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The control of phthalocyanine properties through nitro-group electronic effect

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Abstract

The UV–vis spectra of peripherally substituted tetranitrometallophthalocyanines (TNMPcs) **1a**–**1d** and non-peripherally substituted TNMPcs **2a**–**2d** were investigated. In comparison of **1a** with **2a**, there is the only difference in the substitution position of nitro-groups. The structural diversity of **1a** and **2a** resulted in different electronic effects of nitro-group on Pc rings, which caused them have two kinds of Q bands. The Q band in the UV–vis spectra of **1a**–**1d** was split into two peaks, which were obviously influenced by temperature, while no split was observed in the Q band of **2a**–**2d**. We can draw a conclusion that tuning nitro-group electronic effect is an important approach for controlling the properties of Pcs.

Keywords: Control; Phthalocyanine; Q band split; Inductive effect; Conjugative effect

1. Introduction

Pc derivatives have many applications, such as photodynamic therapeutic agents [1], film materials [2,3] and semiconductor materials [4], etc. Extensively spectral investigations hence have been done for improving their applied potential [5,6]. Symmetry-lowering has great impact on the spectra of Pc and research on symmetry-lowed Pcs has become popular in recent years [7]. There are four series of Pcs that can cause Q band split, namely, symmetric substituted metal free Pcs [8], asymmetric substituted metal Pcs [9], Pcs coordinated by special axial ligand [10] and binuclear Pc [11,12]. Their D_{2h} symmetry is lower than D_{4h} symmetry of normal symmetric metal Pcs [13] and also causes the nondegenerate of their lowest excited singlet (S_1) states, which makes the Q bands in their UV–vis spectra split. In the symmetry-lowering way, the Pc property can be controlled. However, the split span of Q band mentioned in previous literatures [8–12] was not enough to obtain satisfactory results in the control of Pc properties. Hence, we intend to use another approach, namely tuning electronic effect, to gain bigger split span of Q band.

In our previous research work on tetraaminometallophthalocyanines (TAMPcs) [13], both strong inductive effect and strong conjugative effect between the amino groups and the Pc rings of TAMPcs were discussed. We assume that the electron transfer between the substituents and the center M(II) through Pc ring would be influenced greatly with the rotation of substituents if the substituents have strong conjugative effect and are rotational. The nitro-group has strongly not only electron-withdrawing inductive effect, but also electron-withdrawing conjugative effect. Considering the unique 18 π-electron conjugative system of Pc ring, we can say that the electronic effects of nitro-groups in TN-

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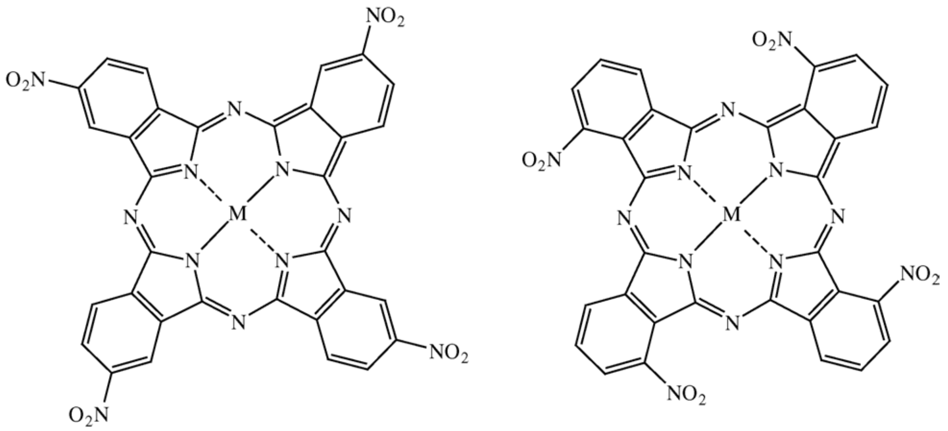
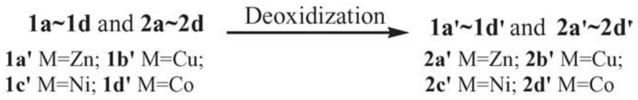


1a M=Zn; **1b** M=Cu;
1c M=Ni; **1d** M=Co

2a M=Zn; **2b** M=Cu;
2c M=Ni; **2d** M=Co

Fig. 1. Peripherally substituted TNMPcs **1a**–**1d** and non-peripherally substituted TNMPcs **2a**–**2d**.



Scheme 1. Deoxidization of TNMPcs **1a**–**1d** and **2a**–**2d**.

MPc on Pc ring will extremely powerful in the comparison with those of other relatively smaller aromatic nitro compounds.

We've done research on the impact of the nitro-group electronic effect, including inductive effect and conjugative effect, on the Q bands of TNMPcs (Fig. 1). The nitro-groups in **1a**–**1d** can make Q band split through their electronic effects, but Q band split phenomenon wasn't found in UV–vis spectra of **2a**–**2d**. The interpretation of these phenomena was given in the present paper.

2. Experimental

According to [13], TNMPcs **1a**–**1d** and **2a**–**2d** were synthesized from 4-nitro-*o*-phenyleneimine and 3-nitro-phthalic anhydride, respectively, and then TNMPcs were deoxidized to obtain TAMPcs **1a**′–**1d**′ and **2a**′–**2d**′ (Scheme 1). Their UV–vis spectra at 0, 20 and 70 °C were recorded on a Cary 500 UV–VIS–NIR spectrophotometer.

3. Results and discussion

3.1. Q band split and analysis on it

As shown in Table 1, there are two obvious peaks in the Q bands of **1a**–**1d** and only one peak in the Q bands of **2a**–**2d**. We take **1a** and **2a** as typical examples to discuss these phenomena. There is the possibility that isomers or dimmers of **1a** would result in the split peaks in Q band. As we all know that if the Q band split of **1a** was caused by isomers or dimmers, Q band would remain split after the reduction of nitro-groups. However, when **1a** was deoxidized to **1a**′ no Q band split was found in UV–vis spectra of **1a**′ (Fig. 2A). What is more, if Q band split of **1a** origined from isomers or dimmers, there should be a Q band split in UV–vis spectra of **2a** although the difference in nitro-group substitution position exits between **1a** and **2a**. The fact is that **2a** do not have a Q band split (Fig. 2B). Furthermore, according to our previous work [13], isomers and dimmers of **1a** were so little that they could be ignored. More importantly, to the best of our knowledge, there are no literatures presently that report the Q band split caused by Pc isomers or dimmers.

In Fig. 2A, we can see that there is two evident split peaks in Q band of **1a** at 648 and 687 nm, respectively. The span (ΔQ = 39 nm) between the two split peaks was wider than the split span (ΔQ = 23 nm) seen before [10]. The split can be interpreted by using Fig. 3.

Table 1
UV–vis spectra parameter of **1a**–**1d** and **2a**–**2d** in DMF (20 °C)

	λ (nm)			
	1a (**2a**)	**1b** (**2b**)	**1c** (**2c**)	**1d** (**2d**)
Q	648, 687 (671)	626.8, 695 (669)	622, 688 (669)	623, 682 (653.36)
ΔQ	39	68.2	66	59