

## Research Article

# Synthesis and Dimerization Behavior of Five Metallophthalocyanines in Different Solvents

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Metallophthalocyanine (MPc) has become one of the metal organic compounds with the largest production and the most widely application, because of its excellent performance in catalytic oxidation. However, aggregation of the MPc in solution, resulting in decreased solubility, greatly limits the performance of application. Studying the behavior of dimerization of MPcs can provide a theoretical basis for solving the problem of the low solubility. So five metallophthalocyanines (FePc, CoPc, NiPc, CuPc, and ZnPc) were prepared with improved method and characterized. Dimerization of the five MPcs was measured by UV-Vis spectroscopy separately in *N,N*-dimethyl formamide (DMF) and dimethylsulfoxide (DMSO). The red-shift of maximum absorption wavelength and deviations from Lambert-Beer law with increasing the concentration were observed for all the five MPcs. The dimerization equilibrium constants (*K*) of the five MPcs in DMF were arranged in order of CoPc > ZnPc > CuPc > FePc > NiPc, while in DMSO they were arranged in order of ZnPc > CoPc > FePc > CuPc > NiPc. The type of the central metal and nature of the solvent affect the dimerization of the MPcs.

## 1. Introduction

As multifunctional materials, metallophthalocyanine (MPc) compounds are widely used not only in industrial printing, optical information recording materials [1, 2], nonlinear optical materials [3], fuel cell electrocatalytic materials, conductive polymers, and other fields [4–6], but also in the field of catalysis, particularly in the application of light oil deodorizing in petroleum refining industry [7]. Because thiol is malodorous, the standard requires that the content of thiol in gasoline [8] is less than  $10 \mu\text{g}\cdot\text{g}^{-1}$ . In the oil refining industry, the MPc is the best catalyst for catalytic oxidation of thiols to disulfide, so MPc had been widely used in gasoline, liquefied petroleum gas, and other light oil sweetening, to achieve the purpose of light oil deodorization in almost all refineries.

However, MPc compounds tend to be polymerization of dimers or multimers in solvents [9, 10], and this polymerization is generally a process of dimerization or multimeric complexes from monomer [11]. Polymerization enhanced van der Waals attraction between the phthalocyanine, combined acting together with the disturbance of electronic structure of

the phthalocyanine and made changes between the ground state and the excited state, which has a significant influence on the optical properties, catalyst activity, and stability of MPc [12]. It is generally believed that the gathering force between phthalocyanine molecules includes the role of intermolecular  $\pi$ - $\pi$ , van der Waals forces, and hydrogen bonding, which is relevant to the structural properties of phthalocyanine complexes. For further research on the dimerization properties of the MPcs in different solvents, five MPcs were synthesized with improved method, and the dimeric equilibrium constants were determined to compare and understand how the structure of MPc affects their stability in solvent.

## 2. Materials and Methods

**2.1. Materials and Synthesis.** All reagents were used as supplied by State Chemicals Corp. of analytical pure grade without further purification. MPcs were prepared by the solid-phase synthesis (synthetic route in Figure 1) based on literatures [13] with the improved procedures. The major improvement in the synthesis was to increase the usage amount of urea, which used not only as the reactant, but also

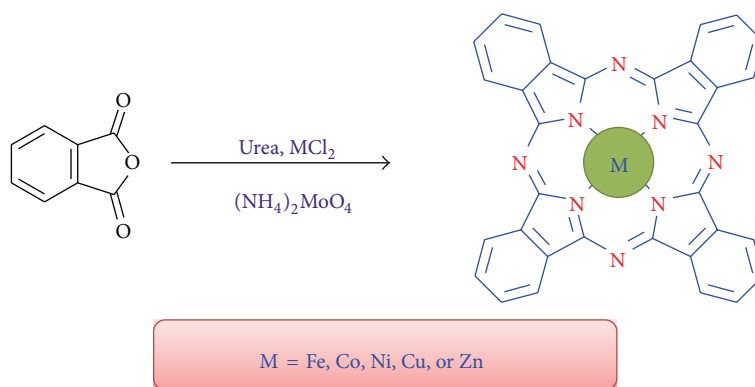


FIGURE 1: The reaction of solid-phase synthesis of MPC.

as reaction solvent after the reactant mixture melted. And we improved the product purification methods by washing the blue product powder in the thimble of a Soxhlet apparatus with alcohol and acetone separately and to optimize the reaction temperature in order to improve the reaction efficiency. A detailed experimental procedure and product characterization were showed in the Supplementary Material available online at <http://dx.doi.org/10.1155/2014/914916>.

**2.2. Physical Measurements.** All the prepared crystalline materials were characterized by powder X-ray diffraction (XRD) and were recorded with an X'Pert Pro MPD diffractometer (Panalytical) employing Cu-K $\alpha$  radiation. The scanning speed was 8° per minute and receiving slits were used in conjunction with a 0.3 mm scatter slit. The scanning range of  $2\theta$  was 5–75°. The morphologies of the five MPC complexes were observed with the Hitachi S-4800 cold field emission scanning electron microscope (SEM). Resolution was 15 kV : 1.0 nm, 1 kV : 2.0 nm; accelerating voltage was 0.5 to 30 kV and magnification was  $30 \times 800000$ ; cold field emission electron gun was used.

**2.3. Dimerization Constant Measurements.** Generally aggregation of MPCs leads to deviation from Lambert-Beer law in the UV-Vis spectroscopy; thus dimerization can be determined by measuring the relations of absorbance and concentration of MPCs [14]. At first five MPCs were accurately weighed and dissolved in DMF (or DMSO), respectively, under ultrasonic oscillation. Using the method of stepwise dilution, solution of MPC in DMF (or DMSO) with the certain concentration was all prepared, respectively. UV-Vis absorption spectrometry was collected on a Hitachi U-3900H UV-V which is spectrophotometer equipped with a temperature controller (Julabo labortechnik GmbH). All of the sample solutions were freshly made and the absorbance was measured on the same day to avoid absorption of the MPCs on the cuvette, and the absorbance was corrected for volume changes of the solutions at various temperatures.

### 3. Results and Discussion

**3.1. XRD Analysis.** By comparison with the standard profile [15], each of the XRD patterns of the MPC in Figure 2

is consistent with the standard pattern. In addition, the baseline is uneven and irregular in the patterns of CoPc and FePc, which is different from others. This is because the X-ray diffractometer using a copper target, diffracted wave can interfere with the detection of the cobalt, iron, and manganese metal and lead to the irregular patterns.

**3.2. SEM Analysis.** The CoPc showed irregular morphology of crystal packing, and NiPc showed crooked rod with different diameters in Figure 3. CuPc appeared irregularly shaped cauliflower. A rod of FePc can be observed with varying lengths and thicknesses and mixed with some crystal grain accumulation [16]. The morphology of ZnPc was strip with different width, and there were crystal grains deposited on the surface of the strip.

**3.3. Dimerization Constant of Metallophthalocyanines in Different Solvents.** As a typical instance, the absorbance versus wavelengths for CoPc is shown in Figures 4 and 5, and the absorbance at maximum absorption wavelength along with the changes of concentration of CoPc is also listed in inset of Figures 4 and 5, respectively. The maximum absorption wavelengths were red-shift with increasing the concentration of CoPc no matter in DMF or in DMSO, which is generally to be considered as caused by dimerization of MPC [17, 18]. Deviations from Lambert-Beer law were all observed for CoPc and the other four MPCs, respectively, in DMF and in DMSO, which further reveals that the aggregation becomes stronger with increasing the concentration of MPC in solvents [19, 20]. The dimerization equilibrium constant  $K$  could be calculated for each MPC according to the literature [18] by plotting the  $\epsilon \sim \epsilon^2 [M]_0$  curves ( $\epsilon$  represents the absorption coefficient and  $[M]_0$  represents the initial concentration of MPC). The  $K$  of other MPCs was calculated using the same method and listed in Table 1. It shows that, under the same experimental conditions, the dimerization equilibrium constants of the five MPCs in DMF were in the order of CoPc > ZnPc > CuPc > FePc > NiPc, while in DMSO the order is ZnPc > CoPc > FePc > CuPc > NiPc. Obviously CoPc and ZnPc had the bigger equilibrium constants for dimerization, followed by CuPc and FePc, and the equilibrium constant of NiPc was the smallest. This means that CoPc and ZnPc

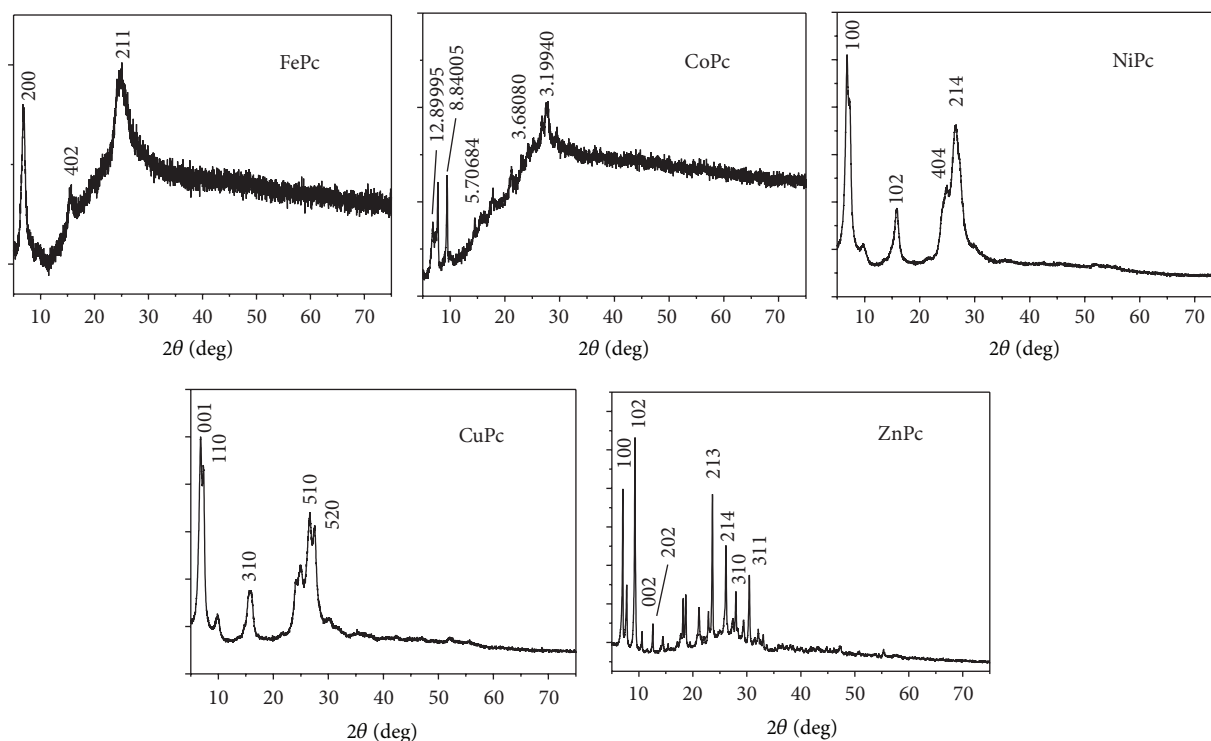


FIGURE 2: XRD patterns of the MPcs.

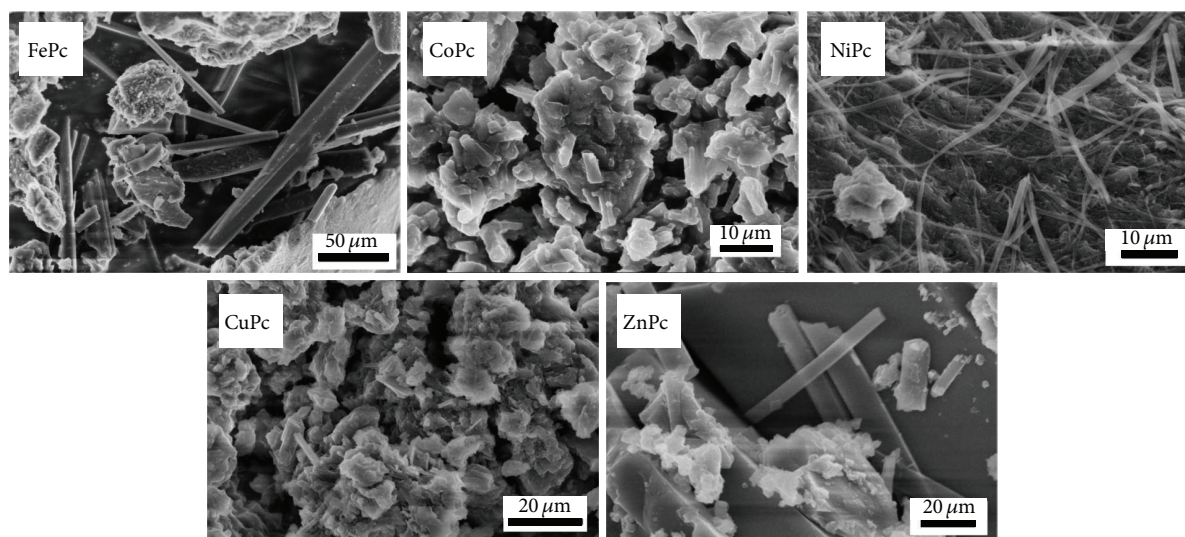


FIGURE 3: The electron micrographs of MPcs.

have the great tendency towards aggregation in polar aprotic solvent. However NiPc was relatively weak for dimerization in the same solvents. The type of the central metal affects the dimerization of the MPc, and the impact is complicated. The central metal atom coordinated with the four nitrogen atoms in phthalocyanine, which result in the decrease of charge density of the inner phthalocyanine. And finally the electron density of the phthalocyanine conjugated system decreased, which could lead to different role of intermolecular  $\pi$ - $\pi$  stacking of MPc in aggregation [21]. On the other hand,

the  $\text{Ni}^{2+}$  has the smallest cationic radius among the five metal ions ( $\text{Fe}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Cu}^{2+}$ , and  $\text{Zn}^{2+}$ ), and the smaller the cationic radius, the stronger the chemical action and the polarization. Thus it can be deduced that NiPc has greater chemical stability and relatively small tendency for dimerization in solvents among the five MPcs, which is in good agreement with the experiment results in Table 1.

It also can be seen from Table 1 that the  $K$  in DMF are greater than that in DMSO for CoPc and ZnPc; however the situation is the reverse for FePc, CuPc, and NiPc. This shows

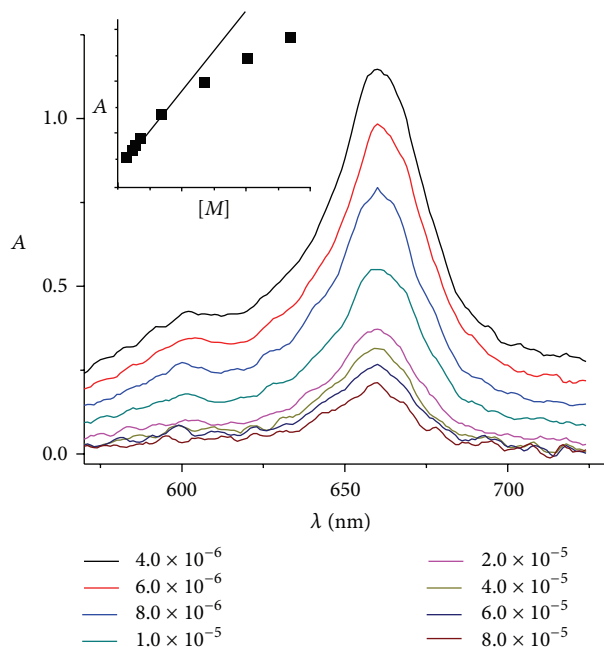


FIGURE 4: UV-Vis spectrum of CoPc in DMF with different concentration (mol/L) (the inset is the relationship between the absorbance at maximum absorption wavelength and the concentration).

TABLE 1: The dimerization equilibrium constant  $K$  of the five MPcs (30°C).

MPcs	$K$ in DMF/mol <sup>-1</sup> ·L	$K$ in DMSO/mol <sup>-1</sup> ·L
CoPc	$4.07 \times 10^5$	$5.54 \times 10^3$
ZnPc	$7.59 \times 10^3$	$7.09 \times 10^3$
CuPc	$2.63 \times 10^3$	$2.70 \times 10^3$
FePc	$6.54 \times 10^2$	$3.36 \times 10^3$
NiPc	$1.30 \times 10^2$	$2.59 \times 10^2$

that the effects of solvent on the  $K$  are different for different MPcs. It was reported that, in polar protic solvent [22, 23], such as in H<sub>2</sub>O, CH<sub>3</sub>OH, the aggregation tendency of MPcs becomes stronger with increasing the polarity of solvents. This may have relations with the enhancement to aggregation by hydrogen bonding formation by the active hydrogen atom in polar protic solvents. Polar aprotic solvents, such as DMSO and DMF used in this research, have no active hydrogen atoms to form hydrogen bonding with phthalocyanine. Thus the relations of aggregation of MPcs with the polarity of aprotic solvents are not obvious.

#### 4. Conclusion

Five MPcs (FePc, CoPc, NiPc, CuPc, and ZnPc) were prepared with improved method at yields of over 75%. The maximum absorption wavelengths were found to be red-shift and deviations from Lambert-Beer law were observed with increasing the concentration for all the five MPcs, respectively, in DMF and in DMSO. The dimerization equilibrium constants of the five MPcs in DMF were in the order of CoPc > ZnPc > CuPc >

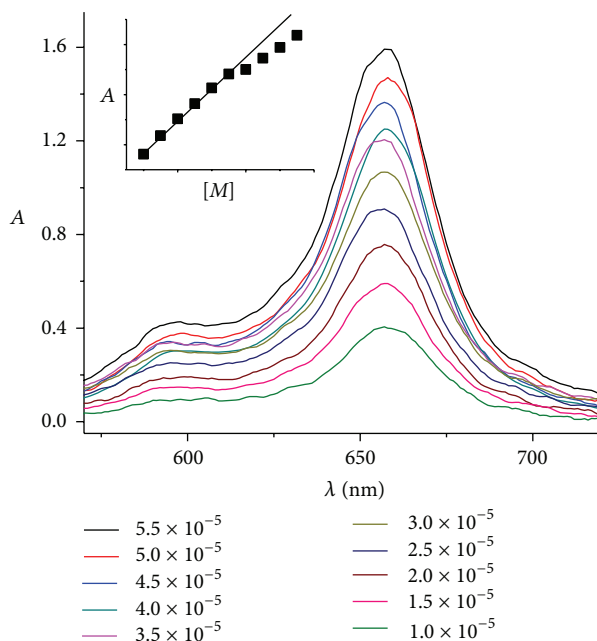


FIGURE 5: UV-Vis spectrum of CoPc in DMSO with different concentration (mol/L) (the inset is the relationship between the absorbance at maximum absorption wavelength and the concentration).

FePc > NiPc, while in DMSO the order is ZnPc > CoPc > FePc > CuPc > NiPc. The type of the central metal and nature of the solvent affect the dimerization of the MPcs and the relations of aggregation of MPcs with the polarity of aprotic solvents are not obvious.

#### Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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