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The spectra and stabilities of alkoxyl-substituted phthalocyaninatometals I. The effect of axial coordination abilities of the center metals on their stabilities in benzoyl peroxide

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Abstract

The stabilities of phthalocyaninatometals are reduced seriously by the substitution of bulky alkoxyl substituents. In the toluene, tetra-α-(2,2,4-trimethyl-3-pentoxy)phthalocyaninatometals can be decomposed by the benzoyl peroxide, and the order of decomposition rate sorted with the center metals is Fe > Co > Cu > Ni > Pd, which showed a consistency with the axial coordination abilities of the center metals.

Keywords: Phthalocyanine; Spectra; Decomposition

1. Introduction

Phthalocyanines (Pcs) have been widely studied for many potential applications because of their excellent optical and electronic properties [1–3] as well as their facile structural adjustabilities [4–6]. The introduction of peripheral substituents is a usual method to optimize their physical and chemical properties. However, it can also weaken their some intrinsic merits, such as chemical, thermal and light stability [7]. To study the stabilities of substituted MPcs in detail, we synthesized a series of substituted phthalocyaninatometals and checked their stabilities in reactions with oxygen, peroxide, and acids.

In a preceding presentation [8], we have reported that the donor substituents could lead to the easy decomposition of phthalocyaninatoiron where the oxygen or peroxide acting at the center metal and the ring. As a reasonable consideration, the nature of center metal will also affect the stabilities of the MPcs. Here we compare the stabilities of bulky alkoxy α-substituted MPcs with different center atoms in the benzoylperoxide (BPO) oxidation.

2. Experimental

2.1. Materials

The title compounds (Scheme 1), tetra-α-(2,2,4-trimethyl-3-pentoxy)phthalocyaninatometals, were synthesized as described in literature [8–10]. All other reagents and solvents were of reagent grade and used without further purification.

2.2. Measurements

The UV/vis spectra were recorded on a PE-Lambda 9 UV/vis spectrophotometer using 1 cm path length cuvettes hermetically at room temperature. The stabilities of phthalocyaninatometals were studied according to the varieties of the Q bands, where the solution of BPO in toluene were added to the solutions of MPc in toluene, then the varieties of their UV/vis spectra were determined.

3. Results and discussion

3.1. The spectra of title compounds in benzoylperoxide oxidation

It is well known that some alkoxy-substituted phthalocyaninatoirons (FePcs) are decomposed easily in the non-coordinated

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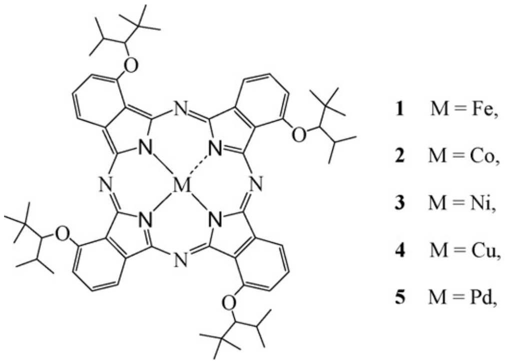

Scheme 1. The structures of the title compounds. The C_{4h} isomer is used to represent the products which may consist of four possible isomers.

solvents [11]. In the previous paper [8], we have investigated the effect of substituents on the stabilities of FePcs in the oxidation atmosphere (oxygen or oxidant BPO) and found that the donor substituents at α position can increase their absorption wavelength and accelerate their decomposition. Considering the relative stabilities in the oxygen for other MPcs, in this paper, we only study their spectra and stabilities in oxidant BPO.

As shown in Fig. 1, all the substituted MPcs are decomposed in toluene/BPO exhibiting the strengths of the Q bands decreased. For compound **1**, a new band at 746 nm was found at the longer wavelength side of Q band, and its intensity increase accompanied the intensity decreasing of Q band. This new band has been assigned to an intermediate that the BPO are bridged at the center atom and *meso* N atom of compound **1** (**1a** in Scheme 2) [8]. For other compounds, there was not any new band at the longer wavelength side of Q band, which perhaps can be attributed to the relatively weaker axial coordinating ability of these Pcs. But in the spectrum of phthalocyaninatocobalt **2**, it was found that the Q band red shifted about 8 nm (from 697 to 705 nm) in a few minutes after BPO was added, then the shift stopped in the further decrease of Q band. However, this red shift neither be observed in the decompositions of the other three MPcs.

Considering the red shift of Q band of **2** is most possibly resulting from the axial coordination on the center Co atom, a small quantity of pyridine was added to the solution of **2** in toluene to examine it. As expected, the observed red shift of Q band by adding pyridine was nearly the same to that observed by adding BPO. Wherein, the bulky substituents forming a space between the two neighbor MPc molecules for the axial coordination are also necessary. From this result, we conjectured that the axial coordinated phthalocyaninatocobalt is an intermediate in the reaction of **2** with BPO (**2a** in Scheme 2). Therefore, the axial

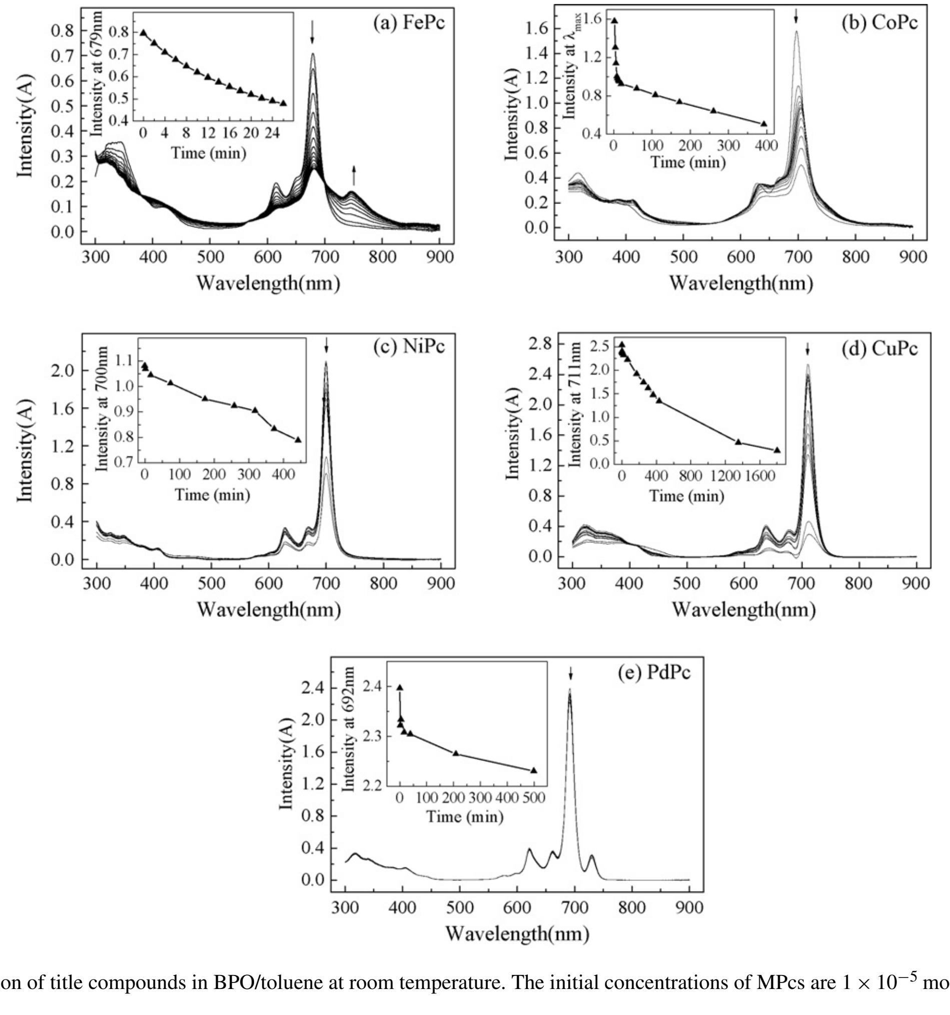

Fig. 1. The spectra variation of title compounds in BPO/toluene at room temperature. The initial concentrations of MPcs are 1×10^{-5} mol/L, and those of BPO are 5×10^{-3} mol/L.