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The facile synthesis and characterization of tetraimido-substituted zinc phthalocyanines

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Abstract

Peripherally tetraimido-substituted zinc phthalocyanines were synthesized by the reaction of tetraamino-substituted zinc phthalocyanine with maleic anhydride, phthalic anhydride and tetrachlorophthalic acid, respectively. The compounds were characterized by MS, ^{1}H NMR, UV–vis, IR and elemental analysis, the results of which were consistent with the proposed structures. UV–vis spectra showed that the wavelengths of the Q bands followed the order: $Q_{2c} > Q_{2b} > Q_{2a}$; the strengths of the Q bands varied inversely with temperature. The compounds were stable in acid but unstable in alkali.

Keywords: Phthalocyanine; Synthesis; Acidylation; Characterization; Property; UV–vis

1. Introduction

Phthalocyanines (Pcs) and their derivatives have attracted world-wide interests because of their properties such as the high thermal stability, semiconductivity, photoconductivity, etc. [1]. As function materials, phthalocyanines also display many interesting applications in photodynamic therapeutic agents [2], dye-sensitized solar cells [3], liquid crystals [4], nonlinear optics [5], film materials [6] and the like. The functions are associated with the aromatic 18-π electron system in Pc macromolecule [7], which causes them to show a characteristic Q band absorbance at around 700 nm. Therefore, the Pc researchers would pay more attention to the characterization [8] and alteration [9] of Q bands, which might reveal some significant information on the potential applications of Pc compounds [10,11].

In our previous studies on the property of peripherally tetranitro-substituted zinc Pc (TNZPc), it was ever found that the Q band absorbance could be controlled by altering the two electronic effects, inductive effect and conjugative effect, of nitro-group around Pc ring, with temperature [12]. In order to understand the impact of substituents and corresponding factors (temperature and acid/base) on the Q band of Pcs, we prepared several new Pc derivatives with maleic imido-group, phthalic imido-group and tetrachlorophthalic imido-group, respectively, for this study.

The common method to synthesize substituted Pcs is to prepare the phthalonitrile precursors with required substituents, then synthesize the corresponding Pcs by cyclotetramerization of the substituted phthalonitriles [13–15]. This was because the solubility of many Pc compounds was poor in organic solvents or water [16]. It was difficult for them as substrates to synthesize Pc derivatives by reacting with other reagents in solution. However, the traditional way usually required more than two reaction steps and time-consuming performance, e.g.

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column chromatogram separation during the course of purifying the substituted phthalonitriles or the resultant Pcs [17,18]. So it is necessary to search a facile strategy to prepare new Pc compounds.

We have ever prepared tetraamino-substituted zinc Pc (TAZPc) **1** bearing functional amino-group and having good solubility in some organic solvents, such as dimethyl formamide (DMF), dimethyl sulfoxide (DMSO) and pyridine, etc. [19]. Its advantageous for us to explore the novel way to synthesize Pc compounds from **1**. In this paper, we synthesized three peripherally tetraimido-substituted zinc Pcs (TIZPcs) **2a**–**2c** by the reaction of **1** with maleic anhydride, phthalic anhydride and tetrachlorophthalic acid, respectively (Scheme 1). The obtained Pc compounds were characterized by MS, ^{1}H NMR, UV–vis, IR and elemental analysis, which were all consistent with proposed structures. Furthermore, the properties of them were investigated in terms of the impacts of substituents, temperature and acid/base on UV–vis spectra and chemical stability.

2. Experimental

2.1. Materials and methods

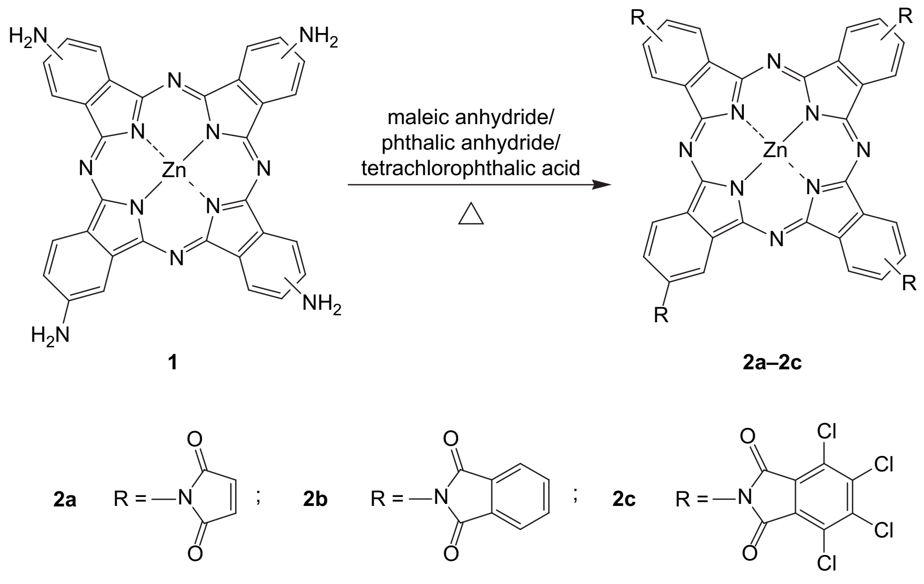
Compound **1** was prepared according to the method in the literature [19]. Maleic anhydride, phthalic anhydride, tetrachlorophthalic acid and other reagents are all commercially available and used without further purification. Mass spectra were obtained on an LDI-1700 MALDI-TOF MS spectrometer. ^{1}H NMR spectra were recorded on an INOVA-500 spectrometer. UV–vis spectra were recorded on a Cary 500 UV–vis–NIR SPECTROPHOTOMETER. IR spectra were recorded on an Aipha-Centuart FT-IR spectrometer (KBr). Microanalysis for C, H and N were performed on a Perkin-Elmer 2400 elemental analyzer.

2.2. Synthesis of **2a**–**2c**

The synthesis of **2a**, a typical procedure: 0.64 g (1 mmol) black green powder of **1** and 2.0 g (20 mmol) finely ground maleic anhydride were put into a 100 mL beaker whose mouth was covered with a watch glass. Then the beaker was kept in an oven at 170 °C for half an hour. After the resulting reaction mixture was cooled down to room temperature, 20 mL acetic acid was added in the beaker and boiled slightly for 20 min. The black blue solid was filtered out and washed twice by 10 mL acetic acid. The product was dried at 80 °C to afford **2a**: yield: 0.72 g (75%). MS (TOF): *m/z* required, 958.1 [M$^+$]; found, 958.4 [M$^+$]. ^{1}H NMR (DMSO): δ 8.889–9.012 (d, 4H ArH); 8.196 (s, 4H ArH); 7.551 (s, 4H ArH); 6.116 (s, 8H 4 COCHCHCO). UV–vis (DMF): λ_{max} 348, 612, 676 nm. IR (KBr): 1714 vs cm^{-1} (C=O). Anal. Required ($C_{48}H_{20}N_{12}O_8Zn$): C 60.17, H 2.10, N 17.54; found: C 60.01, H 2.03, N 17.11.

Using phthalic anhydride as acidylation reagent instead of maleic anhydride, the above synthetic performance generated black blue solid **2b**: yield: 0.94 g (81%). MS (TOF): *m/z* required, 1158.4 [M$^+$]; found, 1158.6 [M$^+$]. ^{1}H NMR (DMSO): δ 8.921–9.140 (four, 4 H ArH); 8.354 (d, 4H ArH); 7.941 (d, 4H ArH); 8.300 (s, 8H PhH); 7.793 (s, 8H PhH). UV–vis (DMF): λ_{max} 349, 612, 678 nm. IR (KBr): 1719 vs cm^{-1} (C=O). Anal. Required ($C_{64}H_{28}N_{12}O_8Zn$): C 66.36, H 2.44, N 14.51; found: C 65.76, H 2.55, N 14.63.

Using tetrachlorophthalic acid as acidylation reagent instead of maleic anhydride and keeping reaction temperature at 255 °C, the resulting product was black blue **2c**: yield: 1.25 g (73%). MS (TOF): *m/z* required, 1709.5 [M$^+$]; found, 1709.4 [M$^+$]. ^{1}H NMR (DMSO): δ 8.692 (s, 4 H ArH); 7.850 (s, 4H ArH); 7.345 (s, 4H ArH). UV–vis (DMF): λ_{max} 343, 638, 679 nm. IR (KBr): 1723 vs cm^{-1} (C=O). Anal. Required ($C_{64}H_{12}Cl_{16}N_{12}O_8Zn$): C 44.97, H 0.71, N 9.83; found: C 44.56, H 0.83, N 9.61.



Scheme 1. Synthesis and molecular structures of **2a**–**2c**.

3. Results and discussion

3.1. Synthesis

The synthesis of **1** was successfully carried out by the reduction of nitro-group around TNZPc with sodium sulfide [19], which presented us a reference to get new Pc derivatives by acidylation of amino-group around **1** with some suitable molecules, e.g. anhydrides and acids (Scheme 1). At 170 °C, the melted maleic anhydride or phthalic anhydride could be used not only as an acidylation reagent, but also as a solvent during the synthetic course of **2a** or **2b**. Under this condition, 0.5 h was enough for the reaction of **1** with anhydrides. Certainly in the preparation of **2c**, the reaction must occur at 255 °C for the high melting point of tetrachlorophthalic acid. On the other hand, all the aforementioned acidylation reagents could finely dissolve in heated acetic acid, but the solubility of products **2a**–**2c** was poor. It is convenient for us to separate and purify the aimed products from other compounds by washing with heated acetic acid. Herein the synthetic strategy of acidylation of amino-group comprises only one step reaction and simple washing purification, which differs from the common method by cyclotetramerization of substituted phthalonitriles. The followed characterization confirmed the rational structure and the better purity of **2a**–**2c**.

3.2. Characterization

Compounds **2a**–**2c** were characterized by MS, ^{1}H NMR, UV–vis, IR and elemental analysis, which were consistent with the proposed structures (seen in Section 2.2). The new compounds can dissolve in DMF, DMSO and pyridine, which benefit the characterization of them by MS, ^{1}H NMR and UV–vis spectra. The results recorded by MS show that the m/z of M^+ approximates to the molecular weight for every new Pc compound. The ^{1}H NMR spectra of them display the existence of characteristic hydrogen around Pc ring and the disappearance of amino-hydrogen as a result of acidylation, e.g. **2a**. In its ^{1}H NMR spectra (Fig. 1), there are four sorts of hydrogens tagged as 1, 2, 3 and 4, respectively. Comparing the ^{1}H NMR spectra of **2a** with **1** [19], the hydrogens 1, 2 and 3 around Pc ring keep down the alike wide peaks and the same chemical shift order, but the split of three peaks is not good. The property that the three peaks being wide is one of the characters of Pc compounds with M(II) at the center of Pc ring, and the poor peak split may be ascribed to the finite solubility of **2a**. Moreover, the wide peak of amino-hydrogen at 6.23 disappeared and instead a steep peak at 6.12, namely the hydrogen atom 4 in the maleic imido-group, appeared. Further, the following UV–vis spectra reveal some special properties of **2a**–**2c** in terms of the impact of substituent, temperature and acid/base on Q bands.

3.3. Impact of substituents on UV–vis spectra

The UV–vis spectra of **2a**–**2c** show that the wavelengths of Q bands are approximative, but follows an order: $Q_{2c} > Q_{2b} > Q_{2a}$ (Fig. 2). The order is consistent with the bulk and conjugative structure sizes of three substituents: tetrachlorophthalic imido-group > phthalic imido-group > maleic imido-group (Scheme 1). Based on the molecular structures of **2a**–**2c** and the property-controlled investigations of Pc compounds [12,20], it is concluded that the factors having impact on the Q band absorbance of **2a**–**2c** should involve the electron-pulling inductive effect (−I) and the electron-pulling conjugative effect (−C) of three imido-groups, as well as the enlargement of conjugative structure (+S) of three Pc molecules.

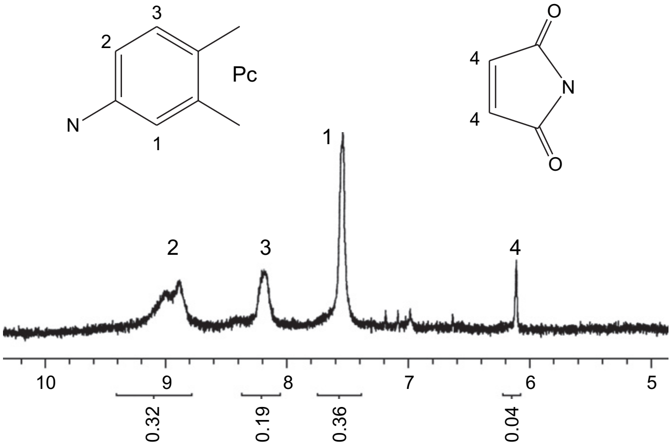


Fig. 1. The ^{1}H NMR spectra of **2a**: 1, 2, 3 and 4 represent four sorts of hydrogen atoms, respectively; 1, 2 and 3 locate around the Pc ring and 4 lies in the maleic imido-group.

In the previous study on peripherally substituted TNZPc, the nitrogen atom of nitro-group around Pc ring bonds with ambient atoms by sp^2 hybrid orbit, which allows its conjugative plane to be parallel with Pc ring and leads to a strong π–π conjugation between them. The competition between −C and −I of nitro-group results in the Q band split of peripherally substituted TNZPc [12]. In the molecules of **2a**–**2c**, both the −C and the +S cannot compete with the −I even if the conjugative structures of the three

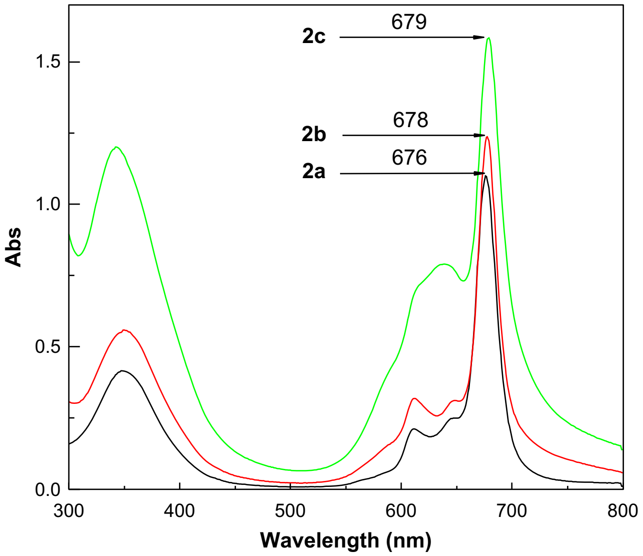


Fig. 2. UV–vis spectra of **2a**–**2c** in DMF (10^{-5} M).

imido-groups are larger than that of the nitro-group in peripherally substituted TNZPc. This is because the nitrogen atom of imido-group around Pc ring bonds with other atoms by sp^3 hybrid orbit, which hinders the imido-group plane to be parallel with Pc ring. As a result, the halfway parallelism disturbs not only the effective π−π conjugation between imido-group and Pc ring, but also the effective +S of Pc molecules. Whereas the −I isn't impacted by the halfway parallelism. So the −I of imido-groups have main impact on the UV−vis spectra of **2a**−**2c** and cause the Q bands of them to display single peaks without Q band split.

As far as the above order of Q band wavelength is concerned, it is mainly related to the difference among several imido-groups. Considering the −I of chlorine atoms and electron-deficient benzene ring, the −I of the three substituents should offer a reverse contribution to the order considering the electron-pulling action of substituent caused the Q band to blue shift [19]. Contrarily, the −C of the three substituents might generate a consistent contribution to the order because of the electron-pushing conjugative effect (+C) of chlorine atom and benzene ring under their chemical circumstances. Moreover, the +S of **2a**−**2c**, caused by the three imido-groups, also brings a consistent contribution to the order considering the conjugative structure sizes are uniform with the +S, which causes the Q band to red shift [21]. All in all, because the difference among three imido-groups is small, the −I gives a reverse contribution to the order of Q band wavelength compared with the −C and the +S. So the co-functionary results of −I, −C and +S are that the wavelengths of Q bands have an order $Q_{2c} > Q_{2b} > Q_{2a}$ and the gaps between two adjacent Q bands are less than 2 nm. In addition, the wide shoulder peak around 638 nm in the UV−vis spectrum of **2c** might be the result of easily intermolecular congregation due to the enlarged conjugative system of molecule [22,23].

3.4. Impact of temperature on UV−vis spectra

Although the imido-groups around Pc rings of **2a**−**2c** have largely conjugative structures, the π−π conjugation between imido-group and Pc ring is less effective considering the halfway parallelism discussed in Section 3.3. So no Q band split and no corresponding impact of temperature on split peaks can be found in their UV−vis spectra. But still their Q bands rise a little at 0 °C and descend at 80 °C like the non-peripherally substituted TNZPc [12], (e.g. the Q band of **2a**, Fig. 3). Here, the reasons that temperature alters Q band strength may be attributed to two aspects. One is that the π−π* electronic transition is limited at high temperature because electronic fluidity in the π conjugate plane of Pc ring becomes difficult with the rising temperature [24]. The other is that the distortion of nearly planar Pc ring due to a result of thermal vibration, is strengthened with the rising temperature and then leads to the hypochromic effect of Pcs, namely that the Q band descends [25].

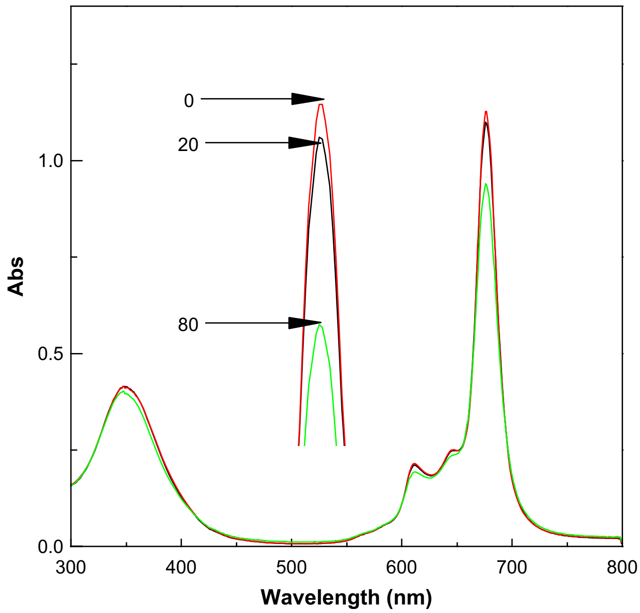


Fig. 3. The impact of temperature on Q band absorbance of **2a** in DMF (10^{-5}): at 0, 20 and 80 °C.

3.5. Impact of acid/base on UV−vis spectra

In view of that the UV−vis spectra of **2a**−**2c** showed similar phenomenon after the solutions of them in DMF were treated with acid/base, and that the UV−vis spectra of **2c** would give much information considering a wide shoulder peak appeared around 638 nm. So the UV−vis spectrum of **2c** was selected to account for the impacts of acid/base on UV−vis absorbance. From Fig. 4, it was found that the wide shoulder peak lowered a little and the Q band rose slightly after treatment with acid. It is concluded that the acid caused the intermolecular congregation to weaken and then the lowering of wide shoulder peak. Accordingly the molecular monomers increased and then the Q band absorbance strengthened [22]. The acid action might

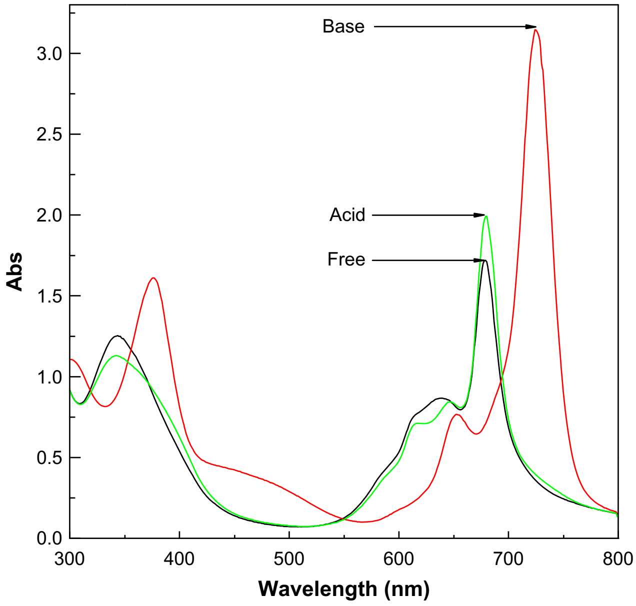


Fig. 4. The UV−vis spectra of **2c** in DMF (10^{-5} M). Before being detected, the three parts of solution of **2c** in absorption cells were treated by adding a drop of 0.1 M HCl in water, adding a drop of 0.1 M NaOH in water and freeing treatment with acid/base, respectively.

be that the H$^+$ from acid attacked acyl oxygen in imido-group, but the action was not strong enough to redistribute electronic cloud of Pc ring considering no Q band shift was found. Except for the Q bands' rising, the shoulder peaks of **2a** and **2b** had no other changes after treatment with acid. Moreover, all the solutions of **2a**–**2c** in DMF had blue color before and after treatment with acid. On the other hand, after treatment with base, all the solutions of them changed quickly from blue to green. The Q bands of them shifted to 726 nm and had an enhanced absorbance, and also a wide absorbance band from 400 to 500 nm appeared (Fig. 4). The new absorbance characters of Q band were similar to that of **1**. The degraded product was further analyzed to be **1** by the method in the literature [19]. So we concluded that the **2a**–**2c** could be rapidly decompounded to **1** by NaOH in DMF through Gabriel reaction, i.e. their stabilities were very poor under basic condition with OH$^-$.

4. Conclusion

Three new Pc compounds **2a**–**2c** were synthesized, in one step, by the reaction of **1** with melted maleic anhydride, phthalic anhydride and tetrachlorophthalic acid, respectively. The synthetic strategy differed from the common method by cyclotetramerization of substituted phthalonitriles, which usually required time-taking performance, e.g. column chromatogram. The proposed molecular structures were confirmed with the results of characterization by general methods, especially with the structural information revealed by ^{1}H NMR. The −I, −C and +S together caused that the wavelength of Q bands has an order $Q_{2c} > Q_{2b} > Q_{2a}$. The nitrogen atom of imido-group around Pc ring bonded with other atoms by sp^3 hybrid orbit, which disturbed $\pi-\pi$ conjugation between the imido-group and the Pc ring. So no Q band splits were found even if the imido-groups have large conjugative structures. The temperature could cause the strength of Q to alter conversely. The acid with H$^+$ gave a little impact on the UV–vis spectra of **2a**–**2c**, but the base with OH$^-$ quickly decompounded them to **1** and their UV–vis spectra were converted to the UV–vis spectra similar to that of **1**. Namely, the obtained compounds could stably exist in the acid with proton but couldn't in the base with hydroxyl anion.

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