Phthalocyaninodehydroannulenes

Michael J. Cook* and Martin J. Heeney[a]

Abstract: 4-Bromo- and 4,5-dibromo-3,6-dibutoxyphthalonitrile have been prepared and treated with 3,6-didecylphthalonitrile in cross tetramerisation reactions in the presence of nickel acetate to afford monobromo- and dibromo-dibutoxyhexadecylphthalocyaninato nickel(II) complexes. Sonogashira and Stille coupling reactions on these compounds displaced the bromine substituents by ethynyl groups. Oxidative coupling of the monoethynyl derivatised nickel phthalocyanine afforded a butadiynyl-linked dinuclear phthalocyanine. The corresponding coupling reaction of the diethynylated phthalocyanine gave a mixture of phthalocyaninodehydroannulenes. Separation of the mixture yielded the diphthalocyaninodehydro[12]annulene as the major product. Electrospray mass spectrometry provides evidence for its aggregation in solution. The corresponding cyclic trimer, the triphthalocyaninodehydro[18]annulene, has been identified as a minor product. Both compounds show a large splitting of the Q-band absorption in the visible region spectrum. Most of the mononuclear phthalocyanine precursors exhibit discotic liquid crystal behaviour. The diphthalocyaninodehydro[12]annulene also enters a mobile phase on heating, but undergoes an irreversible change at 220 °C. MALDI-TOF mass spectrometry of the product reveals that the compound undergoes oligomerisation at this temperature.

Keywords: annulenes · liquid crystals · phthalocyanines · phthalocyaninoannulenes

Introduction

Phthalocyanines (Pcs) are macrocyclic compounds whose 18 π electron system provides the basis for their remarkable photophysical, optoelectronic and conductiometric properties.[1] The compounds have a characteristic bright blue-green colour arising from an intense $\pi-\pi^*$ transition in the visible region, the Q-band, a property widely exploited for well over 60 years in the dye and pigment industry.[2] More recently, phthalocyanines have made an impact in "high tech" areas, as exemplified by their use as the charge carriers in electrophotography[3] and as the dye component in optical data storage systems.[4] Furthermore, their properties have been identified as having potential for exploitation in a number of other fields including gas sensing,[5] photovoltaic cells,[6] optical limiting[7] and the photodynamic therapy of cancer.[8] The versatility of these macrocycles has led to the development of more elaborate derivatives. In particular, attention has been given to devising means whereby the π system is extended or distorted. Compounds containing two Pc cores that share a common benzene ring have been synthesised and provide interesting, elongated planar structures.[9] The last few years has also seen the successful application of palladium-catalysed coupling reactions in phthalocyanine synthesis, and this has provided access to alkynyl Pcs[10–13] of which some monoalkynyl derivatives[13] have been oxidatively coupled to give "dinuclear" Pcs linked through an ethynyl or butadiynyl moiety. Examples of some of these compounds and related structures have interesting NLO effects.[14]

The research described herein exploits similar coupling chemistry to synthesise yet more complex structures in which Pc moieties are conjugated through fusion to a dehydroannulene, a ring system which is currently attracting a resurgence of interest in its own right.[15, 16] The oxidative coupling step (Scheme 1) provides a diphthalocyaninodehydro[12]annulene

Scheme 1. A schematic representation of the oxidative coupling of a diethynylphthalocyanine into a dehydroannulene; *n* is an integer.

($n=1$ in Scheme 1) as the major product. A minor product has been identified as the corresponding triphthalocyaninodehydro[18]annulene ($n=2$). Both compounds have been shown to undergo oligomerisation, apparently by reaction at the dialkynyl moiety.

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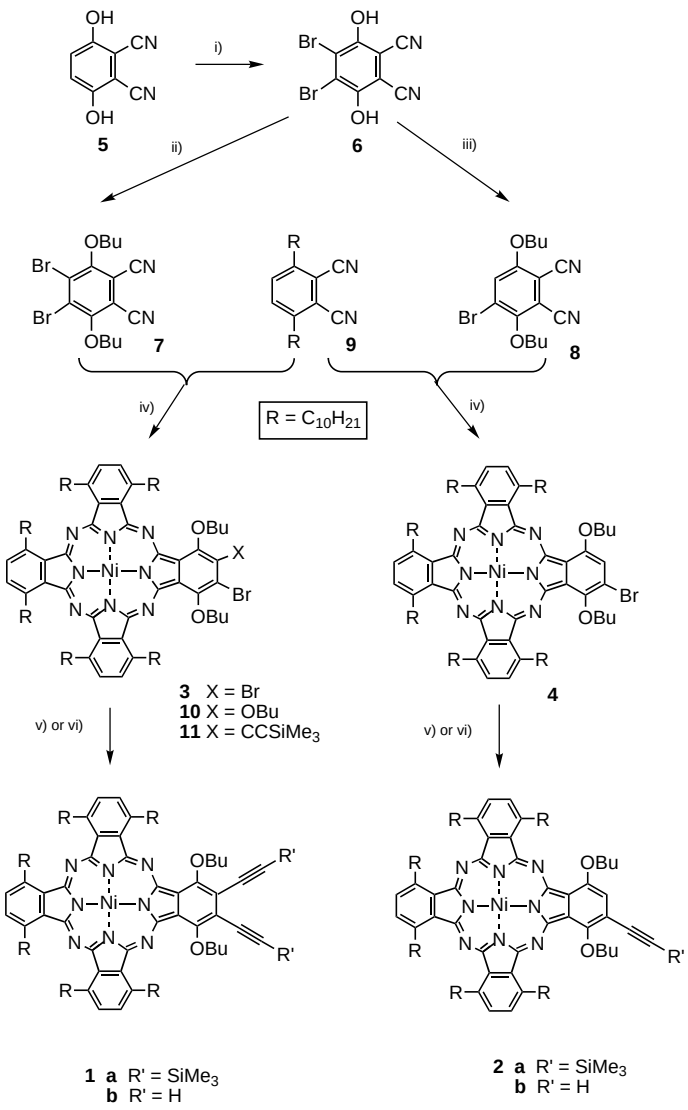
Results and Discussion

Synthesis

General considerations: The chemistry represented in Scheme 1 requires a phthalocyanine that carries two adjacent ethynyl groups on one of the four benzenoid rings. Hitherto, Leznoff and co-workers[12] have reported the synthesis of an octaalkynylphthalocyanine (with two alkynyl groups on all four benzenoid rings) from dialkynylphthalonitrile, the latter synthesised from the corresponding diiodophthalonitrile. These authors commented upon the phthalocyanine's propensity to self aggregate. In the present work, structure **1** (TMS-protected (**1a**, TMS = trimethylsilyl) or unprotected (**1b**), Scheme 2) was designed as a key synthetic intermediate. It has a number of substituent chains in the nonperipheral (1, 4, 8, 11, 15, 18, 22, 25) sites designed both to limit aggregation and to promote solubility in organic solvents.[17] As a model for the subsequent oxidative coupling reaction, we also required the corresponding monoalkynyl phthalocyanines **2a** and **2b**. Access to **1** and **2** was sought from the corresponding di- and mono-bromo analogues **3** and **4**, respectively (Scheme 2). Therefore, compounds **3** and **4** provided the first synthetic targets.



Scheme 2. Synthetic pathway to the required diethynylated phthalocyanine intermediates **1a** and **1b** and the monoethynylated phthalocyanine analogues **2a** and **2b**. R = decyl throughout. i) NBS, $Na_2S_2O_5$. ii) DIAD, Ph_3P, BuOH. iii) K_2CO_3, BuI. iv) LiOBu/BuOH, $(AcO)_2Ni.4H_2O$. v) For **3** → **1a** (and **11**) and **4** → **2a**: HCC-$SiMe_3$, $[Pd(PPh_3)_2Cl_2]$, Ph_3P, CuI. vi) For **3** → **1b** and **4** → **2b**: HCC-$SnBu_3$, $[Pd(PPh_3)_4]$.

*Synthesis of brominated Pcs **3** and **4***: Compounds **3** and **4** are examples of so-called 3:1 phthalocyanines, that is, derivatives in which three of the benzenoid rings have common substituents and the fourth bears different substituents. Such compounds can, in principle, be prepared by several methods;[14, 18] here we have utilised the cross-cyclotetramerisation approach, the reaction together of two appropriately substituted phthalonitriles. The precursors used for the synthesis of **3** and **4** are outlined in Scheme 2. The synthetic pathway commences with the bromination of 2,3-dicyanohydroquinone **5** to afford the dibrominated product **6.** In our hands the use of Guenther's method,[19] bromine in acetic acid, provided a product which gave a low analysis for bromine. However, bromination of **5** by using *N*-bromosuccinamide (NBS),[20] followed by sodium metabisulfite reduction of the 2,3-dibromo-4,5-dicyanobenzoquinone so-formed, gave **6** in 66% yield. Alkylation of compound **6**, unexpectedly and fortuitously, provided access to both **7** and **8**. Hence iodobutane in the presence of potassium carbonate in methyl ethyl ketone (MEK) gave a mixture of **7** (6%) and **8** (39%). The latter was formed exclusively (42%) by delaying addition of iodobutane to the basic solution. This implies that the role of the base is to eliminate HBr from **6**, presumably via its tautomer. The resulting monobromobenzoquinone may then be reduced back to the monobromohydroquinone, which then undergoes conventional Williamson's ether synthesis. Conditions could not be found which favoured the formation of **7** over **8** in this type of alkylation reaction. Instead, compound **7** was obtained conveniently and in satisfactory yield (84%) from **6** by using Mitsunobu conditions.

Mixed cyclotetramerisation of **7** and **9** ($R = C_{10}H_{21}$),[21] ratio 1:9, was undertaken by using lithium butoxide in butanol in the presence of nickel acetate. Chromatographic separation readily removed the self condensation product of **9**, namely 1,4,8,11,15,18,22,25-octadecylphthalocyaninato nickel(II), as the first fraction. The second fraction contained two components which were separated on a second column. One proved to be the required compound **3**, identified by a cluster at 1714 D in the low-resolution FAB-mass spectrum, elemental analysis and an ^1H NMR spectrum, which were consistent with the expected structure. The second was identified as compound **10** on the basis of elemental analysis and the MALDI-TOF mass spectrum. The latter gave a signal for the molecular ion at 1707 D; FAB-MS showed a cluster corresponding to $[M - C_4H_9O]^+$. ^{13}C NMR confirmed the presence of three different butoxy groups in the molecule.

The formation of **10** was unexpected; phthalocyanines formed from 3,6-dialkoxy-4,5-dichlorophthlonitrile show evidence of *ipso* displacement of the alkoxy group by alkoxide derived from the solvent, but not displacement of the halogen.[22] Attempts to convert **3** into **10** under the conditions of the cyclotetramerisation reaction failed; this suggests that

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the butoxy group displaced the bromine atom on the phthalonitrile **7** prior to cyclisation. Subsequent preparations of **3** were performed by using either 0.5 equivalents of lithium butoxide in butanol, or NH_3 in DMAE to suppress formation of undesired **10**. No evidence of bromide displacement was found during the corresponding cross cyclotetramerisation of **8** and **9** to give **4** although not all components of the product mixture were identified systematically.

Synthesis of ethynylated Pcs ***1a***, ***1b***, ***2a*** *and* ***2b***: The conversions of **3** and **4** into the ethynylated compounds were investigated by using both the Sonogashira coupling method,[23] which led to the TMS-protected derivatives **1a** and **2a** (TMS = trimethylsilyl), and the Stille procedure,[24] which led directly to the unprotected compounds **1b** and **2b**.

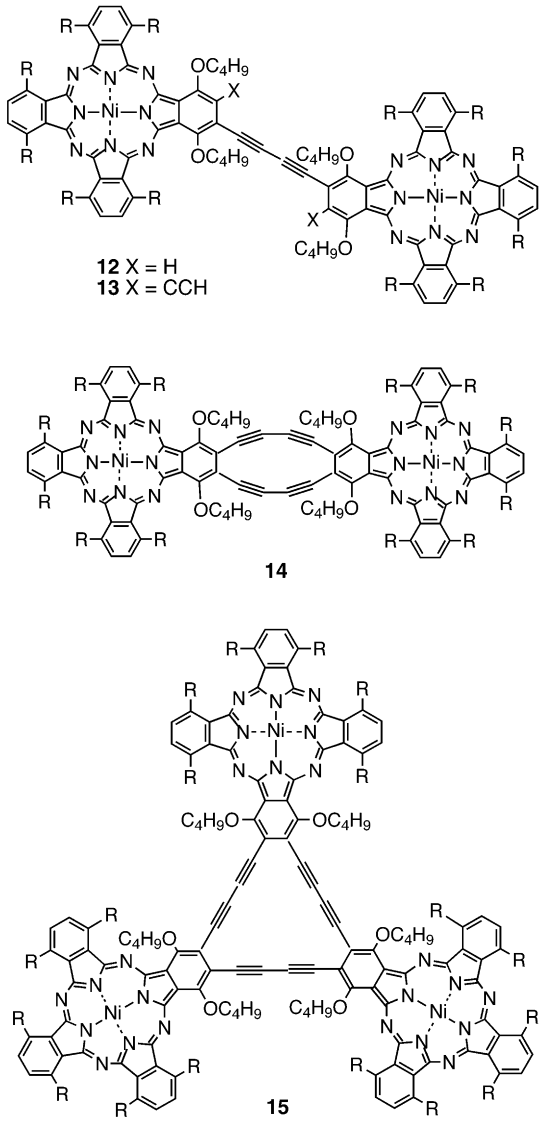
Sonogashira coupling was first applied to **4** with Et_3N as solvent. The compound was treated with trimethylsilylethyne (6 equivalents) at 80 °C for 36 hours in the presence of $[Pd(PPh_3)_2Cl_2]$ (20 mol %) and CuI (30 mol %) with additional catalyst added after 24 h. No cross coupling occurred. However, change of solvent to THF/Et_3N (5:1), an increase in the amount of CuI (39 mol %) and addition of PPh_3 satisfactorily converted **4** into the TMS-protected ethynyl Pc **2a**. This was obtained in 62 % yield after chromatographic purification. The product gave a cluster corresponding to the molecular ion at 1653 D in the FAB mass spectrum and a ^{1}H NMR signal at $\delta = 0.49$ for the nine trimethylsilyl protons. Stille coupling of **4** with tributyl(ethynyl)tin and $[(Ph_3P)_4Pd]$ as catalyst, stabilised by added Ph_3P and lithium chloride, was less satisfactory, affording **2b** in 48 % yield. The compound was characterised by elemental analysis and ^{1}H NMR spectroscopy.

The Sonogashira conditions used above were applied to the conversion of **3** into **1a**, but with only limited success. Despite varying conditions, the required product **1a** was never obtained in a yield greater than 35 % and was always accompanied by the incompletely reacted compound **11.** Compound **1a** was identified by a cluster at 1747 D in the MALDI-TOF mass spectrum and a characteristic 18 proton singlet in the ^{1}H NMR spectrum for the trimethylsilyl protons. ^{13}C NMR spectroscopy provided further confirmation of the structure. All 16 of the expected aromatic ^{13}C signals were well resolved and the two ethynyl carbons gave signals at $\delta =$ 104.74 and 100.97. Deprotection of **1a** by using aqueous KOH in THF/methanol medium afforded **1b** in 79 % yield. This was characterised by a cluster at 1606 D in the FAB mass spectrum, elemental analysis and ^{1}H and ^{13}C NMR spectra, which showed signals fully consistent with the structure given.

The Stille coupling procedure, used above, satisfactorily converted **3** directly into **1b** in 60 % yield. Hence, in this case Stille coupling offered a significant improvement over the Sonogashira method in terms of overall yield. Furthermore, there was less difficulty in separating the fully and partially coupled product, which required careful chromatography in the case of the Sonogashira procedure.

In summary, the coupling methods described above provided satisfactory stocks of **2a** and **1b** for oxidative coupling experiments.

Oxidative coupling of 2a and 1b: Deprotection of **2a** to give **2b** and the subsequent copper-mediated coupling of **2b** into the butadiynyl-linked dinuclear phthalocyanine **12** (Scheme 3),



Scheme 3. Structures of compounds; R = decyl throughout. Compound **12** is obtained from **2a** via **2b**. Compounds **14** and **15** are recovered from the oxidative coupling of **1b**. Compound **13** is an intermediate in the conversion of **1b** into **14** and **15**.

was undertaken in one pot. The preferred conditions utilised potassium carbonate and copper(II) acetate in dry THF/pyridine/methanol (3:1:1). Compound **12**, obtained in 61 % yield, gave a MALDI-TOF mass spectrum showing a cluster at 3161 D and a satisfactory elemental analysis. The ^{1}H NMR spectrum ([D_6]benzene) was broadened at room temperature, but aggregation was sufficiently disrupted at 50 °C for the spectrum at this temperature to show signals consistent with the structure given. In particular the two types of butoxy groups were apparent from the two triplets for the $-CH_2O$ protons at $\delta = 5.03$ and 4.46.

Though the synthesis of **12** was undertaken as a model study for the main theme of the work, its isolation provided a novel example for the limited number of butadiynyl-linked dinu-

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clear phthalocyanines currently known.[13] It is distinguished from those reported previously during the development of this class of compound by Torres' group in so far as the substitution pattern here ensures that the product is obtained as a single isomer. The product also bears alkoxy groups, substituents known to cause a bathochromic shift of the Q-band. The Q-band is split: $\lambda_{max} = 702$ and 752 nm. Split Q-bands are expected for metallated macrocycles of lower symmetry than D_{4h}[25] and are indeed observed for all of the mononuclear precursor phthalocyanines prepared in this study, see Table 1. However, for **12** the splitting is much greater, compare with the precursor **2**, $\lambda_{max} = 700$ and 722 nm,

Table 1. UV/Vis spectroscopic data of solutions (in toluene).

	2- and 3-substituents	λ_{max} [nm] ($\log \varepsilon$)
1a	$CCSiMe_3$, $CCSiMe_3$	732 (4.99), 702 (4.95)
1b	CCH, CCH	729(4.99), 698 (4.88)
2a	$CCSiMe_3$, H	722 (5.09), 700 (5.02)
2b	CCH, H	721 (5.07), 701 (5.01)
3	Br, Br	716 (5.10), 698 (5.03)
4	Br, H	714 (5.10), 700 sh.
10	Br, OBu	714 (5.21), 698 sh.
12	butadiynyl (dinuclear Pc)	752 (5.43), 702 (5.27)
14	dehydro[12]annulene	823 (5.32), 691 (4.93)
15	dehydro[18]annulene	780, 698[a]

[a] Insufficient material available for a quantitative evaluation of ε.

Table 1. Large splittings have been reported for other butadiynyl-linked dinuclear phthalocyanines with the notable exception of a nickel-containing derivative.[13]

Oxidative coupling of **1b** mediated by copper(II) acetate in THF/pyridine/methanol (4:4:1) was investigated over a variety of conditions and was monitored by visible-region spectroscopy. Compound **1b** exhibits a split Q-band absorption, $\lambda_{max} = 698$ and 729 nm (Figure 1, top, line i). The spectrum of the reaction mixture taken after 20 minutes at 50 °C is broadened and there are prominent peaks at $\lambda_{max} =$ 701 and 756 nm. These maxima are closely similar to the Q-band absorptions of compound **12**, see above, and are consistent with the presence of the partially coupled intermediate **13** (Scheme 3). Continuation of the reaction transformed the spectrum and led to a new absorption at 822 nm. The intensity of this band did not increase further after 48 hours (Figure 1, top, line ii). The same spectrum was also obtained from the product mixture of a separate coupling reaction of **1b** (39 mg) after eight hours at 80 °C. The crude reaction products were filtered through silica (eluent: petrol/THF 9:1) to remove copper salts and polymeric material. The MALDI-TOF mass spectrum showed clusters centred at 3206 D (100 %), and lower intensity clusters at 4809 and 6412 D. These correspond to a cyclic dimer, trimer and tetramer, that is, $n = 1$, 2 and 3 in Scheme 1. Preparative size-exclusion chromatography with Sephadex™ LH-20 did not effect a satisfactory separation. However, a partial separation over silica (petrol/THF 19:1) afforded a larger fraction (9.5 mg) and a smaller fraction (3.2 mg). A much smaller third fraction was discarded.

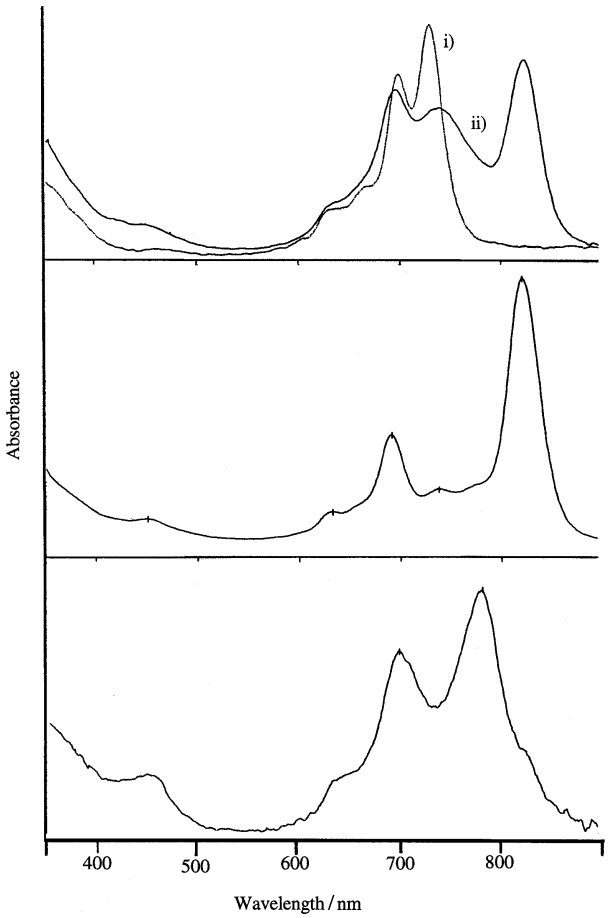

Figure 1. UV-visible spectra (toluene) measured in 1 mm pathlength cells. Top: Line i): compound **1b**; line ii): spectrum of the oxidative cross coupling product from **1b** after 48 h at 50 °C. Middle: Spectrum of **14**. Bottom: Spectrum of **15**.

The first fraction, $\lambda_{max} = 691$ and 822 nm (Figure 1, middle), gave a MALDI-TOF mass spectrum showing an isotopic cluster at 3206 D which corresponds to a singly charged molecular ion of the diphthalocyaninodehydro[12]annulene (**14**, Scheme 3). Scanning to 6500 D gave no indication of higher molecular weight species. The second fraction, $\lambda_{max} =$ 698, 783, shoulder at 822 nm, gave two clusters in the MALDI-TOF spectrum. The smaller one, about 15 % of the base peak, corresponds to **14** (accounting for the shoulder at 822 nm in the absorption spectrum). The base peak at 4809 D corresponds to the cyclic trimerisation product **15**. The preferential formation of the dehydro[12]annulene derivative **14** over the trimerisation product **15** (Scheme 3) and other higher molecular weight cyclisation products is in accord with the results of oxidative couplings of other dialkyne systems.[15, 16]

A sample of **14** and the fraction that contained **15** contaminated with **14** were further examined by gel-permeation chromatography (GPC). Compound **14** exhibited a single peak, retention time 93.3 min, with $M_w = 3430$ and $M_n = 3373$ (polystyrene equivalent molecular mass) to give a polydispersity (M_w/M_n) of 1.02, which corresponds to a single component. The mass data are in satisfactory agreement with the expected molecular mass. The second fraction exhibited

two peaks, retention times 90.3 min and 93.3 min, in an approximate 8:1 ratio. The first peak corresponded to the trimerisation product **15**, with $M_w = 4909$ and $M_n = 4867$ ($M_w/M_n = 1.01$), and was collected. The second peak corresponded to the small amounts of **14** which had not been completely separated from **15** by the earlier column chromatographic purification.

Characterisation of the phthalocyaninoannulenes 14 and 15: The high-resolution FT-ICR electrospray ionisation mass spectrum of **14** in THF is shown in Figure 2 (top). The base signal corresponds to the doubly charged $[M]^{2+}$ ion at 1601.1211 (requires 1601.1235). The isotopic distribution, Figure 2 (middle), shows a 0.5 D mass difference between each peak. Signals for the single and triple charged ions, $[M]^{+}$ and $[M]^{3+}$, are also present, at about 3206 D (poorly resolved) and at 1067.4227 ($[M]^{3+}$ requires 1067.4157), respectively. Further signals are also present which indicate the presence of aggregated structures. The peak cluster at 2135 D and its mass spacings (Figure 2, bottom) correspond to a triply charged, two-molecule aggregate. The very low intensity peak at approximately 2400 corresponds to a quadruply charged, three-molecule aggregate.

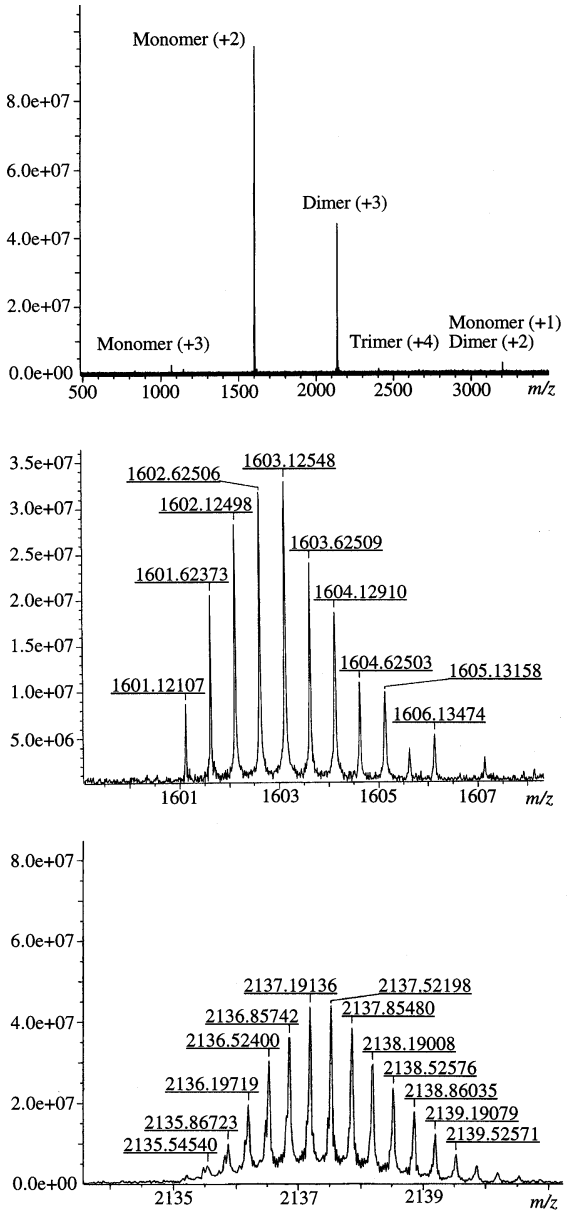

Figure 2. Top: The high-resolution FT-ICR electrospray ionisation mass spectrum of **14** in THF over the mass range 500 to 4000D. "Monomer" refers to unaggregated molecules, "Dimer" and "Trimer" to two and three molecule aggregates, respectively. (+1), (+2) and (+3) refer to the number of charges per species deduced from the peak separations, not shown, within the individual clusters (see text). Middle: The isotopic cluster at 1601 corresponding to the $[M]^{2+}$ species. Bottom: The isotopic cluster at 2135 corresponding to the triply charged dimeric aggregate.

The molecular weight of **15** is beyond the range of the FT-ICR electrospray equipment used to characterise **14** and its structure was confirmed by MALDI-TOF MS. The isotopic cluster for **15** is shown in Figure 3 and is superimposable on the calculated distribution for $[M+H]^{+}$. This correspondence precludes the presence of an incompletely coupled, open chain, trinuclear phthalocyanine.

The ^{1}H NMR spectrum of **14** (4.5 mg per 0.5 mL [D_6]benzene) shows broadening of the signals for the aromatic, OCH_2 and benzylic protons. Introduction of [D_5]pyridine failed to inhibit aggregation at this concentration. At higher dilution (ca. 0.9 mg per 0.5 mL [D_6]benzene) and at 40 °C the ^{1}H NMR spectrum is well resolved. Apart from the expected mutiplets for the aliphatic protons, the spectrum shows overlapping signals for the aromatic protons, an eight-proton triplet at $\delta = 4.91$ for the OCH_2 protons, a triplet for eight benzylic protons at $\delta = 4.76$ and a 16-proton multiplet for the remaining benzylic protons centred at $\delta = 4.62$. The ^{1}H NMR spectral data for **15** were collected under similar conditions from a sample from column chromatography and prior to GPC separation from small amounts of **14**. The spectrum showed signals consistent with the structure given and also revealed that the ratio of **14**:**15** was about 1:8. Interestingly, this spectrum showed clearly that the signals for the OCH_2 protons of **15** ($\delta = 5.12$) are downfield of those of **14**, ($\delta = 4.91$). Matzger and Vollhardt[26] recently appraised ^{1}H NMR spectral data for dibenzodehydro[12]annulene and tribenzodehydro[18]annulene and ascribed the difference in chemical shifts of the *ortho* aromatic protons of these planar molecules to the fact that the former is paratropic (anti-aromatic), whereas the latter is diatropic (aromatic). The difference observed in the chemical shifts of the OCH_2 protons in **14** and **15** can be attributed similarly.

The most striking feature of the Q-band absorptions for **14** and **15** is the splitting, which is much greater than for the butadiynyl-linked dinuclear phthalocyanine **12**. Of the two, the splitting observed in the spectrum of **14** is the larger which may reflect the greater strain in the system.

Mesophase behaviour: The phthalocyanine precursors to the dinuclear and dehydroannuleno derivatives were investigated for liquid crystallinity as a routine element of their characterisation. Hitherto, we have described the columnar mesophase properties of a large number of nonperipherally substituted phthalocyanines both uniformly substituted, with either eight alkyl[27] or eight alkyloxymethyl groups,[28] and 3:1 non-uniformly substituted derivatives bearing at least six alkyl

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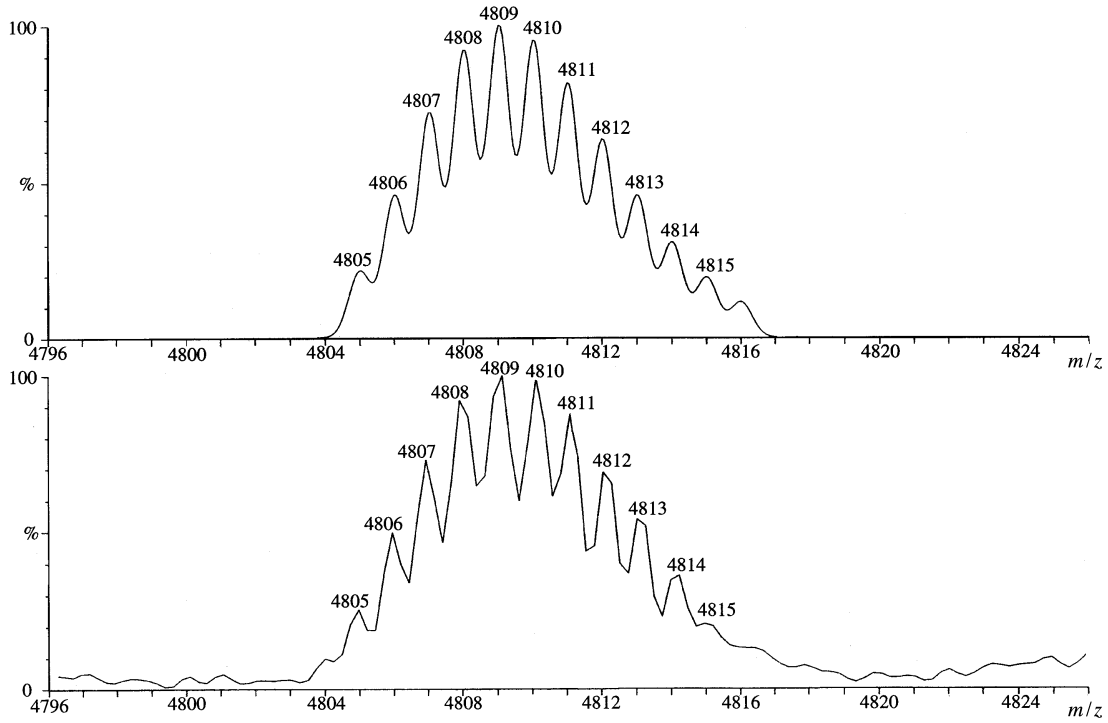

Figure 3. Lower plot: The MALDI-TOF spectrum of the $[M+H]^+$ species for compound **15.** Upper plot: The calculated isotopic cluster for this species.

chains.[29] Non-peripherally substituted octaalkoxy derivatives do not show mesophase behaviour.[22]

The liquid crystal behaviour of the present 3:1 Pcs was examined by optical polarising microscopy, and the results are summarised in Table 2; K refers to the crystal state, D to a mesophase (discotic) and I is the isotropic liquid. All but **1a** exhibited mesophase behaviour; this indicates that inclusion of two alkoxy groups in the nonperipheral positions does not inhibit liquid crystallinity. Without exception, the first mesophase observed upon cooling gave rise to a "fanlike" birefringence texture, which is characteristic of a discotic hexagonal disordered phase (D_{hd}) in accordance with the examples referred to above.[27–29] The monobromo derivative, **4**, exhibited a second mesophase, but only during cooling. This phase was mobile and distorted under external pressure. It gave rise to an indistinct texture and has not been identified. Here we denote it as D_x.

The symmetry of the molecule has a marked affect upon the mesophase behaviour. Hence, the nona-substituted Pcs, **2a**, **2b**, and **4** and the deca-substituted compound **10** are of C_s symmetry, whilst the remaining deca-substituted Pcs have C_{2v} symmetry. The C_s Pcs exhibit lower $K \rightarrow D_{hd}$ transitions than the analogous C_{2v} Pcs. This can be attributed to the more symmetrical Pcs forming better packed crystals. Secondly, the C_s Pcs exhibit higher clearing points ($K \rightarrow I$ or $D_{hd} \rightarrow I$) than their C_{2v} counterparts. The D_{hd} mesophase of the C_s Pcs was much more mobile and less viscous than for the C_{2v} Pcs. The C_s Pcs also had a tendency towards supercooling, with crystallisation occurring upon standing overnight at room temperature. By contrast, the C_{2v} Pcs crystallised directly upon cooling. The transition to the crystal was characterised by a colour change, not a change in texture, the "fans" becoming a lighter green. Replacement of the bromine atoms with unprotected ethynyl groups increased clearing transitions.

The butadiynyl derivative **12** melted directly into the isotropic liquid phase. On cooling, a texture was generated similar to the fan texture referred to above. However, this is assigned to a crystal phase because differential scanning calorimetry showed single, broad endotherms for the $K \rightarrow I$ and $I \rightarrow K$ transitions, rather than the sharp peaks associated with mesophase transitions. Furthermore, crystallisation occurred with some degree of supercooling. In contrast, a sample of the dehydro[12]annulene derivative **14** entered a mobile phase at about 110 °C; a phase which gave rise to a birefringence pattern. Thus we tentatively conclude that this complex molecule also exhibits mesophase behaviour. However, further heating produced an

Table 2. Transition temperatures measured for "mononuclear phthalocyanines".

Compound[a]		Transition temperatures [°C][b]							
	Substituents	$K \rightarrow D_{hd}$	$D_{hd} \rightarrow I$	$K \rightarrow I$	$I \rightarrow K$	$I \rightarrow D_{hd}$	$D_{hd} \rightarrow D_x$	$D_x \rightarrow K$	$D_{hd} \rightarrow K$
1a	$2 \times CCSiMe_3$			69	< RT				
1b	$2 \times CCH$	83	91			88			76
2a	$CCSiMe_3$	46	113			112			< RT
2b	CCH	36	131			130			< RT
3	$2 \times Br$			72		67.5			57
4	Br	30	106			104	35	< RT	
10	Br, OBu	65	87			84			< RT

[a] Central ion is nickel. [b] Transition temperatures measured by polarised light microscopy on the first heating and cooling cycle. [c] The higher temperature mesophase is assigned as D_{hd}. The lower temperature mesophase D_x is unknown.

irreversible change, see below, which hindered mesophase characterisation.

Thermal polymerisation experiments: Acyclic dialkynes are well known to polymerise[30] under thermal and photochemical conditions, but much less is known about cyclic dialkynes.[16] A sample of the butadiynyl derivative **12** was maintained at 220 °C for two hours. After cooling, the visible region spectrum of the material in solution and the TLC behaviour were identical to those of the starting material. Compounds **14** and **15**, the latter contaminated with **14**, were investigated similarly. After five minutes at 220 °C, **14** gave a spectrum (toluene solution) that showed reduction in absorbance of the two main components of the Q-band and growth of a broad band between them. This change was irreversible. Continued heating for 30 minutes gave a sample whose spectrum showed the disappearance of the original bands and their replacement by a featureless band envelope extending over the region 680–820 nm. The sample of **15** showed similar changes, but over a much longer timespan. The heated sample of **14** gave a MALDI-TOF spectrum with a series of broadened peaks for high molecular weight species, the highest at approximately 19000 D. These were spaced at multiples of the molecular weight of **14**. A second series of peaks appear at intervening molecular weights. Clearly the material has undergone oligomerisation, but interpretation is complex because of the possible presence of multiply charged ions. The compound's facility for reaction contrasts with that of **12** and **15**, and this can be attributed to the strain associated with the inevitable distortion of the dialkyne moiety in the dehydro[12]annulene system. Further work is required to characterise the high molecular mass structures in more detail.

Conclusion

The synthesis of highly substituted 3:1 phthalocyanine derivatives whose substituents include one or two bromine atoms on one of the benzenoid rings has been achieved. These compounds have been converted into the corresponding ethynyl and trimethylsilylethynyl derivatives by Stille and Sonogashira coupling methods. Oxidative coupling of the monoethynyl compound provides a butadiynyl-linked binuclear phthalocyanine derivative that is isomerically pure. Under similar conditions, the diethynylphthalocyanine derivative yielded a mixture of compounds which contains a diphthalocyaninodehydro[12]annulene as the major product. It shows a substantial splitting of the Q-band absorption to the extent that the lower energy component absorbs at 822 nm. Mass spectrometry provides evidence of self aggregation in the solution phase. On heating the compound on a hotstage to about 110 °C, it enters a liquid crystal phase. However, on further heating to 220 °C there is an irreversible change arising from an oligomerisation process, which presumably occurs through the diyne unit in the annulene ring. A minor product of the oxidative coupling of the diethynylphthalocyanine has been identified as the cyclic trimer, a triphthalocyaninodehydro[18]annulene. Compared with the diphthalocyaninodehydro[12]annulene, the compound shows a less strongly split Q-band, and the chemical shifts of protons in proximity to the annulene ring are deshielded. The compound also undergoes oligomerisation, but less readily than the diphthalocyaninodehydro[12]annulene.

These compounds extend the range of highly elaborated phthalocyanine derivatives available; they also add to the type of annelated dehydroannulene compounds which are known. In addition, the results indicate that the thermally induced oligomerisation processes undergone by the annulene moiety in this type of system provides an entry to novel phthalocyanine-networked polymers, a topic we shall investigate in more detail in future work.

Experimental Section

IR spectra were recorded on a Perkin–Elmer 297, 298 or a FTIR 1720 spectrophotometer as either neat liquids or as nujol mulls of solids. ^{1}H NMR spectra were measured at 270 MHz with a JEOL EX270 spectrometer and at 300 MHz with a Varian Gemini 2000, with TMS or the residual solvent peak as the reference. Routine mass spectra were recorded on a Kratos model MS25 magnetic sector mass spectrometer with electron impact ionisation. FAB-MS (LSIMS) were obtained by using nitrobenzyl alcohol as the matrix and were measured with the EPSRC's VG ZAB-E low-resolution equipment at Swansea University. MALDI-TOF mass spectra were obtained on a Kratos Kompact MALDI3 spectrometer with a dithranol matrix at the University of Manchester. FT-ICR electrospray mass spectra were obtained of a solution of **14** in THF with a Bruker 9.4-T FT-ICR at the University of Warwick. GPC analysis was carried out at the University of Manchester by using a system that incorporated a Gilson 307 pump operating at 0.3 $cm^3 mL^{-1}$ through four Polymer Labs 3 μ Mixed E columns in tandem followed by a GBC LC1240 differential refractometer for detection. The eluent was chloroform. UV/visible spectra of solutions were measured using a Hitachi U-3000 spectrophotometer. Melting points and thermotropic mesophase transitions were determined by using an Olympus BH-2 polarising microscope in conjunction with a Linkam TMS 92 thermal analyser and a Linkam THM 600 cell. Differential scanning calorimetry (DSC) was undertaken by using a Thermal Analyst 2000 in conjunction with a DSC 10 differential scanning calorimeter from TA Instruments. Silica gel (Merck 7734) was used in chromatographic separations. TLC was performed using silica gel (Merck 5554) supported on aluminium sheets. Solvents were dried, where appropriate, over sodium or calcium hydride and distilled under an atmosphere of dry nitrogen.

4,5-Dibromo-3,6-dihydroxyphthalonitrile (6): NBS (7 g, 38.8 mmol) was added portionwise over 15 min to a stirred solution of 2,3-dicyanohydroquinone (3 g, 18.7 mmol) in *tert*-butyl alcohol (12 mL) at 45 °C. Stirring was continued for 2 h and then additional NBS (7 g, 38.8 mmol) was added over 15 min. After a further 2 h, the reaction was cooled to room temperature and poured into an aqueous solution of sodium metabisulfite (6 g in 60 mL, excess) at 0 °C with vigorous stirring. The mixture was stirred for 10 min, the precipitate filtered and washed with cold water (30 mL). The product was dried under vacuum at 60 °C for 24 h to yield **6** as a cream powder (3.94 g, 66.1 %). This was used without further purification, but an analytical sample was prepared by recrystallisation from acetone/water. M.p. 248 °C (decomp) (literature value 250 °C[19]); ^{13}C NMR (270 MHz, [D$_6$]acetone): $\delta = 151.74$ (C–O), 123.08 (C–Br), 113.07 (CN), 102.46 (C-CN); IR (nujol): $\tilde{\nu} = 3250$ (br), 2232 cm^{-1} (m); elemental analysis calcd (%) for $C_8H_2O_2N_2Br_2$ (317.92): C 30.22, H 0.63, N 8.81, Br 50.27; found C 30.47, H 0.42, N 8.70, Br 50.22.

4,5-Dibromo-3,6-dibutoxyphthalonitrile (7): A mixture of compound **6** (2.50 g, 7.86 mmol), triphenylphosphine (4.95 g, 18.9 mmol), and 1-butanol (1.5 g, 20.2 mmol) was dissolved in dry THF (80 mL) and cooled to 0 °C. A solution of diisopropyl azodicarboxylate (4.35 g, 21.5 mmol) in THF (30 mL) was added dropwise over 30 min. The solution was allowed to warm to RT and stirred for an additional 10 h. The THF was removed under reduced pressure to give a dark red oil, which was dissolved in diethyl ether (20 mL). The solution was filtered to remove undissolved triphenylphos-

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phine oxide, concentrated and separated by column chromatography over silica (eluent: CH_2Cl_2/petrol 1:2). The product was recrystallised from cyclohexane to afford compound **7** as white crystals (2.75 g, 83.6%). M.p. 72–73 °C; ^{1}H NMR (270 MHz, $CDCl_3$): $\delta = 4.24$ (t, $J = 6.4$ Hz, 4H), 1.92 (quint, $J = 7.0$ Hz, 4H), 1.67–1.53 (m, 4H), 1.04 (t, $J = 7.3$ Hz, 6H); ^{13}C (270 MHz, $CDCl_3$): $\delta = 156.37$ (ArC–O), 129.61 (ArC–Br), 112.33 (CN), 109.22 (Ar*C*-CN), 76.43, 31.95, 18.92, 13.73; MS (70 eV, EI): *m/z* (%): 432 (3.1), 430 (5.2), 428 (3.5) $[M]^+$; IR (nujol): $\tilde{\nu} = 2230$ cm^{-1} (m); elemental analysis calcd (%) for $C_{16}H_{18}N_2O_2Br_2$ (430.14): C 44.68, H 4.22, N 6.51, Br 37.15; found: C 44.51, H 4.28, N 6.47, Br 37.33.

4-Bromo-3,6-dibutoxyphthalonitrile (8): A mixture of compound **6** (3 g, 9.4 mmol), finely crushed potassium carbonate (3 g, excess) and *N*,*N*,*N*-tributyl-1-butananinium bromide (TBAB, 0.26 g, 0.7 mmol) was heated under reflux in MEK (80 mL) for 12 h. The reaction was cooled and 1-iodobutane (3.70 g, 20 mmol) was added. Heating under reflux was continued for a further 72 h. Upon cooling, the reaction was filtered and washed with ethyl acetate. The organics were removed under reduced pressure, and the residue dissolved in ethyl acetate (100 mL). This was washed with 5% HCl (25 mL), saturated K_2CO_3 (25 mL), water (25 mL) and brine (25 mL), dried (MgSO4), filtered and concentrated under reduced pressure. The crude product was purified by column chromatography over silica (eluent: petrol/CH_2Cl_2 2:1) and recrystallised from cyclohexane to afford compound **8** (1.43 g, 43%). M.p. 102.5–104 °C; ^{1}H NMR (270 MHz, [D$_6$]acetone): $\delta = 7.88$ (s, 1H), 4.30 (t, $J = 6.4$ Hz, 2H), 4.18 (t, $J = 6.4$ Hz, 2H), 1.86 (m, 4H), 1.56 (m, 4H), 1.00 (t, $J = 7.3$ Hz, 3H), 0.99 (t, $J = 7.3$ Hz, 3H); ^{13}C NMR (300 MHz, [D$_6$]acetone): $\delta = 157.68$ (ArC–O), 152.80 (ArC–O), 124.94, 123.33 (ArC–H), 112.81 (CN), 112.69 (CN), 111.39 (Ar*C*–CN), 103.83 (Ar*C*–CN), 75.75, 70.40, 31.81, 30.57, 18.70, 18.66, 13.07, 12.98; MS (70 eV, EI): *m/z* (%): 350.1 (4.8), 352.1 (4.5) $[M]^+$; IR (nujol): $\tilde{\nu} = 2230$ cm^{-1} (m); elemental analysis calcd (%) for $C_{16}H_{19}N_2O_2Br_1$ (351.24): C 54.85, H 5.47, N 8.00, Br 22.54; found C 54.71, H 5.43, N 7.89, Br 22.67.

1,4-Dibutoxy-2,3-dibromo-8,11,15,18,22,25-hexakis(decyl)phthalocyaninato nickel(II) (3): Freshly cleaned lithium (ca. 50 mg, 7.5 mmol) was added to 3,6-didecylphthalonitrile[21] (2.56 g, 6.27 mmol) and **7** (0.30 g, 0.70 mmol) in refluxing butanol (20 mL) under argon. The reaction was heated under reflux in the dark for 16 h, cooled, nickel acetate tetrahydrate (0.53 g, 2.1 mmol) was added and heating under reflux was continued for 2 h. After cooling, the solvents were removed under reduced pressure, and the residue triturated with methanol to afford a green solid. Purification by column chromatography over silica (eluent: petrol) afforded 1,4,8,11,15,18,22,25-octakis(decyl)phthalocyaninato nickel(II) (0.71 g, 24%) as the first fraction; changing the eluent to petrol/dichloromethane (1:1) afforded a second fraction. The latter was further purified by column chromatography over silica (eluent: petrol/dichloromethane 19:1) to afford **3** (45.7 mg, 3.8%) after recrystallisation from THF/methanol. M.p. 72 °C (K → I), 67 °C (I → D), 57 °C (D → K); ^{1}H NMR (300 MHz, [D$_6$]benzene): $\delta = 7.82$ (s, 4H), 7.81 (s, 2H), 4.75 (t, $J = 7.5$ Hz, 4H), 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 (3.68×10^{-6} M in toluene): λ_{max} (log ε) = 716 (5.10), 698 (5.03), 636 nm (4.39); MS (FAB): *m/z*: isotopic cluster at 1716 $[M+H]^+$; elemental analysis calcd (%) for $C_{100}H_{150}N_8O_2Br_2Ni_1$ (1715.84): C 70.04, H 8.82, N 6.53; found C 70.40, H 8.90, N 6.30.

Further elution (petrol/dichloromethane 1:1) afforded a second fraction, and compound **10** (38.2 mg, 3.2%) was isolated after recrystallisation from THF/methanol. M.p. 65 °C (K → D), 87 °C (D → I); ^{1}H NMR (270 MHz, $CDCl_3$): $\delta = 7.78$ (s, 4H), 7.72 (s, 2H), 4.59–4.43 (m, 10H), 4.30 (br t, 8H), 2.13–1.89 (m, 18H), 1.75–1.08 (m, 90H), 0.95 (t, 3H), 0.91 (t, 3H), 0.85–0.76 (br t, 21H); ^{13}C NMR (67.5 MHz, $CDCl_3$): $\delta = 151.73$, 149.58, 147.39, 147.35, 147.26, 147.12, 146.81, 145.57, 143.49, 143.06, 139.05, 137.88, 137.70, 134.59, 134.41, 134.36, 130.66, 130.60, 130.21, 130.21, 129.69, 125.52, 117.00, 75.31 (OCH_2), 75.04 (OCH_2), 74.54 (OCH_2), 32.69, 62.62, 32.38, 32.33, 32.19, 32.11, 32.01, 31.84, 31.75, 31.45, 30.59, 30.44, 30.23, 30.17, 30.03, 29.89, 29.72, 29.64, 29.60, 29.44, 29.33, 29.29, 22.63, 19.52 ($OCH_2CH_2CH_2$), 19.34 ($OCH_2CH_2CH_2$), 19.19 ($OCH_2CH_2CH_2$), 14.10, 14.04; UV/Vis (1.92×10^{-6} M in toluene): λ_{max} (log ε) = 714 (5.21), 694 (sh), 636 nm (4.57); MS (FAB): *m/z*: isotopic cluster at 1635 $[M - OC_4H_9]^+$; MS (MALDI): *m/z*: 1707 $[M - H]^+$; elemental analysis calcd (%) for $C_{104}H_{159}N_8O_3Br_1Ni_1 \cdot CH_3OH$ (1740.09): C 72.48, H 9.44, N 6.44; found C 72.04, H 9.12, N 6.49.

1,4-Dibutoxy-2,3-(2′-trimethylsilylethynyl)-8,11,15,18,22,25-hexakis(decyl)phthalocyaninato nickel(II) (1a) and compound 11: Bis(triphenylphosphine)palladium(II) chloride (7 mg, 10 μmol), copper(I) iodide (2.2 mg, 11.6 μmol) and trimethylsilylamine (TMSA, 25 mg, 255 μmol) were added in that order and at 10 min intervals to a stirred solution of **3** (40 mg, 23.3 μmol) in dry degassed triethylamine (3.5 mL) under Ar in a dry screw-cap pressure tube. Under a fast stream of Ar the rubber septum was removed and the screw-cap sealed; the reaction mixture was heated and stirred in an oil bath at 100 °C for 16 h. The tube was cooled, and further bis(triphenylphosphine)palladium(II) chloride (4.1 mg), copper(I) iodide (1.7 mg) and TMSA (25 mg) were added under Ar. The reaction was heated at 100 °C for a further 12 h. The mixture was cooled, filtered and concentrated under reduced pressure. The residue was dried at 0.5 mmHg for 12 h to remove excess TMSA and triethylamine traces, and further purified by column chromatography over silica (eluent: petrol/dichloromethane 97:3). The first fraction was unreacted starting material (3.4 mg). The second fraction contained a mixture; subsequent green fractions containing minor amounts of material were discarded. The second fraction was further purified by column chromatography over silica (eluent: petrol/dichloromethane 98.5:1.5 then 97:3) to afford compound **11** (8.0 mg, 22%) as the first eluted component; ^{1}H NMR (270 MHz, $CDCl_3$): $\delta = 7.76$ (br s, 4H), 7.73 (br s, 2H), 4.63 (t, $J = 6.9$ Hz, 2H), 4.50–4.39 (m, 6H), 4.34–4.25 (m, 8H), 2.13–1.84 (m, 16H), 1.62–1.03 (m, 88H), 0.96–0.91 (2 × t, 6H), 0.78 (br t, 18H), 0.42 (s, 9H).

Further elution gave a second fraction and compound **1a** (13.2 mg, 35%) was isolated after recrystallisation from THF/methanol. M.p. 69 °C; ^{1}H NMR (270 MHz, $CDCl_3$): $\delta = 7.78$ (br s, 4H), 7.75 (s, 2H), 4.60 (t, $J = 7.2$ Hz, 4H), 4.47 (t, $J = 6.9$ Hz, 4H), 4.35–4.26 (m, 8H), 2.10–1.90 (m, 16H), 1.60–1.08 (m, 88H), 0.95 (t, $J = 7.4$ Hz, 6H), 0.80 (t, $J = 6.6$ Hz, 12H), 0.79 (t, $J = 6.6$ Hz, 6H), 0.43 (s, 18H); ^{13}C NMR (67.5 MHz, $CDCl_3$): $\delta = 154.18$ (Ar*C*O), 147.99, 139.19, 138.13, 137.77, 134.75, 134.66, 134.43, 130.83, 130.47, 130.29, 130.19, 129.16, 128.17, 127.81, 127.47, 104.74 (*C*–CSi), 100.97 (C–*C*Si), 75.43 (OCH_2), 32.66, 32.56, 32.18, 31.88, 31.50, 30.53, 29.90, 29.85, 29.72, 29.67, 29.61, 29.45, 29.31, 22.64, 22.55, 19.37, 14.20, 14.07, 0.20; UV/Vis (2.80×10^{-6} M in toluene): λ_{max} (log ε) = 732 (4.99), 702 nm (4.95); MS (FAB): *m/z*: isotopic cluster at 1747 $[M+H]^+$; IR (KBr): $\tilde{\nu} = 2929$ (s), 2861 (m), 2155 (w), 1598 (w), 1457 (w), 1200 (w), 1092 cm^{-1} (m).

1,4-Dibutoxy-2,3-di(ethynyl)-8,11,15,18,22,25-hexakis(decyl)phthalocyaninato nickel(II) (1b): Tetrakis(triphenylphosphine)palladium(0) (10.5 mg, 9.0 μmol) was added to a solution of **3** (48.6 mg, 28.3 μmol), anhydrous lithium chloride (10 mg, 233 μmol) and triphenylphosphine (9.5 mg, 36 μmol) in dry degassed toluene (6 mL) under argon. After stirring for 10 min, tributyl(ethynyl)tin (60 mg, 190 μmol) was added, and the reaction heated at 100 °C for 16 h. The reaction was cooled, and the toluene removed under reduced pressure. The residue was triturated with acetone to remove excess tributyl(ethynyl)tin and washed from the filter paper with THF. The THF was removed under reduced pressure, and the residue was purified by column chromatography (eluent: petrol/dichloromethane 19:1) and recrystallised from THF-methanol to afford compound **1b** (27.2 mg, 60%). M.p. 83 °C (K → D), 91 °C (D → I); ^{1}H NMR (270 MHz, [D$_6$]benzene): $\delta = 7.81–7.78$ (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, $J = 7.4$ Hz, 6H), 0.92–0.81 (m, 18H); ^{13}C NMR (67.5 MHz, [D$_6$]benzene): $\delta = 154.86$, 148.47, 148.40, 142.86, 139.57, 138.37, 138.01, 135.40, 135.31, 131.45, 130.93, 130.89, 130.00, 121.68, 87.63, 80.13, 75.87, 33.23, 32.93, 32.20, 31.16, 31.09, 30.57–29.6, 23.04, 23.01, 19.70, 14.33, 14.26; UV/Vis (2.51×10^{-6} M in toluene): λ_{max} (log ε) = 729 (4.99), 698 (4.88), 666 (4.44), 628 (4.23) nm; MS (FAB): *m/z*: isotopic cluster at 1606 $[M+H]^+$; elemental analysis calcd (%) for $C_{104}H_{152}N_8O_2Ni_1 \cdot CH_3OH$ (1637.14): C 77.03, H 9.60, N, 6.84; found C 76.99, H 9.56, N 6.98.

1,4-Dibutoxy-2,3-di(ethynyl)-8,11,15,18,22,25-hexakis(decyl)phthalocyaninato nickel(II) (1b) from 1a: Potassium hydroxide solution (0.1 mL of a solution containing 1 flake in 0.5 mL of H_2O) was added to a solution of **1a** (9.2 mg, 5.3 μmol) in THF (5 mL) and methanol (1 mL), and the reaction was stirred under Ar in the dark for 12 h. One drop of 5% HCl was added, and the solvents were removed under reduced pressure. The residue was triturated with methanol and further purified by column chromatography over silica (eluent: petrol/dichloromethane 10:1) to afford **1b** as a green solid (6.7 mg, 79%) identical to the sample obtained above.

1,4-Dibutoxy-2-bromo-8,11,15,18,22,25-hexakis(decyl)phthalocyaninato nickel(II) (4): Compound **4** was prepared from a mixed cyclotetramerisation of **8** and **9** (R = decyl) by using the method which afforded **3** above. Yield 4%. M.p. 30 °C (K → D), 106 °C (D → I); ^{1}H NMR (300 MHz, [D$_6$]ben-

zene): $\delta = 7.82$ (br s, 4H), 7.77 (s, 2H), 7.68 (s, 1H), 4.83–4.78 (br t, 4H), 4.66 (t, $J = 7.0$ Hz, 2H), 4.63–4.57 (2 × t, 8H), 4.22 (t, $J = 6.8$ Hz, 2H), 2.34–2.22 (m, 14H), 2.13 (quint, $J = 7.2$ Hz, 2H), 1.93–1.10 (m, 88H), 0.99 (t, $J = 7.4$ Hz, 3H), 0.91–0.76 (m, 21H); ^{13}C NMR (67.5 MHz, $CDCl_3$) δ 151.54, 147.74, 147.67, 147.46, 147.13, 146.70, 146.52, 143.68, 142.61, 139.03, 138.94, 137.93, 137.70, 137.66, 134.84, 134.77, 134.70, 134.65, 134.47, 134.38, 130.87, 130.28, 130.17, 130.10, 125.19, 119.52, 116.37, 75.10 (OCH_2), 69.76 (OCH_2), 32.74, 32.62, 32.31, 32.15, 31.86, 31.81, 31.65, 31.48, 31.16, 30.46, 30.26, 29.90, 29.80, 29.71, 29.65, 29.62, 29.45, 29.36, 29.29, 29.24, 22.63, 22.57, 19.45, 19.36, 14.05; UV/Vis (3.37×10^{-6} M in toluene): λ_{max} ($\log\varepsilon$) = 714 (5.10), 700 (sh), 635 nm (4.47); elemental analysis calcd (%) for $C_{100}H_{151}N_8O_2Br_1Ni_1$ (1635.95): C 73.42, H 9.30, N 6.85; found C 74.08, H 9.52, N 6.19.

1,4-Dibutoxy-2-(2′-trimethylsilylethynyl)-8,11,15,18,22,25-hexakis(decyl)phthalocyaninato nickel(II) (2a): Compound **2a** was prepared from **4** by following the procedure for **1a** above using dry THF/Et_3N (5:1) as solvent. Yield (62%). M.p. 46 °C (K → D), 113 °C (D → I); ^{1}H NMR (270 MHz, [D_8]toluene): $\delta = 7.81$ (s, 6H), 7.65 (s, 1H), 4.86–4.78 (br t, 6H), 4.68–4.58 (2 × t, 8H), 4.26 (br t, 2H), 2.38–2.20 (m, 16H), 1.90–1.10 (m, 88H), 0.99–0.76 (m, 24H), 0.49 (s, 9H); UV/Vis (3.44×10^{-6} M in toluene): λ_{max} ($\log\varepsilon$) = 722 (5.09), 700 (5.02), 640 (4.43), 346 nm (4.59); MS (FAB): *m/z*: isotopic cluster at 1653 $[M+H]^+$; elemental analysis calcd (%) for $C_{105}H_{160}N_8O_2Si_1Ni_1$ (1653.25): C 76.28, H 9.75, N 6.78; found C 76.95, H 9.67, N 6.84.

1,4-Dibutoxy-2-(ethynyl)-8,11,15,18,22,25-hexakis(decyl)phthalocyaninato nickel(II) (2b): Compound **2b** was prepared from **4** by following the procedure used to prepare **1b** above. Yield (48%). M.p. 36 °C (K → D), 131 °C (D → I); ^{1}H NMR (270 MHz, [D_6]benzene): $\delta = 7.81–7.78$ (m, 6H), 7.75 (s, 1H), 4.87–4.82 (m, 6H), 4.66–4.55 (m, 8H), 4.27 (t, $J = 7.0$ Hz, 2H), 3.28 (s, 1H), 2.31–2.23 (m, 16H), 1.98–1.06 (m, 88H), 0.99 (2 × t, 6H), 0.94–0.77 (m, 18H); UV/Vis (5.20×10^{-6} M in toluene): λ_{max} ($\log\varepsilon$) = 721 (5.07), 701 (5.01), 641 (4.39), 347 nm (4.54); IR (KBr): $\tilde{\nu} = 3304$ (m), 2965 (sh), 2927 (s), 2853 (s), 1468 (m), 1318 (m), 1187 (m), 1102 cm^{-1} (m); elemental analysis calcd (%) for $C_{102}H_{152}N_8O_2Ni_1$ (1518.07): C 77.49, H 9.69, N 7.09; found C 77.80, H 9.68, N 7.09.

One pot conversion of 2a, via 2b, into 1,4-bis-2[(1,4-dibutoxy-8,11,15,18,22,25-hexakis(decyl)phthalocyaninato nickel(II)]butadiyne (12): A solution of **2a** (46 mg, 27.8 μmol), anhydrous copper(II) acetate (200 mg, 1.1 mmol) and finely crushed K_2CO_3 (210 mg, 1.5 mmol) in dry pyridine/methanol/THF (1:1:3, 10 mL) was stirred under Ar at 55 °C for 16 h. The reaction was cooled, filtered and washed with THF until the washings were colourless. The filtrate was concentrated under reduced pressure, and the Pc was redissolved in THF and filtered to remove copper salts. The crude product was concentrated and purified by column chromatography over silica (eluent: petrol/dichloromethane/Et_3N 95:5:0.1). The first fraction was concentrated and recrystallised from THF/methanol to afford compound **12** (27 mg, 61%). M.p. 159 °C; ^{1}H NMR (270 MHz, [D_6]benzene, 50 °C): $\delta = 7.87–7.83$ (m, 12H), 7.74 (s, 2H), 5.03 (t, $J = 6.9$ Hz, 4H), 4.91–4.86 (m, 8H), 4.66–4.59 (m, 16H), 4.46 (t, $J = 7.1$ Hz, 4H), 2.46–2.22 (m, 32H), 1.97–1.04 (m, 176H), 0.89–0.80 (m, 48H); UV/Vis (4.94×10^{-6} M in toluene): λ_{max} ($\log\varepsilon$) = 752 (5.43), 702 (5.27), 634 (4.71), 438 (4.52), 353 (4.95), 307 nm (5.06); MS(MALDI): *m/z*: isotopic cluster at 3161 $[M+H]^+$; IR (KBr): $\tilde{\nu} = 2960$ (sh), 2919 (s), 2848 (s), 1606 (m), 1526 (m), 1468 (m), 1181 (m), 1096 cm^{-1} (s); elemental analysis calcd (%) for $C_{204}H_{302}N_{16}O_4Ni_2$ (3160.13): C 77.54, H 9.63, N 7.09; found C 77.14, H 9.50, N 6.90.

Oxidative coupling of 1b to give 14 and 15: Copper(II) acetate (180 mg, 0.1 mmol) was added to a solution of **1b**, (39.0 mg, 24.3 μmol) in dry THF/pyridine/methanol (1:1:0.25, 45 mL). The solution was stirred in the dark under Ar for 8 h at 80 °C. The reaction was cooled, filtered and washed with THF. The solution was concentrated under reduced pressure and filtered through silica (eluent: petrol/THF 9:1). The solution was concentrated under reduced pressure and further purified by column chromatography (eluent: petrol/THF 19:1); the fractions were analysed by UV-visible spectrometry. The first fraction was collected and recrystallised from THF-methanol to afford the diphthalocyaninodehydro[12]annulene **14** (9.5 mg, 24%). ^{1}H NMR (270 MHz, [D_6]benzene, 40 °C): $\delta = 7.86–7.80$ (m, 12H), 4.91 (t, 8H), 4.80–4.72 (m, 8H), 4.68–4.56 (m, 16H), 2.35–2.18 (m, 32H), 1.95–1.12 (m, 176H), 1.02–0.84 (m, 48H); MS (MALDI): *m/z*: isotopic cluster at 3206 $[M+H]^+$; HRMS (FT-ICR): calcd for $C_{208}H_{300}N_{16}O_4Ni_2$ 1601.1235 $[M]^{2+}$; found 1601.1211; UV/Vis (2.81×10^{-5} M in toluene): λ_{max} ($\log\varepsilon$) = 822 (5.32), 691 nm (4.93).

The second fraction was collected and recrystallised once from THF-acetone and once from THF-methanol to afford the triphthalocyaninodehydro[18]annulene **15** (3.2 mg, 8%) admixed with about 10% (by ^{1}H NMR) of **14**. For **15**, ^{1}H NMR (270 MHz, [D_6]benzene, 45 °C): $\delta = 7.95$ (d, $J = 8.1$ Hz, 6H), 7.87 (d, $J = 8.1$ Hz, 6H), 7.85 (s, 6H), 5.12 (t, 12H), 5.00–4.88 (m, 12H), 4.70–4.57 (m, 24H), 2.45–2.15 (m, 48H), 2.02–1.08 (m, 264H), 1.05–0.82 (m, 72H); MS (MALDI): *m/z*: isotopic cluster at 4809 $[M+H]^+$; UV/Vis (3.22×10^{-5} M in toluene) $\lambda_{max} = 780$, 698 nm.

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