A Novel Method for the Peripheral Modification of Phthalocyanines. Synthesis and Third-Order Nonlinear Optical Absorption of *β*-Tetrakis(2,3,4,5,6-pentaphenylbenzene)phthalocyanine

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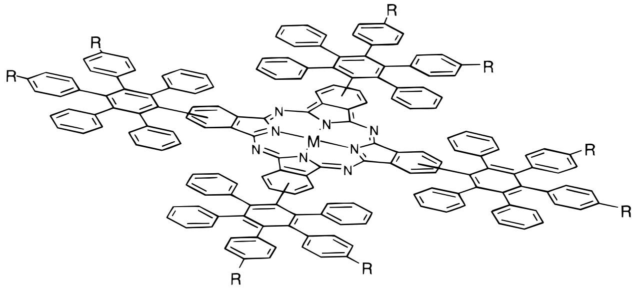
There continues to be intense interest in the development of synthetic strategies for the preparation of new phthalocyanine (Pc) and metallophthalocyanine (MPc) derivatives[1] for optical, electrical, and magnetic applications.[2] In this Laboratory, we have been investigating new synthetic approaches to prepare novel Pc and MPc derivatives to be used in nonlinear optical (NLO) applications and have focused on enhancing the third-order NLO absorptions or $\chi^{(3)}$ in Pcs and MPcs.[3,4] Earlier, we showed that certain axial substituents on silicon MPcs dramatically improve the solubility as well as the $\chi^{(3)}$.[4] Although peripheral substituents improve solubility, there appears to be no correlation between the substituent and $\chi^{(3)}$.[5] To our knowledge, no studies have appeared in which the peripheral substituents have been aromatic. In our initial studies to develop a new method for peripheral modification of Pcs which allows the incorporation of polyaromatic and heteroaromatic moieties, we have found large enhancements in the $\chi^{(3)}$. In this paper, we report the synthesis and third-order nonlinearity of *β*-tetrakis(pentaphenylbenzene)phthalocyanines.

The structures for this class of materials are shown in Figure 1. There are several advantages to this type of design. First, the polyphenylated design renders the Pc soluble in common organic solvents. Second, the peripheral pentaphenylbenzene substituent has extensive electronic interaction with the Pc macrocycle which leads to large bathochromic shifts in the ground-state electronic absorption spectra and enhanced NLO absorptions. Finally, the synthetic scheme is very general and the possibilities are only highlighted by this preliminary study. The scheme allows for the incorporation of alkyl- or alkoxy-substituted benzenes, and could be extended to include heteroaromatic moieties such as carbazole, a molecule of particular interest in our laboratory.[6]



Compound	R	M	Yield (%)
1a	H	2H	10
b	-OC_4H_9	2H	21
c	-OC_4H_9	Ni	25
d	-OC_4H_9	Pb	27
e	-$OC_{12}H_{25}$	2H	20

Figure 1. Structures of *β*-tetrakis(2,3,4,5,6-pentaarylbenzene)phthalocyanines, **1a**−**e**.

The synthesis of polyaromatic systems has been well developed, and the use of [4 + 2] cycloaddition reactions has been shown to be a powerful tool for building diverse polyphenylated compounds and polymers.[7] The preparation of phthalocyanines, on the other hand, relies on the availability of the precursor phthalonitriles which undergo cyclotetramerization to form the macrocycles.[8] These two requirements, Diels−Alder cycloaddition to form the dicyano-functionalized hexaphenylbenzene moiety and its cyclotetramerization, became the key steps in the preparation of the desired materials.

The synthesis of the dinitrile phthalocyanine precursor, 4-(2,3,4,5,6-pentaphenylbenzene)phthalonitrile, **5**, is shown in Scheme 1. Reduction of 4-nitrophthalonitrile, **2**, using powdered iron,[9] gave 4-aminophthalonitrile in 85% yield. Subsequent diazotization using sodium nitrite in 50% sulfuric acid, and reaction of the diazonium salt with potassium iodide, gave 4-iodophthalonitrile, **3**, in 92% yield.[10] Cross-coupling of **3** with phenylacetylene, catalyzed by $Pd(PPh_3)_4$ and CuI, according to Sonogashira[11] and Alami[12] proved to be simple when nonnucleophilic amine bases such as diisopropylamine were used, and provided 4-(phenylethynyl)phthalonitrile, **4**, in 93% yield.[13]

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[13] All spectral analyses of new compounds fully support the given structures.

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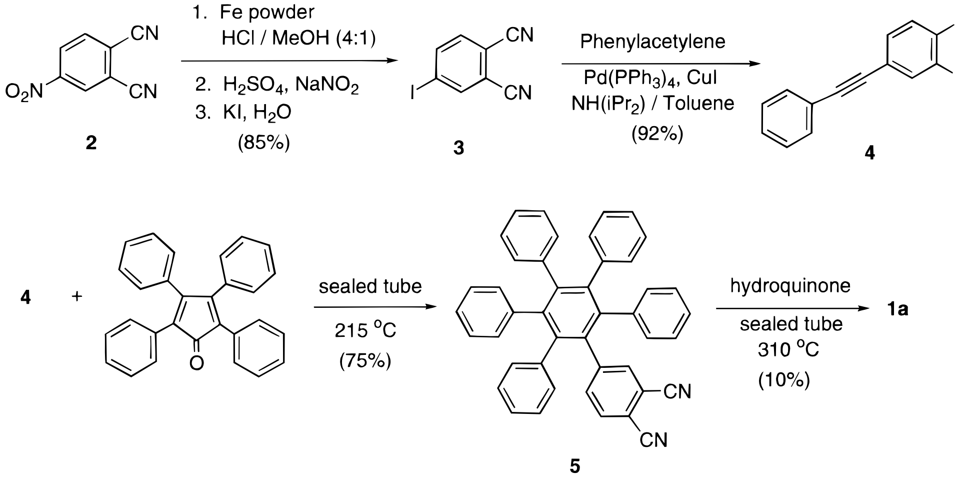
Scheme 1

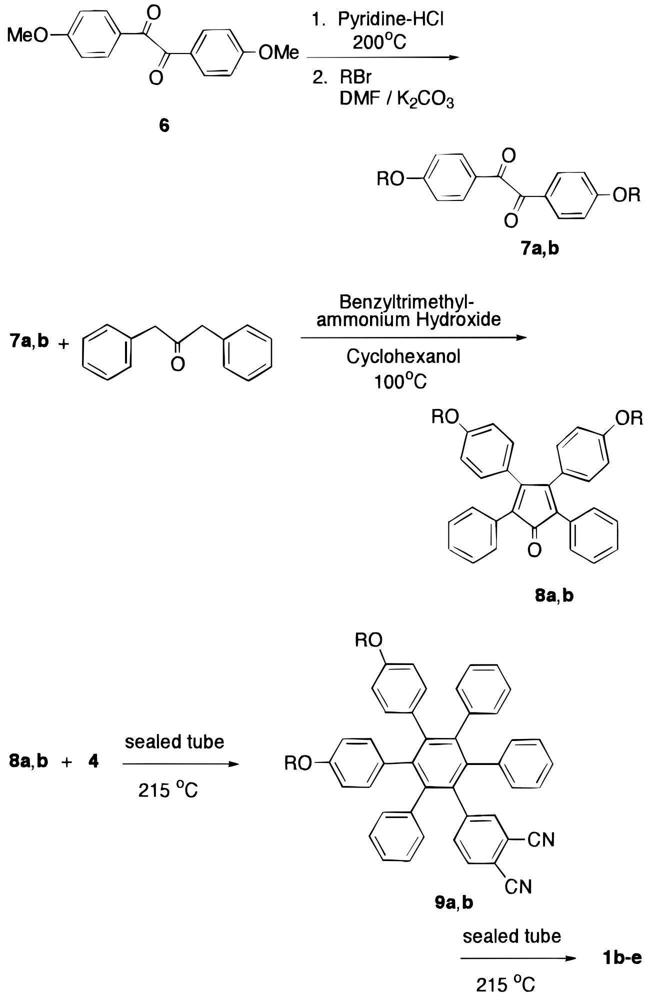


Although alkynylated phthalonitriles have been reported,[14] no attempts have been made to use the alkyne group selectively as a dieneophile to form functionalized phthalonitriles. In fact, **4** is a versatile dieneophile that reacts well with dienes to form polyaromatic phthalonitriles. A [4 + 2] cycloaddition reaction between **4** and 2,3,4,5-tetraphenylcyclopenta-2,4-diene-1-one (tetracyclone) was performed as a melt in a sealed tube for 6 h and gave the desired dinitrile, **5**, in 75% yield. Longer reaction times caused competing cyclotetramerization and only decreased the yields. In addition, there was no evidence of competing cycloaddition with the dieneophilic cyano groups.[15]

Cyclotetramerization of dinitrile **5** proved challenging. When **5** was dissolved in *n*-octanol and the base 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) was added, no phthalocyanine formed after refluxing for 24 h. When the dinitrile was heated under reflux in *n*-octanol with DBU and zinc acetate, again no phthalocyanine formed. The tetramerization of **5** was successful only when the reaction was conducted neat, as a melt at 310 °C in the presence of 5 mol % hydroquinone[16] and gave the desired product **1a**, in 10% yield. It was not surprising to find that at such high temperatures the majority of the material had decomposed or formed insoluble polymeric byproducts. To address this problem, softening alkoxy groups were incorporated into the phthalonitrile to lower the required temperature for cyclotetramerization.

As shown in Scheme 2, dimethoxybenzil, **6**, was demethylated using pyridinium hydrochloride.[17] Alkylation of both free hydroxyl groups using butyl or dodecyl bromide, in DMF with potassium carbonate, gave the alkoxy-substituted diketones **7a**,**b** in 85% and 88% yields, respectively. These diketones **7a**,**b** condensed smoothly with diphenylacetone in cyclohexanol, when 1 equiv of base was used, and yielded the alkoxy-substituted tetracyclones, **8a**,**b** in 55% and 58% yields, respectively.[18]

Scheme 2



These tetracyclones reacted smoothly with the dieneophile, **4**, to give the alkoxy-substituted pentaarylbenzenephthalonitriles, **9a**,**b**, in 57% and 65% yields, respectively.[19] Dinitrile **9a** melted at 205 °C and **9b**

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(18) Data for **8a**. Mp: 134−136 °C. FTIR (neat): 1704, 1605, 1289, 1249, 1176, 1112 cm^{-1}. UV/vis (dichloromethane): 510.0, 466.1, 377.7, 285.5 nm. ^{1}H NMR (300 MHz CDCl$_3$): δ 7.30−7.13 (m, 10H), 6.86 (d, 4H), 6.712 (d, 4H), 3.94 (t, 4H), 1.71 (q, 4H), 1.54 (q, 4H), 1.00 (t, 6H). ^{13}C NMR (75 MHz CDCl$_3$): δ 200.7, 159.8, 454.5, 131.6, 131.5, 130.5, 128.4, 127.5, 125.4, 124.9, 114.2, 68.03, 31.71, 19.67, 14.31. Analysis: calcd for $C_{37}H_{36}O_3$ C, 84.06; H, 6.86; found C, 84.02; H, 6.81.

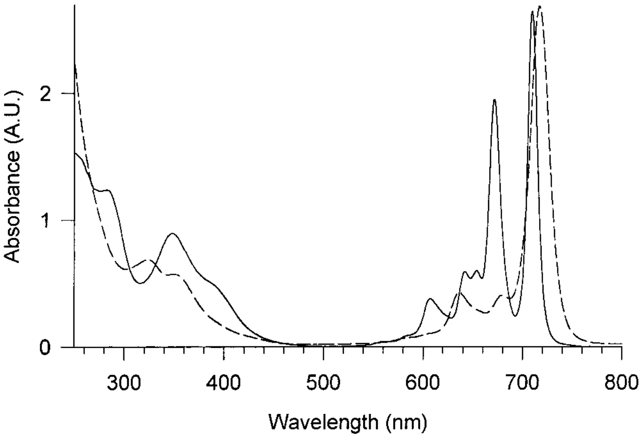

Figure 2. Electronic Absorption Spectra of **1b** (solid line) and **1d** (dashed lined) in toluene.

melted at 180 °C, significantly lower than that of dinitrile **5**. When **9a**,**b** were cyclotetramerized as a melt at 215 °C in the presence of hydroquinone,[16] alkoxy-substituted polyphenylated phthalocyanines **1b** and **1f** were isolated in 21% and 20% yield, respectively.[20] Tetramerization of **9a** in the presence of nickel acetate and lead oxide gave the corresponding nickel MPc **1c**, in 25% yield and the lead MPc **1d**, in 28% yield.

The polyphenylated Pcs and MPcs exhibit different physical properties, but all maintain similar electronic properties. All the materials synthesized are soluble in common organic solvents such as aromatic and chlorinated hydrocarbons, ethers, and hydrocarbons such as hexane and cyclohexane. The high solubility is outstanding for Pcs and MPcs. The unsubstituted polyphenylated Pc **1a**, is crystalline, but Pcs **1b** and **1e** are more amorphous and form films readily from solution.

The ground-state electronic absorption spectra of **1b** and **1d**, in toluene, are shown in Figure 2. The metal-free derivative **1b**, shows a split Q-band with $\lambda_{\max}$ at 712 nm. This absorption is red-shifted ~40 nm compared to unsubstituted Pc. Alkoxy substitution of the pentaphenylbenzene substituent has no additional effect on the $\lambda_{\max}$ of the Q-band absorption. As expected, the position of the Q-band and B-band are influenced by the presence of a metal. The lead derivative **1e**, has the farthest red-shifted Q-band, placed at 724 nm. All the Pcs and MPcs have the typical window in which there is little or no ground-state absorption between 500 and 600 nm.

Third-order NLO properties of Pc **1a** were measured in 1,4-dioxane solution by degenerate four-wave mixing (DFWM) technique in the conventional counterpropagating pump beam geometry. The measurements were carried out at 1064 nm using a mode-locked Q-switched and Nd:YAG laser (Coherent Antares). Details of the experiment and set up have been described previously.[3] The third-order nonlinear optical absorption, $\chi^{(3)}$, of **1a** was determined by comparing the signal intensity with that of CS_2. The $\chi^{(3)}$ value of CS_2 was taken as 6.8×10^{-13} esu. It was found that metal-free Pc **1a** has very high $\chi^{(3)}$ for tetrasubstituted Pcs with $\chi^{(3)} = 0.52 \times 10^{-10}$ esu and $\langle\gamma\rangle = 6.12 \times 10^{-32}$ esu, measured at 1064 nm. This value is among the highest $\chi^{(3)}$ values reported for tetrasubstituted Pcs and is especially remarkable for a metal-free Pc. In fact the $\chi^{(3)}$ is comparable to naphthalocyanines.[5] We believe the influence the aromatic substituents have on the phthalocyanine core, as evidenced by the red-shifted Q-band in the electronic absorption spectrum, is the main reason for the enhancement in $\chi^{(3)}$.

In conclusion, a new type of polyphenylated phthalocyanines has been synthesized via cyclotetramerization of pentaphenylbenzenephthalonitriles. The phthalonitriles were obtained by Diels–Alder-type cycloaddition reactions between phenylethynyl-phthalonitrile and substituted tetracyclones. We are currently exploring the influence heteroaromatic substituents have on the electronic properties of these molecules, in particular, carbazole, thiophene, and pyridine.

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Supporting Information Available: ^{1}H and ^{13}C NMR spectra for compounds **1b 1c 1e**, **7a**,**b**, **8a**,**b**, and **9a**,**b**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(19) Data for **9a**. Mp: 205–206 °C. ^{1}H NMR (300 MHz $CDCl_3$): δ 7.28 (d, 2H), 7.25 (d, 2H), 7.17 (d, 2H), 7.14 (d, 2H), 7.0–6.9 (m, 8H), 6.83–6.74 (m, 6H), 6.72–6.65 (m, 2H). 6.43 (d, 2H). ^{13}C NMR (75 MHz $CDCl_3$): δ 157.1, 147.9, 142.6, 141.6, 141.4, 140.5, 140.3, 139.9, 139.8, 139.7, 136.6, 136.2, 132.5, 132.3, 132.2, 131.6, 131.5, 127.9, 127.8, 127.7, 127.6, 127.2, 126.6, 125.9, 114.4, 113.4, 67.7, 31.6, 19.5, 14.3. Analysis: calcd for $C_{52}H_{44}N_2O_2$ C, 85.68; H, 6.08; N, 3.84; found C, 85.51; H, 5.92; N, 3.74.

(20) Data for **1b**. ^{1}H NMR (300 MHz $CDCl_3$): δ 7.75–7.62 (m, 4H), 7.27–6.4 (m, 100H), 3.87–3.80 (m, 16H), 1.76–1.58 (m, 16H), 1.04–0.92 (m, 40H), −0.63 (s, 2H). ^{13}C NMR (75 MHz $CDCl_3$): δ 156.9, 141.5, 141.4, 141.3, 141.2, 140.9, 140.7, 140.6, 140.5, 140.4, 133.4, 133.3, 132.8, 131.9, 127.1, 125.7, 122.2, 113.4, 67.8, 31.7, 19.6, 14.3. Analysis: calcd for $C_{208}H_{178}N_8O_8$ C, 85.62; H, 6.15; N, 3.84; found C, 85.49; H, 6.13; N, 3.60.