# Synthesis of a phthalocyanine derivative containing easily oxidised sterically-hindered phenolic substituents

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A novel phthalocyanine containing four redox-active 3,5-di-*tert*-butyl-4-hydroxyphenyl substituents is readily oxidised in aerated, basified solution to give a complex product mixture; the oxidation is apparently localised on the phenolic moieties without disturbing the structure of the phthalocyanine core.

Phthalocyanines (Pcs) are of continuing interest as organic materials which possess interesting electronic and optical properties.[1] Recent synthetic work has sought to modify the electronic behaviour of the Pc macrocycle by the attachment of redox-active moieties based on ferrocene,[2] fullerene[3] and tetrathiafulvalene.[4] Sterically hindered phenols are readily oxidised to stable radical species (*e.g.* the galvinoxyl radical) and are used as radical scavengers for the stabilisation of monomers, polymers and solvents. They may also undergo further oxidation to form quinones. Previous studies concerning *meso*-tetrakis(3,5-di-*tert*-butyl-4-hydroxyphenyl)porphyrin **1** reveal that cooperative quinone formation occurs rapidly across the porphyrin ring system on addition of base to an aerated solution.[5] This process results in a dramatic distortion of the porphyrin ring system and loss of aromaticity.[6] It is of interest to establish whether similar cooperative processes may occur *via* the related Pc macrocycle. This communication describes the synthesis of a novel Pc derivative containing four 3,5-di-*tert*-butyl-4-hydroxyphenyl (DTBHP) substituents and the results of a preliminary examination of its behaviour under oxidative conditions.

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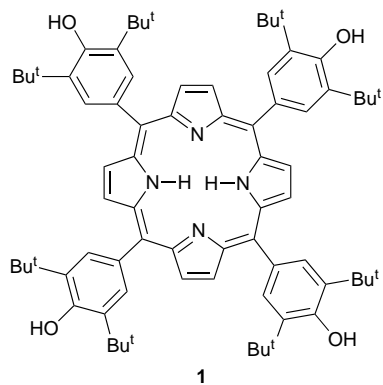
Aromatic nucleophilic substitution of the nitro group of commercially available 4-nitrophthalonitrile **2**, using oxygen, nitrogen or sulfur nucleophiles, is a well established method of preparing phthalonitrile precursors to tetra-substituted Pc derivatives with enhanced solubility.[7] This is exemplified by the reaction between **2** and the anion of 3,5 di-*tert*-butylphenol **3** in DMF which gives 4-(3,5-di-*tert*-butylphenoxy)phthalonitrile **5** in 70–80% yield (Scheme 1). Several previous studies have illustrated the ability of the anion of 2,6-di-*tert*-butylphenol **4** to behave as a carbon nucleophile in the preparation of biphenyl derivatives *via* aromatic nucleophilic substitution.[8]

Encouragingly, we found that the anion of **4** reacts with **2** as a carbon nucleophile efficiently displacing the nitro group to give the novel 4-(3,5-di-*tert*-butyl-4-hydroxyphenyl)phthalonitrile **6** in 75–85% yield. The structure of **6** was assigned using ^{1}H NMR and IR spectroscopy and by a strong bathochromic shift from 345 to 505 nm in the λ_{max} of its UV–VIS absorption spectrum on addition of base, which is characteristic of the formation of a conjugated phenolic anion.† In addition, its biphenyl structure was confirmed by a single crystal X-ray diffraction study. Cyclotetramerisation of phthalonitriles **5** or **6** is catalysed by lithium pentanolate in refluxing pentanol to give Pcs **7** and **8**, respectively, in 10–30% yield. These two isomeric Pcs are each composed of four inseparable regioisomers and give ^{1}H NMR, UV–VIS absorption, IR, fast atom bombardment (FAB) mass spectra and elemental analyses which are consistent with their proposed structures.†

The cyclic voltammetry (CV) of deaerated solutions of Pcs **7** and **8** in CH_2Cl_2 give very similar results consistent with previous CV studies of soluble metal-free Pcs.[9] However, on the addition of excess tetrabutylammonium hydroxide (TBAH), Pc **8** exhibits a strong reversible redox transition ($E_{1/2}$ = 50 mV *vs.* Ag+/Ag) of an intensity consistent with a four-electron oxidative process to give the tetra-phenolic radical species.

The UV–VIS absorption spectra of CH_2Cl_2 solutions of Pc **7** (λ = 701 and 667 nm) and **8** (λ = 715 and 683 nm) both exhibit the characteristic split Q-band of metal-free Pc [Fig. 1(*a*)]. On the addition of an excess of TBAH the Q-band of Pc **7** changes appearance to give a single sharp band at 690 nm [similar to Fig. 1(*c*)] consistent with the formation of a Pc²⁻ anion due to the loss of the two protons from the central cavity. No change in this spectrum is seen over an extended period of time. However, the Q-band of Pc **8** exhibits an initial strong bathochromic shift to 796 nm on addition of the base [Fig. 1(*b*)]. This dramatic shift demonstrates that the deprotonated DBTHP substituents interacts strongly with the Pc macrocycle resulting in a Q-band position which is similar to that shown by naphthalocyanines, of interest as IR-absorbing dyes. If left to stand in aerated conditions the bathochromic shift gradually reduces until, after
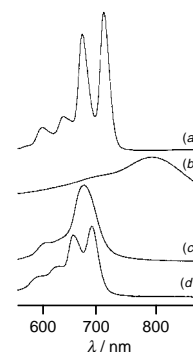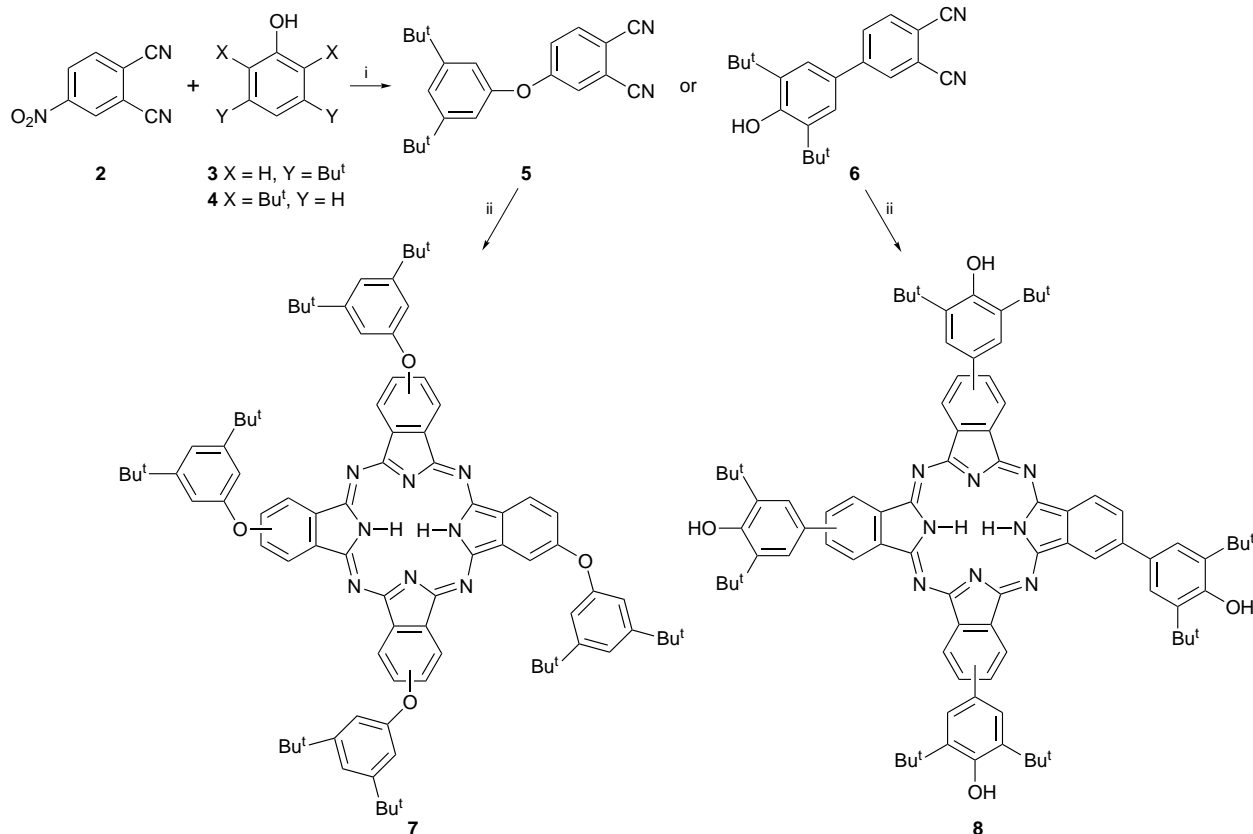

Fig. 1 UV–VIS absorption spectra of Pc **8** in aerated CH_2Cl_2 (*a*) under neutral conditions; (*b*) immediately after the addition of excess TBAH; (*c*) after leaving the solution for 72 h; (*d*) upon addition of excess acetic acid

Scheme 1 *Reagents and conditions*: i, anhydrous K₂CO₃, DMF, 40 °C; ii, C₅H₁₁OLi, C₅H₁₁OH, 135 °C

a period of 2–3 days, a characteristic Pc²⁻ visible absorption spectrum [Fig. 1(*c*)] is obtained ($\lambda = 680$ nm) similar to that observed for the Pc²⁻ anion of **7**. On neutralisation with acetic acid, the familiar split Q-band of a metal-free Pc is regained [Fig. 1(*d*)], although slightly blue-shifted ($\lambda = 700$ and 665 nm) relative to the original Q-band position of **8**. We conclude from these observations that, in contrast to the simple, rapid and cooperative oxidative process observed for porphyrin **1**, the structural integrity of the planar Pc macrocycle is retained and that oxidation is localised on the DTBHP subunits.

TLC and ¹H NMR analysis of Pc **8** subsequent to the oxidation process suggests the formation of a highly complex product mixture from which no discrete compounds could be isolated by chromatography. FAB MS analysis of the product mixture was unhelpful due to the lack of ions with mass greater than 500 Da. However, the IR analysis (KBr disc) of the oxidised material indicates the presence of quinone type functionality ($\nu = 1640$ and 1670 cm⁻¹). Elemental analyses, although irreproducible between different batches of oxidised **8**, indicate the presence of additional oxygen. It is highly likely that the DTBHP substituents undergo the various complex, but well understood, transformations of 4-aryl-2,6-di-*tert*-butylphenols in aerated basic solution.[10] These include the formation of 4-aryl-2,6-di-*tert*-butyl-4,5-epoxy-6-hydroxycyclohex-2-enones, 4-aryl-2,6-di-*tert*-butyl-5,6-epoxy-4-hydroxycyclohex-2-enones and 3-aryl-2,5-di-*tert*-butylcyclopenta-2,4-dienones *via* subsequent decomposition of the initially formed 2- and 4-hydroperoxycyclohexadienone anions. Each resulting Pc molecule would possess a combination of oxidised DTBHP fragments, hence the complex nature of the product mixture.

It is clear from this initial study that the synthesis of novel phthalonitrile precursor **6** allows the preparation of DTBHP containing metal-free or metal ion containing Pc derivatives, with symmetrical or unsymmetrical substitution.[11] Studies of the synthesis and redox properties of these Pcs under deaerated conditions are in progress.

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