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Study on synthesis, characterization and self-assemble nanotubes of a new asymmetrical nickel phthalocyanine

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A new asymmetrical Nickel phthalocyanine was synthesized by increasing the temperature of the classical synthetic method, and characterized by MS, IR and UV-Vis spectroscopy. The nanotubes of NiPc2 were prepared in large scale by self-assembling via a simple solvent diffusion method. The size of them was 50-120 nm in diameter and 2-10μm in length. The nanostructure, disclosed by XRD and UV-Vis, was a kind of highly long-range ordered lamellar arrangement of molecules. UV-Vis spectra demonstrated that the nanostructure is a J-type aggregate because of the red shift of the Q-band of the nanotubes. And the formation mechanism of nanotube has been proposed.

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Keywords: Asymmetrical phthalocyanine, Synthesis, Self-assemble, Nanotubes, J-type aggregate

1. Introduction

Recently, a great scientific interest has been focused on the synthesis of asymmetrical phthalocyanines due to the widespread application of them as functional molecules in gas sensors [1], molecular rectifiers [2], field-effect transistors [3] and fluorescent tagging of biomolecules [4]. However, the most asymmetrical phthalocyanines were synthesized by statistical methods [5-7] or ring expansion of subphthalocyanine complexes [8], which had many disadvantages such as low yield and various products. The difficulty synthesis greatly restricted the application of them. Therefore, the simple method to obtain pure asymmetrical phthalocyanines needed to be studied in time. In this paper, we reported a facile way to synthesize a new asymmetrical phthalocyanine, which was modified the classical cycloaddition reaction by altering the reaction temperature rightly.

2. Experimental

2.1. Materials and equipment

The Pc precursor, 4-(4-tert-Butyl-phenoxy)-phthalonitrile, was provided by the Northeast Normal University. The other chemicals were purchased from commercial suppliers and used without purification. IR spectra (KBr) were recorded on a Magna-560 FTIR spectrophotometer. UV-Vis spectra were measured on a Cary 500 UV-VIS-NIR spectrophotometer. MS spectra were obtained on a QUSTAR-TOF mass spectrometer.

2.2. Synthesis

According to classical method [9, 10], namely treating the precursor 4-(4-tert-Butyl-phenoxy)-phthalonitrile with $NiCl_2$ and BDU (1,8-Diazabicyclo[5.4.0]undec-7-ene) in 1-octanol under N_2 at 135℃for 8h, a symmetrical nickel phthalocyanine (NiPc1) could be synthesized. When the reaction occurred at 170℃,The synthetic product was a mixture of NiPc1 and asymmetrical phthalocyanine (NiPc2 for short) (Scheme 1), which was separated and purified by column chromatography on silica gel. They were characterized by UV-Vis, MS and IR. In order to find out the formation of NiPc2, a hypothetical mechanism was suggested. Firstly, the intermediate product 4-(4-tert-Butyl-phenoxy)-phthalonitrile coordinated with nickel ion (molar ratio, 1:1). Then DBU attacked the carbon atom of *tert*-butyl group in the aforesaid intermediate at high reaction temperature 170℃, and as a result a methyl was removed from *tert*-butyl group, which was accordingly converted into isopropyl group. Finally, the intermediate with an isopropyl group reacted with the others with *tert*-butyl group (molar ratio, 1:3) to form asymmetrical NiPc2.

Nickel 2,9(10),16(17),23(24)-Tetra(4-*tert*-butylphenoxy)phthalocyanine (NiPc1)

Yield: 215mg (37.1%). UV-Vis ($CHCl_3$): λ_{max}nm=298, 331, 609, 674; MS (MALDI-TOF, $CHCl_3$): m/z=1162.9[M]; IR

(KBr): 1238cm^{-1} (C-O-C).

Nickel 2-(4-isopropyl)-9(10),16(17),23(24)-Tri(4-*tert*-butylphenoxy)phthalocyanine (NiPc2)

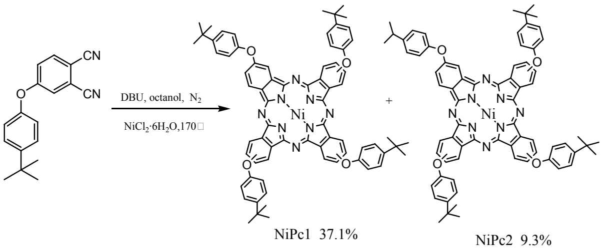
Yield: 53mg (9.3%). UV-Vis ($CHCl_3$): λ_{max}nm=287, 385, 614, 675; MS (MALDI-TOF, $CHCl_3$): m/z=1148.7[M], 1128.6[M – isopropyl + Na^+]; IR (KBr): 1231cm^{-1}(C-O-C); HRMS: 1148.42695, $C_{71}H_{62}N_8O_4Ni$ requires 1148.42420.

2.3. Synthesis of asymmetrical NiPc2 nanotubes

The NiPc2 molecules could self-aggregate nanotubes via a simple solvent diffusion method [11, 12]. When methanol was added dropwise into NiPc2 chloroform solution (~2.7 mg/ml), then the asymmetrical NiPc2 molecules self-aggregated into nanotubes. Then the tubes were washed carefully by ethanol to remove chloroform.

3. Results and discussion

According to TOF-MS spectra of NiPc1 and NiPc2 (Fig. 1), the peaks of singly charged molecular ions are obvious in the range of *m*/*z* from 0 to 3000 but peaks of impurities can hardly be found. But no dimmer peaks were found in the spectra of them. In the Fig.1a, a sharp peak was found at *m/z* 1162.9, corresponding to NiPc1 (*calc*, 1162.4).In the Figure1b, a sharp peak at *m/z* 1148.7 was assigned to be asymmetrical NiPc2 (*calc*, 1148.4). The weak peak at *m/z* 1128.6 in the Fig.1b was considered to be derived from the fragment of NiPc2, which lost an isopropyl and combined with a sodium ion. Here the mass spectrum indirectly offered evidence that the asymmetrical NiPc2 lacked a methyl group compared with the symmetrical NiPc1.



Scheme 1 Synthesis and chemical structures of NiPc1 and NiPc2.

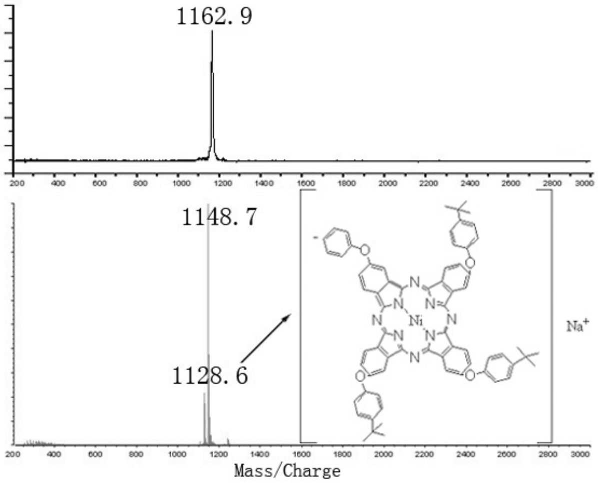


Fig. 1 MS spectra of NiPc1 (a) and NiPc2 (b).

Fig. 2 reveals the typical HRTEM micrographs of the asymmetrical NiPc2 aggregates. Most of which are arranged in tubular nanostructures. The tubes are 50-120 nm in width and 2-10 μm in length, by which the aspect ratio is calculated to be 40-80. The wall thickness of the tubes is 5-10 nm. But each tube is uniform and smooth. And from the micrograph of the sample, we can see that the tubes have a completely hollow structure with blockages.

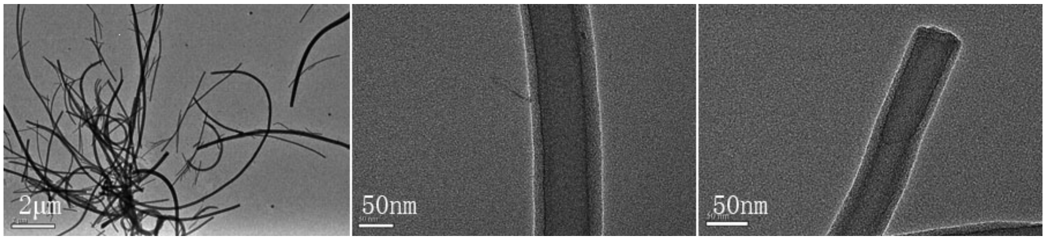


Fig. 2 The HRTEM micrographs of the NiPc2 nanotubes.

From the UV-Vis spectra (Fig. 3), it is found that the optical absorption has a great difference between the solution of NiPc2 in chloroform (5×10^{-5} mol/L) and the nanotubes of NiPc2. The former displayed the characteristic B band at 385 nm and Q bands at 675nm and 614nm. The additional band at 287nm was derived from the absorption of benzene rings in substituted phenoxy moieties of the NiPc2. But the latter presented broad absorption bands. Moreover, the B band shifted blue to 382 nm and the Q bands changed from 675 nm to 687 nm. The B band absorption is related to the front orbitals of the central metals in the metal-hthalocyanines, thus this means that the surrounding conditions of the central Ni ions are changed in the nanotubes of the asymmetrical NiPc2 which excludes the formation of Ni-O coordination bond between the neighbor phthalocyanines. The Q band aborption is related to front orbitals of the metal-phthalocyanine rings, thus this indicates a tight packing between the asymmetrical NiPc2 rings by strong π-π interaction in the nanotubes [13]. The broadened band of 287 nm in the nanotubes shows that there was a tight packing between the benzene rings of peripheral substituted phenoxy moieties of the asymmetrical NiPc2.

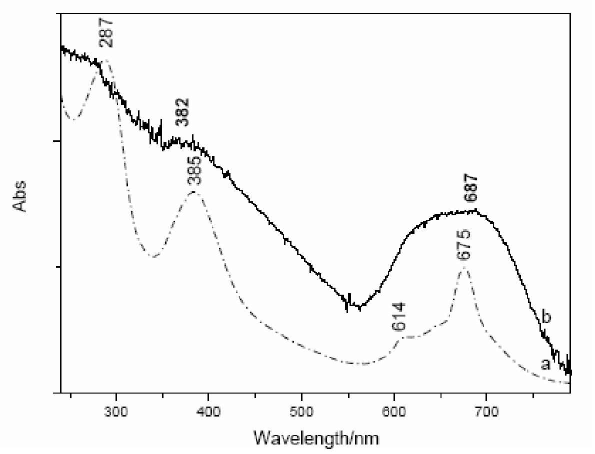


Fig. 3 UV-Vis absorption spectura of the NiPc2 solution (a) and the NiPc2 nanotubes (b).

Fig. 4 showed the XRD of the NiPc2 nanotubes as deposited on a quartz substrate at room temperature. In the XRD spectrum, two clear diffraction peaks were found at 4.32° and 27.36°, whose plane separations were approximately 20.4 Å (d_1) and 3.3 Å (d_2) respectively. The distance of d_1 is similar to the single molecule of NiPc2, which is about 20 Å (optimized with the MM2 force field using the Chem3D program). The broad peak at 20° should be due to the reflection from the quartz substrate. The two peaks of the nanotubes showed that the NiPc2 molecules have been arranged in highly long-range ordered lamellar structure [14], and d_1 and d_2 were the interlayer spacing of the nanotubes [15].

The formation of NiPc2 nanotubes was embodied in the XRD and UV-Vis spectra, which could be understood by three interactions of molecules. First of all, it was the π-π stacking of the asymmetrical NiPc2 rings that drives molecules to aggregate. This was because Pcs were macrocyclic molecules with 18-π electron frameworks formed by alternated carbon with nitrogen atoms, whose structures were prone to form π-π stacking. The π-π stacking interactions cause the UV-Vis spectra of NiPc2 nanotubes have a red shift change compared with the solution of it (Fig. 3), which implied the nanotubes were formed according to a J-type of aggregate method [10, 16]. The second interaction was the CH-π interaction between the benzene rings and isopropyl or t-butyl of the peripheral phenoxy groups around NiPc2 rings [17]. The third interaction was a coordination of the central Ni ion of one molecule and the oxygen atoms in the aryloxy group of another molecule. The inset of fig. 4 depicted the stacking patterns of the NiPc2 molecules.

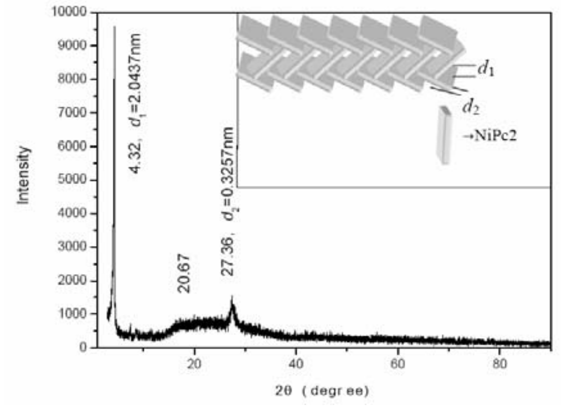


Fig. 4. XRD pattern the NiPc2 nanotubes (inset is the possible molecular staking patterns of the nanotubes).

Fabrication the nanotubes was related to solubility of NiPc2 in the solutions and the densities of the solutions. Methanol and chloroform were chosen as two solvents to prepare nanotubes because they have large difference in the densities, 0.79 g/cm^3 and 1.49g/cm^3 respectively. And the NiPc2 dissolved in chloroform and didn't dissolve in methanol. Methanol was dropped on the surface of chloroform with NiPc2 laggardly, the solutions layered. With methanol molecules diffusing to the chloroform, NiPc2 molecules self-assembled to nanotubes slowly and precipitated gradually.

4. Summary

In summary, a new asymmetrical Nickel phthalocyanine (NiPc2) was synthesized by a modified classical method and characterized by IR, MS and UV-Vis spectroscopy. And the NiPc2 nanotubes were obtained by self-assembling via a simple and reproducible solvent diffusion method. Based on the XRD and UV-Vis studies, the main interaction to form NiPc2 nanotubes were considered to be the π-π interactions of NiPc molecules, the Ni-O coordination and the CH-π interaction between the benzene rings and the isopropyl or t-butyl of the peripheral substitutes, respectively. The NiPc2 nanotubes have potential application on organic function devices [17,18].

Acknowledgments

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