Octaarylethynyl and octaarylbutadiynyl phthalocyanines

Clifford C. Leznoff and Bohdan Suchozak

Abstract: 4,5-Diphenylethynylphthalonitrile, 4,5-di(*p*-*tert*-butylphenylethynyl)phthalonitrile, 4,5-di(*p*-neopentoxyphenylethynyl)phthalonitrile, and 4,5-di(*p*-neopentoxyphenyl-1,3-butadiynyl)phthalonitrile were prepared via 4,5-diiodophthalonitrile and the appropriate alkyne in palladium-catalyzed coupling reactions. Condensation of the above alkynylphthalonitriles with lithium 1-octanolate in 1-octanol afforded the desired polyalkynylphthalocyanines, but only 2,3,9,10,16,17,22,23-octa (*p*-neopentoxyphenylethynyl)phthalocyanine and 2,3,9,10,16,17, 22,23-octa (*p*-neopentoxyphenylbutadnyl)phthalocyanine were soluble enough to be suitably characterized.

Key words: phthalocyanines, phenylacetylenes, 1-phenyl-1,3-butadiynes.

Résumé : On a préparé le 4,5-diphényléthynylphtalonitrile, le 4,5-di(*p*-*tert*-butylphényléthynyl)phtalonitrile, le 4,5-di-(*p*-néopentoxyphényléthynyl)phtalonitrile, le 4,5-di-(*p*-néopentoxyphénylbuta-1,3-diynyl)phtalonitrile en procédant au couplage catalysé par le palladium du 4,5-diiodophtalonitrile avec l'alcyne approprié. La condensation des alcynylphtalonitriles mentionnés plus haut avec de l'octan-1-olate de lithium dans l'octan-1-ol permet d'obtenir les polyalcynylphtalocyanines recherchées; toutefois seules la 2,3,9,10,16,17,22,23-octa(*p*-néopentoxyphényléthynyl)phtalocyanine et la 2,3,9,10,16,17,22,23-octa-(*p*-néopentoxyphénylbutadiynyl)phtalocyanine sont suffisamment solubles pour être caractérisées de façon adéquate.

Mots clés : phtalocyanines, phénylacétylènes, 1-phénylbuta-1,3-diynes.

[Traduit par la Rédaction]

Introduction

2,3,9,10,16,17,23,24-Octa-substituted phthalocyanines are well-known (1), and have been studied for applications in a wide variety of areas, including dyes (2), chemical sensors (3), nonlinear optics (4), and photodynamic therapy of cancer (5, 6). Recently, poly(phenylalkynyl) benzenes (7) and alkynylporphyrins (8) have been described as possible compounds for use in nonlinear optics and arrays (8, 9). With this in mind, a series of 2,3,9,10,16,17,23,24-octaalkynylphthalocyanines were prepared (10) and their ^{1}H NMR spectra studied with respect to their variation in chemical shifts with concentration and temperature. Alkynyl-substituted phthalocyanines (Pcs) have been found to be particularly interesting in that each alkynyl group causes a red shift of 4–6 nm in the Q-band region of the spectrum, and can hence be applied in "fine-tuning" a Pcs absorption spectrum.

Not investigated in our original series of octaalkynylphthalocyanines were those substituted with phenylethynyl groups, which would be expected to give a greater red shift due to more extensive π-electron delocalization. Reports of enhanced nonlinear effects in molecules with extreme bond-length alternations (11), including conjugated diynyl systems (12) have also prompted our interest in butadiynyl substituted phthalocyanines. In this paper, the synthesis of some 2,3,9,10,16,17,23,24-octa(phenylethynyl)phthalocyanines will be described. The synthesis of a 4,5-di(butadiynyl)-substituted phthalonitrile is also outlined and its condensation reaction with lithium 1-octanolate will be discussed.

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Dedicated to Professor Brian James on the occasion of his 65th birthday.

C.C. Leznoff[1] and B. Suchozak. Department of Chemistry, York University Toronto, ON M3J 1P3, Canada.
[1]Corresponding author (telephone: (416) 736-2100 ext. 33838; fax: (416) 736-5936; e-mail: leznoff@yorku.ca).

Results and discussion

Using catalytic quantities of $Pd(PPh_3)_2Cl_2$ and CuI in triethylamine (TEA), 4,5-diiodo-phthalonitrile (**1**) was coupled with 2 molar equiv of phenylacetylene (**2**), to afford 4,5-di(phenylethynyl)phthalonitrile (**3**) in 70% yield (Scheme 1). Subsequent condensation of **3** with lithium 1-octanolate in 1-octanol gave, after work-up, a dark green solid which was extremely insoluble in most organic solvents (see Scheme 3 below). Purification of this product, which is believed to be 2,3,9,10,16,17,23,24-octa(phenylethynyl)phthalocyanine (**4**), was made extremely difficult due to its insolubility, and consequently failed to afford satisfactory proton NMR or FAB mass spectra. A recently acquired MALDI-TOF mass spectrometer has allowed us to record the parent ion cluster at (1314) of **4**. However, a UV–vis spectrum of a probe from the reaction mixture at 20 h seems to suggest the formation of an MPc. This is indicated by a strong absorption maximum at 720 nm, which would correspond to the expected Q-Band absorption of the dilithium Pc.

The high degree of insolubility displayed by the product of this reaction, assuming that it is indeed **4**, was believed to

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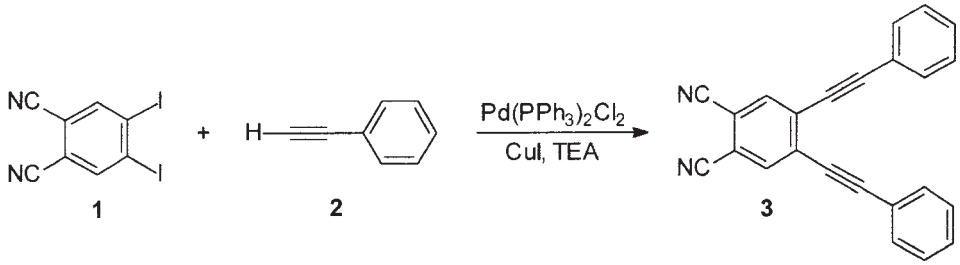
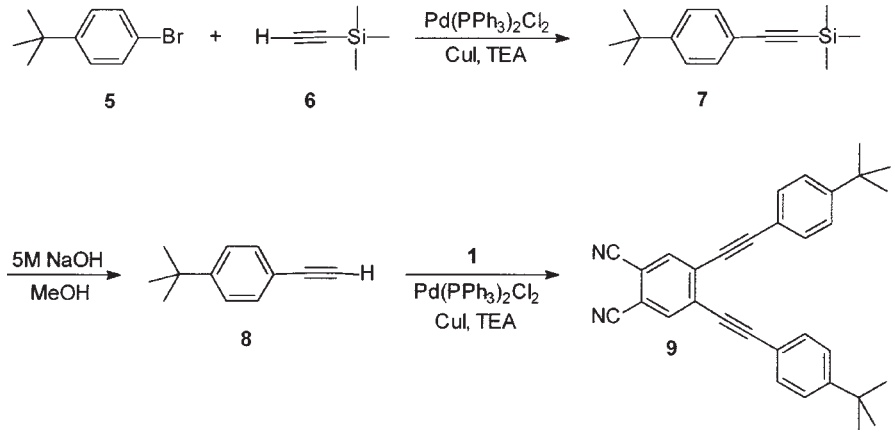
Scheme 1.



Scheme 2.



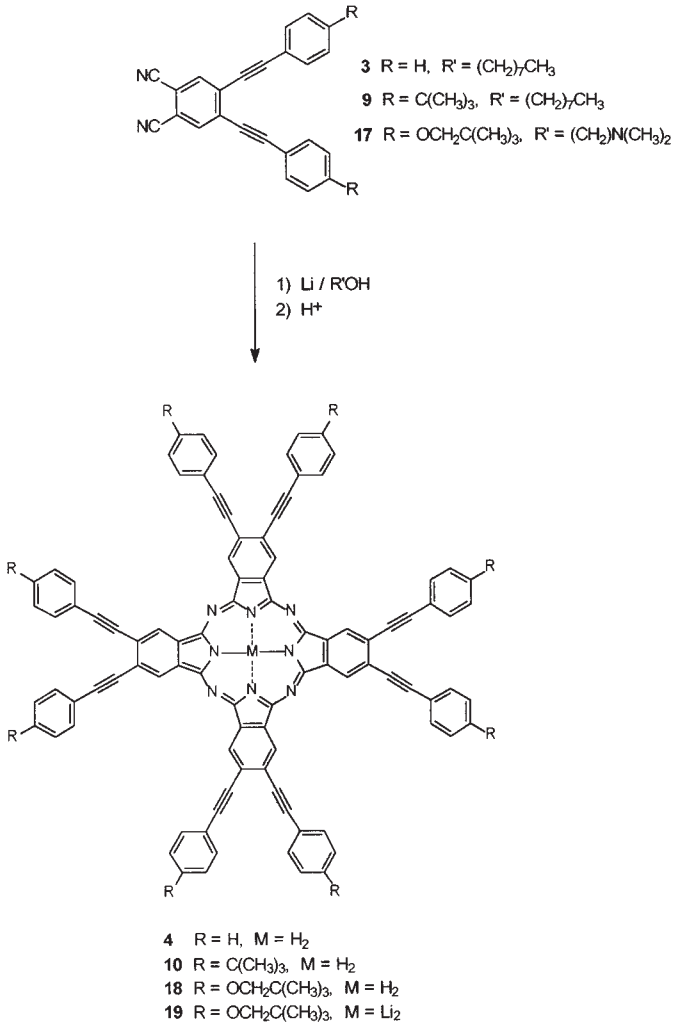
be due to aggregation. In an attempt to minimize these intramolecular aggregative effects, the phenylacetylene moiety was functionalized with the bulky *tert*-butyl group. Thus, 1-bromo-4-*tert*-butylbenzene (**5**) was coupled with trimethylsilylacetylene (**6**) using $Pd(PPh_3)_2Cl_2$ and CuI in TEA in a pressure bottle at 95°C, to give 1-trimethylsilyl-2-(*p*-*tert*-butylphenyl)acetylene (**7**) in 75% yield. This compound was then deprotected by treatment with aqueous 5 M NaOH in methanol to give *p*-*tert*-butylphenylacetylene (**8**) in 98% yield. This was subsequently coupled with 4,5-diiodophthalonitrile (**1**), again using $Pd(PPh_3)_2Cl_2$ and CuI, to afford 4,5-di(*p*-*tert*-butylphenylethynyl)phthalonitrile (**9**) in 88% yield (Scheme 2).

Condensation of **9** to the corresponding Pc (**10**) was performed using lithium 1-octanolate in 1-octanol at 100°C (see Scheme 3 below). A UV–vis probe of this reaction after 22 h revealed an absorption at 722 nm, believed to be the Q-band absorption of the intermediate dilithium Pc. An acid work-up of the reaction was performed to obtain the metal free Pc **10**, but the dark-green product isolated from this reaction was found to be just as insoluble in organic solvents as Pc **4**. Similar difficulties were also encountered in trying to obtain satisfactory NMR and mass spectra, although a MALDI-TOF mass spectrum of **10** exhibited a parent ion cluster at 1762 amu. If phthalocyanine **10** had indeed formed in this reaction, as suggested by the UV–vis spectrum, then it seemed evident that the *tert*-butyl groups did little to enhance the solubility of these Pcs in their metal-free state.

Previous work in our laboratory has shown that neopentoxy groups are highly effective at increasing the solubility of Pcs (13). It was therefore hoped that by replacing the *tert*-butyl groups with neopentoxy groups, a more soluble octaphenylethynyl Pc could be synthesized and full characterization might be facilitated. The synthesis was initiated with the tosylation of neopentyl alcohol (**11**) in pyridine to give neopentyl tosylate (**12**), which was obtained in 85% yield. Tosylate **12** then reacted with *p*-iodophenol (**13**) to give *p*-iodoneopentoxybenzene (**14**) in 82% yield. This was subsequently coupled with trimethylsilylacetylene (**6**) using $Pd(PPh_3)_2Cl_2$ to give 1-trimethylsilyl-2-(*p*-neopentoxyphenyl)acetylene (**15**) in 88% yield. The trimethylsilyl group was then cleaved from **15** using 5 M aq NaOH in methanol to give, in 97% yield, *p*-neopentoxyphenylacetylene (**16**). Terminal alkyne **16** was then coupled with 4,5-diiodophthalonitrile (**1**), again using $Pd(PPh_3)_2Cl_2$ as a catalyst, to give 4,5-di(*p*-neopentoxyphenylethynyl)phthalonitrile (**17**) in 70% yield (Scheme 4). Subsequent condensation of **17** in Li–DMAE at 100°C (Scheme 3) yielded 2,3,9,10,16,17,23,24-octa(*p*-neopentoxyphenylethynyl)phthalocyanine (**18**) as a dark green solid, after work-up. Although not exceedingly soluble, Pc **18** was found to dissolve appreciably well in benzene, toluene, $CHCl_3$, CH_2Cl_2, and THF. Purification of this compound was accomplished by column chromatography using flash silica gel and CH_2Cl_2 as eluent, followed by gel permeation chromatography using SX-2 Biobeads® and THF as eluent. This was followed by reprecipitation from benzene–ethanol and then further chromatography, again using flash silica gel and CH_2Cl_2. After exhaustive purification, **18** was obtained in an overall yield of 8%.

The UV–vis absorption spectrum of phthalocyanine **18** in THF is shown in Fig. 1. A broad absorption band was observed in the 600–800 nm region with an absorption max at 678 nm and a shoulder at 720 nm. Neither dilution of the so-

Scheme 3.



lution, nor heating to 60°C caused any observable changes in its spectral patterns. Although the known metal-free octa(*alkyl*)ethynyl phthalocyanines show a pair of sharp Q-band absorptions in the same region (10), this is not the case for **18**. The corresponding dilithium Pc (**19**) was formed by treating **18** with lithium metal in THF at 50°C. The UV–vis spectrum of this compound in THF, shown in Fig. 2, displays the same sharp Q-band absorption at 720 nm as observed in the spectral probes for the condensation reactions of **3** and **9**. This result lends evidence supporting the formation of Pcs **4** and **10** in the aforementioned reactions.

A comparison of the electronic spectrum of **19** with unsubstituted dilithium phthalocyanine, which displays a Q-band absorption at 688 nm (14), suggests that the eight peripheral *p*-neopentoxyphenylethynyl groups impart a red-shift of approximately 32 nm. Further comparison with the electronic spectrum of a representative octa*alkyl*ethynyl Pc, dilithium-2,3,9,10,16,17,23,24-octapentynylphthalocyanine, which displays a Q-band absorption at 700 nm (15), suggests that the eight peripheral phenyl groups on **19** have the effect of increasing the red-shift in dilithio-octaalkynylphthalocyanines by an additional 20 nm.

Phthalocyanines **18** and **19** were also characterized by ^{1}H NMR spectroscopy in toluene-d_8 at 300 K, at a concentration of 1.0×10^{-3} M. The spectrum of **18** exhibited three broad signals in the aromatic region, one corresponding to the protons on phthalocyanine itself, and the other two corresponding to the protons on the peripheral neopentoxyphenyl rings. The outer neopentoxy groups were observed as a pair of broad singlets, one at 3.48 ppm, corresponding to the OCH_2 hydrogens and the other at 1.16 ppm, corresponding to the hydrogens on the terminal $C(CH_3)_3$ groups. The two protons on the inner nitrogens however were not observed, and a series of high-temperature ^{1}H NMR experiments were subsequently conducted to determine whether aggregation may have any effect in obscuring this signal. The same sample was rerun at incrementally higher temperatures, ranging from 300 to 363 K, but the signal still remained absent. Only after extreme vertical expansion of the spectra was a very broad singlet detected at –4.8 ppm. Additionally, the previously broad aromatic singlets at 300 K began to sharpen, and eventually appeared as a pair of doublets (Fig. 3). FAB-MS analysis of **18** exhibited the parent ion (M + 1, m/z = 2004), but the elemental analysis exhibited somewhat low carbon values, typical of some Pc compounds. The MALDI-TOF mass spectrum also exhibited a parent ion at 2002 amu. The FAB-MS spectrum for **19** did not show a molecular ion peak, but exhibited rather, two ion clusters that are consistent with the loss of one and two lithium atoms; (M – Li) centred around m/z = 2010 and (M – 2 Li) centred around m/z = 2004.

The synthesis of a 4,5-di(butadiynyl)-substituted phthalonitrile was achieved via a palladium-catalyzed cross-coupling between a monosubstituted butadiyne and 4,5-diiodophthalonitrile (**1**). This was accomplished first, by treatment of **16** with an ethyl Grignard and iodine to give 1-iodo-2-(*p*-neopentoxyphenyl)acetylene (**20**) in 26% yield, along with an undesired by-product, 1,4-di(*p*-neopentoxyphenyl)-1,3-butadiyne (**21**). This was followed by a palladium-catalyzed coupling with trimethylsilylacetylene (**6**) to give 1-(trimethylsilyl)-4-(*p*-neopentoxyphenyl)-1,3-butadiyne (**22**) in 29% yield. Subsequent desilylation using 5 M aq NaOH in MeOH at room temperature afforded 1-(*p*-neopentoxyphenyl)-1,3-butadiyne (**23**) in 95% yield. This was followed immediately by a palladium-catalyzed cross-coupling with **1** to give 4,5-di[4-(*p*-neopentoxyphenyl)-1,3-butadiynyl]phthalonitrile (**24**) in 75% yield (Scheme 5). Slow heating of this compound on a melting point apparatus showed no melting point below 300°C, but the addition of a crystal on a hot Kofler block exhibited a sharp decomposition point at 223°C.

Condensation of **24** to 2,3,9,10,16,17,23,24-octa[4-(*p*-neopentoxyphenyl)-1,3-butadiynyl]phthalocyanine (**25**) was attempted using lithium 1-octanolate in 1-octanol at 80°C (Scheme 6). After 18 h, a UV–vis probe of the dark-green reaction mixture in THF revealed a sharp absorption at 738 nm, which was believed to correspond to the Q-band absorption of the dilithium derivative of **25**. A standard workup procedure was attempted whereby the reaction mixture was treated with dilute aqueous acid, followed by several dissolution–reprecipitation cycles from EtOH–H_2O. Unexpectedly, upon contact with aqueous acid or water, the previously dark-green reaction mixture turned brown and

Scheme 4.

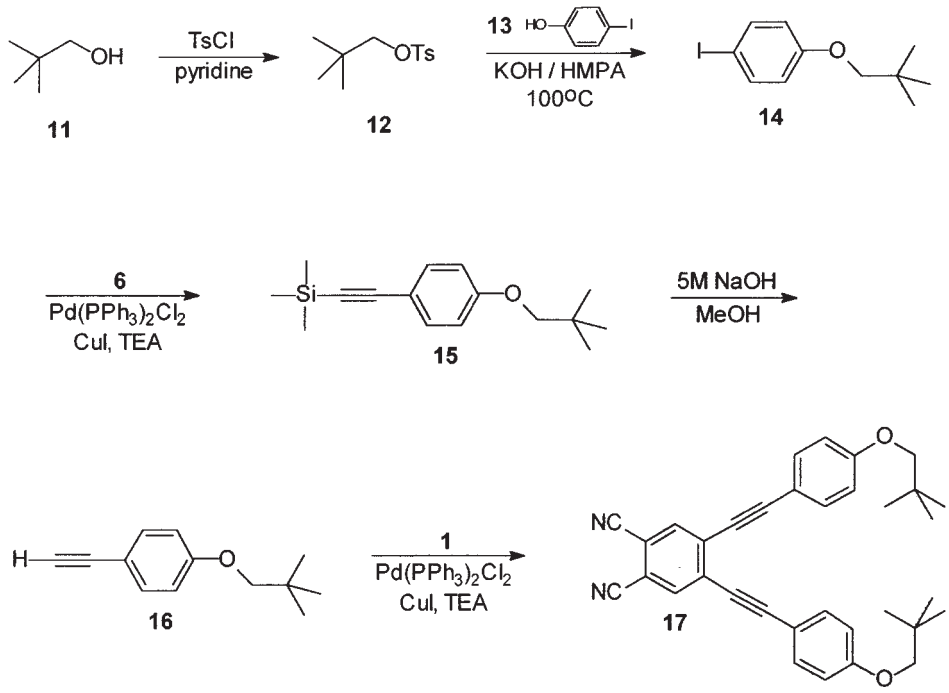


Fig. 1. The UV–vis absorption spectrum of Pc **18**.

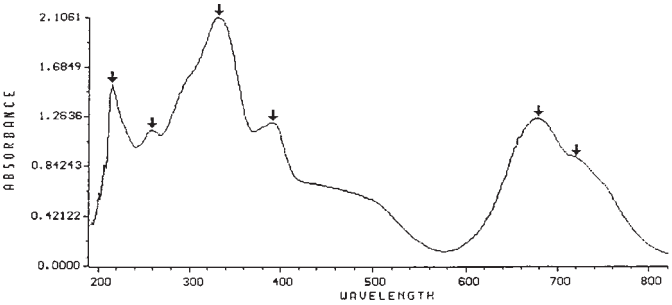
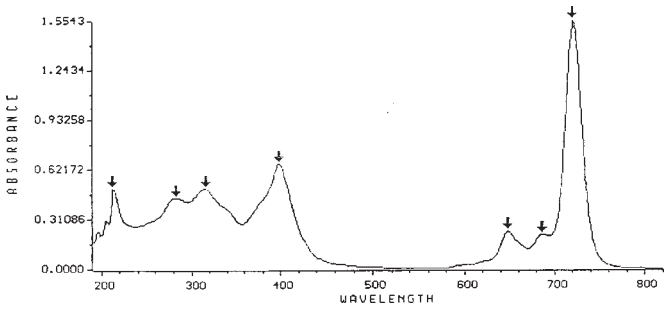


Fig. 2. The UV–vis absorption spectrum of Pc **19**.

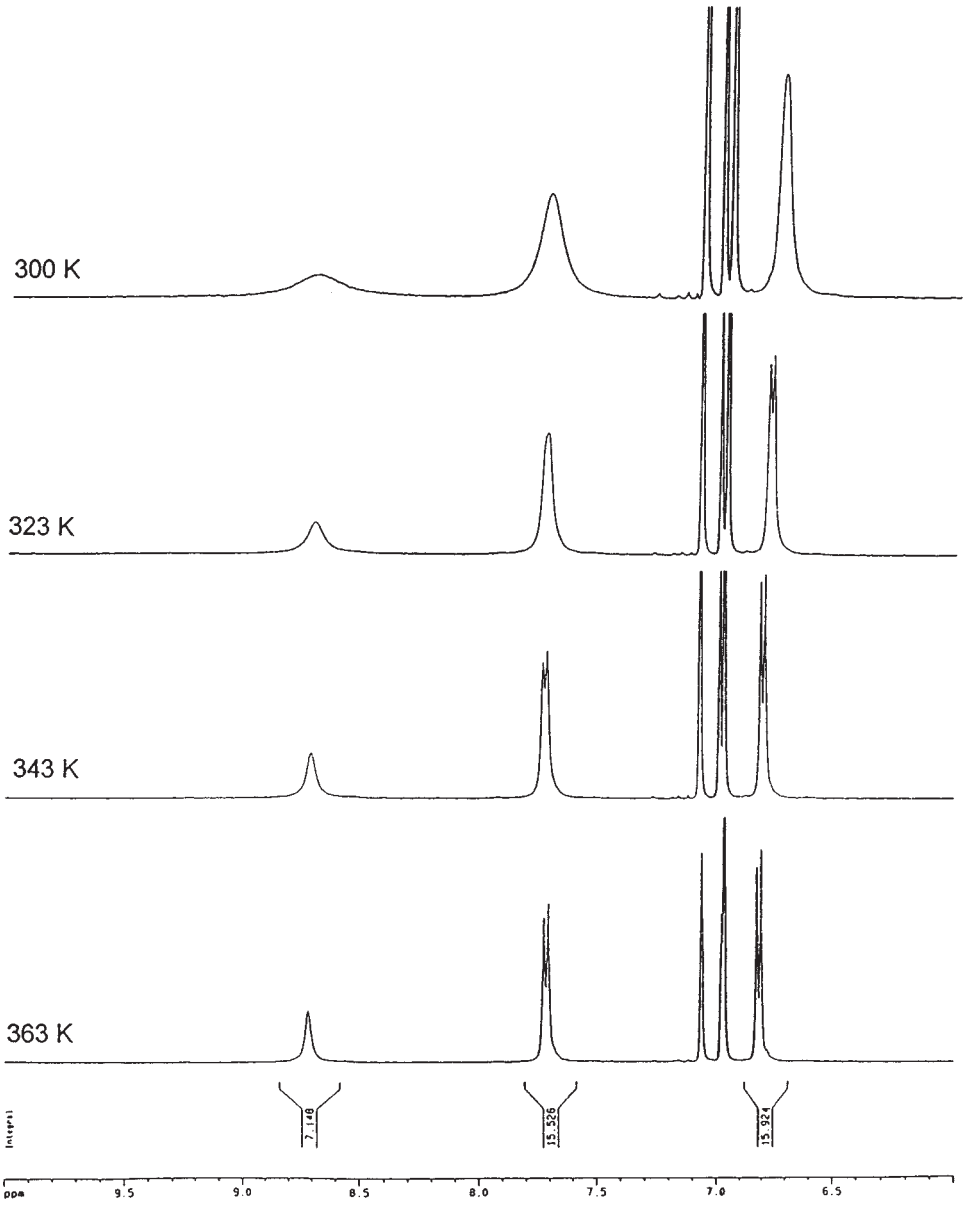


formed a highly insoluble precipitate. A UV–vis spectrum of this material showed almost no absorption in the Q-band region, a result which suggested to us that the Pc had decomposed or polymerized. Attempts were, therefore, made at isolating the intermediate dilithium Pc (**26**) under anhydrous conditions by precipitating the reaction mixture into hexane, followed by gel permeation chromatography of the crude product using dry THF and SX-2 Biobeads®. A dark-green solid was isolated from the column after evaporation of the solvent. An electronic spectrum of this material in THF is shown in Fig. 4. Proton NMR analysis of this material in pyridine-d_5 at 300 K showed a spectrum which was consistent with the structure of **26**. Two singlets were observed at 1.08 and 3.61 ppm, which would correspond to resonances arising from the protons of the eight neopentoxy groups. The aromatic signals arising from the outer neopentoxyphenyl groups corresponded to two doublets centered around 6.92 and 7.67 ppm, and the eight benzo protons on the Pc macrocycle corresponded to a singlet observed at 9.98 ppm. Although, this compound proved to be too unstable to give either a satisfactory elemental analysis or FAB mass spectrum, MALDI-TOF mass spectrometry of **26** did provide a parent ion minus one lithium ion at 2200 amu.

Experimental

Unless otherwise noted, all reaction processes were performed using magnetic stirring methods under an inert atmosphere of Matheson high-purity argon. All organic solvents were dried by appropriate methods and distilled before use. Ultrasound activation was carried out using a Branson 1200 sonicator. Thin layer chromatography (TLC) was performed using Merck silica gel 60 F_{254} polyester-backed plates and column chromatography was performed using Caledon flash grade silica gel 60 of particle size 40–63 μm. Gel permeation chromatography was performed with Bio-Rad SX-2 Biobeads®, using THF as the eluting solvent. Infrared (IR) spectra were recorded on a Unicam Mattson 3000 FT IR spectrometer using samples prepared as KBr discs, unless otherwise noted. Ultraviolet-visible (UV–vis) spectra were recorded on a Hewlett–Packard HP8451A diode array spectrophotometer using THF as the solvent. Melting points (mp) were determined using a Kofler hot stage melting point apparatus and are reported uncorrected. Nuclear magnetic resonance (NMR) spectra for proton and carbon were recorded on a Bruker ARX 400 high field Fourier transform

Fig. 3. The temperature dependent ^{1}H NMR spectra of Pc **18**.



instrument at room temperature unless otherwise stated. Chemical shifts are reported in ppm relative to a tetramethylsilane (TMS) internal standard. Splitting patterns of proton resonances are described as singlets (s), doublets (d), triplets (t), quartets (q), doublet of doublets (dd), multiplets (m), or as broad signals (br). Coupling constants for signals other than singlets and multiplets are reported in Hz. Resonances are reported as the proton decoupled chemical shifts for ^{13}C NMR spectra. Electron-impact mass spectral analyses (EI-MS) were performed by Dr. B. Khouw (York University, Toronto, Ontario, Canada) and Ms. Lisa Nelson (York University, Toronto, Ontario, Canada). MALDI-TOF mass spectra were performed neat using a Voyager Str instrument. Fast atom bombardment (FAB) and high resolution mass spectrometric analyses (HR-MS) were performed by Dr. R. L. Cerny (Nebraska Center for Mass Spectrometry, University of Nebraska-Lincoln, Lincoln, Nebraska, U.S.A.). Microanalyses were performed by Guelph Chemical Laboratories Ltd., Guelph, Ontario, Canada.

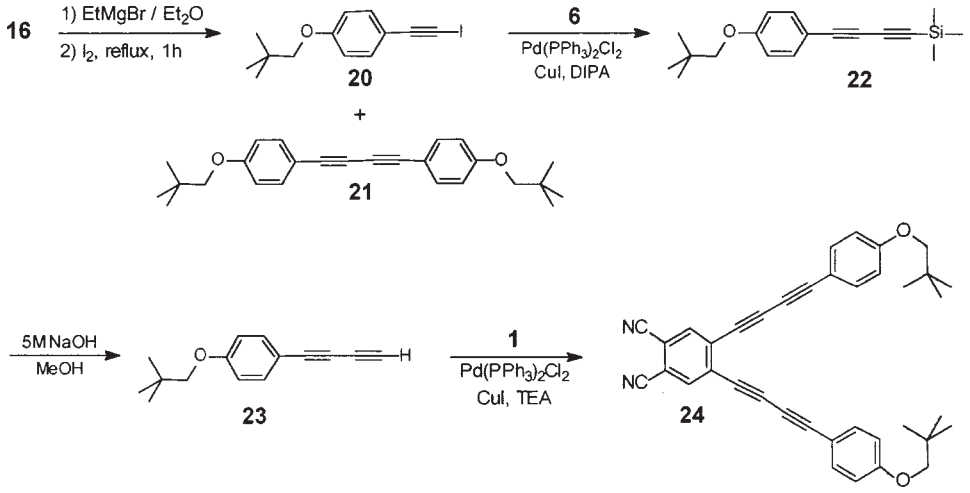
4,5-Diiodophthalonitrile (1)

This compound was prepared in three steps according to a published procedure (10) (overall yield 50% from phthalimide); mp 216–217°C (lit. value (10), 216 to 217°C).

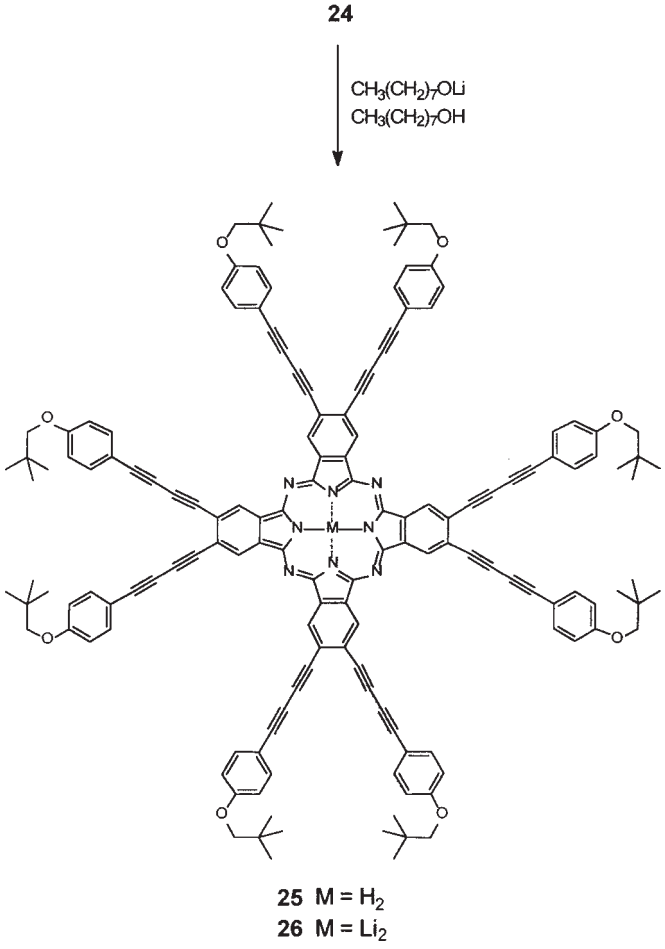
4,5-Di(phenylethynyl)phthalonitrile (3) general procedure

To a solution of 200 mg (0.53 mmol) of 4,5-diiodophthalonitrile (**1**) dissolved in 30 mL of triethylamine (TEA) was added 36 mg (0.051 mmol) of $Pd(PPh_3)_2Cl_2$, 10 mg (0.051 mmol) of CuI, and then 0.13 mL (0.11 g, 1.2 mmol) of phenylacetylene (**2**). The reaction was heated to 60°C for 2 h under argon and then allowed to cool to room temperature overnight. The reaction was analyzed by

Scheme 5.



Scheme 6.



TLC using benzene as eluent, and judged complete by the disappearance of the starting material. The solvent was removed by rotary evaporation at 40°C, the residue was suspended in ethyl acetate, suction filtered through celite, and then the solvent was removed from the filtrate in vacuo at 40°C. This brown residue was chromatographed with flash grade silica gel using 98:2 hexane:ethyl acetate to afford **3** as a yellow solid (121 mg, 70% yield), mp 190–192°C. EI-MS *m*/*z* (%): 328 (M^+, 100). UV–vis (THF) λ_{max} (nm): 222, 276, 301, 345. IR (KBr) (cm^{-1}): 2217 (C≡N). ^1H NMR ($CDCl_3$) δ: 7.93 (s, 2H), 7.59 (d, *J* = 7.1 Hz, 4H), 7.43 (m, 6H). ^{13}C NMR ($CDCl_3$) δ: 136.34, 132.22, 131.09, 130.21, 128.92, 121.72, 114.90, 114.27, 100.70, 85.74. Anal. calcd. for $C_{24}H_{12}N_2$: C 87.79, H 3.68, N 8.53; found: C 87.72, H 3.66, N 8.42.

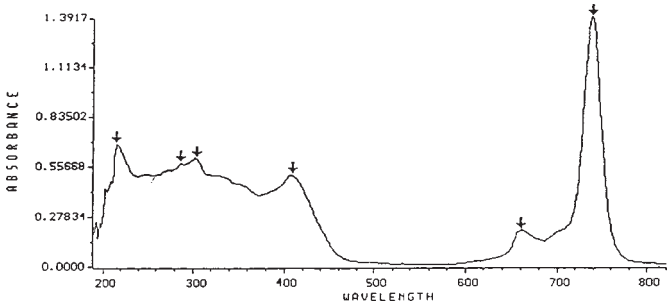
2,3,9,10,16,17,23,24-Octa(phenylethynyl)phthalocyanine (4)

Lithium metal (20 mg, 2.9 mmol) was added to 2 mL of 1-octanol at 60°C and allowed to dissolve over 20 h under argon. After all of the lithium had dissolved, the mixture was cooled to room temperature and then 50 mg (0.15 mmol) of **3** was added. The reaction was heated to 80°C and allowed to stir at this temperature for 6 h. The reaction was monitored by TLC using benzene as the eluent. After all of the starting material had disappeared, the reaction was stopped by the addition of 20% ethanol–water and several drops of 1 M HCl. The reaction mixture was centrifuged, the precipitate was collected, and then washed several times with methanol until the filtrate was colourless. The remaining dark green solid was dried in vacuo to give 10 mg of **4** in a crude yield of 20%. Due to its extreme insolubility in most solvents, this material could not be further purified. MALDI-MS *m*/*z*: 1321.5 (M^+ + Li), 1315.5 (M^+). UV–vis (pyridine) λ_{max} (nm): 726, 650, 396, 306.

1-(*p*-*tert*-Butylphenyl)-2-trimethylsilylacetylene (7)

Into a 100 mL pressure bottle was placed 0.87 mL (1.1 g, 5.0 mmol) of 1-bromo-4-*tert*-butylbenzene (**5**), 0.23 g (0.32 mmol) of $Pd(PPh_3)_2Cl_2$, 19 mg (0.10 mmol) of CuI, and 50 mL of TEA. This yellow suspension was degassed with argon for approximately 5 min, and then 1.5 mL (1.0 g, 10 mmol) of (trimethylsilyl)acetylene (**6**) was added. The bottle was sealed and heated in an oil bath at 95°C overnight. The reaction mixture was allowed to cool to room temperature and was then filtered through celite. The solids were washed with ethyl ether until the washings were colourless and the filtrate was evaporated to dryness under reduced pressure. The residue was chromatographed with

Fig. 4. The UV–vis absorption spectrum of Pc **26**.



flash grade silica gel using hexane as the eluent to give **7** as a pale yellow oil (898 mg, 78% yield). EI-MS *m*/*z* (%): 230 (M^+, 58), 215 (100). ^{1}H NMR ($CDCl_3$) δ: 7.40 (d, *J* = 8.6 Hz, 2H), 7.31 (d, *J* = 8.5 Hz, 2H), 1.31 (s, 9H), 0.25 (s, 9H). The ^{1}H-NMR spectrum matched that of the previously reported compound (16).

p-*tert*-Butylphenylacetylene (8)

To a stirred solution of 200 mg (0.87 mmol) of 1-(*p*-*tert*-butylphenyl)-2-trimethylsilylacetylene (**7**) dissolved in 10 mL of MeOH was added 0.5 mL (2.5 mmol) of 5 M NaOH. After 15 min, the reaction mixture was acidified with 1 M HCl, extracted twice with hexane, and the extracts were dried over $MgSO_4$. Filtration, followed by evaporation of the filtrate in vacuo gave **8** as a pale yellow liquid (134 mg, 98%). IR (neat) (cm^{-1}): 2109 (C≡C). ^{1}HNMR ($CDCl_3$) δ: 7.44 (d, *J* = 8.6 Hz, 2H), 7.35 (d, *J* = 8.1 Hz, 2H), 3.03 (s, 1H), 1.32 (s, 9H). The ^{1}H NMR spectrum matched that of the previously reported compound (16).

4,5-Di(*p*-*tert*-butylphenylethynyl)phthalonitrile (9)

The same procedure was used as for the synthesis of **3**, using 1.0 g (2.6 mmol) of **1**, 1.0 g (6.3 mmol) of **8**, 222 mg (0.32 mmol) of $Pd(PPh_3)_2Cl_2$, 30 mg (0.16 mmol) of CuI, and 30 mL of TEA to give 1.0 g of **9** in 88% yield, mp 168 to 169°C. EI-MS *m*/*z* (%): 440 (M^+, 60), 426 (100). UV–vis (THF) λ_{max} (nm): 214, 279, 309, 354. IR (KBr) (cm^{-1}): 2213 (C≡N). ^{1}H NMR ($CDCl_3$) δ: 7.91 (s, 2H), 7.53 (d, *J* = 8.4 Hz, 4H), 7.43 (d, *J* = 8.6 Hz, 4H), 1.36 (s, 18H). ^{13}C NMR ($CDCl_3$) δ: 153.81, 136.36, 132.09, 131.23, 125.96, 118.79, 115.04, 113.99, 101.09, 85.45, 35.27, 31.34. Anal. calcd. for $C_{32}H_{28}N_2$: C 87.24, H 6.41, N 6.36; found: C 87.25, H 6.42, N 6.12.

2,3,9,10,16,17,23,24-Octa(*p*-*tert*-butylphenylethynyl)phthalocyanine (10)

Lithium metal (16 mg, 2.3 mmol) was added to 3 mL of 1-octanol at 80°C and allowed to dissolve over 20 h under argon. After all of the lithium had dissolved, the mixture was cooled to room temperature and then 200 mg (0.45 mmol) of **9** was added. The reaction was heated to 110°C and allowed to stir at this temperature for 15 h. The reaction was monitored by TLC using benzene as the eluent. After all of the starting material had disappeared, the reaction was stopped by the addition of 20% ethanol–water and several drops of 1 M HCl. The reaction mixture was centrifuged, the precipitate was collected, and then washed several times with methanol until the filtrate was colourless. The remaining dark-green solid was dried in vacuo to give 30 mg of **10** in a crude yield of 15%. Due to its extreme insolubility in most solvents, this material could not be further purified. MALDI-MS *m*/*z*: 1770.8 (M^+ + Li), 1764.8 (M^+). UV–vis (pyridine) λ_{max} (nm): 726, 656, 398, 316.

Neopentyl tosylate (12)

To a stirred, ice water cooled solution of 50 g (0.57 mol) of neopentyl alcohol (**11**) in 350 mL of pyridine was slowly added a solution of 162 g (0.85 mol) of *p*-toluenesulfonyl chloride in 200 mL pyridine. The resulting cloudy brown mixture was allowed to stir overnight at room temperature, after which time the pyridine was removed by rotary evaporation at 45°C. To the remaining residue was added 300 mL of ice-cold water, and the mixture was stirred for 1 h. The mixture was extracted three times with 200 mL portions of ethyl ether, and the combined organic layers were washed with successive 200 mL portions of 1 M HCl, sat. $NaHCO_3$, H_2O, and then brine. The extract was dried over $MgSO_4$, filtered, and the solvent was removed in vacuo to leave **12** as an amber oil. This crude product was crystallized from MeOH–H_2O to afford a white crystalline solid (116 g, 85% yield), mp 48 to 49°C (lit. value (17), 47 to 48°C). ^{1}H NMR ($CDCl_3$) δ: 7.76 (d, *J* = 8.4 Hz, 2H), 7.32 (d, *J* = 8.1 Hz, 2H), 3.63 (s, 2H), 2.42 (s, 3H), 0.87 (s, 9H). ^{13}C NMR ($CDCl_3$) δ: 144.75, 133.20, 129.91, 127.97, 79.59, 31.71, 26.10, 21.69.

p-Iodoneopentoxybenzene (14)

A mixture of 10 g (45 mmol) of 4-iodophenol (**13**), 12.1 g (50 mmol) of neopentyl tosylate (**12**), and 2.8 g (50 mmol) of potassium hydroxide in 30 mL of hexamethylphosphoramide (HMPA) (Caution: Carcinogen) was vigorously stirred at 100°C for 3 days. This mixture was then poured into 300 mL of H_2O and extracted three times with 100 mL portions of ethyl ether. The combined ether extracts were successively washed with 100 mL portions of H_2O, 1 M HCl, H_2O, and then brine, followed by drying over $MgSO_4$, filtration and removal of the solvent by rotary evaporation. The remaining amber oil was chromatographed using silica gel and hexane as eluent to afford **14** as a clear, colourless liquid (10.8 g, 82% yield). EI-MS *m*/*z* (%): 290 (M^+, 60), 220 (100). UV–vis (THF) λ_{max} (nm): 234, 282. ^{1}H NMR ($CDCl_3$) δ: 7.54 (d, *J* = 8.8 Hz, 2H), 6.68 (d, *J* = 8.8 Hz, 2H), 3.55 (s, 2H), 1.03 (s, 9H). ^{13}C NMR ($CDCl_3$) δ: 159.65, 138.27, 117.17, 82.50, 78.16, 32.05, 26.78. Anal. calcd. for $C_{11}H_{15}IO$: C 45.54, H 5.21; found: C 45.47, H 5.36.

1-Trimethylsilyl-2-(*p*-neopentoxyphenyl)acetylene (15)

The same procedure was used as for the synthesis of **3**, using 8.0 g (28 mmol) of **14**, 4.7 mL (3.3 g, 33 mmol) of trimethylsilylacetylene (**6**), 968 mg (1.4 mmol) of $Pd(PPh_3)_2Cl_2$, 263 mg (1.4 mmol) of CuI, and 300 mL of TEA, except that the entire reaction was carried out at room temperature. The crude product was chromatographed using silica gel and hexane as eluent to afford **15** as a white solid (6.3 g, 88% yield), mp 78 to 79°C. EI-MS *m*/*z* (%): 260 (M^+, 40), 245 (20), 190 (50), 175 (100). UV–vis (THF) λ_{max} (nm): 214, 261. IR (KBr) (cm^{-1}): 2157 (C≡C). ^{1}H NMR ($CDCl_3$) δ: 7.39 (d, *J* = 8.4 Hz, 2H), 6.81 (d, *J* = 8.6 Hz, 2H), 3.59 (s, 2H), 1.04 (s, 9H), 0.25 (s, 9H). ^{13}C NMR

($CDCl_3$) δ: 160.02, 133.62, 115.17, 114.60, 105.63, 92.39, 78.08, 32.08, 26.80, 0.32. Anal. calcd. for $C_{16}H_{24}OSi$: C 73.79, H 9.29; found: C 73.40, H 9.23.

p-Neopentoxyphenylacetylene (16)

The same procedure was used as for the synthesis of **8**, using 10 g (38 mmol) of **15**, 23 mL (115 mmol) of 5 M NaOH, and 600 mL of MeOH to afford **16**. The crude product was chromatographed using silica gel and hexane as eluent giving the title compound as a clear, colourless oil (6.5 g, 95% yield). EI-MS *m*/*z* (%): 188 (M^+, 10), 118 (100). UV–vis (THF) λ_{max} (nm): 213, 252, 293, 318, 343. IR (neat) (cm^{-1}): 2107 (C≡C). ^1H NMR ($CDCl_3$) δ: 7.42 (d, *J* = 8.7 Hz, 2H), 6.84 (d, *J* = 8.6 Hz, 2H), 3.60 (s, 2H), 2.99 (s, 1H), 1.04 (s, 9H). ^{13}C NMR ($CDCl_3$) δ: 160.21, 133.73, 114.71, 114.03, 84.05, 78.11, 75.81, 32.08, 26.78. Anal. calcd. for $C_{13}H_{16}O$: C 82.94, H 8.57; found: C 82.20, H 8.39.

4,5-Di(*p*-neopentoxyphenylethynyl)phthalonitrile (17)

The same procedure was used as for the synthesis of **3**, using 760 mg (2.0 mmol) of **1**, 791 mg (4.2 mmol) of **16**, 147 mg (0.32 mmol) of $Pd(PPh_3)_2Cl_2$, 40 mg (0.16 mmol) of CuI, and 25 mL of TEA to give 700 mg of **17** in 70% yield, mp 168–170°C. EI-MS *m*/*z* (%): 501 (M^+, 18), 500 (55), 360 (100). UV–vis (THF) λ_{max} (nm): 214, 252, 284, 325, 366. IR (KBr) (cm^{-1}): 2209 (C≡N). ^1H NMR ($CDCl_3$) δ: 7.87 (s, 2H), 7.51 (d, *J* = 8.6 Hz, 4H), 6.92 (d, *J* = 8.7 Hz, 4H), 3.64 (s, 4H), 1.06 (s, 18H). ^{13}C NMR (acetone-d_6) δ: 162.37, 137.24, 134.80, 131.70, 116.33, 116.03, 114.91, 114.66, 101.51, 86.12, 79.12, 32.69, 27.02. Anal. calcd. for $C_{34}H_{32}N_2O_2$: C 81.57, H 6.44, N 5.60; found: C 81.00, H 6.45, N 5.44.

2,3,9,10,16,17,23,24-Octa(*p*-neopentoxyphenylethynyl)phthalocyanine (18)

To 2.5 mL of dimethylaminoethanol (DMAE) was added 30 mg (4.3 mmol) of lithium metal. After the metal had completely dissolved, 200 mg (0.4 mmol) of **17** was added to the well-stirred alkoxide solution, and the reaction mixture was heated to 100°C for 15 h. After this time, the reaction mixture was cooled to room temperature and diluted with 10 mL of 20% MeOH–H_2O. After being allowed to stand for 90 min, the reaction mixture was centrifuged and the crude Pc was collected, dissolved in THF and precipitated from hexane. This crude pigment was chromatographed using silica gel and CH_2Cl_2 as eluent, followed by gel permeation chromatography using SX-2 Biobeads® and THF as eluent. This material was further purified by reprecipitation from benzene–ethanol and then by chromatography using silica gel and CH_2Cl_2 as eluent to give **18** as a dark green solid (64 mg, 8% yield). FAB-MS: 2004. MALDI-MS *m*/*z*: 2003.9 (M^+). UV–vis (THF) λ_{max} (nm) (log ϵ): 716 (6.08), 678 (6.19), 390 (6.18), 330 (6.41), 258 (6.14), 216 (6.23). ^1H NMR (toluene-d_8, 1.0×10^{-3} M, 363 K) δ: 8.71 (br, 8H), 7.71 (d, *J* = 7.8 Hz), 6.81 (d, *J* = 8.1 Hz), 3.58 (s, 16H), 1.14 (s, 72H), –4.81 (br, 2H). Anal. calcd. for $C_{136}H_{130}N_8O_8$: C 81.49, H 6.54, N 5.59; found: C 80.06, H 5.80, N 5.27.

[2,3,9,10,16,17,23,24-Octa(*p*-neopentoxyphenylethynyl)phthalocyaninyl]dilithium (19)

To a suspension of 10 mg (0.72 mmol) of lithium metal in 2 mL of dry THF was added 2 mg (1.0×10^{-3} mmol) of Pc **18**. The mixture was stirred at 50°C for 5 days, after which time the excess lithium was removed by filtration and the solvent was removed in vacuo at 40°C to give **19** (2 mg, 100% yield). FAB-MS: 2010 (M – Li), 2004 (M – 2Li). UV–vis (THF) λ_{max} (nm) (log ϵ): 720 (6.89), 686 (6.04), 648 (6.07), 398 (6.52), 316 (6.40), 282 (6.35), 212 (6.40). ^1H NMR (pyridine-d_5, 4.0×10^{-4} M, 333 K) δ: 8.86 (br, 8H), 7.75 (br, 16H), 6.79 (d, *J* = 7.4 Hz), 3.53 (s, 16H), 1.12 (s, 72H).

1-Iodo-2-(*p*-neopentoxyphenyl)acetylene (20)

To 11.5 mL (35 mmol) of ethylmagnesium bromide (3.0 M solution in ether) was slowly added a solution of 5.0 g (27 mmol) of *p*-neopentoxyphenylacetylene (**16**) in 15 mL of anhydrous ether. The reaction mixture was then heated to reflux as 6.7 g (23 mmol) of powdered iodine was slowly added through the top of the condenser. The solution was refluxed for another hour, allowed to cool to room temperature and then poured into 150 mL of H_2O. The mixture was acidified with glacial acetic acid, the ether layer was separated, and the aqueous layer was extracted twice with 50 mL portions of ether. The combined organic extracts were washed with sat. $Na_2S_2O_3$, sat. $NaHCO_3$, H_2O, and brine, then dried over $MgSO_4$, filtered and evaporated under reduced pressure. The title compound (**20**) was obtained as a white solid after recrystallization from MeOH–H_2O (2.2 g, 26% yield), mp 54 to 55°C. EI-MS *m*/*z* (%): 314 (M^+, 35), 244 (100), 118 (65). UV–vis (THF) λ_{max} (nm): 214, 262. IR (KBr) (cm^{-1}): 2166 (C≡C). ^1H NMR ($CDCl_3$) δ: 7.36 (d, *J* = 8.7 Hz, 2H), 6.83 (d, *J* = 8.7 Hz, 2H), 3.59 (s, 2H), 1.03 (s, 9H). ^{13}C NMR ($CDCl_3$) δ: 160.26, 133.94, 115.45, 114.62, 94.38, 78.13, 32.08, 26.79, 3.56. Anal. calcd. for $C_{13}H_{15}IO$: C 49.70, H 4.81; found: C 50.06, H 4.78.

The by-product, 1,4-di-(*p*-neopentoxyphenyl)-1,3-butadiyne (**21**), was obtained in 59% yield (2.9 g) as a white solid, mp 189–191°C. UV–vis (THF) λ_{max} (nm): 214, 269, 282, 300, 320, 343. IR (KBr) (cm^{-1}): 2388, 2139, 1601, 1503, 1291, 1247, 1166, 1016, 831. ^1H NMR ($CDCl_3$) δ: 7.44 (d, *J* = 8.7 Hz, 2H), 6.85 (d, *J* = 8.7 Hz, 2H), 3.60 (s, 2H), 1.04 (s, 9H). ^{13}C NMR ($CDCl_3$) δ: 160.50, 134.19, 114.89, 113.85, 81.59, 78.16, 73.10, 32.09, 26.78. EI-MS *m*/*z* (%): 374 (M^+, 50), 234 (100). Anal. calcd. for $C_{26}H_{30}O_2$: C 83.38, H 8.07; found: C 82.90, H 8.40.

1-(Trimethylsilyl)-4-(*p*-neopentoxyphenyl)-1,3-butadiyne (22)

To a solution containing 200 mg (0.64 mmol) of **20** dissolved in 5 mL of THF were added 22 mg (0.032 mmol) of $Pd(PPh_3)_3Cl_2$, 3.0 mg (0.016 mmol) of CuI, 0.16 mL (116 mg, 1.15 mmol) of diisopropylamine (DIPA), and then 0.36 mL (250 mg, 2.55 mmol) of trimethylsilylacetylene (**6**). The reaction mixture was allowed to stir overnight at room temperature, after which time the solvent was evaporated in vacuo, the residue was suspended in hexane and then filtered through a bed of celite. The filtrate was concentrated under reduced pressure, chromatographed using silica gel and hexane as eluent, and then recrystallized from EtOH–H_2O to

give **22** as a white, crystalline solid (53 mg, 29% yield). EI-MS *m*/*z* (%): 284 (M^+, 65), 214 (65), 199 (100). UV–vis (THF) λ_{max} (nm): 214, 240, 275, 291, 309. IR (KBr) (cm^{-1}): 2203, 2103, 1603, 1509, 1299, 1249, 1172, 1108, 1048, 1014, 847, 760, 694. ^1H NMR ($CDCl_3$) δ: 7.41 (d, *J* = 8.7 Hz, 2H), 6.83 (d, *J* = 8.7 Hz, 2H), 3.59 (s, 2H), 1.03 (s, 9H), 0.23 (s, 9H). ^{13}C NMR ($CDCl_3$) δ: 160.72, 134.49, 114.89, 113.06, 90.03, 88.41, 78.13, 77.48, 73.13, 32.08, 26.77, –0.10. Anal. calcd. for $C_{18}H_{24}OSi$: C 76.00, H 8.50; found: C 76.07, H 8.20.

1-(*p*-Neopentoxyphenyl)-1,3-butadiyne (23)

To a stirred solution of 1.0 g (3.5 mmol) of (**22**) dissolved in 50 mL of MeOH was added 2.1 mL (11 mmol) of 5 M NaOH. After 15 min, the reaction mixture was acidified with 1 M HCl, extracted twice with hexane, and the extracts were dried over $MgSO_4$. Filtration, followed by evaporation of the filtrate in vacuo gave a grey solid, which after chromatography through a plug of silica gel using hexane, afforded 709 mg of **23** as a white solid, which rapidly darkened on exposure to light and air (95% yield). (This material was used immediately in the synthesis of **24**). EI-MS *m*/*z* (%): 212 (M^+, 20), 142 (100). UV–vis (THF) λ_{max} (nm): 214, 281, 298. IR (KBr) (cm^{-1}): 2204, 1896, 1602, 1562, 1509, 1473, 1400, 1364, 1295, 1255, 1170, 1109, 1048, 1017, 921, 834, 624. ^1H NMR ($CDCl_3$) δ: 7.45 (d, *J* = 8.6 Hz, 2H), 6.85 (d, *J* = 8.7 Hz, 2H), 3.61 (s, 2H), 2.46 (s, 1H), 1.04 (s, 9H). ^{13}C NMR ($CDCl_3$) δ: 160.86, 134.59, 114.93, 112.74, 78.18, 75.99, 72.50, 70.87, 68.69, 32.09, 26.76.

4,5-Di[4-(*p*-neopentoxyphenyl)-1,3-butadiynyl]phthalonitrile (24)

The same procedure was used as for the synthesis of **3**, using 631 mg (1.66 mmol) of **1**, 740 mg (3.49 mmol) of **23**, 122 mg (0.174 mmol) of $Pd(PPh_3)_2Cl_2$, 33.2 mg (0.174 mmol) of CuI, and 40 mL of TEA, except that the entire reaction was carried out at room temperature. After 18 h, the solvent was removed in vacuo and then the residue was dissolved in CH_2Cl_2, washed with H_2O and brine, dried over $MgSO_4$ and filtered. The solvent was removed from the filtrate under reduced pressure and the brown residue was triturated twice with ethyl ether to leave **24** as a golden-yellow solid (683 mg, 75% yield), mp 233°C (decomp.). HR-MS (*m*/*z*) calcd. for $C_{38}H_{32}N_2O_2$: 548.2464; found: 548.2464. UV–vis (THF) λ_{max} (nm): 218, 262, 280, 294, 308, 386. IR (KBr) (cm^{-1}): 2203 (C≡N). ^1H NMR ($CDCl_3$) δ: 7.86 (s, 2H), 7.52 (d, *J* = 8.7 Hz, 4H), 6.89 (d, *J* = 8.7 Hz, 4H), 3.63 (s, 4H), 1.05 (s, 18H). ^{13}C-NMR (acetone-d_6) δ: 162.76, 138.72, 135.69, 131.19, 116.38, 116.24, 115.64, 113.14, 88.62, 85.03, 79.13, 77.41, 72.81, 32.67, 26.96. Anal. calcd. for $C_{38}H_{32}N_2O_2$: C 83.18, H 5.88, N 5.11; found: C 81.14, H 5.64, N 4.76.

Dilithium-2,3,9,10,16,17,23,24-octa[4-(*p*-neopentoxyphenyl)-1,3-butadiynyl]phthalocyanine (26)

To a vigorously stirred suspension containing 25 mg (0.046 mmol) of **24** in 0.4 mL of 1-octanol, was added 4 mg (0.58 mmol) of lithium metal (rolled to a foil in an argon purged plastic bag). The reaction mixture was heated to 80°C overnight, after which time the colour turned from bright yellow to dark green. The reaction mixture was diluted with 10 mL of hexane and then centrifuged. The supernatant liquid was discarded, the crude pigment was dissolved in anhydrous THF, reprecipitated into 5 mL of hexane and centrifuged again. This cycle was repeated four times until the octanol was removed and the supernatant liquid was colourless. The remaining crude Pc was dissolved in 2-mL of anhyd THF and loaded onto a gel permeation column consisting of SX-2 Biobeads® and anhyd THF as the eluting solvent. A single green band was collected in five, 2 mL fractions, each of which were analyzed by UV–vis spectroscopy. The fractions containing the least intense absorptions in the 200–500 nm region of the spectrum were combined and the solvent removed in vacuo to give what is believed to be **26** as a dark green solid (7 mg, 28% yield). MALDI-MS *m*/*z*: 2202 (M^+ – Li). UV–vis (THF) λ_{max} (nm): 214, 304, 408, 660, 738. ^1H NMR (pyridine-d_5, 4.53×10^{-4} M, 300 K) δ: 9.98 (br, 8H), 7.67 (d, *J* = 8.4 Hz, 16H), 6.92 (d, *J* = 8.4 Hz, 16H), 3.60 (s, 16H), 1.08 (s, 72H).

Conclusion

We have demonstrated that it is possible to prepare octaarylethynyl and octaarylbutadiynyl phthalocyanines, but that solubility and stability problems may make their use in nonlinear optics and other applications difficult. Solubilizing groups on the aryl groups *ortho* to the alkyne groups may provide the dual goal of solubilization and stabilization.

Note added in Proof

One different octaarylethynylphthalocyanine has recently been reported (see R. Faust and F. Mitzel. J. Chem. Soc. Perkin Trans. 1, 3746 (2000)).

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