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Synthesis and properties of copper tetra(4-triphenylmethyl)phthalocyanine

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The synthesis of copper tetra(4-triphenylmethyl)phthalocyanine has been developed by treatment of 2-bromo-1-iodo-4-(triphenylmethyl)benzene with copper cyanide.

Chemical modification of phthalocyanine by introducing substituents into the benzene rings is an effective method of obtaining compounds with predictable physico-chemical properties. For example, introduction of bulky substituents such as *tert*-butyl[1,2] results in much greater solubility in nonpolar organic solvents. The triphenylmethyl group is even more bulky than *tert*-butyl, and it is interesting to investigate the influence of this group upon the properties of phthalocyanine.

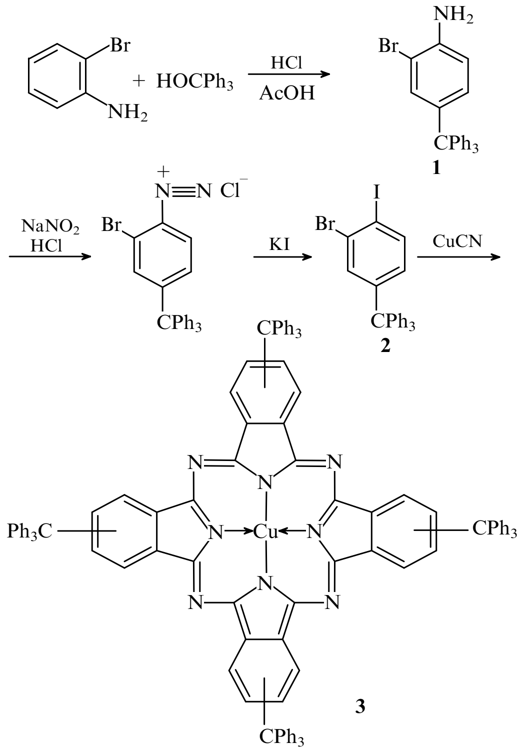
Copper tetra(4-triphenylmethyl)phthalocyanine was obtained by heating 2-bromo-1-iodo-4-(triphenylmethyl)benzene **2** with copper(I) cyanide at 220 °C for 4 h. The initial 2-bromo-4-(triphenylmethyl)aniline **1** was obtained by heating *o*-bromoaniline and triphenylmethanol under conditions employed for the tritylation of 2-chloroaniline.[3] Compound **2** was obtained by diazotation of **1** in acetone solution and by substitution of the diazonium group for iodine (Scheme 1).[†]

The compound obtained in this way can be separated by extraction with benzene. The purification was carried out by chromatography of this benzene solution on silica gel using benzene as eluent. The purity of copper tetra(4-triphenylmethyl)phthalocyanine was confirmed by TLC.

[†] 2-*Bromo*-4-(*triphenylmethyl*)*aniline* **1**. Triphenylmethanol (6.5 g, 0.025 mol), conc. hydrochloric acid (2.5 ml, 0.025 mol) and *o*-bromoaniline (4.67 g, 0.027 mol) were boiled in glacial acetic acid (30 ml). After 12 h the solution was cooled and the precipitate of **1** was filtered and washed with 10% sodium carbonate and water. After crystallization from 90% acetone **1** was obtained [yield 8.3 g (80%); mp 198–200 °C]. (Anal: Calc. for $C_{25}H_{20}NBr$: C, 72.4; H, 4.9; Br, 19.3. Found: C, 71.1; H, 4.9; Br, 19.3%.)

2-*Bromo*-1-*iodo*-4-(*triphenylmethyl*)*benzene* **2**. 4.45 g (0.01 mol) **1** and 1.28 ml conc. hydrochloric acid were dissolved in acetone (200 ml). 0.69 g (0.01 mol) sodium nitrite in 2 ml water was added to the solution at 0 °C. After 2 h, 3.14 g (0.02 mol) potassium iodide in 5 ml water was added to the acetone solution. After 12 h the reaction mixture was heated for 1 h at 50 °C. The mixture was added to 200 ml water and the resulting precipitate was filtered off. Recrystallization of the precipitate from ethanol afforded **2** (3.8 g, 73%) as yellowish needles, mp 190–192 °C. (Anal: Calc. for $C_{25}H_{18}BrI$: Hal, 38.3. Found: Hal, 38.3%.)

Tetra(4-*triphenylmethyl*)*phthalocyanine copper* **3**. 2-Bromo-1-iodo-4-(triphenylmethyl)benzene (5.25 g, 0.01 mol) and copper(I) cyanide (3.6 g, 0.04 mol) were heated at 220 °C for 4 h and the resulting green solid was extracted by benzene. The solution was evaporated and the residue was chromatographed in CCl_4 on silica gel (L40/200). A blue zone was washed away from the column, which was then eluted with benzene. Evaporation of the latter eluate afforded a blue powder of **3** (1.13 g, 29%). (Anal: Calc. for $C_{108}H_{72}N_8Cu$: C, 83.8; H, 4.6; N 7.5; Cu, 4.1. Found: C, 84.25; H, 4.8; N, 7.0; Cu, 3.9%.) IR: KBr, ν/cm^{-1} 2920, 2870, 1616, 1560, 1472, 1136, 976, 747, 704, 632, 560, 472, 456 cm^{-1}. UV (max): benzene λ/nm (lg ε) 684.1 (5.04), 615.2(4.58), 351.8 (4.64); CCl_4, 683.9 (4.96), 616.4 (4.34), 346.0 (4.59).



Scheme 1

This substance is very soluble in most organic solvents (ethers, benzene, DMF, pyridine, chloroform, CCl_4, hexane, acetonitrile and toluene), but only slightly soluble in alcohols and acetone. The substance under consideration proved to be slightly soluble in concentrated sulfuric acid because of the steric influence of the substituents on exocyclic nitrogen atoms.

The proposed structure of this substance was confirmed by elemental analysis, absorption and IR spectroscopy.

Introduction of triphenylmethyl groups into the phthalocyanine molecule results in a 7–8 nm bathochromic shift of the absorption spectrum as compared with the copper tetra(4-*tert*-butyl)phthalocyanine.[1]

The spectra of $(4\text{-}Ph_3C)_4PcCu$ in benzene and hexane given in Figure 1 confirm the phthalocyanine character of the compound obtained.

The bathochromic shift appears to result because the triphenylmethyl group has a more pronounced inductive effect than the *tert*-butyl group.

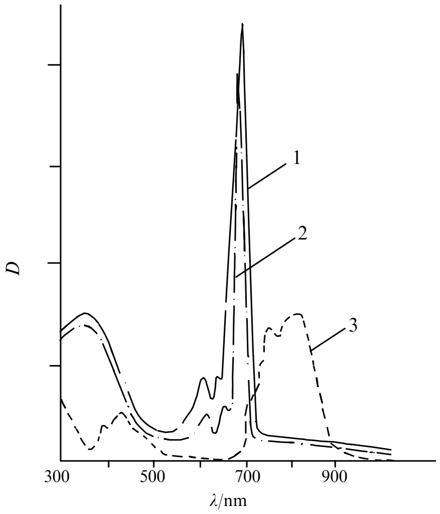


Figure 1 Absorption spectra for $(4\text{-}Ph_3C)_4PcCu$ in benzene (1), hexane (2) and sulfuric acid monohydrate (3).

On adding a small quantity of sulfuric acid monohydrate to a toluene solution of compound **3**, the protonated form is precipitated. This brown-coloured form may be separated and transformed into the initial form $(4\text{-}Ph_3C)_4PcCu$ by addition of water.

We succeeded in dissolving only a small quantity of protonated **3** complex in sulfuric acid monohydrate, but were able to measure the absorption spectrum shown in Figure 1. In this case a considerable extension of all absorption bands and their bathochromic shifts were observed in comparison with the organic solution spectra. This is in good agreement with the changes observed for copper tetra(4-*tert*-butyl)phthalocyanine.[1]

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