Microwave-assisted Synthesis of Phthalocyanine Metal Complexes: Relationship between Yield and Maximum Temperature Reached by Microwave Irradiation

Kanta Abe, Satoshi Katano, and Kazuchika Ohta

Smart Materials Science and Technology, Interdisciplinary Graduate School of Science and Technology, Shinshu University, 3-15-1 Tokida, Ueda, Nagano 386-8567, JAPAN

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Multifunctional phthalocyanine metal complexes are very useful for many applications, such as electroconductivity, electrochromism and liquid crystalline formation, so the syntheses of phthalocyanine derivatives have attracted much interest in recent years. Previously, we noticed that no template effect was observed for the microwave-assisted synthesis of phthalocyanine copper complex, which we thought might be due to dielectric loss coefficient of the added metal salt. However, the dielectric loss coefficient of metal salt in a dilute solution is very difficult to directly measure. Since the heat quantity is proportional to the dielectric loss coefficient from basic microwave theory, the maximum temperature of a solution containing a metal salt heated by microwave irradiation can be an indirect index of the dielectric loss coefficient. In this study, glycerin solutions containing one of twelve different metal salts (MC12, MSO4, M(OAc)2; M = Co, Ni, Cu, Zn) were heated by microwave irradiation. The maximum temperature of the solution reached was measured for each of the metal salts. Then, the corresponding phthalocyanine metal complexes (C8S)8PcM (M = Co, Ni, Cu, Zn) were prepared using these twelve different metal salts by microwave heating. The findings showed a proportional relationship between the yields and the maximum temperatures reached by microwave irradiation. This relationship may provide a useful guideline in microwave-assisted synthesis of organic metal complexes.

Keywords
Microwave-assisted synthesis, Microwave heating, Microwave irradiation, Phthalocyanine metal complex, Metal salt, Dielectric loss coefficient

1. Introduction

Microwave heating has become an interesting technique in the field of organic chemistry, because the reaction mixture can be very rapidly heated to a target temperature, so that the reaction can be promoted in a very short time as compared with oil bath heating.

First of all, we consider the difference between oil bath heating and microwave heating. With conventional oil bath heating, the reaction solvent receives heat from an oil bath, and heat convection occurs in the solvent. Therefore, this heating method is called external heating. With the thermal convection of the solvent, the solute molecules of the reactive species have increased translational motion and reaction occurs by intermolecular collision controlled by the translational energy of the reactive species. Therefore, the temperature of the reaction solution has a large influence on the yield of the reaction product. In contrast, with microwave heating, the solvent and solute molecules directly absorb the irradiated microwave energy, and the rotational motion of the molecules is excited. Relaxation of the rotational motion from the excited state to the ground state releases energy into the surrounding reaction solution as heat. Therefore, this heating method is called internal heating. Internal heating by microwave irradiation can rapidly heat the reaction solution compared to external heating.

With internal heating, the solute molecules of reactive species obtain increases in both rotational and translational motions, so that the reaction occurs by intermolecular collision controlled by both the translational and rotational energies of the reactive species. Therefore, even at the same temperature of the solution, the reactant molecules have greater chances to collide at the optimum reactive points with microwave heating, compared with conventional oil bath heating. Consequently, the yield obtained by microwave heating is much better than that by oil bath heating.

In general, the ease of heating by microwaves de-
The following equation represents the heat quantity of material heated by microwaves.

\[ Q = 0.556 \times 10^{-10} \times f \times E^2 \times \varepsilon_r \cdot \tan \delta \]  

**Q**: Power absorbed by the dielectric material = heat quantity,

\( f \): Frequency of the microwave (constant for domestic microwave ovens; \( f = 2.45 \text{ GHz} \)),

\( E \): Electric field strength (fixed for a domestic microwave oven),

\( \varepsilon_r \): Relative permittivity specific to the dielectric material,

\( \tan \delta \): Dielectric loss angle specific to the dielectric material.

Here, \( \varepsilon_r \cdot \tan \delta \) is called the dielectric loss coefficient. This equation shows that the heat quantity \( Q \) is proportional to the dielectric loss coefficient \( \varepsilon_r \cdot \tan \delta \) specific to the material. Therefore, larger dielectric loss coefficient \( \varepsilon_r \cdot \tan \delta \) allows easier heating by microwave irradiation. Accordingly, the synthetic yield may be better for materials with higher dielectric loss coefficient. Moreover, the reactivities of materials can be compared by direct comparison of their dielectric loss coefficients \( \varepsilon_r \cdot \tan \delta \). However, the dielectric loss coefficient \( \varepsilon_r \cdot \tan \delta \) of the dilute reactive species is very difficult to measure in a solution. Therefore, dielectric loss coefficients are not easy to directly compare.

Reconsideration of the physical meaning of Eq. (1) indicates that as the dielectric loss coefficient \( \varepsilon_r \cdot \tan \delta \) is proportional to heat quantity \( Q \), the dielectric loss coefficients can be compared indirectly from the heat quantities. Therefore, the pure reaction solvent without solutes is heated by microwave irradiation, and the maximum temperature \( (T_0) \) is measured for the pure solvent. Next, a solution containing one type of reactive species is heated by microwave irradiation, and the maximum temperature \( (T) \) is measured for this solution. The difference \( \Delta T = T - T_0 \) provides an indirect measurement of the dielectric loss coefficient specific to the reaction species.

To date, we have rapidly synthesized phthalocyanine (Pc)-based compounds by using our hand-made microwave heating apparatus based on a remodeled domestic microwave oven as illustrated in Fig. 1. We could rapidly synthesize octakisoctylthiophthalocyanine \((\text{C}_8\text{S})_8\text{PcH}_2\) as shown in Fig. 2. The reaction time was 24 h for the synthesis using oil bath heating, but only 10-15 min for the synthesis using microwave heating as summarized in Table 1. Thus, microwave heating greatly shortens the reaction time. Moreover, the yield was improved from 56 to 71%.

The yield of phthalocyanine metal (PcM) complexes is generally higher than that of the metal-free form \((\text{PcH}_2)\) using conventional oil bath heating due to the template effect, which refers to the coordination of multiple ligands around a metal. Therefore, we expected that the yield of the corresponding copper metal complex, \((\text{C}_8\text{S})_8\text{PcCu}\), might improve due to the template.
effect using microwave heating. However, the yield did not improve, as can be seen from Table 1. Thus, the template effect could not be observed for synthesis by microwave heating\(^7\), possibly due to the effects on the dielectric constant and dielectric loss coefficient of the metal salt added.

In this study, glycerin solutions containing one of twelve different metal salts (MCl\(_2\), MSO\(_4\), M(OAc)\(_2\); M = Co, Ni, Cu, Zn) were irradiated with microwaves. The maximum temperature of the solution was measured for each of the metal salts. Then, phthalocyanine metal complexes (C\(_8\)S)\(_8\)PcM (M = Co, Ni, Cu, Zn) were prepared using these twelve different metal salts by microwave heating. As a result, we found an interesting relationship between the yields and the maximum temperatures reached by microwave irradiation, which may provide a good guideline for microwave-assisted synthesis of organic metal complexes.

2. Results and Discussion

2.1. Influence of Metal Salt on Maximum Temperature of Solution

Each of twelve different metal salts (MCl\(_2\), MSO\(_4\), M(OAc)\(_2\); M = Co, Ni, Cu, Zn in Table 2) was selected, and 0.12 mmol of the metal salt was dissolved in 2.00 mL of glycerin as a microwave-absorbing solvent. The solution in a quartz test tube was irradiated by microwaves (2.45 GHz), and the solution temperature was measured every 30 s for 15 min. The solution temperatures are plotted against the microwave irradiation time in Fig. 3.

The vertical and horizontal axes of Fig. 3 show the temperature and the microwave irradiation time, respectively. The red, green and blue plots show the solution temperatures of the metal chloride, metal sulfate, and metal acetate, respectively. The boiling point of glycerin is 290.3 °C. The black solid line shows the temperatures of 2.00 mL of pure glycerin. Since the amount of solvent was small and the test tube was cooled with nitrogen gas flow at room temperature, the solution temperature reached a plateau at around 160 °C.

The maximum temperatures reached in the cases of cobalt salt, nickel salt and zinc salt were higher in the order of acetate < sulfate < chloride. Only in the case of copper salt the maximum temperatures were higher in the order of acetate < chloride < sulfate\(^9\). Therefore, the dielectric loss coefficients of these metal salts are increased in the same order as the maximum temperatures, based on Eq. (1) showing the relationship between heat quantity \(Q\) and dielectric loss coefficient. Therefore, the yields of the Pc metal complexes, (C\(_8\)S)\(_8\)PcM (M = Co, Ni, Cu, Zn) may become better in the same order. Further experiments investigated our hypothesis that "higher maximum temperature of metal salt (reactant) solution with microwave heating results in higher yield of the corresponding Pc metal complex (product) in microwave-assisted synthesis."

2.2. Syntheses of Octakisoctylthiophthalocyaninato Metal(II) (C\(_8\)S)\(_8\)PcM: (1a-d) and Effect of Metal Salt on the Yields

Phthalocyanine metal complexes (C\(_8\)S)\(_8\)PcM (1a-d) were synthesized using twelve different metal salts (MCl\(_2\), MSO\(_4\), M(OAc)\(_2\); M = Co, Ni, Cu, Zn in Table 2) according to Scheme 1. For each of the metal salts, the syntheses of the corresponding phthalocyanine metal complexes (C\(_8\)S)\(_8\)PcM were carried out at 10 °C intervals from 180 to 240 °C using microwave heating. The microwave irradiation time was set as 5, 10 and 15 min.

The yields of the phthalocyanine metal complexes (C\(_8\)S)\(_8\)PcM are plotted against the temperature for each metal (M = Co, Cu, Zn) in Figs. 4-6. In these figures, the solid circles, squares and triangles indicate the yields for the reaction times of 5, 10 and 15 min, re-
respectively. The dotted line shows the yield of the (C8S)8PcM complexes synthesized by the oil bath method.

2.2.1. Cobalt Salt

Figure 4 shows the yields of (C8S)8PcCo for the cobalt salts. Figure 4A shows that the yields for cobalt chloride became higher in the order of reaction times of 15, 5 and 10 min. Thus, the reaction time greatly affected the yields. The highest yield was 72% at the reaction temperature of 200°C and reaction time of 10 min, which was significantly higher than the yield of 53% with the oil bath method.

Figure 4B shows that the yields for cobalt sulfate heptahydrate became higher in the order of reaction time of 5, 15 and 10 min. The highest yield was 53% at 200°C for 10 min. This yield was the same as that of 53% with the oil bath method.

Figure 4C shows that the yields for cobalt acetate tetrahydrate had a different trend, as the yields remained almost constant and low with temperature. The highest yield of 47% with the microwave method was obtained at 210°C for 5 min and 190°C for 10 min. This yield was lower than that of 57% with the oil bath method. Therefore, the type of counter anion of the three cobalt salts greatly affected the yield of product (C8S)8PcCo. In the case of synthesis of (C8S)8PcCo, the highest yield of 72% with the microwave method was obtained at 200°C for 10 min, and was considerably higher than the yield of 57% with the oil bath method.

(i) C6H5SH/K2CO3/DMSO, (ii) Metal salt/DBU/1-hexanol at b.p. (156°C)/N2, (iii) Metal salt/DBU/glycerin at 180-240°C/N2. DMSO = dimethyl sulfoxide. DBU = 1,8-diazabicyclo[5.4.0]undec-7-ene.

Scheme 1 Synthetic Routes of (C8S)8PcM
2.2.2 Copper Salt

Figure 5 shows the yields of (C₈S)₈PcCu for the copper salts. Figure 5A shows that the yields for copper chloride became higher in the order of 15, 5 and 10 min at temperatures over 210 °C. No maximum yields were obtained at about 200 °C in contrast to the case of cobalt chloride. The highest yield with the microwave method was 54 %, which was much lower than the yield of 74 % with the oil bath method.

Figure 5B shows that the yields for copper sulfate became higher almost linearly with higher temperature from 180 to 240 °C. This tendency was totally different from the other metal salts. The highest yield was 64 % at 240 °C for 5 min, and was almost the same as the yield of 62 % with the oil bath method.
Figure 5C shows that the yields for copper acetate monohydrate had a different trend from the previous two copper salts (Figs. 5A, 5B). The yield peaked at around 210-220 °C. The highest yield with the microwave method was 47% at 210 °C for 5 min, and was much lower than the yield of 63% in the oil bath method.

The counter anions of the three types of copper salts greatly affected the yield of (C8S)8PcCu. Also, in the case of synthesis of (C8S)8PcCu, the highest yields with the microwave method were generally poor as compared with the yields with the oil bath method.

2.2.3. Zinc Salt
The zinc complex (C8S)8PcZn was also synthesized using three zinc metal salts by the microwave method. Figure 6A shows the yields for zinc chloride. The maximum yields peaked at around 210 °C. The highest yield was 82% at 210 °C for 15 min, which was much higher than the yield of 42% with the oil bath method. Figures 6B and 6C show the yields for zinc sulfate heptahydrate and zinc acetate dihydrate, respectively. The highest yields with the microwave method were nearly the same as the yields with the oil bath method.

2.2.4. Nickel Salt
The syntheses of nickel complex (C8S)8PcNi by the microwave method gave extremely different results from the other three metals.

The (C8S)8PcNi complex was synthesized by the microwave method using nickel chloride at 10 °C intervals from 160 to 240 °C for 10 min. Very interestingly, the microwave method for nickel chloride gave a mixture of the metal complex (C8S)8PcNi and the metal-free compound (C8S)8PcH2. The polarities of (C8S)8PcNi and (C8S)8PcH2 are almost the same, so were impossible to separate and purify by column chromatography. Therefore, the ratio of these two products was estimated from the UV-vis spectra, as shown in Fig. 7A. For comparison, the spectrum of the pure (C8S)8PcNi complex synthesized by the oil bath method is also shown.

The product synthesized by the oil bath method had a sharp single Q-band (Peak β) at 701 nm characteristic of the pure (C8S)8PcNi complex as shown in Fig. 7A. Therefore, the oil bath method using nickel chloride afforded only the pure Ni complex. On the other hand, the products synthesized by the microwave method using the same nickel salt, nickel chloride, had two split Q-bands located at 732 nm (Peak α) and 701 nm (Peak β) for all reaction temperatures. These two split Q-bands originated from the metal-free phthalocyanine (C8S)8H2. These wavelengths coincided well with the literature values, 732 nm and 700 nm8,9). Therefore, a mixture of (C8S)8PcNi and (C8S)8PcH2 was produced by the microwave method using nickel chloride.

The mixture of (C8S)8PcNi and (C8S)8PcH2 was produced despite using a large excess of nickel chloride. Therefore, this phenomenon was not caused by simple raw material shortage. This previously unknown phenomenon occurred only in the synthesis of (C8S)8PcNi by the microwave heating method, and was completely different from the syntheses of the other metal com-
plexes \((\text{C8S})_8\text{PcCo}, (\text{C8S})_8\text{PcCu}, (\text{C8S})_8\text{PcZn}\).

To confirm whether this phenomenon occurs only for nickel chloride, syntheses of \((\text{C8S})_8\text{PcNi}\) by the microwave heating method were also carried out using nickel sulfate hexahydrate and nickel acetate tetrahydrate at 10 \(\degree\) intervals from 180 to 250 \(\degree\) for 10 min. A mixture of \((\text{C8S})_8\text{PcNi}\) and \((\text{C8S})_8\text{PcH}_2\) was obtained in most reactions of nickel sulfate hexahydrate and nickel acetate tetrahydrate. The ratio of these two products was estimated from the ratio of the absorbencies of Peak \(\alpha\) and Peak \(\beta\) \((A_\alpha/A_\beta)\). The ratio \(A_\alpha/A_\beta\) is plotted against temperature in Fig. 7B. The red circles, green squares and blue triangles represent the ratios for nickel chloride, nickel sulfate hexahydrate, and nickel acetate tetrahydrate, respectively. The dotted lines at the top and bottom of this figure correspond to the ratios of the pure \((\text{C8S})_8\text{PcH}_2\) and \((\text{C8S})_8\text{PcNi}\) compounds, respectively. Therefore, the values between these two dotted lines correspond to a mixture of \((\text{C8S})_8\text{PcNi}\) and \((\text{C8S})_8\text{PcH}_2\).

Using nickel chloride (red circle), only \((\text{C8S})_8\text{PcH}_2\) was produced at 160 \(\degree\), but the relative amount of \((\text{C8S})_8\text{PcH}_2\) gradually decreased at higher reaction temperatures. However, only a mixture of \((\text{C8S})_8\text{PcH}_2\) and \((\text{C8S})_8\text{PcNi}\) was obtained at all temperatures from 170 to 240 \(\degree\). Using nickel sulfate hexahydrate (green square), the relative amount of \((\text{C8S})_8\text{PcNi}\) was the highest at 160 \(\degree\) but smaller than that using nickel chloride. Only pure \((\text{C8S})_8\text{PcNi}\) complex was obtained at reaction temperatures higher than 210 \(\degree\). Using nickel acetate tetrahydrate (blue triangle), \((\text{C8S})_8\text{PcNi}\) was predominantly obtained even at lower reaction temperatures 160-170 \(\degree\). However, \((\text{C8S})_8\text{PcH}_2\) was always formed even if the reaction temperature was higher. Therefore, pure \((\text{C8S})_8\text{PcNi}\) could not be obtained under any conditions using nickel acetate tetrahydrate (blue triangle). Further research is necessary to reveal this unique mixture phenomenon in the microwave-assisted synthesis of \(\text{PcNi}\) complex using nickel salts.

To obtain the pure \((\text{C8S})_8\text{PcNi}\) complex by the microwave method, we should carry out the reaction using nickel sulfate hexahydrate in a temperature range of 210-240 \(\degree\) as demonstrated in Fig. 7B. However, the yields were extremely low from a few percent to 27 \% (Table 2), which is much lower than the yield of 63 \% (Table 2) by the oil bath method using the same nickel sulfate hexahydrate. Therefore, it is better to synthesize \((\text{C8S})_8\text{PcNi}\) by the conventional oil bath method.

These findings show that the yields of \((\text{C8S})_8\text{PcM}\) (M = Co, Ni, Cu, Zn) in microwave-assisted syntheses strongly depend on the types of metal ion and counter anion.

### 2.3. Proportional Relationship between Yield and Maximum Temperature Reached by Microwave Irradiation

Table 3 summarizes the highest yields of \((\text{C8S})_8\text{PcM}\) synthesized by both the microwave method and oil bath method, using the 12 types of metal salts (MCl\(_2\), MSO\(_4\cdot n\text{H}_2\text{O}\), M(OAc)\(_2\cdot n\text{H}_2\text{O}\); M = Co, Ni, Cu, Zn). Using cobalt salts in the microwave method, the yields of \((\text{C8S})_8\text{PcCo}\) became higher in the order of acetate < sulfate < chloride. Using zinc salts in the microwave method, the yields of \((\text{C8S})_8\text{PcZn}\) became higher in the same order of acetate < sulfate < chloride. Using copper salts in the microwave method, the yields of \((\text{C8S})_8\text{PcCu}\) became higher in a different order of

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**Table 3**: Summary of maximum yields of \((\text{C8S})_8\text{PcM}\) synthesized by both the microwave and oil bath methods

| Metal Ion | Yield (Microwave) | Yield (Oil Bath) |
|-----------|------------------|------------------|
| Co        | 63 %             | 90 %             |
| Ni        | 50 %             | 80 %             |
| Cu        | 35 %             | 70 %             |
| Zn        | 27 %             | 65 %             |
acetate < chloride < sulfate.

These findings demonstrate the very interesting correlation that the orders of the yields of (C₈S)₈PcM (M = Co, Cu, Zn) in microwave-assisted syntheses are the same orders of the maximum temperatures induced by microwave irradiation in the glycerin solutions containing these metal salts (see Fig. 3). In other words, “higher maximum temperature of metal salt (reactant) solution reached by microwave irradiation results in higher yield of the corresponding Pc metal complex (product) in microwave-assisted synthesis.” We are convinced that this proportional relationship between yield and maximum temperature will provide an important guideline for syntheses of organic metal complexes using microwave heating.

3. Conclusion

In this study, glycerin solutions containing one of twelve different metal salts (MCl₂, MSO₄, M(OAc)₂; M = Co, Ni, Cu, Zn) were heated by microwave irradiation. The maximum temperature of the solution reached by microwave irradiation was measured in detail for each of the metal salts. The maximum temperatures reached in the cases of cobalt salt, nickel salt and zinc salt were higher in the order of acetate < sulfate < chloride. Only in the case of copper salt, the maximum temperatures increased in a different order of acetate < chloride < sulfate. Therefore, the dielectric loss coefficients of these solute metal salts may increase in the same orders of the maximum temperatures, based on the relationship between heat quantity Q and dielectric loss coefficient.

The phthalocyanine metal complexes (C₈S)₈PcM (M = Co, Ni, Cu, Zn) were prepared by microwave heating using these twelve different metal salts. Using cobalt and zinc salts in the microwave method, the yields of (C₈S)₈PcCo and (C₈S)₈PcZn became higher in the order of acetate < sulfate < chloride, respectively. Using copper salts in the microwave method, the yields of (C₈S)₈PcCu became higher in a different order of acetate < chloride < sulfate. Very interestingly, these orders of the yields of (C₈S)₈PcM (M = Co, Cu, Zn) in microwave-assisted syntheses were the same orders of the maximum temperatures reached by microwave irradiation to the glycerin solutions containing the metal salt.

Our findings indicate an interesting proportional relationship between the yields and the maximum temperatures reached by microwave irradiation. Such a proportional relationship may provide an important guideline in the microwave-assisted syntheses of organic metal complexes.

4. Experimental

4.1. Synthesis

The synthetic routes for the (C₈S)₈PcM (M = Co, Ni, Cu, Zn) complexes are shown in Scheme 1. The microwave-assisted syntheses of these PcM complexes were carried out using our handmade apparatus based on a domestic microwave oven (Fig. 1).

4,5-Bisoctylthiophthalonitrile (2)

A mixture of 4,5-dichlorophthalonitrile (2.00 g, 10.2 mmol) and 1-octanethiol (3.56 g, 24.3 mmol) in dry DMSO (40 mL) was heated up to 100 °C with stirring under a nitrogen atmosphere. Dry finely powdered K₂CO₃ was added (5 × 1.40 g, one portion every 5 min). The mixture was stirred at 100 °C for 15 min. After cooling to room temperature, the reaction mixture was diluted with chloroform. The organic layer was washed with brine and dried over Na₂SO₄. After removal of the solvent, purification was carried out by column chromatography (silica gel, CHCl₃, Rf = 0.55) and then by recrystallization twice from ethanol with activated carbon to afford 2.89 g of white crystals.

Yield: 68.2%.

M.p. 60.3-60.5 °C (lit. 58.8-59.0 °C)10). IR (KBr, cm⁻¹): 2929 (~CH₂~), 2229 (~CN), 1562 (Aryl).

4.1.1. Oil Bath Method

The metal complexes octakisoclythiophthalocyaninato metal(II) (1a-d) could be prepared by the same oil bath method reported in our previous work10). Therefore, the representative copper complex (1c) is described in detail and the characterization data for the other complexes (1a, 1b and 1d) only are described here.

Octakisoclythiophthalocyaninato copper(II) (1c)10,11)

A mixture of 4,5-bisoclythiophthalonitrile (0.250 g,
0.60 mmol), DBU (0.120 g, 0.77 mmol) and copper salt (0.17 mmol, Table 2) in 1-hexanol (2.5 mL) was refluxed for 24 h. The reaction mixture was cooled and methanol was added. The resulting precipitate was separated by filtration, then washed with methanol and AcOEt. The residue was purified by column chromatography (silica gel, CHCl3, Rf = 1.00) and then solid-liquid extraction with AcOEt to afford the pure compound as dark green crystals.

**Yield:** see Table 3.

**IR (KBr, cm⁻¹):** 2921, 2851 (−CH₂), 1593 (Aryl), 748 (S−CH₂).

**MALDI-TOFF Mass spectrum, found (calculated):**

UV-Vis spectrum in CHCl₃: nm (log ε): 709 (5.31), 675 (4.66), 636 (4.65), 340 (4.90), 320 (4.91). **Octakisoctylthiophthalocyaninato nickel(II) (1a)**  

**Yield:** see Table 3.

**IR (KBr, cm⁻¹):** 2925, 2854 (−CH₂), 1598 (Aryl), 749 (S−CH₂).

**MALDI-TOFF Mass spectrum, found (calculated):** 1722.899 (1722.863).  

UV-Vis spectrum in CHCl₃: nm (log ε): 701 (5.07), ca. 670(shoulder), 633(4.54), 437(4.12), 328(5.02). **Octakisoctylthiophthalocyaninato cobalt(II) (1b)**  

**Yield:** see Table 3.

**IR (KBr, cm⁻¹):** 2924, 2853 (−CH₂), 1593 (Aryl), 748 (S−CH₂).

**MALDI-TOFF Mass spectrum, found (calculated):** 1723.899 (1723.861).  

UV-Vis spectrum in CHCl₃: nm (log ε): 701(5.07), ca. 670(shoulder), 633(4.54), 437(4.12), 328(5.02). **Octakisoctylthiophthalocyaninato zinc(II) (1c)**  

**Yield:** see Table 3.

**IR (KBr, cm⁻¹):** 2924, 2853 (−CH₂), 1594 (Aryl), 741 (S−CH₂).

**MALDI-TOFF Mass spectrum, found (calculated):** 1728.919 (1728.857).  

UV-Vis spectrum in CHCl₃: nm (log ε): 709 (5.48), 679 (4.69), 637 (4.71), 441 (4.39), 364 (4.95), 330 (4.80).

**4.1.2. Microwave Method**

**Octakisoctylthiophthalocyaninato metal(II) (1a-d)**

A mixture of 4.5-bisocetylthiophthalonitrile (2: 0.050 g, 0.12 mmol), metal salt (0.12 mmol, Table 1), DBU (5 drops) and glycerin (2.00 mL) was poured into a 35 mL of quartz test tube. The air in the test tube was replaced by N₂ gas stream for 10 min. It was heated by microwave irradiation and kept at a certain temperature for a certain time (see Scheme 1 and Figs. 4-7). After cooling to r.t., it was extracted with chloroform, washed with water. Then, the organic layer was dried over Na₂SO₄, filtered and evaporated. The crude product was purified by column chromatography (silica gel, CHCl₃) to afford the pure compound as dark green solid.

**Yield:** see Figs. 4-7.

**4.2. Measurements**

All products synthesized here were identified by FT-IR spectroscopy (Nicolet NEXUS 670). The phthalocyanine derivatives 1a-d prepared here were confirmed by electronic absorption spectroscopy (Hitachi U-4100 spectrophotometer) and MALDI-TOF mass spectroscopy (Bruker Daltonics Autoflex III-2S). The melting points of these compounds were measured using a polarizing microscope (Olympus BH2), equipped with a heating plate controlled by a thermoregulator (Mettler FP80HT hot stage, Mettler FP90 Central Processor).

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要 旨

フタロシアニン金属錯体のマイクロ波加熱合成
一収率とマイクロ波照射による最高到達温度との関係一

安部 寛太，片野 聡，太田 和親

信州大学大学院総合工学系研究科スマート材料工学講座, 386-8567 長野県上田市常田 3-15-1

多官能性フタロシアニン金属錯体は、導電性、エレクトロクロミズムおよび液晶形成などの多くの用途に非常に有用であるため、近年、フタロシアニン誘導体の合成が非常に興味を引いている。以前我々は、フタロシアニン銅錯体のマイクロ波加熱による合成において、テンプレート効果が観察されてなかったことに気づいた。これは、添加金属塩の誘電損失係数に起因すると考えた。しかし、希薄溶液中の金属塩の誘電損失係数を直接測定することは非常に困難である。基礎的なマイクロ波理論によると、マイクロ波照射により得られる熱量は誘電損失係数に比例するため、マイクロ波照射により到達した金属塩を含む溶液の最高温度は誘電損失係数の間接的な指標となり得ると考えられる。そこで本研究では、12種類の金属塩 (MCl₂, MSO₄, M(OAc)₂: M = Co, Ni, Cu, Zn) をそれぞれ含むグリセリン溶液にマイクロ波を照射し、マイクロ波照射によって到達した溶液の最高温度を各金属塩について測定した。次に、これらの12種類の金属塩を用いて、マイクロ波加熱により対応するフタロシアニン金属錯体 (C₈S)₈PcM (M = Co, Ni, Cu, Zn) を合成した。その結果、大変興味深いことに、マイクロ波加熱による (C₈S)₈PcM の合成は、最高到達温度を与えた金属塩（反応種）の順番に、(C₈S)₈PcM の最高収率も与えることを見出した。これは、今後、マイクロ波加熱を用いた有機金属錯体の合成において重要な指針となるだろう。