Carbon Networks Based on Dehydrobenzoannulenes: Part 2[+]

Synthesis of Expanded Graphdiyne Substructures

W. Brad Wan, Stephen C. Brand, Joshua J. Pak, and Michael M. Haley*[a]

Abstract: Graphdiyne (**1**) is a member of a novel family of interesting and potentially important allotropes of carbon. Reported herein are the synthesis and spectroscopic characterization of model substructures **2**–**6**. The macrocycles were prepared by the intramolecular cyclization of suitable α,ω-polyynes. Key to the success of this approach was the development of an in situ protiodesilylation/alkynylation reaction utilizing reactive phenylbutadiyne synthons. This new method has allowed for the preparation of the largest, most complete substructures of the graphdiyne network to date (**3**–**6**).

Keywords: alkynes · annulenes · aromaticity · carbon allotropes · macrocycles

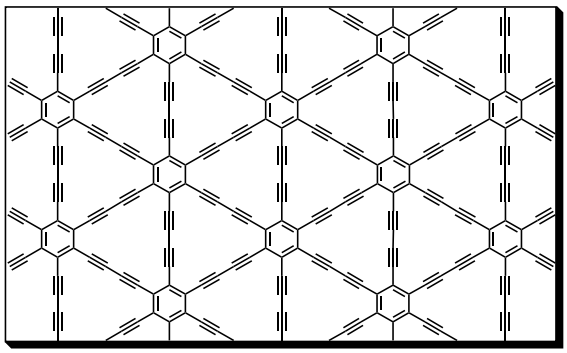
Introduction

As we begin the new millennium and the Electronics Age is just reaching adolescence, there exists an ever-growing demand for the next generation of electronic devices. Conventional electronic materials have been pushed nearly to the limits, and industry is turning more and more towards the development of novel organic materials with interesting electrical, optical, and structural properties.[1] Organic materials are particularly attractive as they offer adaptability with respect to the design and tailoring of materials with specialized properties for specific applications (i.e., liquid crystals, optical switches, conductors, insulators, etc.). Likely candidates for these purposes include conjugated polymers, perfluorinated polymers, carbon-rich molecules, and all-carbon networks.[2]

In 1968, a group of theoreticians led by Alexandru Balaban published an article in which they put forth a variety of imaginative, nonnatural, two- and three-dimensional carbon allotropes, many of which comprised sp^2 and/or sp^3 carbon scaffolding.[3] The extended π-conjugation of such networks creates a foundation for a wealth of interesting technologically important attributes. In addition to the aforementioned materials applications, other desirable qualities that might be expected of these networks include nonlinear optical (NLO) behavior, hardness, chemical inertness, and thermal resistance.[2]

Building upon Balaban's work, others have proposed a wide array of nonnatural networks—some practical, most impractical.[4] Despite predictions of numerous favorable attributes, the majority of the proposed allotropes have not been seriously investigated other than from a theoretical standpoint (calculated physical properties, crystal packing, energies of formation, etc.).[2–4] Many of these systems are considered to be unsuitable synthetic targets as monomeric precursors do not exist or are too reactive to be isolated. Furthermore, several of the proposed allotropes incorporate strained rings within the matrix, which markedly increases the overall energy. Such networks are susceptible to *graphitization*, the facile rearrangement into a more thermodynamically stable state, most likely graphite.

One of the more "synthetically approachable" allotropes is graphdiyne (**1**), a planar network comprised entirely of benzene rings and alkyne units.[5] With a heat of formation



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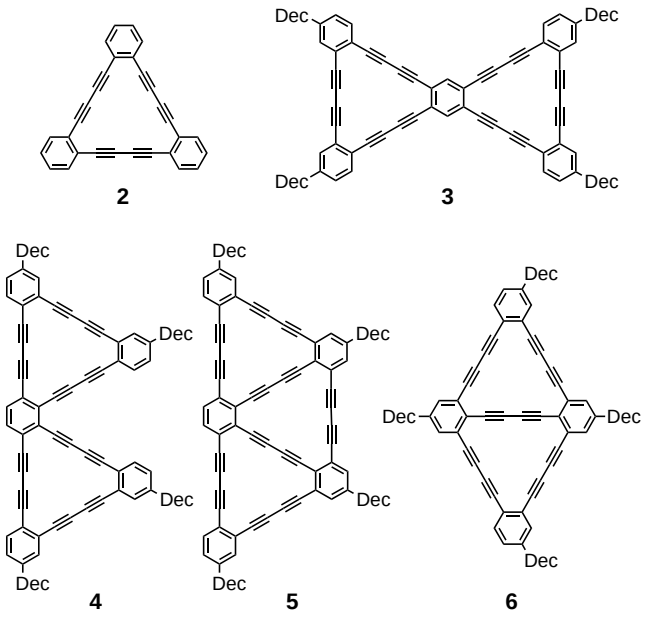
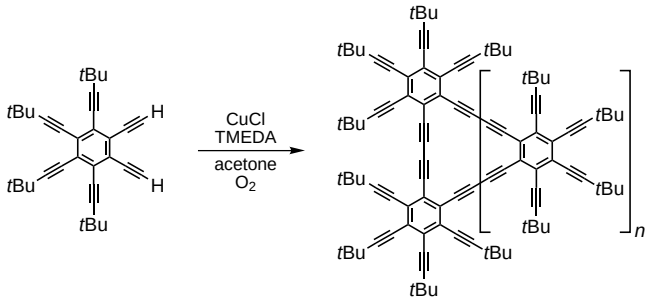
of 18.3 kcal per g-atom C, allotrope **1** is the most stable carbon network containing diacetylenic linkages.[2] Virtually strain free, graphdiyne is not expected to readily rearrange to graphite, while at the same time retaining relatively high-temperature stability and mechanical properties similar to graphite. The extended π-conjugation of **1** should also give rise to the aforementioned materials properties (NLO activity, conductivity or superconductivity, enhanced redox activity). The large holes in the planar sheets of graphdiyne (ca. 2.5 Å) also afford a method of dopant storage that is not available to graphite, namely intrasheet intercalation. None of these properties have been confirmed, however, as a viable synthetic route for the formation of **1** is beyond the limits of current methodology.



An alternative strategy to investigate the potential properties of graphdiyne is the preparation and study of model "oligomers" such as substructures **2**–**6**.[1d] By monitoring a variety of physical properties as a function of oligomer size, extrapolation towards the behavior of network **1** may be possible. The smallest macrocyclic substructure of network **1**, dodecadehydrotribenzo[18]annulene (**2**), has been pursued as a synthetic target since the late 1950s,[6] yet only recently was the isolation and characterization of the parent hydrocarbon reported.[7] Throughout the literature, the most prevalent method for the preparation of derivatives of **2** has been copper-mediated cyclotrimerization of an appropriate *o*-diethynylbenzene.[8] A representative example of this method is the formation of perethynylated derivative **8b** (Scheme 1).[9]

While simple in execution, the unavoidable pitfall of this synthetic approach is the formation of other cyclooligomeric products. In this case, cyclooligomerization of **7** under Hay coupling conditions gave predominantly dimer **8a** (25% yield) and an inseparable mixture of trimer **8b** and tetramer **8c** (13% combined yield); thus, the chemical and physical properties of expanded graphdiyne subunit **8b** are as yet unknown. Despite possible synthetic and purification short



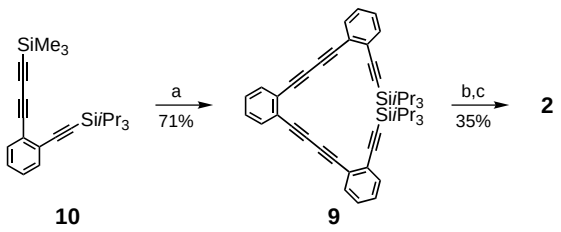
Scheme 1.

comings,the vast majority of related compounds found in the literature have been prepared by this method. Efforts to manipulate the relative ratio of dimer, trimer, and tetramer by varying the reaction conditions (i.e., concentration, temperature, catalyst, solvent)[10] have met with limited success as a mixture of products is almost always recovered. Owing to their similarity in composition, structure, and solubility, it is often difficult (or impossible) to isolate a specific macrocycle from the product mixture. Surprisingly, the cyclooligomerization approach purportedly failed to provide the parent macrocycle **2**.[6, 10] It is also noteworthy that derivatives of **2** prepared by this route are restricted to uniform D_{nh} substitution patterns. Thus, this synthetic method is not applicable or conducive towards the preparation of larger, more complex graphdiyne substructures.

To avoid the aforementioned problems, we developed an improved, more efficient synthesis of [18]annulenes which incorporates an intramolecular cyclization of an α,ω-polyyne performed under pseudo high-dilution conditions to complete the macrocycle.[7, 11] Unlike the "nonspecific" synthesis discussed above, our method insures the generation of the desired macrocycle exclusively in moderate to good overall yield. Although the preparation of the appropriate macrocycle precursor necessitates the manipulation of highly reactive phenylbutadiyne moieties,[12] we described recently a convenient and efficient method of cross-coupling functionalized phenylbutadiyne moieties with iodoarenes.[11] Utilizing this new strategy, we report herein the synthesis and characterization of models **2**–**6**, the most complete substructures of graphdiyne reported to date, as well as the first examples of macrobicyclic and macrotricyclic mimics of nonnatural carbon networks.[13]

Syntheses

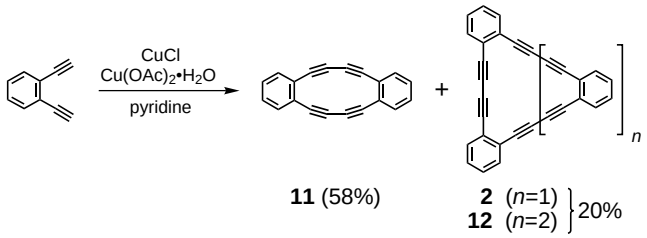
Slow addition of triyne **10**[11] to a dilute suspension of 1,2-diiodobenzene and cross-coupling catalysts, in the presence of aqueous KOH, gave hexayne **9** in 71% yield (Scheme 2). This modification of typical Sonogashira conditions generated the reactive phenylbutadiyne species in situ by selective removal of the smaller, more labile trimethylsilyl protecting group. In this manner the concentration of the butadiyne intermediate remained low, and cross-coupling to the substrate occurred



Scheme 2. Reagents: a) 1,2-diiodobenzene, $[PdCl_2(PPh_3)_2]$, CuI, Et_3N, THF, aq KOH; b) Bu_4NF, EtOH, THF; c) CuCl, $Cu(OAc)_2 \cdot H_2O$, pyridine.

with minimal self-polymerization. The in situ protiodesilylation/alkynylation sequence has proven to be quite versatile and has led to the preparation of a large family of dehydrobenzoannulenes.[11, 14] Desilylation of **9** with Bu_4NF followed by intramolecular cyclization with CuCl and $Cu(OAc)_2$ in pyridine furnished **2** as the sole product in modest yield (35%). We attributed the low yield to the solubility of the parent [18]annulene, which was very poor in common organic solvents.

The poor solubility of **2** provided an important clue as to why its isolation was elusive prior to our work. We noted that dichloromethane was superior to diethyl ether, the solvent most commonly used during reaction work-up of Cu-mediated alkyne couplings. Indeed, repetition of the cyclooligomerization experiment with 1,2-diethynylbenzene (Scheme 3)

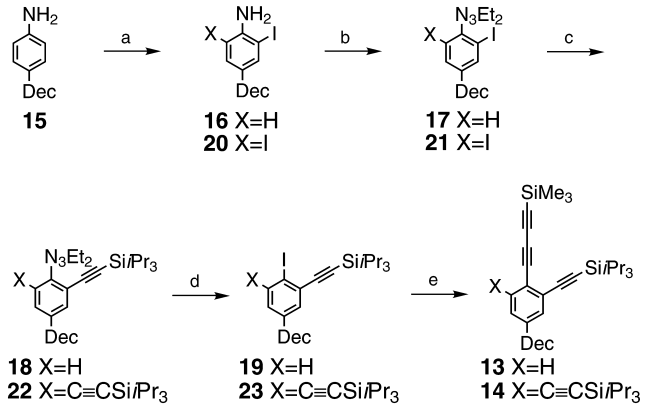


Scheme 3.

followed by careful work-up and chromatography provided dimer **11** (58%) *and* an inseparable 3:2 mixture of **2:12** (20%). The ^1H NMR spectrum of the two-component mixture was identical to an overlay of the individual spectra obtained for **2** and **12**,[11] which were synthesized independently by our intramolecular strategy. Therefore, it is likely **2** was generated in the previous studies and then was discarded as an insoluble by-product!

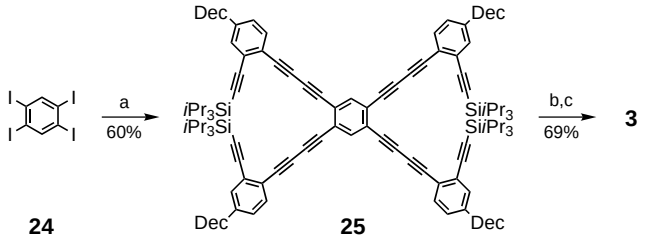
The problems in manipulating **2** indicated that the larger structures (**3**–**6**) would require the incorporation of pendant alkyl chains in order to enhance solubility. Subsequently, all phenylbutadiyne building blocks incorporate decyl chains. Fortunately though, the symmetry of macrocycles **3**–**6** required the construction of only two basic components, triyne **13** and tetrayne **14**, and their preparation is shown in Scheme 4.

Treatment of 4-decylaniline (**15**) with one equivalent of $BnEt_3N^+ ICl_2^-$ gave iodoaniline **16** as tan needles in 96% yield.[15] Conversion of the amino group to a diethyltriazene moiety resulted in the formation of triazene **17** in 96% yield.[16] Palladium-catalyzed alkynylation of **17** with (triisopropylsilyl)acetylene afforded **18**, which was followed by conversion of the triazene functionality into an iodide upon treatment with iodomethane at 120°C.[16] Cross-coupling of the resultant iodoarene (**19**) with excess (trimethylsilyl)butadiyne[17] produced triyne **13** in 89% yield. Tetrayne **14** is structurally similar, and was assembled in approximately 60% overall yield following virtually the same pathway, using instead two equivalents of the appropriate reagents in steps a and c (Scheme 4).



Scheme 4. Reagents: a) $(BnNEt_3) \cdot ICl_2$, CH_2Cl_2, $CaCO_3$, MeOH; b) 1. $NaNO_2$, HCl, H_2O, CH_3CN, THF, Et_2O; 2. Et_2NH, K_2CO_3, H_2O, CH_3CN; c) $iPr_3SiC{\equiv}CH$, $[PdCl_2(PPh_3)_2]$, CuI, Et_3N; d) MeI, 120°C; e) $Me_3SiC{\equiv}CC{\equiv}CH$, $[PdCl_2(PPh_3)_2]$, CuI, Et_3N.

With the necessary precursors in hand, substructures **3**–**6** were constructed readily. The first and least complex graphdiyne substructure synthesized was bis-annulene **3**, dubbed the "bow tie" (Scheme 5).



Scheme 5. Reagents: a) **13**, $[PdCl_2(PPh_3)_2]$, CuI, Et_3N, THF, aq KOH; b) Bu_4NF, EtOH, THF; c) CuCl, $Cu(OAc)_2 \cdot H_2O$, pyridine.

Sonogashira cross-coupling of 1,2,4,5-tetraiodobenzene[18] (**24**) with excess triyne **13** by the in situ protiodesilylation/alkynylation sequence gave the tetra-coupled product **25** in 60% yield. Subsequent removal of the four triisopropylsilyl groups with Bu_4NF followed by double intramolecular oxidative coupling with CuCl and $Cu(OAc)_2$ led to the formation of bow tie **3** in 69% yield.[19]

Bis-annulene **4**, the angular analogue of **3**, was prepared by a similar synthetic route (Scheme 6). Cross-coupling of four equivalents of triyne **13** with 1,2,3,4-tetraiodobenzene[18, 20] (**26**) using our "in situ" method gave dodecayne **27** in 58% yield. Desilylation and intramolecular oxidative cyclization furnished "boomerang" **4** in 30% yield. We attribute the low yield of **4** (relative to the synthesis of **3**) to a competitive cyclization pathway in which the terminal acetylenic appen-

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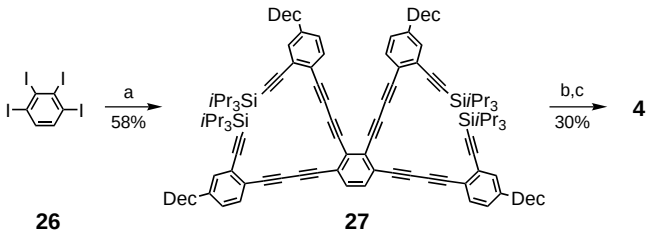
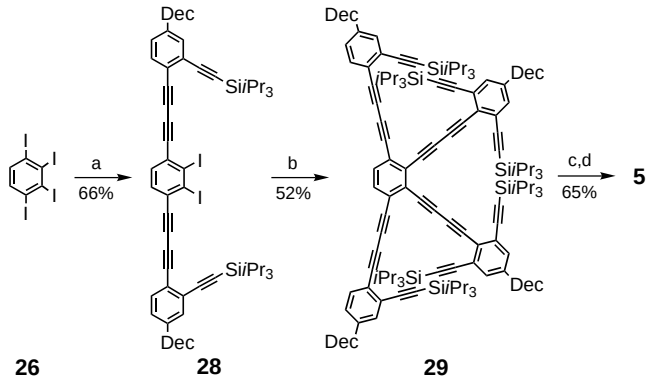


Scheme 6. Reagents: a) **13**, $[PdCl_2(PPh_3)_2]$, CuI, Et_3N, THF, aq KOH; b) Bu_4NF, EtOH, THF; c) CuCl, $Cu(OAc)_2 \cdot H_2O$, pyridine.

dages at the 2- and 3-positions intramolecularly couple first. Subsequent Cu-mediated oligomerization/polymerization of the free alkynes in the resulting intermediate (at the 1- and 4-positions) would produce insoluble and/or intractable species.

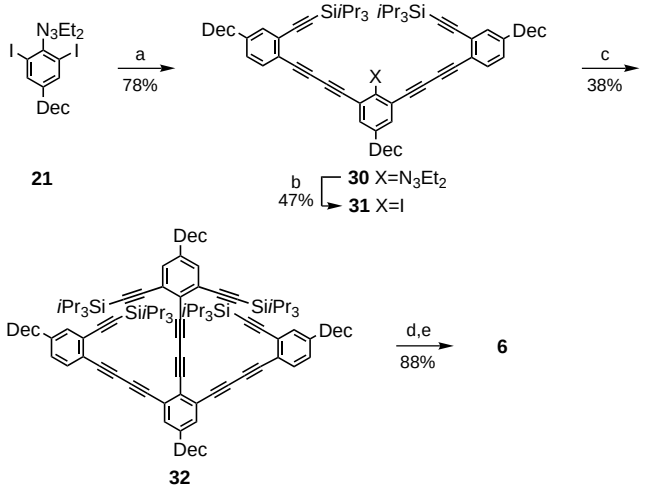
During the synthesis of boomerang **4**, we established that the first two equivalents of coupling partner (triyne **13**) add preferentially to the more accessible 1- and 4-positions of **26**. This reactivity is consistent with results published by Vollhardt et al. in regards to an analogous system.[21] Accordingly, we were able to take advantage of this regioselectivity for the preparation of the "half wheel" (**5**), as outlined in Scheme 7.



Scheme 7. Reagents: a) **13**, $[PdCl_2(PPh_3)_2]$, CuI, Et_3N, THF, aq KOH; b) **14**, $[PdCl_2(PPh_3)_2]$, CuI, Et_3N, THF, aq KOH; c) Bu_4NF, EtOH, THF; d) CuCl, $Cu(OAc)_2 \cdot H_2O$, pyridine.

Alkynylation of **26** at the 1- and 4-positions with two equivalents of triyne **13** using the in situ protiodesilylation/alkynylation sequence at room temperature produced the desired *para*-substituted diiodohexayne **28** in 66% yield. Cross-coupling of tetrayne **14** at the two remaining iodines in **28** furnished tetradecayne **29** in 52% yield. Removal of the triisopropylsilyl groups and oxidative intramolecular coupling gave half wheel **5** in 65% yield.

Both bow tie **3** and boomerang **4** can be envisioned as two [18]annulenes that are fused in an end-to-end fashion at a common benzene ring. The "diamond" substructure (**6**) represents a laterally fused bis-annulene, or rather two [18]annulenes with an entire side in common. Half wheel **5** also represents a laterally fused tris-annulene in which three [18]annulenes share a common diphenylbutadiyne side among any two of the macrocycles; moreover, the central benzene is common for all three cycles. Although more involved than the previous syntheses, diamond **6** was prepared readily from existing precursors (Scheme 8).



Scheme 8. . Reagents: a) **13**, $[PdCl_2(PPh_3)_2]$, CuI, Et_3N, THF, aq KOH; b) MeI, 120 °C; c) **14**, $[PdCl_2(PPh_3)_2]$, CuI, Et_3N, THF, aq KOH; d) Bu_4NF, EtOH, THF; e) CuCl, $Cu(OAc)_2 \cdot H_2O$, pyridine.

Two equivalents of triyne **13** were cross-coupled to intermediate **21** to give triazene **30** as a dark brown oil in 78% yield. Treatment with iodomethane at 120 °C afforded iodohexayne **31** in 47% yield. Tetrayne **14** was cross-coupled with **31** by the in situ protiodesilation/alkynylation protocol to produce polyyne **32** as a dark oil in 38% yield. Desilylation with Bu_4NF followed by copper-mediated cyclization furnished diamond **6** in 88% yield.

Discussion

All of the macrocycles were isolated as bright yellow, microcrystalline solids. Even with four appended decyl moieties, the product solubility of annulenes **3**–**6** decreased appreciably with increasing molecule size. Most notably, completion of the third macrocyclic ring going from **4** to **5** resulted in a marked drop in product solubility.

All annulenic structures and intermediates were identified unequivocally and characterized spectroscopically. Particularly instructive to the present study were the ^1H NMR and UV/Vis spectra of **2**–**6**. Each of the graphdiyne subunits possesses $(4n+2)$ π-electron circuits, which suggests that the macrocycles might be able to sustain an induced ring current and thus exhibit a degree of aromatic character. Consistent with our previous studies of dehydrobenzo[18]annulene derivatives,[14c, d] the benzene resonances of expanded macrocycles **3**–**6** showed small but distinct downfield shifts ($\Delta\delta =$ 0.15–0.30 ppm) relative to their acyclic precursors, indicating the presence of a weak diatropic ring current in the 18-membered ring. For example, the two proton resonance on

the central benzene of **27** appeared as a singlet at $\delta = 7.40$, yet moved to $\delta = 7.68$ in **4**. Comparison of this same arene resonance of **4** with that in **5** revealed a slight downfield shift of the protons ($\Delta\delta = 0.06$ ppm) and thus illustrates enhanced delocalization due to completion of the third macrocyclic unit. Whether this is due to the presence of "superdelocalization"[21b] in tris-macrocycle **5** is subject for further study.

The predicted materials properties, particularly the NLO and electrical properties, presumably arise from the extended, two-dimensional π-conjugation of the network or network fragment. The extent of delocalization is manifested by a bathochromic shift in the UV absorption spectra, the magnitude of which should be a function of substructure size and conjugation length. The electronic absorption spectra of **2**–**6** are shown in Figure 1. Comparison of four diagnostic peaks is presented in Table 1.

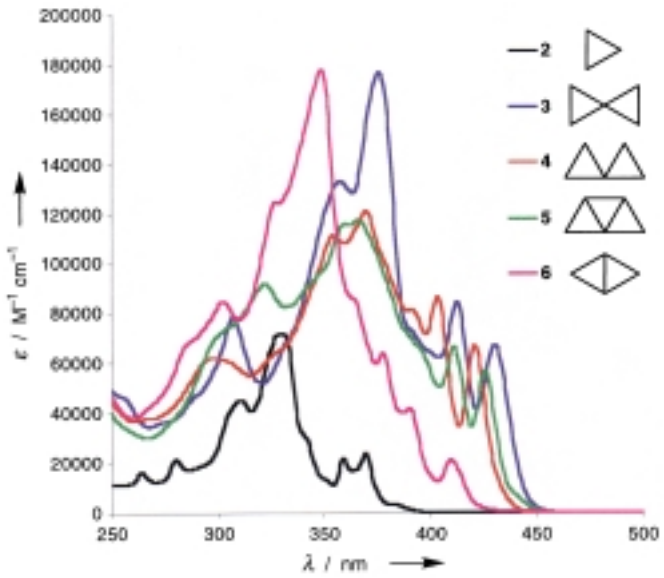


Figure 1. Electronic absorption spectra of macrocycles **2**–**6**.

Table 1. Selected peaks (nm) from the electronic absorption spectra of **2**–**6**.

Compound	Peak 1	Peak 2	Peak 3	Peak 4
2	309	330	359	369
3	357	376	413	431
4	354	366	404	420
5	360	366	411	426
6	325	347	390	410

The absorption spectrum of **2** (Figure 1) exhibits the characteristic pattern associated with the dodecadehydro[18]annulene core. Throughout the series of macrocycles, the same general trend in diagnostic peak intensities ($2 \rightarrow 1 \rightarrow 3,4$) is maintained. The absorption bands at longer wavelengths (peaks 3 and 4) are attributed to the interaction of the ^1L_a-state of the benzene nucleus with the diyne chromophore.[22] Diamond **6**, the next smallest in the series after **2**, comprises multiple 1,4-diphenylbutadiyne chromophores. The peak at 347 nm for **6** is comparable to that of parent **2** (330 nm); however, the intensity is approximately double due to the increase in π-conjugation density. Fusion of the two [18]annulenes leads to an appreciable bathochromic shift (ca. 40 nm) of the low-energy bands.

The remaining substructures also incorporate 1,4-diphenylbutadiyne chromophores, accompanied by one or more elongated chromophores, that is, *para*-bis(phenylbutadiynyl)-benzene units. Thus, macrocycles **4** and **5** (both containing a single long chromophore) exhibit a maximum absorption at 366 nm, which is a bathochromic shift of about 35 nm with respect to **2**. More importantly, the effect of completing the third macrocycle can be observed in the low-energy region. Boomerang **4** produces moderately strong absorptions at 404 nm and 420 nm, whereas the analogous bands in half wheel **5** appeared at 411 nm and 426 nm, respectively. Bow tie **3**, the structural isomer of **4**, shows the greatest bathochromic shifts of the series, primarily because **3** now possesses two long chromophores as opposed to only one such unit in **4** or **5**. The result is a maximum absorption at 376 nm (a shift of ca. 45 nm from **2**), and low-energy absorptions at 413 and 431 nm. The above results indicate that the electronic absorption behavior of the graphdiyne subunits is a function of effective conjugation length, and not of macrocycle size or molecular weight.

Both as solids and in solution, macrocycles **2**–**6** proved quite robust, remaining spectroscopically unchanged over a period of several months. Decomposition could be induced thermally in the solid state around 200 °C. Differential scanning calorimetry (DSC) analysis showed this to be an exothermic process, occurring over a narrow 10–15 °C range. Attempts to examine the thermoproducts from the DSC experiments were hampered due to complete insolubility of the shiny, black materials in common organic solvents. Some clue as to the type of polymerization might be given by analysis of the solid state packing of **2**–**6**. Unfortunately, efforts to grow X-ray quality crystals of the macrocycles have been unsuccessful. Therefore, the structures of the thermoproducts as well as the nature of thermal transformation remain uncertain. In-depth studies are required to determine whether the graphdiyne subunits undergo topochemical solid-state polymerization to form polydiacetylenes; these studies are currently underway.

Conclusion

Our in situ protiodesilylation/alkynylation protocol in conjunction with the intramolecular cyclization strategy has permitted the preparation and characterization of novel substructures **2**–**6**, the most complete "oligomers" of the graphdiyne network synthesized to date. While the electronic absorption properties of **2**–**6** suggest a strong dependence on the effective conjugation length of the subunits, the preparation and study of even larger, more complex subunits such as "radiation symbol" **33** and "full wheel" **34** will corroborate this hypothesis and hopefully permit extrapolation to **1**. Their syntheses, as well as NLO studies of all graphdiyne substructures, are in progress.

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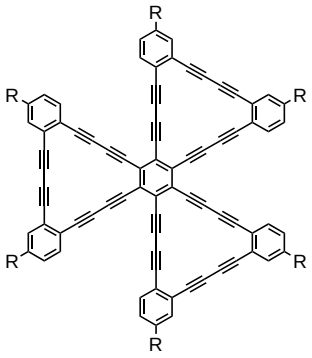

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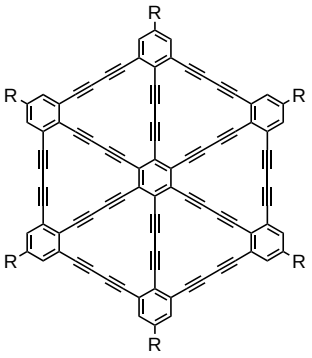

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Experimental Section

General: ^{1}H and ^{13}C NMR spectra were recorded using a Varian Unity Inova 300 (^{1}H: 299.95 MHz, ^{13}C: 75.43 MHz) spectrometer and were obtained in $CDCl_3$ unless otherwise noted. Chemical shifts (δ) are expressed in ppm downfield from tetramethylsilane using the residual non-deuterated solvent as internal standard ($CDCl_3$ $\delta(^1H)$ 7.26, $\delta(^{13}C)$ 77.0; CD_2Cl_2 $\delta(^1H)$ 5.32, $\delta(^{13}C)$ 54.0; [D_8]THF $\delta(^1H)$ 3.58, $\delta(^{13}C)$ 67.57). Coupling constants are expressed in Hz. Melting points are uncorrected. Dichloromethane, triethylamine (TEA), and pyridine were distilled from calcium hydride under an atmosphere of nitrogen prior to use. Tetrahydrofuran and diethyl ether were distilled from sodium and benzophenone under an atmosphere of nitrogen 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). Pre-coated silica gel plates (EM Separations Technology, 60 PF_{254}, $200 \times 50 \times 0.20$ mm) were used for analytical thin-layer chromatography. Solvent mixtures for elution are v:v ratios.

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 TEA (25 mL per mmol) was degassed with bubbling nitrogen, or by method of freeze-pump-thaw. The terminal acetylene (1.5 equiv per iodine) was added in three portions in 1 h intervals with stirring at 60 °C under nitrogen. The reaction was monitored by TLC. 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 crude product was purified by column chromatography or by Chromatotron.

General in situ desilylation–alkynylation procedure B: An iodoarene (1 equiv) was dissolved in THF/TEA (1:5, v:v, 25 mL per mmol). To this was added $PdCl_2(PPh_3)_2$ (0.03 equiv), CuI (0.06 equiv), and aqueous KOH (1M, 10 equiv). The reaction mixture was degassed by bubbling nitrogen, or by method of freeze-pump-thaw. In a separate vessel, the (trimethylsilyl)-butadiyne coupling partner (1.2 equiv per coupling) was dissolved in a small volume of TEA and was degassed. The acetylene solution was added by syringe pump over 12–24 h to the iodoarene solution under nitrogen atmosphere at 60 °C. The reaction was monitored by TLC. Upon completion, the mixture was concentrated in vacuo, suspended in CH_2Cl_2, and filtered through a bed of silica gel. The filtrate was concentrated, and the crude product was purified by column chromatography or by Chromatotron.

General triazene conversion (to an iodoarene) procedure C: A mixture of aryl diethyltriazene (1 equiv) and freshly distilled iodomethane (5 equiv) was stirred in a sealed pressure reactor at 120 °C for 6–24 h. The reaction mixture was cooled, diluted with hexanes, filtered, and concentrated in vacuo. The crude product was then purified (as necessary) by flash chromatography or by Chromatotron.

General macrocyclization procedure D: To the silyl-protected oligo(acetylenic) substrate dissolved in THF (ca. 25 mL per mmol) was added EtOH (10–20 drops) and Bu_4NF solution (1M 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 (ca. 25 mL per mmol of substrate), washed three times with water, twice with brine, and dried over $MgSO_4$. 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. The deprotected acetylene was added by syringe pump to a suspension of CuCl and $Cu(OAc)_2 \cdot H_2O$ (20 equiv of each per coupling) in pyridine (ca. 250 mL per mmol of α,ω-polyyne) at 60 °C. The addition was done over 16–20 h. The reaction was monitored by TLC. Upon completion, the mixture was concentrated in vacuo and extracted with CH_2Cl_2. The organic layer was subsequently washed with dilute HCl solution and several times with water. The organic layer was dried over $MgSO_4$, filtered, evaporated, and purified by column chromatography or by Chromatotron.

1-(Trimethylsilyl)-1,3-butadiyne: Prepared in 8–10 g amounts by the method of Brandsma.[17] **Warning**: the procedure involves use of butadiyne gas, which is highly explosive. It is important not to store the diethyl ether solution of dissolved gas overnight, but rather to continue until the distillation of pure (trimethylsilyl)butadiyne is complete. ^{1}H NMR: $\delta =$ 0.21 (s, 9H), 2.11 (s, 1H).

Hexayne 9: Triyne **10**[11] (1.65 g, 4.36 mmol) was treated with 1,2-diiodobenzene (480 mg, 1.45 mmol) as described in general in situ coupling procedure B. Chromatography on silica gel (5:1 hexanes:CH_2Cl_2) gave polyyne **9** (705 mg, 71% yield) as a orange gum. ^{1}H NMR: $\delta = 1.16$ (s, 42H), 7.25–7.38 (m, 6H), 7.47–7.57 (m, 6H); ^{13}C NMR (CD_2Cl_2): $\delta = 11.95$, 19.10, 78.12, 78.68, 80.95, 82.39, 96.87, 105.11, 125.06, 125.62, 127.81, 128.72, 129.60 (2), 132.90, 133.41, 134.04; UV/Vis (CH_2Cl_2): λ_{max} (ε) = 221 (30100), 238 (25800), 267 (15400), 316 (9800), 337 (8600), 361 (6300) nm; IR (CH_2Cl_2): $\tilde{\nu} = 2210, 2159$ cm^{-1}; MS (70 eV, EI): m/z (%): 686 ([M^+], 13), 643 (11), 601 (20), 559 (18), 517 (12); $C_{48}H_{54}Si_2$ (687.11): calcd: C 83.90, H 7.92; found: C 83.50, H 7.71.

Dodecadehydrotribenzo[18]annulene (2): Polyyne **9** (400 mg, 0.58 mmol) was deprotected as described in general procedure D. Cyclization was performed using CuCl (175 mg, 20 equiv) and $Cu(OAc)_2 \cdot H_2O$ (320 mg, 20 equiv) in pyridine. Purification by column chromatography on silica gel (CH_2Cl_2) followed by recrystallization in hot CH_2Cl_2 furnished a bright yellow microcrystalline solid (76 mg, 35% yield). Once purified, the product exhibited poor solubility. M.p. 210 °C (decomp); ^{1}H NMR: $\delta = 7.42$ (AA′m, 6H), 7.68 (BB′m, 6H); ^{13}C NMR: $\delta = 77.21$, 80.73, 125.29, 128.81, 132.72; UV/Vis (CH_2Cl_2): λ_{max} (ε) 226 (13400), 280 (18900), 309 (42500), 330 (69400), 359 (19000), 369 (21100) nm; IR (CH_2Cl_2): $\tilde{\nu} = 3054$, 2207 cm^{-1}; MS (70 eV, EI): m/z (%): 372 ([M^+], 100), 371 (8), 370 (26), 368 (11), 91 (24); $C_{30}H_{12}$ (372.42): calcd: C 96.75, H 3.25; found: C 96.55, H 3.15.

Cyclooligomerization of 1,2-diethynylbenzene: 1,2-Diethynylbenzene (126 mg, 1.0 mmol) was added to a suspension of CuCl (297 mg, 30 mmol) and $Cu(OAc)_2 \cdot H_2O$ (600 mg, 30 mmol) in pyridine (100 mL) at 60 °C. After stirring for 12 h, the mixture was concentrated in vacuo and extracted with CH_2Cl_2. The organic layer was subsequently washed with dilute HCl solution and four times with water. The organic layer was dried over $MgSO_4$, filtered, evaporated, and purified by Chromatotron (2 mm plate, 9:1 hexanes:CH_2Cl_2) to give dimer **11** (71 mg, 58%) and a 3:2 mixture of trimer **2** and tetramer **12** (25 mg, 20%). The NMR spectral data of each compound were identical to those reported in the literature (**11**,[6c] **12**[11]) or to the sample prepared above (**2**).

4-Decyl-2-iodoaniline (16): 4-Decylaniline (2.5 g, 10.7 mmol) was dissolved in CH_2Cl_2 (200 mL) and MeOH (75 mL). To this was added $BnEt_3N^+$ ICl_2^-[15] (4.34 g, 11.1 mmol) and $CaCO_3$ (3.44 g, 34.4 mmol). The suspension was stirred at room temperature for 3 h. The mixture was filtered through a bed of celite and was concentrated in vacuo to approximately 1/3 volume. The reaction mixture was washed with 5% $NaHSO_3$ solution, saturated $NaHCO_3$ solution, water, and brine. The organic layer was dried over $MgSO_4$, filtered, and concentrated to give an orange solid. The residue was recrystallized from EtOH/H_2O to afford **16** (3.70 g, 96% yield) as light brown needles. M.p. 44–46 °C. ^{1}H NMR: $\delta = 0.88$ (t, $J = 6.6$ Hz, 3H), 1.26 (m, 14H), 1.50–1.57 (m, 2H) 2.45 (t, $J = 7.7$ Hz, 2H), 3.95 (br s, 2H), 6.67 (d, $J = 8.2$ Hz, 1H), 6.95 (dd, $J = 8.2$, 2.1 Hz, 1H), 7.46 (d, $J = 2.1$ Hz); ^{13}C NMR: $\delta = 14.12$, 22.68, 29.17, 29.32, 29.48, 29.57, 29.60, 31.64, 31.89, 34.48, 84.37, 114.64, 129.39, 134.87, 138.41, 144.41; IR (KBr): $\tilde{\nu} = 3407$, 3311,

3204, 1619, 1498, 1466 cm^{-1}; $C_{16}H_{26}IN$ (359.29): calcd: C 53.49, H 7.29, N 3.90; found: C 54.18, H 7.40, N 3.83.

***N,N*-Diethyl-*N'*-(4-decyl-2-iodophenyl)triazene (17)**: Iodoaniline **16** (2.0 g, 5.6 mmol) was dissolved in Et_2O (20 mL), THF (15 mL), and CH_3CN (2.5 mL). A solution of HCl (4.1 mL concentrated HCl in 5.5 mL H_2O) was added dropwise, then the reaction mixture was cooled in a salted ice bath. A solution of $NaNO_2$ (1.31 g, 19 mmol) dissolved in H_2O (7 mL) and CH_3CN (2.5 mL) was added dropwise, and the reaction was allowed to stir for 30 min at -5 to 0 °C. The reaction mixture was poured into a chilled solution of K_2CO_3 (3.69 g, 28 mmol) and Et_2NH (13 mL, 72 mmol) in H_2O (25 mL) and CH_3CN (55 mL). After stirring for 30 min, the mixture was extracted twice with Et_2O. The combined diethyl ether layers were washed twice with brine, dried over $MgSO_4$, filtered, and concentrated. Purification of the crude material by column chromatography on silica gel (20:1 hexanes:CH_2Cl_2) gave **17** (2.37 g, 96 % yield) as a yellow oil. ^1H NMR: $\delta =$ 0.90 (br t, 3H), 1.25 – 1.36 (m, 20H), 1.52 – 1.60 (m, 2H), 2.53 (t, $J = 7.5$ Hz, 2H), 3.78 (q, $J = 7.2$ Hz, 4H), 7.09 (dd, $J = 8.2$, 1.8 Hz, 1H), 7.28, (d, $J = 8.2$, 1H), 7.68 (d, $J = 1.8$ Hz, 1H); ^{13}C NMR: $\delta = 14.11$, 22.65, 29.14, 29.30, 29.45, 29.58 (2), 31.39, 31.87, 34.87, 42.04, 49.05, 96.52, 117.02, 128.80, 138.60, 141.50, 148.21; IR (neat): $\nu = 1592$, 1549, 1465 cm^{-1}; $C_{20}H_{34}IN_3$ (443.41): calcd: C 54.17, H 7.73, N 9.48; found: C 54.48, H 7.66, N 9.28.

***N,N*-Diethyl-*N'*-[4-decyl-2-(triisopropylsilylethynyl)phenyl]triazene (18)**: Iodotriazene **17** (2.12 g, 4.8 mmol) was treated with (triisopropylsilyl)acetylene (1.6 mL, 7.14 mmol) according to general alkynylation procedure A. The reaction mixture was purified by column chromatography (20:1 hexanes:CH_2Cl_2) to afford **18** (2.28 g, 96 % yield) as an orange oil. ^1H NMR: $\delta = 0.89$ (br t, 3H), 1.15 (s, 21H), 1.24 – 1.38 (m, 20H), 1.56 – 1.66 (m, 2H), 2.55 (t, $J = 7.6$ Hz, 2H), 3.79 (q, $J = 7.2$ Hz, 4H), 7.06 (dd, $J = 8.2$, $J = 2.1$ Hz, 1H), 7.29 (d, 2.1 Hz, 1H), 7.35 (d, $J = 8.2$ Hz, 1H); ^{13}C NMR: $\delta = 11.41$, 14.12, 18.67, 22.61, 29.69, 29.25, 29.34, 29.52, 29.34, 31.48, 31.91, 35.23, 41.85, 48.95, 93.28, 105.86, 116.49, 118.14, 129.19, 133.51, 139.21, 150.46. IR (neat): $\tilde{\nu} = 2148$, 1599, 1465 cm^{-1}; $C_{31}H_{55}N_3Si$ (497.87): calcd: C 74.78, H 11.13, N 8.44; found: C 74.91, H 11.04, N 7.93.

4-Decyl-1-iodo-2-[(triisopropylsilyl)ethynyl]benzene (19): Triazene **18** (2.0 g, 4.0 mmol) was treated with iodomethane (25 mL) as described in general procedure C to give **19** (2.06 g, 98 % yield) as a pale yellow oil, with no need for further purification. ^1H NMR: $\delta = 0.89$ (br t, 3H), 1.18 (s, 21H), 1.25 – 1.36 (m, 14H), 1.52 – 1.60 (m, 2H), 2.51 (t, $J = 7.5$ Hz, 2H), 6.82 (dd, $J = 8.2$, 2.1 Hz, 1H), 7.32 (d, $J = 2.1$ Hz, 1H), 7.71 (d, $J = 8.2$ Hz, 1H); ^{13}C NMR: $\delta = 11.35$, 14.14, 18.74, 22.71, 29.22, 29.34, 29.46, 29.58, 29.61, 31.21, 31.91, 35.23, 94.59, 97.08, 108.23, 129.76, 129.95, 133.25, 138.41, 142.75; IR (neat): $\tilde{\nu} = 2152$, 1459 cm^{-1}. $C_{27}H_{45}SiI$ (524.64): calcd: C 61.81, H 8.65; found: C 61.72, H 8.54.

4-Decyl-2-[(triisopropylsilyl)ethynyl]-1-[4-(trimethylsilyl)-1,3-butadiynyl]-benzene (13): Iodoarene **19** (2.0 g, 3.8 mmol) was treated with (trimethylsilyl)butadiyne (700 mg, 5.7 mmol) according to general alkynylation procedure A. Purification by column chromatography on silica gel (hexanes) furnished **13** (1.76 g, 89 % yield) as a dark orange syrup. ^1H NMR: $\delta = 0.24$ (s, 9H), 0.89 (br t, 3H), 1.19 (s, 21H), 1.25 – 1.36 (m, 14H), 1.52 – 1.60 (m, 2H), 2.57 (t, $J = 7.5$ Hz, 2H), 7.05 (dd, $J = 8.1$, 1.5 Hz, 1H), 7.28 (d, $J = 1.5$ Hz, 1H), 7.36 (d, $J = 8.1$ Hz, 1H); ^{13}C NMR: $\delta = -0.40$, 11.33, 14.13, 18.71, 22.69, 29.25, 29.33, 29.45, 29.56, 29.60, 31.0, 31.91, 35.76, 75.54, 77.31, 88.26, 90.86, 95.40, 104.72, 121.73, 127.44, 128.32, 132.14, 132.56, 144.24; IR (neat): $\tilde{\nu} = 2206$, 2152, 2103, 1599, 1464 cm^{-1}; $C_{34}H_{54}Si_2$ (518.96): calcd: C 78.69, H 10.49; found: C 78.17 H 10.33.

4-Decyl-2,6-diiodoaniline (20): 4-Decylaniline (3.75 g, 16.1 mmol) was dissolved in CH_2Cl_2 (200 mL) and MeOH (75 mL). To this was added $BnEt_3N^+\ ICl_2^-$[15] (13.1 g, 33.6 mmol) and $CaCO_3$ (5.15 g, 51.4 mmol). The suspension was stirred at 50 °C overnight. Upon completion, the mixture was filtered through a bed of celite and was concentrated in vacuo to approximately 1/3 volume. The reaction mixture washed with 5 % $NaHSO_3$ solution, saturated $NaHCO_3$ solution, water, and brine. The organic layer was dried over $MgSO_4$, filtered, and concentrated to yield an off-white solid. The residue was recrystallized from EtOH/H_2O to give **20** (7.80 g, 81 % yield) as light brown needles. M.p. 87 – 88 °C. ^1H NMR: $\delta = 0.88$ (br t, 3H), 1.25 – 1.36 (m, 14H), 1.52 – 1.60 (m, 2H), 2.40 (t, $J = 7.8$ Hz, 2H), 4.46 (br s, 2H), 7.45 (s, 2H); ^{13}C NMR: $\delta = 14.13$, 22.69, 29.10, 29.32, 29.42, 29.54, 29.60, 31.49, 31.89, 33.92, 81.54, 136.30, 139.15, 143.87; IR (KBr): $\tilde{\nu} =$ 3410, 3327, 1608, 1466 cm^{-1}; $C_{16}H_{25}I_2N$ (485.19): calcd: C 39.61, H 5.19, N 2.89; found: C 39.74, H 5.14, N 2.68.

***N,N*-Diethyl-*N'*-(4-decyl-2,6-diiodophenyl)triazene (21)**: Diiodoaniline **20** (980 mg, 2.0 mmol) was dissolved in Et_2O (7 mL), THF (6 mL), and CH_3CN (1 mL). A solution of HCl (1.5 mL concentrated HCl in 2 mL H_2O) was added dropwise, and the reaction mixture was cooled in a salted ice bath. A solution of $NaNO_2$ (477 mg, 6.9 mmol) dissolved in H_2O (2.5 mL) and CH_3CN (1 mL) was added dropwise, and the reaction was allowed to stir for 30 min at -5 to 0 °C. The reaction mixture was poured into a chilled solution of K_2CO_3 (1.34 g, 10.1 mmol) and Et_2NH (8.4 mL, 46.4 mmol) in H_2O (10 mL) and CH_3CN (20 mL). After stirring for 30 min, the reaction mixture was extracted twice with Et_2O. The combined ether layers were washed twice with brine, dried over $MgSO_4$, filtered, and concentrated. The crude product was purified by column chromatography on silica gel (50:1 hexanes:EtOAc) to give **21** (1.03 g, 89 % yield) as a dark brown gum. ^1H NMR: $\delta = 0.89$ (br t, 3H), 1.22 – 1.40 (m, 20H), 1.52 – 1.60 (m, 2H), 2.47 (t, $J = 7.8$ Hz, 4H), 3.79 (q, $J = 7.0$ Hz, 6H), 7.64 (s, 2H); ^{13}C NMR: $\delta =$ 14.06, 22.63, 29.02, 29.30, 29.34, 29.48, 29.60, 31.18, 31.85, 34.15, 41.61, 49.05, 90.85, 139.24, 142.79, 149.86; IR (neat): $\tilde{\nu} = 3462$, 3366, 1578, 1522, 1466 cm^{-1}.

***N,N*-Diethyl-*N'*-[2,6-bis{(triisopropylsilyl)ethynyl}-4-decylphenyl]triazene (22)**: Diiodotriazene **21** (1.0 g, 1.75 mmol) was treated with (triisopropylsilyl)acetylene (1.2 mL, 5.25 mmol) according to general alkynylation procedure A. The reaction mixture was purified by column chromatography (50:1 hexanes:EtOAc) to afford **22** (1.14 g, 96 % yield) as an orange syrup. ^1H NMR: $\delta = 0.89$ (br t, 3H), 1.09 (s, 42H), 1.22 – 1.40 (m, 20H), 1.52 – 1.60 (m, 2H), 2.50 (t, $J = 7.7$ Hz, 2H), 3.75 (q, $J = 7.1$ Hz, 4H), 7.23 (s, 2H); ^{13}C NMR: $\delta = 11.35$, 14.13, 18.70, 22.71, 29.24, 29.36, 29.49, 29.64 (2), 31.39, 31.92, 34.98, 40.75, 48.61, 93.00, 105.18, 116.65, 134.11, 138.71, 153.12; IR (neat): $\tilde{\nu} = 2143$, 1587, 1567, 1485 cm^{-1}.

1,3-Bis[(triisopropylsilyl)ethynyl]-5-decyl-2-iodobenzene (23): Triazene **22** (1.14 g, 1.7 mmol) was treated with iodomethane (25 mL) as described in general procedure C to give **23** (1.08 g, 92 % yield) as a pale yellow oil, with no need for further purification. ^1H NMR: $\delta = 0.89$ (br t, 3H), 1.18 (s, 42H), 1.22 – 1.36 (m, 14H), 1.52 – 1.60 (m, 2H), 2.50 (t, $J = 7.8$ Hz, 2H), 7.22 (s, 2H); ^{13}C NMR: $\delta = 11.37$, 14.13, 18.74, 22.72, 29.29, 29.34, 29.45, 29.60, 29.62, 31.13, 31.92, 35.04, 94.89, 103.77, 108.51, 131.00, 132.58, 142.55; IR (neat): $\tilde{\nu} = 2150$, 1554, 1460 cm^{-1}; $C_{38}H_{65}Si_2I$ (705.00): calcd: C 64.74, H 9.29; found: C 64.39, H 8.95.

1,3-Bis[(triisopropylsilyl)ethynyl]-5-decyl-2-[4-(trimethylsilyl)-1,3-butadiynyl]benzene (14): Iodoarene **23** (1.08 g, 1.5 mmol) was treated with (trimethylsilyl)butadiyne (280 mg, 2.3 mmol) according to general alkynylation procedure A. Purification by column chromatography on silica gel (hexanes) furnished **14** (1.04 g, 95 % yield) as a dark orange syrup. ^1H NMR: $\delta = 0.21$ (s, 9H), 0.88 (br t, 3H), 1.16 (s, 42H), 1.23 – 1.30 (m, 14H), 1.50 – 1.60 (m, 2H), 2.52 (t, $J = 7.0$ Hz, 2H), 7.21 (s, 2H); ^{13}C NMR: $\delta = -0.42$, 11.31, 14.13, 18.70, 22.66, 29.31, 29.42, 29.54, 29.60, 30.98, 31.60, 31.89, 36.56, 74.22, 81.41, 88.51, 91.76, 95.75, 104.35, 124.79, 127.58, 131.83, 143.58; IR (neat): $\tilde{\nu} = 2206$, 2152, 2103, 1586, 1546, 1463 cm^{-1}.

Dodecayne 25: 1,2,4,5-Tetraiodobenzene (**24**, 50 mg, 0.086 mmol) was treated with triyne **13** (270 mg, 0.52 mmol) using general in situ coupling procedure B. Purification by column chromatography (50:1 hexanes: EtOAc) gave **25** (98 mg, 60 % yield) as a dark orange gum. ^1H NMR: $\delta =$ 0.89 (t, $J = 7.2$ Hz, 12H), 1.17 (s, 84H), 1.24 – 1.35 (m, 56H), 1.52 – 1.64 (m, 8H), 2.58 (t, $J = 7.5$ Hz, 8H), 7.09 (dd, $J = 8.1$, 1.6 Hz, 4H), 7.31 (d, $J =$ 1.6 Hz, 4H), 7.45 (d, $J = 8.1$ Hz, 4H), 7.59 (s, 2H); ^{13}C NMR (CD_2Cl_2): $\delta =$ 11.92, 14.47, 19.08, 23.28, 29.79, 29.91, 30.02, 30.14, 30.18, 31.62, 32.49, 36.29, 77.17, 79.19, 81.50, 84.38, 96.38, 105.24, 121.91, 126.01, 127.69, 129.16, 132.87, 133.43, 138.11, 145.67; UV (CH_2Cl_2): λ_{max} (ε) = 280 (79360), 357 (90720), 402 nm (71050); IR (neat): $\tilde{\nu} = 2211$, 2153, 1597, 1465 cm^{-1}; MS (121 mV, FAB positive ions): m/z (%): 1857.3 ([$M^+ + 2H$], 100), 1856.3 (98), 1855.3 (58), 1814.3 (34); $C_{130}H_{182}Si_4$ (1857.18): calcd: C 84.07, H 9.88; found: C 83.80, H 9.75.

Bow tie 3: Dodecayne **25** (98 mg, 0.053 mmol) was deprotected as described in procedure D. Cyclization was performed by using CuCl (200 mg, 40 equiv) and $Cu(OAc)_2 \cdot H_2O$ (350 mg, 40 equiv) in pyridine. After work-up, the reaction mixture was concentrated to give a yellow solid. Trituration with Et_2O afforded **3** (45 mg, 69 % yield) as an amorphous yellow solid. M.p. 220 °C (decomp). ^1H NMR: $\delta = 0.89$ (t, $J = 7.2$ Hz, 12H), 1.24 – 1.35 (m, 56H), 1.58 – 1.69 (m, 8H), 2.65 (t, $J = 7.3$ Hz, 8H), 7.24 (dd, $J = 7.9$, 1.2 Hz, 4H), 7.49 (d, $J = 1.2$ Hz, 4H), 7.60 (d, $J = 7.9$ Hz, 4H), 7.88 (s, 2H); ^{13}C NMR: $\delta = 14.13$, 22.69, 29.20, 29.33, 29.44, 29.53, 29.60, 30.94,

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31.89, 35.82, 77.20, 77.87, 79.19, 80.82, 81.05, 82.73, 122.22, 125.15, 125.33, 129.36, 132.60, 132.80, 136.26, 144.74; UV (CH_2Cl_2): λ_{max} (ε) = 307 (20700), 357 (35400), 375 (48600), 413 (22800), 430 (18000), 369 nm (21100); IR (KBr): $\tilde{\nu}$ = 2198, 1620, 1598, 1446 cm^{-1}; MS (MALDI): $C_{94}H_{98}$ (1227.78): *m*/*z*: 1227.75 [M^+].

Dodecayne 27: 1,2,3,4-Tetraiodobenzene (**26**, 77 mg, 0.133 mmol) was treated with triyne **13** (413 mg, 0.8 mmol) using general in situ coupling procedure B. Purification by Chromatotron (2 mm plate, 50:1 hexanes:CH_2Cl_2) gave **27** (140 mg, 58% yield) as a dark orange gum. ^{1}H NMR (CD_2Cl_2): δ = 0.91 (br t, 12H), 1.11 (s, 42H), 1.16 (s, 42H), 1.23–1.34 (m, 56H), 1.53–1.64 (m, 8H), 2.57 (br t, 8H), 7.04 (br d, *J* = 8.1 Hz, 2H) 7.07 (br d, *J* = 8.1 Hz, 2H), 7.28 (br s, 2H), 7.30 (br s, 2H), 7.40 (s, 2H), 7.43 (d, *J* = 8.1 Hz, 2H), 7.45 (d, *J* = 8.1 Hz, 2H); ^{13}C NMR (CD_2Cl_2): δ = 11.33, 14.13, 18.73, 22.71, 29.25, 29.33, 29.46, 29.58, 29.61, 31.08, 31.90, 35.78, 77.08, 77.28, 77.68, 79.23, 81.17, 83.56, 83.68, 84.05, 95.68, 95.83, 104.60, 104.72, 121.84, 121.99, 126.41, 127.02, 127.18, 128.20, 128.32, 129.07, 132.23 (2), 132.55, 132.79, 133.14, 144.22, 144.43; UV (CH_2Cl_2): λ_{max} (ε) = 351 nm (79780); IR (neat): $\tilde{\nu}$ = 2210, 2157, 1607, 1460 cm^{-1}; $C_{130}H_{182}Si_4$ (1857.18): calcd C 84.07, H 9.88; found C 84.05, H 9.31.

Boomerang 4: Dodecayne **27** (140 mg, 0.075 mmol) was deprotected as described in procedure D. Cyclization was performed using CuCl (300 mg, 40 equiv) and $Cu(OAc)_2 \cdot H_2O$ (545 mg, 40 equiv) in pyridine. Purification by column chromatography on silica gel (9:1 hexanes:CH_2Cl_2) afforded **4** (28 mg, 30% yield) as an amorphous yellow solid. M.p. 192 °C (decomp). ^{1}H NMR (CD_2Cl_2): δ = 0.89 (br t, 12H), 1.20–1.40 (m, 56H), 1.60–1.68 (m 8H), 2.66 (q, *J* = 6.5 Hz, 8H), 7.27 (dd, *J* = 8.0, 1.2 Hz, 2H), 7.34 (dd, *J* = 8.0, 1.2 Hz, 2H), 7.54 (d, *J* = 1.2 Hz, 2H), 7.56 (d, *J* = 1.2 Hz, 2H), 7.62 (d, *J* = 8.0 Hz, 2H), 7.68 (s, 2H), 7.78 (d, *J* = 8.0 Hz, 2H); ^{13}C NMR (CD_2Cl_2): δ = 14.46, 23.27, 29.76, 29.91, 30.00, 30.12, 30.18, 31.54, 32.49, 36.33, 77.49, 77.60, 77.98, 78.05, 78.88, 80.16, 81.27, 81.43, 81.47, 83.24, 83.46, 83.95, 122.50 (2), 125.59 (2), 126.44, 128.61, 130.20 (2), 132.95, 133.15, 133.31, 133.40, 133.67, 145.87, 145.91; UV (CH_2Cl_2): λ_{max} (ε) = 297 (60780), 354 (109820), 370 (119760), 404 (85370), 421 nm (65970); IR (KBr): $\tilde{\nu}$ = 2197, 1593, 1456 cm^{-1}; MS (MALDI): $C_{94}H_{98}$ (1227.78): *m*/*z*: 1227.62 [M^+].

Diiodohexayne 28: 1,2,3,4-Tetraiodobenzene (**26**, 250 mg, 0.43 mmol) was treated with triyne **13** (468 mg, 0.9 mmol, 2.1 equiv) using general in situ coupling procedure B, performed at room temperature. Purification by Chromatotron (2 mm plate, 50:1 hexanes:CH_2Cl_2) furnished *para*-coupled product **28** (345 mg, 66% yield) as an amorphous yellow solid. M.p. 105–107 °C. ^{1}H NMR: δ = 0.88 (br t, 6H), 1.17 (s, 42H), 1.25–1.35 (m, 28H), 1.50–1.60 (m, 4H), 2.59 (br t, 4H), 7.10 (dd, *J* = 8.1, 1.5 Hz, 2H), 7.32 (d, *J* = 1.5 Hz, 2H), 7.40 (s, 2H), 7.44 (d, *J* = 8.1 Hz, 2H); ^{13}C NMR: δ = 11.35, 14.16, 18.82, 22.71, 29.29, 29.34, 29.46, 29.58, 29.62, 31.05, 31.92, 35.81, 76.43, 80.10, 84.34, 84.48, 95.74, 104.74, 115.50, 121.55, 127.16, 128.44, 130.52, 132.18, 132.34, 132.82, 144.68; IR (KBr): $\tilde{\nu}$ = 2210, 2157, 1554, 1460 cm^{-1}; $C_{68}H_{92}Si_2I_2$ (1219.45): calcd: C 66.98, H 7.60; found: C 66.82, H 7.46.

Tetradecayne 29: Diiodohexayne **28** (100 mg, 0.082 mmol) was coupled with tetrayne **14** (233 mg, 0.32 mmol, 4 equiv) using general in situ coupling procedure B. Purification by Chromatotron (2 mm plate, 50:1 hexanes: EtOAc) gave polyyne **29** (95 mg, 52% yield) as an orange gum. ^{1}H NMR: δ = 0.89 (br t, 12H), 1.08 (s, 84H), 1.14 (s, 42H), 1.23–1.38 (m, 56H), 1.53–1.64 (m, 8H), 2.25–2.61 (m, 8H), 7.06 (dd, *J* = 8.4, 1.5 Hz, 2H), 7.22 (s, 4H), 7.29 (d, *J* = 1.5 Hz, 2H), 7.39 (s, 2H), 7.42 (d, *J* = 8.4 Hz, 2H); ^{13}C NMR:[23] δ = 11.31, 14.13, 18.73, 29.24, 29.28, 29.34, 29.46, 29.61, 31.05, 31.61, 31.91, 35.54, 35.78, 77.25, 78.27, 79.28, 81.18, 81.23, 82.61, 83.56, 83.64, 95.58, 96.08, 104.19, 104.76, 121.92, 124.46, 126.69, 127.17, 127.73, 128.25, 128.69, 132.10, 132.22, 132.56, 132.64, 143.47, 144.30; UV (CH_2Cl_2): λ (ε) = 335 (130250), 357 nm (185280); IR (neat): $\tilde{\nu}$ = 2210, 2157, 1587, 1547, 1467 cm^{-1}; $C_{152}H_{222}Si_6$ (2217.90): calcd: C 82.31, H 10.09; found: C 82.54, H 9.80.

Half wheel 5: Dodecayne **29** (85 mg, 0.038 mmol) was deprotected as described in general procedure D. Cyclization was performed with 60 equiv each of CuCl and $Cu(OAc)_2 \cdot H_2O$. Purification by passing through a short plug of silica gel (CH_2Cl_2) followed by evaporation and trituration with Et_2O afforded **5** (31 mg, 65% yield) as a yellow solid. M.p. 218 °C (decomp). ^{1}H NMR (1:1 CS_2/CD_2Cl_2): δ = 0.91 (m, 12H), 1.26–1.42 (m, 56H), 1.64–1.74 (m, 8H), 2.63–2.74 (m, 8H), 7.55 (d, *J* = 1.2 Hz, 2H), 7.61 (dd, *J* = 7.8, 1.2 Hz, 2H), 7.62 (s, 2H), 7.63 (d, *J* = 7.8 Hz, 2H), 7.74 (s, 2H); ^{13}C NMR[23] ([D$_8$]THF): δ = 14.62, 23.76, 26.55, 30.42, 30.45, 30.49, 30.62, 30.72, 30.78, 30.89, 32.01, 32.14, 35.27, 36.51, 36.70, 78.19, 78.47, 78.99, 79.24, 80.46, 80.51, 80.90, 81.32, 81.89, 81.91, 82.10, 82.49, 83.66, 83.94, 123.17, 125.98, 126.07, 126.17, 126.55, 126.71, 126.87, 129.30, 130.93, 133.48, 133.94, 134.12, 134.60, 146.13, 146.41; UV (CH_2Cl_2): λ_{max} (ε) = 322 (91850), 360 (115950), 366 (117570), 411 (66600), 426 nm (57370); IR (KBr): $\tilde{\nu}$ = 2200, 1584, 1544, 1464 cm^{-1}; MS (MALDI): $C_{98}H_{96}$ (1273.81): *m*/*z*: 1273.47 [M^+].

Hexayne 30: Triazene **21** (130 mg, 0.23 mmol) was treated with triyne **13** (265 mg, 0.51 mmol) according to general in situ coupling procedure B. Purification by column chromatography (50:1 hexanes:EtOAc) provided hexayne **30** (217 mg, 78% yield) as a dark yellow gum. ^{1}H NMR: δ = 0.89 (br t, 9H), 1.17 (s, 42H), 1.25–1.30 (m, 48H), 1.56–1.62 (m, 6H), 2.57 (t, *J* = 7.5 Hz, 6H), 3.82 (q, *J* = 7.0 Hz, 4H), 7.07 (dd, *J* = 7.5 Hz, 1.5 Hz, 2H), 7.29 (br s, 4H), 7.38 (d, *J* = 7.8 Hz, 2H); ^{13}C NMR:[23] δ = 11.32, 14.11, 18.71, 22.67, 29.02, 29.25, 29.31, 29.36, 29.43, 29.51, 29.55, 29.58, 29.67, 29.71, 30.99, 31.09, 31.89, 31.92, 34.84, 35.72, 42.01, 49.15, 76.92, 77.74, 80.41, 81.26, 95.24, 104.97, 115.04, 122.48, 126.87, 128.31, 132.26, 132.53, 134.99, 138.57, 143.83, 154.54; IR (neat): $\tilde{\nu}$ = 2209, 2152, 1465 cm^{-1}.

Iodohexayne 31: Hexayne **30** (148 mg, 0.12 mmol) was treated with iodomethane as described in general procedure C. Purification by column chromatography (20:1 hexanes:EtOAc) gave iodohexayne **31** (69 mg, 47% yield) as an orange syrup. ^{1}H NMR: δ = 0.88 (br t, 9H), 1.19 (s, 42H), 1.25–1.32 (m, 42H), 1.52–1.65 (m, 6H), 2.58 (t, *J* = 7.5 Hz, 6H), 7.09 (dd, *J* = 8.1 Hz, 1.5 Hz, 2H), 7.27 (s, 2H), 7.31 (d, *J* = 1.5 Hz, 2H), 7.44 (d, *J* = 8.1 Hz, 2H); ^{13}C NMR: [22] δ = 11.34, 14.13, 18.80, 22.69, 29.02, 29.26, 29.32, 29.36, 29.43, 29.55, 29.59, 29.67, 31.05, 31.93, 35.77, 76.73, 77.80, 82.32, 83.28, 95.59, 103.13, 104.81, 121.11, 127.11, 128.40, 130.05, 132.30, 132.70, 134.01, 142.94, 144.42; IR (neat): ν = 2216, 2153, 1598, 1464 cm^{-1}.

Decayne 32: Iodohexayne **31** (47 mg, 0.038 mmol) was treated with tetrayne **14** (35 mg, 0.05 mmol) as described in general procedure B. Purification by preparative TLC (hexanes) afforded **32** (25 mg, 38% yield) as a dark orange gum. ^{1}H NMR: δ = 0.89 (br t, 12H), 1.11 (s, 42H), 1.14 (s, 42H), 1.25–1.32 (m, 56H), 1.55–1.68 (m, 8H), 2.50–2.64 (m, 8H), 7.05 (dd, *J* = 8.1 Hz, 1.5 Hz, 2H), 7.23 (s, 2H), 7.28 (d, *J* = 1.5 Hz, 2H), 7.30 (s, 2H), 7.41 (d, *J* = 1.5 Hz, 2H); ^{13}C NMR: [23] δ = 11.31, 14.13, 18.72, 22.69, 29.10, 29.23, 29.31, 29.36, 29.44, 29.56, 29.59, 29.67, 29.70, 30.63, 31.06, 31.88, 31.93, 35.36, 35.53, 35.75, 77.32, 78.66, 79.10, 79.64, 81.43, 81.73, 82.13, 82.21, 95.43, 96.02, 104.27, 104.81, 122.07, 124.80, 125.02, 126.36, 127.12, 127.56, 128.26, 132.05, 132.18, 132.72, 133.81, 143.33, 143.27, 144.11; UV (CH_2Cl_2): λ_{max} (ε) = 291 (57710), 340 (56230), 364 nm (35840); IR (neat): $\tilde{\nu}$ = 2212, 2154, 1598, 1546, 1463, cm^{-1}.

Diamond 6: Decayne **32** (25 mg, 0.014 mmol) was cyclized using procedure D with 40 equiv each of CuCl and $Cu(OAc)_2 \cdot H_2O$. After work-up, the reaction mixture was dried over $MgSO_4$, and filtered though a bed of celite. Removal of the solvent resulted in the precipitation of the product as a yellow powder. The product was purified by preparative TLC (9:1 hexanes:CH_2Cl_2) to give **6** as a yellow solid (14 mg, 88% yield). M.p. 165 °C (decomp). ^{1}H NMR (CD_2Cl_2): δ = 0.89 (br t, 12H), 1.21–1.39 (m, 56H), 1.58–1.70 (m, 8H), 2.62–2.72 (m, 8H), 7.29 (dd, *J* = 7.9 Hz, 1.5 Hz, 2H), 7.54 (d, *J* = 1.5 Hz, 2H), 7.58 (s, 2H), 7.60 (s, 2H), 7.62 (d, *J* = 7.9 Hz, 2H); ^{13}C NMR[23] (CD_2Cl_2): δ = 14.46, 23.26, 29.68, 29.75, 29.90, 29.94, 29.99, 30.11, 30.12, 30.16, 30.23, 31.38, 31.54, 32.50, 32.47, 36.12, 36.29, 77.56, 77.73, 78.44, 78.55, 80.58, 80.68, 80.97, 81.08, 81.79 (3C), 81.90, 122.67, 125.30, 125.74, 125.90, 125.94, 126.02, 130.28, 133.38 (3C), 133.66, 133.80, 145.04, 145.61; UV (CH_2Cl_2): λ_{max} (ε) = 302 (84900), 328 (124510), 349 (178080), 362 (87310), 378 (64070), 390 (41970), 410 nm (21370); IR (KBr): $\tilde{\nu}$ = 2216, 2193, 1583, 1539, 1465, 1423 cm^{-1}. MS (MALDI) $C_{84}H_{94}$ (1103.65): *m*/*z*: 1103.78 [M^+].

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