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Mixed cyclisations giving phthalocyanine–naphthalocyanine hybrids

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ABSTRACT

Mixed cyclisations have been performed to give phthalocyanine–naphthalocyanine hybrids bearing solubilising substituents. Reactivity differences between the two phthalonitrile precursors result in inefficient mixed-macrocyclisation under standard, non-templating conditions leading to predominant formation of symmetrical phthalocyanine. Templated mixed-macrocyclisation leads to the hybrids. However, the reaction proceeds with unexpected selectivity with only one of the possible 2:2 products observed.

Phthalocyanines are important molecular materials because of the potential for such molecules to form the functional component of optoelectronic devices.[1,2] Their use in such applications typically requires a combination of molecular (optical absorption/band gap, redox, etc.) and bulk (processability, self-assembly, mesophase formation, etc.) properties. For this reason a large number of phthalocyanine derivatives have been prepared. Some phthalocyanines are discotic liquid crystals,[3] an important sub-class of liquid crystals to emerge since their discovery around 30 years ago.[4] Phthalocyanine itself can be modified extensively to tune both molecular and bulk properties. Such modifications can focus on a combination of variation of the (organic) core structure (e.g., introduction of substituents to change absorption and/or solubility properties) and central metal ion (more than 70 elements can be introduced).

Extension of the aromatic core has also been investigated and is known to give rise to perturbed properties. In particular, extension of the π-system of the molecule results in longer wavelength electronic absorption (red-shifted spectra) and a number of fused and modified core structures are now known where, for example, the benzene units of parent phthalocyanines are replaced by naphthalene, anthracene or perylene.[5] The intense and tunable electronic absorption of phthalocyanines and related macrocycles has led to investigation of their potential as solar light collectors in energy conversion systems, most notably photovoltaic devices.[6] Ruthenium derivatives have proved particularly promising and we have recently reported convenient methods for controlled synthesis of ruthenated phthalocyanines bearing either one or two replaceable axial ligands.[7]

An ideal solar collector should absorb across the full range of incident irradiation and we reasoned that a simple strategy to broaden and extend the absorption profile of phthalocyanine chromophores would be to prepare π-extended derivatives in which the core symmetry is broken.[8] Our main target molecules were 3:1 phthalocyanine–naphthalocyanine hybrids **1** and **2**, designed to have solubilising alkyl substituents on the three benzenoid units. The remaining naphthalene unit was designed to incorporate either a carboxylic acid functional group (to promote binding to inorganic substrates employed in photovoltaic cells) or a *tert*-butyl group (Fig. 1).

Mixed cyclisation employing a 3:1 ratio of 3,6-dioctylphthalonitrile **3** and 6-*tert*-butylnaphthalene-2,3-dicarbonitrile **4** proceeded smoothly and as expected under the standard conditions commonly employed for synthesis of metal-free phthalocyanines (reflux in pentanol, lithium). Work-up of the crude mixture with acetic acid gave a mixture of the metal-free phthalocyanine products from which the symmetric octa-alkyl phthalocyanine and 3:1 hybrid **5**[9] (5%) were isolated by careful column chromatography (Scheme 1). Hybrid **5** was converted to its zinc derivative **6** by treatment with zinc acetate, and to its ruthenium carbonyl derivative **7** by following our previously reported method.[7] Absorption spectra are red shifted by around 20 nm compared to the corresponding symmetrical phthalocyanines and cover a broader range (e.g., for **5**, absorption covers the range 575–780 nm). Further characterisation of metal-free hybrid **5** surprisingly revealed that it exhibits a stable columnar mesophase below 242 °C. The parent symmetrical phthalocyanines are well known to form liquid crystals,[10] but breaking the molecular symmetry and introduction of the bulky *tert*-butyl group are expected to destabilise or destroy the mesophase behaviour.

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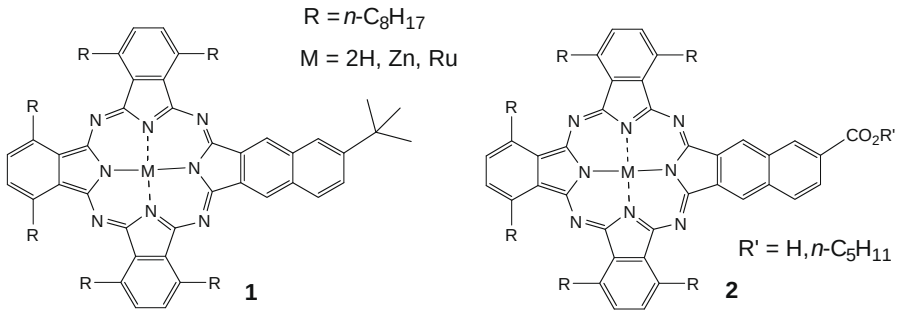
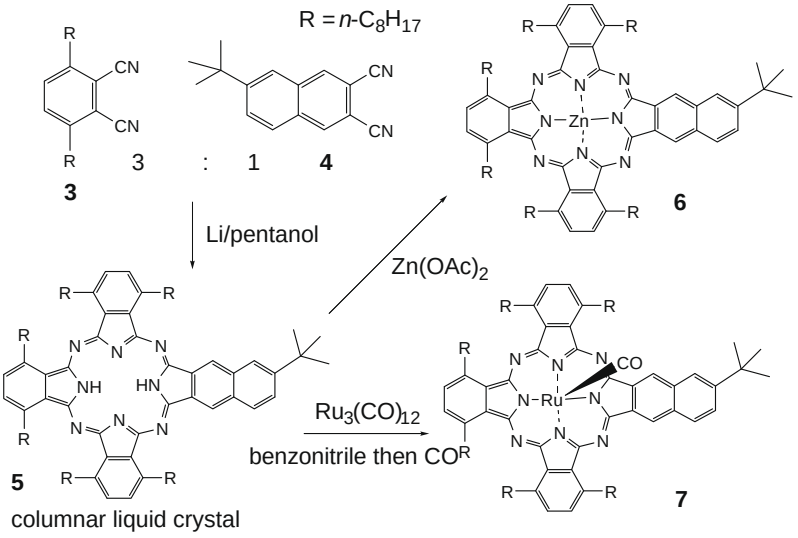


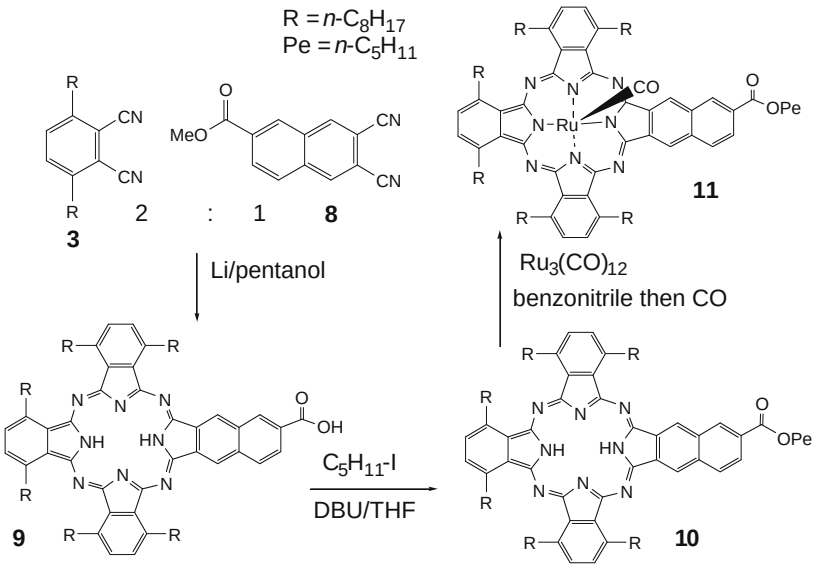
Figure 1. Target phthalocyanine/naphthalocyanine hybrids.



Scheme 1. Synthesis of *tert*-butyl-substituted 3:1 hybrids and metallation.

Attempts to prepare the corresponding 3:1 hybrid between phthalonitrile **3** and naphthalonitrile **8** proved to be less straightforward. Indeed, under the same reaction conditions (**3**:**8** = 3:1, Li/pentanol/reflux) no 3:1 hybrid was formed. Instead, symmetrical phthalocyanine (plus a trace of the symmetrical naphthalocyanine) were the only macrocyclic products observed. This result implies that there exists a significant reactivity difference between the two substrates resulting in preferential consumption of the phthalonitrile to give symmetrical phthalocyanine as the dominant product.

The phthalonitrile/naphthalonitrile ratio was changed (**3**:**8** = 2:1) in order to overcome this reactivity difference and the 3:1 hybrid was indeed obtained (Scheme 2). Characterisation revealed that the material isolated was not the expected ester **10**

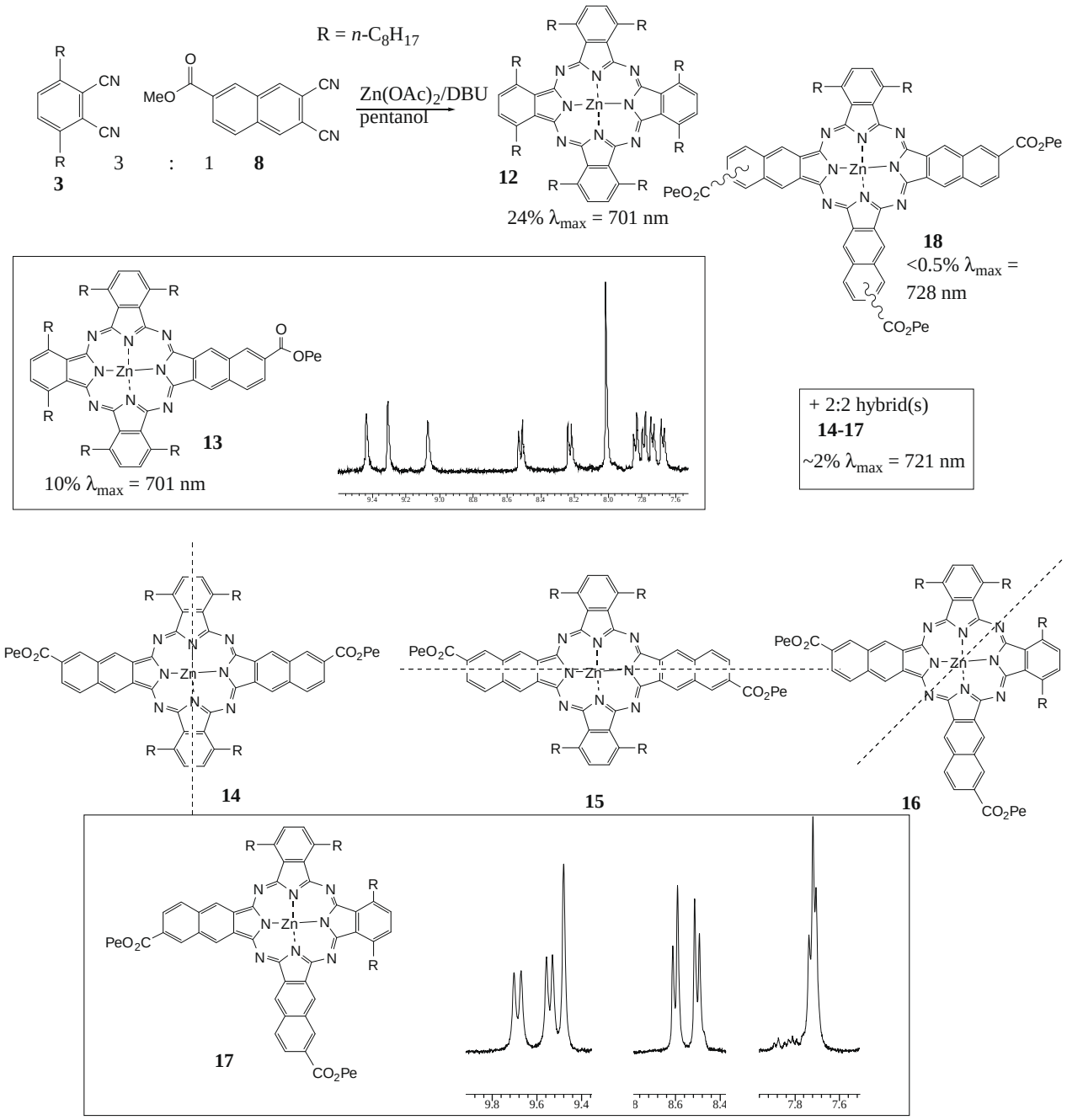


Scheme 2. Synthesis of metal-free 3:1 hybrids bearing carboxyl functional groups on the naphthyl units.

(transesterification is expected under the reaction conditions) but rather the carboxylic acid **9**. Esterification of **9** was achieved smoothly by treatment with iodopentane/DBU in THF, and the resulting ester **10** metallated as before.

Mixed cyclisations under templating conditions[11] gave different results. Cyclisation of a 3:1 mixture of **3**:**8** using zinc as the template [$Zn(OAc)_2$/DBU/pentanol] led to a mixture of hybrids in a ratio closer to that expected statistically. Under these conditions the ester products were isolated. Careful column chromatography allowed their separation and sufficient quantity of the 2:2 hybrid was obtained to permit detailed characterisation. We expected to obtain the product as a mixture of regioisomers **14**–**17** (the other symmetric adjacent isomer is not shown) but ^{1}H NMR spectroscopy revealed that, somewhat surprisingly, a single isomer had been isolated. There is no evidence for the presence of any significant quantity of other 2:2 hybrids. The important region of the ^{1}H NMR spectrum, along with four of five possible isomers **14**–**17** is shown in Scheme 3. Isomers **14**–**16** can be eliminated on symmetry grounds (for each, three singlets and an AB pattern are expected for the naphthalene protons) leaving **17** as the only possible product.

In conclusion, mixed cyclisations have been performed to give phthalocyanine–naphthalocyanine hybrids bearing solubilising substituents. The outcome of the reactions, under standard conditions, depends on the relative reactivity of each dinitrile precursor. Reactivity differences between the two phthalonitrile precursors can therefore result in inefficient mixed-macrocyclisation under standard, non-templating conditions leading to predominant formation of symmetrical phthalocyanine. Templated mixed-macrocyclisation overcomes the reactivity difference to a large extent



Scheme 3. Template synthesis of phthalocyanine/naphthalocyanine hybrids.

and leads to the hybrids. However, in our case the reaction proceeds with unexpected selectivity with only one of the possible 2:2 products observed.

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9. *Hybrid* **5**: liquid crystalline (LC) below 247 °C; ^{1}H NMR (C_6D_6) δ −1.79 (br s, 2H), 0.39 (s, 9H), 0.97–0.77 (m, 18H), 1.69–1.15 (m, 48H), 2.07–1.70 (m, 12H), 2.47–2.17 (m, 12H), 3.98 (m, 2H), 4.11 (m, 2H), 4.43 (m, 4H), 4.51 (m, 4H), 7.60 (m, 2H), 7.70 (m, 2H), 7.81 (s, 2H), 7.83 (d, J = 8.4 Hz, 1H), 8.32 (d, J = 8.4 Hz, 1H), 8.37 (s, 1H), 9.05 (s, 1H), 9.20 (s, 1H); MALDI MS *m/z* isotopic cluster at 1293.0 M^+; $C_{88}H_{124}N_8$ requires: C, 81.68; H, 9.66; N, 8.66%. Found: C, 81.85; H, 9.64; N, 8.28; UV–vis (THF) λ_{max} 744 (log ε = 5.43), 702 (5.42) nm. *Hybrid* **7**: IR 1950 cm^{-1}; ^{1}H NMR (C_6D_6) δ 1.04–0.70 (m, 27H), 1.14–1.03 (m, 36H), 1.73–1.14 (m, 12H), 1.93–1.78 (m, 7H), 2.28–2.14 (m, 5H), 2.55–2.36 (m, 7H), 2.82–2.66 (m, 5H), 4.98–4.74 (m, 12H), 7.79 (d, J = 8.8 Hz, 1H), 7.92–7.85 (m, 6H), 8.49 (d, J = 8.8 Hz, 1H), 8.58 (s, 1H), 10.03 (s, 1H), 10.08 (s, 1H); MALDI MS *m/z* isotopic cluster at 1420.8 M^+, 1393.9 $(M-CO)^+$, 2786.8 $(M-CO+M-CO)^+$; λ_{max} 673 (log ε = 4.68) nm. *Hybrid* **9**: mp >300 °C; IR 1686 cm^{-1}; ^{1}H NMR (THF) δ −2.16–2.44 (br s, 2H), 1.07–0.60 (m, 4H), 1.80–1.02 (m, 14H), 2.31–1.82 (m, 72H), 4.50–3.20 (m, 12H), 7.42 (br m, 1H), 7.49 (d, J = 5.9 Hz, 1H), 7.58 (d, J = 5.9 Hz, 1H), 7.65 (br s, 3H), 7.86 (d, J = 6.6 Hz, 1H), 8.08 (d, J = 6.6 Hz, 1H), 8.14 (s, 1H), 8.41 (s, 1H), 8.68 (s, 1H), 11.78–11.46 (br s, 1H); MALDI MS *m/z* isotopic cluster at 1281.0 $(M+H)^+$; λ_{max} 740 (log ε = 5.08), 703 (5.07) nm. *Hybrid* **10**: mp 290 °C; IR 1716 cm^{-1}; ^{1}H NMR (C_6D_6, 70 °C) δ −1.15–1.64 (br s, 2H), 1.11–0.65 (m, 21H), 1.70–1.09 (m, 50H), 2.06–1.72 (m, 14H), 2.64–2.06 (m, 14H), 4.88–3.80 (m, 14H), 8.02–7.55 (m, 6H), 8.17–8.01 (m, 1H), 8.40 (s, 1H), 9.33–8.54 (m, 3H); MALDI *m/z* isotopic cluster at 1352.1 M^+; λ_{max} 737 (log ε = 5.01), 702 (5.02) nm. Hybrid **13**: mp 292 °C; IR 1720 cm^{-1}; ^{1}H NMR (C_6D_6+C_5D_5N) δ 1.07–0.75 (m, 21H), 1.65–1.15 (m, 50H), 2.04–1.79 (m, 14H), 2.62–2.25 (m, 14H), 4.05 (br t, 2H), 4.27 (br t, 2H), 4.53 (t, J = 6.9, Hz, 2H), 4.70−4.80 (m, 4H), 4.92 (m, 4H), 7.67 (d, J = 7.3 Hz, 1H), 7.73 (d, J = 7.7 Hz, 1H), 7.78 (d, J = 7.3 Hz, 1H), 7.83 (d, J = 7.7 Hz, 1H), 8.01 (s, 2H), 8.22 (d, J = 8.8 Hz, 1H), 8.51 (d, J = 8.8 Hz, 1H), 9.07 (s, 1H), 9.30 (s, 1H), 9.43 (s, 1H); MALDI MS *m/z* isotopic cluster at 1415.0 M^+; λ_{max} 713 (log ε = 5.36) nm. 2:2 *Hybrid* **17**: mp >300 °C; IR 1719 cm^{-1}; ^{1}H NMR (C_6D_6 + C_5D_5N) δ 0.80–0.85 (m, 12H), 0.91 (t, J = 6.2 Hz, 6H), 1.73–1.19 (m, 40H), 1.98–1.79 (m, 4H), 2.20–2.00 (m, 8H), 2.62–2.41 (m, 8H), 4.20–4.90 (m, 12H), 7.68–7.76 (m, 4H), 8.50 (d, J = 8.8 Hz, 2H), 8.60 (d, J = 8.8 Hz, 2H), 9.48, (s, 2H), 9.53 (s, 1H), 9.56 (s, 1H), 9.67 (s, 1H), 9.70 (s, 1H); MALDI MS *m/z* isotopic cluster at 1355.6 M^+; λ_{max} 721 (log ε = 5.15) nm.
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