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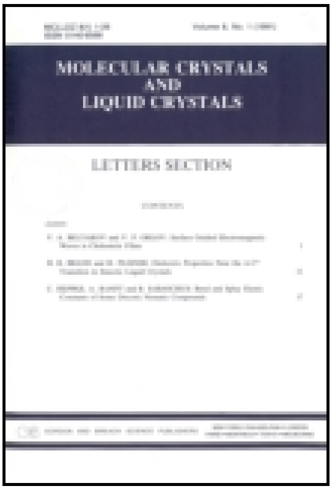

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Effects of Substituents on the Size of Water-Dispersible Phthalocyanine Colloids Synthesized by Reprecipitation

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Phthalocyanine derivatives have become very well-known compounds because of their optical, electrical, and magnetic properties. We studied water-dispersible phthalocyanine colloids synthesized using a conventional reprecipitation method. The average phthalocyanine colloid diameter was closely related to the central metal and the peripheral phthalocyanine substituent. The average 4-phenylsulfonylphthalocyanine colloid diameter was much lower than that of 4-phenylsulfinylphthalocyanine because of the larger molecular size of the phthalocyanine macrocycle with sulfonyl substituent. Ni-phthalocyanine with sulphonyl substituent was found to have the lowest diameter of 28.0 nm.

Keywords Phthalocyanine; reprecipitation method; water-dispersible colloid

Introduction

Phthalocyanine derivatives have been extensively used as dyes and pigments in many industrial components because of their extremely intense blue and green colors, photostability, insolubility in most organic solvents, and chemical inertness [1–4]. Their importance has been rapidly growing in many other applications, especially in organic semiconductor devices, including organic light-emitting diodes (OLEDs) [5] and organic photovoltaic (OPV) cells [6–8]. The potential to be useful in such a wide range of applications originates from their singular chemical structure, high degree of aromaticity, unique electronic properties, and the flexibility involved in their synthesis. Some applications, such as those proposed for phthalocyanine, require compounds with distinct and well-defined physical, chemical, and electronic properties.

A disadvantage in producing a thin phthalocyanine film using normal solution processes is the extreme insolubility of unsubstituted phthalocyanine derivatives. This can be attributed to the extreme hydrophobicity of the aromatic core and the phthalocyanine planarity, which leads to a π–π stacking tendency [9, 10]. A number of functional groups have been attached to the peripheral benzene rings of the phthalocyanine macrocyclic framework to induce solubility [11–17]. Simple functional groups such as alkyl chains, higher

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*Address correspondence to Takeshi Fukuda, Department of Functional Materials Science, Saitama University, 255 Shimo-Ohkubo, Sakura-ku, Saitama, Japan. E-mail: fukuda@fms.saitama-u.ac.jp order aromatics, ethers, amines, thiols, and various acid groups have been used to improve the overall phthalocyanine properties. A few previous studies have shown that several kinds of soluble phthalocyanine derivatives can be used in organic semiconducting devices [18–20].

Most chemically well-dissolved phthalocyanine derivatives have quite low carrier mobilities because of the weak π–π tacking, resulting in the poor performance of organic photoconductive devices [20]. Water-soluble Cu-phthalocyanine has been prepared; it causes little environmental damage and is easy to use in mass production systems [21, 22]. However, the photoconversion efficiency of an OPV device using the water-soluble Cu-phthalocyanine. was relatively low compared to that of a conventional one built with a thermal evaporation method, even though water-solubility is required for organic device applications [21]. We have been studying water-dispersible phthalocyanine colloids synthesized by reprecipitation with the aim of improving OPV device performance using phthalocyanine derivatives in the solution process [23, 24].

We present a study of the influence of the substituent and the central metal in soluble phthalocyanines on the average diameters of the water-dispersible phthalocyanine colloids.

Experimental Procedure

All reagents were of analytical grade. All commercially available reagents were used without further purification. 4-Nitrophthalonitrile was supplied by Orient Chemical Industries Co., Ltd. (Osaka, Japan). Column chromatography was performed using silica gel (50–200 μm) from Fuji Silysia Chemical Ltd. and aluminum oxide 90 (standardized) from Merck Ltd. Preparative thin layer chromatography (TLC) was conducted on aluminum sheets (1 mm thick) using Merck TLC Silica gel 60 F_{254} (Merck Ltd.).

^{1}H nuclear magnetic resonance (NMR) spectra were recorded on a Bruker Avance 400 spectrometer at 400.12 MHz, using $CDCl_3$ as the solvent and tetramethylsilane as the internal reference. High-resolution mass spectra (HRMS) were obtained using a MALDI-TOF mass spectrometer (Auto Flex Speed III Bruker spectrometer; laser 337 nm; 100 Hz; 2,5-dihydroxybenzoic acid matrix; Flex analysis processing software). Mass spectra (MS) were obtained using a JMS-700AM (JEOL Co.), and Fourier transform infrared (FTIR) spectra were recorded on an FT/IR-4200 spectrophotometer (JASCO Corporation) using KBr disks.

The shape and size distribution of the synthesized phthalocyanine colloids were estimated using a scanning electron microscope (SEM; S-4800 instrument; Hitachi) and a dynamic light scattering (DLS) instrument (DLS; Zetasizer Nano S; Malvern), respectively. Elemental analyses of C, H, and N were performed using a Flash EA-1112 recorder (Thermo Fisher Scientific K.K.).

1,2-Dicyano-4-phenylsulfanylbenzene (**1**) (henceforth referred as "S-substituent") and 1,2-dicyano-4-phenylsulfanylbenzene (**3**) (henceforth referred as "SO_2-substituent") were synthesized following a published procedure [25–31]. 1,2-Dicyano-4-phenylsulfinylbenzene (**2**) (henceforth referred as "SO-substituent") was synthesized following a literature published procedure with modifications [25–31].

A mixture of 1,2-dicyano-4-phenylsulfanylbenzene (**1**) (300 mg) and *m*-chloroperbenzoic acid (283 mg) in 10 mL of CH_2Cl_2, at 0 °C, was stirred for 1 hr. The mixture was evaporated and the residue was purified using silica gel column chromatography (silica gel, $Rf = 0.2$, eluted with $CHCl_3$). Yield 69%; white solid; ^{1}H NMR (400 MHz,

$CDCl_3$) δ 7.48 (dd, 1H), 7.54 (d, 1H), 7.63 (d, 1H), 7.5–7.8 (m, 5H); MS m/z 252 [M^+]; IR (KBr) 2235, 1085, 1053, 848, and 750 cm^{-1}. Anal. calcd for $C_{14}H_8N_2OS$: C 66.65, H 3.20, N 11.10; found: C 66.88, H 3.73, N 11.23.

4-Substituted phthalocyanines were mixtures of the four corresponding regioisomers. Therefore, they were characterized without further isolation from their FTIR spectra and HRMS.

General Procedure for Synthesizing Phthalocyanine Metal Complexes

A phthalonitrile with a substituent at the 4-position (1 eq.) and a metal salt (4 eq.) were placed in a two-necked flask sealed on one neck with a rubber septum and with a reflux condenser joined to a vacuum pump fitted to the other neck. The atmospheric air was replaced with argon, and 2-dimethylaminoethanol (5 mL) was added using a syringe through the rubber septum. The mixture was stirred overnight under reflux. It was then added to vigorously stirred water (ca. 500 mL) and filtered. The filtrate was chromatographically separated on aluminum oxide with $CHCl_3$ as the mobile phase to purify the desired product, which was collected as the first blue band.

Synthesis of Tetrakis-(4-pentylsulfanyl)phthalocyaninato Nickel(II) (4a). Following the general procedure, 4-phenylsulfanylphthalonitrile (**1**) (100 mg) and nickel(II) acetate tetrahydrate (104 mg) were used. (*Rf* = 0.7, eluted with $CHCl_3$). Yield 46%; MALDI-TOF-MS m/z found = 1002.039 [M^+], calcd monoisotopic mass for $C_{56}H_{32}N_8S_4Ni$ = 1002.098.

Synthesis of Tetrakis-(4-pentylsulfanyl)phthalocyaninato Copper(II) (4b). Following the general procedure, 4-phenylsulfanylphthalonitrile (**1**) (200 mg) and copper(II) chloride (128 mg) were used. (*Rf* = 0.5, eluted with $CHCl_3$). Yield 32%; MALDI-TOF-MS m/z found = 1007.131 [M^+], monoisotopic mass calcd for $C_{56}H_{32}N_8S_4Cu$ = 1007.092.

Synthesis of Tetrakis-(4-pentylsulfanyl)phthalocyaninato Zinc(II) (4c). Following the general procedure, 4-phenylsulfanylphthalonitrile (**1**) (200 mg) and zinc(II) acetate dihydrate (154 mg) were used. (*Rf* = 0.4, eluted with $CHCl_3$). Yield 37%; MALDI-TOF-MS m/z found = 1008.068 [M^+], monoisotopic mass calcd for $C_{56}H_{32}N_8S_4Zn$ = 1009.096.

Synthesis of Tetrakis-(4-pentylsulfanyl)phthalocyaninato Free Base (4d). Ammonia gas was introduced into a two necked flask containing 4-phenylsulfanylphthalonitrile (500 mg) (**2**) in 2-dimethylaminoethanol (10 mL). The mixture was stirred overnight under reflux. The color of the solution changed to bright blue. The reaction mixture was then added to vigorously stirred water (ca. 500 mL) and filtered. The filtrate was chromatographically separated on aluminum oxide with $CHCl_3$ as the mobile phase to purify the desired product, which was collected as the first blue band. (*Rf* = 0.7, eluted with $CHCl_3$). Yield 32%; MALDI-TOF-MS m/z found = 964.133 [M^+], monoisotopic mass calcd for $C_{56}H_{34}N_8S_4$ = 946.178.

Synthesis of Tetrakis-(4-pentylsulfinyl)phthalocyaninato Nickel(II) (5a). Following the general procedure, 4-phenylsulfinylphthalonitrile (**2**) (500 mg) and nickel(II) acetate tetrahydrate (494 mg) were used. (*Rf* = 0.5, eluted with $CHCl_3$). Yield 29%; FAB-MS m/z 1067 [M^+]; IR (KBr) 1139, 1022 cm^{-1}. Anal. calcd for $C_{56}H_{32}N_8O_4S_4Ni$: C 62.99, H 3.02, N 10.49; found: C 63.01, H 2.89, N 10.12.

Synthesis of Tetrakis-(4-pentylsulfinyl)phthalocyaninato Copper(II) (5b). Following the general procedure, 4-phenylsulfinylphthalonitrile (**2**) (500 mg) and copper(II) chloride (338 mg) were used. (*Rf* = 0.3, eluted with $CHCl_3$). Yield 34%; FAB-MS m/z 1072 [M^+]; IR (KBr) 1091, 1051 cm^{-1}. Anal. calcd for $C_{56}H_{32}N_8O_4S_4Cu$: C 62.70, H 3.01, N 10.45; found: C 63.02, H 3.40, N 10.00.

Synthesis of Tetrakis-(4-pentylsulfinyl)phthalocyaninato Zinc(II) (5c). Following the general procedure, 4-phenylsulfinylphthalonitrile (**2**) (500.0 mg) and zinc(II) acetate dihydrate (496.7 mg) were used. (*Rf* = 0.2, eluted with $CHCl_3$). Yield 34%; FAB-MS m/z 1072 [M^+]; IR (KBr) 1093, 1045 cm^{-1}. Anal. calcd for $C_{56}H_{32}N_8O_4S_4Zn$: C 62.60, H 3.00, N 10.43;. found: C 61.76, H 3.40, N 10.12.

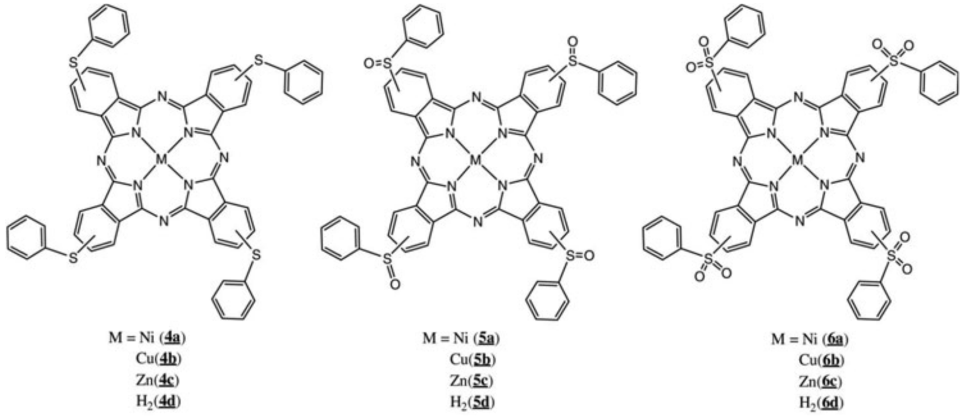
Synthesis of Tetrakis-(4-pentylsulfinyl)phthalocyaninato Free Base (5d). Ammonia gas was introduced into a two necked flask containing 4-phenylsulfinylphthalonitrile (500 mg) (**2**) in 2-dimethylaminoethanol (10 mL). The mixture was stirred overnight under reflux. The color of the solution changed to bright blue. The reaction mixture was then added to vigorously stirred water (ca. 500 mL) and filtered. The filtrate was chromatographically separated on aluminum oxide with $CHCl_3$ as the mobile phase to purify the desired product, which was collected as the first blue band. (*Rf* = 0.7, eluted with $CHCl_3$). Yield 30%; FAB-MS m/z 1010 [M^+]; IR (KBr) 1058, 1047 cm^{-1}. Anal. calcd for $C_{56}H_{34}N_8O_4S_4$: C 66.52, H 3.39, N 11.08; found: C 66.20, H 3.65, N 11.32.

Synthesis of Tetrakis-(4-pentylsulfonyl)phthalocyaninato Nickel(II) (6a). Following the general procedure, 4-phenylsulfonylphthalonitrile (**3**) (500.0 mg) and nickel(II) acetate tetrahydrate (464 mg) were used. (*Rf* = 0.7, eluted with $CHCl_3$). Yield 34%; IR (KBr) 1307, 1155, 1061 cm^{-1}. MALDI-TOF-MS m/z found = 1130.061 [M^+], monoisotopic mass calcd for $C_{56}H_{32}N_8O_8S_4Ni$ = 1130.057.

Synthesis of Tetrakis-(4-pentylsulfonyl)phthalocyaninato Copper(II) (6b). Following the general procedure, 4-phenylsulfonylphthalonitrile (**3**) (500.0 mg) and copper(II) chloride (313 mg) were used. (*Rf* = 0.4, eluted with $CHCl_3$). Yield 32%; IR (KBr) 1307, 1122, 1101 cm^{-1}. MALDI-TOF-MS m/z found = 1134.864 [M^+], monoisotopic mass calcd for $C_{56}H_{32}N_8O_8S_4Cu$ = 1135.052.

Synthesis of Tetrakis-(4-pentylsulfonyl)phthalocyaninato Zinc(II) (6c). Following the general procedure, 4-phenylsulfonylphthalonitrile (**3**) (500.0 mg) and copper(II) chloride (313 mg) were used. (*Rf* = 0.4, eluted with $CHCl_3$). Yield 27%; IR (KBr) 1153, 1099 cm^{-1}. MALDI-TOF-MS m/z found = 1135.888 [M^+], monoisotopic mass calcd for $C_{56}H_{32}N_8O_8S_4Zn$ = 1136.051.

Synthesis of Tetrakis-(4-pentylsulfonyl)phthalocyaninato Free Base (6d). Ammonia gas was introduced into a two necked flask containing 4-phenylsulfonylphthalonitrile (500 mg) (**3**) in 2-dimethylaminoethanol (5 mL). The mixture was stirred overnight under reflux. The color of the solution changed to bright blue. The reaction mixture was then added to vigorously stirred water (ca. 500 mL) and filtered. The filtrate was chromatographically separated on aluminum oxide with $CHCl_3$ as the mobile phase to purify the desired product, which was collected as the first blue band. (*Rf* = 0.8, eluted with $CHCl_3$). Yield 33%; IR (KBr) 1307, 1155, 1107, and 1010 cm^{-1}. MALDI-TOF-MS m/z found = 1074.043 [M^+], monoisotopic mass calcd for $C_{56}H_{34}N_8O_8S_4$ = 1074.138.



Scheme 1. Synthesized soluble phthalocyanine derivatives (**4**, **5**, and **6**) with different substituents and M means Ni, Cu, Zn, and H_2.

The compounds obtained are illustrated in scheme 1 and the yields are summarized in Table I.

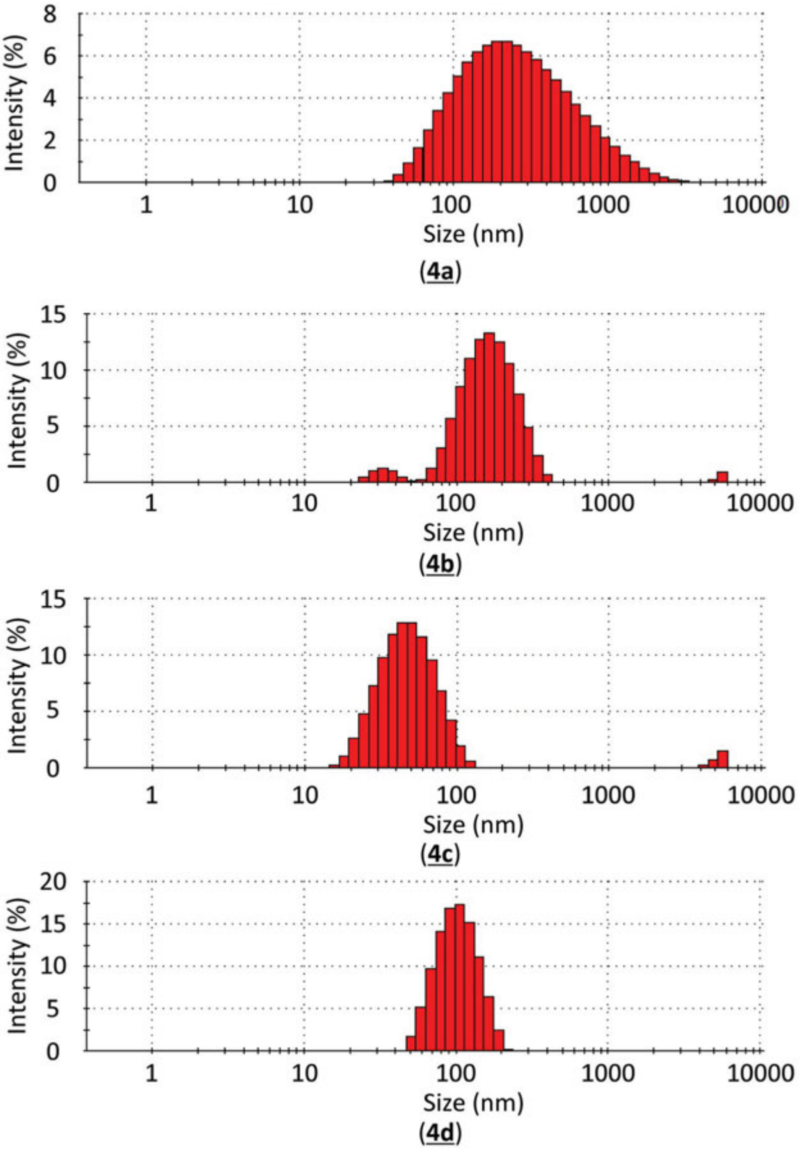
Water-dispersible phthalocyanine colloids were synthesized by reprecipitation [32]. The synthesized soluble phthalocyanine (0.1 mg) was dissolved in a suitable solvent (tetrahydrofuran, 5 mL) and the solution was then added very slowly to a poor solvent (water, 60 mL) with stirring. The mixture was filtered through a membrane filter (pore diameter: 0.45 μm), and tetrahydrofuran was evaporated under reduced pressure. The shape and size distribution of the synthesized phthalocyanine colloids were estimated using the SEM and DLS instrument, respectively.

Results and Discussion

Figure 1 shows the size distributions of the colloidal phthalocyanine derivatives with the S-substituent (**4a–d**) dispersed in water. The average diameters of **4a**, **4b**, **4c**, and **4d** were 358.0, 172.0, 50.1, and 105.0 nm, respectively, all of which were rather large for use in OLEDs and OPVs. In general, organic devices consist of an organic layer with thickness less than 100 nm [33–35] because of the short exciton diffusion lengths of common organic materials [36, 37]. It is, therefore, desirable that the average phthalocyanine colloid size is 100 nm or less.

Table 1. Yields of synthesis process for all the phthalocyanine derivatives with different center metals (Ni, Cu, Zn, and H) and substituents (S, SO, and SO_2)

	Center metal			
Substituent	Ni	Cu	Zn	H_2
	46	32	37	32
	29	34	34	30
	34	32	27	33



(**4a**)

(**4b**)

(**4c**)

(**4d**)

Figure 1. Size distributions of colloidal phthalocyanine derivatives (**4a**, **4b**, **4c**, and **4d**) with S-substituents measured by the DLS.

Figure 2 shows the size distributions of the phthalocyanine colloids with the SO-substituent (**5a–5d**) dispersed in water. The average diameters of **5a**, **5b**, **5c**, and **5d** were 203.0, 94.1, 40.2, and 36.6 nm, respectively. The average diameters of **5a**–**5d** were lower than those of **4a**–**4d** for all the central metals (Ni, Cu, Zn, and H_2). This result can be explained by the distance between adjacent phthalocyanine molecules. The additional oxygen atom in the substituent in **5a**–**5d** causes further distance between adjacent phthalocyanine rings, resulting in a small colloidal size, illustrated in Figures 1 and 2.

Two or three peaks appeared in the size distribution of the synthesized water-dispersible phthalocyanine colloids. This indicates that the colloids have broad diameter-distributions.

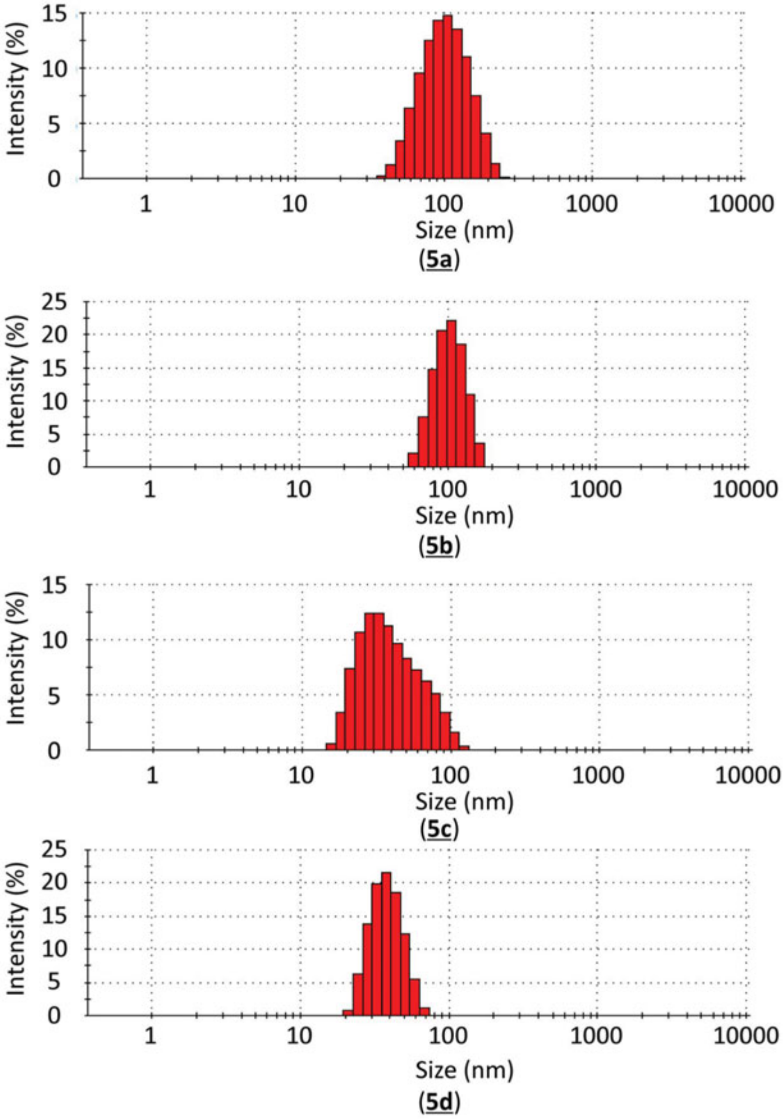


Figure 2. Size distributions of colloidal phthalocyanine derivatives (**5a**, **5b**, **5c**, and **5d**) with SO-substituents dispersed in water measured by the DLS.

A sharp diameter-distribution is an important factor in producing a smooth, thin organic film, and further method optimization is necessary to produce films with smaller diameter and a sharp diameter-distribution.

Figure 3 shows the size distributions of the phthalocyanine colloids with the SO_2-substituent (**6a–d**) dispersed in water. The average diameters of **6a**, **6b**, **6c**, and **6d** were 28.0, 32.3, 47.9, and 54.5 nm, respectively. The average diameters of **6a–6d** were lower than those of **4a–d** and **5a–d** with the same central metal. This is probably explained by the coordination ability of the central metal in the synthesized soluble phthalocyanine. It is clear that the molecular size of the substituent influenced the average diameter

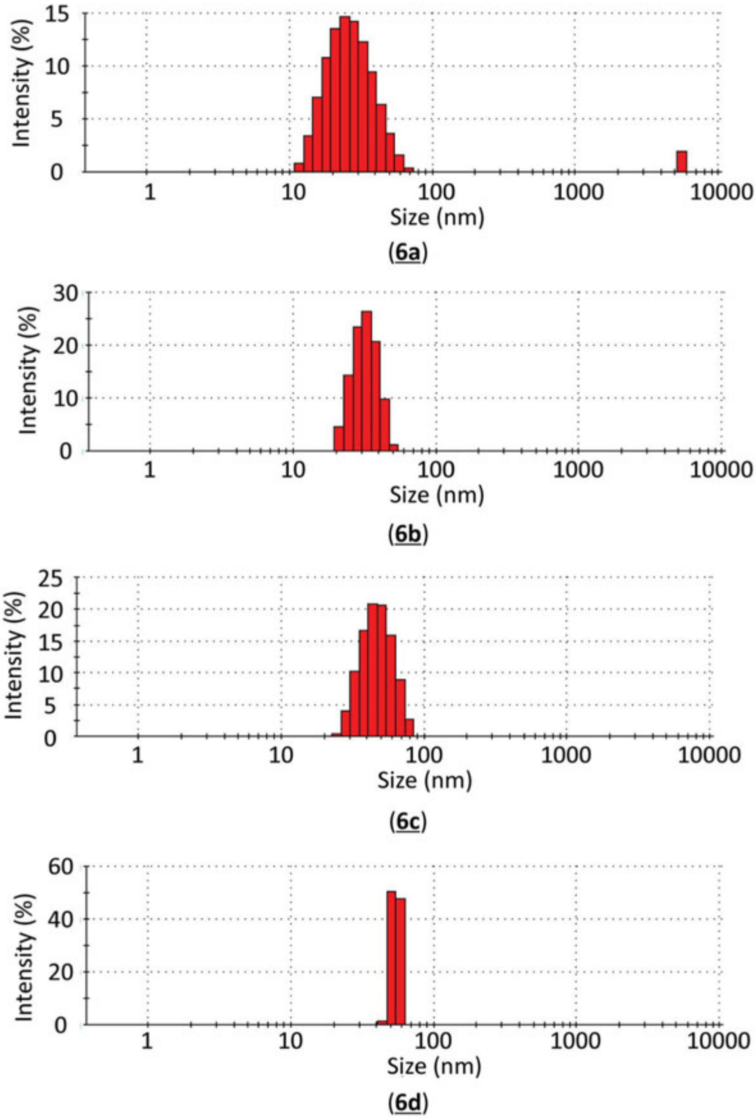


Figure 3. Size distributions of colloidal phthalocyanine derivatives (**6a**, **6b**, **6c**, and **6d**) with SO_2-substituent in water measured by the DLS.

of the water-dispersible phthalocyanine colloid. In general, the SO_2 (4-phenylsulfonyl) group is larger than the SO (4-phenylsulfinyl) and sulfur (S) groups because of the additional S=O bond. The cohesive energy density of phthalocyanine is low when adjacent molecules are far apart. Therefore, weak intermolecular interactions exist between 4-phenylsulfonylphthalonitrile (**3**), resulting in a lower average-diameter in the synthesized colloid.

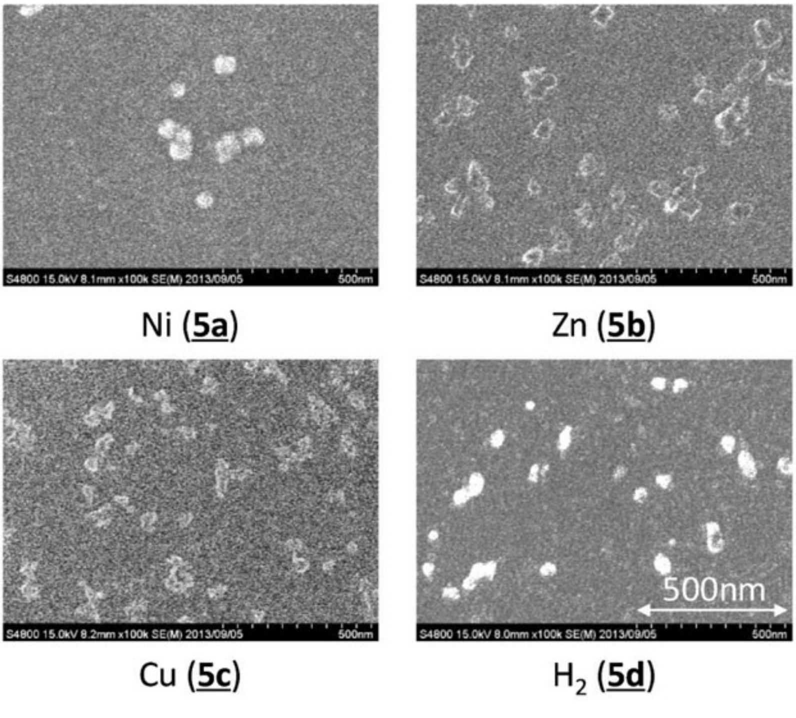
The DLS measurement results for the phthalocyanine colloids with the SO_2-substituents (**6**) (Figure 3) showed that the average diameter increased in the order Ni $<$ Cu $<$ Zn $<$ H_2.

Table 2. Average diameters of DLS measurement result for soluble phthalocyanine colloids with different substituents (S, SO, and SO_2) and center metals (Ni, Cu, Zn, and H_2)

	Center metal			
Substituent	Ni	Cu	Zn	H_2
S (**4**)	358	172	50.1	105
SO (**5**)	119	104	42.9	38.8
SO_2 (**6**)	28.0	32.3	47.9	54.5

Table II shows the average diameter calculated from the DLS results shown in Figures 1–3. The water-dispersible phthalocyanine colloids were stable for several days without aggregating. The average diameter was closely related to the central metal and the peripheral substituents.

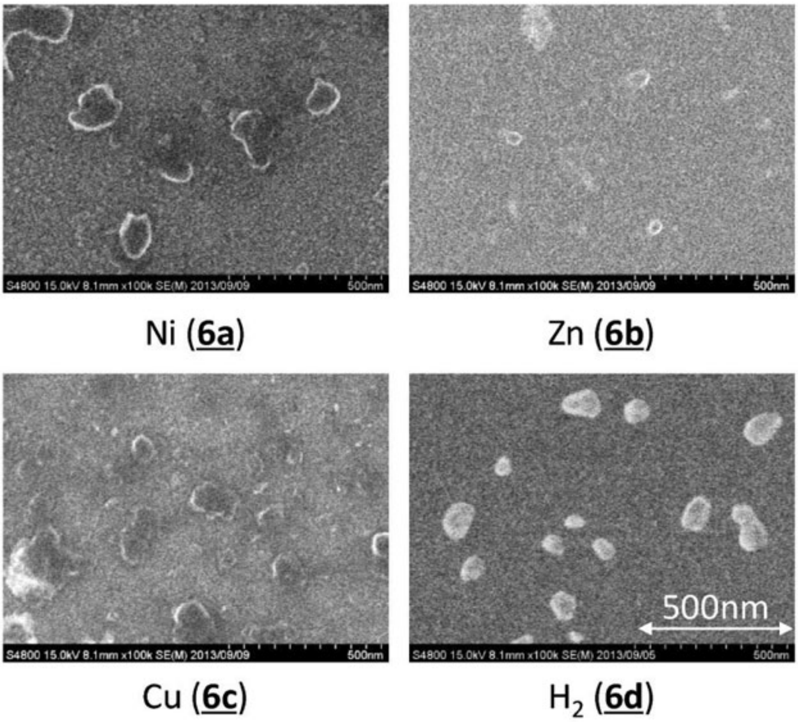
Figures 4 and 5 show SEM images of the phthalocyanine colloids **5** and **6,** with different central metals, which have 4-phenylsulfinyl and 4-phenylsulfonyl substituents, respectively. As clearly shown in these figures, phthalocyanine colloids with diameters less than 100 nm were formed.



Ni (**5a**) Zn (**5b**)

Cu (**5c**) H_2 (**5d**)

Figure 4. SEM images of water-dispersible SO(4-phenylsulfinylphthalocyanine) colloids (**5a**, **5b**, **5c**, and **5d**) with different center metals.



Ni (**6a**)

Zn (**6b**)

Cu (**6c**)

H_2 (**6d**)

Figure 5. SEM images of water-dispersible SO_2(4-phenylsulfonylphthalocyanine) colloids (**6a**, **6b**, **6c**, and **6d**) with different center metals.

Conclusions

We successfully synthesized water-dispersible phthalocyanine colloids using a conventional reprecipitation method. The average diameters of the synthesized phthalocyanine colloids could be controlled by changing the substituent and the central metal. The smallest synthesized phthalocyanine colloid had an average diameter of 28.0 nm, which is small enough to be useful in realizing organic thin film devices.

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