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

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Copper phthalocyanine in the metastable α crystal polymorph can be obtained directly from phthalonitrile or from phthalimide, which would normally give the more stable β crystal form, by the inclusion of 3% or greater of the sulfide 2 **or the diimide** 3**. The resulting α form material does not revert to the β form upon treatment in boiling xylene, unlike conventionally prepared α copper phthalocyanine.**

Copper phthalocyanine and its derivatives constitute one of the main classes of commercially important organic pigments[1]. Like other such compounds, copper phathalocyanine is crystal polymorphic, i.e. crystallizes in at least two different forms which differ in their crystal structures[2], and the different polymorphs have different commercial value. At least four polymorphs of copper phthalocyanine are known, the α-, β- γ- and ε-forms[3], of which the β- and α-forms are the most commercially significant. The less valuable β-form is that which is generally obtained directly by preparation of copper phthalocyanine, whereas the more valuable α-form is obtained by further treatment of the β-form material with concentrated sulfuric acid or by other industrial processes[1]. The crystal structure of the β-form is well established[4], having a herringbone-like arrangement as illustrated in Fig 1 (top). The structure of the α-form has been more difficult to establish, however recent work[5] has suggested that it features copper phthalocyanine molecules stacked in molecular columns as in Fig 1 (bottom). The β-form is the more thermodynamically stable, for example, treatment of a suspension of the α-form in refluxing xylene gives complete reversion to the β-form after 2 hours[6]. Gradual reversion of α form to β form can also be observed as 'greening' of pigment products containing the α form.

Transformation of the metastable α-form to the more stable β-form requires a re-ordering of the copper phthalocyanine molecules within the crystal. It is possible that the presence of some quantity of tethered phthalocyanines within the α–form structure could 'reinforce' the α-form structure against such a re-ordering and so stablize that form. Rather than attempt to incorporate tethered phthalocyanines directly into existing copper phthalocyanine crystals, a more feasible approach would be to carry out copper phthalocyanine preparation in such a manner as to generate a small quantity of tethered phthalocyanine within the product crystals.

This approach may also 'direct' the initial formation of copper phthalocyanine solid to give α-form rather than β–form crystals, as the tethered phthalocyanine would not be well accommodated within the β-form structure as it would be incompatible with the herringbone arrangement. By contrast, it could be possible for tethered phthalocyanines to occupy adjacent molecular columns of the α structure.

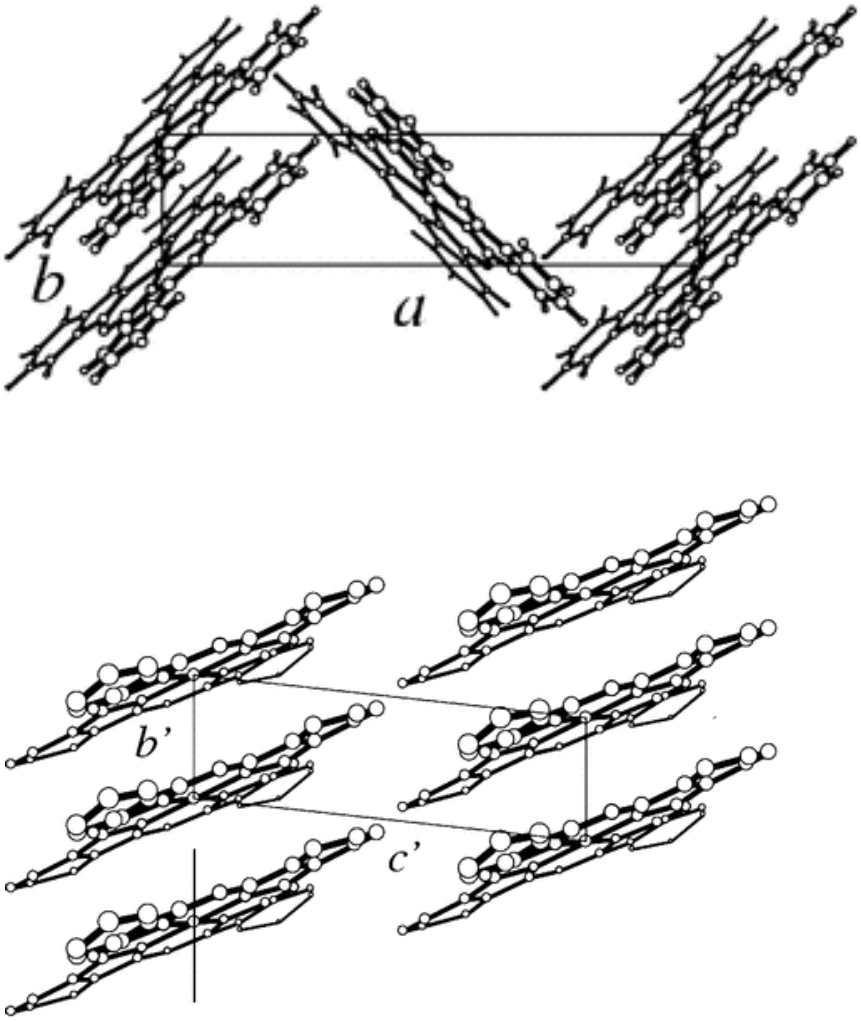


Fig. 1 Illustration of the crystal packing in (top) copper phthalocyanine β form and (bottom) α form. (reproduced with permission from reference 5; copyright International Union of Crystallography http://journals.iucr.org/.)

To examine this approach for the direction of crystallization and stabilization of crystal forms, we carried out preparations of copper phthalocyanine from phthalonitrile and phthalodiimide starting materials in the presence of tethered phthalonitriles and phthalodiimides. The requirement for selection as possible tethered phthalonitriles and phthalodiimides were, firstly, synthetic accessibility and, secondly, likely compatibility of the linker group with the juxtaposition of phthalocyanine molecules in the α-form. Compounds based on a biphenyl or diphenyl ether core were initially examined but these were found to be ineffective. However, compounds based on a diphenylsulfide and a benzophenone core structure were found to provide the required activity.

Specifically the tethered compounds examined where the phthalonitriles **1** and **2**, and the phthalodiimide **3**[7]. These were incorportated into established preparations of copper phthalonitrile from phthalonitrile[8] or phthalodiimide[9], Eqn 1. The results are presented in Table 1.

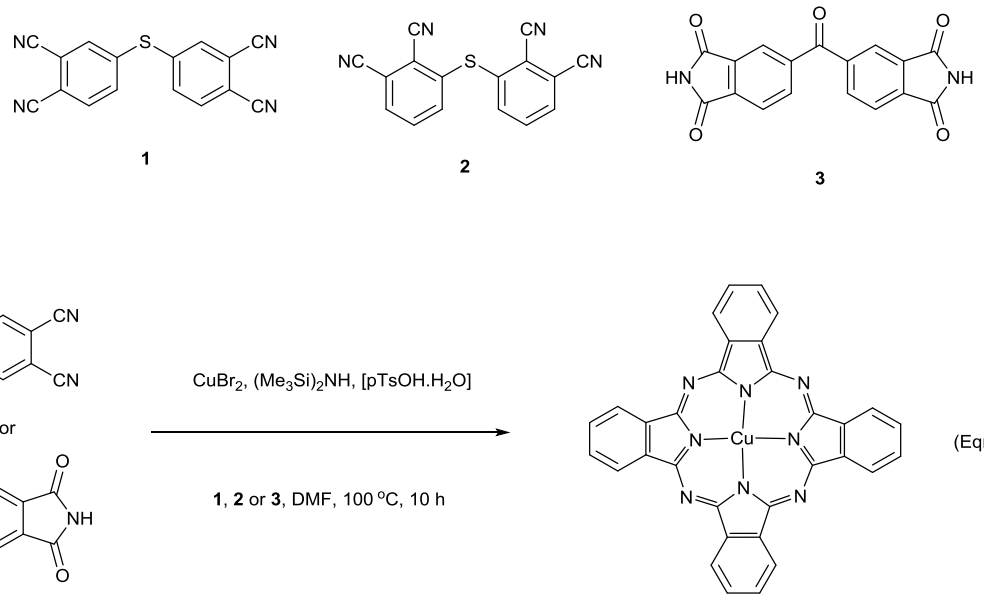


Table 1 Outcomes of copper phthalocyanine preparations in the presence of tethered compounds **1**, **2** and **3**.

Starting material.	tethered compound	% w/w[a]	crystal form obtained[b]	crystal form stability[c]
-	-	-	α[d]	β
nitrile	-	-	β	-
diimide	-	-	β	-
nitrile	**1**	5	β	-
nitrile	**2**	> 3	α	α
diimide	**3**	> 2	α	α

[a] mass of tethered compound added as percentage of mass of starting material.
[b] Polymorphic form determined by IR and PXRD.
[c] crystal form obtained after suspension in xylene heated to reflux for 2 h.
[d] commercial α form copper phthalocyanine.

The data in Table 1 show that addition of quantities of nitrile **2** and diimide **3**, but not nitrile **1**, result in an α-directing and stabilizing effect. Not only does this effect result in the direct precipitation of α form crystals from the reaction, rather than the usual β form, but the α form material that results is also resistant to reversion to the β form upon treatment in refluxing xylene. This α-directing and protecting

effect can be attributed to the formation of small quantities of tethered copper phthalocyanine molecules which become incorporated into the copper phthalocyanine crystals produced, blocking formation of the β form structure and reinforcing the resulting α form structure against re-ordering to the β structure.

The α form copper pthalocyanine material obtained in this manner could also be viewed as a solid solution of tethered phthalocyanine in α copper phthalocyanine crystals. The tethered phthalocyanines can be tolerated by the α form structure sufficiently for crystals to form, but reduce the freedom of the phthalocyanine molecules in the α form to re-order into the β structure. The tethered phthalocyanines are completely incompatible with the herringbone-like β form and inhibit its formation. It is interesting that inclusion of sulfide **2** but not sulfide **1** results in this effect, as sulfide **1** has the same pattern of substitution as diimide **3**. The tethered phthalocyanines produced by compound **1** may not be compatible with either the α or β form structures, whereas compounds **2** and **3** give rise to tethered phthalocyanines which can be tolerated by the α, but not the β, structure.

These findings demonstrate a new approach to obtaining and stabilizing a metastable crystal form though exploitation of the process chemistry so as to deliberately generate a structure-directing impurity. This approach may be applicable to obtaining and stabilizing crystal metastable forms of some scientifically and commercially important materials, provided the presence of the structure-directing compound does not prove to be an unacceptable impurity.

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Notes and references

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† Electronic Supplementary Information (ESI) available: [includes procedures and characterisation data for the preparations of sulfides **1** and **2**, and diimide **3**; typical processes for the preparation of copper phthalocyanine from phthalonitrile and phthalimide; examples of IR spectra and PXRD patterns characterizing the α and β polymorphs of copper phthalocyanine]. See DOI: 10.1039/b000000x/

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2. J. Bernstein, *Polymorphism in Molecular Crystals*, IUCr Oxford Science Publications, Oxford, 2002.
3. P. Erk, *Curr. Op. Solid State and Material Science*, 2001, **5**, 155-160; B. N. Achar and K. S. Lokesh, *J. Solid State Chem.*, 2004, **177**, 1987-1993.
4. C. J. Brown, *J. Chem. Soc (A)*, 1968, 2488-2493.
5. A. Hoshino, Y. Takenaka, H. Miyaji, *Acta Cryst.*, 2003, **B59**, 393-403.
6. F. H. Moser and A. L. Thomas, *Phthalocyanine*, Reinhold, New Youk, 1963.
7. Sulfides **1** and **2** were prepared from the corresponding iodophthalonitriles, and the bis(diimide) **3** from the correspodning bis(anhydride); experimental details are given in the supplementary information.
8. H. Uchida, H. Tanaka, H. Yoshiyama, P. Y. Reddy, S. Nakamura and T. Toru, *Synlett*, 2002, **10**, 1649-1652.
9. H. Uchida, P. Y. Reddy, S. Nakamura, T. Toru,, *J. Org. Chem.*, 2003, **68**, 8736-8738.

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

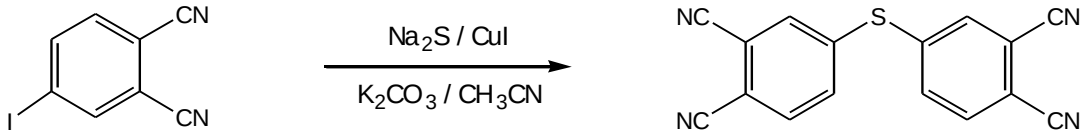
Humphrey A. Moynihan* and Geraldine Claudon

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}. ^{1}H 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.

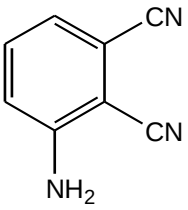
4,4'-Thiodiphthalonitrile **1**



70 %

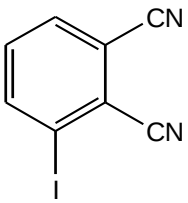
A solution of 4-iodophthalonitrile (1.0 g) and anhydrous K_2CO_3 (0.5 eq ; 0.28 g) in acetonitrile (15 mL) is made by heating on an oil bath for a few minutes. After the addition of anhydrous Na_2S (0.55 eq ; 0.17 g) and CuI (0.1 eq ; 0.08 g), the mixture is refluxed for 4 days. Water (50 mL) is then 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 C≡N) ; 115.4 ; 117.7 (4 C-CN) ; 134.5 ; 134.9 (2) (6 CH) ; 140.5 (2 C-S).

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



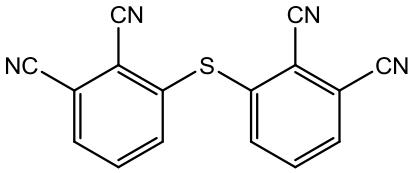
3-Aminophthalonitrile :

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 :

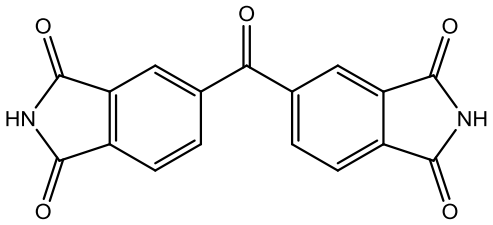
Amine (0.40 g, 2.8 mmoles) was mixed with concentrated hydrochloric acid (8 mL) and ice (20 g), sodium nitrite (0.30 g, 4.3 mmoles) in water (3 mL) was added in one portion. After 1.5 hour at 5°C, the solution was filtered. The diazonium salt solution was added dropwise to a stirred cool solution of 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, ^{4}J = 1.5 Hz, ^{3}J = 7.5 Hz) : **^{13}C NMR (DMSO-d^6) :** 114.5, 115.9 (4 C≡N), 117.3, 117.8 (4 C-CN), 134.2, 135.2, 137.6 (6 CH), 138.7 (2 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.

3,3',4,4'-benzophenonetetracarboxylic diimide **3** :



3,3',4,4'-benzophenonetetracarboxylic diimide :

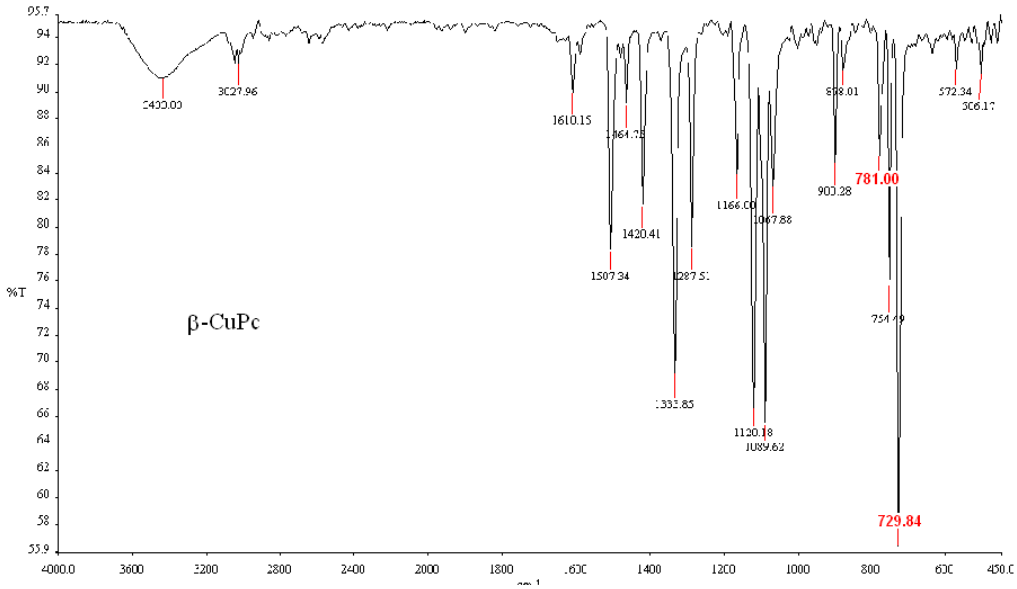
Benzophenone-3,3',4,4'-tetracarboxylic dianhydride (5 mmoles, 0.16 g) was heated under stirring in formamide (5 mL) for 4 hours at 200ºC. After cooling the precipitate was filtered, washed with water and acetone. (90%) **^{1}H NMR (300 MHz, DMSO d^6) :** 11.7 ppm (bs, 2H) ; 8.15 ppm (dd, J=1.4 Hz, J=7.7 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.

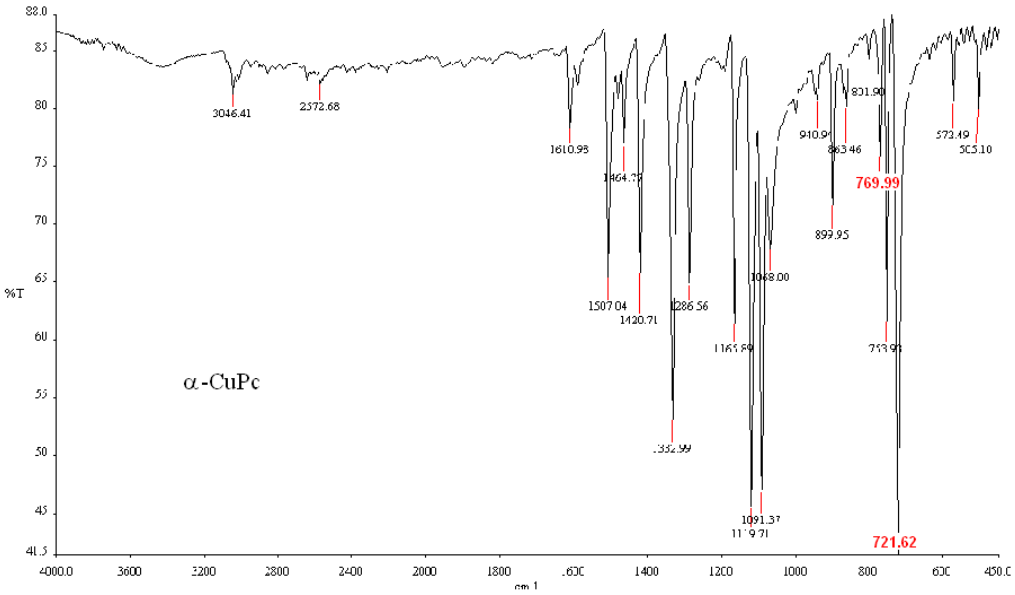
Copper Phthalocyanine Processes

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 %)

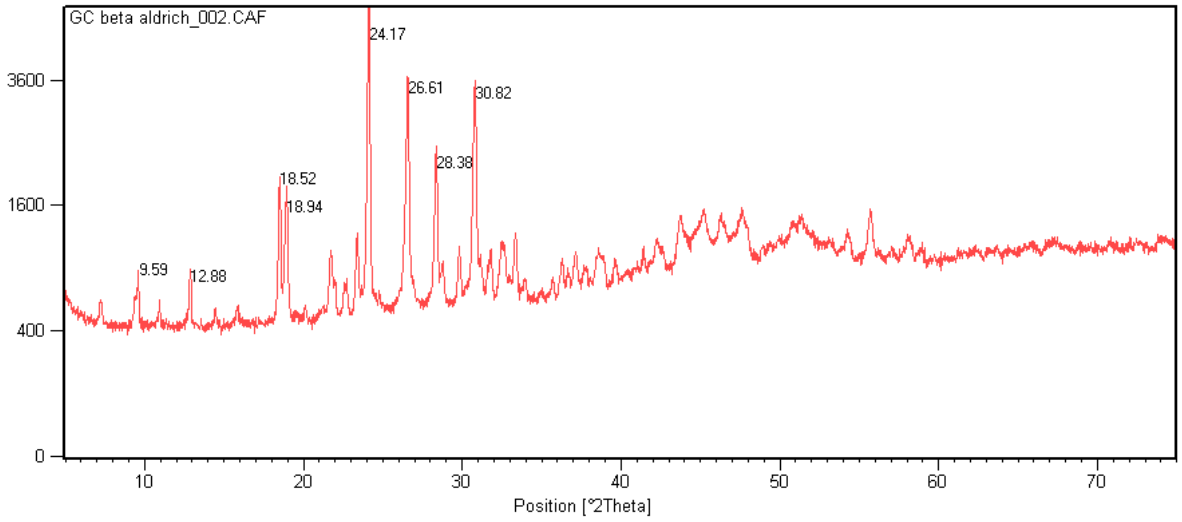
Copper Phthalocyanine from Phthalimide: A mixture of phthalimide (1.47 g, 10 mmoles), copper (II) bromide (0.58 g, 2.6 mmoles), *p*-TsOH.H_2O (0.19 g, 1 mmole) and HMDS (8.30 mL, 40 mmoles) in 0.77 mL of DMF was heated at 100°C for 10 hours. The precipitate was filtered off and washed with water, methanol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

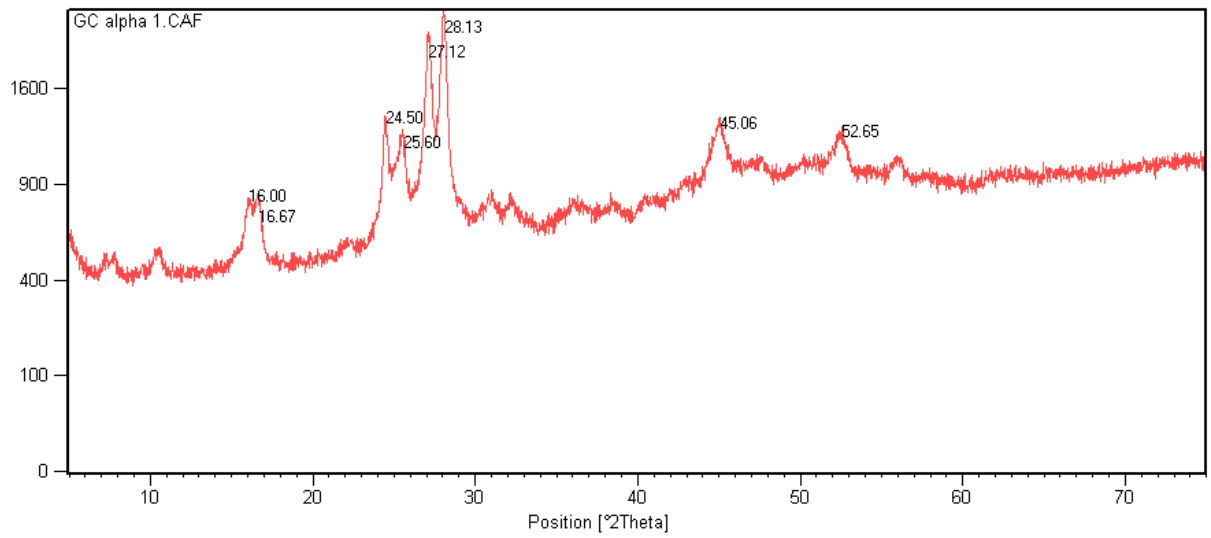
IR spectra of β- and α-Copper Phthalocyanine





PXRD patterns of β- and α-Copper Phthalocyanine





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