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Macrodiscotic triphenylenophthalocyanines

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The first heavily substituted triphenylenophthalocyanines have been synthesised and found to be mesogenic.

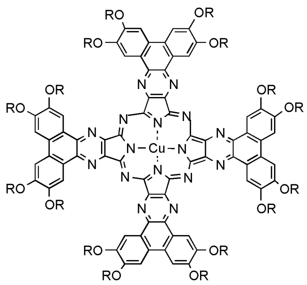
Phthalocyanines are extremely useful and versatile materials.[1] The synthesis of new derivatives has been the subject of widespread research over recent decades with the aims typically being to improve processability (unsubstituted derivatives are typically poorly soluble) and properties. Many substituted phthalocyanines are discotic liquid crystals (a feature which dramatically aids materials processing) and for some time we have been aiming to prepare new derivatives which absorb in the near IR region and maintain liquid crystallinity. To this end we have been interested in the effects of extending the phthalocyanine core[2] and evaluating the properties of the resulting materials.

To date the largest macrodiscotic compound based on a phthalocyanine-type structure is the pyrazinoporphyrazine **1**.[3–5] Synthesis of the parent structure is far more complex and in this paper we report the first heavily substituted triphenylenophthalocyanines **3–5**. Non-planar, 'open' structures **2** have been described by Simon and were found to be mesogenic.[6] Their structures, however, are more closely related (in terms of properties) to the parent phthalocyanines. We expected that planarising the system (formation of triphenylene) would have the effect of changing both the absorption (shift to longer wavelength) and the mesogenic properties.

The synthesis of the novel phthalocyanines was achieved from the precursor dinitriles and, as is often the case in phthalocyanine syntheses, the challenge revolved around preparation of these intermediates (Schemes 1 and 2).

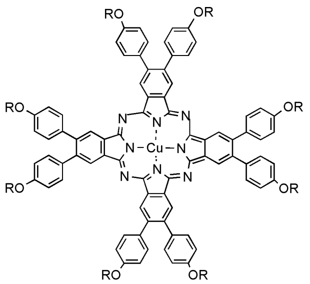
Phthalocyanines **3** and **4** were synthesised following similar routes. Terphenyls **7** and **12** were synthesised by (Suzuki) coupling the (*p* or *m*) hexyloxyphenylboronic acid with 4,5-dibromoveratrole. These intermediates were converted to the corresponding tetraalkoxytriphenylenes (**8** and **14** respectively) using ferric chloride (**13**) or photochemically (**7**).[7] Selective demethylation (lithium diphenylphosphide[8]) and reaction with triflic anhydride gave triphenylene ditriflates which were converted to the required dinitriles by treatment with $Zn(CN)_2$–$Pd_2(dba)_3$–DPPF.[9] Phthalocyanine synthesis was most conveniently accomplished by treating the dinitriles with $Zn(OAc)_2$–DBU in refluxing hexanol.

The dicyanotriphenylene bearing four alkoxide substituents was most conveniently synthesised following an alternative route. 4-Bromoveratrole was coupled with benzeneboronic acid to yield biphenyl **17**. Oxidative coupling with veratrole (using ferric chloride)[10] yielded tetramethoxytriphenylene **18** which was demethylated (HBr–HOAc) and realkylated affording **19**.



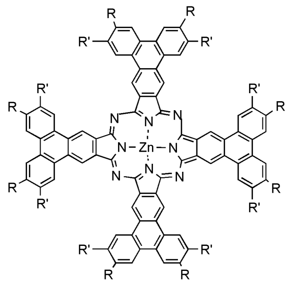
1 [Ref. 3]

R = $C_{10}H_{21}$

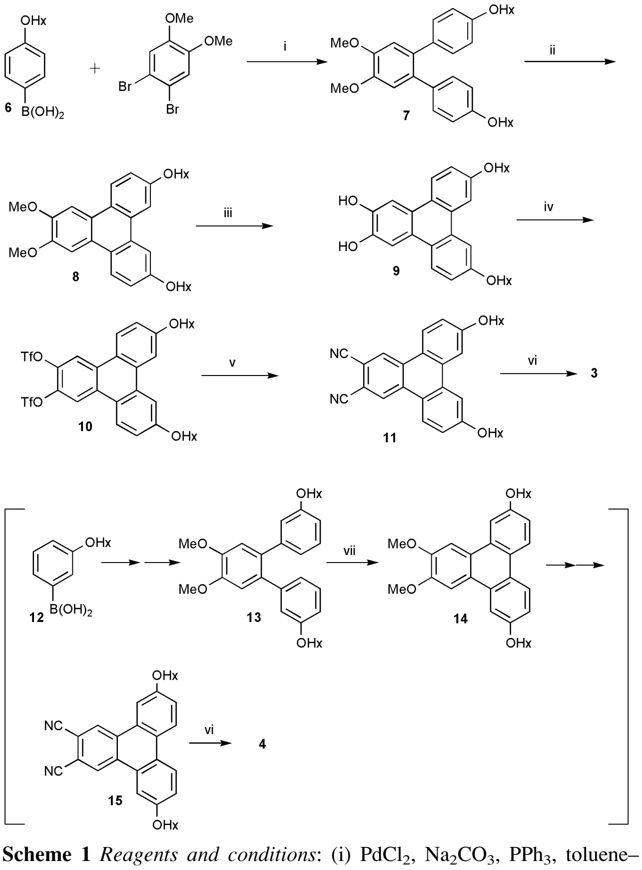


2 [Ref. 6]

R = C_8H_{17}, $C_{10}H_{21}$, $C_{12}H_{25}$, $C_{18}H_{37}$, $CH_2CH(C_2H_5)C_4H_9$



3 R = OC_6H_{13}, R' = H
4 R = H, R' = OC_6H_{13}
5 R = R' = OC_6H_{13}



Scheme 1 *Reagents and conditions*: (i) $PdCl_2$, Na_2CO_3, PPh_3, toluene–EtOH–H_2O, reflux, 24 h, 70% (ii) hν, I_2, benzene, 96 h, 58% (iii) $LiPPh_2$, THF, 75% (iv) Tf_2O, CH_2Cl_2, pyridine, −20 °C, 68% (v) $Zn(CN)_2$, $Pd_2(dba)_3$, DPPF, DMF, 140 °C, 24 h, 28% (vi) DBU, hexanol, $Zn(OAc)_2$, reflux, 24 h, 5% (vii) $FeCl_3$, CH_2Cl_2, 2 h then MeOH, 57%

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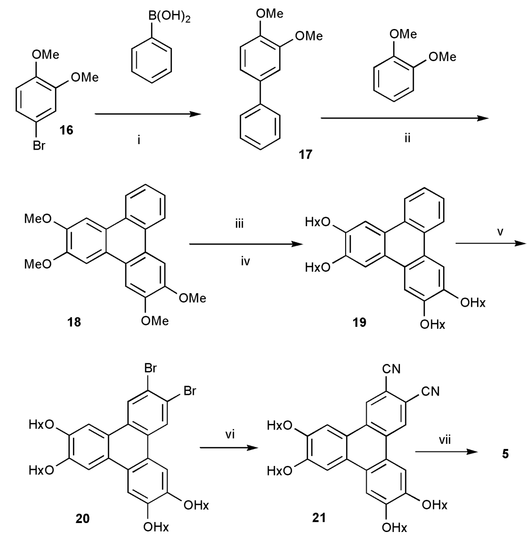

Scheme 2 *Reagents and conditions*: (i) $PdCl_2$, Na_2CO_3, PPh_3, toluene–EtOH–H_2O, reflux, 24 h, 62% (ii) $FeCl_3$, CH_2Cl_2, 2 h then MeOH, 72% (iii) HBr, HOAc, reflux, 10 h, 96% (iv) K_2CO_3, $C_6H_{13}Br$, EtOH, reflux, 24 h, 95% (v) Br_2, CH_2Cl_2, 0 °C, 60% (vi) $Zn(CN)_2$, $Pd_2(dba)_3$, DPPF, DMF, 140 °C, 24 h, 28% (vii) DBU, hexanol, $Zn(OAc)_2$, reflux, 24 h, 8%.

Bromination and reaction of the resulting dibromide **20** with CuCN gave dinitrile **21** which was cyclised to phthalocyanine **5**, again using DBU–$Zn(OAc)_2$–hexanol.

All three phthalocyanines were purified by column chromatography and reprecipitation and gave satisfactory elemental analyses and mass spectra (MALDI). The final yields of the phthalocyanines are relatively low, mostly due to the extensive purification procedures carried out in order to obtain samples of sufficient purity for mesophase characterisation. The materials are soluble in common organic solvents but NMR spectra show broadened signals indicating a high degree of aggregation. Running spectra at elevated temperatures had a marginal effect on resolution. UV–Vis spectra of highly dilute solutions are typical of metallophthalocyanines. λ_{max} is shifted (compared with unsubstituted zinc phthalocyanine) by 50–90 nm due to the extra conjugation (**3** = 748 nm, **4** = 745 nm and **5** = 765 nm). Preliminary investigation of the mesophase behaviour of these macrodiscotic phthalocyanines indicated that all form columnar liquid crystals. Phthalocyanine **2** has a high melting point (270 °C) whereas the isomer **3** melts at 185 °C. Both are liquid crystalline above 300 °C. The most heavily substituted derivative **4** exhibits an extremely wide mesophase range and appears to be liquid crystalline at RT– > 300°C. The samples do not form isotropic liquids at accessible temperatures so characterisation of the mesophase by microscopy was not possible. We assume that columnar mesophases are formed because they are highly viscous.

The syntheses of the first heavily substituted triphenylenophthalocyanines has therefore been achieved. These materials are the largest macrodiscotic phthalocyanines prepared to date. The highly conjugated materials show a high tendency to aggregate and this observation appears to be consistent with the behaviour of neat samples which remain liquid crystalline at temperatures above 300 °C.

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