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Synthetic Routes toward Carborane-Wheeled Nanocars

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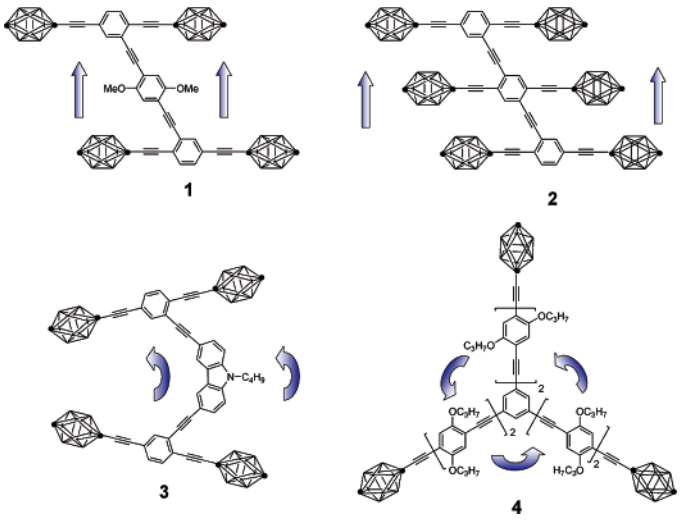

A new set of aryleneethynylene derivatives bearing three, four, and six *p*-carboranes as potential wheels attached to a semirigid chassis have been designed and synthesized. These molecules are expected to move in predetermined patterns on atomically smooth surfaces, depending on their specific configuration.

Introduction

The development of microscopy tools, particularly scanning tunneling microscopy (STM), has allowed scientists to study biological[1] and artificial[2] molecular machines on surfaces. The quickly expanding field of nanomachines has been reviewed.[3] Because translational motion is the easiest to monitor by STM, much effort has been devoted to observe single molecule translational movement on flat metallic surfaces. For instance, a family of molecular barrows with triptycene moieties as wheels has been developed.[4] Although these molecules can be imaged and manipulated by STM in the direction perpendicular to the axles, calculations suggest sliding rather than rolling of the molecules due to the lack of positive interactions with the surface.[4a] Furthermore, other molecules have been imaged to slide or migrate across surfaces.[5] To improve directionality, four fullerene-wheeled nanocars were recently synthesized by our group.[3a,6] Fullerene's spherical and smooth shape, and most importantly its affinity toward gold surfaces, have produced directional rolling motions of the nanocars on the gold surface upon heating or electrostatic control.[6a] However, synthetic

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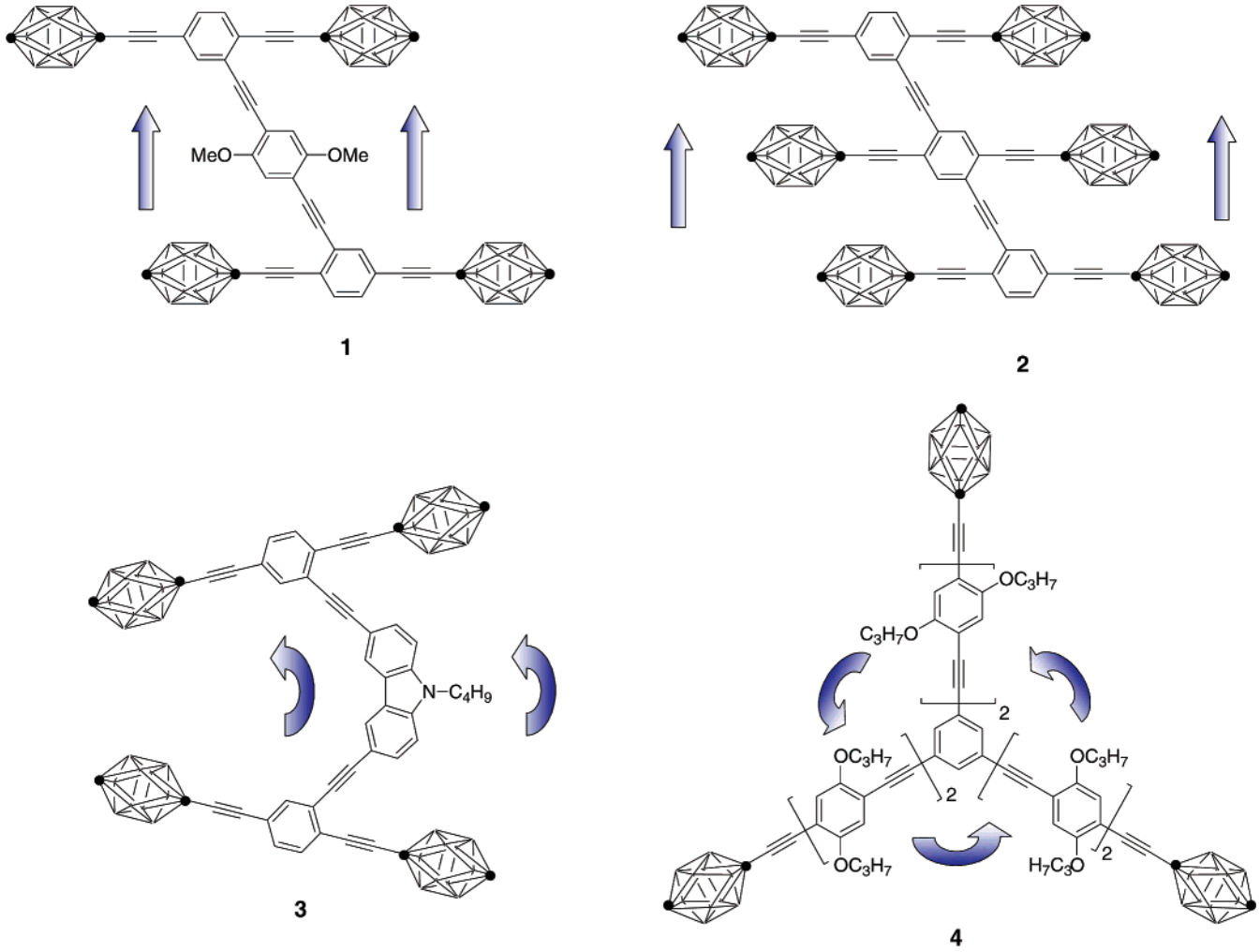

FIGURE 1. Molecular structures of **1**−**4** and the expected directionality of motion.

problems arise when using fullerenes. First, fullerenes and fullerene-containing molecules have very poor solubility. Long alkyl chains are incorporated to alleviate the solubility problems, but in return this addition increases the number of synthetic steps required to construct the nanocar. Second, because of their tendency to deactivate metal-catalyzed reactions, fullerenes have to be introduced onto the nanocar at the final step of the synthesis, resulting in a low-yielding tetra-substitution reaction. Additionally, the electronic nature of fullerene makes it unsuitable for the development of more complex nanomachines with use of light as the power input due to the rapid energy transfer to the fullerenes.[7]

We report here the synthesis of four different nanovehicles: nanocars **1** and **3**, nanocaterpillar **2**, and trimer molecule **4**, all bearing *p*-carboranes (Figure 1). *p*-Carborane was our choice for the potential development of rolling molecules because of its spherical shape and its aromatic nature[8] that allow for easy substitution reactions at one or both of the carbon atoms positioned para to each other.[9] Moreover, they are robust, and unlike fullerenes, are very soluble in common organic solvents, thus allowing for the synthesis of smaller molecular machines in fewer synthetic steps. Last, carboranes can be introduced at any stage of the synthesis because they do not inhibit organometallic coupling reactions (unlike fullerenes). The work presented here is an extension of our previous work on the fullerene-containing nanocar[3a,6] and the first step toward development of easily accessible functional nanomachines to address molecular rolling on surfaces. As shown in Figure 1, molecules **1**−**4** are designed to move in specific patterns on the surface. Nanocar **1** and nanocaterpillar **2** are expected to translate in a one-dimensional fashion since the axles are parallel to each other. The difference in the number of wheels will assist in the dimensional analysis of the molecules sliding or rolling on the surface by STM. Nanocar **3** was designed to make small circular motions on the surface. This movement could be useful for monitoring surface motion by using the STM.[6a] Trimer **4** was designed to pivot on

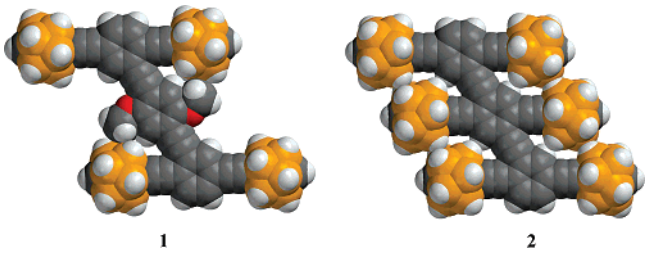

FIGURE 2. CPK models of planar conformations of **1** and **2**.

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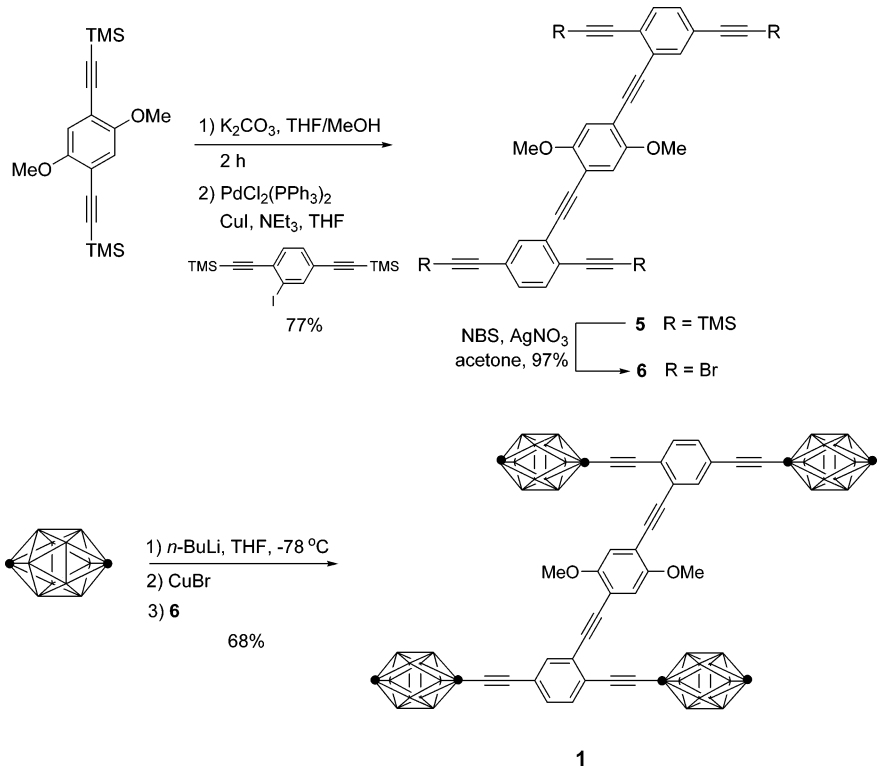
SCHEME 1. Synthesis of the Nanocar 1[a]



[a] Every vertex on the starting carborane is BH except the darkened sites that are CH. The product nanocar, **1**, has the internal carborane carbon alkynyl-substituted.

the surface with no translational movement, analogous to the pattern observed for the related fullerene trimers.[3a,6]

Results and Discussion

Synthesis. Two different strategies were used to synthesize nanocar **1** and nanocaterpillar **2**. For **1**, the four wheels were introduced at the end of the synthetic pathway on the tetra-(bromoalkyne) moiety. On the other hand, the wheels on **2** were coupled to the axle prior to the synthesis of the central part of the chassis. This allowed us to compare both routes in terms of synthetic feasibility and efficiency.

In Scheme 1, the methoxy groups were installed to increase the polarity of the molecules, which was necessary in order to chromatographically separate the large excess of nonpolar unreacted *p*-carborane from the desired product. The starting compound 1,4-dimethoxy-2,5-bis(trimethylsilylacetylene)benzene was synthesized in two steps following known procedures.[10,11] The alkynes were then deprotected. Due to the unstable nature of the free alkyne intermediate, the deprotection step was carried out immediately prior to the coupling with the 1-iodo-2,5-bis(trimethylsilyacetylene)benzene that was previously synthesized.[7] The four TMS protecting groups were removed by desilyl bromination[12] to give **6** in good yield. Finally, the *p*-carborane moieties were introduced at the four bromoalkyne positions to give **1** in 68% yield. The nanocar **1** is quite soluble in common organic solvents such as chloroform, acetone, THF, and toluene. Thermogravimetric analysis (TGA) was performed on **1** to obtain information on its thermal stability. At a scan rate of 20 deg/min (under N_2), gradual decomposition of **1** from its original mass was observed around 390 °C. This result suggests that the alkyne−carborane bond is stronger and more stable than the alkyne−fullerene bond, which showed decomposition around 300 °C upon heating, and these data will be essential as substrate heating[6] is used to propel the nanocars.

A CPK model of the planar conformation of **1** was generated by using Spartan X. As shown in Figure 2, the wheel-to-wheel distance for **1** is approximately 14 Å in both directions (parallel and perpendicular to the axles), meaning that **1** is nearly a square molecule. Although **1** is one of the simplest nanocars we can synthesize, the square configuration limits its usefulness for STM studies. Since we can only image the wheels and not the inner chassis due to the relative differences in their density of states, we will not be able to distinguish the orientation of **1** on the surface. Thus addressing directionality will be even more difficult.

To bypass this problem, nanocaterpillar **2**, with three axles rather than two, was synthesized. The CPK model (Figure 2) of the planar conformation of **2** shows minimal spacing between the aligned carborane wheels. The UV data, explained in the latter section, confirm the steric hindrance between the wheels that might lead to problems for surface rolling. The strategy used for the synthesis of **2** is depicted in Scheme 2.

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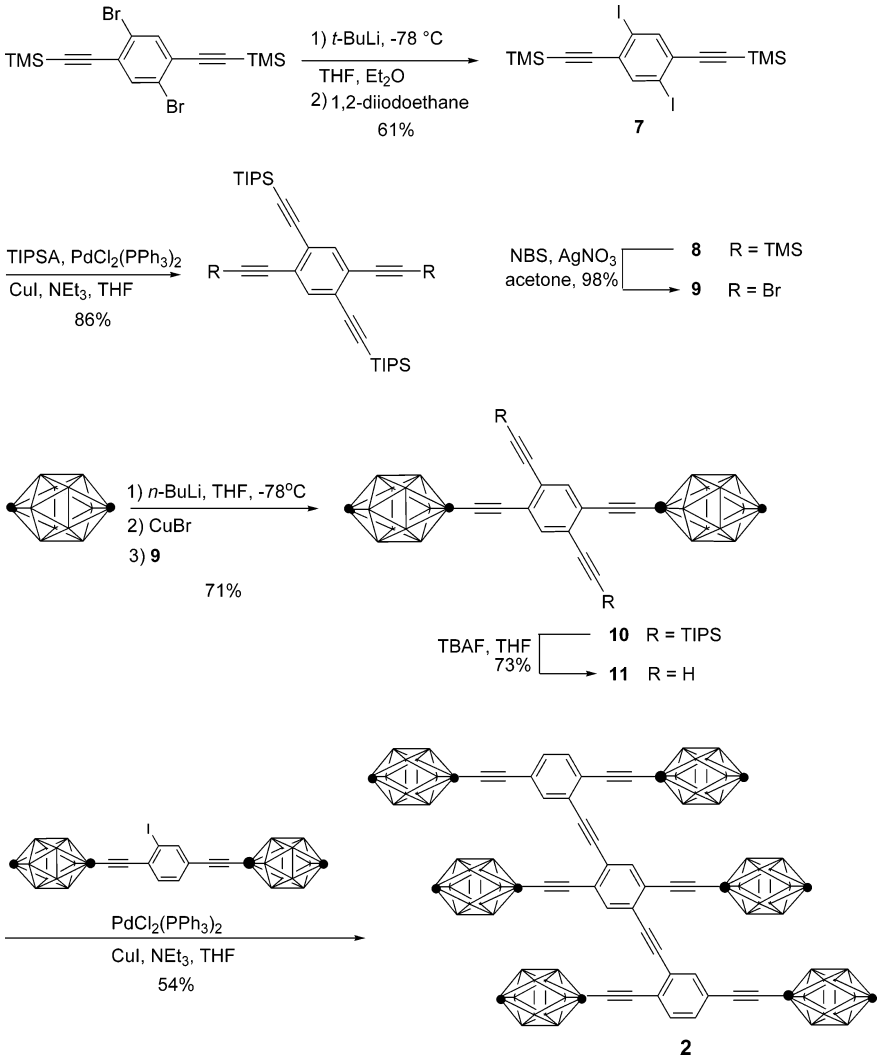
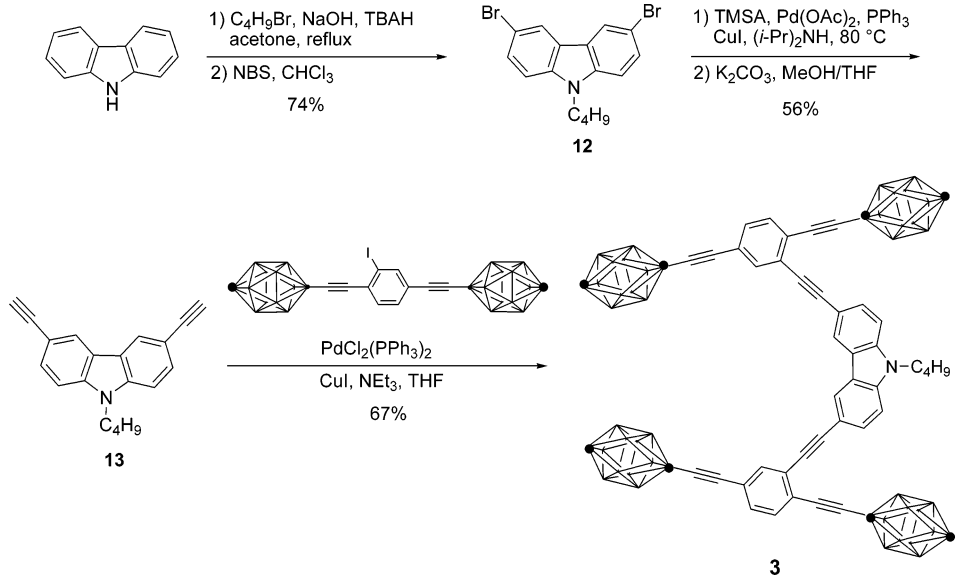
SCHEME 2. Synthesis of the Nanocaterpillar 2



SCHEME 3. Synthesis of the "Curved" Nanocar 3



Following known procedures,[13,14] 1,4-dibromo-2,5-bis(trimethylsilylacetylene)benzene was synthesized in two steps from 1,4-dibromobenzene. The bromides were replaced by iodides by using *tert*-butyllithium followed by 1,2-diiodo-

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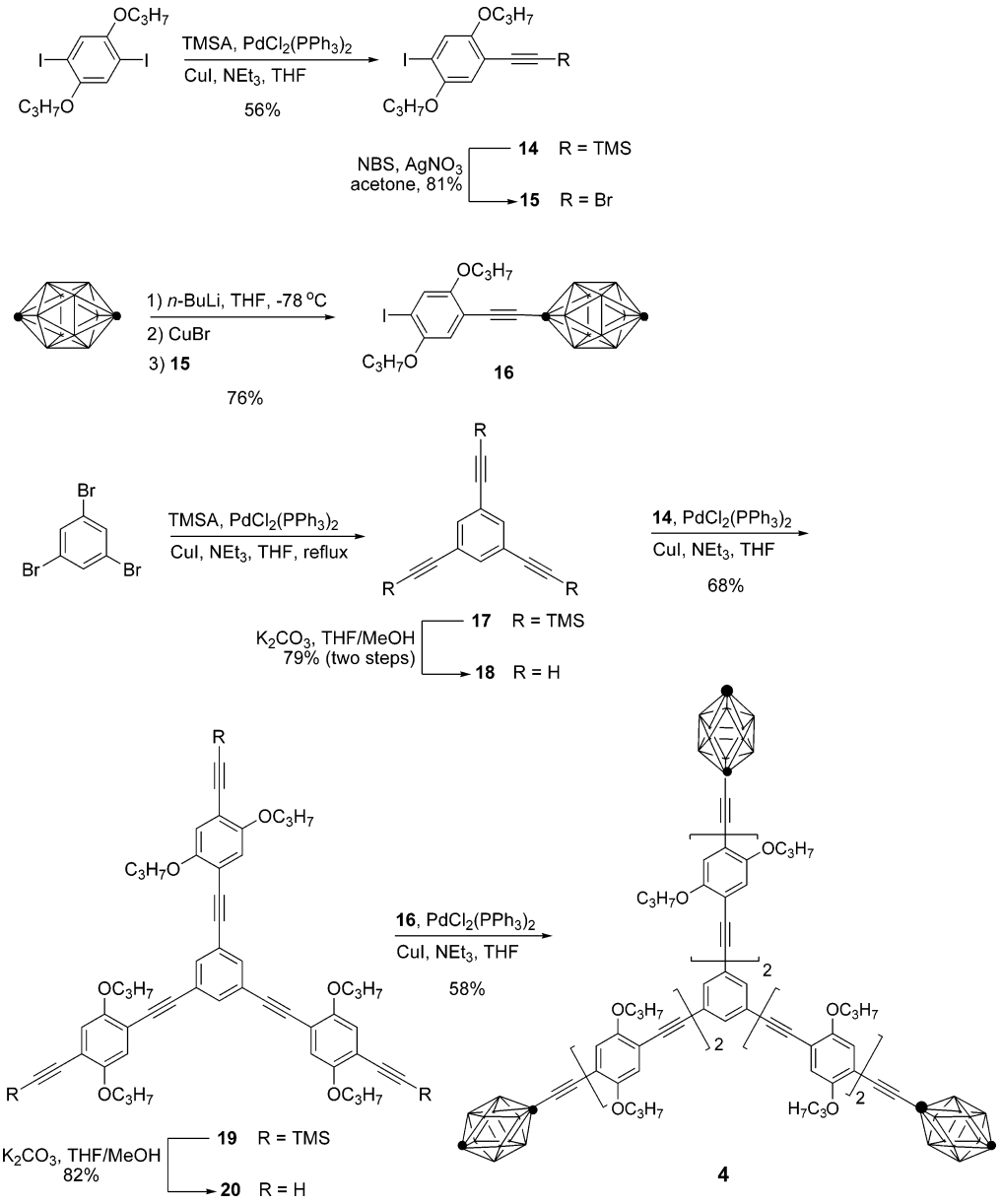
SCHEME 4. Synthesis of the Trimer 4, Designed To Rotate about Its Center on the Surface



ethane. This step was necessary in order to perform the Sonogashira coupling reaction between the iodide-containing axle and the central chassis.[15] The TIPS-acetylene groups were introduced on **7** by standard Sonogashira coupling to provide **8** in good yield. Selective desilyl bromination of the TMS-acetylene groups[12b] was achieved by using NBS and $AgNO_3$ in acetone to give **9** in almost quantitative yield. The *p*-carborane wheels were introduced to give **10** followed by deprotection of the TIPS-acetylene groups. The resulting **11** was then coupled with wheel/axle (1-iodo-2,5-bis(*p*-carboraneacetylene)benzene)[7] to give the nanocaterpillar **2**. As with **1**, **2** is also soluble in common organic solvents.

The wheel/axle (1-iodo-2,5-bis(*p*-carboraneacetylene)benzene)[7] is a versatile tool and can be used in combination with several different chassis to create nanovehicles having specific conformations for accomplishing different tasks, hence Scheme 2 is preferable over Scheme 1. In this regard, we synthesized nanocar **3** (Scheme 3), which is expected to move in a circular motion due to its "curved" conformation (Figure 1). The chassis **13** of nanocar **3** bearing two terminal alkynes was synthesized in four straightforward steps.[16] Compound **13** was then coupled to the wheel/axle to give nanocar **3** in 67% yield.

The CPK models of **3** and **4** (Figure 3) were modeled by Spartan X. Despite the "curved" feature of the inner chassis of **3**, the model shows no overlapping of the inner carborane wheels. Unlike **1**, the distances perpendicular and parallel to the axis are distinct. This will allow for an easier assessment of molecular orientation and movement on the surface. Trimer **4** was designed to rotate on the surface with the center of rotation coincident with the center of the molecule. A similar molecule, bearing fullerene wheels instead of *p*-carborane, proved to be

(15) *Caution*: It is known that 1,2-dialkynyl benzene derivatives can decompose or explode violently upon heating.

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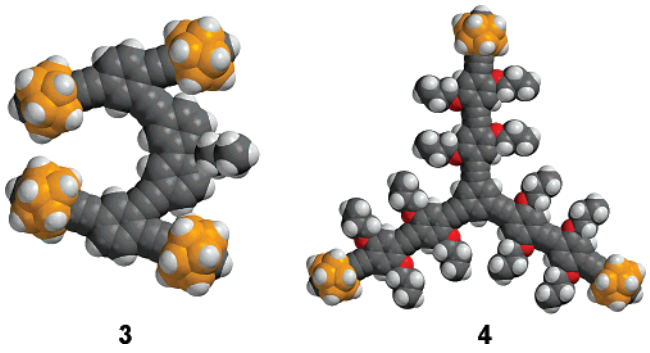

FIGURE 3. CPK models of planar conformations of **3** and **4**.

useful in studying the pivot-rolling mechanism with STM, since it did not show translational movement on a gold surface.[6a]

To synthesize **4** (Scheme 4), we first tried a linear strategy involving the successive addition of phenylacetylene moieties onto a 1,3,5-trisubstituted benzene ring followed by addition of the three carborane wheels. However, we found that desilyl bromination of the long oligo(phenylene ethynylene) (OPE) gave a low yield and led to various side products. Compound **4** was instead synthesized by using a convergent strategy involving a triangular central part and a carborane-containing substituted phenylacetylene moiety. Thus, the triangular core was synthesized in two steps from 1,3,5-dibromobenzene by using a Sonogashira coupling reaction followed by a deprotection reaction to provide **18** in 79% overall yield.[17] Compound **18** was then coupled to **14**, synthesized in three steps from hydroquinone,[18] using the Sonogashira coupling reaction to afford **19** in 68% yield. The carborane-containing moiety was synthesized in two steps from 1,4-bis(propyloxy)-2,5-diiodobenzene[19] by desilyl bromination[12] followed by reaction with carborane−copper adduct as described above. In this case, the latter reaction proceeded slowly and 48 h were necessary for the reaction to be completed. This can be attributed to the electron-donating nature of the propyloxy groups present on the phenyl ring that partially deactivate the alkynyl bromide toward oxidative addition. Compound **20** was then coupled to **16** to give **4** in good yield.

Optical Properties. There are few reports on the optical properties of carborane-containing conjugated molecules; therefore, the optical properties of molecules **1**−**4** were investigated by using solution phase absorption and fluorescence spectroscopy. As an alternative to STM, it is possible that the optical properties could be exploited to image these molecules on a nonmetallic surface by using fluorescence, hence these studies are essential. As shown in Figure 4, **1**−**4** absorb light in the regions λ_{max} = 375−410 nm, as commonly observed for OPEs containing three phenyl rings.[20] Compound **4** absorbs light at the longest wavelength out of the four (λ_{max} = 410 nm), which can be attributed to the electron-donating nature of the four propyloxy groups and the increased conjugation length of the

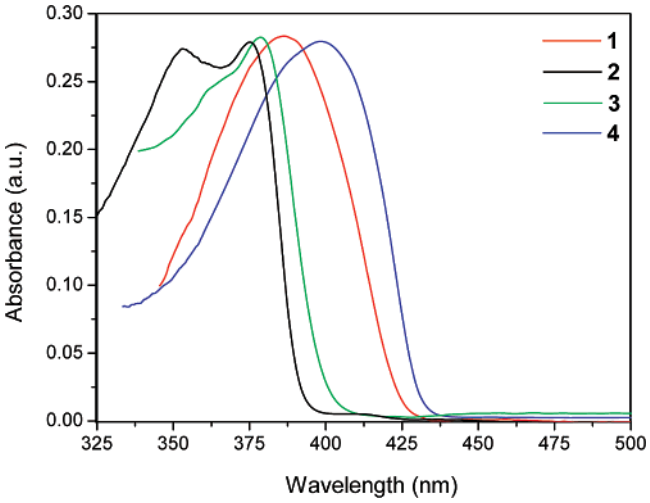

FIGURE 4. UV−visible absorption spectra of **1**−**4** (1.0×10^{-5} M) in chloroform.

OPE. Electron-donating substituents are known to increase the energy of the HOMO level and, consequently, the band gap of π-conjugated systems. A portion of this effect can be attributed to the aromatic character of carborane,[8] acting to extend the conjugated length of the molecule. Next, compound **1** (λ_{max} = 385 nm) is further red-shifted than **2** and **3** due to again the electron-donating methoxy groups. However, lower conjugation of this molecule results in a shorter wavelength than that of compound **4**. Compound **3** contains no significant electron-withdrawing groups, resulting in a shorter wavelength. The interesting feature is that the spectrum of **3** shows a slight absorbance at ~362 nm, which may indicate a rigid conformation.[21] On the other hand, the UV−visible spectrum of **2** is blue-shifted compared to **1**, **3**, and **4**. This blue shift can be attributed to the steric hindrance between carborane wheels of different axles, which leads to a high dihedral angle between phenyl rings of the molecule's core, thereby possibly limiting its usefulness on a surface. However, the surface−carborane attraction might be sufficient to make the system planar; therefore we are waiting expectantly the surface analyses. Additionally, the UV−visible spectrum of **2** shows two distinct maxima (353 and 375 nm) indicating that **2** adopts a rigid conformation in its ground state. This type of vibronic structure is frequently observed in cases of rigid ladder-shaped molecules.[21] The energy difference between the two maxima (about 0.20 eV) is consistent with a C═C stretching mode that would be expected to couple strongly to the electronic structure.[22] In comparison, **1**, **3**, and **4** do not show significant vibronic structure, indicating that they have a fairly flexible conformation in the ground state.

To determine the specific effect of the carboranes on the optical properties of conjugated molecules, UV−visible spectra of **1** and its TMS-substituted precursor **5** were compared. As expected, the λ_{max} of **1** (386 nm) is red-shifted compared to its precursor **5** (379 nm). This can be attributed to an increase in the conjugation length of the molecule containing carborane, therefore underscoring the conjugation effect of the carboranes.

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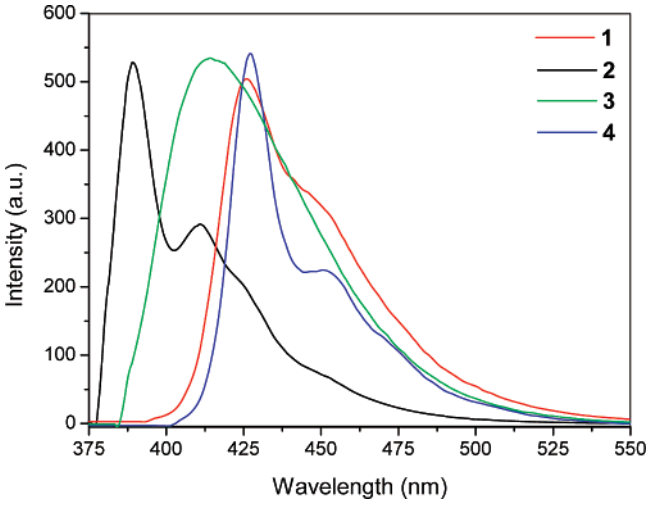

FIGURE 5. Fluorescence spectra of **1**−**4** (1.0×10^{-7} M) in chloroform.

TABLE 1. Optical Properties of Compounds 1−4

compd	Abs (λ_{max})[a]	Emi (λ_{max})[a]	E_g (eV)[b]
1	386	426	2.89
2	375 (353)	389 (411)	3.14
3	379	414	3.05
4	399	427 (451)	2.85

[a]Spectra in chloroform. [b]Band gap (optical), determined from the lower energy onset of the absorption spectra.

The electron-withdrawing nature of carborane can be part of an intramolecular charge-transfer complex with the 1,4-dimethoxy moiety of the core, decreasing the band gap. Furthermore, the introduction of carborane does not induce significant steric hindrance between the two axles since both spectra have a similar shape with no vibronic structure.

The fluorescence properties of **1**−**4** were investigated with the results summarized in Figure 5 and Table 1. As expected, all four compounds fluoresce in chloroform in the UV-blue region. The wavelength of the emission maxima increases in the order of **2** < **3** < **1** < **4** reflecting the extent of conjugation plus the influence of electron-rich moieties of the propoxyl, methoxyl, and butyl carbazole groups. A reversed result is seen with the band gap (optical, E_g, from the lower energy onset of the absorption spectra) in the order of **4** < **1** < **3** < **2**, as expected. Interestingly, **2** and **4** show fine vibronic structure, generally associated with a rigid conformation in the excited state. The small Stoke shift observed for compound **2** (14 nm) is characteristic of a molecule having a rigid conformation.[23] Table 1 summarized the optical data.

Conclusion

The design and the synthesis of four potential nanovehicles bearing *p*-carborane as wheels is reported. The use of *p*-carboranes overcomes several synthetic problems observed in fullerene-wheel nanovehicles: no long-chain alkyl groups are necessary to obtain soluble structures and addition of the wheels at different stages in the synthesis is possible. STM imaging analysis of the **1**−**4** is underway to investigate the movement of these nanovehicles on a metallic surface. The synthesis of more complex functional nanomachines is also underway.

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Experimental Procedures

General Synthetic Methods. ^{1}H NMR and ^{13}C NMR spectra were recorded at 400 and 100 MHz, respectively. Proton chemical shifts (δ) are reported in ppm downfield from tetramethylsilane (TMS). Mass spectrometry was performed at the Rice University and University of South Carolina Mass Spectrometry Laboratory. Infrared spectra (IR) assignments have 2 cm^{-1} resolution. Reagent grade tetrahydrofuran (THF) and diethyl ether (Et_2O) were distilled from sodium and benzophenone under a N_2 atmosphere. Triethylamine (NEt_2) and CH_2Cl_2 were distilled from CaH_2 under N_2 atmosphere unless otherwise stated. THF and NEt_2 were degassed with a stream of argon for 1 h before being used in the Castro−Stephens−Sonogashira coupling. All other reagents were purchased from commercial suppliers and used without further purification. Trimethylsilylacetylene (TMSA) was donated by FAR Research Inc. or Petra Research. *n*-BuLi 1.7 M in pentane, and *t*-BuLi 2.5 M in hexanes from Sigma-Aldrich Co. were used. Flash chromatography was carried out with silica gel (grade 60, mesh size 230−400, EM science). Thin layer chromatography (TLC) was performed with use of glass silica gel plates (40 F_{254} 0.25 mm layer thickness, Merck). Melting points were measured on a Mel-Temp instrument (uncorrected). All reactions were conducted under a dry oxygen-free atmosphere with oven-dried glassware unless otherwise stated. $PdCl_2(PPh_3)_2$,[1] 1,4-dimethoxy-2,5-diiodobenzene,[5] 1,4-dimethoxy-2,5-bis(trimethylsilylacetylene)benzene,[6] 1,4-dibromo-2,5-diiodobenzene,[7] 1,4-dibromo-2,5-bis(trimethylsilylacetylene)benzene,[8] and 1,4-bis(propyloxy)-2,5-diiodobezene[9] were prepared using literature procedures.

General Procedure for the Palladium-Catalyzed Coupling Reaction of Terminal Alkynes and Aryl Bromides or Aryl Iodides (Castro−Stephens−Sonogashira Coupling). An oven-dried round-bottomed flask equipped with a magnetic stir bar was charged with the terminal alkyne (1 equiv), aryl halide (1 equiv), $PdCl_2(PPh_3)_2$ (3−5 mol % per halide), CuI (6−10 mol % per halide), triethylamine (4 equiv per halide), and THF ([aryl halide] = 0.1−0.3 M). If the halide was an aryl iodide, the mixture was stirred at room temperature for 24 h. In the case of an aryl bromide, PPh_3 (6−10 mol % per halide) was added and the mixture was stirred at 70 °C for the same period of time. After that period, saturated NH_4Cl was added and the mixture was extracted twice with dichloromethane. The combined organic layers were washed with water and dried over $MgSO_4$. The mixture was filtered, the solvent was removed, and the desire product was isolated with column chromatography (silica gel as stationary phase) to provide the product.

General Procedure for Deprotection of Trimethylsilyl-Protected Alkynes. In a round-bottomed flask equipped with a magnetic stir bar, the protected alkyne was dissolved in a mixture of THF and MeOH ([protected alkyne] = 0.05−0.1 M). Then, K_2CO_3 (2 equiv per alkyne) was added. The mixture was stirred at room temperature for 2 h or until the reaction was complete (monitored by TLC). After that period, brine was added and the mixture was extracted twice with dichloromethane. The combined organic layers were washed with water and dried over $MgSO_4$. The solvent was removed and the desired product was isolated with column chromatography (silica gel as the stationary phase) to provide the product.

1,4-Dimethoxy-2,5-bis[(2′,5′-trimethylsilylacetylenebenzene)-acetylenebenzene] (5). A 100 mL round-bottomed flask equipped with a magnetic stirrer was charged with 1,4-dimethoxy-2,5-(trimethylsilylacetylene)benzene[10,11] (0.75 g, 2.27 mmol), K_2CO_3 (1.26 g, 9.07 mmol), THF (25 mL), and MeOH (25 mL). The mixture was stirred at room temperature for 2 h and poured into water. The mixture was extracted three times with dichloromethane and the combined organic layers were washed twice with water

and dried over $MgSO_4$. The solvent was removed under reduced pressure to provide a yellow solid that was used for the Sonogashira coupling without further purification. See general procedure for Castro−Stephens−Sonogashira coupling. The compounds used were 1,4-dimethoxy-2,5-diacetylenebenzene (100 mg, 0.54 mmol), **5** (639 mg, 1.61 mmol), CuI (10.2 mg, 0.05 mmol), $PdCl_2(PPh_3)_2$ (18.8 mg, 26.8 μmol), well-degassed dry triethylamine (0.6 mL), and THF (5 mL) at room temperature for 16 h. The resulting orange brown solid was purified by column chromatography (silica gel, 25% dichloromethane in hexanes as eluent) to provide 300 mg of the desired product as a white amorphous solid (77%): mp 199−201 °C; IR (KBr) 2955, 2155, 1503, 1248, 843, 858, 759 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, ppm) δ 7.67 (dd, J = 1.6 and 0.4 Hz, 2H), 7.43 (dd, J = 8.1 and 0.4 Hz, 2H), 7.33 (dd, J = 8.1 and 1.7 Hz, 2H), 7.03 (s, 2H), 3.88 (s, 6H), 0.253 (s, 18H), 0.251 (s, 18H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 154.2, 135.5, 132.3, 131.3, 126.3, 125.3, 123.3, 116.1, 113.8, 103.9, 103.3, 100.8, 97.1, 93.0, 90.2, 56.7, 0.1, 0.0; HRMS calcd for $C_{44}H_{50}O_2Si_4$ 722.2888, found 722.2884.

1,4-Dimethoxy-2,5-bis[(2′,5′-bromoacetylenebenzene)acetylenebenzene] (6). A 25 mL round-bottomed flask equipped with a magnetic stirrer was charged with **5** (100 mg, 0.14 mmol) and acetone (10 mL). Then, freshly purified and dried *N*-bromosuccinimide (113 mg, 0.64 mmol) and $AgNO_3$ (2.3 mg, 13.8 μmol) were added in order. The mixture was stirred in the dark at room temperature for 2 h and poured into methanol (100 mL). After 5 min of vigorous stirring, the yellow precipitate formed was collected by filtration, rinsed thoroughly with water followed by MeOH, and dried under reduced pressure for 24 h to provide 101 mg of **6** as a bright yellow solid (97%): mp >250 °C; IR (KBr) 1509, 1482, 1458, 1381, 1281, 1222, 1208, 1037, 830 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, ppm) δ 7.65 (d, J = 1.4 Hz, 2H), 7.43 (d, J = 8.4 Hz, 2H), 7.32 (dd, J = 8.1 and 1.6 Hz, 2H), 7.07 (s, 2H), 3.95 (s, 6H). This compound was not soluble enough for ^{13}C NMR analysis; HRMS calcd for $C_{32}H_{14}Br_4O_2$ 750.12, found both electrospray and direct exposure probe failed.

Nanocar 1. An oven-dried 25 mL round-bottomed flask equipped with a magnetic stirrer was charged with *p*-carborane (144 mg, 1.00 mmol) and dry THF (3 mL). The solution was cooled to −78 °C and *n*-BuLi (0.41 mL, 1.02 mmol) was added dropwise. The solution was allowed to warm to room temperature and stirred for 30 min before it was cooled again at −78 °C. Copper(I) bromide (179 mg, 1.25 mmol) was then added and the mixture was allowed to warm at room temperature for 30 min. A solution of **6** (75 mg, 1.00 μmol) in dry THF (2 mL) was then added and the resulting mixture was allowed to stir at room temperature for 16 h. A few drops of water were added and the mixture was filtered on a silica gel pad with dichloromethane as eluent. The resulting greenish solid was purified by column chromatography (silica gel, 15% dichloromethane in hexanes as eluent) to provide 68 mg of the title product as a white powder (68%): mp >250 °C; IR (KBr) 2613, 1504, 1410, 1222, 1063, 820, 726 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, ppm) δ 7.48 (d, J = 1.5 Hz, 2H), 7.23 (d, J = 8.1 Hz, 2H), 7.15 (dd, J = 8.1 and 1.6 Hz, 2H), 7.07 (s, 2H), 4.00 (s, 6H), 3.34−1.47 (br m, 44H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 154.2, 135.5, 132.3, 131.1, 126.7, 124.0, 122.1, 115.8, 113.5, 92.1, 91.2, 90.9, 88.0, 78.1, 78.0, 69.6, 69.3, 60.5 (2C), 56.6; HRMS calcd for $C_{40}H_{58}B_{40}O_2$ 1003.8445, found 1003.9116.

1,4-Diiodo-2,5-bis(trimethylsilylacetylene)benzene (7). An oven-dried 250 mL round-bottomed flask equipped with a magnetic stirrer was charged with 1,4-dibromo-2,5-bis(trimethylsilylacetylene)-benzene[8] (2.59 g, 6.05 mmol), diethyl ether (60 mL), and THF (60 mL). The mixture was cooled −78 °C and *t*-BuLi (16.0 mL, 27.2 mmol) was added over 15 min. The resulting deep red solution was stirred for 1 h at −78 °C and 1,2-diiodoethane (5.45 g, 19.4 mmol) was added quickly. The solution was stirred for 1 h at −78 °C and an additional 16 h at room temperature. The red solution was poured into water and extracted twice with dichloromethane. The combined organic layers were washed with 0.1 M sodium bisulfite and water and dried over $MgSO_4$. The solvent was removed under reduced pressure and the resulting orange solid was purified by column chromatography (silica gel, hexanes as eluent) to provide 1.93 g of the title product as a white waxy solid (61%): mp 129−131 °C; IR (KBr) 1453, 1248, 1048, 887, 860, 837, 796, 761 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, ppm) δ 7.87 (s, 2H), 0.27 (s, 18H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 141.8, 131.0, 104.8, 102.3, 99.7, −0.1; HRMS calcd for $C_{16}H_{20}I_2Si_2$ 521.9193, found 521.9191.

1,4-Bis(triisopropylsilylacetylene)-2,5-bis(trimethylsilylacetylene)benzene (8). See the general procedure for Castro−Stephens−Sonogashira coupling. The compounds used were **7** (1.20 g, 2.30 mmol), triisopropylsilylacetylene (1.24 mL, 5.51 mmol), CuI (43.8 mg, 0.23 mmol), $PdCl_2(PPh_3)_2$ (80.6 mg, 0.11 mmol), well-degassed dry triethylamine (2.6 mL), and THF (25 mL) at room temperature for 16 h. The resulting brown oil was purified by column chromatography (silica gel, hexanes as eluent) to provide 1.25 g of the title product as a pale yellow solid (86%): mp 152−154 °C; IR (KBr) 2959, 2943, 2865, 1481, 1249, 1186, 876, 842, 769, 759 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, ppm) δ 7.53 (s, 2H), 1.15 (s, 42H), 0.24 (s, 18H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 137.2, 125.4, 125.3, 104.2, 102.4, 100.6, 97.5, 19.0, 11.5, 0.1; HRMS calcd for $C_{38}H_{62}Si_4$ 630.3929, found 630.3940.

1,4-Bis(triisopropylsilylacetylene)-2,5-bis(bromoacetylene)-benzene (9). A 25 mL round-bottomed flask equipped with a magnetic stirrer was charged with **8** (675 mg, 1.07 mmol) and acetone (10 mL). Freshly purified and dried *N*-bromosuccinimide (438 mg, 2.46 mmol) and silver(I) nitrate (27.2 mg, 0.16 mmol) were added, in that order. The mixture was stirred in the dark at room temperature for 2 h and poured into water (100 mL). After 5 min of vigorous stirring, the white precipitate formed was collected by filtration, rinsed thoroughly with water, and dried under reduced pressure for 24 h to provide 679 mg of **9** as a white solid (98%): mp 170−175 °C; IR (KBr) 2955, 2942, 2863, 1481, 1460, 1016, 902, 875, 779, 680, 655 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, ppm) δ 7.5 (s, 2H), 1.1 (s, 42H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 136.1, 126.1, 125.5, 103.6, 98.3, 78.0, 56.5, 18.8, 11.4; HRMS calcd for $C_{32}H_{44}Br_2Si_2$ 644.1331, found 644.1329.

1,4-Bis(triisopropylsilylacetylene)-2,5-bis(1′,12′-dicarba-*closo*-dodecaborane)benzene (10). An oven-dried 50 mL round-bottomed flask equipped with a magnetic stirrer was charged with *p*-carborane (246 mg, 1.71 mmol) and dry THF (20 mL). The solution was cooled to −78 °C and *n*-BuLi (0.68 mL, 1.71 mmol, 2.5 M in hexanes) was added dropwise. The solution was allowed to warm to room temperature and stirred for 30 min before it was cooled again at −78 °C. Copper(I) bromide (267 mg, 1.86 mmol) was then added and the mixture was allowed to warm to room temperature for 30 min. A solution of compound **9** (500 mg, 0.78 mmol) in THF (5 mL) was then added and the resulting mixture was allowed to stir at room temperature for 16 h. A few drops of water were added and the mixture was filtered on silica gel pad with dichloromethane as eluent. The resulting greenish solid was purified by column chromatography (silica gel, hexanes as eluent) to provide 425 mg of **10** as a white powder (71%): mp >250 °C; IR (KBr) 2943, 2865, 2614, 1488, 1064, 882, 841, 708, 675 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, ppm) δ 7.28 (s, 2H), 3.33−1.42 (m, 22H), 1.14 (s, 42H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 137.5, 125.4, 123.8, 103.3, 98.6, 91.0, 69.4, 60.6, 19.0, 11.5; HRMS calcd for $C_{36}H_{66}B_{20}Si_2$ 771.6703, found 771.6713.

1,4-Bis(acetylene)-2,5-bis(1′,12′-dicarba-*closo*-dodecaborane)-benzene (11). An oven-dried 50 mL round-bottomed flask equipped with a magnetic stirrer was charged with **10** (300 mg, 0.39 mmol), THF (40 mL), and tetrabutylammonium fluoride (TBAF) (1.94 mL, 1.94 mmol, 1.0 M in THF, Aldrich Co.). The resulting solution was stirred at room temperature for 4 h and poured into water (ca. 100 mL). The mixture was extracted twice with dichloromethane and the combined organic layers were washed with water. The organic layer was dried over $MgSO_4$ and the solvent was removed under reduced pressure leaving an off-white powder (**11**) that was

used for the next step without further purification (73%): mp >250 °C; IR (KBr) 2617, 1488, 1062, 906, 727, 655, 626 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, ppm) δ 7.36 (s, 2H), 3.34 (s, 2H), 3.25−1.40 (m, 22H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm). This compound is not soluble enough for ^{13}C NMR analysis; HRMS calcd for $C_{18}H_{26}B_{20}$ 458.4052, found 458.4040.

Nanocaterpillar 2. See general procedure for Castro−Stephens−Sonogashira coupling. The compounds used were **11** (65.0 mg, 0.14 mmol), 1-iodo-2,5-bis(*p*-carboraneacetylene)benzene[7] (232 mg, 0.43 mmol), CuI (2.74 mg, 14.4 μmol), $PdCl_2(PPh_3)_2$ (5.1 mg, 7.21 μmol), well-degassed dry triethylamine (0.2 mL), and THF (2 mL) at room temperature for 16 h. The resulting brown oil was purified by column chromatography (silica gel, 5% dichloromethane in hexanes as eluent) to provide 98 mg of the title product as a yellow solid (54%): mp >250 °C; IR (KBr) 2612, 1492, 1062, 901, 831, 727, 705 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, ppm) δ 7.50 (s, 2H), 7.47 (d, J = 1.1 Hz, 2H), 7.23 (d, J = 8.2 Hz, 2H), 7.18 (dd, J = 8.2 and 1.5 Hz, 2H), 3.45−1.43 (m, 66H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 135.6, 135.4, 132.1, 131.6, 125.9, 125.6, 124.3, 124.2, 122.2, 92.8, 91.7, 91.6, 91.1, 88.0, 77.9, 77.5, 77.3, 69.3 (2C), 60.7 (2C), 60.4 (2C); MALDI-TIF MS *m*/*z* (no natrix; positive ion mode) calcd for $C_{46}H_{74}B_{60}$ 1287.24, found 1287.

Nanocar 3. See general procedure for Castro−Stephens−Sonogashira coupling. The compounds used were **13**[16](75 mg, 0.28 mmol), 1-iodo-2,5-bis(*p*-carboraneacetylene)benzene[7] (408 mg, 0.76 mmol), CuI (4.2 mg, 22.1 μmol), $PdCl_2(PPh_3)_2$ (7.8 mg, 11.0 μmol), well-degassed triethylamine (0.5 mL), and THF (3.0 mL) at room temperature for 16 h. The white precipitate formed during the course of the reaction was filtered, rinsed thoroughly with methanol, and recrystallized twice from ethyl acetate to give 202 mg of **3** as a white solid (67%): mp >250 °C; IR (KBr) 2613, 2209, 1592, 1492, 1212, 1063, 804, 727 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, ppm) δ 8.40 (s, 2H), 7.67 (d, J = 7.6 Hz, 2H), 7.43 (d, J = 8.5 Hz, 2H), 7.39 (s, 2H), 7.24 (d, J = 8.2 Hz, 2H), 7.11 (dd, J = 8.0 and 1.3 Hz, 2H), 4.35 (t, J = 7.0 Hz, 2H), 3.45−1.37 (br m, 48H), 1.00 (t, J = 7.3 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 141.2, 135.0, 132.60, 132.58, 129.9, 127.5, 125.4, 124.0, 123.0, 122.2, 113.8, 110.0, 109.5, 96.5, 91.2, 88.0, 85.6, 78.44, 78.39, 77.6, 68.4, 60.7 (4C), 43.7, 31.5, 26.0, 21.0, 14.3; MALDI-TIF MS *m*/*z* (no matrix; positive ion mode) calcd for $C_{48}H_{65}B_{40}N$ 1095.88, found 1096.

1,4-Bis(propyloxy)-2-iodo-5-trimethylsilylacetylenebenzene (14). See general procedure for Castro−Stephens−Sonogashira coupling. The compounds used were 1,4-bis(propyloxy)-2,5-diiodobenzene[9] (3.35 g, 7.51 mmol), TMSA (1.06 mL, 7.51 mmol), CuI (86 mg, 0.45 mmol), $PdCl_2(PPh_3)_2$ (158 mg, 0.23 mmol), well-degassed triethylamine (5 mL), and THF (75 mL) at room temperature for 16 h. The resulting brown oil was purified by column chromatography (silica gel, 8% dichloromethane in hexanes as eluent) to provide 1.77 g of **14** as a yellow solid (56%): mp 34−36 °C; IR (KBr) 2149, 1495, 1464, 1376, 1248; 1216, 860, 845 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, ppm) δ 7.26 (s, 1H), 6.84 (s, 1H), 3.90 (m, 4H), 1.81 (m, 4H), 1.07 (t, 6H, J = 7.4 Hz), 0.25 (9H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 155.3, 152.1, 124.4, 116.7, 113.9, 101.2, 99.9, 88.3, 72.0, 71.8, 23.1, 23.0, 11.2, 10.9, 0.4; HRMS calcd for $C_{17}H_{25}IO_2Si$ 416.0669, found 416.0671.

1,4-Bis(propyloxy)-2-iodo-5-bromoacetylenebenzene (15). A 25 mL round-bottomed flask equipped with a magnetic stir bar was charged with **14** (400 mg, 0.96 mmol) and acetone (12 mL). Then, freshly purified and dried *N*-bromosuccinimide (205 mg, 1.15 mmol) and silver(I) nitrate (16 mg, 96 μmol) were added. The mixture was stirred in the dark at room temperature for 2 h and poured into water (100 mL). The resulting slurry was extracted twice with dichloromethane and the combined organic layers were dried with $MgSO_4$. The solvent was removed under reduced pressure and the resulting orange-red oil solid was purified by column chromatography (silica gel, 10% dichloromethane in hexanes as eluent) to provide 330 mg of **15** as an orange oil (81%): IR (KBr) 2961, 2933, 2872, 2200, 1586, 1487, 1461, 1375, 1262, 1214, 1060, 1048, 1009, 974, 853, 837, 731; ^1H NMR (400 MHz, $CDCl_3$, ppm) δ 7.27 (s, 1H), 6.82 (s, 1H), 3.90 (m, 4H), 1.82 (m, 4H), 1.06 (q, J = 7.5 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 155.1, 151.8, 124.1, 116.6, 113.1, 88.3, 76.4, 71.69, 71.63, 54.1, 22.7 (2C), 10.9, 10.6; HRMS calcd for $C_{14}H_{16}BrIO_2$ 421.9378, found 421.9374.

1,4-Bis(propyloxy)-2-iodo-5-(1′,12′-dicarba-*closo*-dodecaborane)benzene (16). An oven-dried 50 mL round-bottomed flask equipped with a magnetic stir bar was charged with *p*-carborane (135 mg, 0.94 mmol) and THF (20 mL). The solution was cooled to −78 °C and *n*-BuLi (0.39 mL, 0.98 mmol, 2.5 M in hexanes) was added dropwise. The solution was allowed to warm to room temperature and stirred for 30 min before it was cooled again to −78 °C. Copper(I) bromide (146 mg, 1.02 mmol) was then added and the mixture was allowed to stir at room temperature for 30 min. A solution of **15** (330 mg, 0.78 mmol) in THF (10 mL) was then added and the resulting mixture was allowed to stir at room temperature for 48 h. A few drops of water were added and the mixture was filtered through a silica gel pad with dichloromethane as the eluent. The resulting greenish solid was purified by column chromatography (silica gel, 20% dichloromethane in hexanes as eluent) to provide 288 mg of **16** as a white powder (76%): mp 96−98 °C; IR (KBr) 2614, 1496, 1486, 1463, 1383, 1212, 1064, 1026, 979 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, ppm) δ 7.19 (s, 1H), 6.63 (s, 1H), 3.83 (m, 4H), 3.39−1.39 (br m, 15H), 1.05 (t, J = 7.4 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 155.2, 151.8, 124.0, 116.1, 111.8, 90.3, 88.9, 76.0, 71.9, 71.4, 60.18, 60.15, 22.94, 22.85, 11.0, 10.8. HRMS calcd for $C_{16}H_{27}B_{10}IO_2$ 488.1986, found 488.1984.

1,3,5-Tris[1′,4′-bis(propyloxy)-2′-(trimethylsilylacetylene)-5′-acetylenebenzene] (19). See general procedure for Castro−Stephens−Sonogashira coupling. The compounds used were **18**[17] (100 mg, 0.68 mmol), **14** (1.13 g, 2.72 mmol), CuI (16 mg, 84 μmol), $PdCl_2(PPh_3)_2$ (29 mg, 41 μmol), well-degassed triethylamine (2 mL), and THF (7 mL) at room temperature for 16 h. The resulting orange oil was purified by column chromatography (silica gel, 30% dichloromethane in hexanes as eluent) to provide 471 mg of **19** as a yellow solid (68%): mp 158−160 °C; IR (KBr) 2962, 2151, 1500, 1387, 1240, 1214, 860, 840, 758 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, ppm) δ 7.62 (s, 3H), 6.97 (s, 3H), 6.96 (s, 3H), 3.96 (m, 12H), 1.85 (m, 12H), 1.09 (td, J = 7.4 and 2.3 Hz, 18H), 0.27 (s, 27H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 154.6, 154.0, 134.4, 124.6, 117.7, 117.6, 114.68, 114.67, 114.2, 101.5, 100.8, 93.6, 87.5, 71.53, 71.49, 23.1, 11.01, 11.00, 0.4; MALDI-TIF MS *m*/*z* (no matrix; positive ion mode) calcd for $C_{63}H_{78}O_6Si_3$ 1014.51, found 1015.

1,3,5-Tris[1′,4′-bis(propyloxy)-2′-(acetylene)-5′-acetylenebenzene] (20). See general procedure for deprotection of TMS-protected alkyne. The compounds used were **19** (350 mg, 0.35 mmol), K_2CO_3 (573 mg, 4.15 mmol), THF (5 mL), and methanol (5 mL) at room temperature for 2 h. The resulting crude yellowish solid was dissolved in a minimum amount of dichloromethane and poured into 100 mL of cold methanol. The bright yellow solid was collected by filtration and dried under reduced pressure to provide 225 mg of **20** as a bright yellow solid (82%): mp 140−142 °C; IR (KBr) 2963, 1578, 1500, 1420, 1388, 1275, 1218, 851 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, ppm) δ 7.63 (s, 3H), 6.99 (s, 6H), 3.98 (m, 12H), 3.36 (s, 3H), 1.86 (m, 12H), 1.08 (m, 18H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 154.3, 153.7, 134.2, 124.3, 118.1, 117.3, 114.3, 113.3, 93.4, 87.1, 82.8, 80.1, 71.4, 71.3, 22.9, 22.8, 10.8, 10.7; HRMS calcd for $C_{54}H_{54}O_6$ 799.3998, found 799.3990.

4. See general procedure for Castro−Stephens−Sonogashira coupling. The compounds used were **20** (95 mg, 0.12 mmol), **16** (233 mg, 0.48 mmol), CuI (2.2 mg, 12 μmol), $PdCl_2(PPh_3)_2$ (5.0 mg, 7.2 μmol), well-degassed triethylamine (0.2 mL), and THF (1.5 mL) at room temperature for 16 h. The resulting yellow solid was purified by column chromatography (silica gel, 40% dichloromethane in hexanes as eluent) to provide 129 mg of **4** as a yellow

solid (58%): mp 166−168 °C; IR (KBr) 2963, 2611, 1505, 1423, 1385, 1274, 1215, 1062 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, ppm) δ 7.63 (s, 3H), 7.011 (s, 3H), 7.006 (s, 3H), 6.92 (s, 3H), 6.76 (s, 3H), 3.99 (m, 12H), 3.94 (t, $J = 6.5$ Hz, 6H), 3.86 (t, $J = 6.2$ Hz, 6H), 3.30−1.51 (br m, 68H), 1.08 (m, 36H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 154.6, 154.0, 153.7, 153.5, 134.2, 124.5, 117.60, 117.56, 117.4, 117.3, 115.4, 114.9, 113.9, 112.2, 93.6, 92.0, 91.7, 91.0, 87.4, 76.5, 71.5, 71.4, 71.2, 60.3, 60.2, 23.04, 23.01, 22.98, 10.9; MALDI-TIF MS *m*/*z* (no matrix; positive ion mode) calcd for $C_{102}H_{132}B_{30}O_{12}$ 1879.25, found 1879.

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Supporting Information Available: ^1H and ^{13}C NMR spectra for compounds **1**−**11**, **14**−**16**, **19**, and **20**. This material is available free of charge via the Internet at http://pubs.acs.org.

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