

## Synthesis and hypochromic effect of phthalocyanines and metal phthalocyanines

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### Abstract

Several series of phthalocyanines (Pcs) and metallophthalocyanines (MPcs) were prepared and characterized by MS, <sup>1</sup>H NMR, UV–vis and elemental analysis, which were consistent with the proposed structures. These Pcs and their metal complexes are synthesized using 3-(2-isopropyl-5-methylphenoxy)phthalonitrile or 4-(2-isopropyl-5-methylphenoxy)phthalonitrile as the starting material in the presence of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) as the catalyst. An original UV–vis absorption investigation of these compounds is performed. Obvious hypochromic effect of Q-bands was found with the increment of temperature from 293 K to 333 K. B-bands did not show the analogous tendency. The hypochromic effect originates from conversion of Pc framework as a result of thermal vibration, which reduces the localization of  $\pi$ -electron system.

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### 1. Introduction

Phthalocyanines (Pcs) are macrocyclic complexes whose  $\pi$  systems, localized over an arrangement of alternated carbon and nitrogen atoms, provide their unique chemical and physical properties [1,2], rendering these complexes applicable in different areas, especially in materials science. Due to the significance of  $\pi$  system of Pcs, studying the nature of  $\pi$  system and attempting to modulate  $\pi$  system have been extensively and intensively investigated. Typical examples are the preparation of subphthalocyanines (subPcs) [3] and super-phthalocyanines [4], both of which enrich the number of Pc family

and provide the theoretical and applied foreground for Pcs. Mainly owing to the  $\pi$  system, Pcs and metallated Pcs display excellent thermal stability. However, they were found to undergo photooxidative cleavage, particularly in the solution phase, leading to phthalimide derivatives [5].

Pcs' metal complexes generated by the replacement of the hydrogen atoms in central cavity are usually called metallophthalocyanines (MPcs). Central metals play a critical role in tuning the properties of MPcs [6]. What is more, coordination of the Pc ligand with metal and some metalloid will result in the alteration of molecular conformation. In general, since the structural arrangement of metallophthalocyanines (MPcs) is determined by the size and location of the metal center with respect to the mean plane of the aromatic Pc ligand, several conformations are known [7]. Those have been named according to their molecular shape. The most common conformations are planar, ruffled, waved, domed, and skew domed [7]. For

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instance, Pcs metallated with Pb or Sn show the domed conformation [7,8]. The essentially planar conformation of Pcs can also be distorted by substituents alone through conformational stress [9]. In remarkable contrast with the intensive studies of the effect of macrocycle distortion of porphyrins on physicochemical properties, e.g. redox potential and light absorbance [10], few reports [9,11] have mentioned the connections of Pc ring contortion with the properties. In fact, the effect of macrocycle distortion on the properties can be attributed to the alteration in planarity of  $\pi$ -electron system.

Hyperchromic effect or hypochromic effect of Pcs usually accompany the changes in  $\lambda_{\max}$  and  $\epsilon$  values (or absorbance) of Q-band and B-band. Generally, these two effects can be attributed to the alteration in  $\pi$ -electron systems. According to the previous reports [12], formation of dimers, coordination to the central metal with certain ligands and enlargement of  $\pi$  system are the three factors giving rise to hyperchromicity or hypochromicity. In our synthetic laboratory at Dalian University of Technology, we found a hypochromic effect induced by temperature without precedent in the published literatures, which was related to the distortion of  $\pi$ -electron system. In this paper, we describe the synthesis and characterization of series of Pcs and MPcs ( $M = \text{Cu}$ ,  $\text{Zn}$ ,  $\text{TiO}$  and  $\text{InCl}$ ) (Fig. 1). By using these compounds, we study the hypochromic effect related to temperature.

## 2. Experimental

### 2.1. Materials and instruments

The chloronaphthalene was purchased from J&K Chemical Ltd., which is a mixture of  $\alpha$ -chloronaphthalene (90%) and  $\beta$ -chloronaphthalene (10%). Chloronaphthalene was predried by stirring with  $\text{CaCl}_2$  and then distilled from  $\text{P}_2\text{O}_5$  prior to use. CuPc was purchased from the market. All other chemicals used were of reagent grade. All other solvents were dried and purified as described by Perrin and Armarego [13].

Syntheses of **1–3b**, **1–3c**, **1d**, and **1e** were carried out according to the relevant literatures [6b,14,15].

High-resolution  $^1\text{H}$  NMR spectra were recorded on a Bruker AV 500 spectrometer unless otherwise stated. UV–vis spectra were taken on a UV-3100 UV–vis–NIR Recording Spectrophotometer (SHIMADZU, Japan). MS spectra were obtained on an LDI-1700-TOF mass spectrometer (Linear Scientific Inc., USA) or a Kratos MALDI-TOF mass spectrometer (SHIMADZU, Japan). Elemental analyses were performed on a Flash EA1112 Elemental Analyzer (ThermoQuest, Italy).

### 2.2. UV–vis absorption operation

UV–vis spectra were performed on a UV-3100 Spectrophotometer equipped with a low-constant-temperature bath using water as the heating and cooling media. Cycled water can pass the colorimetric stand through the insulating hoses to make the sample solution in quartz flow-cell (10 mm path length) maintain the same temperature as water. Although water temperature is indicated by an electronic meter furnished in this spectrophotometer, a thermometer is still put into water to show correct water temperature. Before measurements, the solutions were saturated for 10 min with dry nitrogen (oxygen-free), which was carried out directly in the quartz flow-cell. The quartz flow-cell was sealed tightly with a quartz cover to prevent volatility of chloronaphthalene causing the increment of sample concentration. Shortly after sometime water was poured into the constant-temperature bath, it was cooled to 293 K by a cooling pump and beginning at this temperature we obtained the UV–vis absorption data for each sample. The highest temperature up to which water in constant-temperature bath can be heated is 333 K, therefore, we cannot get UV–vis absorptions measured at accurate temperatures higher than 333 K. The sample solution in quartz flow-cell can be cooled to 273 K and 283 K, but at those temperatures small water droplet appeared on the surface of flow-cell. Hence, we chose to carry out UV–vis measurements between 293 K and 333 K.

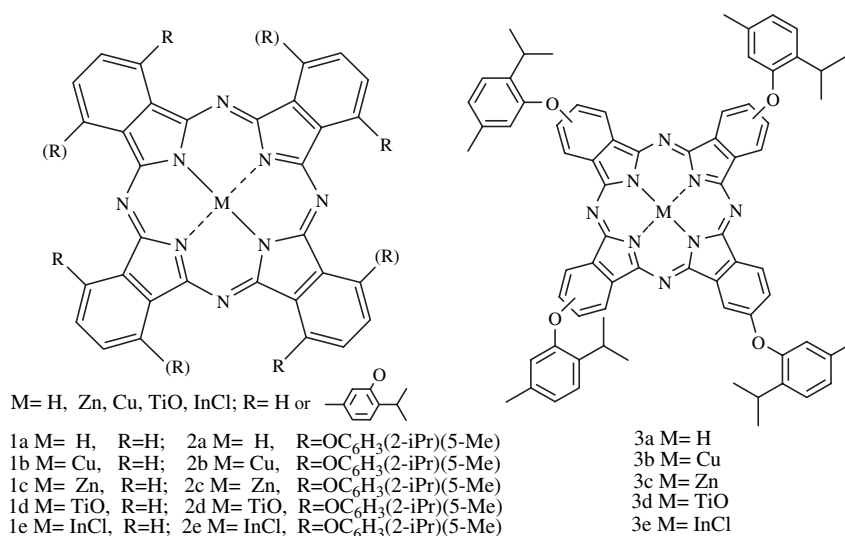


Fig. 1. Structures of **1a–e**, **2a–e** and **3a–e**.

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