Direction of copper phthalocyanine crystallization using *in situ* generated tethered phthalocyanines

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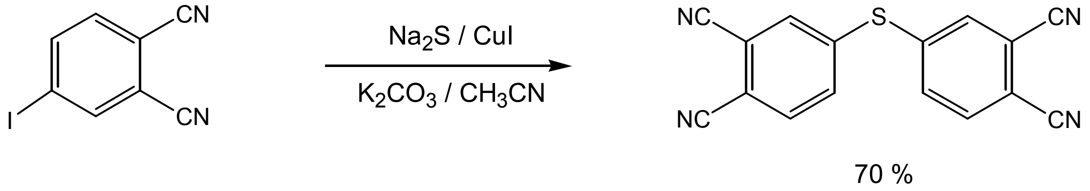
Supplementary Information

All materials were purchased from Sigma-Aldrich, except for the α-copper phthalocyanine which was supplied by Kromachem. Infrared spectra (pressed KBr discs) were recorded on a PERKIN-ELMER 1000 spectrometer in the range 4000 to 450 cm^{-1}. ^1H NMR spectra were recorded at 300 MHz and ^{13}C NMR spectra were recorded at 75 MHz on a BRUKER AVANCE 300 spectrometer at 20°C. Chemical shifts are reported in parts per million (ppm) downfield from TMS. Coupling constants (J) are given in Hertz and splitting patterns are indicated as : s (singlet), br s (broad singlet), d (doublet), t (triplet), dd (doublet of doublets) and m (multiplet). Flash column chromatography was performed on silica gel 60 (220-440 mesh). Elementary analyses were performed at the microanalytical laboratory, UCC on a PERKIN-ELMER 240 elemental analyser for carbon, hydrogen and nitrogen.

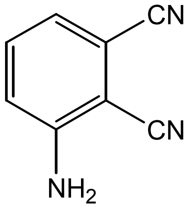
Powder X-ray diffraction was performed using a PHILIPS PANanlytical X'Pert PRO diffractometer with a PW 3830 generator, a PW 3710 MPD diffractometer and an X'Celerator detector operated with an anode current of 40 mA and an accelerating voltage of 45 kV. Samples were ground into powder and back filled into aluminium holders and exposed to CuKα radiation at diffraction angles (2θ) from 5° to 75° in continuous scan mode using a step size of 0.0167° and a step time of 10.16 s.

4,4'-Thiodiphthalonitrile **1**



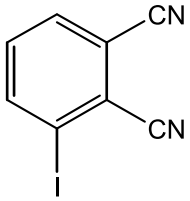
A solution of 4-iodophthalonitrile (1.0 g) and anhydrous K_2CO_3 (0.5 eq ; 0.28 g) in acetonitrile (15 mL) is made by heating on an oil bath for a few minutes. After the addition of anhydrous Na_2S (0.55 eq ; 0.17 g) and CuI (0.1 eq ; 0.08 g), the mixture is refluxed for 4 days. Water (50 mL) is then added, and the mixture is boiled with activated carbon. It is filtered while hot. The water diluted reaction mixtures are extracted with chloroform (3 x 10 mL). The combined organic phase is washed with 2 M NaOH (3 x 5 mL), and dried over $MgSO_4$. The solvent is removed to give the desired compound (70 %). 4,4'-thiodiphthalonitrile : **^{1}H NMR (300 MHz, $CDCl_3$) :** 7.67 ppm (dd, J=1.8 Hz, J=8.2 Hz, 2 H) ; 7.74 ppm (d, J=1.8 Hz, 2 H) ; 7.83 ppm (d, J=8.2 Hz, 2 H). **^{13}C NMR (75 MHz, $CDCl_3$) :** 114.2 ; 114.5 (4 $\underline{\mathrm{C}}$N) ; 115.4 ; 117.7 (4 $\underline{\mathrm{C}}$-CN) ; 134.5 ; 134.9 (2) (6 CH) ; 140.5 (2 $\underline{\mathrm{C}}$-S).

3-[(2,3-Dicyanophenyl)thio]phthalonitrile **2**



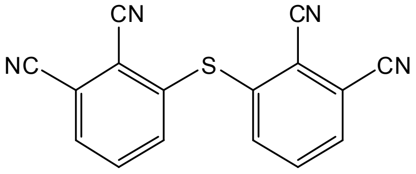
3-Aminophthalonitrile :

3-Nitrophthalonitrile (0.87 g, 5 mmoles) was added to a mixture of methanol (16 mL) and concentrated hydrochloric acid (3.5 mL) and the suspension heated to boiling. Iron powder (0.8 g) was added in small portions over 45 min. During addition the nitro-compound gradually went into solution, and towards the end of the reaction (1 h.) a yellow solid was deposited. The mixture was then poured into cold water and the precipitate filtered off. Yellowish solid, mp = 196°C (lit. mp 195-198°C), 50 %. **^{1}H NMR ($CDCl_3$) :** 4.73 (s, 2H, NH_2), 6.97 (d, 1H, J = 8.1 Hz), 7.09 (d, 1H, J = 8.1 Hz), 7.41 (t, 1H, J = 8.1 Hz).



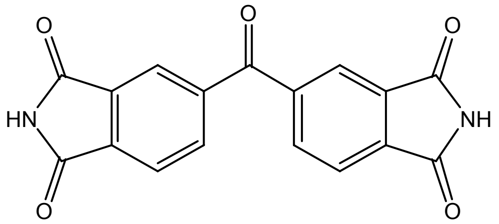
3-Iodophthalonitrile :

Amine (0.40 g, 2.8 mmoles) was mixed with concentrated hydrochloric acid (8 mL) and ice (20 g), sodium nitrite (0.30 g, 4.3 mmoles) in water (3 mL) was added in one portion. After 1.5 hour at 5°C, the solution was filtered. The diazonium salt solution was added dropwise to a stirred cool solution of potassium iodide in 5 mL water. The resulting dark brown mixture was stirred for 0.5 hour. This mixture was added to toluene and the solution was washed with cold water, cold 5 % $NaHCO_3$, cold water, cold saturated $Na_2S_2O_3$, and again with cold water. The toluene solution was dried over anhydrous magnesium sulfate and filtered. White solid, 65 %, **^{1}H NMR ($CDCl_3$) :** 7.41 (t, 1H, ^{3}J = 8.3 Hz, ArH-5), 7.80 (dd, 1H, ^{4}J = 1.2 Hz, ^{3}J = 8.3 Hz, ArH-4), 8.18 (dd, 1H, ^{4}J = 1.2 Hz, ^{3}J = 8.3 Hz, ArH-6).



3-[(2,3-Dicyanophenyl)thio]phthalonitrile :
A suspension of 3-iodophthalonitrile (0.51 g, 2 mmoles) and anhydrous K_2CO_3 (0.14 g, 0.5 eq) in DMF (15 mL) is made by heating for a few minutes. After the addition of anhydrous Na_2S (0.09 g, 0.55 eq) and CuI (0.04 g, 0.1 eq) the mixture is refluxed under a nitrogen atmosphere for 78 hours. Water (50 mL) is then added, and the mixture is boiled with activated carbon. It is filtered while hot into an excess of 6M HCl (10 mL). The precipitate formed on cooling to room temperature is filtered and washed with water. Column chromatography of the residue on silica gel using a mixture of hexane/ethyl acetate (75:25) affords a white solid (70 %). **^{1}H NMR (CDCl$_3$) :** 7.73-7.87 (m, 6H, ArH), **^{1}H NMR (CD$_3$CN) :** 7.62-7.72 (m, 2H, ArH), 7.85 (dd, 1H, $^4J = 1.5$ Hz, $^3J = 7.5$ Hz) : **^{13}C NMR (DMSO-d^6) :** 114.5, 115.9 (4 $\underline{C}$N), 117.3, 117.8 (4 $\underline{C}$-CN), 134.2, 135.2, 137.6 (6 $\underline{C}$H), 138.7 (2 $\underline{C}$-S). mp 225-227°C. $C_{16}H_6N_4S$ calc. : C 67.12, H 2.11, N 19.57, S 11.20. found : C 67.07, H 2.22, N 19.22, S 11.36.

<u>3,3’,4,4’-benzophenonetetracarboxylic diimide **3**</u> :



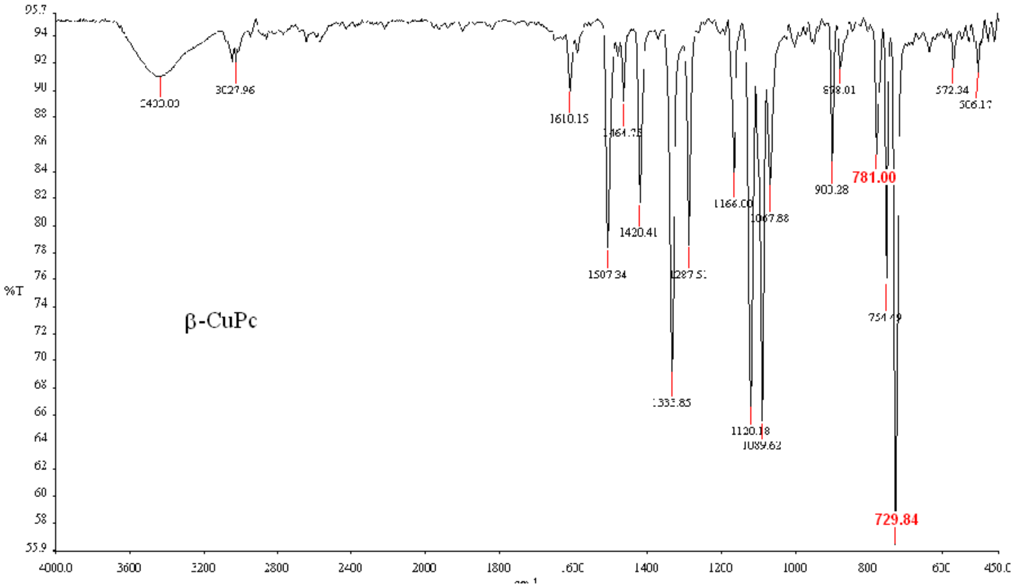
3,3’,4,4’-benzophenonetetracarboxylic diimide :
Benzophenone-3,3’,4,4’-tetracarboxylic dianhydride (5 mmoles, 0.16 g) was heated under stirring in formamide (5 mL) for 4 hours at 200ºC. After cooling the precipitate was filtered, washed with water and acetone. (90%) **^{1}H NMR (300 MHz, DMSO d^6) :** 11.7 ppm (bs, 2H) ; 8.15 ppm (dd, J=1.4 Hz, J=7.7 Hz, 2 H) ; 8.00 ppm (m, 4 H). **IR (KBr) :** ν 3230 ; 3070 ; 1781 ; 1709 ; 1665 ; 1356 ; 1244 ; 1100 ; 1043 ; 749 ; 720 cm^{-1}. m.p. : 380-385°C (lit.[i]) K. Kacprzak, *Synthetic Commun.*, 33, 9, **2003**, 1499.

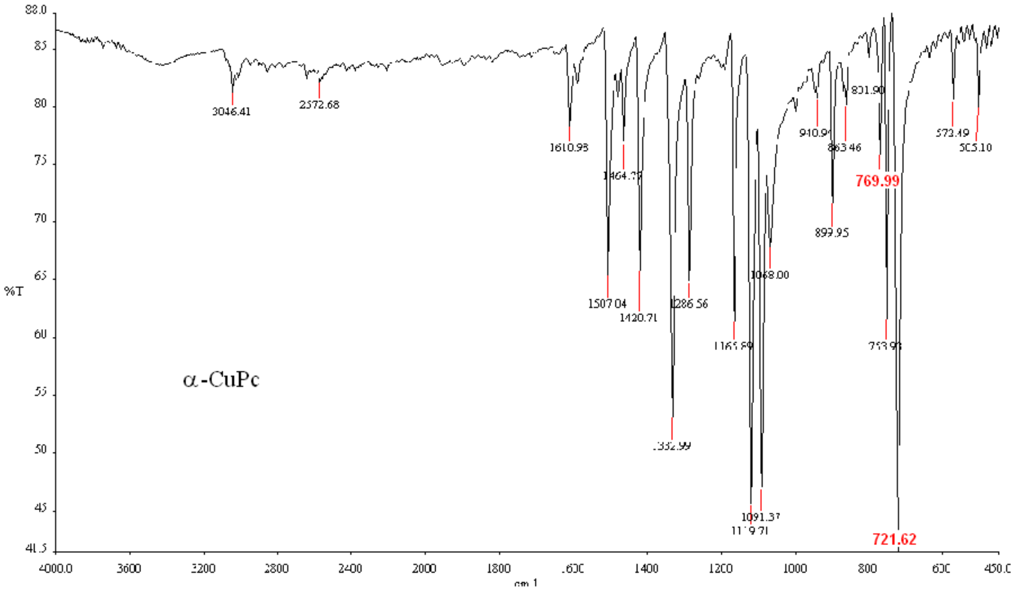
Copper Phthalocyanine Processes

Copper Phthalocyanine from Phthalonitrile : A mixture of phthalonitrile (2.56 g, 20 mmoles), copper (II) bromide (1.12 g, 5 mmoles) and hexamethyldisilazane (4.16 mL, 20 mmoles) in 10 mL of DMF was heated at 100°C for 10 hours. The precipitate was filtered and washed with acetone. (Blue solid, 70-75 %)

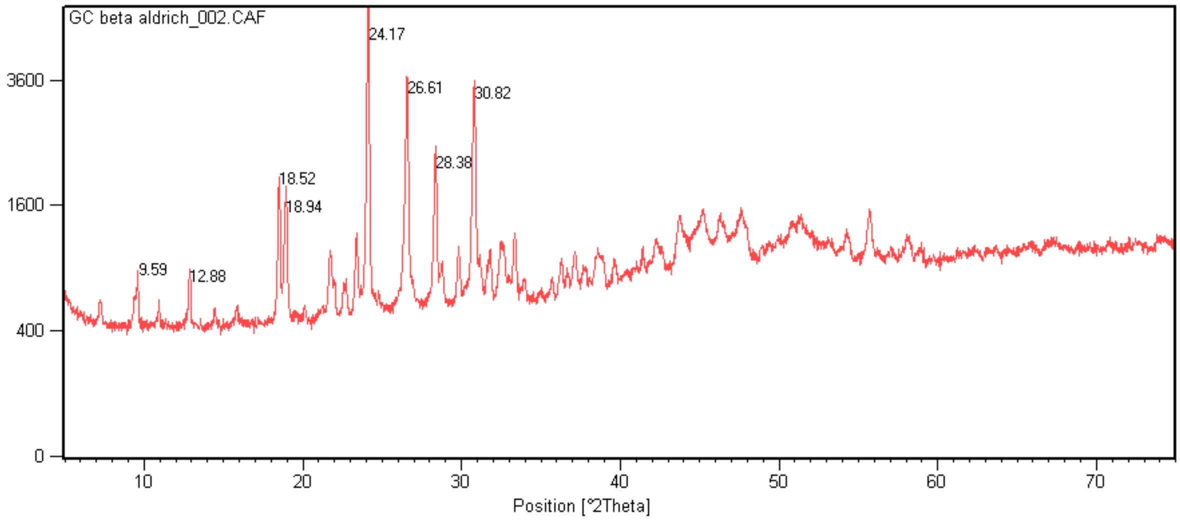
Copper Phthalocyanine from Phthalimide: A mixture of phthalimide (1.47 g, 10 mmoles), copper (II) bromide (0.58 g, 2.6 mmoles), *p*-TsOH.H_2O (0.19 g, 1 mmole) and HMDS (8.30 mL, 40 mmoles) in 0.77 mL of DMF was heated at 100°C for 10 hours. The precipitate was filtered off and washed with water, methanol and then acetone. (Blue solid, 60-65 %)

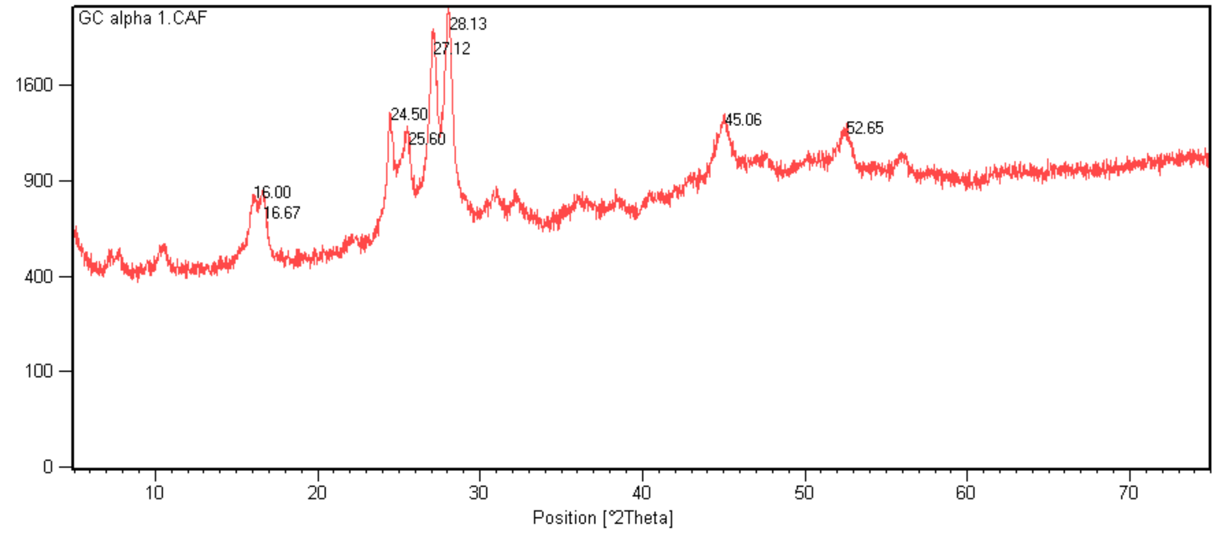
IR spectra of β- and α-Copper Phthalocyanine





PXRD patterns of β- and α-Copper Phthalocyanine





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[i] K. Kacprzak, *Synthetic Commun.*, 33, 9, **2003**, 1499.