Preparation and Characterization of Tetraphenylporphyrin Dyes

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Abstract: Porphyrin compounds exist widely in nature and are a key part of photosynthesis and photosynthesis. Because of its good photothermal stability and many unique physical and chemical properties, it has been widely used in the research and development of sensitized dye solar cells. As a new type of solar cell, dye-sensitized solar cell has attracted extensive attention and research due to its simple manufacturing process, relatively cheap price, high photoelectric conversion efficiency and environmental protection. In this paper, control experiments were carried out to synthesize tetrabenzoporphyrin with higher yield and purity by changing the solvent and washing solvent. The samples were characterized by uv-vis spectra. The results showed that the tetraphenylporphyrin crystals with better comprehensive effect could be obtained by using ethanol solution as sample solution and distilled water as washing solvent.

1. Introduction
Tetraphenylporphyrins were synthesized in 1935 by Rothemund under acidic conditions by the reaction of benzaldehyde and pyrrole in a sealed tube for 24 – 48 h under 150°C. But the yield obtained by this method is very low.
In 1967, Adler improved Rothemund's method. Tetraphenylporphyrin was prepared by the reaction of benzaldehyde and pyrrole in propionic acid at 141 °C for 30 min. After cooling and filtering , the filter cake with methanol and water respectively. The yield rate of tetraphenylporphyrin reached 20% .
The method of preparing tetraphenylporphyrins by condensation and cyclization of pyrrole with Aldehydes can also be used to synthesize simple meso-substituted porphyrins. This is a widely used method in the field of porphyrin synthesis.
2. Experiment

2.1 First preparation
The liquid paraffin was poured into the Constant temperature heating Magnetic stirrer, so that the liquid level reached two thirds of its volume. 180 mL xylene and 3.0 g salicylic acid were added into a 500 mL round bottom three-port bottle, magnets, insert thermometer (measuring range 200 °C), condensing tube and constant pressure drop funnel respectively, placing the rounded bottom flask in the center of the Constant temperature heating Magnetic stirrer on a metal stand.
When the initial temperature was 16 °C and the reflux phenomenon began at 128 °C, the mixture of 20 mL xylene and 0.04 mol pyrrole was added to the reaction solution of round bottom flask through a constant pressure drop funnel. (within 5 min) The reaction liquid changed from light yellow to violet black very quickly. Continue refluxing for 3 h, stop heating, and cool to room temperature. Adding the same volume of distilled water, leaving for 8 h, washing with Water 4 times, the bright purple crystal was obtained. (net weight : 3.0 g) The yield rate was about 48.9%.

2.2 Second and third preparation
1.0 g salicylic acid, 0.013 mol benzaldehyde and 60 mL xylene were added into the round bottom three mouth bottle of the same equipment, stirring and heating. The mixture of 0.013 mol pyrrole and 6.7 ml xylene were added through a constant pressure drop funnel after the reflux started (within about 2 minutes). The reaction liquid changed from light yellow to violet black very quickly. Continue reflux for 3 h, stop heating, cool to room temperature. After adding the same volume of ethanol, leaving for 8 hours, washing twice with water and ethanol, bright violet crystal was obtained. (net weight 0.57 g or 0.6 g) The yield was about 27.7% and 29.3%.

2.3 Fourth preparation
3.0 g salicylic acid, 0.04 mol benzaldehyde and 180 mL xylene were added into the round bottom three mouth bottle of the same equipment, stirring and heating. The mixture of 0.04 mol pyrrole and 20 mL xylene were added through a constant pressure drop funnel under agitation (within about 2 min) . The reaction liquid changed from light yellow to purple black quickly. Continue reflux for 3 h, then stopped heating and cooled to room temperature. After adding the same volume of ethanol and leaving it for 8 hours, washing twice with water and ethanol, the bright purple crystal was obtained (net weight : 1.2 g) . The yield rate was about 19.5% .

3. Result and discussion

3.1 The yield rate of tetraphenylporphyrin
Yield Rate = Actual Output / Shouldbe Output= Sample Weight / 6.14 g
Table 3-1 experimental results of porphyrin preparation by four different methods

|   | 1            | 2      | 3     | 4     |
|---|--------------|--------|-------|-------|
| 1 | weight of salicylic acid | 3.0g   | 1.0g  | 1.0g  | 3.0g  |
|   | resting      | water  | ethanol| water | ethanol|
|   | washing      | water (4 times) | water (4 times) | water (twice) + ethanol (twice) | water (twice) + ethanol (twice) |
| 2 | weight of sample | 3.0g  | 1.7g  | 1.80g | 1.2g  |
| 3 | yield        | 48.9%  | 27.7% | 29.3% | 19.5% |

The first preparation of porphyrin: The crystal was violet black, surface attached black flocs, yield was 48.9% ;
The second preparation of porphyrin: The crystal was bright purple, uniform thickness, yield was 27.7% ;
The third preparation of porphyrin: The crystal was bright purple, but the size of the crystal was different, the yield was 29.3% ;
The fourth preparation of porphyrin: The crystal was bright purple, uniform thickness, but the yield was 19.5% .

The conclusion drawn from the preparation of tetrabenzoporphyrin was as follows: The purified product can be obtained by washing with ethanol rather than distilled water alone; However, washing the sample with ethanol would lead to its dissolution in the solution, resulting in too little product, and yield was too low.

3.2 Detection of ultraviolet spectrum
Weigh 0.0003g of the product and dissolve it in dichloromethane, titrate to 100mL. The 4 kinds of solutions were blue and purple, with No. 4 being the darkest, No. 2 and No. 3 the second, and No. 1 the lightest. The four solutions were tested by uv-vis spectroscopy. The results were showed in Figure 1: UV spectra of 450-700nm.
The typical UV-vis Absorption Spectra of porphyrins had a strong Soret band near 420 nm and four relatively weak q-band peaks between 450 nm and 700 nm. The maximum absorption peak of sample 1–4 was at 418 nm, and there were four relatively weak absorption peaks at 450–700 nm. The absorption intensity of sample 1 was the lowest, and that of sample 4 was the highest. It can be concluded that sample 4 has the highest purity.

4. Conclusion
In this thesis, tetrabenzoporphyrin with high yield and purity was synthesized by changing the sample static solvent and washing solvent. The samples were characterized by UV-vis Spectra. The effects of different solvents and concentrations on the photoelectric conversion rate of solar cells were studied. The results are as follows:
1. When tetraphenylporphyrin was prepared by four methods, the method of preparing tetraphenylporphyrin with absolute alcohol and washing with distilled water is the best, the yield can reach 19.5%;

2. The porphyrin samples were prepared by using anhydrous ethanol to rest and distilled water to wash the samples when the four samples were analyzed by UV.

Reference
[1] Lin P, Clegg W and R Harrington Synthesis and structures of 5-(pyridyl) tetrazole complexes of Mn(II) 2005 J. Dalton Trans 45 2388–2394
[2] Zhao H and Xiong R G In situ hydrothermal synthesis of tetrazole coordination polymers with interesting physical properties2008 J. Soc. Rev. 37 84–100.
[3] Wong C P, William D and Horrocks W New Metalloloporphyrins: Thorium and Yttrium Complexes of Tetr phenylporphrin 1975 J. Tetrahedron Lett.16 2637–2640.
[4] Timothy D L, Michael J H and John D S Conjugated Macrocycles Related to the Porphyrins. 21. Synthesis, Spectroscopy, Electrochemistry, and Structural Characterization of Carbaporphyrins 2002 J. J. Org. Chem. 67 4860–4874.

[5] Adler Alan D, Long Frederick R and William S Mechanistic investigations of porphyrin syntheses I: preliminary studies on ms-tetraphenylporphin 1964 J. J. Am. Chem. Soc. 86 234–238.

[6] Gao J, Hide F and Wang H Efficient photodetectors and photovoltaic cells from composites of fullerenes and conjugated polymers: Photoinduced electron transfer 1997 J. Syntheticmetals. 84 979–980.