiber					
	Acetate	Cotton	Nylon	PET	Acrylic	Wool
3	4-5	4-5	4-5	5	5	4-5

Table 4. Deodorizing rate of cotton fiber treated with compound 3

Time (min)	Deodorizing rate on NH ₄ gas(%)
	Dyed with compound 3
30	81
60	84
90	88
120	91

4. Conclusion

Three kinds of iron phthalocyanine derivatives were synthesized and analyzed by a MASS, FT-IR and SEM/EDS. Compound 3 was dyed onto cotton fiber by an exhaust dyeing method. Exhaustion yields and K/S values for 90°C dyeings were higher than those for 60°C dyeings due to their big size of phthalocyanine ring. Very similar exhaustion yields for compound 1 and compound 3 were observed, whereas final dyeing yield of compound 3 containing triazinyl reactive groups was found to be higher than that of compound 1 indicating the formation of covalent bonds between compound 3 and cellulosic fiber.

Wash fastness of compound 3 tested using by multi-fibers was evaluated as ratings 4-5 or 5.

In terms of deodorizing rate, cotton fiber dyed with compound 3(3% o.w.f.) at 90°C provided an outstanding rate of 91% for ammonium gas after passing time of 120min.

Acknowledgment

The authors wish to acknowledge that this research was supported by Kyungpook National University Research Fund, 2013.

References

1. F. H. Moser and A. L. Thomas, "Phthalocyanine Compounds", Reinhold, New York, 1963.
2. K. Jaekel and U. Majer, Determination of the Critical Constants of the Binary Aniline-cyclohexane System near the Critical Concentration by Light Scattering Measurements, *Ber. Bunsenges. Phys. Chem.*, **77**, 843(1973).
3. C. S. Marvel and J. H. Rassweiler, Polymeric Phthalocyanines, *J. Am. Chem. Soc.*, **80**, 1197(1958).
4. D. R. Boston and J. C. Bailar, Phthalocyanine Derivatives from 1,2,4,5-tetracyanobenzene or Pyromellitic Dianhydride and Metal Salts, *Inorg. Chem.*, **11**(4), 1578(1972).
5. H. Shirai, S. Yagi, A. Suzuki, and N. Hojo, Functional Metal-porphyrzine Derivatives and Their Polymers 1, *Makromol. Chem.*, **178**, 1889(1977).
6. H. Shirai, K. Kobayashi, Y. Takemae, A. Suzuki, and O. Hirabaru, Functional Metal-porphyrzine Derivatives and Their Polymers 2: Synthesis and Properties of Polyimides Containing Metal-phthalocyanines, *Makromol. Chem.*, **180**, 2073(1979).
7. H. Shirai, A. Maruyama, J. Takano, K. Kobayashi, and N. Hojo, Functional Metal-porphyrzine Derivatives and Their Polymers: Catalytic Activity of Fe(III)-3,4,3',4',3r',4",3"',4'''-octacarboxyphthalocyanine for Decomposition of Hydrogen Peroxide, *Makromol. Chem.*, **181**, 565(1980).
8. H. Shirai, A. Maruyama, J. Takano, K. Kobayashi, and N. Hojo, Functional Metal-porphyrzine Derivatives and Their Polymers: Synthesis of Poly(styrene) bonded Fe(III)- as well as Co(II)-4,4",4"',4'''-tetracarboxyphthalocyanine and Their Catalase-like Activity, *Makromol. Chem.*, **181**, 575(1980).
9. Y. Washino, "Functional Fibers: Trends in Technology and Product Development in Japan", Toray Reserch Center Inc., Otsu, pp.216-219, 1993.
10. J. L. Petersen, C. S. Schramm, D. R. Stojakovic, B. M. Hoffma, and T. J. Marks, A New Class of Highly Conductive Molecular Solids: The Partially Oxidized Phthalocyanines, *J. of American Chem. Soc.*, **1**, 99(1977).
11. H. Shirai, A. Maruyama, K. Kobayashi, and N. Hojo, Synthesis and Catalase-like Activity of Polystyrene-bonded Iron(III)-phthalocyanine, *J. of Polymer Sci.*, **17**, 661(1979).
12. J. P. Collin and J. P. Sauvage, Electrochemical Reduction of Carbon Dioxide Mediated by Molecular Catalysts, *Coordinuiun Chem. Review*, **93**, 245(1989).

13. M. Kimura and H. Shirai, "The Porphyrin Handbook vol. 19", Elsevier Science, New York, pp. 151-177, 2003.
14. C. C. Leznoff and A. B. P. Lever, "Phthalocyanines: Properties and Applications", VCH, New York, 1989.
15. Y. Washino, "Functional Fibers: Trends in Technology and Product Development in Japan", Toray Reserch Center Inc., Otsu, pp.222-244, 1993.
16. E. M. Kim and J. H. Jang, Reactive Dyeing of Photografted *para*-Aramid Fabrics, *Textile Coloration and Finishing(J. of Korea Soc. Dyers and Finishers)*, **23**(3), 155(2011).
17. Y. Y. Dong and J. H. Jang, Photoinitiator-free Photo-reactive Coloration of Wool Fabrics Using C.I. Reactive Black 5, *Textile Coloration and Finishing(J. of Korea Soc. Dyers and Finishers)*, **24**(2), 97(2012).
18. C. Preston, "The Dyeing of Cellulosic Fibres; Dyers Company Publications Trust", Bradford, England, pp.142-146, 1986.
19. Y. Washino, "Functional Fibers: Trends in Technology and Product Development in Japan", Toray Reserch Center Inc., Otsu, pp.220-221, 1993.