

# A diphthalocyanino-dehydro[12]annulene

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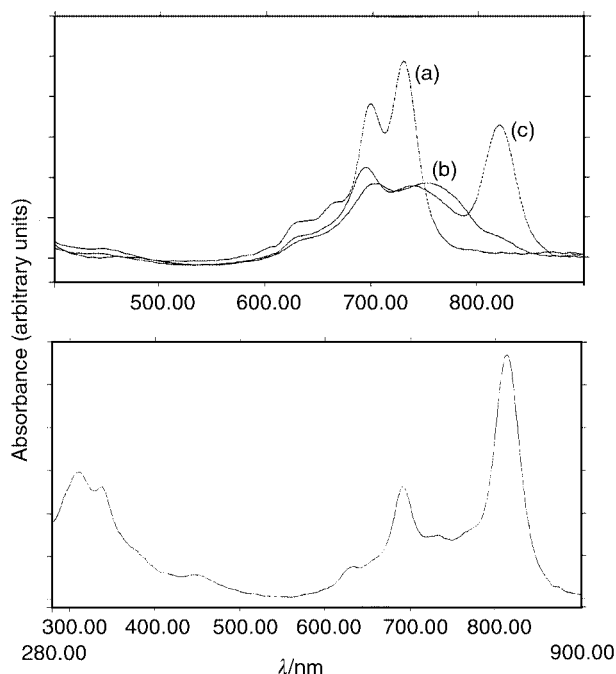
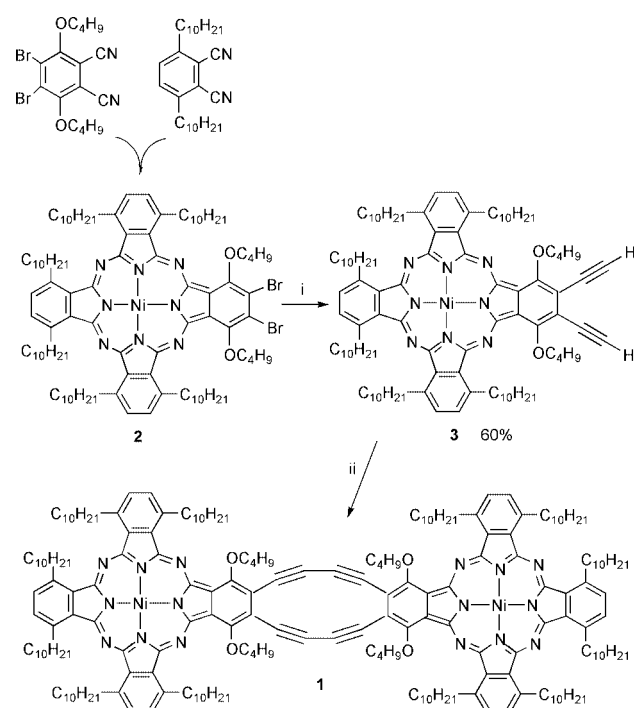
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**A diphthalocyanino-dehydro[12]annulene, synthesised by oxidative coupling of a dialkynylphthalocyanine, has been characterised by mass spectrometry and UV–VIS spectroscopy and shown to undergo thermal oligomerisation.**

Phthalocyanines (Pcs) are important functional materials, their  $18\pi$  electron system providing the basis for their characteristic photophysical, optoelectronic and conductometric properties.<sup>1</sup> More complex structures such as covalently linked binuclear Pc structures are attracting attention because of interesting effects arising from the further extension of the  $\pi$  conjugation.<sup>2</sup> Formally planar structures in which two Pc cores share a common benzene ring have been characterised satisfactorily<sup>3</sup> and applications of palladium coupling reactions have provided access to alkynyl Pcs<sup>4–6</sup> of which some monoalkynyl derivatives<sup>6</sup> have been coupled to give both ethynyl and butadiynyl linked Pcs. These coupling methods are here applied to the synthesis of the first example of a diphthalocyanino-dehydroannulene **1** which is highly substituted to promote solubility in organic solvents. A report that annulenes are polymerisable at a diyne unit<sup>7</sup> indicates that phthalocyanino-dehydroannulenes could act as useful precursors for the synthesis of novel phthalocyanine network polymers. Preliminary studies of the thermolysis of **1** are described.

The synthesis of **1** is summarised in Scheme 1. The principal features are that the dehydroannulene ring is constructed in the last stage, requiring a non-uniformly substituted Pc as precursor. The latter is the dibromo derivative **2**,† obtained by a conventional mixed condensation of 3,6-didecylphthalonitrile<sup>8</sup> and 3,6-dibutoxy-4,5-dibromophthalonitrile<sup>9</sup> (ratio 6:1). Stille

coupling,<sup>10</sup> converted **2** into **3**.† The conversion of **3** into **1** was achieved by copper(II) acetate mediated oxidative coupling in dry THF–pyridine–methanol (1:1:0.25). The reaction was investigated under various conditions, its progress monitored by visible region spectroscopy. Fig. 1 (top) shows the spectrum of **3**, line (a), with the visible region (Q-band) absorptions at 698 and 729 nm. The spectrum of the reaction mixture after 20 min at 50 °C under an argon atmosphere shows a broadened spectrum, line (b), with prominent peaks at  $\lambda_{\text{max}}$  701 and 756 nm. After further time, there is a gradual appearance of a new peak at 822 nm, whose intensity maximises after 48 h. This same absorption band envelope was also obtained in a separate coupling reaction of **3** (39 mg) after 8 h at 80 °C, Fig. 1 (top), line (c). The crude reaction products were filtered through silica (eluent: light petroleum (bp 40–60 °C)–THF, 9:1) to remove copper salts and polymeric material. MALDI-TOF MS of the filtrate gave a base peak corresponding to **1** with smaller peaks attributable to a cyclic trimer and cyclic tetramer. Size exclusion chromatography failed to separate the mixture. However, purification by repeated column chromatography over silica (eluent: light petroleum (bp 40–60 °C)–THF, 19:1) afforded **1** as the major fraction (9.5 mg); MALDI-TOF showed an isotopic cluster at  $m/z$  3206 corresponding to a singularly charged molecular ion. Scanning to higher mass gave no indication of higher molecular weight species. The high resolution FT-ICR MS of **1** using electrospray ionisation in THF confirmed the structure. The base signal corresponds to the doubly charged  $M^{2+}$  ion at  $m/z$  1601.1211 (requires 1601.1235),



**Fig. 1** UV–VIS spectra: (top) line (a), compound **3** as a solution in toluene; line (b), spectrum (toluene) of oxidative cross-coupling product from **3** after 20 min at 50 °C; line (c), the oxidative cross-coupling product from **3** after 8 h at 80 °C. (Bottom) spectrum of **1** as a solution in cyclohexane, showing the split Q-band. There is also evidence of splitting of the Soret band in the UV region.

isotopic distribution showing a mass difference between each peak of 0.5 u. Signals are also present for  $M^+$  at  $m/z$  ca. 3206 (poorly resolved) and  $M^{3+}$ ,  $m/z$  1067.4227 (requires 1067.4157). The spectrum also indicates the presence of aggregated structures. A peak cluster at  $m/z$  ca. 2138 corresponds to a triply charged two molecule aggregate of **1** and a very weak peak at  $m/z$  ca. 2400 corresponds to a quadruply charged trimeric aggregate.

Aggregation is also apparent from the  $^1\text{H}$  NMR spectrum. Thus unlike the spectra of **2** and **3**, the spectrum of **1** (4.5 mg per 0.5 ml benzene- $d_6$ ) shows broadening of the signals for the aromatic protons, and the  $-\text{OCH}_2$  and benzylic protons. Addition of pyridine- $d_5$  failed to inhibit aggregation at this concentration. Aggregation of **1** implies the possibility that  $\pi$ - $\pi$  interactions lead to a supramolecular structure involving Pc units stacking to encapsulate a  $\pi$  electron rich channel formed by the dihydroannulene units. At higher dilution, (ca. 0.9 mg per 0.5 ml benzene- $d_6$ ), and at 40 °C the  $^1\text{H}$  NMR spectrum is better resolved. Apart from aliphatic protons, there are overlapping signals for the aromatic protons, an 8 proton triplet at  $\delta$  4.91 ( $\text{OCH}_2$  protons), a multiplet for 8 benzylic protons at  $\delta$  4.76 and a 16 proton multiplet for the remaining benzylic protons at  $\delta$  4.62.

The Q-band absorption for **1** is split,  $\lambda_{\text{max}}$  822 and 691 nm, Fig. 1 (bottom). This is expected for metallated macrocycles of lower symmetry than  $D_{4h}^{11}$  and is indeed observed for compounds **2** and **3**. However, the splitting is much more significant for compound **1**. A sample of **1** was heated on a hotstage and analysed by visible region spectroscopy. After heating for 5 min at 220 °C, the solution phase spectrum of the material shows reduction in absorbance of the two main components of the Q-band and growth of a broad band between them. Continued heating gives a sample whose spectrum shows an irreversible disappearance of the original bands and a featureless band envelope in the region 680–820 nm. The MALDI-TOF spectrum of the product shows broadened high molecular mass clusters corresponding to multiples of  $m/z$  3206, the highest centered at  $m/z$  ca. 19200. This provides a clear indication that oligomerisation has occurred. The potential for developing large and potentially well organised phthalocyanine networks from these and related materials is under investigation.

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## Notes and references

† Compound **2**: found C 70.40, H 8.90, N 6.30.  $\text{C}_{100}\text{H}_{150}\text{N}_8\text{O}_2\text{Br}_2\text{Ni}$  requires C 70.04, H 8.82, N 6.53%.  $^1\text{H}$  NMR (300 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  7.82 (s, 4H), 7.81 (s, 2H), 4.75 (t, 4H,  $J$  7.5 Hz), 4.66–4.57 (3 overlapping t, 12H), 2.34–2.17 (m, 16H), 1.92–1.11 (m, 88H), 0.95 (t, 6H,  $J$  7.4 Hz), 0.87–0.80 (m, 18H); UV–VIS ( $3.68 \times 10^{-6}$  M in toluene, log  $\epsilon$ ) 1716 (5.10), 698 (5.03), 636 (4.39) nm; MS (FAB): isotopic cluster at  $m/z$  1716  $[\text{M} + \text{H}]^+$ ; requires 1715.84.

Compound **3**: found C 76.99, H 9.56, N 6.98.  $\text{C}_{104}\text{H}_{152}\text{N}_8\text{O}_2\text{Ni}\cdot\text{CH}_3\text{OH}$  requires C 77.03, H 9.60, N 6.84%.  $^1\text{H}$  NMR (270 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  7.81–7.78 (m, 6H), 4.83–4.76 (m, 8H), 4.61–4.56 (m, 8H), 3.53 (s, 2H), 2.33–2.21 (m, 16H), 1.93–1.11 (m, 88H), 0.96 (t, 6H,  $J$  = 7.4 Hz), 0.92–0.81 (m, 18H). UV–VIS ( $2.51 \times 10^{-6}$  M in toluene, log  $\epsilon$ ) 1729 (4.99), 698 (4.88), 666 (4.44), 628 (4.23) nm; MS (FAB): isotopic cluster at  $m/z$  1606  $[\text{M} + \text{H}]^+$ , requires 1605.1.

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