Synthesis of 2,3,9,10,16,17,23,24-Octaalkynylphthalocyanines and the Effects of Concentration and Temperature on Their ^{1}H NMR Spectra

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The syntheses of 3,4- and 4,5-diiodophthalonitriles are described. Coupling of the latter compound with $Pd(PPh_3)_2Cl_2$ and 1-octyne, 1-heptyne, 1-hexyne, 1-pentyne, and 3,3-dimethyl-1-butyne gave a series of 4,5-dialkynylphthalonitriles. Hydrogenation of 4,5-bis(1-pentynyl)phthalonitrile and 4,5-bis(3,3-dimethyl-1-butynyl)phthalonitrile gave 4,5-dipentylphthalonitrile and 4,5-bis(3,3-dimethylbutyl)phthalonitriles. Condensation of the dialkynylphthalonitriles with lithium 1-pentoxide in 1-pentanol gave 2,3,9,10,16,17,23,24-octaalkynylphthalocyanines, while intervention of the intermediate dilithium phthalocyanines with zinc acetate gave the related zinc(II) phthalocyanines. ^{1}H NMR spectroscopy of these octaalkynylphthalocyanines exhibited large chemical shifts (1−2 ppm) of the internal and aromatic protons at concentrations ranging from 10^{-2} to 10^{-5} M and at temperatures from 27 to 147 °C. The effects of aggregation phenomena are discussed. The importance of reporting concentration and temperature values for NMR spectra of phthalocyanines is stressed.

Introduction

2,3,9,10,16,17,23,24-Octasubstituted phthalocyanines and other phthalocyanines have found wide applications[1] in a number of areas, outside their traditional uses as dyes,[2] including liquid crystals,[3] chemical sensors,[1,4] nonlinear optics,[5] and electrical and even biological applications.[1,6] The description of hexaalkynylbenzenes[7] as possible compounds for use in nonlinear optics has piqued our interest in related polyalkynylphthalocyanines. Although 2,3,9,10,16,17,23,24-octaalkoxyphthalocyanines,[8] 2,3,9,10,16,17,23,24-octakis(alkoxymethyl)-phthalocyanines,[3,9] and 2,3,9,10,16,17,23,24-octaalkylphthalocyanines[10−12] have been known for some time now, the methods used for their preparation are not applicable to the syntheses of the *alkynyl*phthalocyanines described herein. Both 4-iodophthalonitrile[13,14] and 3-iodophthalonitrile[15] have been used to prepare monoalkynylphthalonitriles[14,15] which have been used to synthesize alkynylphthalocyanines, but 4,5-dialkynylphthalonitriles have hitherto been rarely accessible for elaboration into polyalkynylphthalocyanines.[16] Since monoiodophthalonitriles are key starting materials for monoalkynylphthalonitriles, the preparation of some unknown polyiodophthalonitriles was a prerequisite for preparing polyalkynylphthalonitriles.

Results and Discussion

Synthesis. Electrophilic aromatic iodination of aromatic compounds containing two electron-withdrawing groups is quite rare but can be accomplished using iodine in fuming sulfuric acid at temperatures greater than 60 °C.[17,18] Thus, phthalimide (**1**) was directly iodinated with iodine in 30% fuming sulfuric acid at 70−75 °C to give 4,5-diiodophthalimide (**2**), a trace of 3,4-diiodophthalimide (**3**), and 4,5-diiodophthalic acid (**4**) from which **2** and **4** were isolated in 75 and 20% yields, respectively. If the reaction was allowed to proceed at 85−90 °C, a larger amount of **3** (inseparable from **2**) was produced. Pure **2**, on treatment with concentrated ammonia, gave pure 4,5-diiodophthalamide (**5**), while similar treatment of a mixture of **2** and **3** gave a mixture of **5** and 3,4-diiodophthalamide (**6**). Treatment of **5** with trifluoroacetic anhydride in pyridine,[19,20] gave 4,5-diiodophthalonitrile (**7**) in 79% yield, while similar treatment of the

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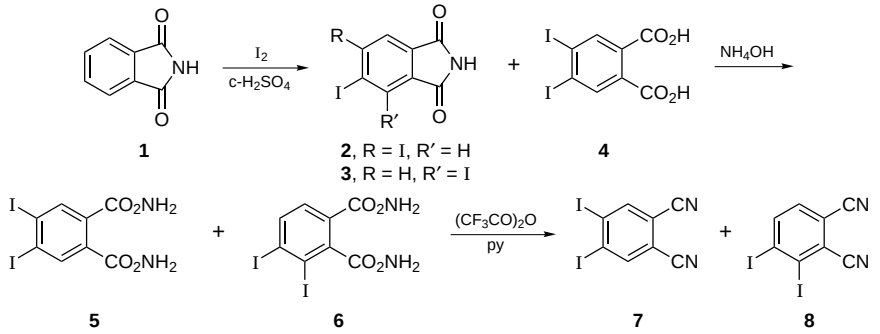
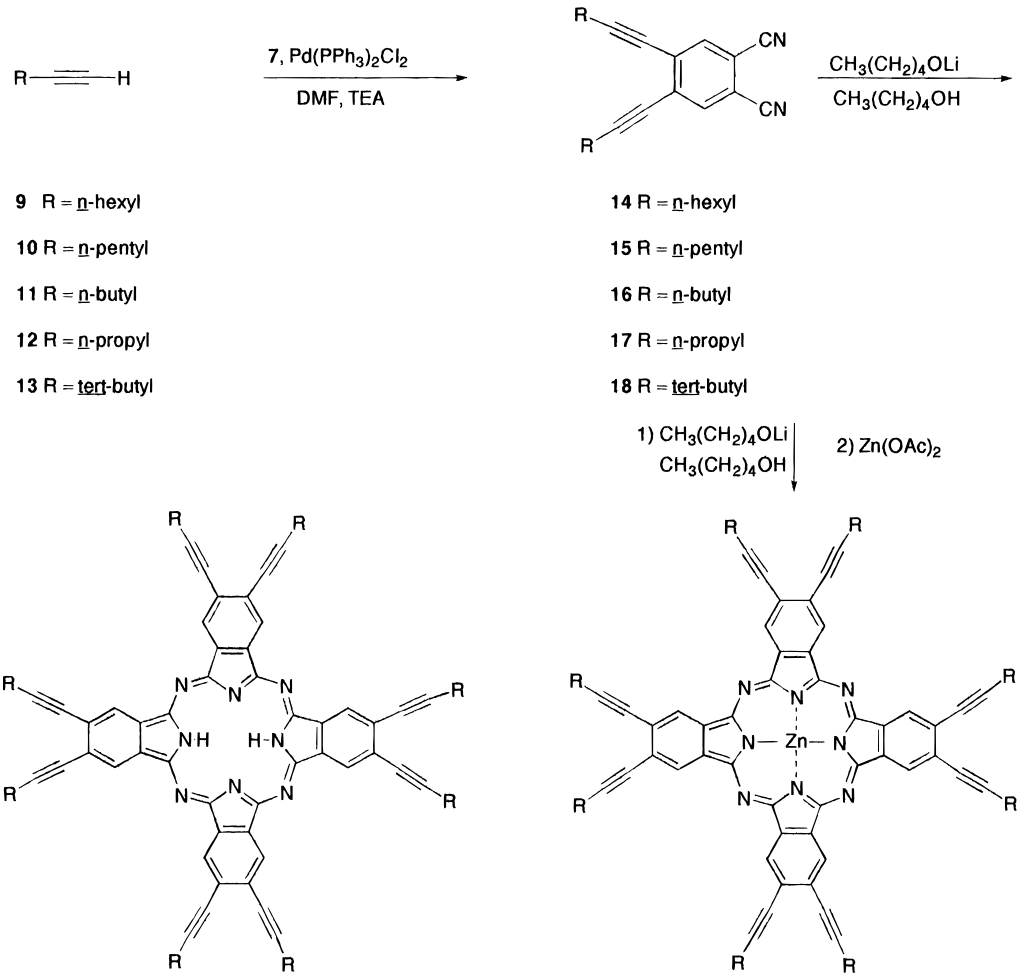
Scheme 1



Scheme 2



9 R = n-hexyl
10 R = n-pentyl
11 R = n-butyl
12 R = n-propyl
13 R = tert-butyl

14 R = n-hexyl
15 R = n-pentyl
16 R = n-butyl
17 R = n-propyl
18 R = tert-butyl

19 R = n-hexyl
20 R = n-pentyl
21 R = n-butyl
22 R = n-propyl
23 R = tert-butyl

24 R = n-hexyl
25 R = n-pentyl
26 R = n-butyl
27 R = n-propyl
28 R = tert-butyl

mixture of **5** and **6** gave **7** and 3,4-diiodophthalonitrile (**8**) isolated in 80% and 10% yields, respectively (Scheme 1).

Coupling of an excess of the terminal alkynes **9**−**12** with 4,5-diiodophthalonitrile (**7**) in triethylamine (TEA) at 110 °C using $Pd(PPh_3)_2Cl_2$ as a catalyst[21] or 3,3-dimethyl-1-butyne (**13**) in TEA at room temperature using $Pd(PPh_3)_2Cl_2$ and CuI as catalysts[22,23] gave the 4,5-dialkynylphthalonitriles **14**−**18** in 70−90% yields. Compounds **14**−**18** were readily soluble in most organic solvents and were converted using lithium 1-pentoxide

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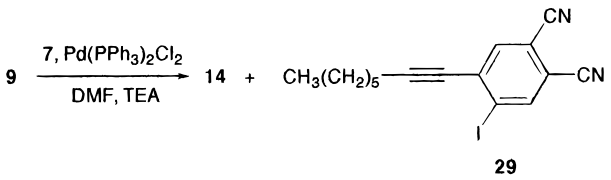
Scheme 3



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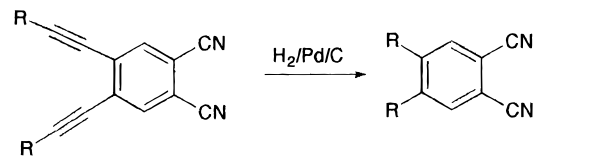
Scheme 4



17 R = n-propyl
18 R = tert-butyl
30 R = n-pentyl
31 R = $(CH_3)_3CCH_2CH_2$

in 1-pentanol[24,25] at 110 °C into their respective metal-free 2,3,9,10,16,17,23,24-octaalkynylphthalocyanines **19**−**23**. Attempts at converting the metal-free Pcs **19**−**23** into zinc Pcs using $Zn(OAc)_2$ in *N*,*N*-dimethylformamide (DMF) at 120 °C was unsuccessful in that incomplete metalation and some bleaching of the pigment occurred. Consequently, the dilithium Pcs, prepared as nonisolated intermediates in the preparation of **19**−**23**, were treated *in situ* with $Zn(OAc)_2$ at 60 °C to provide the fully metaled zinc(II) 2,3,9,10,16,17,23,24-octaalkynylphthalocyanines **24**−**28** in 35−45% yields, respectively (Scheme 2). Although the zinc(II) Pcs **24**−**28** were somewhat less soluble in organic solvents than the metal-free Pcs **19**−**23**, they were still quite soluble in most organic solvents. The relative mobilities of the zinc(II) Pcs on thin-layer chromatography using $CHCl_3$ as eluent are **28** > **24** > **25** > **26** > **27**, as expected with the bulky *tert*-butyl groups of **28**, reducing aggregation and increasing its mobility.

It is important to note that although **19**−**23** and **24**−**28** exhibit Q-bands typical of metal-free and metalated Pcs, respectively, the λ_{max} values of the most red-shifted band is red-shifted by approximately 1 eV per alkynyl group compared to unsubstituted phthalocyanines so that the λ_{max} of **23**, for example, is 732 nm and that of **28** is 712 nm.

When **7** was coupled as before but in triethylamine (TEA) and with only 2 equiv of 1-octyne (**9**), a mixture of **14** and the monocoupled product 4-iodo-5-(1-octynyl)-phthalonitrile (**29**) were produced in 40 and 30% yields, respectively (Scheme 3). Although the identity of 4,5-diiodophthalonitrile (**7**) is firmly based on NMR chemical shift data, the isolation of **29** exhibiting two different *singlets* in its NMR spectrum clearly corroborates that **7** could not be 3,6-diiodophthalonitrile, whose monocoupled product would yield two different *doublets*.

Catalytic hydrogenation of 4,5-bis(1-pentynyl)phthalonitrile (**17**) or 4,5-bis(3,3-dimethyl-1-butynyl)phthalonitrile (**18**) with hydrogen over a Pd/C catalyst gave 4,5-dipentylphthalonitrile (**30**) and 4,5-bis(3,3-dimethylbutyl)phthalonitrile (**31**) in yields greater than 95% (Scheme 4).

It should be noted that the preparation of 4,5-dialkylphthalonitriles **30** and **31** via **7** and a terminal alkyne followed by hydrogenation is a desirable alternative to other multistep preparations of 4,5-dialkylphthalonitriles[10−12] which require low-yield reactions using CuCN.

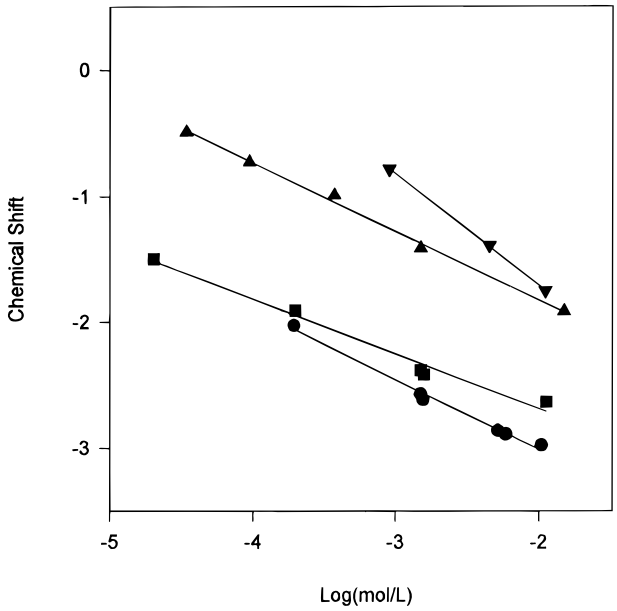


Figure 1. Chemical shift of internal protons of metal-free phthalocyanines as a function of log concentration (mol/L). ^{1}H NMR in C_6D_6 at 27 °C: ▲, $(3,3\text{-dimethylbutynyl})_8PcH_2$ (**23**); ●, $(hexynyl)_8PcH_2$ (**21**); ■, $(heptynyl)_8PcH_2$ (**20**). ^{1}H NMR in $CDCl_3$ at 27 °C; ▼, $(3,3\text{-dimethylbutynyl})_8PcH_2$ (**23**).

Concentration and Temperature Effects in ^{1}H NMR Spectroscopy of the Phthalocyanines. Some earlier work on the effect of concentration on tetrasubstituted phthalocyanines[14] was limited due to the facts that mixtures of tetrasubstituted isomers were always present and lower field instrumentation did not allow the collection of data on very dilute solutions. The octaalkynylphthalocyanines described herein are all single isomers, and both internal and aromatic protons give simple singlets. Initial ^{1}H NMR spectra obtained for Pcs at 10^{-2} M in benzene-d_6 showed that the internal protons of the *tert*-butylethynyl Pc **23** were further downfield than the internal protons of the other four Pcs **19**−**22** at the same concentration. This observation can be readily explained by the fact that the bulky *tert*-butylethynyl groups prevent aggregation far better than the linear alkynyl groups. These results bring up an interesting point. What is the actual absorption value of the internal and aromatic protons of an unaggregated Pc in a specific solvent?

It was decided that a series of concentration and temperature ^{1}H NMR studies would be carried out on the Pcs described in Scheme 2. The results of these experiments are depicted in Figures 1−5. The effect of concentration on the ^{1}H NMR chemical shifts of the Pcs was studied over the concentration range of 10^{-2}−10^{-5} M in benzene-d_6. It is apparent that for the internal NH protons the chemical shifts changes by almost 2 ppm downfield as the concentration approaches 10^{-5} M (Figure 1). At this latter concentration the Pc solution is almost colorless, and 20 000 scans were required to obtain satisfactory spectra. The chemical shift changes with concentration are readily explained by the high aggregation[26,27] of phthalocyanines and the fact that the cone of aromaticity of one Pc ring generally causes upfield

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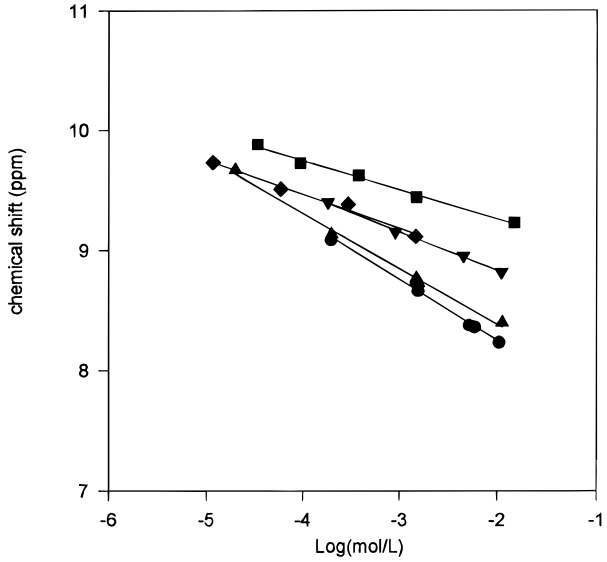

Figure 2. Chemical shift of aromatic protons of metal free phthalocyanines, as a function of log concentration (mol/L). ^{1}H NMR in C_6D_6 at 27 °C: ■, (3,3-dimethylbutynyl)$_8$PcH$_2$ (**23**); ●, (hexynyl)$_8$PcH$_2$ (**21**); ▲, (heptynyl)$_8$PcH$_2$ (**20**). ^{1}H NMR in $CDCl_3$ at 27 °C; ▼, (3,3-dimethylbutynyl)$_8$PcH$_2$ (**23**). ^{1}H NMR in nitrobenzene-d_5 at 27 °C: ■, (3,3-dimethylbutynyl)$_8$PcH$_2$ (**23**).

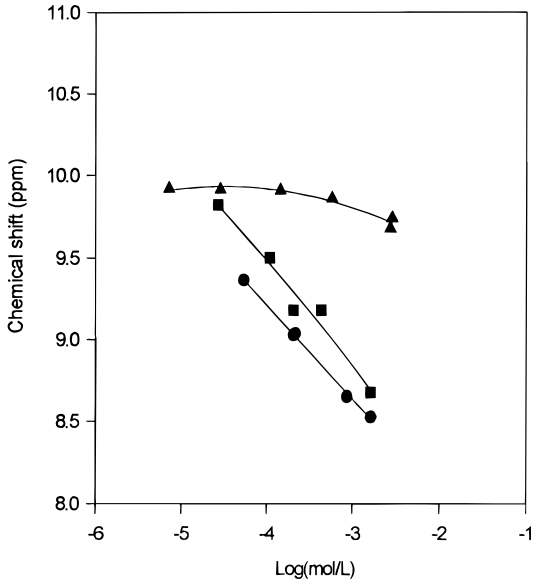

Figure 3. Chemical shift of aromatic protons of zinc phthalocyanines, as a function of log concentration (mol/L). ^{1}H NMR in C_6D_6 at 27 °C: ▲, (3,3-dimethylbutynyl)$_8$PcZn (**28**); ●, (hexynyl)$_8$PcZn (**26**); ■, (octynyl)$_8$PcZn (**24**).

shifts of its aggregated partners. It is likely that the aggregated dimers and oligomers are not static in solution and can slide over each other and rotate.[28] The maximum concentration of the Pcs was limited by their solubility, while the lowest concentration was limited by the acquisition times on the NMR instrument available. The ^{1}H chemical shifts of the internal and aromatic protons at high concentrations were broad likely due to the formation of polymeric aggregates. When a solution of a Pc becomes more and more diluted, the signals become sharp, which would be typical for ^{1}H NMR spectra of monomeric species. At about 10^{-3} M Pc we often were able to discern two peaks for internal protons where the second peak had an intensity about 10% that of the major peak. This peak actually disappeared at both lower and higher concentrations and may be due to discrete "dimer" aggregates.

As expected, the internal protons of **19**−**23** are more sensitive to changes in concentration than aromatic protons (Figure 2) as they are closer to the cone of aromaticity in aggregated species.

We also wished to study the effects of concentration on the ^{1}H NMR chemical shifts of the zinc(II) octaalkynylphthalocyanines **24**−**28**. For these Pcs we observe that there is still a strong concentration dependence for the linear alkynyl Pcs **24**−**27** but that the ^{1}H NMR chemical shift of the aromatic protons of the *tert*-butylethynyl Pc **28** is only slightly concentration dependent (Figure 3). When a 10 times excess of pyridine-d_5 or pyrazine was added to concentrated solutions of Pcs the ^{1}H NMR chemical shifts of the aromatic protons of **24**−**27** approached the value of the unaggregated Pc at 9.92−9.94 ppm in benzene-d_6. A similar concentration study of the ^{1}H NMR chemical shifts of the aromatic protons of **23** in nitrobenzene-d_5 exhibited a limiting value at 9.73 ppm.

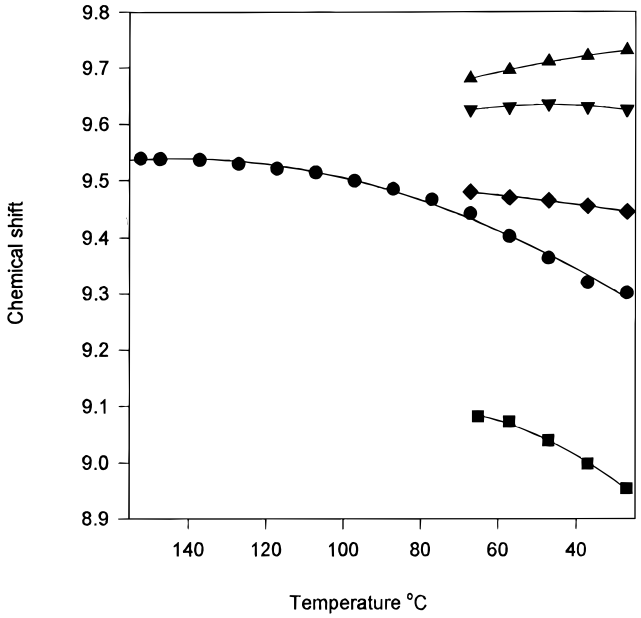

Figure 4. Dependence on temperature of the chemical shift of aromatic protons of metal-free (3,3-dimethylbutynyl)$_8$PcH$_2$ (**23**): ●, in nitrobenzene-d_5 (1.1×10^{-3} M); ■, in $CDCl_3$ (3.6×10^{-3}). In C_6D_6: ◆, 1.5×10^{-3}; ▼, 4.0×10^{-4}; ▲, 9.4×10^{-5} mol/L.

We wished to examine the effect of temperature on the ^{1}H NMR chemical shifts of the Pcs, but to examine a suitably wide temperature range we used nitrobenzene-d_5 as the solvent. Using a 10^{-3} M concentration of **23**, it was shown that the ^{1}H NMR chemical shift of the aromatic protons of **23** moved downfield from 9.30 ppm at 27 °C to 9.53 ppm at 137 °C at which point no further downfield shifts occurred even at higher temperatures (Figure 4). Similarly, the ^{1}H NMR chemical shifts of the internal protons shifted from −1.35 ppm to +0.30 ppm at 157 °C at which point further downfield shifts are less

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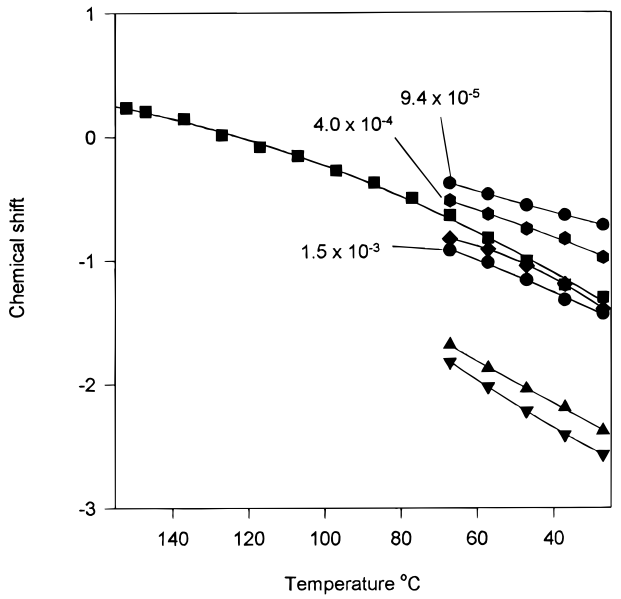

Figure 5. Dependence on temperature of the chemical shift of internal protons of metal-free phthalocyanines: ●, (3,3-dimethylbutynyl)$_8$PcH$_2$ (**23**) in C_6D_6 (different concentrations), ■, in nitrobenzene-d_5 (1.1×10^{-3} M); ◆, in $CDCl_3$ (3.6×10^{-3} M); ▲, Pc(hexynyl)$_8$H$_2$ (**21**) in C_6D_6 (1.5×10^{-3} M), ▼, Pc-(heptynyl)$_8$H$_2$ (**20**) in C_6D_6 (1.5×10^{-3} M).

likely (Figure 5). It should be noted that the *aliphatic* protons were unaffected by the effects of both concentration and temperature.

We know now that the limiting downfield chemical shift for the aromatic protons of **23** at 10^{-5} M is 9.92 ppm in benzene-d_6 and 9.73 ppm in nitrobenzene-d_6. We can see that simply raising the temperature of a concentrated solution is not entirely sufficient to determine the chemical shifts of "unaggregated" Pcs.

Conclusion

We have developed reliable syntheses of 4,5-diiodophthalonitrile (**7**) from which dialkynylphthalonitriles and dialkylphthalonitriles can be prepared. Some of these phthalonitriles were condensed to 2,3,9,10,16,17,23,24-octaalkynylphthalocyanines and their zinc derivatives. ^{1}H NMR studies of these compounds at different concentrations and temperatures clearly demonstrate the importance of quoting concentration and temperature values when reporting ^{1}H NMR spectra of phthalocyanines. The fact that one alkynyl group causes a red shift of the Q band by 1 eV allows one to "fine-tune" this absorption band when designing Pcs.

Experimental Section

General. See ref 15.

4,5-Diiodophthalimide (2) and 4,5-Diiodophthalic Acid (4). To 60 mL of 30% fuming sulfuric acid was added 14.7 g (0.1 mol) of phthalimide (**1**) and 25.4 g (0.2 mol) of iodine. The reaction mixture was heated to 75−80 °C for 24 h. This mixture was then poured onto 400 g of ice, and the precipitated solids were filtered off using a funnel with a glass frit. The solids were washed twice with water, once with a 2% solution of K_2CO_3, once with a saturated solution of $Na_2S_2O_3$, and water and dried at room temperature. The solids were extracted with acetone (1 L) in a Soxhlet extractor for 48 h. The resulting precipitate which formed in the solvent vessel consisted of 4,5-diiodophthalic acid (**4**) (mp 220−222 °C (lit.[18] mp 221−222 °C)). Compound **4** was filtered from the acetone, and 100 mL of water was added. This solution was concentrated to 500 mL and cooled to give 20 g of a bright-yellow precipitate of 4,5-diiodophthalimide (**2**). The mother liquors were reduced in volume to 100 mL and cooled to give 15 g of a 4:1 mixture of **2** and **4**. Chromatography on silica gel of this mixture using $CHCl_3$−EtAc (4:1) as eluent gave **2** and **4** in isolated yields of 75 and 20% respectively.

Compound **2**: mp 297−299 °C; IR (KBr) 3150 (NH), 1750 (C═O), 1700 (C═O) cm^{-1}; ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.25 (s, 2H), 11.41 (s, 1H); MS *m*/*z* (rel intensity) 399 M$^+$, 82). Anal. Calcd for $C_8H_3I_2NO_2$: C, 24.09; H, 0.76; N, 3.51. Found: C, 24.07; H, 0.66; N, 3.32.

4,5-Diiodophthamide (5). To 220 mL of concd aqueous ammonia was added 20 g (50 mmol) of pure 4,5-diiodophthalimide (**2**). The rapidly stirred mixture was heated to 50−60 °C for 1.5 h. The white solid was filtered and washed three times with ice-cold water and with methanol to remove any trace amounts of ammonia and **2**. The solid was dried overnight at room temperature to give intermediate **5** (17.0 g, 81%) as a white powder: mp 297−299 °C; IR (KBr) [3390, 3280, 3130(NH)], [1680, 1640, (C═O)], 1590 cm^{-1}; ^{1}H NMR (DMSO-d_6, 27 °C) δ 7.91 (s, 2H), 7.80, 7.39 (bs, 4H).

4,5-Diiodophthalonitrile (7). To an ice-cooled stirred suspension of 8.3 g (20 mmol) of **5** in 80 mL of dry dioxane and 18 mL of dry pyridine was added 16 mL of trifluoroacetic anhydride at 0−5 °C. After the addition was complete, the reaction mixture was warmed to room temperature, stirred overnight, and poured onto ice. The product was extracted three times with EtOAc. The organic layer was washed with water, 1 M HCl, dilute Na_2CO_3, and water and dried over $MgSO_4$. The solvent was removed under vacuum, and the product was recrystallized from ethanol to give **7** (6.0 g, 79% yield) as yellow-white needles: mp 216−217 °C; IR (KBr) 2210 (CN) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 8.19 (s); MS *m*/*z* (rel intensity) 380 (M$^+$, 100). Anal. Calcd for $C_8H_3I_2N_2$: C, 25.29; H, 0.53; N, 7.37. Found: C, 25.61; H, 0.50; N, 7.24.

3,4-Diiodophthalimide (3), 3,4-Diiodophthalamide (6), and 3,4-Diiodophthalonitrile (8). When **1** was treated as above for the preparation of **2**, but at 85−90 °C, an inseparable mixture of **2** and **3** was obtained. This mixture was treated as above for the preparation of **5** to give another inseparable mixture of **5** and **6**. Finally, treatment of 1.0 g of the mixture of **5** and **6** as above for the preparation of **7** gave a mixture of **7** and **8**. Separation of **7** and **8** on silica gel chromatography using ethyl acetate−hexane (1:9) as eluent gave **7** (0.8 g, 80% yield) and **8** (0.1 g, 10% yield): mp 201−202 °C; IR (KBr) 2215 (CN) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 8.19 (d, J = 8.7 Hz, 1H), 7.80 (d, J = 8.7 Hz); MS *m*/*z* (rel intensity) 380 (M$^+$, 89). Anal. Calcd for $C_8H_3I_2N_2$: C, 25.29; H, 0.53: N, 7.37. Found: C, 25.61; H, 0.51; N, 7.24.

4,5-Di(1-octynyl)phthalonitrile (14). General Procedure. To a solution of 500 mg (1.3 mmol) of 4,5-diiodophthalonitrile (**7**) dissolved in 20 mL of TEA was added 580 mg (5.3 mmol) of 1-octyne (**9**) and a 5% molar amount of $Pd(PPh_3)_2Cl_2$. The reaction was heated to 110 °C under argon. The reaction was monitored by TLC using hexane−benzene (1:1) as eluent. After 30 min, all of the starting phthalonitrile had completely reacted and the reaction was cooled to room temperature. The reaction mixture was then suction filtered on a glass fritted funnel, and the collected precipitate was washed with diethyl ether until the filtrate was colorless. The filtrate was then evaporated to dryness under reduced pressure and then preabsorbed onto classical silica gel. A column using classical silica gel with *n*-hexane as eluent removed all unreacted 1-octyne. The solvent was then changed to hexane−benzene (1:1), and the first fraction collected (280 mg) was the desired product. This product was further purified by recrystallization in *n*-hexane to give a waxy yellow solid in 68% yield: mp 42−44 °C; ^{1}H NMR ($CDCl_3$) δ 7.72 (s, 2H), 2.49 (t, J = 7.0 Hz, 4H), 1.59 (m, 4H), 1.45 (m, 4H), 1.31 (m, 8H), 0.90 (t, J = 6.7 Hz, 6H); IR (KBr) 2930 (s), 2230 (s), 1500 (s) cm^{-1}; MS *m*/*z* 344 (70), 259 (50), 245 (80), 231 (95), 217 (100), 203 (90), 191 (85), 179 (75). Anal. Calcd for $C_{24}H_{28}N_2$: C, 83.67; H, 8.14; N, 8.14. Found: C, 83.38; H, 8.23; N, 8.17.

4.5-Di(1-heptynyl)phthalonitrile (15). The same procedure as described above for **14**, from **7** and 1-heptyne (**10**), was

used to prepare **15** in 80% yield: mp 42−43 °C; ^{1}H NMR ($CDCl_3$) δ 7.71 (s, 2H), 2.49 (t, J = 7.0 Hz, 4H), 1.60 (m, 4H), 1.44 (m, 4H), 1.36 (m, 4H), 0.92 (t, J = 6.8 Hz, 6H); IR (KBr) 2958 (s), 2861 (m), 2229 (s), 1589 (m) cm^{-1}; MS m/z 316 (M^+, 73). Anal. Calcd for $C_{22}H_{24}N_2$: C, 83.50; H, 7.64; N, 8.85. Found: C, 83.75; H, 7.80; N, 8.91.

4,5-Di(1-hexynyl)phthalonitrile (16). The same procedure as described above for **14** using 1 g of 4,5-diiodophthalonitrile (**7**) and 1-hexyne (**11**) was used. After the reaction was complete, the reaction mixture was diluted with toluene and washed in a separatory funnel once with water, once with brine, and again with water. The organic layer was then dried over $MgSO_4$. To the toluene layer was added 1.5 g of classical silica gel, and the toluene was removed under reduced pressure. A classical silica gel column using toluene as eluent gave two fractions; the first was unreacted **11** and the second was the desired product **15** in 76% yield: mp 84−86 °C; ^{1}H NMR ($CDCl_3$) δ 7.71 (s, 2H,), 2.50 (t, J = 7.0 Hz, 4H), 1.61 (m, 4H), 1.49 (m, 4H), 0.95 (t, J = 6.8 Hz, 6H); IR (KBr) 2957 (s), 2873 (m), 2227 (s), 1589 (m) cm^{-1}; MS m/z 288 (M^+, 58). Anal. Calcd for $C_{20}H_{20}N_2$: C, 83.30; H, 6.99; N, 9.71. Found: C, 83.59; H, 7.10; N, 9.78.

4,5-Di(1-pentynyl)phthalonitrile (17). The same procedure as described for **16** was used from **7** and 1-pentyne (**12**) to give **17** in 82% yield: mp 102−104 °C; H NMR ($CDCl_3$) δ 7.73 (s, 2H), 2.50 (t, J = 7.0 Hz, 4H), 1.65 (m, 4H), 1.07 (t, J = 6.9 Hz, 6H); IR (KBr) 2974 (s), 2878 (m), 2230 (s), 1585 (m) cm^{-1}; MS m/z 260 (M^+, 100). Anal. Calcd for $C_{18}H_{16}N_2$: C, 83.04; H, 6.19; N, 10.76. Found: C, 82.88; H, 6.24; N, 10.85.

4,5-Bis(3,3-dimethyl-1-butynyl)phthalonitrile (18). To a solution of 60 mL of TEA was dissolved 1 g (2.6 mmol) of 4,5-diiodophthalonitrile (**7**), 0.53 g (6.5 mmol) of 3,3-dimethyl-1-butyne (**13**), CuI (3.75 mmol), and 60 mg of $Pd(PPh_3)_2Cl_2$. All reactants were allowed to stir under argon at room temperature. The reaction was monitored by TLC (with hexane−benzene (1:1) as the eluting solvent), and after 1 h most of the starting material had reacted. At this point an additional 0.3 g of alkyne along with 0.1 g of CuI and 40 mg of catalyst were added. After 6 h the reaction was complete.

The reaction mixture was suction filtered on a glass fritted funnel, and the collected precipitate was washed with diethyl ether until the filtrate was colorless. The filtrate was then evaporated under reduced pressure to give an orange solid which was recrystallized from hexane to give 0.65 g of **18** as white crystals in 85% yield: mp 177−179 °C; ^{1}H NMR ($CDCl_3$) δ 7.82 (s, 2H), 1.36, (s, 18H); IR (KBr) 2235 cm^{-1}; MS m/z 288 (M^+, 78). Anal. Calcd for $C_{20}H_{20}N_2$: C, 83.30; H, 6.99; N, 9.71. Found C, 83.30; H, 7.12; N, 9.55.

2,3,9,10,16,17,23,24-Octa(1-octynyl)phthalocyanine (19). To 2.5 mL of 1-pentanol was added 30 mg of lithium metal and the solution was stirred under argon at 60 °C. After all of the lithium metal had dissolved, the solution was cooled to room temperature and 300 mg of **14** was added. The reaction mixture was then heated to 110 °C under argon. The reaction was monitored by TLC with benzene as eluent. After 3 h all of the starting phthalonitrile **14** was gone, and the reaction was then cooled to room temperature and diluted with 10 mL of 20% methanol/water. After 90 min the reaction mixture was then centrifuged and the precipitate collected. The precipitate was further washed with methanol and collected by centrifugation. This process was continued until the filtrate was colorless. At this point the crude pigment was further purified by flash column chromatography using benzene as eluent. The first band collected was the desired Pc **19** and was further purified by a second flash silica gel column to remove all insoluble impurities. Final purification involved the reprecipitation of **19** from THF/ethanol which gave 130 mg of the desired Pc in 43% yield: ^{1}H NMR (benzene-d_6, 1.5 × 10^{-3} M) δ 8.77 (s, 8H), 2.8 (t, J = 6.9 Hz, 16H), 1.9 (m, 16H), 1.65 (m, J = Hz, 16 H), 1.5 (m, 32H), 1.1 (t, J = 7.1 Hz, 24H), −2.38 (br, 2H); UV−vis λ_{max} (THF) (log e) 730 (5.44), 694 (5.38), 636 (4.89), 364 (5.29) nm; FABMS 1379 (M + 1, 40). Anal. Calcd for $C_{96}H_{114}N_8$: C, 83.59; H, 8.27; N, 8.13. Found: C, 84.15; H, 8.40; N, 8.23.

2,3,9,10,16,17,23,24-Octa(1-heptynyl)phthalocyanine (20). Pc **20** was prepared using the same method as described above using 200 mg of **17** to give 76 mg of **20** in 38% yield: ^{1}H NMR (benzene-d_6, 1.5 × 10^{-3} M) δ 8.77 (s, 8H), 2.82 (t, J = 6.9 Hz, 16H), 1.92 (m, 16H), 1.67 (q, 16H), 1.5 (m, 16H), 1.1 (t, J = 7.1 Hz, 24H), −2.82 (bs, 2H); UV−vis λ_{max} (THF) (log e) 730 (5.47), 694 (5.35), 636 (4.92), 364 (5.32) nm; FABMS 1266 (M + 1). Anal. Calcd for $C_{88}H_{98}N_8$: C, 83.33; H, 7.79; N, 8.84. Found: C, 82.67; H, 7.12; N, 9.39.

2,3,9,10,16,17,23,24-Octa(1-hexynyl)phthalocyanine (21). The same method as described above for **19** was used, except that 100 mg of **16** was used to give 40 mg of **21** in 40% yield: ^{1}H NMR (benzene-d_6, 1.5 × 10^{-3} M) δ 8.73 (s, 8H), 2.83 (t, J = 6.6 Hz, 16H), 1.92 (m, 16H), 1.8 (m, 16H), 1.15 (t, J = 7.4 Hz, 24H) −2.82 (br, 2H); UV−vis λ_{max} (THF) (log e) 730 (5.22), 694 (5.19), 366 (5.04 nm); FABMS 1154 (M + 1). Anal. Calcd for $C_{80}H_{82}N_8$: C, 83.25; H, 7.15; N, 8.68. Found: C, 82.98; H, 7.76; N, 8.68.

2,3,9,10,16,17,23,24-Octa(1-pentynyl)phthalocyanine (22). The same method as described above for **19** was used except that 250 mg of **17** was used. As a result of the poor solubility of the desired Pc **22**, it was necessary to use $CHCl_3$ as the eluent for flash column chromatography instead of benzene. Two columns were run on the crude pigment, and the final product was reprecipitated from THF/ethanol to give 75 mg of the desired Pc **22** in 30% yield: ^{1}H NMR (benzene-d_6, 1.8 × 10^{-3} M) δ 8.79 (s, 8H), 2.88 (t, J = 6.9 Hz, 16H), 2.03 (m, 16H), 1.44 (t, J = 7.4 Hz, 24 H), −2.64 (br, 2H); UV−vis λ_{max} (THF) (log e) 728 (5.03), 694 (5.00), 628 (4.55), 363 (4.27) nm; FABMS 1042 (M + 1).

2,3,9,10,16,17,23,24-Octakis(3,3-dimethyl-1-butynyl)-phthalocyanine (23). The same method as described above using 100 mg of **18** gave 36 mg of **23** in 36% yield: ^{1}H NMR (400 MHz, benzene-d_6, 1.5 × 10^{-3} M) δ 9.44 (s, 8H), 1.45 (s, 72H), −1.42 (br, 2H); UV−vis λ_{max} ($CHCl_3$) (log e) 734 (5.32), 694 (5.27), 666 (4.72), 632 (4.59), 368 (5.03), 314 (4.89) nm; FAB MS (M + 1, 1154). Anal. Calcd for $C_{80}H_{82}N_8$: C, 83.14, H, 7.16, N, 9.70. Found: C, 83.05; H, 7.36, N, 9.36.

[2,3,9,10,16,17,23,24-Octa(1-octynyl)phthalocyaninyl]zinc(II) (24). To 2.5 mL of 1-pentanol was added 30 mg of lithium metal. The solution was stirred under argon at 60 °C until all of the lithium had dissolved. At this point the alkoxide solution was cooled to room temperature, and 250 mg of **19** was added. The reaction mixture was then heated under argon to 110 °C for 3 h. After this time the reaction temperature was lowered to 80 °C, and 300 mg of $Zn(OAc)_2$ was added. The reaction mixture was allowed to stir for an additional 2 h at 80 °C. The reaction mixture was then cooled to room temperature and diluted with 10 mL of 20% methanol/water. After being allowed to stand for 90 min the reaction mixture was centrifuged and the crude zinc Pc **24** collected. The crude pigment was further washed with 20% methanol/water until the filtrate was colorless. It was then washed with methanol and acetonitrile. The crude Pc **24** was further purified by flash column chromatography with benzene as eluent, and the first band collected was the desired Pc. This material was further purified by a second flash silica gel column with benzene as eluent to give 100 mg of the desired **24** in 40% yield: ^{1}H NMR (benzene-d_6, 1.6 × 10^{-3} M) δ 8.68 (s, 8H), 2.81 (t, J = 6.8 Hz, 16H), 1.95 (m, 16H), 1.77 (m, 16H), 1.62 (m, 32H), 1.16 (t, J = 7.1 Hz, 24H); UV−vis λ_{max} (THF) (log e) 708 (5.57), 636 (4.81), 370 (5.21) nm; FABMS 1444.6 (M + 1). Anal. Calcd for $C_{96}H_{112}N_8Zn$: C, 79.75; H, 7.75; N, 7.75. Found: C, 79.40; H, 7.88; N, 7.73.

[2,3,9,10,16,17,23,24-Octa(1-heptynyl)phthalocyaninyl]-zinc(II) (25). The same procedure as described above to make **24** was used to give 112 mg of **25** in 45% yield: ^{1}H NMR (benzene-d_6, 1.5 × 10^{-3} M) δ 8.85 (s, 8H), 2.80 (t, J = 7.1 Hz, 16H), 1.95 (m, 16H), 1.77 (m, 16H), 1.63 (m, 16H), 1.18 (t, J = 6.9 Hz, 24H); UV−vis λ_{max} (THF) (log e) 706 (5.54), 636 (4.77), 370 (5.12) nm; FABMS 1329.8 (M + 1). Anal. Calcd for $C_{88}H_{96}N_8Zn$: C, 79.41; H, 7.22; N, 8.42. Found: C, 79.47; H, 7.27; N, 8.16.

[2,3,9,10,16,17,23,24-Octa(1-hexynyl)phthalocyaninyl]-zinc(II) (26). The same procedure as outlined above for **24** was used to give 95 mg of **26** in 38% yield: ^{1}H NMR (benzene-d_6, 1.6 × 10^{-3} M) δ 8.73 (s, 8H), 2.83 (t, J = 7.1 Hz, 16H), 1.96 (m, 16H), 1.85 (m, 16H), 1.21 (t, J = 6.9 Hz, 24H); UV−vis

λ_{max} (THF) (log e) 708 (5.52), 634 (4.73), 370 (5.12) nm; FABMS 1216.9 (M + 1). Anal. Calcd for $C_{80}H_{80}N_8Zn$: C, 78.89; H, 6.57; N, 9.20. Found: C, 79.36; H, 6.92; N, 8.72.

[2,3,9,10,16,17,23,24-Octa(1-pentynyl)phthalocyaninyl]-zinc(II) (27). The same procedure as described above for **24** was used, except $CHCl_3$ was used as eluent instead of benzene for column chromatography to give 95 mg of **27** in 38% yield: ^{1}H NMR (pyridine-d_5, 4.5×10^{-4} M) δ 9.79 (s, 8H), 2.84 (t, J = 7.1 Hz, 16H), 1.96 (m, 16H), 1.27 (t, J = 6.9 Hz, 24H); UV−vis λ_{max} (THF) (log e) 706 (5.45), 638 (4.74), 368 (5.14) nm; FABMS 1108 (M + 1). Anal. Calcd for $C_{72}H_{64}N_8Zn$: C, 78.05, H, 5.78, N, 10.12. Found: C, 78.16, H, 5.86, N, 10.12.

Synthesis of [Octakis(3,3-dimethyl-1-butynyl)phthalocyaniyl]zinc(II) (28). The same procedure as outlined above was used to give 67 mg of **28** in 25% yield: ^{1}H NMR (400 MHz, benzene-d_6, 2.7×10^{-3} M) δ 9.74 (s, 8H), 1.46 (s, 72H); UV−vis λ_{max}($CHCl_3$) (log e) 714 (5.40), 640 (4.61), 370 (5.00) nm; FAB MS (M + 1) 1216.9. Anal. Calcd for $C_{80}H_{80}N_8Zn$: C, 78.83; H, 6.62; N, 9.19. Found: C, 77.94; H, 6.62; N, 8.57.

4-Iodo-5-(1-octynyl)phthalonitrile (29). To a solution of 3.8 g (10 mmol) of 4,5-diiodophthalonitrile (**7**) dissolved in a 40 mL mixture of TEA and DMF (1:1) was added 3 mL (20 mmol) of 1-octyne (**9**) and a 5% molar amount of $Pd(PPh_3)_2Cl_2$. The reaction mixture was heated to 100 °C under argon for 1 h, cooled to room temperature, diluted with 200 mL of ethyl acetate, extracted three times with water, 5% HCl, and water, a 2% solution of $NaHCO_3$, and water, and dried with $MgSO_4$. The solvent was evaporated under reduced pressure, and the oil residue was separated by column chromatography on silica gel, using hexane and ethyl acetate (19:1), to give 4,5-di(1-octynyl)phthalonitrile (**14**) (1.4 g, 40%) and 4-iodo-5-(1-octynyl)phthalonitrile **(29)** (1.1 g, 30%) as white needles: mp 46−47 °C; IR (KBr) 2256, 2210 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 8.19, (s, 1H), 7.21, (s, 1H), 2.86 (t, J = 7.0 Hz, 2H) 2.69, (m, 2H), 1.52 (m, 2H) 1.33, (m, 2H) 0.93, (t, J = 6.8 Hz, 3H); MS m/z 362 (M^+, 10). Anal. Calcd for $C_{16}H_{15}N_2I$: C, 53.06; H, 4.17; N, 7.73. Found: C, 53.36; H, 4.10; N, 7.56.

4,5-Dipentylphthalonitrile (30). To 0.3 g (1 mmol) of **17** dissolved in 50 mL of absolute ethanol was added 0.2 g of palladium on barium sulfate catalyst . The reaction mixture was placed to a Parr hydrogenation bottle, and the bottle was installed in a Parr-Shaker apparatus and pressurized to 36 psi. After 1 h the reaction was complete, the catalyst was filtered, and the solvent was evaporated. The residue was purified by column chromatography using ethyl acetate and hexane (1:9) as eluent. The first few fractions, containing the desired product, were combined and rotary evaporated to yield white crystals. Recrystallization from hexane gave 0.3 g of pure 4,5-di(1-pentyl)phthalonitrile[29] (**30**) in 95% yield as white crystals: mp 41−43 °C (lit.[30] mp 39 °C); ^{1}H NMR (CH_3CN) δ 7.70 (s, 2H), 2.68 (t, J = 7.8 Hz, 4H), 1.93 (m, 4H), 1.56 (m, 4H), 1.33 (m, 4H), 0.90 (t, J = 4 Hz, 6H); IR (KBr) 2230 (CN) cm^{-1}; MS m/z 268 (M^+, 85). Anal. Calcd for $C_{18}H_{24}N_2$: C, 80.59; H, 8.95; N, 10.45. Found: C., 80.33; H, 9.23; N, 10.24.

4,5-Bis(3,3-dimethylbutyl)phthalonitrile (31). The same method as described above for **30** was used except that 1.44 g (5 mmol) of **18** was used and gave us 1.40 g in 95% yield of pure 4,5-di(3,3-dimethylbutyl)phthalonitrile (**31**) as white crystals: mp 127−129 °C; IR (KBr) 2235 (CN) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (s, 2H), 266 (m, 44), 1.44 (m, 4H), 1.02 (s, 18H); MS m/z 292 (M^+, 82). Anal. Calcd for $C_{20}H_{28}N_2$: C, 81.03; H, 9.52; N, 9.45. Found: C, 81.28; H, 9.51; N, 9.46.

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