Carbon Networks Based on Dehydrobenzoannulenes. 4. Synthesis of "Star" and "Trefoil" Graphdiyne Substructures via Sixfold Cross-Coupling of Hexaiodobenzene

W. Brad Wan and Michael M. Haley*

Department of Chemistry and the Materials Science Institute, University of Oregon, Eugene, Oregon 97403-1253

haley@oregon.uoregon.edu

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The synthesis and characterization of star- and trefoil-shaped polyethynyl aromatic structures, which represent model substructures of the all-carbon network graphdiyne, are described. Assembly of these macrocycles is accomplished via 6-fold Sonogashira cross-coupling of hexaiodobenzene using $Pd[P(o\text{-}Tol)_3]_2$ and CuI as the catalytic system. The development of these modified Sonogashira conditions is detailed. This work has led to the synthesis of a new family of hexakis(phenylbutadiynyl)benzene derivatives (**4a**−**c**), the largest of which is the D_{3h}-symmetric "trefoil" **2** and is composed of three [18]annulenes fused at a common benzene ring. Attempts at the synthesis of "wheel" **3** are also described. Compound **2** represents the largest fragment of the graphdiyne network to date. UV−vis spectroscopic studies indicate enhanced electron delocalization throughout the extended π-system.

Introduction

As part of our ongoing work toward the synthesis and study of nonnatural carbon networks,[1] we have focused on the preparation of increasingly larger fragments of graphdiyne (**1**).[2] Such molecules fall under the category of electron-rich, reactive hydrocarbons with high C:H ratios and can serve as precursors or mimics of carbon allotropes (e.g., graphdiyne).[3] Furthermore, their extended π-conjugation may give rise to interesting materials properties such as high third-order nonlinear optical (NLO) susceptibility and novel discotic liquid crystalline behavior.[2,4] Hexaethynylbenzene (HEB)[5] would be the ideal monomer for graphdiyne; however, the high reactivity of this molecule results in random cross-linking and incomplete cross-coupling, eliminating it as a viable network scaffold. Instability problems also complicate and often prevent extensive synthetic studies with the molecule. Only computational chemistry has allowed insight into the interesting electronic and magnetic properties of HEB.[6]

In a prior publication, we discussed the synthesis and properties of several related graphdiyne subunits, most of which were constructed from tetraiodobenzenes.[1b] The next logical step is the preparation of a class of larger, more complex analogues of HEB—"trefoil" **2** and "wheel" **3**, the core of which is "star" molecule **4**. In theory, derivatives of **4** could be readily assembled by affixing 6 equiv of a phenylbutadiyne species to hexaiodobenzene[7] via common Pd-catalyzed cross-coupling conditions. In practice, this required substantial experimentation and modification of the Sonogashira alkynylation protocol.[8]

There are several publications describing the preparation of HEB derivatives.[9] For molecules possessing D_{6h} symmetry,[5,9a−c] the simplest systems, the synthetic procedures are specific for certain substrate/coupling partner combinations. Difficulties often arise (primarily incomplete addition) when adapting these conditions to other reactants.[10] In 1992, Vollhardt et al. reported the first and only published synthesis of hexabutadiynylbenzene derivatives.[11] Using high-temperature Sonogashira conditions, they prepared **5a**−**c** in low to modest yield. Similar to the monoalkyne counterparts, Vollhardt and

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(8) Sonogashira, K. In *Metal-Catalyzed Cross-Coupling Reactions*; Stang, P. J., Diederich, F., Eds.; VCH: Weinheim, 1997; Chapter 5.

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(10) Representative examples include: (a) Mongin, M.; Hoyler, N.; Gossauer, A. *Eur. J. Org. Chem.* **2000**, 1193−1197. (b) Kayser, B.; Altman, J.; Beck, W. *Chem. Eur. J.* **1999**, *5*, 754−758.

(11) Boese, R.; Green, J. R.; Mittendorf, J.; Mohler, D. L.; Vollhardt, K. P. C. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 1643−1645.

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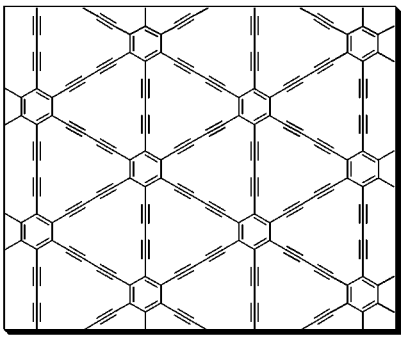

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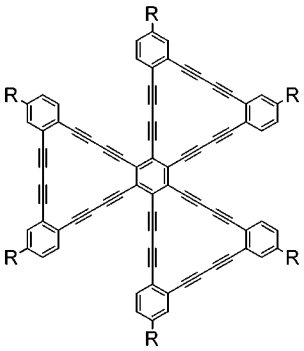
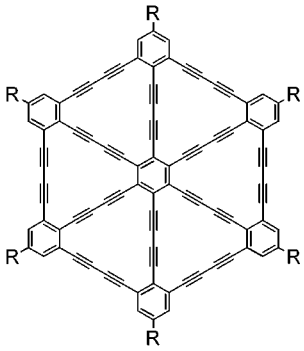
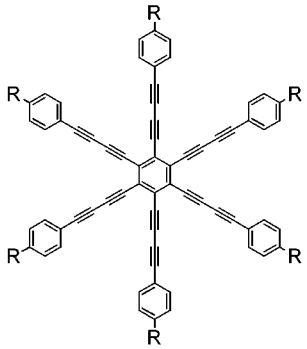


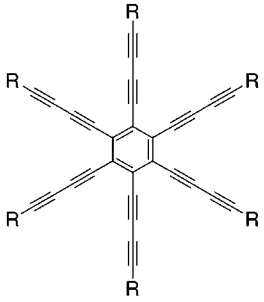
2a (R = *t*-Bu)
2b (R = *n*-Dec)



3a (R = *t*-Bu)
3b (R = *n*-Dec)



4a (R = *t*-Bu)
4b (R = *n*-Dec)
4c (R = OMe)

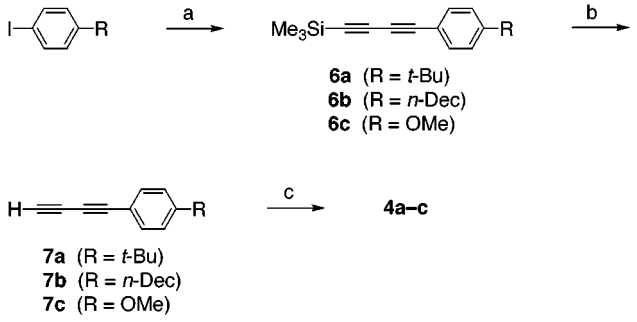


5a (R = *t*-Bu)
5b (R = Si*i*-Pr$_3$)
5c (R = SiMe$_2$Th)

Th = 1,1,2–trimethylpropyl

co-workers were limited specifically to these three systems, purportedly due to the instability of other butadiyne species. In particular, they were unable to obtain phenylbutadiyne derivatives such as **4a**−**c**, which are essential for the preparation of **2** and/or **3**.[12] Previously we have relied on a method in which reactive phenylbutadiyne species are generated in situ under Sonogashira conditions.[1,13] In this manner the concentration of the unstable diyne at any given time is low, and thus this reactive species has the opportunity to cross-couple to the haloarene substrate before decomposition. The in situ protiodesilylation/alkynylation approach is quite effective for the construction of graphdiyne fragments containing butadiyne linkages,[1] as well as for the assembly of a wide variety of dehydrobenzoannulenes.[13] Consequently, we hoped that this technique could be applied to the preparation of hexabutadiynylbenzene derivatives such as **4a**−**c**, and thus **2** and **3**.

Scheme 1[a]



[a] Key: (a) $Me_3SiC{\equiv}CC{\equiv}CH$, $PdCl_2(PPh_3)_2$, CuI, Et_3N; (b) K_2CO_3, MeOH, THF, Et_2O; (c) C_6I_6, $Pd[P(o\text{-}Tol)_3]_2$, CuI, Et_3N, NMP.

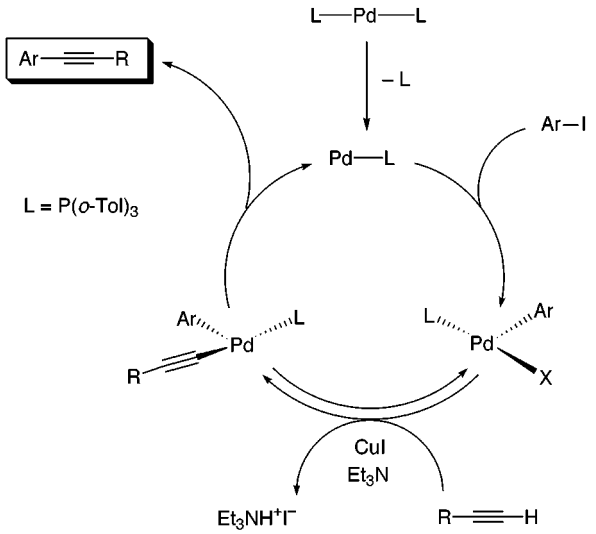
Results and Discussion

Synthesis of Star-Shaped Subunits. Coupling partners **6a**−**c** were quickly assembled via Sonogashira coupling of (trimethylsilyl)butadiyne[12] with the requisite iodobenzenes (Scheme 1). The initial target was dodecayne **4a**, which could be constructed by reacting **6a** with C_6I_6 via the aforementioned in situ desilylation/alkynylation procedure. Despite numerous attempts, the results were less than satisfactory. The majority of material recovered was a mixture of 4-fold- and 5-fold-coupled products with no evidence of the formation of **4a**. In addition, a significant amount of crystalline material was obtained, which upon further inspection proved to be pure, *stable* crystals of diyne **7a**. This result was surprising given the reported instability problems of other phenylbutadiyne derivatives.[1,12,13] At this point we cannot offer a logical explanation for the stability of **7a**, especially considering the fact that both **7b** and **7c** were found to be considerably less stable. Despite numerous perturbations of various reaction conditions (reaction times, temperature, pressure, solvent(s), choice of amine, catalyst loading, etc.), complete addition was never

(12) Brandsma, L. *Preparative Acetylenic Chemistry*; Elsevier: Amsterdam, 1971. The first edition contained the preparation of 1-phenyl-1,3-butadiyne, but stated that the molecule proved to be very unstable. This procedure was deleted from the second edition (1988). (b) Other groups have reported similar problems using free phenylbutadiynes in synthesis: Godt, A. *J. Org. Chem.* **1997**, *62*, 7471−7474. (c) Use of tin butadiynes: Bunz, U. H. F.; Enkelmann, V. *Organometallics* **1994**, *13*, 3823−3833.

(13) (a) Haley, M. M.; Pak, J. J.; Brand, S. C. *Top. Curr. Chem.* **1999**, *201*, 81−130. (b) Haley, M. M.; Bell, M. L.; English, J. J.; Johnson, C. A.; Weakley, T. J. R. *J. Am. Chem. Soc.* **1997**, *119*, 2956−2957. (c) Wan, W. B.; Kimball, D. B.; Haley, M. M. *Tetrahedron Lett.* **1998**, *39*, 6795−6798. (d) Pak, J. J.; Weakley, T. J. R.; Haley, M. M. *J. Am. Chem. Soc.* **1999**, *121*, 8182−8192. (e) Sarkar, A.; Haley, M. M. *J. Chem. Soc., Chem. Commun.* **2000**, 1733−1734. (f) Bell, M. L.; Chiechi, R. C.; English, J. J.; Johnson, C. A.; Kimball, D. B.; Matzger, A. J.; Wan, W. B.; Weakley, T. J. R.; Haley, M. M. *Tetrahedron*, in press.

Scheme 2



achieved, even after abandoning the in situ approach. In the past we have relied heavily upon $PdCl_2(PPh_3)_2$ as the catalyst in our cross-coupling reactions. The fact that predominantly unreacted phenylbutadiyne was recovered consistently, however, indicated that the catalyst was insufficiently active under these reaction conditions and that other options needed to be explored.

One particular catalyst that has garnered considerable attention in recent literature is $Pd[P(o\text{-}Tol)_3]_2$.[14] This highly coordinatively unsaturated Pd species is more commonly employed in Heck reactions and Stille couplings and is rather unorthodox for use in Sonogashira couplings. The catalyst is typically generated in situ by the addition of $Pd(dba)_2$ and $P(o\text{-}Tol)_3$ to the reaction mixture; however, Hartwig et al. recently reported a method to synthesize and isolate the $Pd[P(o\text{-}Tol)_3]_2$ catalyst as stable yellow crystals.[14a] The bulk of the work in this report was carried out with the preformed version of the catalyst.

A simplified coupling cycle, based on one proposed by Hartwig, is shown in Scheme 2.[14b] The most significant difference between $PdCl_2(PPh_3)_2$ and $Pd[P(o\text{-}Tol)_3]_2$ is the cone angle of the phosphine ligands (PPh_3 = 145°, $P(o\text{-}Tol)_3$ = 195°).[15] To accommodate the bulkier $P(o\text{-}Tol)_3$ ligands, the palladium−phosphorus bond must be elongated and therefore is weakened. As a result, the larger phosphine is much more labile and readily dissociates to create a highly coordinatively unsaturated species that is more reactive than $PdCl_2(PPh_3)_2$. More importantly, this species is much less sterically hindered, having only one remaining ligand. Therefore, it should be much easier for an iodoarene to undergo oxidative addition to the active palladium species, transmetalation to introduce the alkyne moiety, and reductive elimination to generate the desired product.[16]

Sixfold cross-coupling using $Pd[P(o\text{-}Tol)_3]_2$ and stable butadiyne **7a** furnished **4a** in 42% yield (Scheme 1). The structure was confirmed by NMR spectroscopy, matrix-assisted laser desorption time-of-flight (MALDI-TOF) mass spectrometry, and X-ray crystallography. The crystal structure (see Supporting Information) confirmed the correct connectivity; however, poor diffraction of the crystals precluded accurate structural details save that the molecule is highly disordered with respect to the orientation of the phenyl rings and the *tert*-butyl substituents.

While this new catalytic system was effective for the formation of **4a**, the reaction conditions needed to be modified for the coupling of more reactive species, such as **7b**,**c**. Unfortunately, $Pd[P(o\text{-}Tol)_3]_2$ proved to be unstable or ineffective under the basic conditions (KOH and K_2CO_3) required for the in situ deprotection. It was therefore necessary to abandon the in situ method and readdress ways to generate and/or manipulate free diynes. As mentioned previously, phenylbutadiyne derivatives have historically been too reactive to isolate, with **7a** being a rare exception. Inspired by the robust nature of **7a**, we reinvestigated the stability of our diacetylene moieties and determined that several phenylbutadiyne derivatives are in fact moderately stable. If handled carefully (dilute solution, minimal exposure to oxygen), it is possible to manipulate these highly reactive species for short periods of time. As expected, there is a direct correlation between phenylbutadiyne stability and product yield (*t*Bu ≫ *n*Dec > OMe). The general procedure used to achieve the 6-fold Sonogashira coupling is as follows: the trimethylsilyl protecting group of butadiyne species **6a**−**c** was removed upon treatment with methanolic K_2CO_3. Upon careful workup, the deprotected material (10 equiv) was concentrated, Et_3N was added, and the mixture was deoxygenated thoroughly with bubbling nitrogen. The deprotected butadiyne solution was then added to a deoxygenated *N*-methylpyrrolidinone (NMP) suspension of C_6I_6 and catalysts (3% $Pd[P(o\text{-}Tol)_3]_2$ and ca. 10% CuI per iodine).[17] The reaction mixture was stirred overnight at 60 °C under a dry N_2 atmosphere. After routine workup and purification, model systems **4a**−**c** were isolated in low to moderate yields. Although optimization of the reaction conditions is still ongoing, these results were encouraging enough to proceed with the assembly of **2** and **3**.

Synthesis of Trefoil-Shaped Subunits. Construction of macrocycles **2** and **3** required the preparation of the necessary phenylbutadiyne derivatives, i.e., triyne **8** and tetrayne **9**, respectively (Scheme 3). Solubilizing alkyl groups were engineered into **8** and **9** to combat anticipated solubility problems. Treatment of 4-*tert*-butylaniline with 1 equiv of $(BnEt_3N)\cdot ICl_2$ gave iodoaniline **10** as a viscous red oil in 90% yield.[18] Conversion of the amino group to a diethyltriazene furnished **11** in 92% yield.[19] Pd-catalyzed alkynylation of triazene **11** with (triisopropylsilyl)acetylene afforded **12**, which was converted to the corresponding iodoarene upon treatment with iodomethane at 120 °C.[19] Cross-coupling of **13** with excess (trimethylsilyl)butadiyne produced triyne **8a** in

(14) (a) Paul, F.; Patt, J.; Hartwig, J. F. *Organometallics* **1995**, *14*, 3030−3039. (b) Hartwig, J. F.; Paul, F. *J. Am. Chem. Soc.* **1995**, *117*, 5373−5374. (c) Hartwig, J. F.; Paul, F.; Richards, S.; Baranano, D. *J. Am. Chem. Soc.* **1996**, *118*, 3626−3633. (d) Wagaw, S.; Rennels, R. A.; Buchwald, S. L. *J. Am. Chem. Soc.* **1997**, *119*, 8451−8458. (e) Farina, V.; Krishnan, B. *J. Am. Chem. Soc.* **1991**, *113*, 9585−9595.

(15) Tolman, C. A. *Chem. Rev.* **1977**, *77*, 313−348.

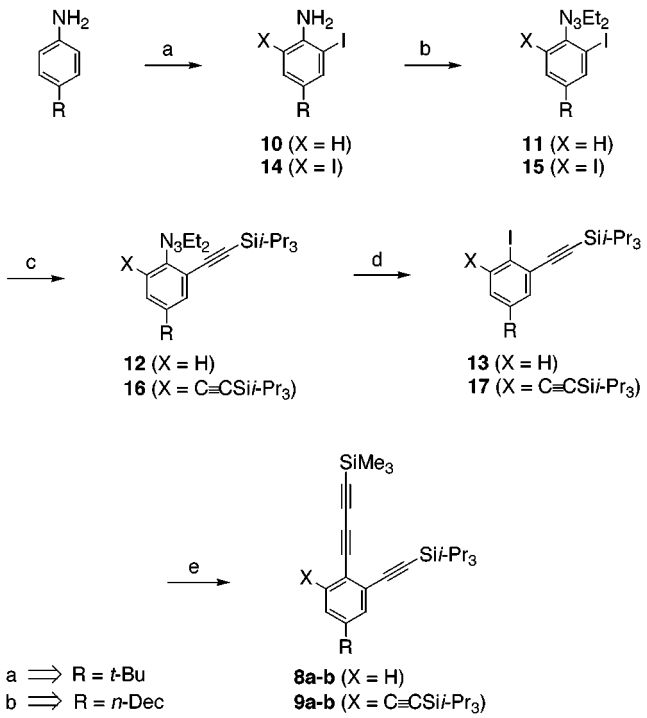
(16) The use of the bulky, electron-rich phosphine $P(t\text{-}Bu)_3$ in Sonogashira reactions was recently reported. (a) Hundertmark, T.; Littke, A. F.; Buchwald, S. L.; Fu, G. C. *Org. Lett.* **2000**, *2*, 1729−1731. (b) Böhm, V. P. W.; Herrmann, W. A. *Eur. J. Org. Chem.* **2000**, 3679−3681.

(17) Allow catalysts to stir with C_6I_6 for ca. 30 min prior to addition of acetylene. NMP was used as solvent (50 mL per mmol C_6I_6).

(18) Kajigaeshi, S.; Kakinami, T.; Yamasaki, H.; Fujisaki, S.; Okamoto, T. *Bull. Chem. Soc. Jpn.* **1988**, *61*, 600−603.

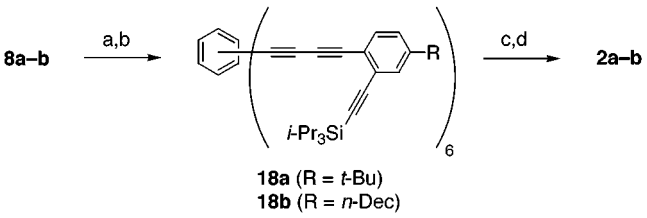
(19) Moore, J. S.; Weinstein, E. J.; Wu, Z. *Tetrahedron Lett.* **1991**, *32*, 2465−2466.

Scheme 3[a]



[a] Key: (a) $(BnEt_3N)\cdot ICl_2$, CH_2Cl_2, $CaCO_3$, MeOH; (b) [i] $NaNO_2$, HCl, H_2O, CH_3CN, THF, Et_2O; [ii] Et_2NH, K_2CO_3, H_2O, CH_3CN; (c) *i*-$Pr_3SiC{\equiv}CH$, $PdCl_2(PPh_3)_2$, CuI, Et_3N; (d) MeI, 120 °C; (e) $Me_3SiC{\equiv}CC{\equiv}CH$, $PdCl_2(PPh_3)_2$, CuI, Et_3N.

Scheme 4[a]

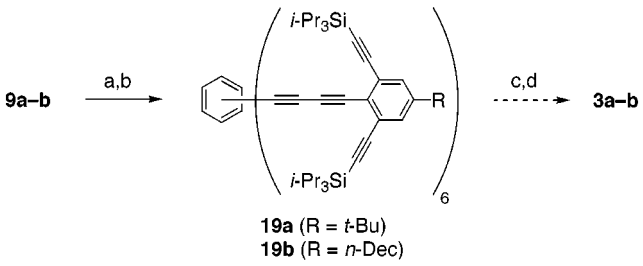


[a] Key: (a) K_2CO_3, MeOH, THF; (b) C_6I_6, Pd[P(*o*-Tol)$_3$]$_2$, CuI, Et_3N, NMP; (c) Bu_4NF, EtOH, THF; (d) CuCl, $Cu(OAc)_2\cdot H_2O$, pyridine.

90% yield. Tetrayne **9a**, which is structurally similar, is assembled by following virtually the same pathway (**14** → **17**) in approximately 40% overall yield, with the exception of using 2 equiv of the appropriate reagents in steps a and c (Scheme 3). The corresponding *n*-decyl counterparts (triyne **8b** and tetrayne **9b**) were prepared by using the same strategy.[1b]

It seemed reasonable that the desilylation of **8a**, owing to its structural similarity to **7a**, should furnish a phenylbutadiyne derivative of similar stability. Treatment of triyne **8a** with K_2CO_3 in methanol selectively removed the more labile trimethylsilyl protecting group. The deprotected triyne was successfully coupled to C_6I_6 as described above to give **18a** as yellow needles in ca. 30% yield (Scheme 4). Although the crystals were unsuitable for X-ray crystallography, the correct structure was positively confirmed by ^{1}H and ^{13}C NMR spectroscopy and by mass spectrometry (FAB and MALDI-TOF). Precursor **18a** was treated with Bu_4NF to remove the triisopropylsilyl protecting groups, dissolved in pyridine, and added slowly via syringe pump to a suspension of CuCl and $Cu(OAc)_2$ in pyridine under pseudo-high dilution conditions. Workup and removal of the solvent produced after purification a poorly soluble, amorphous powder. MALDI-TOF MS suggested the formation of the desired product (**2a**), but owing to poor solubility in common organic solvents, indisputable characterization by other spectroscopic techniques was not possible.

Scheme 5[a]



[a] Key: (a) K_2CO_3, MeOH, THF; (b) C_6I_6, Pd[P(*o*-Tol)$_3$]$_2$, CuI, Et_3N, NMP; (c) Bu_4NF, EtOH, THF; (d) CuCl, $Cu(OAc)_2\cdot H_2O$, pyridine.

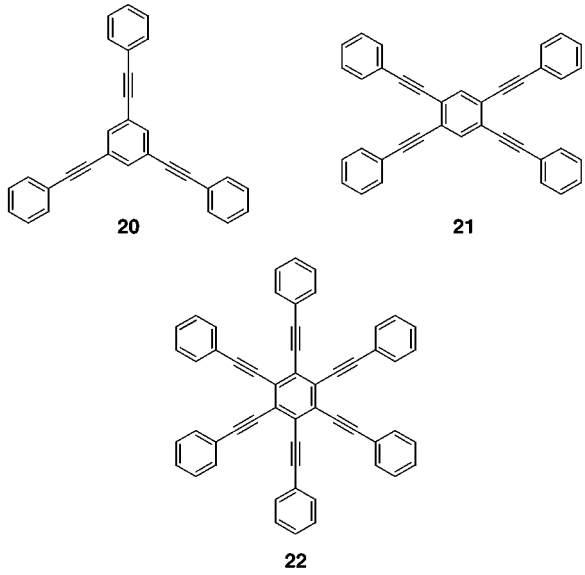
In contrast, attempts to couple **7b** to C_6I_6 using the same procedure failed to produce the pure *n*-decyl precursor **18b**. Despite various separation techniques, the desired product was consistently contaminated with 5-fold material in which the sixth iodine was displaced with a hydrogen atom, as indicated by MALDI-TOF MS and ^{1}H NMR spectroscopy. Unfortunately, it was not possible to estimate the ratio of 5-fold to 6-fold material from the available information. The resulting mixture was subjected to cyclization as described above. The desired product **2b**, which was much more soluble than its *tert*-butyl counterpart **2a**, was isolated in 6% overall yield as an amorphous yellow solid. The identity of the product was confirmed by ^{1}H NMR spectroscopy and MALDI-TOF mass spectrometry.

Attempted Synthesis of Wheel-Shaped Subunits. The ultimate example in this series would be the synthesis of **3**; however, after numerous attempts, results have been inconclusive (Scheme 5). Coupling phenylbutadiyne derivative **9b** to C_6I_6 using the newly developed reaction conditions resulted in the isolation of a material (**19**) that was found (MALDI-TOF MS) to have a molecular weight of 3507 amu (theoretical 3829 amu). This is too large to be 5-fold material (3330 amu), but presently we are unable to justify the fragmentation pattern. The ^{1}H NMR spectrum showed two singlets in the aromatic region, as well as two discrete -Si*i*-Pr_3 resonances. This may be because of an unexpected shielding effect, or perhaps the material is simply an impure mixture of 5-fold and 6-fold material (similar to **18b**). Molecular modeling supports both of these arguments.[20] The six arms of **19** are perpendicular to the central benzene ring; thus, the -Si*i*-Pr_3 groups are held close to the shielding zone of this arene. In addition, the steric bulk offered by the many -Si*i*-Pr_3 units might prevent the transmetalation needed to introduce the sixth arm. Regardless, protiodesilylation and copper-mediated cyclization of this material furnished an amorphous orange-yellow powder. Analysis by MALDI-TOF MS gave a peak at 2304 amu (theoretical 1940 amu). Similar to **2a**, the poor solubility of this material precluded acquisition of meaningful NMR data. At this point,

(20) PM3 calculations were performed on an SGI workstation using Spartan software (Version 5.0).

it is unlikely that **3b** will be prepared via this route; we are currently investigating alternative synthetic pathways for **3**.

Spectroscopic and Physical Properties. The material properties of the molecules presented in this report will likely arise from the extended π-conjugation and enhanced electron delocalization of these star-shaped systems. The amount of delocalization can be qualitatively observed by comparing the electronic absorption spectra of several similar substructures. In 1995, Kondo et al. reported the UV−vis spectra and the third-order NLO properties of a series of phenylethynyl-substituted benzene systems (**20**−**22**).[21] The trend of λ_{max} was 300, 315, and 350 nm, respectively. These results demonstrated a correlation between the number of chromophores per molecule and the absorbance frequency, and also length of conjugation. Their results established that third-order NLO susceptibility, $\chi^{(3)}$, increases with conjugation length. In addition, this class of molecules exhibits a third-order response comparable to that of other organic third-order NLO compounds, including π-conjugated polymers, organic photoconductors, and organic charge-transfer conducting complexes.[22]



Molecules **4a**−**c** can be viewed as elongated derivatives of **22** with superior π-conjugation lengths where the active chromophore is 1,4-bis(phenylbutadiynyl)benzene. As a result, the UV−vis absorbances occur at considerably longer wavelengths (Figure 1). The spectra for **4a**, **4b** (not shown), and **18a** are virtually identical, possessing a characteristic pattern with λ_{max} at ca. 385 nm and a second peak of slightly lower intensity at ca. 415 nm. The spectrum of **4c** shows a similar pattern, but both peaks are slightly red-shifted (ca. 11−13 nm), which is the expected effect of the electron-donating methoxy group. On the basis of these results, it is very likely that the hexakis(phenylbutadiynyl)benzene structures **4a**−**c** and **18** will generate third-order NLO responses equal to, if not greater than, that of **22**.

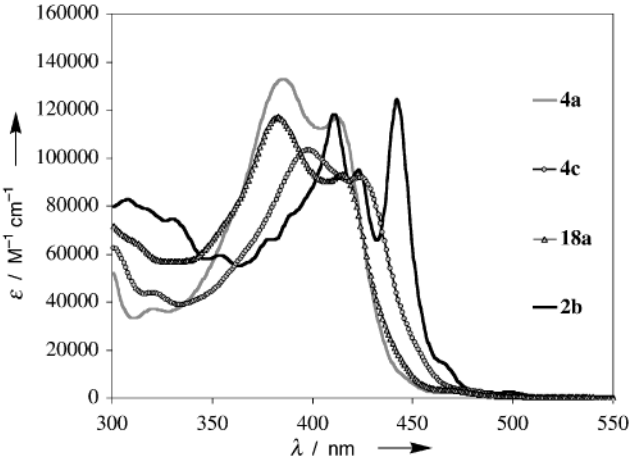
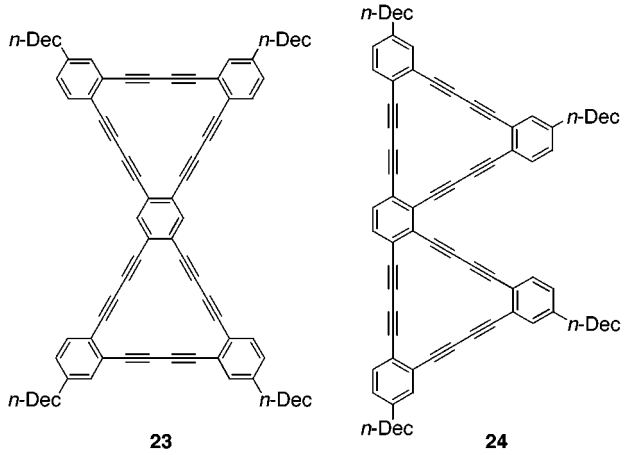


Figure 1. Electronic absorption spectra of molecules **2b**, **4a**, **4c**, and **18a**.

Upon closure of **18b** to generate **2b**, a strong bathochromic shift (25−30 nm) is observed in the UV−vis spectrum (Figure 1). Closure of the three [18]annulene rings locks the entire macrocycle into planarity, which enhances delocalization in the extended π-system and should further enhance the NLO response. The absorption pattern is altered slightly by intensification of the second peak, now λ_{max} (442 nm), and by appearance of a third peak at 423 nm. Interestingly, the UV−vis pattern of **2b** more closely resembles structures **4a**−**c** and **18a** than previous graphdiyne subunits (e.g., **23**−**24**) as the characteristic pattern associated with the dodecadehydro-[18]annulene core (Figure 2) is no longer discernible.[1b]



Consistent with our previous studies of graphdiyne substructures[1] and other planar dehydrobenzoannulenes,[13c,f] the benzene proton resonances of **2b** are shifted downfield ($\Delta\delta \approx 0.15-0.35$ ppm) relative to its acyclic precursor, indicating the presence of a weak diatropic ring current in the [18]annulene rings. Comparison of these resonances with those on the "bay" arenes of **24** reveals only a very slight downfield shift (0.02−0.04 ppm) and thus may be another indicator of the enhanced delocalization observed in the UV−vis spectra.

DSC analysis of the polyynes showed the molecules to be extremely reactive, displaying irreversible exotherms prior to melting (150−250 °C). The reactions occurred over a 20−40 °C range in all cases, which is indicative of

(21) Kondo, K.; Yasuda, S.; Tohoru, S.; Miya, M. *J. Chem. Soc., Chem. Commun.* **1995**, 55−56.

(22) Inter alia: (a) *Molecular Nonlinear Optics − Materials, Physics and Devices*; Zyss, J., Ed.; Academic Press: San Diego, CA, 1994. (b) Kanis, D. R.; Ratner, M. A.; Marks, T. J. *Chem. Rev.* **1994**, *94*, 195−242. (c) *Nonlinear Optics of Organic Molecules and Polymers*; Nalwa, H. S., Miyata, S., Eds.; CRC Press: New York, 1997. (d) Wolff, J. J.; Wortmann, R. In *Advances in Physical Chemistry*; Bethell, D., Ed.; Academic Press: London, UK, 1999; Vol. 32, pp 121−217.

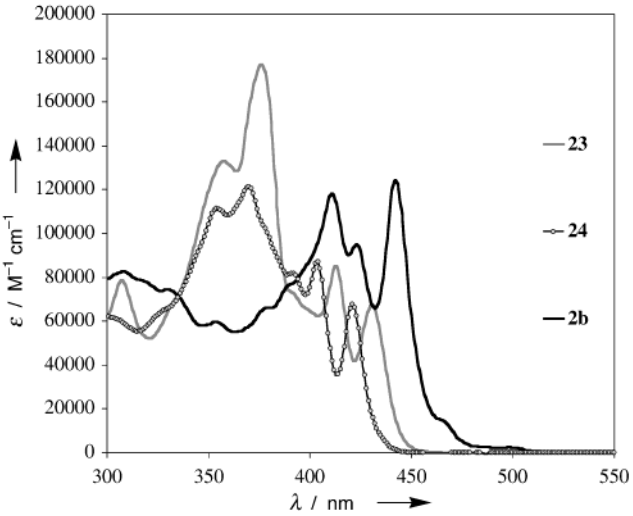


Figure 2. Electronic absorption spectra of molecules **2b**, **23**, and **24**.

random polymerization. The residues were insoluble black materials that could not be adequately analyzed. No others transitions that might suggest liquid crystal behavior were observed, although such behavior might be induced by preparing derivatives of **2** and **4** with different substitution patterns or functional groups (i.e., R = long alkoxy or carboalkoxy linkages).[8d,23]

Conclusion

In summary, we have demonstrated that the catalyst $Pd[P(o\text{-}Tol)_3]_2$ is particularly effective for the construction of sterically hindered systems such as 6-fold Sonogashira cross-coupling reactions. In conjunction with this catalyst, we have developed a method of preparing hexakis(phenylbutadiynyl)benzene derivatives such as **4a**−**c**, which have been unobtainable by conventional routes. Using this method we were able to prepare **2a**,**b**, which are the largest graphdiyne fragments to date. Unfortunately, the synthesis of **3** was elusive, presumably because **18** represents the upper limit of bulky appendages which can be successfully introduced by this technique. Evidence presented suggests that **2** and **4** will exhibit a strong third-order NLO response. Derivatives of **4** with various functional groups might optimize this response as well as induce liquid crystalline behavior. We are currently exploring the NLO properties of all graphdiyne substructures, as well as alternate syntheses of **3**.

Experimental Section

Materials and Methods. ^1H and ^{13}C NMR spectra were recorded using a Varian Unity Inova 300 (^1H, 299.95 MHz; ^{13}C, 75.43 MHz) spectrometer. Chemical shifts (δ) are expressed in ppm downfield from tetramethylsilane using the residual nondeuterated solvent as internal standard ($CDCl_3$ ^1H, 7.26 ppm; ^{13}C, 77.0 ppm; CD_2Cl_2 ^1H, 5.34 ppm; ^{13}C, 54.0 ppm). Coupling constants are expressed in hertz. IR spectra were recorded using a Nicolet Magna-FTIR 550 spectrometer. UV−vis spectra were recorded in CH_2Cl_2 using a Hewlett-Packard 8453 spectrophotometer. Mass spectra were recorded using a Kratos MS50 spectrometer (EI, CI, FAB) or a PerSeptive Biosystems Voyager-DE STR Biospectrometry Workstation (MALDI-TOF) with 2,5-dihydroxybenzoic acid as matrix (calibrated with C_{60} and C_{70}). DSC analyses were performed using a TA Instruments DSC 2920 Modulated DSC. Elemental analyses were performed by Robertson Microlit Laboratories, Inc. Melting points were determined on a Meltemp II apparatus and are uncorrected. CH_2Cl_2 and Et_3N were distilled from CaH_2 under a nitrogen atmosphere prior to use. THF and Et_2O were distilled from sodium and benzophenone under a nitrogen atmosphere prior to use. All other chemicals were of reagent quality and used as obtained from manufacturers. Reactions were carried out in an inert atmosphere (dry nitrogen or argon) when necessary. Column chromatography was performed on Whatman reagent grade silica gel (230−400 mesh). Preparative radial thin-layer chromatography was performed on a Chromatotron using silica gel (60 PF_{254}) plates (1−4 mm). Precoated silica gel plates (EM Separations Technology, 60 PF_{254}, 200 × 50 × 0.20 mm) were used for analytical thin-layer chromatography.

General Acetylene Coupling Procedure A. A suspension consisting of iodoarene (1 equiv), $PdCl_2(PPh_3)_2$ (0.03 equiv), and CuI (0.06 equiv) in Et_3N was deoxygenated by bubbling nitrogen or by the method of freeze−pump−thaw. The terminal acetylene (1.5 equiv per iodine) was added in three portions at 1 h intervals with stirring at 60 °C under nitrogen. Upon completion, the reaction mixture was concentrated in vacuo, suspended in CH_2Cl_2, and filtered through a bed of silica gel. The filtrate was concentrated, and the desired product was purified by column chromatography on silica gel or by Chromatotron.

General Sixfold Coupling Procedure B. The appropriate (trimethylsilyl)butadiyne (10 equiv relative to C_6I_6) was dissolved in a solution of THF, Et_2O, and MeOH (6:3:1 v:v, 25 mL per mmol). K_2CO_3 (2 equiv) was added, and the reaction was stirred vigorously for 1 h. Upon completion, the deprotected material was extracted into hexanes, washed with water and brine, and dried ($MgSO_4$). The solution was filtered and concentrated under reduced pressure to approximately 10% of the original volume. Distilled Et_3N (2 mL) was added, and the mixture was deoxygenated thoroughly by nitrogen bubbling for 10 min. In a separate flask were placed C_6I_6 (1 equiv), $Pd[P(o\text{-}Tol)_3]_2$ (15 mol %), CuI (50 mol %), and NMP (50 mL per mmol C_6I_6), and the mixture was deoxygenated for 30 min. The deprotected butadiyne solution was added to a C_6I_6/catalyst mixture, and the reaction was stirred overnight at 60 °C under nitrogen. Upon completion, the reaction mixture was diluted with CH_2Cl_2 and washed with a 10% HCl solution. The organic layer was washed with water, dried ($MgSO_4$), filtered, and concentrated under vacuum. The residue was preabsorbed onto silica gel and was purified by column chromatography.

General Aryl Diethyltriazene Formation Procedure C. The arylamine (1 equiv) was dissolved in a solution of Et_2O, THF, and CH_3CN (7:6:1 v:v, 7 mL per mmol). A solution of HCl (4.5 M, 9 equiv) was added, and the reaction mixture was cooled to −5 °C. A solution of $NaNO_2$ (3.4 equiv) in CH_3CN and H_2O (2:3 v:v, 2 M) was added dropwise, and the reaction was stirred for 1.5 h at −5 to 0 °C. The mixture was poured into a chilled solution of K_2CO_3 (5 equiv) and Et_2NH (5 equiv) in CH_3CN and H_2O (2:1 v:v, 10 mL per mmol arylamine). After stirring for 1.5 h, the mixture was extracted twice with ether. The combined ether layers were washed twice with brine, dried ($MgSO_4$), filtered, and concentrated by rotary evaporation. The crude product was purified by column chromatography on silica gel or by Chromatotron.

General Macrocyclization Procedure D. The silyl-protected macrocycle precursor was dissolved in THF (25 mL per mmol) and EtOH (10−20 drops). A solution of Bu_4NF was added (1 M in THF, 2.1 equiv) with stirring at room temperature. The reaction was monitored by TLC. Upon completion, the mixture was diluted with Et_2O, washed three times with water and twice with brine, and dried ($MgSO_4$). After filtration through a short pad of silica gel and removal of the solvent, the resulting product was dissolved in a small volume of pyridine and was used immediately in the next step.

(23) Zhang, D.; Tessier, C. A.; Youngs, W. J. *Chem. Mater.* **1999**, *11*, 3050−3057.

The deprotected precursor was added over 16−20 h via syringe pump to a suspension of CuCl and $Cu(OAc)_2 \cdot H_2O$ (20 equiv of each per coupling) in pyridine (250 mL per mmol of α,ω-polyyne) at 60 °C. Upon completion, the mixture was concentrated in vacuo and diluted with CH_2Cl_2. The organic layer was subsequently washed with 10% HCl solution and repeatedly with water. The organic layer was dried ($MgSO_4$), filtered, evaporated, and purified by column chromatography or preparative TLC.

4-*n*-Decyliodobenzene. 4-*n*-Decylaniline (500 mg, 2.14 mmol) was dissolved in glacial AcOH (35 mL). In a separate container, $NaNO_2$ (85 mg, 1.23 mmol) was suspended in chilled, concentrated H_2SO_4 (1 mL). The $NaNO_2$ solution was added slowly to the reaction mixture and was allowed to stir for 2 h. The reaction was poured into a quench solution consisting of KI (1.55 g, 9.34 mmol) and I_2 (320 mg, 1.26 mmol) in H_2O (3 mL), and the resulting mixture was stirred for 2 h. Crushed ice and a 15% NaOH solution were added until the mixture was basic to litmus paper. The mixture was extracted into EtOAc and washed with a 5% $NaHSO_3$ solution, H_2O, and brine. The organics were dried ($MgSO_4$), filtered, and concentrated under vacuum. Purification by chromatotron (4 mm plate, hexanes) gave the desired product (485 mg, 66%) as an orange oil: ^{1}H NMR ($CDCl_3$) δ 7.59 (d, J = 8.2 Hz, 2H), 7.16 (d, J = 8.2 Hz, 2H), 2.55 (t, J = 7.7 Hz, 2H), 1.65−1.52 (m, 2H), 1.38−1.20 (m, 14H), 0.90 (t, J = 6.6 Hz, 3H); ^{13}C NMR ($CDCl_3$) δ 142.47, 137.17, 130.51, 90.49, 35.42, 31.88, 31.28, 29.60, 29.56, 29.45, 29.32, 29.18, 22.68, 14.13; IR (neat) υ 2954, 2924, 2854, 1485, 1466, 1007 cm^{-1}; MS (CI pos) *m*/*z* (%) 344.1 (M^+, 55), 260 (70), 245 (100), 216.9 (41), 91 (63); $C_{16}H_{25}I$ (344.27). Anal. Calcd: C 55.82, H 7.32. Found: C 55.92, H 7.23.

1-*tert*-Butyl-4-(4-trimethylsilyl-1,3-butadiynyl)benzene (6a). 4-*tert*-Butyliodobenzene (998 mg, 3.84 mmol) was reacted with trimethylsilylbutadiyne (705 mg, 5.77 mmol) as described in general procedure A. Purification by column chromatography on silica gel (hexanes) followed by recrystallization from hexanes gave **6a** (928 mg, 95%) as pale yellow needles: mp 87−89.5 °C; ^{1}H NMR ($CDCl_3$) δ 7.43 (d, J = 8.4 Hz, 2H), 7.34 (d, J = 8.4 Hz 2H), 1.30 (s, 9H) 0.23 (s, 9H); ^{13}C NMR ($CDCl_3$) δ 152.81, 132.46, 125.46, 118.22, 90.11, 88.00, 76.59; 73.49, 34.91, 31.06, −0.37; IR (KBr) υ 2958, 2902, 2868, 2206, 2104, 1502, 1461, 1407, 1250, 846 cm^{-1}; MS (CI Pos) *m*/*z* (%) 254.1 (M^+, 60), 239.1 (100); $C_{17}H_{22}Si$ (254.44). Anal. Calcd: C 80.25, H 8.72. Found: C 80.25, H 8.72.

1-*n*-Decyl-4-(4-trimethylsilyl-1,3-butadiynyl)benzene (6b). 4-*n*-Decyliodobenzene (348 mg, 1.01 mmol) was reacted with trimethylsilylbutadiyne (185 mg, 1.51 mmol) as described in general procedure A. Purification by chromatotron (2 mm plate, petroleum ether) gave **6b** (342 mg, 99%) as a viscous, dark orange oil: ^{1}H NMR ($CDCl_3$) δ 7.40 (d, J = 8.1 Hz, 2H), 7.12 (d, J = 8.1 Hz, 2H), 2.59 (t, J = 8.1 Hz, 2H), 1.65−1.52 (m, 2H), 1.38−1.20 (m, 14H), 0.90 (br t, 3H), 0.24 (s, 9H); ^{13}C NMR (CD_2Cl_2) δ 145.76, 133.11, 129.19, 118.68, 90.82, 88.28, 77.52, 73.83, 36.47, 32.46, 31.74, 30.15, 30.11, 29.99, 29.88, 29.77, 23.24, 14.43, −0.18; IR (neat) υ 2961, 2919, 2850, 2208, 2108, 1507, 1464, 1253, 847 cm^{-1}; MS (CI pos) *m*/*z* (%) 338.2 (M^+, 100), 323.2 (65), 244.1 (57), 229 (64), 73 (63); $C_{23}H_{34}Si$ (338.60).

4-(4-Trimethylsilyl-1,3-butadiynyl)anisole (6c). 4-Iodoanisole (500 mg, 2.14 mmol) was coupled with trimethylsilylbutadiyne (275 mg, 2.25 mmol) as described in general procedure A. Purification by column chromatography (2% CH_2Cl_2 in petroleum ether) gave **6c** (426 mg, 87%) as a dark oil: ^{1}H NMR ($CDCl_3$) δ 7.43 (d, J = 8.5 Hz, 2H), 6.83 (d, J = 8.5 Hz, 2H), 3.80 (s, 3H), 0.23 (s, 9H); ^{13}C NMR (CD_2Cl_2) δ 161.24, 134.88, 114.75, 113.48, 90.51, 88.50, 77.46, 73.39, −0.11; IR (neat) υ 3005, 2960 (methoxy CH), 2898, 2839, 2202, 2102, 1605, 1567, 1510, 1463, 1300, 1252 (C−O−C asym), 1172 (C−O−C sym) cm^{-1}; MS (CI pos) *m*/*z* (%) 228.1 (M^+, 85), 213 (89), 108.1 (100), 92 (30), 77(19); $C_{14}H_{16}OSi$ (228.36).

1-(1,3-Butadiynyl)-4-*tert*-butylbenzene (7a). The trimethylsilyl protecting group was removed from **6a** (150 mg, 0.44 mmol) as described in the first step of general procedure B. Purification by column chromatography (petroleum ether) followed by recrystallization (petroleum ether) furnished **7a** (67 mg, 84%) as light orange needles: mp 67−69 °C; ^{1}H NMR ($CDCl_3$) δ 7.41 (d, J = 8.4 Hz, 2H), 7.34 (d, J = 8.4 Hz, 2H), 2.46 (s, 1H), 1.30 (s, 9H); ^{13}C NMR ($CDCl_3$) δ 152.95, 132.48, 125.43, 117.77, 75.52, 70.90, 68.23, 67.65, 34.84, 30.98; IR (KBr) υ 3296, 2964, 2904, 2870, 2212, 1502, 1458 cm^{-1}; MS (CI pos) *m*/*z* (%) 182.1 (M^+, 73), 167.1 (100) 139.0 (22); $C_{14}H_{14}$ (182.26). Anal. Calcd: C 92.26, H 7.74. Found: C 92.12, H 7.78.

Subunit 4a. *tert*-Butyldiyne **6a** (76 mg, 0.30 mmol) was reacted with C_6I_6 (25 mg, 0.03 mmol) as described in general procedure B. Column chromatography on silica gel (20% CH_2Cl_2 in petroleum ether) followed by recrystallization from CH_2Cl_2 gave **4a** as yellow needles (15 mg, 42%): mp 174 °C (dec); ^{1}H NMR ($CDCl_3$) δ 7.53 (d, J = 8.4 Hz, 12H), 7.35 (d, J = 8.4 Hz, 12H), 1.32 (s, 54H); ^{13}C NMR ($CDCl_3$) δ 153.12, 132.55, 128.99, 125.47, 118.37, 86.74, 85.17, 76.91, 73.70, 34.96, 31.08; IR (KBr) υ 2954, 2916, 2848, 2206, 1697, 1600, 1462 cm^{-1}; UV/vis (CH_2Cl_2) λ_{max} (ϵ) 321 (37 200), 385 (132 900), 412 (116 800) nm; MS (FAB pos) *m*/*z* (%) 1159.1 (M^+, 100), 926 (98), 866 (55), 766 (49), 690 (43); MS (MALDI-TOF) $C_{90}H_{79}$ (1159.58) *m*/*z* 1160.15.

Subunit 4b. *n*-Decyldiyne **6b** (100 mg, 0.3 mmol) was reacted with C_6I_6 (25 mg, 0.03 mmol) as described in general procedure B. Purification by preparative TLC (10% CH_2Cl_2 in hexanes) gave **4b** (6.5 mg, 13% yield) as an amorphous yellow solid: mp 164 °C (dec); ^{1}H NMR ($CDCl_3$) δ 7.50 (d, J = 8.0 Hz, 12H), 7.14 (d, J = 8.0 Hz, 12H), 2.61 (t, J = 7.8 Hz, 12H), 1.65−1.52 (m, 12H), 1.38−1.20 (m, 84H), 0.88 (br t, 18H); ^{13}C NMR ($CDCl_3$) δ 145.11, 132.70, 128.96, 128.58, 118.52, 86.76, 85.13, 76.80, 73.72, 36.05, 31.89, 31.14, 29.59, 29.55, 29.46, 29.31, 29.24, 22.67, 14.11; IR (CH_2Cl_2) υ 2924, 2852, 2204, 1465, 1427 cm^{-1}; UV/vis (CH_2Cl_2) λ_{max} (ϵ) 320 (39 600), 386 (115 700), 413 (100 600) nm; MS (MALDI-TOF) $C_{126}H_{150}$ (1664.54) 1662.11.

Subunit 4c. Methoxydiyne **6c** (500 mg, 2.0 mmol) was reacted to C_6I_6 (166 mg, 0.2 mmol) as described in general procedure B. Purification by preparative TLC (50% CH_2Cl_2 in hexanes) gave **4c** (20 mg, 10%) as an amorphous yellow solid: mp 207 °C (dec); ^{1}H NMR ($CDCl_3$) δ 7.53 (d, J = 8.9 Hz, 12H), 6.86 (d, J = 8.9 Hz, 12H), 3.83 (s, 18H); ^{13}C NMR (CD_2Cl_2) δ 161.66, 135.09, 129.34, 114.86, 113.42, 87.68, 85.51, 77.22, 73.10, 55.99; IR (CH_2Cl_2) υ 2960 (methoxy CH), 2924, 2852, 2198, 1602, 1511, 1423, 1295, 1255 (C−O−C asym), 1172 (C−O−C sym) cm^{-1}; UV/vis (CH_2Cl_2) λ_{max} (ϵ) 398 (103 300), 424 (91 800) nm; MS (MALDI-TOF) $C_{72}H_{42}O_6$ (1003.10) *m*/*e* 1004.67. Anal. Calcd: C 86.21, H 4.22. Found: C 86.07, H 4.30.

4-*tert*-Butyl-2-iodoaniline (10). 4-*tert*-Butylaniline (2.0 g, 13.4 mmol) was dissolved in CH_2Cl_2 (200 mL) and MeOH (100 mL). To this were added $(BnEt_3N) \cdot ICl_2$ (5.46 g, 14.0 mmol) and $CaCO_3$ (2.68 g, 26.8 mmol). The suspension was stirred at room temperature for 3 h. The reaction mixture was filtered through a bed of Celite and was concentrated in vacuo to approximately 1/3 volume. The residual mixture was washed with a 5% $NaHSO_3$ solution, a saturated $NaHCO_3$ solution, water, and brine. The organic layer was dried ($MgSO_4$), filtered, and concentrated to give an orange oil. Purification by column chromatography (5% EtOAc in hexanes) furnished **10** (3.33 g, 90%) as a viscous red oil: ^{1}H NMR ($CDCl_3$) δ 7.64 (d, J = 1.8 Hz, 1H), 7.18 (dd, J = 8.4, 1.8 Hz, 1H), 6.71 (d, J = 8.4 Hz, 1H), 3.97 (br s, 2H), 1.27 (s, 9H); ^{13}C NMR ($CDCl_3$) δ 144.24, 143.18, 135.58, 126.49, 114.44, 84.48, 33.78, 31.37; IR (neat) υ 3460, 3367, 2962, 2904, 2867, 1616, 1498, 1265 cm^{-1}; MS (CI pos) *m*/*z* (%) 275 (M^+, 52), 260 (100), 133.1 (18); $C_{10}H_{14}IN$ (275.13). Anal. Calcd: C 43.65, H 5.13, N 5.09. Found: C 43.91, H 5.02, N 5.18.

***N*,*N*-Diethyl-*N*′-(4-*tert*-butyl-2-iodophenyl)triazene (11).** Iodoaniline **10** (3.33 g, 12.1 mmol) was subjected to general procedure C. Purification by column chromatography on silica gel (5% CH_2Cl_2 in petroleum ether) gave **11** (4.01 g, 92%) as an orange oil: ^{1}H NMR ($CDCl_3$) δ 7.88 (d, J = 1.8 Hz, 1H), 7.33 (m, 2H), 3.80 (q, J = 6.9 Hz, 4H), 1.35 (t, J = 7.0 Hz, 4H), 1.34 (s, 9H); ^{13}C NMR ($CDCl_3$) δ 149.64, 148.00, 135.70, 125.79, 116.82, 96.59, 48.85, 42.12, 34.19, 31.25, 14.57, 11.07; IR (neat) υ 3066, 2966, 2933, 2904, 2870, 1589, 1540, 1463, 1380, 1340, 1257, 1236, 1207, 1105 cm^{-1}; MS (CI pos) *m*/*z* (%) 359 (M^+, 50), 287 (40), 259 (100), 132.1 (20), 117.1 (39), 72.1

(21); $C_{14}H_{22}IN_3$ (359.25). Anal. Calcd: C 46.81, H 6.17, N 11.70. Found: C 46.51, H 6.02, N 11.48.

***N,N*-Diethyl-*N*′-[4-*tert*-butyl-2-(triisopropylsilylethynyl)-phenyl]triazene (12).** Iodotriazene **11** (705 mg, 1.96 mmol) was reacted with triisopropylsilylacetylene (0.66 mL, 2.94 mmol) as described in general procedure A. Purification by column chromatography (5% CH_2Cl_2 in petroleum ether) gave **12** (756 mg, 93% yield) as an orange oil: ^{1}H NMR ($CDCl_3$) δ 7.46 (d, J = 2.1 Hz, 1H), 7.35 (d, J = 8.7 Hz, 1H), 7.18 (dd, J = 8.7, 2.1 Hz, 1H), 3.78 (q, J = 6.9 Hz, 4H), 1.31 (s, 9H), 1.26 (br t, 6H triplet), 1.14 (s, 21H); ^{13}C NMR ($CDCl_3$) δ 150.28, 147.37, 130.37, 126.33, 117.76, 116.38, 106.10, 93.09, 49.73, 41.35, 34.25, 31.25, 18.76, 14.32, 11.46, 11.43; IR (neat) υ 2960, 2943, 2866, 2152, 1464, 1387, 1238, 1092 cm^{-1}; MS (CI pos) m/z (%) 413.3 (M^+, 4), 359 (51), 287 (43), 259 (100), 117.1 (39), 72.1 (22); $C_{25}H_{43}N_3Si$ (413.71). Anal. Calcd: C 72.58, H 10.48, N 10.16. Found: C 72.81, H 10.23, N 10.01.

4-*tert*-Butyl-1-iodo-2-[(triisopropylsilyl)ethynyl]benzene (13). Triazene **12** (750 mg, 1.81 mmol) was reacted with freshly distilled CH_3I (8 mL) in a sealed reaction vessel at 120 °C for 24 h. The reaction was cooled, diluted with hexanes, and filtered through a bed of Celite and silica gel. Removal of the solvent by rotary evaporation gave **13** (657 mg, 82% yield) as a dark brown oil in sufficiently pure form: ^{1}H NMR ($CDCl_3$) δ 7.75 (d, J = 8.4 Hz, 1H), 7.49 (d, J = 2.1 Hz, 1H), 7.03 (dd, J = 8.4, 2.1 Hz, 1H), 1.30 (s, 9H), 1.19 (s, 21H); ^{13}C NMR ($CDCl_3$) δ 151.03, 138.29, 130.23, 129.56, 127.13, 108.47, 97.22, 94.37, 34.48, 31.01, 18.75, 11.37; IR (neat) υ 2960, 2943, 2866, 2158, 1461, 1382, 1014 cm^{-1}; MS (CI pos) m/z (%) 440.1 (M^+, 14), 397 (100), 369 (14), 355 (14), 327 (16), 259 (13); $C_{21}H_{33}ISi$ (440.48). Anal. Calcd: C 57.26, H 7.55. Found: C 57.17, H 7.35.

4-*tert*-Butyl-2-[(triisopropylsilyl)ethynyl]-1-[4-(trimethylsilyl)-1,3-butadiynyl]benzene (8a). Iodoarene **13** (600 mg, 3.81 mmol) was reacted with trimethylsilylbutadiyne (252 mg, 2.06 mmol) as described in general procedure A. Purification by column chromatography on silica gel (petroleum ether) gave **8a** (535 mg, 90% yield) as a pale yellow solid: mp 61−63 °C; ^{1}H NMR ($CDCl_3$) δ 7.46 (d, J = 1.8 Hz, 1H), 7.40 (d, J = 8.1 Hz, 1H), 7.28 (dd, J = 8.1, 1.8 Hz, 1H), 1.31 (s, 9H), 1.19 (s, 21H), 0.23 (s, 9H); ^{13}C NMR ($CDCl_3$) δ 152.27, 132.44, 129.05, 127.20, 125.42, 121.64, 104.99, 95.16, 90.82, 88.26, 77.28, 75.50, 34.80, 30.93, 18.71, 11.34, −0.41; IR (KBr) υ 2960, 2866, 2204, 2156, 2102, 1464, 1252 cm^{-1}; MS (CI pos) m/z (%) 434.2 (M^+, 23), 397 (100), 349.1 (32), 307.1 (27), 287 (25), 259 (59) 229 (18), 117.1 (23), 83.9 (25); $C_{28}H_{42}Si_2$ (434.80).

4-*tert*-Butyl-2,6-diiodoaniline (14). 4-*tert*-Butylaniline (2.0 g, 13.4 mmol) was dissolved in CH_2Cl_2 (200 mL) and MeOH (100 mL). To this were added $(BnEt_3N)\cdot ICl_2$ (10.9 g, 28.0 mmol) and $CaCO_3$ (5.4 g, 54 mmol). The suspension was stirred at 40 °C overnight. The reaction mixture was filtered through a bed of Celite and was concentrated in vacuo to approximately 1/3 volume. The residual mixture was washed with a 5% $NaHSO_3$ solution, a saturated $NaHCO_3$ solution, water, and brine. The organic layer was dried ($MgSO_4$), filtered, and concentrated to give an orange oil. Purification by column chromatography on silica gel (5% EtOAc in petroleum ether) first gave monoiodoaniline **10** (1.22 g, 28%), then diiodoaniline **14** (4.62 g, 72%) as a viscous red oil: ^{1}H NMR ($CDCl_3$) δ 7.62 (s, 2H), 4.47 (br s, 2H), 1.24 (s, 9H); ^{13}C NMR ($CDCl_3$) δ 144.52, 143.66, 136.44, 81.74, 33.66, 31.28; IR (neat) υ 3464, 3363, 2955, 2867, 1613, 1457 cm^{-1}; MS (CI pos) m/z (%) 400.8 (M^+, 67), 385.8 (100), 259 (10), 132.1 (12); $C_{10}H_{13}NI_2$ (401.03).

***N,N*-Diethyl-*N*′-(2,6-diiodo-4-*tert*-butylphenyl)triazene (15).** 4-*tert*-Butyl-2,6-diiodoaniline **14** (4.49 g, 11.2 mmol) was subjected to general procedure C. Purification by chromatography over silica gel (5% EtOAc in hexanes) followed by slow evaporation gave **15** (4.78 g, 88%) as a light orange semisolid: ^{1}H NMR ($CDCl_3$) δ 7.81 (s, 2H), 3.79 (q, J = 6.9 Hz, 4H), 1.37 (br t, 6H), 1.28 (s, 9H); ^{13}C NMR ($CDCl_3$) δ 151.15, 149.82, 136.74, 90.94, 49.10, 41.69, 34.08, 31.17, 14.92, 11.35; IR (neat) υ 2964, 2933, 2906, 2870, 1576, 1514, 1465, 1255, 1203, 1107 cm^{-1}; MS (CI pos) m/z (%) 484.9 (M^+, 10), 400.8 (62), 385.8 (100), 259 (13), 132.1 (12); $C_{14}H_{21}N_3I_2$ (485.15). Anal. Calcd: C 34.66, H 4.36, N 8.66. Found: C 34.77, H 4.16, N 8.39.

***N,N*-Diethyl-*N*′-[2,6-bis(triisopropylsilylethynyl)-4-*tert*-butylphenyl]triazene (16).** Diiodotriazene **15** (2.0 g, 4.12 mmol) was reacted with triisopropylsilylacetylene (2.77 mL, 12.12 mmol) as described in general procedure A. Purification by column chromatography (2% EtOAc in petroleum ether) gave **16** (1.93 g, 75%) as a pale orange solid: mp 89.5−90.5 °C; ^{1}H NMR ($CDCl_3$) δ 7.42 (s, 2H), 3.76 (q, J = 6.9 Hz, 4H), 1.30 (s, 9H), 1.26 (br t, 6H), 1.10 (s, 42H); ^{13}C NMR ($CDCl_3$) δ 152.95, 146.81, 131.25, 116.37, 105.43, 92.75, 48.51, 40.73, 34.12, 31.13, 18.68, 14.31, 11.34, 11.15; IR (KBr) υ 2943, 2893, 2866, 2146, 1464, 1394, 1238, 1009 cm^{-1}; MS (CI pos) m/z (%) 593.4 (M^+, 43), 550.4 (24), 521.3 (57), 484.9 (59), 451.3 (78), 412.9 (60), 384.8 (100), 271.2 (56), 131.1 (56); $C_{36}H_{63}N_3Si_2$ (594.08). Anal. Calcd: C 72.78, H 10.69, N 7.07. Found: C 72.51, H 10.46, N 6.95.

1,3-Bis(triisopropylsilylethynyl)-5-*tert*-butyl-2-iodobenzene (17). Triazene **16** (1.90 g, 3.2 mmol) was treated with CH_3I (25 mL) in a sealed reaction vessel at 120 °C for 24 h. The reaction was cooled, diluted with hexanes, and filtered through a bed of Celite and silica gel. Purification by column chromatography (hexanes) gave **17** (1.56 g, 78% yield) as a pale yellow oil: ^{1}H NMR ($CDCl_3$) δ 7.39 (s, 2H), 1.30 (s, 9H), 1.17 (s, 21H); ^{13}C NMR ($CDCl_3$) δ 150.74, 130.80, 129.84, 108.73, 103.91, 94.67, 34.42, 30.90, 18.74, 11.35; IR (neat) υ 2958, 2943, 2866, 2150, 1464, 1390, 989 cm^{-1}; MS (CI pos) m/z (%) 620.1 (M^+, 72), 577.1 (93), 451.2 (100), 430.9 (50); $C_{32}H_{53}ISi_2$ (620.84). Anal. Calcd: C 61.91, H 8.60. Found: C 62.22, H 8.55.

1,3-Bis(triisopropylsilyl)ethynyl-5-*tert*-butyl-2-[4-(trimethylsilyl)-1,3-butadiynyl]benzene (9a). Iodoarene **17** (1.50 g, 2.4 mmol) was reacted with trimethylsilylbutadiyne (445 mg, 3.65 mmol) as described in general procedure A. Purification by column chromatography on silica gel (petroleum ether) followed by recrystallization from petroleum ether (slow evaporation) gave **9a** (1.34 g, 90%) as orange needles: mp 121−123 °C; ^{1}H NMR ($CDCl_3$) δ 7.39 (s, 2H), 1.29 (s, 9H), 1.16 (s, 12H), 0.21 (s, 9H); ^{13}C NMR ($CDCl_3$) δ 151.63, 128.96, 127.45, 124.78, 104.64, 95.51, 91.69, 88.61, 81.43, 74.24, 34.75, 30.87, 18.72, 11.36, −0.45; IR (KBr) υ 2960, 2943, 2893, 2866, 2204, 2152, 2102, 1581, 1538, 1464, 1400, 1251, 999 cm^{-1}; MS (CI pos) m/z (%) 614.2 (M^+, 100), 571.2 (28), 529.1 (42), 487.1 (32), 73 (34); $C_{39}H_{62}Si_3$ (615.17).

α,ω-Polyyne 18a. Triyne **8a** (400 mg, 0.92 mmol) was reacted with C_6I_6 (75 mg, 0.09 mmol) as described in general procedure B. Purification by column chromatography (10% CH_2Cl_2 in petroleum ether), followed by slow evaporation from petroleum ether, produced **18a** (60 mg, 30%) as yellow needles: mp 252 °C (dec); ^{1}H NMR ($CDCl_3$) δ 7.46 (d, J = 8.4 Hz, 6H), 7.44 (d, J = 2.1 Hz, 6H), 7.23 (dd, J = 8.4, 2.1 Hz, 6H), 1.29 (s, 54H), 1.09 (s, 126 H); ^{13}C NMR ($CDCl_3$) δ 152.37, 133.14, 129.11 (2C), 126.78, 125.26, 121.76, 104.82, 95.66, 85.43, 85.27, 77.52, 77.27, 34.83, 30.96, 18.71, 11.31; IR (CH_2Cl_2) υ 2958, 2943, 2864, 2204, 2156, 1461 cm^{-1}; UV/vis (CH_2Cl_2) λ_{max} (ϵ) 383 (117 100), 415 (93 100) nm; MS (FAB) m/z (%) 2240.4 (M^+, 73), 1881.1 (100); (MALDI-TOF) 2264.72 (M^+ + Na), 1913.54 (M^+ − 2 × TIPSA); $C_{156}H_{198}Si_6$ (MW 2241.75).

Subunit 2a. Precursor **18a** (56 mg, 0.025 mmol) was deprotected and cyclized as described in general procedure D. Purification by preparative TLC (5% CH_2Cl_2 in hexanes) gave **2a** (6 mg, 20%) as an amorphous yellow solid that was extremely difficult to redissolve: MS (MALDI-TOF) m/z (%) 1320.8 (M^+ + Na), 1298.0 (M^+). $C_{102}H_{72}$ (MW 1297.66).

α,ω-Polyyne 18b. Triyne **8b** (500 mg, 0.96 mmol) was reacted with C_6I_6 (80.3 mg, 0.096 mmol) as described in general procedure B. After workup, the residue was preabsorbed on silica gel and was purified by flash chromatography. Elution (petroleum ether) gave the homodimer of **8b**; further elution (2% CH_2Cl_2 in petroleum ether) gave **18b** (50 mg) contaminated with partially coupled material: ^{1}H NMR ($CDCl_3$) δ = 7.52 (s, Ar−H of 5-fold material), 7.46−7.41 (m), 7.30−7.25 (m), 7.08−6.99 (m), 1.17−1.09 (4 s); MS (MALDI-TOF) m/z (%)

2703.6 ($M^+ - i$-Pr), 2602.4 ($M^+ -$ Si-i-Pr_3), 2215.8 (5-fold product with H, $-$ 2(i-Pr)). $C_{192}H_{270}Si_6$ (2746.71).

Subunit 2b. An impure mixture of **18b** (50 mg) was deprotected and cyclized as described in general procedure D. Purification by preparative TLC (5% CH_2Cl_2 in hexanes) gave **2b** (11 mg, 6% yield based on C_6I_6) as an amorphous yellow solid: ^{1}H NMR (CD_2Cl_2) δ 7.80 (d, J = 8.1 Hz, 12H), 7.58 (d, J = 1.2 Hz, 12H), 7.36 (dd, J = 8.1, 1.2 Hz, 12H), 2.71 (t, J = 7.8 Hz, 12H), 1.65−1.58 (m, 12H), 1.38−1.20 (m, 84H), 0.88 (br t, 18H); IR (CH_2Cl_2) υ 2923, 2850, 2194, 1592, 1464, 1420 cm^{-1}; UV/vis (CH_2Cl_2) λ_{max} (ϵ) 411 (118 200), 423 (95 000), 442 (124 500) nm; MS (MALDI-TOF) $C_{138}H_{144}$ (1802.62): m/z 1802.7 (M^+).

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Supporting Information Available: ^{1}H and ^{13}C NMR spectra for compounds **2b**, **4a**−**c**, **6b**,**c**, **8a**, **9a 14**, and **18a**,**b** described in the Experimental Section; low-grade X-ray crystal structure of **4a**. This information is available free of charge via the Internet at http://pubs.acs.org.

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