

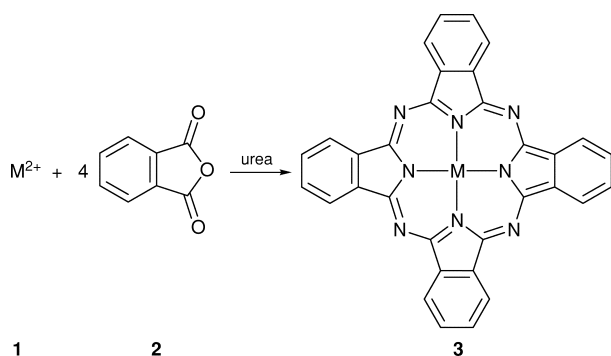
# Synthesis of Metallophthalocyanines under Solvent-free Conditions using Microwave Irradiation†

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The phthalocyanine complexes of Cu, Co, Ni, and Fe are easily prepared upon exposure to microwave radiation under solvent-free conditions and reaction times are considerably reduced.

Phthalocyanines are of interest not only as model compounds for the biologically important porphyrins but also because the intensely colored metal complexes are of commercial importance as dyes and pigments.<sup>1</sup> Preparation of metallophthalocyanines from the reaction between metal salts, particularly CuCl, phthalic anhydride and urea is carried out on a large scale industrially, the copper derivatives being an important blue pigment.<sup>2</sup> Typically, temperatures around 200 °C and reaction times of hours are needed.<sup>3</sup> The reaction is sometimes described as follows:



It is not clear what the reducing reagent is in this process.<sup>4</sup> Such syntheses because of long reaction times and high temperature are often of low yield and giving mixtures of products from which the pure phthalocyanines may be difficult to obtain.

Microwave (MW) irradiation using commercial domestic ovens has recently been used to accelerate organic reactions, the efficient heating giving rise to remarkable rate enhancements.<sup>5,6</sup> Nevertheless, these procedures are seriously limited because of the use of solvents in microwave ovens which gives rise to elevated temperatures and consequently high pressures, thus leading in some cases to dangerous explosions.

Here I describe a facile preparation of phthalocyanine complexes of Cu, Co, Ni and Fe in the absence of any solvent ("dry media" conditions) which reduces consider-

ably reaction times in a process that is accelerated by microwave irradiation. The experimental procedure involves a simple mixing and grinding of reactants and irradiating the reaction mixture in a microwave oven for about 4 to 7 min in the absence of any solvent. The reaction occurred instantly as the melting of the mixture started after about 3 min. The microwave oven was a domestic (Maximum 900 W) National model NN-6653 with five select power levels (two of which were used for this experiment; high 100% wattage, medium 70% wattage). This extremely rapid, manipulatively simple, and inexpensive protocol avoids the use of excess and toxic solvents. The results for various metallophthalocyanines are summarized in Table 1.

In conclusion, I have developed a convenient and rapid procedure for the synthesis of metallophthalocyanines using domestic microwave ovens for a few minutes under solvent-free conditions including "dry" media. Investigations toward extension of this procedure to other metals are in progress.

## Experimental

Elemental analyses were performed using a Heraeus CHN-O rapid analyser. IR spectra were measured on a Shimadzu IR-470 spectrometer. All starting solids used were anhydrous. The IR spectra of these compounds were in excellent agreement with those reported.<sup>10</sup>

The preparation of copper phthalocyanines is representative of the general procedure employed. Phthalic anhydride (26.50 g, 0.18 mol), urea 955.40 g, 0.92 mol), copper chloride (5.00 g, 0.05 mol), and ammonium molybdate (0.75 g, 3.80 mmol) were ground together until homogeneous, placed in a beaker and irradiated in a microwave oven at high power for 6 min. Upon completion of the reaction the product was ground and washed with 5% caustic soda, water, 2% hydrochloric acid and again with water respectively. The dried phthalocyanine thus obtained weighed 23.3 g, 91% of the theoretical amount based on phthalic anhydride. [Cu(pc)] was subsequently recrystallized two times from concentrated H<sub>2</sub>SO<sub>4</sub>. Usually during recrystallization the solution of phthalocyanine in concentrated H<sub>2</sub>SO<sub>4</sub> was poured into distilled water.<sup>11</sup> After complete recrystallization the [Cu(pc)] obtained was purified by Soxhlet extraction using in succession methanol and methylene chloride, yield 86%. After two vacuum sublimations (Found: C, 66.69; H, 2.52; Cu, 11.00; N, 19.18. Calc. for C<sub>32</sub>H<sub>16</sub>CuN<sub>8</sub>: C, 66.74; H, 2.78; Cu, 11.03; N, 19.45%).  $\tilde{\nu}_{\max}$

**Table 1** Synthesis of metallophthalocyanines, M(pc), using MW

Entry	Product	Time/min		Yield (%) <sup>a</sup>		T/°C	Ref
		Found	Reported	Found	Reported		
<b>3a</b>	[Cu(pc)] from CuCl	6 <sup>b</sup>	480	91 (86) <sup>c</sup>	91.8	190–195	7,8
<b>3b</b>	[Co(pc)] from CoCl <sub>2</sub>	5 <sup>b</sup>	480	86 (81)	90	180–190	7,9
<b>3c</b>	[Ni(pc)] from NiCl <sub>2</sub>	4.5 <sup>b</sup>	360	90 (86)	86.5	178	8
<b>3d</b>	[Fe(pc)] from FeCl <sub>2</sub>	7 <sup>d</sup>	660	89 (85)	95	180–190	7,9

<sup>a</sup>Based on the phthalic anhydride. <sup>b</sup>At high power (100% wattage). <sup>c</sup>After Soxhlet extraction. <sup>d</sup>At medium power (70% wattage).

†This is a **Short Paper** as defined in the Instructions for Authors, Section 5.0 [see *J. Chem. Research (S)*, 1998, Issue 1]; there is therefore no corresponding material in *J. Chem. Research (M)*.

(KBr)/cm<sup>-1</sup> 728 vs, 754 s, 779 m, 874 w, 894 m, 1048 m, 1081 s, 1114 s, 1157 m, 1277 m, 1324 s, 1409 m, 1452 w, 1495 m, 1602 w, 3025 vw.

[Co(pc)] (Found: C, 67.30; H, 2.69; Co, 10.08; N, 19.47. Calc. for  $C_{32}H_{16}CoN_8$ ; C, 67.28; H, 2.80; Co, 10.32; N, 19.61%):  $\tilde{\nu}_{\max}$  (KBr)/ $cm^{-1}$  733 vs, 756 s, 780 m, 870 m, 910 m, 1056 m, 1089 vs, 1118 vs, 1157 m, 1283 s, 1327 s, 1419 m, 1458 w, 1515 s, 1598 w, 3040 vw.

[Ni(pc)] (Found: C, 67.23; H, 2.71; N, 19.55; Ni, 10.20. Calc. for  $C_{32}H_{16}Ni_8$ ; C, 67.30; H, 2.80; N, 19.61; Ni, 10.27%):  $\tilde{\nu}_{\max}$  (KBr)/ $cm^{-1}$  727 vs, 752 s, 771 m, 861 w, 907 m, 1055 (sh), 1084 s, 1114 s, 1157 m, 1277 m, 1320 s, 1415 m, 1457w, 1517 m, 1596 w, 3025 vw.

[Fe(pc)] (Found: C, 67.59; H, 2.78; Fe, 9.76; N, 19.57. Calc. for  $C_{32}H_{16}FeN_8$ ; C, 67.64; H, 2.82; Fe, 9.83; N, 19.71%):  $\tilde{\nu}_{\max}$  (KBr)/ $cm^{-1}$  734 vs, 756 s, 780 m, 871 w, 904 m, 1076 s, 1117 s, 1156 m, 1279 m, 1327 s, 1411 m, 1456w, 1501 m, 1598 w, 3035 vw.

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