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Published on Web 04/16/2004

Synthesis of Polyphenylene Dendrimers Related to "Cubic Graphite"

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Abstract: Four large, 6-fold symmetric, polyphenylene hydrocarbons have been prepared by short syntheses that chiefly employed alkyne trimerization, palladium-catalyzed coupling, and Diels−Alder reactions. The two largest of these molecules, hexakis[4′-(pentaphenylphenyl)biphenyl-4-yl]benzene (**4**, $C_{294}H_{198}$) and hexakis[4′-(2,3,4,5-tetraphenylphenyl)biphenyl-4-yl]benzene (**5**, $C_{258}H_{174}$) are substructures of "phenylogous cubic graphite", and the other two, hexakis(2′,3′,4′,5′,6′-pentaphenylbiphenyl-4-yl)benzene (**26**, $C_{258}H_{174}$) and hexakis(2′,3′,4′,5′-tetraphenylbiphenyl-4-yl)benzene (**25**, $C_{222}H_{150}$) are strongly pitched, six-bladed molecular propellers. The X-ray crystal structure of compound **26** has also been determined; dendrimer **26** is at present the largest crystallographically characterized hydrocarbon.

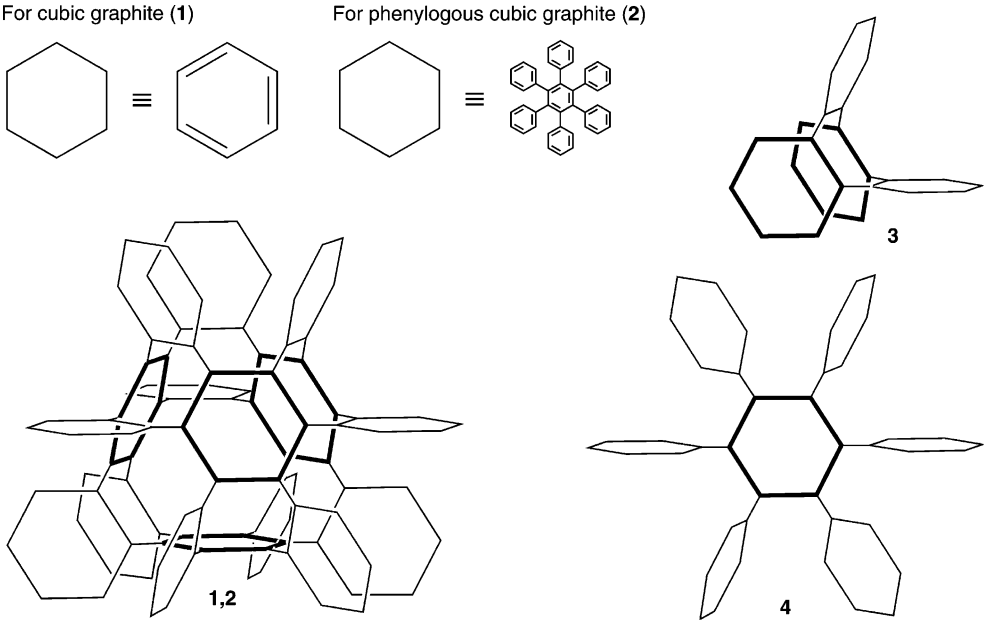
Introduction

"Cubic graphite" (**1**) is a hypothetical carbon allotrope first proposed by Gibson et al. in 1946.[1] Composed entirely of benzene rings, with each benzene ring attached to six other, different benzene rings, cubic graphite is the ultimate polyphenylene structure,[2] but the prospects for its synthesis are poor because of both thermodynamic and kinetic considerations.[3,4] However, the homolog, or phenylog, of cubic graphite **2**,[4] formed from hexaphenylbenzene subunits linked in the same fashion as the benzene rings in cubic graphite, is a better candidate for synthesis because the large cavities in this structure and its larger precursors would permit the easy passage of solvents and reagents.

Polyphenylene nanostructures[2,5] are of great current interest, and substructures of phenylogous cubic graphite (**2**) are attractive examples this class of compounds. We recently reported the synthesis and X-ray structure of compound **3** ($C_{168}H_{112}$),[4] a macrocyclic substructure of **2**, and in this article we describe the synthesis of two larger, dendrimeric substructures of **2**, compounds **4** ($C_{294}H_{198}$) and **5** ($C_{258}H_{174}$), and several related, very large, polyphenylene hydrocarbons (see Schemes 1−3).

Results and Discussion

The polyphenylene dendrimer **4** possesses ideal D_6 symmetry, and thus it has a central benzene ring with six large, but identical, substituents. The trimerization of the bis(polyaryl)-



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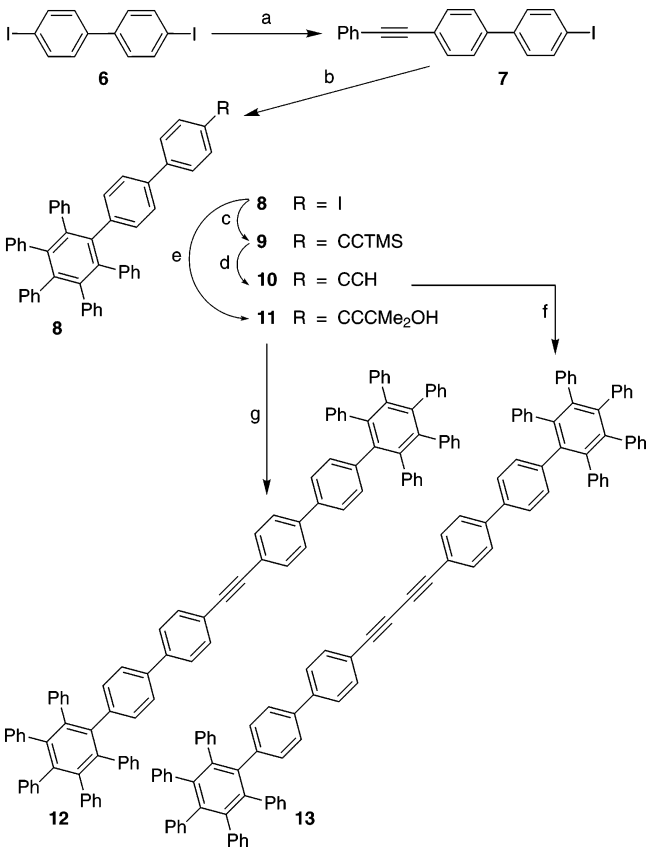
Scheme 1 [a]



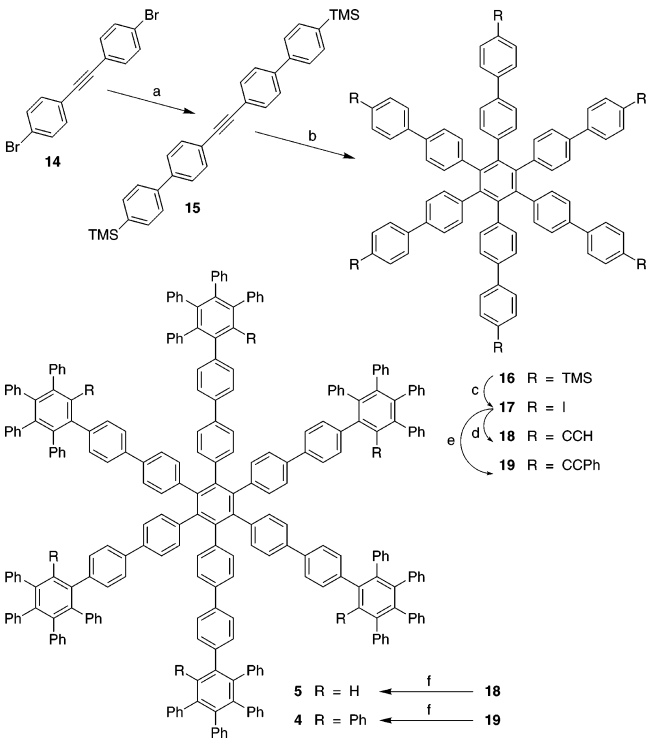
[a] (a) PhCCH, $(Ph_3P)_2PdCl_2$, CuI, piperidine, 50 °C, 62%. (b) Tetracyclone, Ph_2O, 280 °C, 91%. (c) TMSCCH, $(Ph_3P)_2PdCl_2$, CuI, Et_3N, toluene, 50 °C, 96%. (d) TBAF, THF, room temperature, 94%. (e) 2-Methyl-3-butyn-2-ol, $(Ph_3P)_2PdCl_2$, CuI, Et_3N, toluene, 80 °C, 76%. (f) **8**, $(Ph_3P)_4Pd$, CuI, Et_3N, toluene, 50 °C, 47%. (g) **8**, $(Ph_3P)_2PdCl_2$, CuI, NaOH, toluene, Bu_4NI, 80 °C, 22%.

acetylene **12** (Scheme 1) should be a very efficient way to prepare such a molecule, because there is no question of the formation of regioisomers in such a reaction.

A synthesis of the precursor **12** is simple enough on paper, and indeed only the last step was problematic in practice. Sonogashira coupling[6] of 4,4′-diiodobiphenyl (**6**) with 1 equiv of phenylacetylene gave alkyne **7** in 62% yield, and its Diels–Alder reaction with tetracyclone gave the aryl iodide **8** in 91% yield. A second Sonogashira reaction of **8** with trimethylsilylacetylene gave **9**, and treatment of this material with tetrabutylammonium fluoride furnished the corresponding monosubstituted acetylene **10** in 90% yield from **8**. Unfortunately, the third Sonogashira reaction in this sequence was not successful: the coupling of aryl iodide **8** with alkyne **10** gave primarily the bis(polyaryl)butadiyne **13** (the dimer of **10**) instead of the desired **12**.

Various conditions were examined for the ability to suppress the undesired dimerization. The more reactive $Pd_2(dba)_3$ catalyst

Scheme 2 [a]



[a] (a) 4-$TMSC_6H_4B(OH)_2$, $(Ph_3P)_4Pd$, K_2CO_3, toluene, EtOH, 50 °C, 83%. (b) $Hg[Co(CO)_4]_2$, dioxane, 100 °C, 81%. (c) ICl, CH_2Cl_2, 93%. (d) TMSCCH, $(Ph_3P)_2PdCl_2$, CuI, Et_3N, toluene, 60 °C, then TBAF, THF, room temperature, 91%. (e) PhCCH, $(Ph_3P)_2PdCl_2$, CuI, Et_3N, toluene, 50 °C, 84%. (f) Tetracyclone, Ph_2O, 280 °C, 60% for **5**, 80% for **4**.

was employed along with triphenylarsine as an accelerating ligand,[7] but **13** remained the major product. The usual base, triethylamine, was replaced with *n*-butylamine or Hunig's base, but without success. Finally, the method of Chow et al.,[8] in which a masked acetylene (the acetone adduct **11**) is used to generate low concentrations of the free alkyne **10** in situ, enabled the synthesis of compound **12** without the formation of dimer **13**. The 22% yield in this reaction was low, but attempts to optimize the yield were abandoned when a more serious problem was discovered: the insolubility of the alkyne **12**. The vast majority of polyphenyl aromatic compounds are readily soluble in aromatic and halogenated organic solvents, but compound **12** proved to be quite insoluble in all common solvents. Nevertheless, the synthesis of dendrimer **4** was attempted by heating a suspension of **12** in refluxing dioxane in the presence of the trimerization catalyst $Hg[Co(CO)_4]_2$,[9] but only starting material was recovered.

A new synthesis of **4** was devised in which the trimerization of a freely soluble alkyne is carried out at an earlier stage (Scheme 2). Bis(4-bromophenyl)acetylene[10] (**14**) was subjected to a double Suzuki coupling[11] with 4-(trimethylsilyl)benzeneboronic acid to give the alkyne **15** in 83% yield, and trimerization of this material yielded the starlike polyphenylene **16** in 81% yield. It was now necessary to alter six functional groups in *each* of three consecutive reactions to obtain **4**, but this

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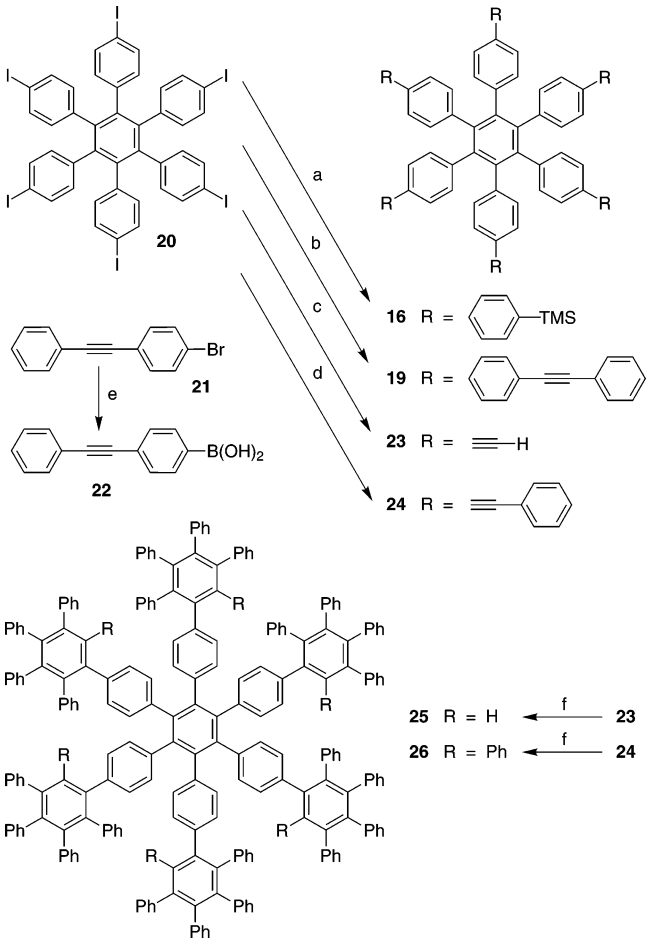
Scheme 3 [a]



[a] (a) 4-TMSC$_6$H$_4$B(OH)$_2$, (Ph$_3$P)$_4$Pd, K$_2$CO$_3$, toluene, EtOH, 80 °C, 64%. (b) **22**, (Ph$_3$P)$_4$Pd, K$_2$CO$_3$, toluene, EtOH, 80 °C, 25%. (c) TMSCCH, (Ph$_3$P)$_2$PdCl$_2$, CuI, Et$_3$N, toluene, 60 °C, then TBAF, THF, room temperature, 75%. (d) PhCCH, (Ph$_3$P)$_2$PdCl$_2$, CuI, Et$_3$N, toluene, 50 °C, 80%. (e) *n*-BuLi, THF, −78 °C, then B(OMe)$_3$, warm to room temperature, 76%. (f) Tetracyclone, Ph$_2$O, 280 °C, 85% for **25**, 81% for **26**.

questionable tactic proved to be surprisingly efficient. Iododesilation[12] of **16** gave **17** in 93% yield, a Sonogashira reaction with excess phenylacetylene converted the six iodines into phenylethynyl groups to give **19** (84%), and Diels−Alder reaction of **19** with excess tetracyclone smoothly gave dendrimer **4** (80%). Thus, the overall yield of **4** from the simple, readily accessible **14** was 42% in a five-step synthesis. We note that Müllen and co-workers have very recently reported a very similar preparation of intermediates **16** and **17** during the synthesis of entirely different targets.[13]

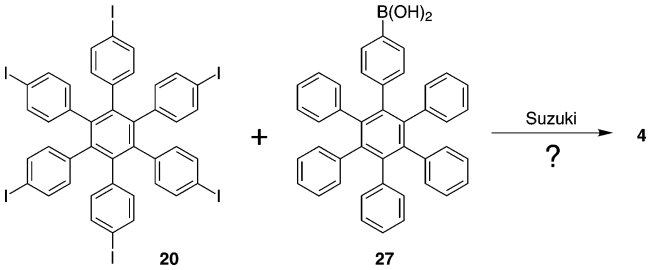
The polyphenylene dendrimer **5**—which lacks six of the phenyl groups found in **4**, but which is also a substructure of phenylogous cubic graphite—was prepared by this general method as well. In that case, hexaiodide **17** was converted to the terminal alkyne **18** by Sonogashira reaction with trimethylsilylacetylene followed by fluoride cleavage in overall 91% yield. The final Diels−Alder reaction gave a more modest 60% yield of **5**, perhaps due to partial polymerization of the six terminal alkyne groups under the relatively harsh reaction conditions (280 °C). Nevertheless, **5** was prepared in 34% overall yield from **14**.

The success of the various 6-fold functional group modifications encouraged us to try a similar strategy for the synthesis of a more crowded set of polyphenylene dendrimers. Whereas compound **4** is composed of six hexaphenylbenzene subunits attached to a central hexaphenylbenzene, compound **26** (Scheme 3) is made of six hexaphenylbenzenes attached to a central *benzene* ring. As such, **26** is not a substructure of phenylogous cubic graphite, and it is much more crowded than **4**. Müllen and co-workers have previously prepared the closely related compound **25**,[14] which lacks six of the phenyl groups of **26**, but even so, the very fine X-ray structure of **25** shows it to be a strongly pitched molecular propeller.[14c]

The synthesis of **26** began with hexakis(4-iodophenyl)benzene[15] (**20**, Scheme 3). The iodines were converted to phenylalkynyl groups via a 6-fold Sonogashira reaction with phenylacetylene to give **24** (80% yield), and a Diels−Alder reaction with tetracyclone gave **26** (81%). In a similar manner, we prepared Müllen's compound **25** by elaboration of **20** to the terminal hexayne (75%), followed by Diels−Alder reaction with tetracyclone (85%). This synthesis is perhaps more succinct than Müllen's, but there is no real synthetic advantage either way.

Finally, compounds **16** and **19** were prepared by Suzuki coupling reactions of hexaiodide **20** with 4-(trimethylsilyl)benzeneboronic acid and the tolaneboronic acid **22**, respectively, thus providing alternative routes to dendrimers **4** and **5**. However, the three-step synthesis of **20** from **14** proceeds in only 48% overall yield,[15] and thus the overall syntheses of **4** and **5** in this manner are not quite as efficient as those illustrated in Scheme 2.

The two- or three-step elaborations of the D_6 symmetric core molecules **16** and **20** gave the target polyphenylene dendrimers **4**, **5**, **25**, and **26** in good yields, despite the fact that the modification of six functional groups was required in each of these steps. Given this success, it is easy to imagine even shorter, convergent syntheses of these molecules by attaching preformed penta- or hexaphenylbenzenes to a D_6 core molecule. For example, a Suzuki reaction of **20** with 6 equiv of the (hexaphenylbenzene)boronic acid **27** should yield compound **4** directly.



Unfortunately, this reaction and similar reactions employing hexakis(4-bromophenyl)benzene instead of the hexaiodide **20** were not successful (data not shown). The products were mainly the polyphenylenes resulting from two, three, and four coupling

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events, and each of these appeared to be mixtures of regioisomers. These results stand in contrast to the ostensibly similar Suzuki coupling reactions used to make **16** and **19** from **20**, which gave reasonable yields (64% and 25%, respectively) of 6-fold reacted products. Even better was Müllen's recent synthesis of **16** by 6-fold coupling of 4-(trimethylsilyl)benzeneboronic acid and hexakis(4-bromophenyl)benzene (92%).[13] Indeed, it has been our experience, in this and related projects, that palladium-catalyzed coupling reactions involving two large reactants generally proceed poorly, even if both are freely soluble and there is no apparent steric encumbrance of the reactive sites, but reactions involving one large reactant and one small one tend to be highly efficient. Of course, this observation may be due to steric hindrance of a slightly different sort: even though the reactive sites are exposed, the large pendant groups of the two reactants may collide with each other or with large phosphine ligands surrounding the palladium in some critical transition state. In any event, it may be wise to avoid the coupling of two large molecules where possible when planning syntheses of highly branched polyphenylenes.

The characterization of large polyphenylenes requires special care. The most useful simple method is mass spectrometry, which, when combined with the knowledge of the structures of the precursors, gives the best evidence of successful reactions. All of the compounds reported here give strong molecular ions in FAB or MALDI mass spectra. Less useful are NMR data. Although the molecules are usually soluble, their ^{1}H NMR spectra are not very informative, and even the ^{13}C NMR spectra of the larger compounds can suffer from overlapping resonances, which are inevitable for molecules composed entirely of benzene rings. However, the ^{13}C NMR spectra do give an indication of the degree of symmetry present in the molecules, and thus provide an important check on the mass spectral data. Compounds **4**, **5**, **25**, and **26** all have relatively simple ^{13}C NMR spectra consistent with their high symmetry (and all are reproduced in the Supporting Information).

Because of the limitations of spectroscopic methods and to determine the conformations of our large polyphenylenes, a special effort has been made to obtain X-ray crystal structures of these molecules. Unfortunately, crystallization experiments with the new dendrimers have failed to yield, with one exception, single crystals large enough for X-ray analysis. This was surprising, because the crystal structure of the known compound **25** has been reported by Müllen and co-workers,[14c] and we have previously reported the X-ray structures of several polyphenylene hydrocarbons containing more than 100 carbon atoms.[4,16,17]

The exception is compound **26**, which gives long needles from many solvent combinations, provided that dichloromethane is one of the components. These crystals are trigonal, and, after data collection, the initial solution of the structure was rapid. Unfortunately, it soon became apparent that the compound crystallizes in the polar space group *R*3*m* with $Z = 3$ (hexagonal setting), which implies that each molecule of **26** resides on a site with crystallographic C_{3v} symmetry. However, compound **26** itself possesses only C_3 symmetry, and thus the entire structure is disordered across the vertical mirror planes. This fact, combined with the presence of large voids filled with disordered dichloromethane molecules, makes a truly satisfactory refinement of the structure impossible (see the Experimental Section for details), but this X-ray structure determination does reveal the composition and conformation of the molecule. A search of the Cambridge Structural Database[18] indicates that compound **26** is the largest hydrocarbon to date to have its structure determined by X-ray crystallography, and it is one of only four crystallographically characterized hydrocarbons containing more than 200 carbon atoms.[14c,19]

The molecular structure of **26** is illustrated in Figure 1. The molecule is a relatively crowded, six-bladed molecular propeller. Compound **25**, which lacks six of the interior phenyls in **26**, is less crowded, and its X-ray structure[14c] shows more variably tilted polyphenylbenzene "blades" than **26**, but neither molecule shows any large distortions due to steric conflicts. This is consistent with the ^{13}C NMR spectra of both molecules, which show resonances that are few and sharp enough to suggest that all of the phenyl groups undergo rapid rotation on the NMR time scale. The packing of one layer of the molecules of **26** is also shown in Figure 1. The crystals contain large channels parallel to the *c* axis of the crystal, and these are filled with severely disordered solvent molecules. Additional solvent molecules are located in cavities above and below the central ring of the dendrimer; overall, this is a highly porous, but also fragile, crystal.

The structures of the larger dendrimers **4** and **5** would be interesting to obtain, because they might be very different than those of **25** and **26**. The six polyphenylbenzene blades in **4** and **5** are further removed from the core, and they would have the opportunity to flatten out to a much greater degree than those in **25** and **26**, perhaps giving discoidal structures approximately 40 Å in diameter. However, it seems unlikely that these structures will be obtained: in addition to the parent hydrocarbons **4** and **5**, extensive crystallization experiments with a variety of halogenated and oxygenated derivatives (a dodecabromo derivative, **4b**, is described in the Experimental Section) have thus far failed to yield satisfactory crystals.

Conclusion

The successful synthesis of the polyphenylene **4** in only five steps and 42% yield from the readily accessible dibromotolane **14**, as well as the preparation of dendrimers **5**, **25**, and **26** by syntheses of comparable brevity and yield, suggest that even more complicated polyphenylene nanostructures should be accessible. The high solubility of these compounds, already containing nearly 300 carbon atoms, encourages us to believe that studies of larger structures can still be accomplished by using conventional chemical methods for synthesis and purification, although common spectroscopic methods will be increasingly strained for the characterization of such molecules. Therefore, having now prepared and characterized both macrocyclic (**3**)[4] and dendrimeric (**4**, **5**) fragments of "phenylogous cubic graphite", we hope to synthesize even more elaborate

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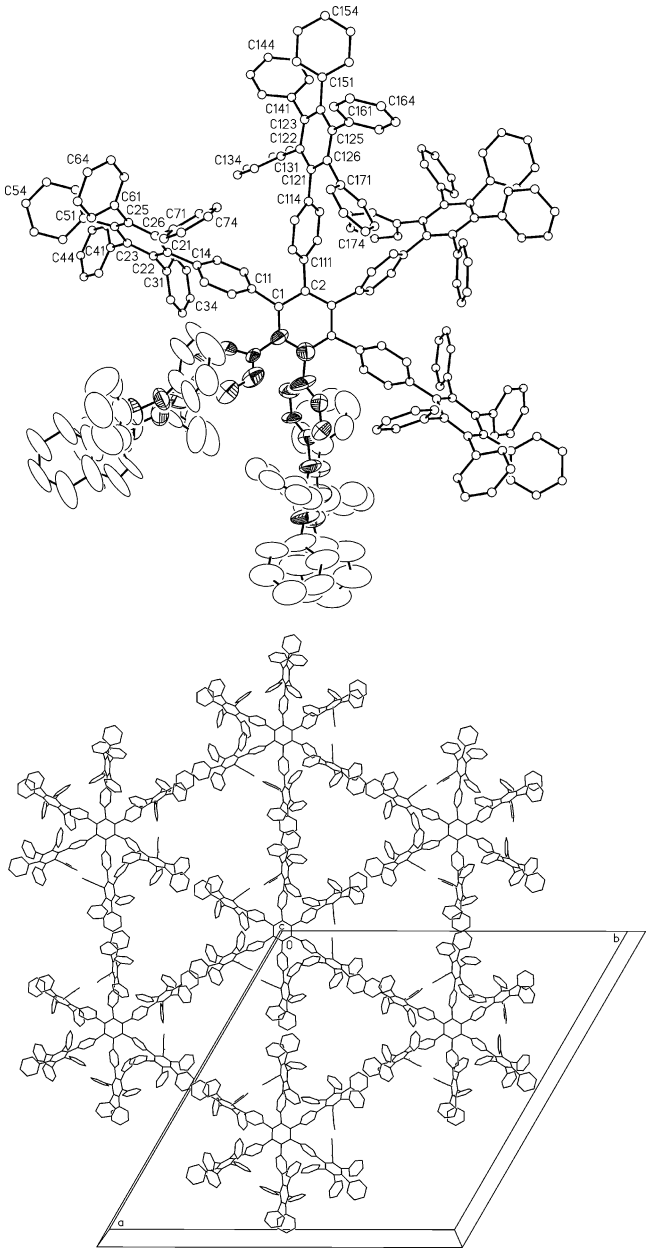

Figure 1. Top: Molecular structure of compound **26**. Hydrogen atoms have been omitted. One symmetry-independent third of the molecule is drawn with 40% probability thermal ellipsoids, and another third shows the crystallographic numbering scheme. Bottom: Unit cell and one layer of the packing of compound **26** viewed down the *c* axis. For clarity, only one of the two disordered molecules at each site is illustrated.

substructures of this material containing multiple macrocycles in a three-dimensional network.

Experimental Section

Bis(4-bromophenyl)acetylene (**14**, mp 183−185 °C [ref 10, 182−184 °C]), 1-bromo-4-(phenylethynyl)benzene (**21**, mp 84−85 °C [ref 20, 83−84 °C]), hexakis(4-iodophenyl)benzene (**20**, mp > 400 °C [ref 15, > 330 °C]), 3,4-bis(bromophenyl)-2,5-diphenylcyclopentadienone (mp 246−247 °C [ref 21, 249.5−250 °C]), and $Hg[Co(CO)_4]_2$[9] were prepared by literature procedures.

4-Iodo-4′-(phenylethnyl)biphenyl (7). 4,4′-Diiodobiphenyl (**6**, 10.0 g, 24.6 mmol), CuI (0.23 g, 1.2 mmol), and $(Ph_3P)_2PdCl_2$ (0.43 g, 0.62 mmol) were stirred in piperidine (120 mL) at 50 °C under argon for 20 min. Phenylacetylene (2.29 g, 22.4 mmol) was added to the reaction mixture over the next 20 min, and stirring was continued for 3 h at 50 °C. Saturated NH_4Cl was added, and the mixture was extracted twice with toluene. The combined extracts were washed with water, dried over Na_2SO_4, and concentrated to dryness. This residue was chromatographed on a silica gel column (4:1 hexanes−benzene), and the fraction with R_f 0.29 (silica gel TLC; 4:1 hexanes−benzene) was collected and concentrated to give compound **7** as a white powder (5.81 g, 15.3 mmol, 62%), mp 218−219 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.32−7.38 (m, 5 H), 7.53−7.62 (m, 6 H), 7.78 (m, 2 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 89.3, 90.6, 93.7, 122.9, 123.4, 127.0, 128.6, 129.0, 131.8, 132.4, 138.2, 140.0, 140.1 (13 of 14 expected resonances). MS (EI) *m*/*z*: 380 (M^+, 100), 252 (M − HI, 57). Exact mass, 380.0050; calcd for $C_{20}H_{13}I$, 380.0062.

4-Iodo-4′-(pentaphenylphenyl)biphenyl (8). Compound **7** (1.15 g, 3.02 mmol), tetracyclone (1.20 g, 3.13 mmol), and diphenyl ether (3 mL) were mixed in a screw-capped Pyrex tube, and the tube was placed in a metal bath heated at 280 °C for 2 h. After cooling, the mixture was dissolved in CH_2Cl_2, and then methanol was added until no more precipitate appeared. Suction filtration gave compound **8** as an off-white powder (2.02 g, 2.75 mmol, 91%), mp 351−353 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.81−6.88 (m, 25 H), 6.89 and 7.08 (AA′BB′ system, 4 H), 7.16 and 7.64 (AA′BB′ system, 4 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 92.7, 125.1, 125.4, 125.5, 126.8, 126.9, 128.8, 131.59, 131.61, 131.62, 132.2, 136.4, 137.8, 139.9, 140.50, 140.52, 140.53, 140.6, 140.70, 140.72, 140.75, 140.76 (22 of 24 expected resonances). MS (EI) *m*/*z*: 736 (M^+, 100). Exact mass, 736.1632; calcd for $C_{48}H_{33}I$, 736.1627.

4-Ethynyl-4′-(pentaphenylphenyl)biphenyl (10). Compound **8** (500 mg, 0.679 mmol), CuI (6.5 mg, 0.034 mmol), and $(Ph_3P)_2PdCl_2$ (11.9 mg, 0.017 mmol) were stirred in toluene (15 mL) and triethylamine (5 mL) at 50 °C under argon for 20 min. Trimethylsilylacetylene (133 mg, 1.36 mmol) was added over 5 min, and stirring was continued for 3 h at 50 °C. Saturated NH_4Cl was added, and the mixture was extracted twice with toluene. The combined extracts were washed with water, dried over Na_2SO_4, and concentrated to dryness. The residue was chromatographed on a silica gel column (2:1 hexanes−CH_2Cl_2), and the fraction with R_f 0.43 (silica gel TLC; 2:1 hexanes−CH_2Cl_2) was collected and concentrated to give 4-(pentaphenylphenyl)-4′-(trimethylsilylethynyl)biphenyl (**9**) as a white powder (461 mg, 0.65 mmol, 96%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.26 (s, 9 H), 6.84−6.88 (m, 25 H), 6.91 and 7.12 (AA′BB′ system, 4 H), 7.37 and 7.43 (AA′BB′ system, 4 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 0.22, 94.8, 105.3, 121.7, 125.3, 125.4, 125.5, 126.6, 126.8, 126.9, 131.59, 131.60, 131.62, 132.1, 132.4, 136.7, 139.9, 140.45, 140.53, 140.64, 140.68, 140.72, 140.76, 140.77, 140.9 (25 of 27 expected resonances).

The silylated alkyne **9** (461 mg, 0.652 mmol) was dissolved in THF (15 mL) at room temperature. Tetrabutylammonium fluoride (1.0 M in THF, 1.3 mL, 1.3 mmol) was added, and the solution was stirred for 2 h. Water was added, and the mixture was extracted twice with ethyl acetate. The combined extracts were washed with water, dried over Na_2SO_4, and concentrated to dryness. The residue was chromatographed on a silica gel column (2:1 hexanes−CH_2Cl_2), and the fraction with R_f 0.34 (silica gel TLC; 2:1 hexanes−CH_2Cl_2) was collected and concentrated to give compound **10** as a white powder (389 mg, 0.613 mmol, 94%), mp 308−311 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.09 (s, 1 H), 6.81−6.88 (m, 25 H), 6.90 and 7.12 (AA′BB′ system, 4 H), 7.39 and 7.46 (AA′BB′ system, 4 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 77.8, 83.9, 120.7, 125.3, 125.4, 125.5, 126.76, 126.81, 126.9, 131.60, 131.62, 131.63, 132.2, 132.5, 136.6, 139.9, 140.5, 140.58, 140.64, 140.70, 140.72, 140.76, 140.77, 141.4 (24 of 26 expected resonances). MS (EI) *m*/*z*: 634 (M^+, 100). Exact mass, 634.2682; calcd for $C_{50}H_{34}$, 634.2660.

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4-(3-Hydroxy-3-methyl-1-butynyl)-4′-(pentaphenylphenyl)biphenyl (11). Compound **8** (500 mg, 0.679 mmol), CuI (12.9 mg, 0.068 mmol), and $(Ph_3P)_2PdCl_2$ (23.7 mg, 0.034 mmol) were stirred in toluene (15 mL) and triethylamine (8 mL) at 80 °C under argon for 20 min. 2-Methyl-3-butyn-2-ol (0.20 mL, 2.06 mmol) was added over 5 min, and stirring was continued for 3 h at 80 °C. Saturated NH_4Cl was added, and the mixture was extracted twice with ethyl acetate. The combined extracts were washed with water, dried over Na_2SO_4, and concentrated to dryness. The residue was chromatographed on a silica gel column (5:1 hexanes−ethyl acetate), and the fraction with R_f 0.12 (silica gel TLC; 5:1 hexanes−ethyl acetate) was collected and concentrated to give compound **11** as a light orange powder (358 mg, 0.517 mmol, 76%), mp 326−329 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.61 (s, 6 H), 6.82−6.87 (m, 25 H), 6.88 and 7.11 (AA′BB′ system, 4 H), 7.37 (s, 4 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 31.7, 65.9, 82.3, 94.3, 121.3, 125.2, 125.4, 125.5, 126.7, 126.8, 126.9, 131.60, 131.62, 131.63, 132.0, 132.1, 136.7, 139.9, 140.4, 140.5, 140.6, 140.68, 140.74, 140.76, 140.78 (25 of 28 expected resonances). MS (EI) *m*/*z*: 692 (M^+, 100), 674 (M − H_2O, 88), 634 (M − CH_3COCH_3, 45). Exact mass, 692.3087; calcd for $C_{53}H_{40}O$, 692.3079.

1,4-Bis[4′-(pentaphenylphenyl)biphenyl-4-yl]-1,3-butadiyne (13). Aryl iodide **8** (42.4 mg, 57.6 mmol), CuI (1.1 mg, 5.8 μmol), and $(Ph_3P)_4Pd$ (3.4 mg, 2.9 μmol) were stirred in toluene (4 mL) and triethylamine (1 mL) at 50 °C under argon for 20 min. Alkyne **10** (36.5 mg, 57.5 mmol) in toluene (1 mL) was added in a dropwise fashion, and the reaction mixture was stirred at 50 °C for 18 h. Saturated NH_4Cl was added, and the mixture was extracted twice with toluene. The combined extracts were washed with water, dried over Na_2SO_4, and concentrated to dryness. The residue was chromatographed on a silica gel column (1:1 hexanes−CH_2Cl_2), and the fraction with R_f 0.19 (silica gel TLC; solvent, 1:1 hexanes−CH_2Cl_2) was collected and concentrated to give compound **13** as a white powder (34 mg, 27 mmol, 47%), mp 385−387 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.82−6.88 (m, 50 H), 6.90 and 7.11 (AA′BB′ system, 8 H), 7.39 and 7.47 (AA′BB′ system, 8 H). FAB MS *m*/*z*: 1268 (M + H [$^{13}C_1$], 100). Because of the very low solubility of **13**, a ^{13}C NMR spectrum was not recorded.

Bis[4′-(pentaphenylphenyl)biphenyl-4-yl]acetylene (12). Aryl iodide **8** (50 mg, 0.068 mmol), alkyne **11** (47 mg, 0.068 mmol), CuI (1.3 mg, 6.8 μmol), $(Ph_3P)_4PdCl_2$ (4.8 mg, 6.8 μmol), and tetrabutylammonium iodide (2.5 mg, 6.8 μmol) were heated in a mixture of toluene (6 mL) and aqueous NaOH (5 M, 0.1 mL, 0.5 mmol) in a screw-capped tube at 80 °C for 24 h. Saturated NH_4Cl was added, and the mixture was extracted twice with toluene. The combined extracts were washed with water, dried over Na_2SO_4, and concentrated to dryness. The residue was chromatographed on a silica gel column (3:2 hexanes−toluene), and the fraction with R_f 0.15 (silica gel TLC; solvent, 1:1 hexanes−toluene) was collected and concentrated to give compound **12** as an off-white powder (18 mg, 0.014 mmol, 22%), mp > 400 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 6.80−6.88 (m, 50 H), 6.88 and 7.16 (AA′BB′ system, 8 H), 7.51 and 7.56 (AA′BB′ system, 8 H). MS (MALDI) *m*/*z*: 1242 (M^+, 100). Because of the very low solubility of **12**, a ^{13}C NMR spectrum was not recorded.

Bis[4′-(trimethylsilyl)biphenyl-4-yl]acetylene (15). Bis(4-bromophenyl)acetylene (**14**, 500 mg, 1.49 mmol) and 4-(trimethylsilyl)-benzeneboronic acid (722 mg, 3.72 mmol) were dissolved in toluene (30 mL). Ethanol (4 mL) and 2 M K_2CO_3 (10 mL) were added, and the mixture was flushed with argon. $(Ph_3P)_4Pd$ (170 mg, 0.15 mmol) was added, and the mixture was heated at 50 °C under argon for 24 h. Addition of ethyl acetate (10 mL) to the reaction mixture induced the crystallization of the desired product **15**, which was collected as off-white plates (590 mg, 1.24 mmol, 83%), mp 269−271 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.31 (s, 18 H), 7.62 (s, 16 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ −0.9, 90.3, 122.5, 126.5, 127.2, 132.3, 134.1, 140.0, 140.9, 141.1 (10 of 10 expected resonances). MS (EI) *m*/*z*: 474 (M^+, 100), 459 (M − CH_3, 61). Exact mass, 474.2193; calcd for $C_{32}H_{34}Si_2$, 474.2199.

Hexakis[4′-(trimethylsilyl)biphenyl-4-yl]benzene (16) (by Trimerization of 15). A mixture of compound **15** (210 mg, 0.442 mmol), $Hg[Co(CO)_4]_2$ (17 mg, 0.031 mmol), and dioxane (25 mL) was sealed in a screw-capped Pyrex tube under argon, and the mixture was stirred at 100 °C for 2 days. After cooling, the mixture was filtered through a short Celite pad to remove the catalyst residue. The filtrate was concentrated to dryness, and the residue was dissolved in CH_2Cl_2. This solution was diluted with methanol to precipitate the desired product **16** as an off-white powder (170 mg, 0.119 mmol, 81%), mp > 400 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.24 (s, 54 H), 6.95 and 7.16 (AA′BB′ system, 24 H), 7.41 and 7.46 (AA′BB′ system, 24 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ −1.0, 125.5, 126.3, 132.2, 133.8, 137.7, 138.9, 140.0, 140.5, 141.2 (10 of 10 expected resonances). FAB MS *m*/*z*: 1422 (M^+, 77), 978 (100).

Hexakis(4′-iodobiphenyl-4-yl)benzene (17). Compound **16** (0.67 g, 0.47 mmol) was dissolved in CH_2Cl_2 (40 mL). A solution of ICl in CH_2Cl_2 (3.3 mL of a 1.0 M solution, 3.3 mmol) was added, and the reaction was stirred under argon for 12 h. Methanol was added to precipitate the desired product **17** as a white powder (0.76 g, 0.44 mmol, 93%), mp > 500 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.93 and 7.10 (AA′BB′ system, 24 H), 7.14 and 7.63 (AA′BB′ system, 24 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 92.9, 125.4, 128.8, 132.2, 137.9, 140.1, 140.3, 140.4 (eight of nine expected resonances). FAB MS *m*/*z*: 1746 (M^+, 100).

Hexakis(4′-ethynylbiphenyl-4-yl)benzene (18). Compound **17** (200 mg, 0.115 mmol), CuI (5 mg, 0.026 mmol), and $(Ph_3P)_2PdCl_2$ (24 mg, 0.034 mmol) were stirred in toluene (30 mL) and triethylamine (7 mL) at 60 °C under argon for 20 min. Trimethylsilylacetylene (132 mg, 1.34 mmol) was added over 5 min, and the reaction mixture was stirred at 60 °C for 18 h. Saturated NH_4Cl was added, and the mixture was extracted twice with toluene. The combined extracts were washed with water, dried over Na_2SO_4, and concentrated to dryness. The solid residue was dissolved in THF (20 mL), and tetrabutylammonium fluoride (1.0 M in THF, 1.1 mL, 1.1 mmol) was added. The solution was stirred for 2 h at room temperature. Water was added, and the mixture was extracted twice with ethyl acetate. The combined extracts were washed with water, dried over Na_2SO_4, and concentrated to dryness. The residue was chromatographed on a silica gel column (3:1 hexanes−ethyl acetate) to give compound **18** as an off-white powder (119 mg, 0.18 mmol, 91%), mp > 400 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.08 (s, 6 H), 6.96 and 7.16 (AA′BB′ system, 24 H), 7.30 and 7.43 (AA′BB′ system, 24 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 77.9, 83.8, 120.8, 125.6, 126.8, 132.1, 132.6, 137.0, 140.2, 140.4, 141.1 (11 of 11 expected resonances). FAB MS *m*/*z*: 1134 (M^+, 100).

Hexakis[4′-(phenylethynyl)biphenyl-4-yl]benzene (19). Compound **17** (300 mg, 0.172 mmol), CuI (6 mg, 0.032 mmol), and $(Ph_3P)_2PdCl_2$ (36 mg, 0.051 mmol) were stirred in toluene (45 mL) and triethylamine (10 mL) at 50 °C under argon for 20 min. Phenylacetylene (214 mg, 2.09 mmol) was added over 5 min, and the reaction mixture was stirred at 50 °C for 18 h. Saturated NH_4Cl was added, and the mixture was extracted twice with toluene. The combined extracts were washed with water, dried over Na_2SO_4, and concentrated to dryness. The residue was chromatographed on a silica gel column. A byproduct, 1,4-diphenyl-1,3-butadiyne, was eluted with solvent 2:1 hexanes−toluene, and compound **19** was then eluted with 1:1 hexanes−toluene. Evaporation of the solvent gave **19** as a light yellow powder (230 mg, 0.144 mmol, 84%), mp > 400 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.99 and 7.21 (AA′BB′ system, 24 H), 7.31−7.34 (m, 18 H), 7.43 and 7.49 (AA′BB′ system, 24 H), 7.50−7.54 (m, 12 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 89.6, 90.2, 122.0, 123.5, 125.6, 126.8, 128.4, 128.5, 131.8, 132.1, 132.2, 137.1, 140.2, 140.5, 140.6 (15 of 15 expected resonances). FAB MS *m*/*z*: 1592 (M + H [$^{13}C_1$], 100).

Hexakis[4′-(2,3,4,5-tetraphenylphenyl)biphenyl-4-yl]benzene (5). Compound **18** (34 mg, 0.030 mmol), tetracyclone (103 mg, 0.27 mmol), and diphenyl ether (1 mL) were mixed in a screw-capped Pyrex tube, and the tube was placed in a metal bath heated at 280 °C for 3 h. After

cooling, CH_2Cl_2 (3 mL) was added, the solution was then added dropwise into methanol (30 mL), and the resulting precipitate was collected. This material was chromatographed on a silica gel column (5:1 hexanes−ethyl acetate) to give compound **5** as a pale yellow solid (60 mg, 0.018 mmol, 60%), mp > 500 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.42−7.00 (m, 174 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 125.3, 125.5, 125.8, 126.1, 126.4, 126.8, 127.1, 127.2, 127.8, 130.1, 130.4, 131.7, 137.1, 138.6, 139.3, 139.4, 139.8, 140.2, 140.4, 140.5, 141.0, 141.9, 142.0 (23 of 31 expected resonances). MS (MALDI) *m*/*z*: 3273 (M^+ [$^{13}C_3$], 100).

Hexakis[4′-(pentaphenylphenyl)biphenyl-4-yl]benzene (4). Compound **19** (40 mg, 0.025 mmol), tetracyclone (87 mg, 0.23 mmol), and diphenyl ether (1 mL) were mixed in a screw-capped Pyrex tube, and the tube was placed in a metal bath heated at 280 °C for 3 h. After cooling, CH_2Cl_2 (3 mL) was added, the solution was then added dropwise into methanol (30 mL), and the resulting precipitate was collected. This material was chromatographed on a silica gel column (1:1 hexanes−CH_2Cl_2) to give compound **4** as a pale yellow solid (75 mg, 0.020 mmol, 80%), mp > 500 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.62−6.96 (m, 198 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 125.2, 125.4, 126.8, 126.9, 131.6, 131.8, 137.47, 137.53, 139.3, 139.4, 140.0, 140.3, 140.50, 140.56, 140.61, 140.8 (16 of 25 expected resonances). MS (MALDI) *m*/*z*: 3731 (M^+ [$^{13}C_5$], 100).

Hexakis{4′-[3,4-bis(4-bromophenyl)-2,5,6-triphenylphenyl]biphenyl-4-yl}benzene (4b). Compound **19** (30 mg, 0.019 mmol), 3,4-bis-(4-bromophenyl)-2,5-diphenylcyclopentadienone (93 mg, 0.17 mmol), and diphenyl ether (1 mL) were mixed in a screw-capped Pyrex tube, and the tube was placed in a metal bath heated at 280 °C for 3 h. Workup and purification as described for **4** gave compound **4b** as a pale yellow solid (50 mg, 0.011 mmol, 57%), mp > 500 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.60−7.20 (m, 186 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 119.9, 125.2, 125.5, 125.7, 126.9, 127.08, 127.13, 130.3, 131.5, 131.6, 131.8, 133.1, 137.4, 137.7, 139.0, 139.1, 139.2, 140.26, 140.32, 140.49, 140.54, 140.59, 140.7, 141.1 (24 of 35 expected resonances). MS (MALDI) *m*/*z*: 4678 (M^+ [$^{13}C_4{}^{79}Br_6{}^{81}Br_6$], 100).

Hexakis[4′-(trimethylsilyl)biphenyl-4-yl]benzene (16) (by Arylation of 20). Compound **20** (1.00 g, 0.78 mmol) and 4-(trimethylsilyl)-benzeneboronic acid (1.80 g, 9.3 mmol) were dissolved in toluene (100 mL). Ethanol (6 mL) and 2 M K_2CO_3 (20 mL) were added, and the mixture was flushed with argon. $(Ph_3P)_4Pd$ (90 mg, 0.078 mmol) was added, and the mixture was heated at 80 °C under argon for 24 h. Water was added, and the mixture was extracted twice with ethyl acetate. The combined extracts were washed with water, dried over Na_2SO_4, and concentrated to dryness. The residue was chromatographed on a silica gel column. A byproduct, 4,4′-bis(trimethylsilyl)biphenyl, was eluted with hexanes, and compound **16** was then eluted with ethyl acetate. Evaporation of the solvent gave **16** as an off-white powder (0.71 g, 0.50 mmol, 64%), mp > 400 °C. (Spectral data are provided above.)

4-(Phenylethynyl)benzeneboronic Acid (22). Compound **21** (2.00 g, 7.78 mmol) was dissolved in freshly distilled THF (30 mL) and cooled to −78 °C under argon. To this solution was added *n*-butyllithium (1.6 M in pentane, 5.3 mL, 8.5 mmol), and after 30 min, trimethyl borate (1.21 g, 11.67 mmol) was added over 15 min. The reaction was allowed to warm to room temperature over 3 h, and it was quenched by adding 2 *N* HCl (50 mL). The resulting mixture was extracted twice with ethyl acetate, and the combined extracts were washed with water, dried over Na_2SO_4, and concentrated to dryness. Crystallization of the crude product from toluene gave pure compound **22** as a white powder (1.32 g, 5.94 mmol, 76%), mp 204−206 °C. ^{1}H NMR (400 MHz, DMSO-d_6): δ 7.42−7.45 (m, 3 H), 7.51 and 7.82 (AA′BB′ system, 4 H), 7.55−7.58 (m, 2 H), 8.19 (s, 2 H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 89.6, 90.1, 122.3, 123.7, 128.8, 128.9, 130.3, 131.4, 134.3 (nine of 10 expected resonances). MS (EI) *m*/*z*: 222 (M^+, 10), 204 (M − H_2O, 8), 178 (M − $B(OH)_2$, 100). Exact mass, 222.0845; calcd for $C_{14}H_{11}BO_2$, 222.0852.

Hexakis[4′-(phenylethynyl)biphenyl-4-yl]benzene (19) (by Arylation of 20). Compound **20** (200 mg, 0.155 mmol) and compound **22** (300 mg, 1.50 mmol) were dissolved in toluene (50 mL). Ethanol (4 mL) and 2 M K_2CO_3 (10 mL) were added, and the mixture was flushed with argon. $(Ph_3P)_4Pd$ (18 mg, 0.016 mmol) was added, and the mixture was heated at 80 °C under argon for 24 h. Water was added, and the mixture was extracted twice with ethyl acetate. The combined extracts were washed with water, dried over Na_2SO_4, and concentrated to dryness. The residue was chromatographed on a silica gel column. Impurities were eluted with 2:1 hexanes−toluene, and compound **19** was then eluted with solvent 1:1 hexanes−toluene. Evaporation of the solvent gave **19** as a light yellow powder (62 mg, 0.039 mmol, 25%), mp > 400 °C. (Spectral data are provided above.)

Hexakis(4-ethynylphenyl)benzene (23). Compound **20** (300 mg, 0.233 mmol), CuI (7 mg, 0.037 mmol), and $(Ph_3P)_2PdCl_2$ (24 mg, 0.034 mmol) were stirred in toluene (20 mL) and triethylamine (5 mL) at 50 °C under argon for 20 min. Trimethylsilylacetylene (271 mg, 2.76 mmol) was added over 5 min, and the reaction mixture was stirred at 50 °C for 18 h. Saturated NH_4Cl was added, and the mixture was extracted twice with ethyl acetate. The combined extracts were washed with water, dried over Na_2SO_4, and concentrated to dryness. The solid residue was dissolved in THF (30 mL), and tetrabutylammonium fluoride (1.0 M in THF, 2.1 mL, 2.1 mmol) was added. The solution was stirred for 2 h at room temperature. Water was added, and the mixture was extracted twice with ethyl acetate. The combined extracts were washed with water, dried over Na_2SO_4, and concentrated to dryness. The residue was chromatographed on a silica gel column (1:1 hexanes−CH_2Cl_2) to give compound **23** as a white powder (119 mg, 0.175 mmol, 75%), mp > 400 °C [ref 13, >300 °C]. ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.98 (s, 6 H), 6.72 and 7.03 (AA′BB′ system, 24 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 77.5, 83.8, 119.7, 131.17, 131.24, 140.0, 140.5 (seven of seven expected resonances). MS (EI) *m*/*z*: 678 (M^+, 100). Exact mass, 678.2350; calcd for $C_{54}H_{30}$, 678.2347.

Hexakis[4-(phenylethynyl)phenyl]benzene (24). Hexakis(4-iodophenyl)benzene (**20**, 300 mg, 0.233 mmol), CuI (7 mg, 0.037 mmol), and $(Ph_3P)_2PdCl_2$ (24 mg, 0.034 mmol) were stirred in toluene (20 mL) and triethylamine (5 mL) at 50 °C under argon for 20 min. Phenylacetylene (288 mg, 2.82 mmol) was added over 5 min, and the reaction mixture was stirred at 50 °C for 18 h. Saturated NH_4Cl was added, and the mixture was extracted twice with ethyl acetate. The combined extracts were washed with water, dried over Na_2SO_4, and concentrated to dryness. The residue was chromatographed on a silica gel column (1:1 hexanes−CH_2Cl_2) to give compound **24** as a light yellow powder (211 mg, 0.186 mmol, 80%), mp > 400 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.82 and 7.12 (AA′BB′ system, 24 H), 7.27−7.32 (m, 18 H), 7.42−7.49 (m, 12 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 89.66, 89.72, 120.7, 123.4, 128.4, 128.5, 130.7, 131.4, 131.7, 140.20, 140.21 (11 of 11 expected resonances). FAB MS *m*/*z*: 1136 (M + H [$^{13}C_1$], 100).

Hexakis(2′,3′,4′,5′-tetraphenylbiphenyl-4-yl)benzene (25). Compound **23** (115 mg, 0.169 mmol), tetracyclone (585 mg, 1.52 mmol), and diphenyl ether (3 mL) were mixed in a screw-capped Pyrex tube, and the tube was placed in a metal bath heated at 280 °C for 3 h. After cooling, CH_2Cl_2 (5 mL) was added, the solution was then added dropwise into methanol (50 mL), and the resulting precipitate was collected. The residue was chromatographed on a silica gel column (3:2 hexanes−CH_2Cl_2) to give compound **25** as an off-white solid (406 mg, 0.144 mmol, 85%), mp > 400 °C [ref 13, > 300 °C]. ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.40 and 6.66 (AA′BB′ system, 24 H), 6.72−6.98 (m, 90 H), 7.14−7.20 (m, 30 H), 7.49 (s, 6 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 125.5, 125.7, 126.4, 126.8, 127.0, 127.1, 127.7, 128.6, 130.2, 131.5, 131.7, 131.8, 131.9, 138.3, 138.6, 139.2, 139.3, 140.1, 140.2, 140.3, 140.6, 140.7, 140.8, 141.86, 141.9 (25 of 27 expected resonances). FAB MS *m*/*z*: 2819 (M + H [$^{13}C_3$], 100).

Hexakis(2′,3′,4′,5′,6′-pentaphenylbiphenyl-4-yl)benzene (26). Compound **24** (70 mg, 0.062 mmol), tetracyclone (213 mg, 0.55 mmol), and diphenyl ether (1 mL) were mixed in a screw-capped Pyrex tube,

and the tube was placed in a metal bath heated at 280 °C for 3 h. After cooling, CH_2Cl_2 (3 mL) was added, the solution was then added dropwise into methanol (30 mL), and the resulting precipitate was collected. The crude product was chromatographed on a silica gel column (5:1 hexanes−ethyl acetate) to give compound **26** as a pale yellow solid (163 mg, 0.050 mmol, 81%), mp > 500 °C. ^{1}H NMR (300 MHz, CD_2Cl_2): δ 5.59 and 6.24 (AA′BB′ system, 24 H), 6.69−7.02 (m, 150 H). ^{13}C NMR (75 MHz, CD_2Cl_2): δ 125.7, 125.8, 127.0, 127.2, 130.7, 131.5, 131.8, 131.9, 132.2, 132.9, 136.7, 137.6, 140.7, 140.8, 141.1, 141.4, 141.59, 141.60, 141.62 (19 of 21 expected resonances). FAB MS *m*/*z*: 3275 (M + H [$^{13}C_3$], 100).

X-ray Crystal Structure of 26. Compound **26** crystallized upon the evaporation of a solution in CH_2Cl_2−$CHCl_3$−benzene at room temperature. A colorless needle was cut to dimensions of 0.12 mm × 0.15 mm × 0.55 mm, sealed in a glass capillary (because of rapid solvent loss by exposed crystals), and transferred to a Nonius Kappa-CCD diffractometer. Frames of data (1400) were collected using Mo Kα radiation (λ = 0.71073 Å) at 298 (2) K with an ω oscillation range of 0.5°/frame and an exposure time of 480 s/deg. A total of 62 392 reflections were collected (θ_{max} = 18.84°), and these were reduced to 8378 unique reflections, of which 5416 had $I > 2\sigma(I)$, by using the program DENZO-SMN.[22] For subsequent refinement in the space group *R*3*m* (see below), the 8378 reflections were merged to 4402 unique reflections by using Siemens SHELXTL.[23] Postrefinement of the unit cell parameters gave $a = b$ = 48.293 (1), c = 11.866 (1), and V = 23,965 (2) Å^3. Axial photographs, systematic absences, and the observed mean |E·E−1| value of 0.658 were consistent with those expected for the noncentric, trigonal space groups *R*3 (No. 146), *R*32 (No. 155), and *R*3*m* (No. 160).

The structure was solved by direct methods in the space group *R*3, and the initial model was refined by full-matrix least-squares on F^2 using SHELXTL. In such a model, each molecule of **26** resides on a special position with crystallographic C_3 symmetry, and, in the hexagonal setting for *R*3, Z = 3. Unfortunately, it soon became apparent that the true space group was *R*3*m* with Z = 3, which implies that each molecule of **26** lies on a site with crystallographic C_{3v} symmetry. However, **26** itself possesses only C_3 symmetry, and thus the *entire structure* is disordered across the vertical mirror planes. For this reason, it was necessary to employ ideal rigid bodies for the benzene rings, restraints on many inter-ring distances, and restraints on the anisotropic displacement coefficients of all non-hydrogen atoms. A riding model was employed for the hydrogen atoms [C−H = 0.93 Å, U(H) = 1.2U(C)], and several molecules of CH_2Cl_2 were included as rigid bodies. Refinement of this discrete atom model converged to $R(F)$ = 0.192 with no peaks in the $\Delta\rho$ map greater than 0.50 e/Å^3, but it was clear that the solvent was very poorly described. For this reason, the SQUEEZE/BYPASS procedure[24] implemented in PLATON[25] was employed to account for the solvent electron density. With only the title molecule model included in the instruction file for PLATON, the SQUEEZE option found a total electron count of 1724 e in a volume of 7947 Å^3 for the solvent regions in the unit cell (33% of the unit cell volume). This electron count corresponds to 41.0 molecules of CH_2Cl_2 (42 e each), and thus the composition of the crystal has been formulated as $C_{258}H_{174}\cdot 14CH_2Cl_2$ (because Z = 3, the number of CH_2Cl_2 molecules in the cell would be 42), but it seems likely that even more solvent is present.

The SQUEEZE-processed data were used for all subsequent cycles of refinement. The refinement converged to $R(F)$ = 0.1321, $wR(F^2)$ = 0.3431, and S = 1.204 for 2777 reflections with $I > 2\sigma(I)$, and $R(F)$ = 0.1545, $wR(F^2)$ = 0.3751, and S = 1.033 for 4402 unique reflections, 601 parameters, and 389 restraints. The maximum Δ/σ in the final cycle of least squares was less than 0.001, and the residual peaks on the final $\Delta\rho$ map ranged from −0.33 to 0.33 e/Å^3.

Acknowledgment. This work was supported by National Science Foundation Grants CHE-0077990 and CHE-0314873, which are gratefully acknowledged.

Supporting Information Available: ^{13}C NMR spectra of compounds **4**, **4b**, **5**, **7**−**11**, **15**−**19**, and **22**−**26** (PDF) and X-ray structural information for compound **26** (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

JA030675C

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