

Raman spectra study of *p*-tert-butylphenoxy-substituted phthalocyanines with different central metal and substitution positions



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ABSTRACT

Metallophthalocyanine (MPc) derivatives show excellent photoelectric and magnetic properties due to their large π -conjugate system. Central metals and peripheral substituents are two important ways to adjust and optimize the properties of MPc via tuning the large π -conjugate system. In this work, Raman scattering spectra of MPc, including ZnPc, CuPc, CoPc, and NiPc, were investigated. The most intense band in the Raman spectra at about 1500 cm^{-1} , owing to the vibration of C–N–C bridge bonds, shifts significantly with the size of the metal ion, indicating a good marker of metal ion effect on the changes of the Raman shift. For the MPc with suitable sizes of metal ions (e.g., Zn^{2+} , Cu^{2+} , Co^{2+} , Ni^{2+}), the structure of phthalocyanine ring is planar. The ring will be distorted according to the different forces of the central metal ions. When the polarization force of the central metal ion enhances ($\text{Zn}^{2+} < \text{Cu}^{2+} < \text{Co}^{2+} < \text{Ni}^{2+}$), the Raman shift of C–N–C would simultaneously increase, and the bigger polarization force could lead to a larger Raman shift ($\text{ZnPc} < \text{CuPc} < \text{CoPc} < \text{NiPc}$). On the other hand, the C–N–C Raman shift of the 3-substituted MPc was relatively smaller than that of the 4-substituted one with the same central metal ion. When the electron density of the phthalocyanine ring was relatively low, the energy of the system would increase and the Raman peak would correspondingly shift distinctly. Our Raman spectra results are consistent with the UV–vis measurement results. This work will provide the basis for structure analysis, and design of new molecular materials, as well as their application.

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1. Introduction

Metallophthalocyanine (MPc) derivatives have attracted an increasing interest not only for their strong coloring as dyes and pigments but also due to their extraordinary optical, electronic, thermal and magnetic properties based on the large two-dimensional 18π -conjugate system [1–3]. As reported, central metals and peripheral substituents are two important ways to modulate the large π -conjugate system, so as to adjust and optimize the corresponding properties of MPc [4]. Recently, the synthesis and characterization of novel MPc complexes, as new molecular materials for different applications, have been extensively and intensively studied [5–8].

Up to present, many metallophthalocyanine (MPc) with different central metal atoms have been extensively studied by

different optical methods, such as absorption ellipsometry, Nuclear magnetic resonance (NMR), FTIR absorption, Raman spectroscopy, X-ray diffraction [9–18]. UV–vis spectra [19–24] are typically used to characterize the synthesis quality of new compounds. Raman spectra for the MPc have been investigated through experimental measurements and theoretical analysis [25–32]. However, there are few reports about the effect of different metals and different peripheral substitution positions on the Raman spectra of MPc.

Identifying and understanding the vibration frequency shifts caused by electron addition to MPc molecules with various substituents positions is the main goal of the present work. Herein, phthalocyanine complexes containing 3- or 4-*p*-tert-butylphenoxy-substituted ZnPc, CuPc, CoPc, and NiPc were synthesized; meanwhile, their UV–Vis spectra and Raman spectra were investigated. According to their UV–Vis and Raman spectra, the changes of Raman shift were analyzed with different central metals and different substituting positions [33]. The characteristic displacement bonds of C–N–C bridge at about 1500 cm^{-1} for 3- and 4-substituted MPc showed the same order

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(ZnPc < CuPc < CoPc < NiPc) with the varying central metal ion, and the 3-substituted MPC was relatively smaller than that of the 4-substituted one with the same central metal ion. This work might be beneficial to design and construct new molecular materials as well as their application.

2. Experimental

2.1. Materials and methods

1-Pentanol (Sigma-Aldrich) was predried by Na before use; dimethyl sulfoxide (analytical purity, Aladdin Industrial Corporation) was predried by BaO. All other reagents and solvents are commercially bought and without further purification, such as 3-nitrophthalonitrile and 4-nitrophthalonitrile (Analytical purity, Meryer Co., Ltd.); *p*-tert-butylphenol (Alfa Chemistry); copper acetate ($\text{Cu}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$), nickel chloride ($\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$), cobalt chloride ($\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$), zincacetate ($\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$) (Analytical purity, Beijing Chemical Works).

2.2. Synthesis of 3- or 4-substituted metal phthalocyanine

The phthalocyanine precursors, 3- and 4-*p*-tert-butylphenoxy substituted phthalonitrile, were synthesized according to the methods in literatures [19,34]. In brief, based on the electrophilic substitution reaction, the nitro groups of 3-nitro or 4-nitro phthalonitrile were substituted by the *p*-tert-butylphenoxy of *p*-tert-butylphenol under the existence of LiOH in anhydrous DMSO at 25 °C, then the 3- or 4-substituted phthalonitrile were prepared for further synthesis of MPC, as described in Fig. 1. According to the

metal template synthesis method, 3- or 4-substituted phthalonitrile, as the starting material, was refluxed in 1-pentanol at 140 °C to cyclize into 3- or 4-*p*-tert-butylphenoxy-substituted ZnPc, CuPc, CoPc and NiPc (3- or 4-ZnPc, CuPc, CoPc, NiPc) with metal salt ($\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$, $\text{Cu}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$, $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$, $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$) and DBU as catalyst under N_2 for 12 h. Then the solids were collected by methanol and purified by column chromatography.

All the prepared samples are characterized by mass spectra, UV-vis spectra, and Raman spectra. The molecular ion peaks of the mass spectra data are consistent with the theoretical calculated results, and no other impurity molecular ion peaks in the mass spectra, which indicate that we have synthesized the MPC successfully with high purity. The following sections will discuss the UV-vis spectra and Raman spectra of the prepared MPC with characteristic peak in detail. These results indicated that the corresponding substituted MPC were prepared successfully.

In this work, the tetrasubstituted phthalocyanines prepared by cyclotramerization of monosubstituted phthalonitriles have four constructional isomers ($D_{2h}:C_s:C_{2v}:C_{4h} = 1:4:2:1$) [19]. These isomers could not be successfully separated by column chromatography, and the conclusions of this paper are statistical results of four isomers and do not focus on a pure isomer, thus we used the mixture of four constructional isomers for the following study.

2.3. UV-vis and Raman spectra acquisition

UV-Vis and Raman spectra acquisition tometer (Lamda950) was used to collect spectra of the as-synthesized MPC with different central metals and different substitution positions, in which the spectral range was from 250 nm to 800 nm, and the used solvent was CHCl_3 . The Raman spectra of the synthesized phthalocyanines, which were powder after extraction, with different central metals and different substituted positions were collected by Raman spectrometer (Horiba Jobin Yvon HR800) with a laser wavelength of 532 nm (semiconductor laser) and a spectral acquisition range of 300–1800 cm^{-1} , and the spectral resolution is better than 2 cm^{-1} . The laser beam was tightly focused on the sample surface through a Leica 50X LWD (long working distance) microscope objective.

3. Results and discussion

3.1. UV-Vis spectra of 3- or 4-*p*-tert-butylphenoxy-substituted ZnPc, CuPc, CoPc, and NiPc

Phthalocyanines are very sensitive to the light owing to their large π -conjugate system, which can be confirmed by the UV-Vis spectra [20–22]. Fig. 2 shows the measured UV-Vis absorption spectra of 3- or 4-*p*-tert-butylphenoxy-substituted MPC, including ZnPc, CuPc, CoPc, and NiPc. The absorption bands of all 3- or 4-substituted MPC are similar, with two strong absorption bands at about 340 nm and 600–700 nm, which are identified as B band (also known as Soret band) and Q band related to the large π conjugated structure [20,33].

To be more specific, the strong absorption band around 700 nm was mainly due to the π - π^* double degenerate transition from a_{1u} to e_g . When the concentration was high, there was a weak shoulder or a small peak before the Q band, which was attributed to the absorption of the dimer of phthalocyanine [19]. The absorption of its monomer was much stronger than that of its dimer, indicating that the large steric hindrance, generated from the substituent group, in the phthalocyanine molecule could effectively prevent the aggregation of phthalocyanine in the solution. The broad B band (or Soret band) was due to the π - π^* jump of electrons from the much lower energy occupying orbit to the Lowest Unoccupied Molecular Orbital (LUMO) e_g . For the same substituent position (3- or 4-*p*-tert-butylphenoxy-substituted) with different metal ions,

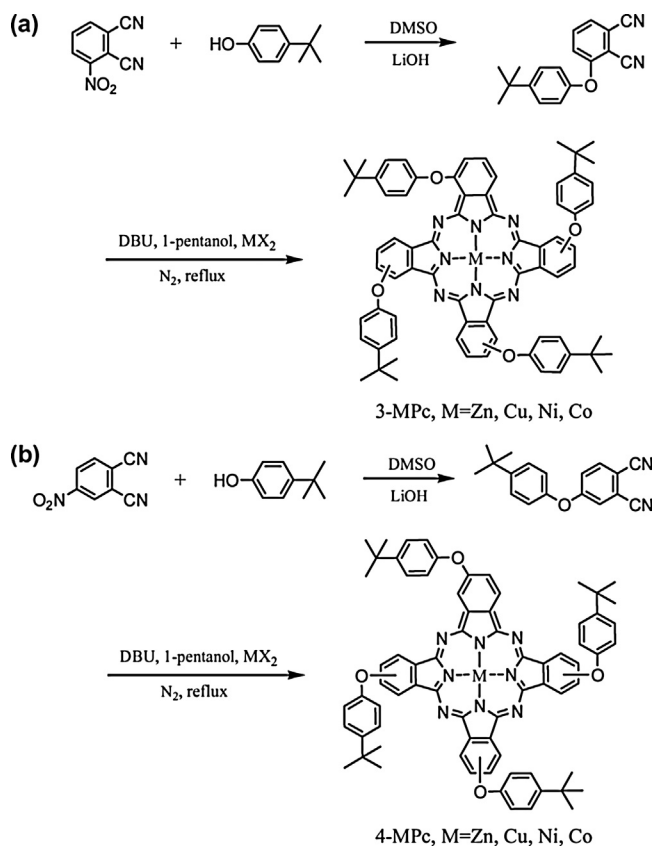


Fig. 1. Synthesis route of 3- or 4-substituted metal phthalocyanines and their precursors according to the literature [18]. (a) 3-*p*-tert-butylphenoxy-substituted metal phthalocyanines (3-MPC, M = Zn, Cu, Ni, Co). (b) 4-*p*-tert-butylphenoxy-substituted metal phthalocyanines (4-MPC, M = Zn, Cu, Ni, Co).

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