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# Synthesis of Fluorescent Dye-Tagged Nanomachines for Single-Molecule Fluorescence Spectroscopy

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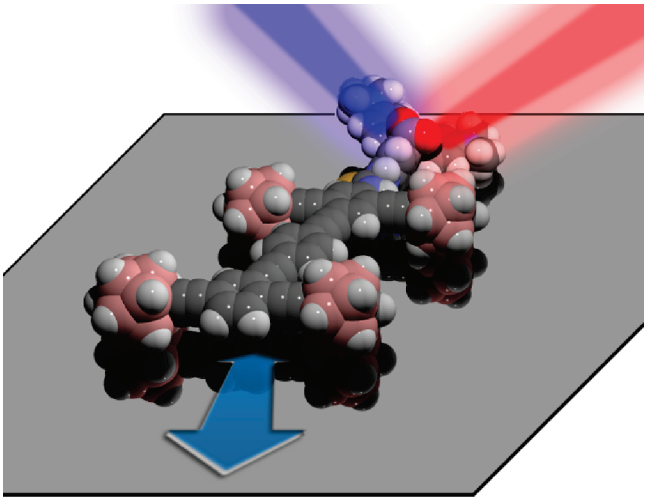

In an effort to elucidate the mechanism of movement of nanovehicles on nonconducting surfaces, the synthesis and optical properties of five fluorescently tagged nanocars are reported. The nanocars were specifically designed for studies by single-molecule fluorescence spectroscopy and bear a tetramethylrhodamine isothiocyanate fluorescent tag for excitation at 532 nm. The molecules were designed such that the arrangement of their molecular axles and *p*-carborane wheels relative to the chassis would be conducive to the control of directionality in the motion of these nanovehicles.

## Introduction

The construction of nanomachines that exhibit controlled movements in solution[1] has lead researchers to explore the design, synthesis, and manipulation of more complex, highly functional devices that can be studied not only as ensembles but also as single entities.[2] Adapting the approach taken by biological systems, synthetic strategies often arrive at these structures via bottom-up construction, quickly generating nanometer-sized configurations from the most basic organic building blocks.[3] Concomitantly, the development of increasingly powerful imaging tools has enabled the study of the individual rotational, translational, and transportation dynamics of biological[4] and synthetic[5] nanomachines on surfaces.

(1) For examples of early work, see: Balzani, V.; Credi, A.; Venturi, M. *Molecular Devices and Machines: A Journey Into the Nanoworld*; Wiley-VCH: Weinheim, Germany, 2003.

(2) For a comprehensive review of molecular machine work, see: Kay, E. R.; Leigh, D. A.; Zerbetto, F. *Angew. Chem., Int. Ed.* **2007**, *46*, 72–191.

(3) For recent synthetic approaches see: (a) Shirai, Y.; Morin, J.-F.; Sasaki, T.; Guerrero, J. M.; Tour, J. M. *Chem. Soc. Rev.* **2006**, *35*, 1043–1055. (b) Jimenez-Bueno, G.; Rapenne, G. *Tetrahedron* **2007**, *63*, 7018–7026. (c) Spruell, J. M.; Dichtel, W. R.; Heath, J. R.; Stoddart, J. F. *Chem.—Eur. J.* **2008**, *14*, 4168–4177. For recent self-assembly approaches see: (d) Saha, S.; Stoddart, J. F. *Molecular Motors and Muscles*; Wiley-VCH: Weinheim, Germany, 2007; pp 295−327. (e) Aprahamian, I.; Yasuda, T.; Ikeda, T.; Saha, S.; Dichtel, W. R.; Isoda, K.; Kato, T.; Stoddart, J. F. *Angew. Chem., Int. Ed.* **2007**, *119*, 4759–4763. (f) Vives, G.; Tour, J. M. *Acc. Chem. Res.* **2009**, *42*, 473–487.

(4) (a) Takano, H.; Kenseth, J. R.; Wong, S.-S.; O'Brien, J. C.; Porter, M. D. *Chem. Rev.* **1999**, *99*, 2845–2890. (b) Soong, R. K.; Bachand, G. D.; Neves, H. P.; Olkhovets, A. G.; Craighead, H. G.; Montemagno, C. D. *Science* **2000**, *290*, 1555–1558. (c) Bachand, G. D.; Soong, R. K.; Neves, H. P.; Olkhovets, A. G.; Craighead, H. G.; Montemagno, C. D. *Nano Lett.* **2001**, *1*, 42–44. (d) Park, H.; Toprak, E.; Selvin, P. R. *Q. Rev. Biophys.* **2007**, *40*, 87–111.

(5) (a) Rosei, F.; Schunack, M.; Naitoh, Y.; Jiang, P.; Gourdon, A.; Laegsgaard, E.; Stensgaard, I.; Joachim, C.; Besenbacher, F. *Prog. Surf. Sci.* **2003**, *71*, 95–146. (b) Tinnefeld, P.; Sauer, M. *Angew. Chem., Int. Ed.* **2005**, *44*, 2642–2671. (c) Sasaki, T.; Guerrero, J. M.; Leonard, A. D.; Tour, J. M. *Nano Res.* **2008**, *5*, 412–419.

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Though interesting results have been obtained using other methods,[5b,c] scanning tunneling microscopy (STM) remains unparalleled in its ability to resolve molecular-sized structures and to track the translational movement of nanoscale objects.[6] To this end, various groups have synthesized landers,[7] wheelbarrows,[3b,8] nanowalkers,[9] and polyaromatic systems[10] for the purpose of observing their behavior on metallic surfaces. Similarly, our group has combined various nanocomponentries with molecular axles containing fullerene, *p*-carborane, or organometallic wheels to construct a number of nanovehicles designed for directed motion and transport along atomically flat surfaces.[3a,f] Proof-of-concept experiments have shown, using STM, the directed movement of fullerene-wheeled nanocars on atomically flat Au(111) surfaces upon thermal and electrogradient activation.[11]

Although STM remains invaluable in the study of atomic detail and mechanism, the experimental conditions that are present are often less than ideal. The STM measurements are time-consuming, conductive substrate surfaces must be used, and cryogenic and high-vacuum settings are often required to obtain clean images.[6b,12] Single-molecule fluorescence spectroscopy (SMFS), which has been widely used to track motion in biological systems,[13] offers a complementary technique to STM to study single molecules but on nonconductive surfaces. While SMFS does not have the atomic resolution of STM, nanometer localization is possible with large photon count rates,[14] and fast measurement of distances as low as several nanometers has been realized on larger scan areas.[15] To exploit these advantages, we recently employed single-molecule fluorescence imaging as a complementary technique to STM for monitoring the motion of fluorescent nanocars on nonconductive glass under ambient conditions.[16]

To obtain accurate measurements of single molecules, it is of paramount importance to ensure that (a) the molecules of interest fluoresce well and (b) fluorescence from impurities, optics, and substrate surfaces is avoided.[17] Molecular design ensures that the first requirement is achieved, while the other is typically met by using excitation light with wavelengths greater than 500 nm since fewer molecules and substrates absorb in this region.[18] In our case, use of such light came with a caveat, as our previously synthesized *p*-carborane nanocars[19] do not possess absorption bands in this region. In general, molecules are tagged with a high-quantum-yield fluorescent dye to enable visualization at longer wavelengths.[20] For our purposes, tetramethylrhodamine isothiocyanate (TRITC) was an attractive dye, as it possesses an excitation wavelength centered at the emission line of our Nd:Vanadate laser (532 nm), has good quantum yield of fluorescence, and is appended to molecular structures via a simple urea formation by reaction with amines.[21] The attachment of TRITC to nanovehicular structures should afford the ability to more easily study the behavior of nanocars on nonconductive surfaces where ultrahigh vacuum is not required.

In an effort to elucidate the mechanism of movement and control the directionality of nanovehicles via specific arrangements of their molecular axles and wheels, reported here are the syntheses and optical properties of five fluorescently tagged nanovehicles (Figure 1) specifically designed for SMFS. The molecules all bear TRITC fluorescent tags for excitation at 532 nm and *p*-carborane wheels. Our main reasons for choosing *p*-carborane were 2-fold: (1) its ability to be substituted at both carbon atoms *para* to one another and (2) its stability toward many organometallic and photoinitiated processes.

As shown in Figure 1, nanocars **1** and **2** were designed to move along a straight trajectory due to the placement of the axles parallel to one another. Nanocar **3** is designed to move in a circular motion, a result of the axles angled toward each other. Analogous to our previous work with fullerene nanomachines, trimer **4** was designed to exhibit a pivoting motion, assessable by polarization experiments, with no translation. Due to the initial results from imaging trimer **4**,[16] nanocar **5** was designed to ascertain the effect of TRITC on wheel rotation and nanocar movement.

## Results and Discussion

**Design and Synthesis.** The strategy to arrive at each target adopts a convergent approach, where the inner components of each nanovehicle are synthesized and then attached to versatile *p*-carborane-containing axles. The design of nanocars **1**, **2**, and **3** dictated the use of two different molecular axles, with one axle bearing a pendant aniline for the attachment to amine-reactive TRITC. To arrive at trimer **4** and nanocar **5**, we used a convergent, symmetric approach to synthesize a late-stage intermediate, followed by statistical attachment of an extended aniline to one wheel for the purpose of TRITC tagging.

In Scheme 1, iodide axle **6**[22] was coupled to the methoxy-containing inner chassis of the nanocar **7**[23] using conventional Sonogashira conditions followed by deprotection to yield the terminal alkyne **8**. Immediate coupling with known aniline axle **9**[23] was performed to give the aniline nanocar **10**.

(6) (a) Avouris, P. *Acc. Chem. Res.* **1995**, *28*, 95–102. (b) Anderson, H. *Angew. Chem., Int. Ed.* **2000**, *39*, 2451–2453.
(7) Rosei, F.; Schunack, M.; Jiang, P.; Gourdon, A.; Legsgaard, E.; Stensgaard, I.; Joachim, C.; Besenbacher, F. *Science* **2002**, *296*, 328–331.
(8) Grill, L.; Rieder, K.-H.; Moresco, F.; Jimenez-Bueno, G.; Wang, C.; Rapenne, G.; Joachim, C. *Surf. Sci.* **2005**, *584*, L153–L158.
(9) Kwon, K.-Y.; Wong, K. L.; Pawin, G.; Bartels, L.; Stolbov, S.; Rahman, T. S. *Phys. Rev. Lett.* **2005**, *95*, 166101–166104.
(10) Gimzewski, J. K.; Joachim, C.; Schlittler, R. R.; Langlais, V.; Tang, H.; Johannsen, I. *Science* **1998**, *281*, 531. (b) Gross, L.; Rieder, K.−H.; Moresco, F.; Stojkovic, S. M.; Gourdon, A.; Joachim, C. *Nat. Mater.* **2006**, *4*, 892.
(11) Shirai, Y.; Osgood, A. J.; Zhao, Y.; Kelly, K. F.; Tour, J. M. *Nano Lett.* **2005**, *5*, 2330–2334.
(12) Eigler, D. M.; Lutz, C. P.; Rudge, W. E. *Nature* **1991**, *352*, 600–603.
(13) Haustein, E.; Schwille, P. *Methods* **2003**, *29*, 153–166 and references within.
(14) (a) Yildiz, A.; Forkey, J. N.; McKinney, S. A.; Ha, T.; Goldman, Y. E.; Selvin, P. R. *Science* **2003**, *300*, 2061–2065. (b) Yildiz, A.; Tomishige, M.; Vale, R. D.; Selvin, P. R. *Science* **2004**, *303*, 676–678.
(15) Thompson, R. E.; Larson, D. R.; Webb, W. W. *Biophys. J.* **2002**, *82*, 2775–2783.
(16) Khatua, S.; Guerrero, J. M.; Claytor, K.; Vives, G.; Kolomeisky, A. B.; Tour, J. M.; Link, S. *ACS Nano* **2009**, *3*, 351–356.
(17) Rueda, D.; Walter, N. G. *J. Nanosci. Nanotechnol.* **2005**, *5*, 1990–2000.
(18) (a) Telford, W. G.; Murga, M.; Hawley, T.; Hawley, R.; Packard, B.; Komoriya, A.; Haas, F.; Hubert, C. *Cytometry, Part A* **2005**, *68*, 36–44. (b) Van Hoof, D.; Pinkse, M. W. H.; Ward-Van Oostwaard, D.; Mummery, C. L.; Heck, A. J. R.; Krijgsveld, J. *Nat. Methods* **2007**, *4*, 678–679. (c) Perfetto, S. P.; Roederer, M. *Cytometry, Part A* **2007**, *71*, 73–79.
(19) Morin, J.−F.; Sasaki, T.; Shirai, Y.; Guerrero, J. M.; Tour, J. M. *J. Org. Chem.* **2007**, *72*, 9481–9490.
(20) Zarrin, F.; Dovichi, N. J. *Anal. Chem.* **1985**, *57*, 2690–2692.
(21) (a) Corrie, J. E. T.; Craik, J. S. *J. Chem. Soc., Perkins Trans.* **1994**, 2967–2973. (b) Buchynskyy, A.; Kempin, U.; Vogel, S.; Hennig, L.; Findeisen, M.; Müller, D.; Giesa, S.; Knoll, H.; Welzel, P. *Eur. J. Org. Chem.* **2002**, 1149–1162. (c) Hernando, J.; van der Schaaf, M.; van Dijk, E. M. H. P.; Sauer, M.; García-Parajó, M. F.; van Hulst, N. F. *J. Phys. Chem. A* **2003**, *107*, 43–52. (d) Reizelman, A.; Wigchert, S. C. M.; del-Bianco, C.; Zwanenburg, B. *Org. Biol. Chem.* **2003**, *1*, 950–959. (e) Sørensen, M. D.; Martins, R.; Hindsgaul, O. *Angew. Chem., Int. Ed.* **2007**, *46*, 2403–2407.
(22) Morin, J.−F.; Shirai, Y.; Tour, J. M. *Org. Lett.* **2006**, *8*, 1713–1716.
(23) Sasaki, T.; Tour, J. M. *Tetrahedron Lett.* **2007**, *48*, 5821–5824.

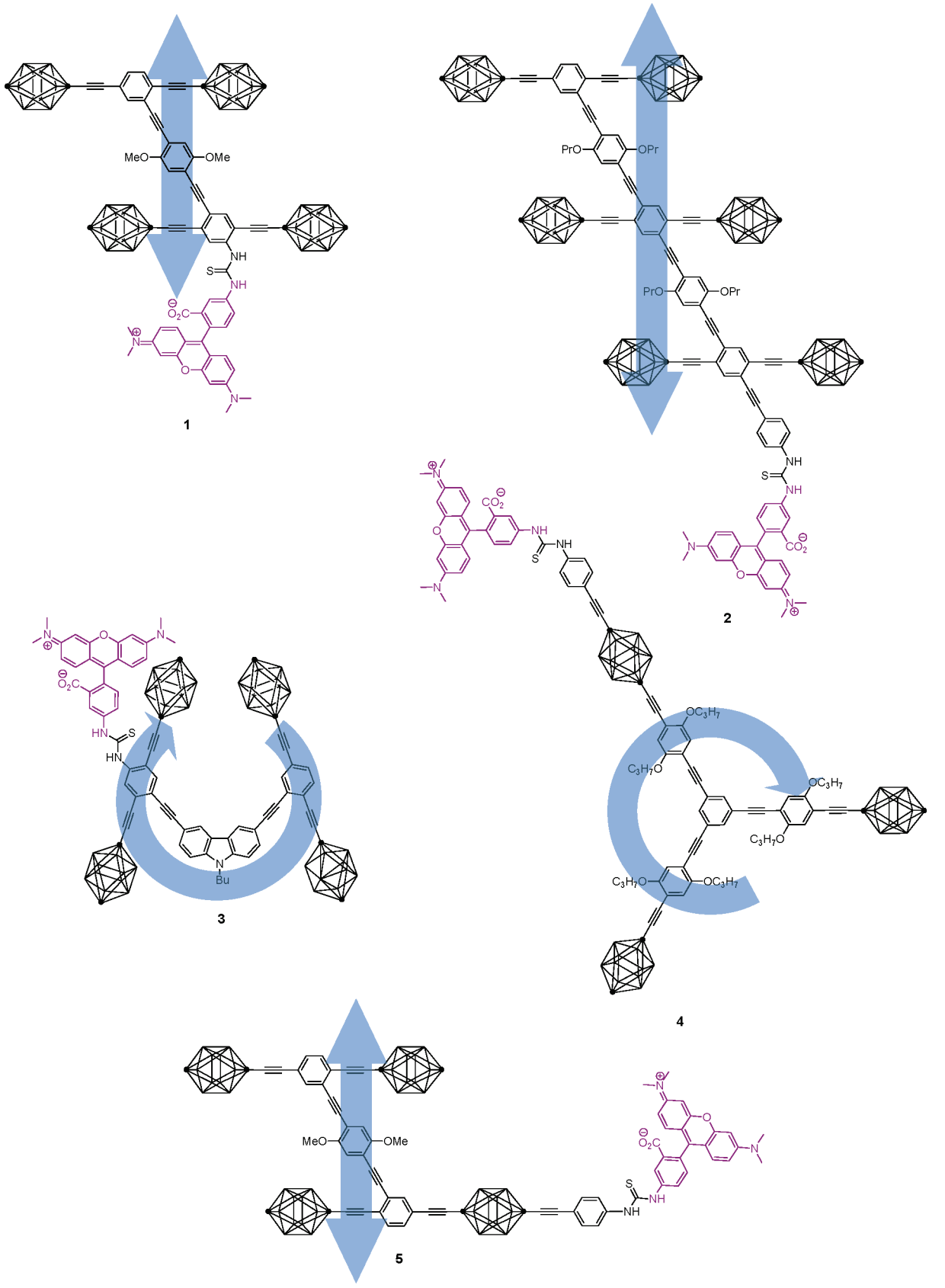
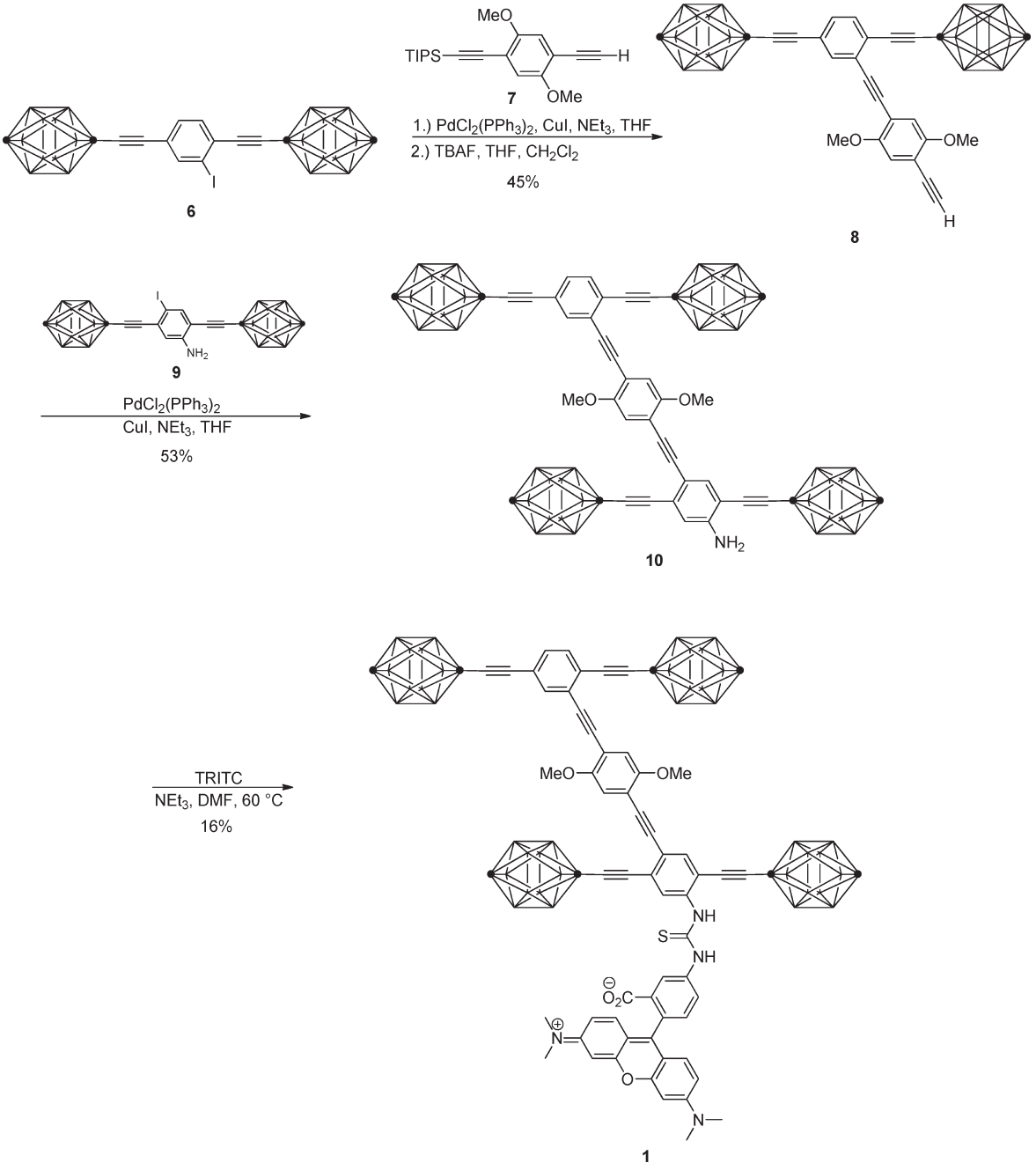



**FIGURE 1.** Structures of the TRITC-tagged nanovehicles and their expected directional motion. Every vertex of the carborane wheel is BH except the darkened sites, where the outer (*para*) is CH and the inner (*ipso*) is an alkynyl-substituted C. Only the 5-isomer adduct of TRITC is shown.

**SCHEME 1. Synthesis of TRITC-Tagged Nanocar 1**



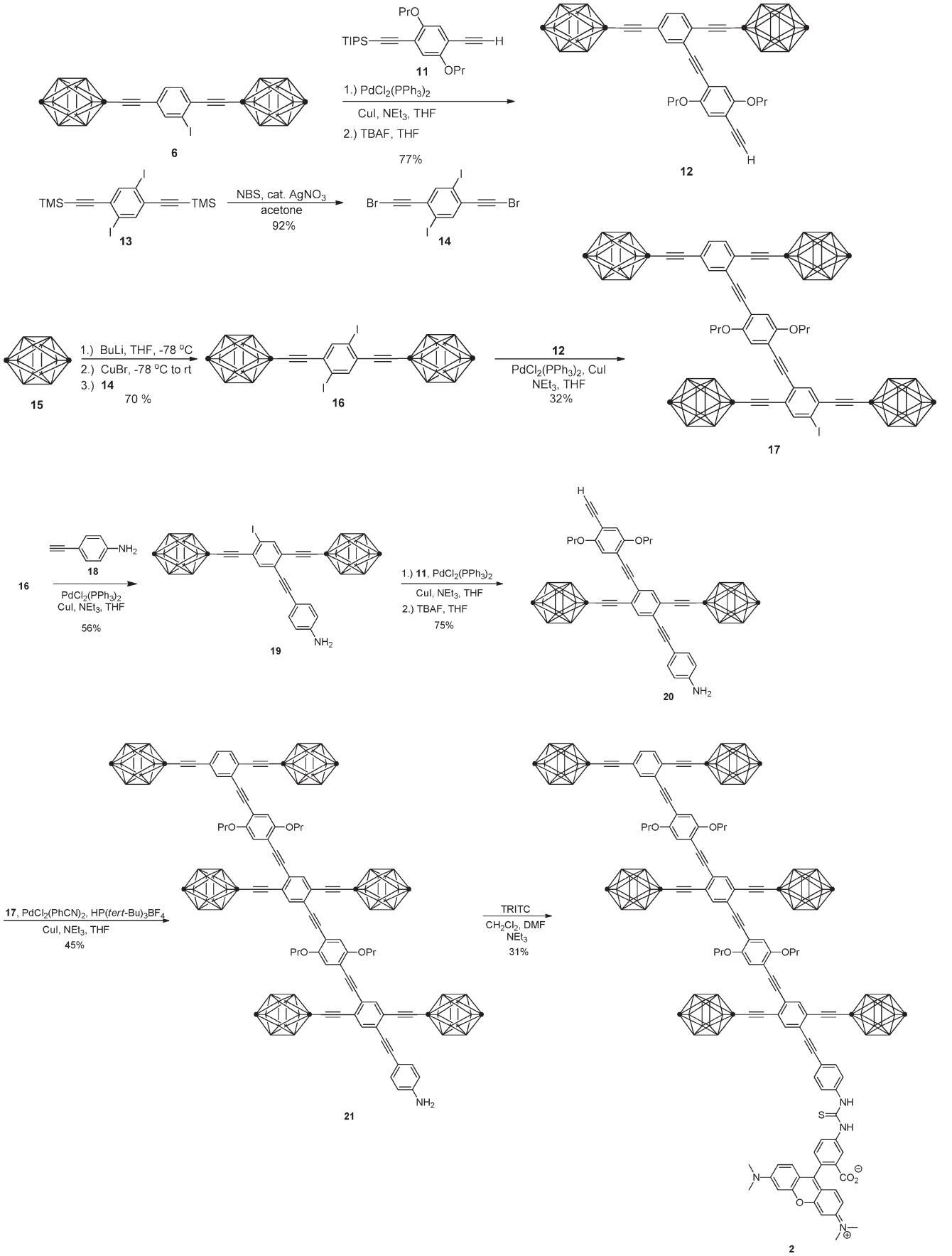

In a final step, the aniline group of **10** was reacted with TRITC in DMF at elevated temperature, with triethylamine as base, to give target nanocar **1** in 16% yield. It is possible that the low yield was a result of steric bulk around the reacting aniline.

SMFS results show that the axle-tagged nanocar **1** has sufficient energy at room temperature to move along a glass surface at high rates of displacement.[16] This was an encouraging result, as the attachment of a relatively large fluorescent tag to the central aromatic moiety of the axle of nanocar **1** demonstrates that transport on the nanoscale is not impeded by the TRITC.

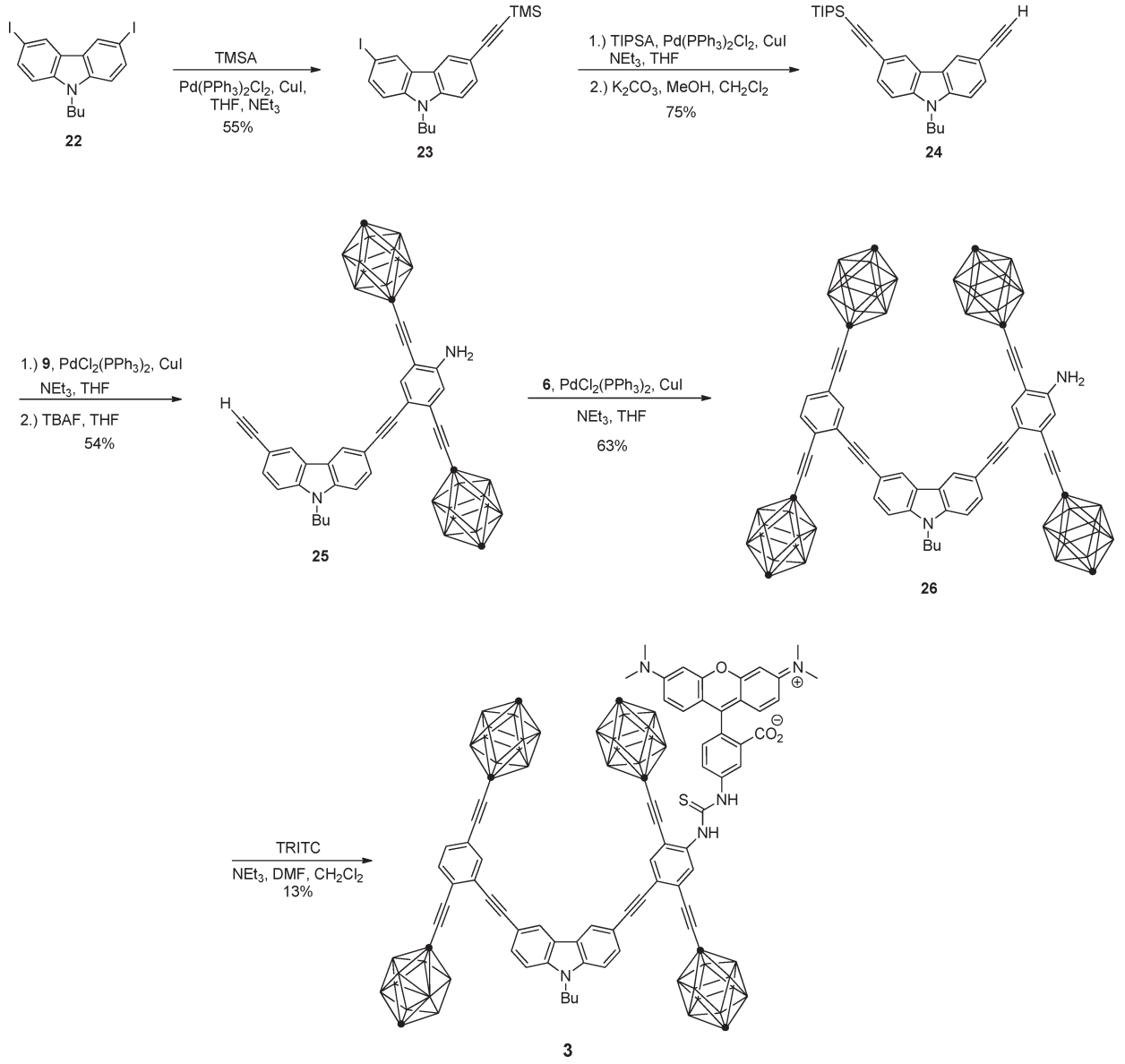
Our proposed mechanism[16] suggests that increasing the number of wheels (thereby increasing the surface interaction) should lead to a more controlled motion over a larger distance, with the possibility that the increase in the number of wheels would produce a concomitant decrease in the speed of the movement.

In an effort to improve controlled straight-line directionality via increased surface interaction, we synthesized an extended-chassis tagged nanovehicle with three axles and six wheels. As shown in Scheme 2, the synthesis was carried out beginning with an intermediate similar to that used for the synthesis of the four-wheeled tagged nanocar. After two straightforward steps, the half-nanocar was once again deprotected to give **12**. Separately, 1,4-diiodo-2,5-bis(trimethylsilylethynyl)benzene (**13**)[19] was subjected to desilyl bromination. The resultant alkynyl bromide **14** was coupled

**SCHEME 2. Synthesis of TRITC-Tagged Six-Wheeled Nanovehicle 2**



**SCHEME 3. Synthesis of TRITC-Tagged Angled Nanocar 3**

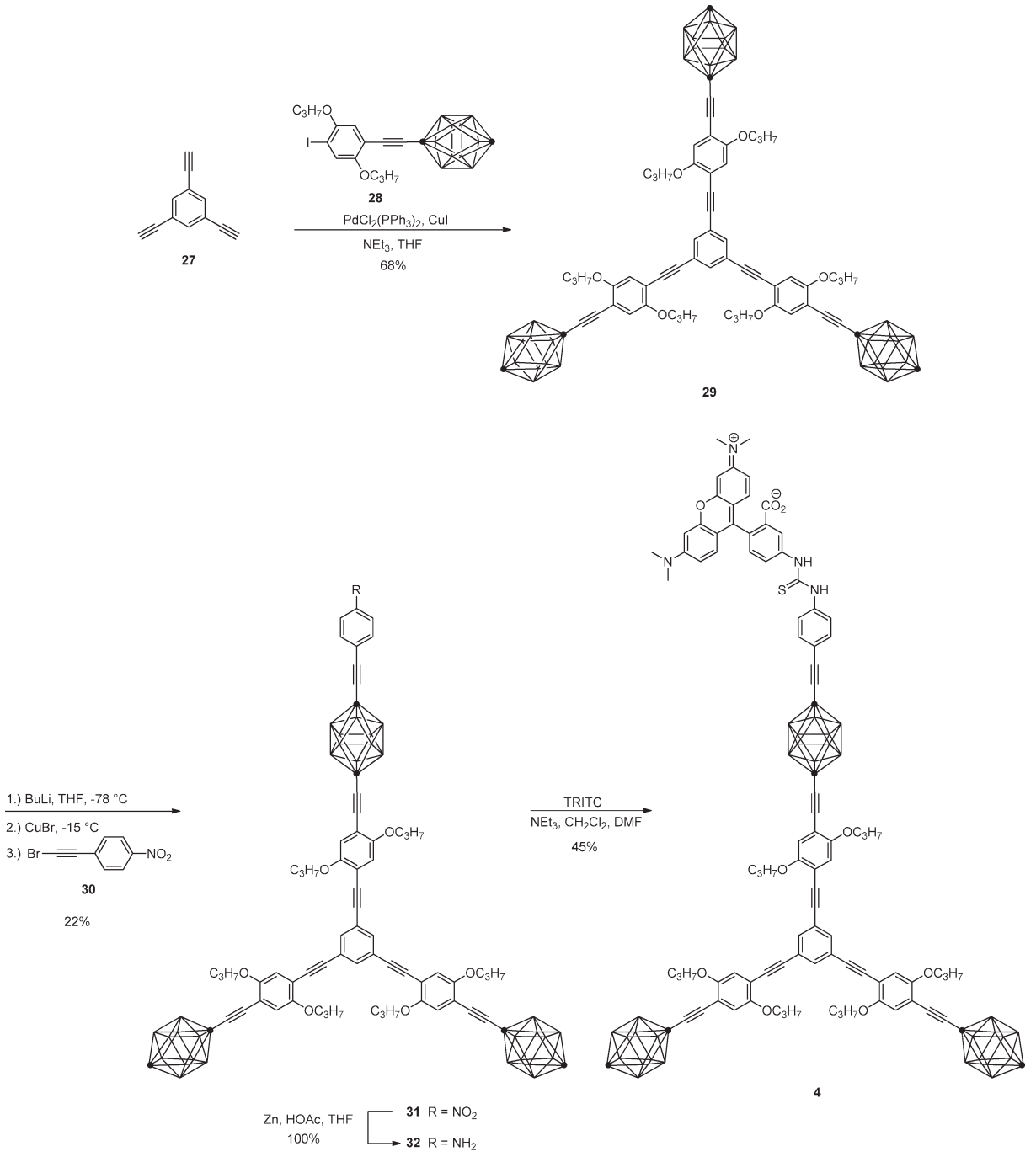



with *p*-carborane (**15**) via a carborane−copper adduct to give diiodide axle **16**. A statistical coupling between axle **16** and **12** gave the four-wheeled iodide nanocar **17**. It should be noted that to increase the solubility of the six-wheeled nanocar the methoxy groups were replaced by more solubilizing propoxy groups. The extended aniline axle **20** was obtained in three steps starting with a statistical Sonogashira coupling between axle **16** and 4-ethynylaniline (**18**).[24] Subsequently, **19** was coupled to the chassis **11**[25] followed by deprotection to yield the extended aniline axle with chassis **20**. A final Sonogashira coupling to four-wheeled iodo-nanocar **17** gave the six-wheeled extended aniline nanocar **21** in 45% yield. The use of the Fu-modified Sonogashira method[26] with the air-stable HP(*tert*-Bu)$_3$BF$_4$ proved to be exceedingly effective since conventional conditions using triphenylphosphine afford only a 18% yield. Room-temperature attachment of the aniline to TRITC was then carried out again in DMF with triethylamine to provide the target six-wheeled tagged nanovehicle **2**.

While changing molecular design by increasing the number of axles and wheels should be a way to improve straight-line trajectory over longer distances, we also aimed to control the directionality by varying the angles of attachment to carborane-wheeled molecular components. Thus, we synthesized a nanocar with a bent chassis structure, designed to produce a circling motion (Scheme 3), by using a differentially substituted carbazole as the angling unit and a combination of iodide axle **6** and aniline axle **9**, the latter being for the TRITC attachment. Although the expected circumference of the circle traveled by nanocar **3** would be smaller than the detection limit of our current SMFS setup, polarization anisotropy measurements have given very accurate rotational measurements, as demonstrated by previous studies on biological motors and our initial SMFS studies.[13,16]

(24) Maya, F.; Chanteau, S. H.; Cheng, L.; Stewart, M. P.; Tour, J. M. *Chem. Mater.* **2005**, *17*, 1331–1345.
(25) Lindner, E.; Zong, R.; Eichele, K.; Ströbele, M. *J. Organomet. Chem.* **2002**, *660*, 78–84.
(26) Netherton, M. R.; Fu, G. C. *Org. Lett.* **2001**, *3*, 4295–4298.

**SCHEME 4. Synthesis of Trimer 4**



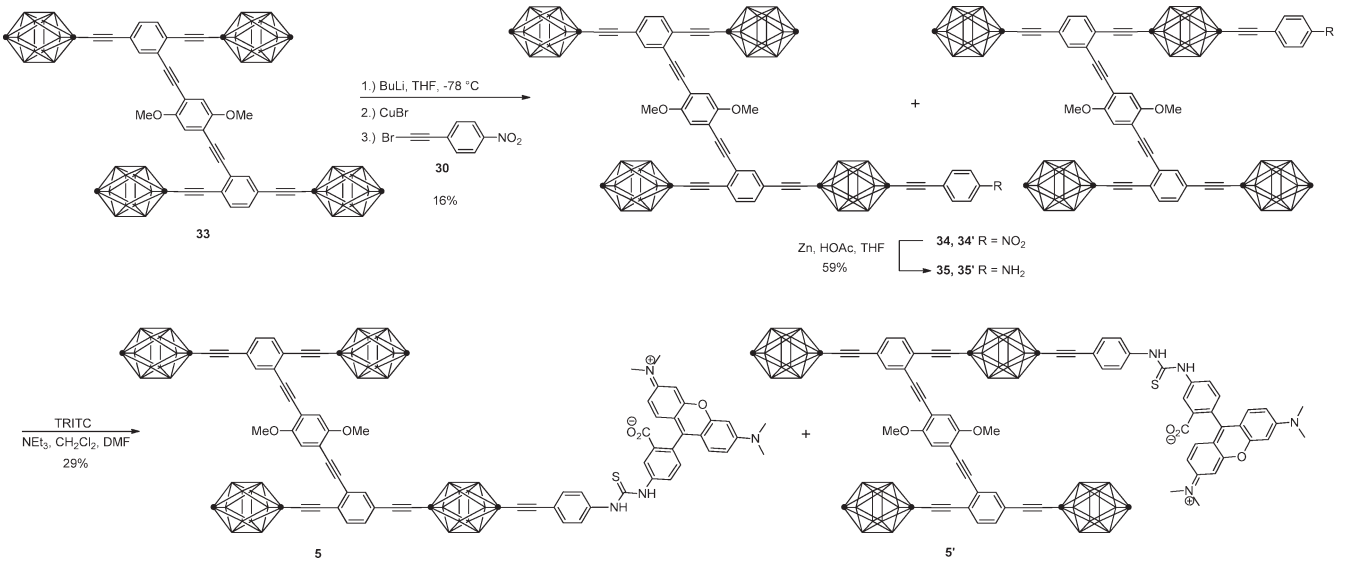

Therefore, **3** was synthesized initially through two consecutive Sonogashira reactions that were carried out on the diiodocarbazole **22**.[27] The first coupling used 0.6 equiv of trimethylsilylacetylene (TMSA) to yield **23**. The coupling that followed, making use of the more robust triisopropylsilylacetylene (TIPSA), gave, after selective TMS deprotection, **24** in a combined yield of 75%. Alkyne **24** was further coupled to aniline axle **9** to give, after deprotection, the half-angled nanocar **25**. A further coupling with the iodo axle **6** gave the angled aniline nanocar **26** that was then reacted with TRITC to give the tagged angled nanocar **3** in 13% yield. Again, the final TRITC coupling was the lowest yielding step of the sequence.

To further explore our ability to study directionality and molecular behavior, trimer **4** was designed and synthesized to have properties analogous to those of a previously studied fullerene-wheeled trimer, where the molecule undergoes no translation but rotates about the central trialkynylated benzene.[11]

To synthesize trimer **4** (Scheme 4), we first attempted to use an early-stage statistical coupling to 1,3,5-tribromobenzene, followed by the coupling of a fully elaborated pendant aniline arm to the benzene core. This method, however, proved to be lengthy and low yielding. Using a late-stage

(27) Zhao, T.; Liu, Z.; Song, Y.; Xu, W.; Zhang, D.; Zhu, D. *J. Org. Chem.* **2006**, *71*, 7422–7432.

**SCHEME 5. Synthesis of Wheel-Tagged Nanocar 5**




statistical approach, trimer **4** was convergently constructed in four synthetic steps, where 1,3,5-triethynylbenzene **27**[19] was coupled to 3 equiv of known carborane arm **28**[19] to give the symmetrical trimer **29** in good yield. Initially, statistical attachment of the *p*-(bromoethynyl)nitrobenzene (**30**) unit was carried out under standard conditions for unsubstituted *p*-carborane functionalization: **29** was deprotonated using 1 equiv of *n*-butyllithium at −78 °C, followed by equilibration at room temperature for 30 min, then cooled again to −78 °C. Transmetalation was then performed by addition of CuBr and allowing the mixture to warm to room temperature, followed by coupling with the alkynyl bromide. Unfortunately, no product was obtained using this protocol, and the starting material was almost totally recovered. In monosubstituted *p*-carboranes, Fox and co-workers have reported an influence of the substituent on the unsubstituted carbon.[28] Substitutions by electron-donating groups increase electron density on the *para*-carbon, following a Hammet $\sigma_p$ plot with good correlation. Hence, modification of the procedure by lowering the temperature of the equilibration steps to −15 °C and increasing the equilibration times to 1 h led to formation of *p*-(bromoethynyl)nitrobenzene-substituted trimer **31** in 22% yield. The pendant nitro was then smoothly reduced using zinc powder and acetic acid in THF to provide the aniline **32** in quantitative yield. Reaction with TRITC provided fluorescently tagged trimer **4** in 45% yield. It should be noted that the less hindered aniline−TRITC coupling yields were considerably higher than in the hindered aniline cases. Hence, a steric retardation on the coupling was likely the cause of the much lower yields of the nanocars **1** and **3**.

SMFS imaging of TRITC-tagged trimer **4** showed that the molecule is stationary, exhibiting no translational motion. While a lack of translational motion was expected, the molecule also failed to show any rotational movement by polarization anisotropy measurements.[16] This lack of rotation could be due to molecular design, where TRITC is attached via a pendant group emanating from one wheel, causing it to act as a brake.

To test this hypothesis, we synthesized a wheel-tagged fluorescent nanocar (Scheme 5). Known nanocooper **33**[19] was subjected to statistical carborane substitution conditions, similar to those developed for the synthesis of the trimer, resulting in a 16% yield of **34** and **34′**; a lower yield when compared to the trimer **4** due to the statistical contribution of one extra wheel. The substitution of only one of the four wheels of nanocar **33** leads to two regioisomers, corresponding to substitution on the *ortho*- or *meta*-positioned ethynyl carborane relative to the inner chassis. The two isomers are obtained as a 1:1 mixture that is inseparable by column chromatography. The current mechanism of translocation suggests that the two isomers should exhibit similar behavior on the glass surface, so the mixture was carried on through the rest of the synthetic sequence. Subsequent reduction to anilines **35** and **35′** and TRITC attachment gave wheel-tagged nanocars **5** and **5′** in a combined 29% yield. Initial SMFS results indicate that TRITC may indeed act as a brake, as only 5% of the nanocars exhibited translational motion, compared to 25% for nanocar **1**.

**Optical Properties.** We recently reported upon the solution-based ensemble absorption and fluorescence spectroscopy measurements of carborane-containing conjugated molecules.[19]

As shown in Figure 2, the aniline precursors show two absorption maxima: the first one in the region $\lambda_{max}$ = 288−294 and the second around 400 nm. A trend can be noted in the relative absorption energies of the alkoxy-functionalized nanovehicles, where increasing conjugation length (and the corresponding number of alkoxy units) causes a decrease in the HOMO−LUMO gap, red-shifting the $\lambda_{max}$ values in the order **21** > **10** ≈ **35** > **26** > **32**. Despite the fact that the aniline precursors show relatively high quantum yields (Table 1), we are unable to use them in SMFS measurements, as none of these molecules can be excited at 532 nm, which our current setup requires.[16]

Although much synthetic effort is required to attach TRITC to our molecules, of paramount importance for the detection of single fluorescent molecules is the elimination of background fluorescence, in particular, fluorescence from luminescent impurities and optical and substrate surfaces. Therefore, by using a fluorescent dye with >500 nm wavelength excitation, we minimize undesired fluorescence, as fewer molecules and substrates are known to undergo absorption and emission in this region.[18]

(28) Fox, M. A.; MacBride, J. A. H.; Peace, R. J.; Wade, K. *J. Chem. Soc., Dalton Trans.* **1998**, 401–411.

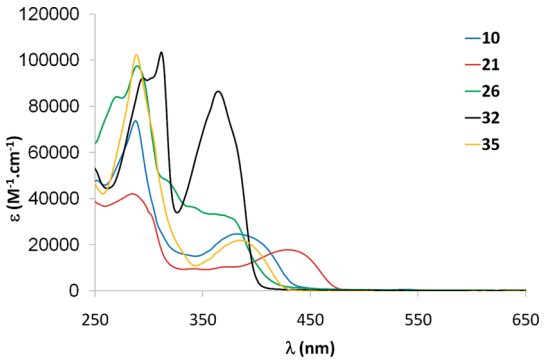



**FIGURE 2.** UV−vis spectra of aniline-substituted nanocars in $CHCl_3$.

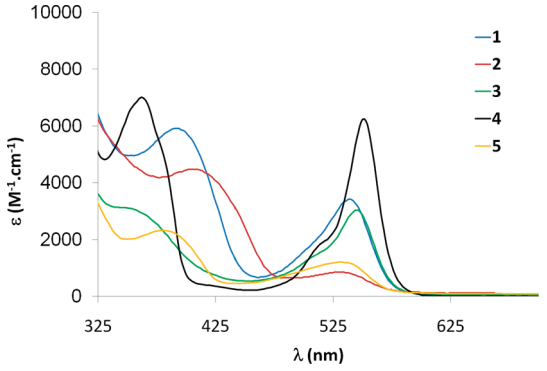



**FIGURE 3.** UV−vis spectra of **1**−**5** in $CHCl_3$.

**TABLE 1. Optical Properties of Key Compounds**[a]

| compound | absorption maxima ($\lambda_{max}$, $\varepsilon$ ($M^{-1}$, $cm^{-1}$)) | $\lambda_{em}$ (nm) | $\Phi_F$[b] |
|---|---|---|---|
| **1** | 286 (18700), 392 (6000), 540 (3400) | 564 | 0.37 |
| **2** | 286 (16200), 406 (4500), 532 (900) | 554 | 0.22 |
| **3** | 286 (8100), 546 (3000) | 564 | 0.40 |
| **4** | 312 (15800), 362 (11000), 552 (9700) | 569 | 0.47 |
| **5** | 288 (11500), 380 (2300), 532 (1200) | 560 | 0.23 |
| **10** | 288 (73800), 382 (24600) | 436 | 0.75 |
| **21** | 284 (25000), 429 (17800) | 471 | 0.22 |
| **26** | 290 (97000), 364 (33100) | 438 | 0.33 |
| **32** | 294 (92000), 366 (86100) | 400 | 0.67 |
| **35** | 288 (102200), 386 (21800) | 428 | 0.65 |

[a]Determined in chloroform solution, ca. $1 \times 10^7$ M. [b]Using rhodamine 6G as reference, $\Phi_F = 0.95$ in EtOH, $\lambda_{exc} = 488$ nm. Excitation was done at the corresponding $\lambda_{max}$—30 nm for compounds **1**−**5**. For other compounds, excitation was done at $\lambda_{max}$.

As shown in the absorption spectra in Figure 3, upon TRITC attachment, all of the nanovehicles exhibit an absorption peak centered between 532 and 552 nm while still maintaining a UV-blue profile near-identical to the main nanovehicle structure. The absence of any vibronic structure is a clear indication that the presence of TRITC does not disturb the molecules' freedom of axle rotation in the ground state, a feature which is necessary for traversing subnanometer surface irregularities when related nanocars were studied on surfaces.[29]

It is interesting to note that the non-tagged aniline precursors all exhibit fluorescence quantum yields higher than those of their TRITC-tagged cousins (Table 1) along with very large Stokes shifts, indicating that large geometric changes occur in their excited states. Nevertheless the TRITC-tagged nanocars display suitable quantum yields for SMFS studies on a glass surface, thereby fulfilling the intent of this synthetic approach.

(29) Shirai, Y.; Osgood, A.; Zhao, Y.; Yao, Y.; Saudan, L.; Yang, H.; Yu-Hung, C.; Alemany, L. B.; Sasaki, T.; Morin, J.-F.; Guerrero, J. M.; Kelly, K. F.; Tour, J. M. *J. Am. Chem. Soc.* **2006**, *128*, 4854–4864.

## Conclusion

The design and synthesis of five fluorescently tagged nanovehicles for the purpose of SMFS imaging is reported. The attachment of the TRITC fluorescent dye label to the nanovehicles was accomplished through the coupling of the isothiocyanate residue of the fluorophore with an aniline-functionalized nanovehicle. Several arrangements of axles on the chassis were used to achieve different directional motion on the surface. Optical studies revealed that the tagging with a TRITC moiety renders the nanocars suitable for SMFS studies with excitation at 532 nm.

## Experimental Section

**General Methods.** $^1$H NMR and $^{13}$C NMR spectra were recorded at 400 or 500 and 100 or 125 MHz, respectively. Proton chemical shifts ($\delta$) are reported in parts per million downfield from tetramethylsilane (TMS). All MALDI-TOF experiments were performed using α-cyano-4-hydroxy-cinnamic acid as the matrix. FTIR spectra were recorded by deposition of the sample on a KBr plate from a $CH_2Cl_2$ solution using a Nicolet FTIR Infrared Microscope with ATR objective with 2 $cm^{-1}$ resolution. All reactions were performed under an atmosphere of nitrogen unless stated otherwise. Reagent grade tetrahydrofuran (THF) was distilled from sodium benzophenone ketyl. Triethylamine (TEA) and $CH_2Cl_2$ were distilled over $CaH_2$. CuBr was purified by suspension in hot MeOH and filtration. Trimethylsilylacetylene (TMSA) was donated by suppliers. All other chemicals were purchased from commercial suppliers and used without further purification. Flash column chromatography was performed using 230−400 mesh silica gel from a supplier. Thin-layer chromatography was performed using glass plates precoated with silica gel 40 $F_{254}$ purchased from a supplier. The syntheses of compounds **6**,[22] **7**,[23] **9**,[23] **11**,[25] **13**,[19] **18**,[24] **22**,[27] **27**,[19] **28**,[19] and **33**[19] were performed according to formerly reported protocols.

**General Procedure for the Coupling of a Terminal Alkyne with an Aryl Halide Using a Palladium-Catalyzed Cross-Coupling (Sonogashira) Protocol.** To an oven-dried round-bottom flask equipped with a magnetic stir bar were added the aryl halide, the terminal alkyne, $PdCl_2(PPh_3)_2$ (ca. 2 mol % per aryl halide), and CuI (ca. 4 mol % per aryl halide). A solvent system of TEA and/or THF was added depending on the substrates. Upon completion, the reaction was quenched with a saturated solution of $NH_4Cl$. The organic layer was then diluted with hexanes, diethyl ether, or $CH_2Cl_2$ and washed with water or saturated $NH_4Cl$ (1×). The combined aqueous layers were extracted with hexanes, diethyl ether, or $CH_2Cl_2$ (2×). The combined organic layers were dried over $MgSO_4$ and filtered, and the solvent was removed from the filtrate in vacuo to afford the crude product, which was purified by column chromatography (silica gel). Eluents and other slight modifications are described below for each compound.

**General Procedure for Deprotection of TIPS-Protected Alkynes using TBAF.** In a round-bottomed flask equipped with a magnetic stir bar, the protected alkyne was dissolved in THF or $CH_2Cl_2$ ([protected alkyne] = 0.05−0.1 M). TBAF in THF (1.0 M, 1.1 equiv per alkyne) was added. The mixture was stirred at rt for 0.5 h or until the reaction was complete (monitored by TLC).

Silica gel was added, and the solvent was removed in vacuo. The resulting product loaded onto silica gel was then purified by column chromatography (silica gel as the stationary phase) to provide the product.

**Compound 8.** See the general procedure for the Pd/Cu coupling reaction. The materials used were **6**[22] (0.150 g, 0.28 mmol), **7**[23] (0.091 g, 0.27 mmol), $PdCl_2(PPh_3)_2$ (0.020 g, 0.028 mmol), CuI (0.012 g, 0.063 mmol), TEA (0.32 mL), and THF (4.0 mL) at rt overnight. The residue was purified by flash column chromatography in silica gel using 20% $CH_2Cl_2$ in hexanes; the product-containing fractions were combined and concentrated, and the residue was subjected to the general procedure for the deprotection of TIPS-protected alkynes. The materials used were the TIPS-protected intermediate (0.090 g, 0.12 mmol), TBAF (0.20 mL, 1.0 M in THF), and $CH_2Cl_2$ (3 mL). The mixture was stirred at rt for 0.5 h and then passed through a silica plug using 30% $CH_2Cl_2$ in hexanes as eluent to yield **8** (0.071 g, 45%, two steps) as an off-white solid. FTIR (KBr) 2926, 2615, 1502, 1463, 1408, 1385, 1221, 1064, 1041, 785, 665 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$ 7.45 (d, $J$ = 1.2 Hz, 1H), 7.22 (d, $J$ = 8.0 Hz, 1H), 7.13 (dd, $J_1$ = 8.0 Hz, $J_2$ = 1.2 Hz, 1H), 7.04 (s, 1H), 7.01 (s, 1H), 3.97 (s, 3H), 3.89 (s, 3H), 3.44 (s, 1H), 3.40−1.45 (br m, 22H); $^{13}C$ NMR (100 MHz, $CDCl_3$) $\delta$ 154.5, 154.0, 135.3, 132.1, 131.0, 126.4, 123.8, 122.0, 116.2, 115.6, 113.4, 112.5, 91.8, 91.0, 90.4, 87.8, 82.8, 79.9, 77.9, 77.7, 60.3, 56.5, 56.4; EI-HRMS $m/z$ calcd for $C_{26}H_{34}B_{20}O_2$ 595.4549, found 595.4552.

**Compound 10.** Terminal alkyne **8** (0.019 g, 0.031 mmol) was subjected to the general Sonogashira protocol, using **9**[23] (0.019 g, 0.034 mmol), $PdCl_2(PPh_3)_2$ (0.002 g, 0.003 mmol), CuI (0.001 g, 0.006 mmol), TEA (1 mL), and THF (5 mL) and stirred at rt overnight. The resulting residue was purified by column chromatography in silica gel with 25% $CH_2Cl_2$ in hexanes to give product **10** (0.017 g, 53%) as a light yellow solid. FTIR (neat) 3493, 3395, 3061, 2924, 2853, 2614, 2358, 2205, 1615, 1507, 1220, 1063, 727 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$ 7.47 (d, $J$ = 1.5 Hz, 1H), 7.33 (s, 1H), 7.22 (d, $J$ = 8 Hz, 1H), 7.13 (dd, $J_1$ = 8 Hz, $J_2$ = 1.5 Hz, 1H), 7.04 (s, 2H), 6.59 (s, 1H), 4.13 (br s, 2H), 3.98 (s, 6H), 2.6 (br m, 44H); $^{13}C$ NMR (100 MHz, $CDCl_3$) $\delta$ 154.0, 153.7, 147.4, 136.1, 135.3, 132.1, 130.8, 126.6, 125.1, 123.7, 121.9, 117.2, 115.5, 115.4, 115.3, 114.1, 112.2, 106.6, 92.7, 92.6, 91.6, 90.94, 90.91, 87.7, 77.9, 77.8, 74.8, 60.2, 56.3, 29.6; MALDI-TOF MS (+eV) $m/z$ calcd for $C_{40}H_{59}B_{40}NO_2$ 1018.9, found 1019.0.

**Nanocar 1.** In a Schlenk tube under nitrogen, **10** (0.021 g, 0.026 mmol) was dissolved in DMF (1.0 mL) and $Et_3N$ (0.1 mL). TRITC (5.8 mg, 0.013 mmol) in solution in DMF (1.0 mL) was added dropwise, and the mixture was heated to 60 °C, then stirred overnight in the dark. The solvents were then removed by rotary evaporation under reduced pressure. The resulting solid was purified by flash column chromatography in silica gel with 10% MeOH in $CH_2Cl_2$ to yield **1** as a purple solid (3 mg, 16%). FTIR (neat) 3349, 2960, 2921, 2851, 2615, 2359, 2342, 1737, 1596, 1510, 1249, 1185, 1112, 1039, 828, 803 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$ 7.98 (br s, 1H), 7.82 (d, $J$ = 8.8 Hz, 1H), 7.48 (m, 1H), 7.15 (m, 6H), 6.82 (m, 2H), 6.69 (d, $J$ = 8.6 Hz, 2H), 6.50 (d, $J$ = 2.0 Hz, 2H), 6.42 (dd, $J_1$ = 7.6 Hz, $J_2$ = 2.0 Hz, 2H), 4.01 (s, 6H), 3.00 (s, 12H), 3.00−1.47 (br m, 44H). The material was not soluble enough for $^{13}C$ analysis. MALDI-TOF MS (+eV) $m/z$ calcd 1461.9, found 1462.2.

**Compound 12.** See the general procedure for the Pd/Cu Sonogashira coupling reaction. The materials used were **6** (60 mg, 0.12 mmol), **11**[25] (53 mg, 0.13 mmol), $PdCl_2(PPh_3)_2$ (10 mg, 0.01 mmol), CuI (5.0 mg, 0.02 mmol), THF (10 mL), and $Et_3N$ (5 mL) at rt overnight. The crude product was purified by column chromatography (silica gel, 10% $CH_2Cl_2$ in hexanes) to yield a white solid (70 mg). The product was then deprotected (see the general procedure for the removal of the TMS/TIPS protecting groups). The materials used were the white solid (70 mg, 0.086 mmol), THF (10 mL), and TBAF (0.40 mL, 0.40 mmol) at rt. The resulting reaction mixture was passed through a plug of silica gel and concentrated to afford the title compound **12** as a yellow solid (56 mg, 77%, two steps). FTIR (KBr) 2925, 2614, 1502, 1463, 1408, 1385, 1221, 1064, 1041, 785 $cm^{-1}$; $^1H$ NMR (500 MHz $CDCl_3$) $\delta$ 7.38 (d, $J$ = 1.6 Hz, 1H), 7.21 (d, $J$ = 8.2 Hz, 1H), 7.12 (dd, $J_1$ = 8.2 Hz, $J_2$ = 1.6 Hz, 1H), 7.02 (s, 1H), 6.99 (s, 1H), 4.06 (t, $J$ = 6.5 Hz, 2H), 3.97 (t, $J$ = 6.5 Hz, 2H), 3.37 (s, 1H), 3.00−1.60 (br m, 26H), 1.09 (m, 6H); $^{13}C$ NMR (126 MHz $CDCl_3$) $\delta$ 154.2, 153.7, 135.4, 132.3, 131.0, 126.9, 123.8, 122.1, 118.0, 117.0, 114.2, 113.3, 91.8, 91.1, 91.0, 88.0, 82.7, 80.1, 78.1, 77.9, 71.25, 71.22, 69.6, 60.4, 22.85, 22.83, 18.3, 18.0, 17.9, 12.7, 12.5, 10.7, 10.6; EI-HRMS calcd for $C_{30}H_{42}B_{20}O_2$ 650.5191, found 650.5163.

**Compound 14.** A 25 mL round-bottomed flask equipped with a stir bar was charged with **13**[19] (320 mg, 0.61 mmol) and acetone (10 mL). Then *N*-bromosuccinimide (229 mg, 1.28 mmol) and $AgNO_3$ (20 mg, 0.12 mmol) were added, in that order. The mixture was stirred in the dark at rt for 2 h, and then the solvent was removed in vacuum. The residue was passed through a silica gel plug using $CH_2Cl_2$ followed by $Et_2O$ as eluents, to give **14** as a white solid (300 mg, 92%). *Caution: alkynyl bromides decompose over time and evolve HBr. Care should be taken when handling*. FTIR (neat) 3072, 2998, 2952, 2919, 2849, 1760, 1453, 1325, 1242 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$ 7.84 (s, 2H); $^{13}C$ NMR (100 MHz, $CDCl_3$) $\delta$ 142.4, 131.0, 99.1, 80.6, 58.1; EI-HRMS $m/z$ calcd for $C_{10}H_2Br_2I_2$ 533.6613, found 533.6606.

**Compound 16.** An oven-dried 50 mL round-bottom flask equipped with a magnetic stir bar was charged with *p*-carborane (**15**) (85 mg, 0.59 mmol) and dry THF (8 mL). The solution was cooled to −78 °C, and BuLi (0.24 mL, 0.60 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. CuBr (121 mg, 0.84 mmol) was then added, and the mixture was allowed to stir at rt for 30 min. A solution of **14** (150 mg, 0.28 mmol) in dry THF (10 mL) was added, and the resulting mixture was allowed to stir overnight at rt. A few drops of water were added, and the mixture was filtered through a silica gel pad using hexanes as the eluent. The resulting greenish solid was purified by column chromatography (silica gel, hexanes as eluent) to provide **16** (130 mg, 70%) as a white powder. FTIR (neat) 2613, 1463, 1384, 1123, 1084, 1064, 1047 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$ 7.63 (s, 2H), 3.40−1.60 (br m, 22H); $^{13}C$ NMR (100 MHz, $CDCl_3$) $\delta$ 141.7, 129.9, 99.7, 91.8, 79.8, 68.9, 61.0; EI-HRMS $m/z$ calcd for $C_{14}H_{24}B_{20}I_2$ 663.1949, found 663.1944.

**Compound 17.** See the general procedure for the Pd/Cu Sonogashira coupling reaction. The materials used were **12** (58 mg, 0.09 mmol), **16** (98 mg, 0.15 mmol), $PdCl_2(PPh_3)_2$ (10 mg, 0.01 mmol), CuI (5.0 mg, 0.02 mmol), THF (10 mL), and $Et_3N$ (5 mL) at rt overnight. The crude product was purified by column chromatography (silica gel, using 20% $CH_2Cl_2$ in hexanes) to yield **17** as a yellow solid (34 mg, 32%). FTIR (neat) 3060, 2963, 2925, 2851, 2618, 2237, 2335, 2214, 1501, 1466, 1422, 1369, 1263, 1219, 1062 $cm^{-1}$; $^1H$ NMR (500 MHz $CDCl_3$) $\delta$ 7.74 (s, 1H), 7.40 (d, $J$ = 1.6 Hz, 1H), 7.33 (s, 1H), 7.22 (d, $J$ = 8.2 Hz, 1H), 7.14 (dd, $J_1$ = 8.2 Hz, $J_2$ = 1.6 Hz, 1H), 7.06 (s, 1H), 7.04 (s, 1H), 4.09 (t, $J$ = 6.5 Hz, 4H), 3.10−1.60 (br m, 48H), 1.13 (m, 6H); $^{13}C$ NMR (126 MHz $CDCl_3$) $\delta$ 153.94, 153.92, 142.0, 135.5, 135.4, 132.3, 131.0, 128.7, 127.0, 126.6, 124.8, 123.9, 122.2, 117.02, 116.98, 114.3, 113.7, 99.5, 92.4, 92.1, 91.9, 91.4, 91.2, 91.1, 88.0, 80.7, 78.2, 78.0, 77.4, 76.5, 71.22, 71.19, 69.7, 69.3, 60.9, 60.7, 60.5, 53.6, 34.9, 29.9, 22.98, 22.96, 22.88, 10.78, 10.77; MALDI-TOF MS (+eV) $m/z$ calcd for $C_{44}H_{65}B_{40}IO_2$ 1185.8, found 1186.0.

**Compound 19.** See the general procedure for the Pd/Cu Sonogashira coupling reaction. The materials used were **16** (150 mg, 0.23 mmol), 4-ethynylaniline (**18**)[24] (16 mg, 0.13 mmol), $PdCl_2(PPh_3)_2$ (157 mg, 0.224 mmol), CuI (85 mg, 0.45 mmol), THF (30 mL), and

$Et_3N$ (10 mL) at rt overnight. The crude product was purified by column chromatography (silica gel, using 50% $CH_2Cl_2$ in hexanes) to yield **19** as a yellow solid (50 mg, 56%). $^1H$ NMR (400 MHz $CDCl_3$) $\delta$ 7.69 (s, 1H), 7.34 (d, $J$ = 8.6 Hz, 2H), 7.32 (s, 1H), 6.66 (d, $J$ = 8.6 Hz, 2H), 3.89 (br s, 2H), 3.10−1.60 (br m, 24H); $^{13}C$ NMR (100 MHz $CDCl_3$) $\delta$ 147.5, 141.9, 134.9, 133.5, 128.4, 127.0, 124.6, 114.9, 111.9, 98.4, 97.0, 91.7, 90.9, 84.3, 80.9, 69.4, 60.7, 53.6, 29.9; EI-HRMS calcd for $C_{22}H_{30}B_{20}IN$ 652.3418, found 652.3410.

**Compound 20.** See the general procedure for the Pd/Cu Sonogashira coupling reaction. The materials used were **19** (30 mg, 46 $\mu$mol), **11**[25] (24 mg, 68 $\mu$mol), $PdCl_2(PPh_3)_2$ (5 mg, 5 $\mu$mol), CuI (2.5 mg, 10 $\mu$mol), THF (10 mL), and $Et_3N$ (5 mL) at rt overnight. The crude product was purified by column chromatography (silica gel, hexanes/$CH_2Cl_2$ 1:1) to yield a yellow solid (33 mg). The product was then deprotected (see the general procedure for the removal of the TMS/TIPS protecting groups). The materials used were the white solid (33 mg, 35 $\mu$mol), THF (5 mL), and TBAF (0.10 mL, 0.10 mmol) at rt. The resulting reaction mixture was passed through a plug of silica gel and concentrated to afford the title compound **20** as a yellow solid (26 mg, 75%, two steps). FTIR (neat) 3063, 2960, 2927, 2863, 2612, 2356, 2338, 2326, 2200, 2167, 2150, 2041, 1979, 1717, 1605, 1513, 1504, 1463, 1416, 1381, 1263, 1216, 1060 $cm^{-1}$; $^1H$ NMR (400 MHz $CDCl_3$) $\delta$ 7.39 (s, 1H), 7.37 (s, 1H), 7.35 (d, $J$ = 8.6 Hz, 2H), 7.02 (s, 1H), 6.99 (s, 1H), 6.67 (d, $J$ = 8.6 Hz, 2H), 4.06 (d, $J$ = 6.5 Hz, 2H), 3.97 (d, $J$ = 6.5 Hz, 2H) 3.91 (br s, 2H), 3.38 (s, 1H), 3.10−1.60 (br m, 26H), 1.09 (m, 6H); $^{13}C$ NMR (100 MHz $CDCl_3$) $\delta$ 154.3, 153.8, 135.8, 135.2, 133.6, 126.6, 125.1, 123.7, 118.0, 117.0, 115.0, 114.2, 113.4, 112.0, 107.7, 92.0, 91.0, 85.0, 82.8, 80.2, 71.3, 68.2, 60.6, 22.9, 18.4, 18.0, 10.7; MALDI-TOF MS (+eV) $m/z$ calcd for $C_{38}H_{47}B_{20}NO_2$ 765.5, found 766.6 [M + H].

**Compound 21.** See the general procedure for the Pd/Cu Sonogashira coupling reaction. The materials used were **17** (12 mg, 10 $\mu$mol), **20** (9 mg, 12 $\mu$mol), $PdCl_2(PhCN)_2$ (2 mg, 5 $\mu$mol), (*tert*-Bu)$_3$PHBF$_4$ (4.5 mg, 15 $\mu$mol), CuI (1 mg, 5 $\mu$mol), THF (5 mL), and $Et_3N$ (2 mL) at 50 °C overnight. The crude product was purified by column chromatography (silica gel, using 50% $CH_2Cl_2$ in hexanes) to yield **21** as a fluorescent yellow solid (8.3 mg, 45%). FTIR (neat) 2925, 2857, 2612, 2480, 2359, 2332, 1725, 1655, 1460, 1377, 1257, 1066, 1036 $cm^{-1}$; $^1H$ NMR (500 MHz $CDCl_3$) $\delta$ 7.42 (s, 2H), 7.40 (m, 3H), 7.36 (d, $J$ = 8.6 Hz, 2H), 7.23 (d, $J$ = 8.2 Hz, 1H), 7.14 (dd, $J_1$ = 8.2 Hz, $J_2$ = 1.6 Hz, 1H), 7.07 (s, 1H), 7.06 (br s, 3H), 6.68 (d, $J$ = 8.6 Hz, 2H), 4.10 (t, $J$ = 6.5 Hz, 8H), 3.91 (br s, 2H), 3.10−1.60 (br m, 74H), 1.13 (m, 12H); $^{13}C$ NMR (126 MHz $CDCl_3$) $\delta$ 154.0, 153.9, 147.5, 135.8, 135.5, 135.2, 133.6, 132.3, 127.0, 126.5, 125.9, 125.1, 123.9, 123.8, 123.7, 123.6, 122.2, 117.0, 114.9, 114.2, 113.9, 112.0, 97.5, 92.9, 92.3, 92.2, 91.2, 91.1, 91.0, 85.1, 71.2, 69.6, 60.5, 59.1, 53.6, 29.9, 23.3, 23.0, 22.9, 14.4, 14.3, 11.8, 10.8; MALDI-TOF MS (+eV) $m/z$ calcd for $C_{82}H_{111}B_{60}NO_4$ 1822.5, found 1823.6 [M + H].

**Compound 2.** In a Schlenk tube under nitrogen, the aniline nanocar **21** (7 mg, 4 $\mu$mol) was dissolved in $CH_2Cl_2$ (1.0 mL) and $Et_3N$ (0.1 mL). TRITC (1.7 mg, 4 $\mu$mol) in solution in DMF (1.0 mL) was added dropwise, and the mixture was stirred overnight at rt in the dark. The solvents were then removed by rotary evaporation under reduced pressure. The resulting solid was purified by column chromatography (silica gel, using 10% MeOH in $CH_2Cl_2$) to yield **2** as a purple solid (2.7 mg, 31%). FTIR (neat) 3349, 3193, 2919, 2851, 2609, 2362, 2338, 2158, 1979, 1716, 1661, 1610, 1510, 1451, 1410, 1372, 1216, 1177, 1104, 1062 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$ 8.28 (s, 2H), 7.66 (d, $J$ = 9.1 Hz, 2H), 7.49 (d, $J$ = 8.5 Hz, 1H), 7.47 (s, 1H), 7.09−7.03 (m, 5H), 6.99−6.97 (m, 2H), 6.69 (d, $J$ = 8.9 Hz, 2H), 6.56−6.50 (m, 4H), 6.34−6.33 (m, 2H), 6.31 (d, $J$ = 2.5 Hz, 1H), 6.02 (s 1H), 3.38 (t, $J$ = 6.5 Hz, 8H), 3.08 (br s, 12H), 3.00−1.47 (br m, 74H), 1.13 (m, 12H). The material was not soluble enough for $^{13}C$ analysis. MALDI-TOF MS (+eV) $m/z$ calcd for $C_{107}H_{132}B_{60}N_4O_7S$ 2266.9, found 2267.4.

**Compound 23.** See the general procedure for the Pd/Cu Sonogashira coupling reaction. The materials used were carbazole **22**[27] (3.54 g, 7.46 mmol), TMSA (0.64 mL, 4.48 mmol), $PdCl_2(PPh_3)_3$ (157 mg, 0.22 mmol), CuI (85 mg, 0.45 mmol), THF (30 mL), and $Et_3N$ (10 mL) at rt overnight. The crude product was purified by column chromatography (silica gel, using 10% $CH_2Cl_2$ in hexanes) to yield **23** as a yellow solid (1096 mg, 55%). FTIR (neat) 3204, 3060, 2960, 2930, 2869, 2353, 2323, 2153, 1858, 1628, 1590, 1478, 1434, 1384, 1345, 1286, 1251, 1210, 1174, 1151, 1130, 1062, 1051, 1012, 897, 839, 803 $cm^{-1}$; $^1H$ NMR (400 MHz $CDCl_3$) $\delta$ 8.34 (d, $J$ = 1.7 Hz, 1H), 8.16 (d, $J$ = 1.4 Hz, 1H), 7.69 (dd, $J_1$ = 8.6 Hz, $J_2$ = 1.7 Hz, 1H), 7.57 (dd, $J_1$ = 8.5 Hz, $J_2$ = 1.6 Hz, 1H), 7.28 (d, $J$ = 8.5 Hz, 1H), 7.16 (d, $J$ = 8.6 Hz, 1H), 4.22 (t, $J$ = 8.0 Hz, 2H), 1.80 (quint, $J$ = 7.5 Hz, 2H), 1.34 (sext, $J$ = 7.5 Hz, 2H), 0.92 (t, $J$ = 7.4 Hz, 3H), 0.29 (s, 9H); $^{13}C$ NMR (100 MHz $CDCl_3$) $\delta$ 140.3, 140.1, 134.4, 130.4, 129.6, 125.1, 124.9, 121.6, 113.9, 111.2, 108.9, 106.5, 92.3, 82.0, 43.2, 31.2, 20.7, 14.0, 0.4; EI-HRMS $m/z$ calcd for $C_{21}H_{24}INSi$ 445.0717, found 445.0723.

**Compound 24.** See the general procedure for the Pd/Cu coupling reaction. The materials used were **23** (1.07 g, 2.4 mmol), TIPSA (1.1 mL, 4.95 mmol), $PdCl_2(PPh_3)_2$ (84 mg, 0.12 mmol), CuI (46 mg, 0.24 mmol), TEA (10 mL), and THF (30 mL) at rt overnight. The residue was purified by flash column chromatography in silica gel with 5% $CH_2Cl_2$ in hexanes; the product-containing fractions were combined and concentrated. The TMS-protected intermediate (983 mg, 1.97 mmol) was dissolved in 30 mL of a 1:1 mixture of THF and MeOH. Then $K_2CO_3$ (542 mg, 3.92 mmol) was added, and the mixture was stirred at rt for 1.5 h. Then it was passed through a silica plug using 30% $CH_2Cl_2$ in hexanes as eluent to yield **24** (763 mg, 75%, 2 steps) as a yellow oil. FTIR (neat) 3311, 3042, 2954, 2942, 2886, 2863, 2721, 2359, 2329, 2147, 2099, 1870, 1678, 1628, 1602, 1478, 1466, 1378, 1351, 1289, 1251, 1213, 1151, 1133, 1068, 998, 918, 883, 803 $cm^{-1}$; $^1H$ NMR (400 MHz $CDCl_3$) $\delta$ 8.23 (d, $J$ = 1.2 Hz, 1H), 8.19 (d, $J$ = 1.4 Hz, 1H), 7.60 (d, $J$ = 1.5 Hz, 1H), 7.57 (d, $J$ = 1.5 Hz, 1H), 7.31 (d, $J$ = 7.1 Hz, 1H), 7.29 (d, $J$ = 7.1 Hz, 1H), 4.26 (t, $J$ = 8.0 Hz, 2H), 3.06 (s, 1H), 1.81 (quint, $J$ = 8.0 Hz, 2H), 1.34 (sext, $J$ = 8.0 Hz, 2H), 1.17 (s, 21 H), 0.92 (t, $J$ = 8.0 Hz, 3H); $^{13}C$ NMR (100 MHz $CDCl_3$) $\delta$ 140.6, 140.4, 130.2, 129.9, 124.8, 124.6, 122.3, 122.2, 114.3, 112.6, 108.9, 108.8, 108.2, 88.3, 84.7, 75.3, 43.0, 31.0, 20.4, 18.7, 13.8, 11.4; EI-HRMS $m/z$ calcd for $C_{29}H_{37}NSi$ 427.2698, found 427.2695.

**Compound 25.** See the general procedure for the Pd/Cu coupling reaction. The materials used were **24** (30 mg, 69.6 $\mu$mol), **9**[23] (32 mg, 58.0 $\mu$mol), $PdCl_2(PPh_3)_2$ (6 mg, 8.7 $\mu$mol), CuI (3.3 mg, 17.4 $\mu$mol), TEA (1 mL), and THF (3 mL) at rt overnight. The residue was purified by flash column chromatography in silica gel with 20% $CH_2Cl_2$ in hexanes; the product-containing fractions were combined and concentrated. The product was then deprotected (see the general procedure for the removal of the TMS/TIPS protecting groups). The materials used were the yellow solid (38 mg, 44.0 $\mu$mol), THF (5 mL), and TBAF (0.33 mL, 0.33 mmol) at rt. Then it was passed through a silica plug using 20% $CH_2Cl_2$ in hexanes as eluent to yield **25** (19.5 mg, 54%, 2 steps) as a yellow solid. FTIR (neat) 3487, 3393, 3308, 3060, 2957, 2925, 2871, 2606, 2362, 2329, 2226, 2208, 2105, 1613, 1596, 1498, 1478, 1381, 1357, 1286, 1210, 1151, 1127, 1062, 1006, 971, 886, 806, 753 $cm^{-1}$; $^1H$ NMR (400 MHz $CDCl_3$) $\delta$ 8.28 (dd, $J_1$ = 12.0 Hz, $J_2$ = 4.0 Hz, 2H), 7.60 (dd, $J_1$ = 12.0 Hz, $J_2$ = 4.0 Hz, 2H), 7.36 (t, $J$ = 8.0 Hz, 2H), 7.31 (s, 1H), 6.61 (s, 1H), 4.30 (t, $J$ = 8.0 Hz, 2H), 4.09 (s, 2H), 3.30−1.50 (br m, 25H), 1.42 (quart, $J$ = 8.0 Hz, 2H), 0.96 (t, $J$ = 8.0 Hz, 3H); $^{13}C$ NMR (100 MHz $CDCl_3$) $\delta$147.2, 140.9, 140.6, 135.7, 130.2, 129.7, 125.3, 125.1, 124.4, 122.7, 122.6, 117.6, 116.3, 114.3, 112.8, 109.1, 106.9, 92.9, 90.1, 85.6, 85.0,

78.4, 75.5, 75.2, 60.3, 43.1, 31.3, 20.7, 14.0; MALDI-TOF MS (+eV) $m/z$ calcd for $C_{34}H_{42}B_{20}N_2$ 694.9, found 695.5.

**Compound 26.** See the general procedure for the Pd/Cu Sonogashira coupling reaction. The materials used were **25** (60 mg, 86.0 $\mu$mol), **6**[22] (42 mg, 78.0 $\mu$mol), $PdCl_2(PPh)_3$ (5.5 mg, 7.8 $\mu$mol), CuI (3.0 mg, 3.0 $\mu$mol), THF (4.5 mL), and $Et_3N$ (1.5 mL) at rt overnight. The crude product was purified by column chromatography (silica gel, using 25% $CH_2Cl_2$ in hexanes) to yield **26** as a yellow solid (54 mg, 63%). FTIR (neat) 3493, 3390, 3066, 3010, 2927, 2654, 2609, 2362, 2323, 2207, 2158, 1610, 1590, 1493, 1460, 1384, 1351, 1286, 1239, 1210, 1148, 1127, 1062, 1004, 968, 877, 806 $cm^{-1}$; $^1H$ NMR (400 MHz $CDCl_3$) $\delta$ 8.37 (dd, $J_1$ = 12.0 Hz, $J_2$ = 4.0 Hz, 2H), 7.66 (dd, $J_1$ = 12.0 Hz, $J_2$ = 1.7 Hz, 1H), 7.64 (dd, $J_1$ = 12.0 Hz, $J_2$ = 4.0 Hz, 1H), 7.41 (m, 3H), 7.24 (s, 1H), 7.24 (d, $J$ = 4.0 Hz, 1H), 7.11 (dd, $J_1$ = 8.0 Hz, $J_2$ = 4.0 Hz, 1H), 6.62 (s, 1H), 4.33 (t, $J$ = 8.0 Hz, 2H), 4.08 (br s, 2H), 3.40−1.40 (br m, 48H), 0.99 (t, $J$ = 7.4 Hz, 3H); $^{13}C$ NMR (100 MHz $CDCl_3$) $\delta$ 147.2, 141.0, 140.6, 135.6, 134.8, 132.4, 130.4, 129.7, 129.5, 127.4, 125.3, 124.7, 123.9, 122.9, 122.8, 122.0, 117.6, 116.4, 114.4, 113.4, 109.4, 109.2, 106.8, 96.5, 93.0, 92.8, 91.0, 90.1, 87.8, 85.6, 85.3, 78.4, 78.3, 78.2, 75.2, 69.9, 69.4, 60.5, 43.4, 31.4, 29.9, 20.8, 14.3, 14.1; MALDI-TOF MS (+eV) $m/z$ calcd for $C_{48}H_{66}B_{40}N_2$ 1103.4, found 1104.0.

**Compound 3.** In a Schlenk tube under nitrogen, the aniline nanocar **26** (19 mg, 17.2 $\mu$mol) was dissolved in $CH_2Cl_2$ (1.0 mL) and $Et_3N$ (0.1 mL). TRITC (8 mg, 17.2 $\mu$mol) in solution in DMF (1.0 mL) was added dropwise and the mixture stirred overnight at 50 °C in the dark. The solvents were then removed under reduced pressure. The resulting solid was purified by column chromatography (silica gel, using 10% MeOH in $CH_2Cl_2$) to yield **3** as a purple solid (3.3 mg, 13%). *Note: It was not possible to obtain a clean $^1H$ NMR spectrum of **3** where all expected signals were observable due to the small amount prepared; however, the presence of the desired compound was confirmed by MALDI MS.* FTIR (neat) 3343, 3060, 2925, 2854, 2618, 2356, 2338, 2209, 1711, 1596, 1493, 1463, 1410, 1348, 1266, 1216, 1189, 1127, 1104, 1062, 930, 827 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$ 7.80 (d, $J$ = 8.5 Hz, 1H), 7.70 (dd, $J_1$ = 6.0 Hz, $J_2$ = 3.5 Hz, 2H), 7.53 (dd, $J_1$ = 6.0 Hz, $J_2$ = 3.5 Hz, 2H), 7.47 (s, 1H), 7.30 (s, 2H), 7.22 (s, 2H), 7.12 (m, 5H), 7.05 (s, 1H), 6.80 (m, 3H), 6.73 (d, $J$ = 8.5 Hz, 1H), 4.22 (m, 2H), 3.35 (s, 12H). The material was not soluble enough for $^{13}C$ analysis. MALDI-TOF MS (+eV) $m/z$ calcd for $C_{73}H_{87}B_{40}N_5O_3S$ 1547.0, found 1548.2 [M + H].

**Compound 29.** Trialkyne **27**[19] (0.100 g, 0.667 mmol) was subjected to the general Sonogashira protocol using **28**[19] (0.978 g, 2.00 mmol), $PdCl_2(PPh_3)_2$ (0.126 g, 0.179 mmol), CuI (0.066 g, 0.346 mmol), TEA (3.0 mL), and THF (10.0 mL), and the mixture was stirred at rt overnight. The resulting residue was purified by column chromatography with 25% $CH_2Cl_2$ in hexanes to give **29** (0.557 g, 68%) as a light yellow solid. FTIR (KBr) 2963, 2613, 1579, 1502, 1423, 1218, 1061 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$ 7.57 (s, 3H), 6.89 (s, 3H), 6.76 (s, 3H), 3.92 (t, $J$ = 5.2 Hz, 6H), 3.87 (t, $J$ = 5.2 Hz, 6H), 3.15−1.90 (br m, 33H), 1.82 (m, 12H), 1.08 (m, 18H); $^{13}C$ NMR (100 MHz, $CDCl_3$) $\delta$ 154.5, 153.7, 134.2, 124.3, 117.2, 117.1, 114.5, 112.5, 93.5, 91.0, 87.1, 76.2, 71.4, 71.1, 22.9, 22.8, 10.8, 10.7; MALDI-TOF MS (+eV) $m/z$ calcd for $C_{60}H_{84}B_{30}O_6$ 1226.0, found 1226.0.

**Compound 30.** 1-Nitro-4-trimethylsilylethynylbenzene (2.19 g, 10.00 mmol) was combined with $AgNO_3$ (0.340 g, 2.00 mmol), *N*-bromosuccinimide (1.80 g, 10.1 mmol), and acetone (100 mL). The mixture was stirred for 2 h at rt in the dark and poured onto a pad of silica gel. The pad was then eluted with 40% $CH_2Cl_2$ in hexanes, and the solvents were removed to yield **30** (2.37 g, 91%) as a light yellow solid. *Caution: alkynyl bromides decompose over time and evolve HBr. Care should be taken when handling.* FTIR (KBr) 3105, 2196, 1772, 1698, 1591, 1508, 1346, 1192, 853, 748 $cm^{-1}$; $^1H$ NMR (500 MHz, $CDCl_3$) $\delta$ 8.18 (d, $J$ = 8.8 Hz, 2H), 7.58 (d, $J$ = 8.8 Hz, 2H); $^{13}C$ NMR (126 MHz, $CDCl_3$) $\delta$ 147.5, 133.0, 129.7, 123.8, 78.6, 56.6; EI-HRMS $m/z$ calcd for $C_8H_4BrNO_2$ 224.9425, found 224.9419.

**Compound 31.** Trimer **29** (0.40 g, 0.33 mmol) was added to an oven-dried, three-neck round-bottom flask, followed by THF (5 mL). The mixture was cooled to −78 °C, and BuLi (2.5 M in hexanes, 0.13 mL, 0.033 mmol) was added dropwise. The mixture was allowed to stir at −15 °C for 1 h, followed by cooling to −78 °C. To the blue mixture was then added CuBr (0.061 g, 0.424 mmol), followed by warming to −15 °C and stirring for 1 h. Alkynyl bromide **30** (0.096 g, 0.424 mmol) was then added all at once as a solid, and the mixture was allowed to warm to rt and stirred overnight. The reaction was quenched by addition of 1 drop of water, followed by elution through a Celite pad with $CH_2Cl_2$. The resulting residue was then purified using flash chromatography with 25% $CH_2Cl_2$ in hexanes as eluent to give product **31** (0.098 g, 22%) as a light yellow solid. FTIR (KBr) 2963, 2925, 2875, 2855, 2615, 1579, 1502, 1467, 1423, 1387, 1343, 1276, 1218, 1062, 1017, 989 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$ 8.14 (d, $J$ = 7.2 Hz, 2H), 7.57 (s, 3H), 7.47 (d, $J$ = 6.8 Hz, 2H), 6.89 (s, 3H), 6.76 (s, 3H), 3.92 (t, $J$ = 5.2 Hz, 6H), 3.86 (t, $J$ = 5.2 Hz, 6H), 3.20−1.90 (br m, 33H), 1.81 (m, 12H), 1.07 (m, 18H); $^{13}C$ NMR (100 MHz, $CDCl_3$) $\delta$ 154.5, 153.7, 147.8, 134.2, 133.1, 128.2, 124.3, 124.2, 123.7, 117.19, 117.17, 117.1, 117.0, 114.8, 114.5, 93.7, 93.5, 91.1, 87.1, 71.40, 71.37, 71.14, 71.07, 29.9, 22.9, 22.8, 10.8; MALDI-TOF MS (+eV) $m/z$ calcd for $C_{68}H_{87}B_{30}NO_8$ 1371.0, found 1371.0.

**Compound 32.** To a round-bottom flask with stir bar was added trimer **31** (0.074 g, 0.054 mmol), Zn powder (0.353 g, 5.39 mmol), 1 drop AcOH, and THF (3.0 mL). The mixture was allowed to stir for 1 h and the reaction quenched by elution through a Celite pad with $CH_2Cl_2$. The resulting residue was then purified using flash chromatography with 25% $CH_2Cl_2$ in hexanes as eluent to give product **32** (0.072 g, 100%) as a light yellow solid. FTIR (neat) 3568, 3386, 2964, 2934, 2876, 2614, 2364, 2229, 1619, 1605, 1578, 1501, 1422, 1386, 1276, 1217, 1062, 1015 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$ 7.57 (s, 3H), 7.11 (d, $J$ = 8.7 Hz, 2H), 6.89 (s, 3H), 6.75 (s, 3H), 6.53 (d, $J$ = 8.7 Hz, 2H), 3.92 (t, $J$ = 6.5 Hz, 6H), 3.86 (t, $J$ = 6.2 Hz, 6H), 3.30−1.60 (br m, 46H), 1.06 (t, $J$ = 7.4 Hz, 18H); $^{13}C$ NMR (100 MHz, $CDCl_3$) $\delta$ 154.49, 154.48, 153.7, 134.2, 133.5, 124.3, 117.2, 117.11, 117.09, 115.7, 114.7, 114.5, 112.5, 93.6, 87.1, 76.8, 76.2, 71.4, 71.1, 29.9, 22.9, 22.8, 10.76, 10.75; MALDI-TOF MS (+eV) $m/z$ calcd for $C_{68}H_{90}B_{30}NO_6$ 1341.0, found 1342.1 [M + H].

**Trimer 4.** Into a Schlenk tube under nitrogen, trimer **32** (15 mg, 0.011 mmol) was dissolved in $CH_2Cl_2$ (1 mL) and TEA (0.1 mL). TRITC (5 mg, 0.011 mmol) in solution in DMF (1 mL) was added dropwise, and the mixture was stirred overnight in the dark at rt. The solvents were removed by rotary evaporation. The resulting residue was then purified using flash chromatography with 10% MeOH in $CH_2Cl_2$ as eluent to give **4** (9 mg, 45%) as a purple solid. FTIR (neat) 3350, 2961, 2924, 2853, 2615, 2369, 1596, 1500, 1421, 1365, 1349, 1218, 1188 $cm^{-1}$; $^1H$ NMR (400 MHz $CDCl_3$) $\delta$ 8.05 (br s, 1H), 7.89 (d, $J$ = 8.8 Hz, 1H), 7.74 (br s, 1H), 7.58 (m, 1H), 7.52 (s, 3H), 7.20 (m, 4H), 7.05 (d, $J$ = 9.5 Hz, 1H), 6.85 (s, 3H), 6.72 (dd, $J_1$ = 8.3 Hz, $J_2$ = 2.0 Hz, 2H), 6.71 (s, 3H), 6.67 (d, $J$ = 2.0 Hz, 2H), 3.88 (t, $J$ = 6.5 Hz, 6H), 3.82 (t, $J$ = 6.5 Hz, 6H), 3.21 (s, 12H), 3.00−1.47 (br m, 33H), 1.77 (m, 12H), 1.02 (m, 18H). The material was not soluble enough for $^{13}C$ analysis. MALDI-TOF MS (+eV) $m/z$ calcd for $C_{93}H_{110}B_{30}N_4O_6S$ 1784.1, found 1785.1 [M + H].

**Compound 34.** A Schlenk tube equipped with a magnetic stir bar was charged with **33**[19] (80 mg, 80 $\mu$mol) and dry THF (3 mL). The solution was cooled to −30 °C, and BuLi (32 $\mu$L, 80 $\mu$mol, 2.5 M in hexanes) was added. The solution was allowed to stir at −30 °C for 15 min before CuBr (17 mg, 118 $\mu$mol) was added, and the mixture was allowed to stir at −30 °C for 15 min.

**30** (18 mg, 80 $\mu$mol) was added, and the resulting mixture was allowed to stir at rt for 16 h. A few drops of water were added, and the mixture was filtered through a silica gel pad using $CH_2Cl_2$ as the eluent. The resulting greenish solid was purified by column chromatography (silica gel, using 50% $CH_2Cl_2$ in hexanes) to provide a mixture of **34** and **34′** as a white powder (15 mg, 16%). FTIR (neat) 3063, 3010, 2960, 2927, 2854, 2609, 2362, 2344, 2209, 1593, 1528, 1501, 1450, 1407, 1378, 1348, 1278, 1257, 1219, 1133, 1059, 1039, 1012, 853, 830 $cm^{-1}$; $^1H$ NMR (400 MHz $CDCl_3$) $\delta$ 8.14 (d, $J$ = 9.0 Hz, 2H), 7.49−7.45 (m, 4H), 7.26−7.23 (m, 2H), 7.17−7.15 (m, 2H), 7.07−7.05 (m, 2H), 4.00 (m, 6H), 3.20−1.60 (br m, 44H); $^{13}C$ NMR (100 MHz $CDCl_3$) $\delta$ 154.27, 154.23, 147.82, 135.53, 133.03, 132.35, 132.28, 131.20, 128.11, 128.06, 126.81, 126.68, 124.26, 124.01, 123.70, 122.39, 122.17, 121.85, 115.82, 113.62, 113.56, 113.40, 11.37, 92.23, 91.18, 92.04, 91.34, 91.17, 91.02, 90.89, 90.85, 90.78, 90.08, 88.18, 88.05, 87.60, 79.61, 79.51, 78.50, 78.42, 78.10, 78.04, 69.69, 69.33, 60.53, 56.66; MALDI-TOF MS (+eV) $m/z$ calcd for $C_{48}H_{61}B_{40}NO_4$ 1148.4, found 1148.7

**Compound 35.** A Schlenk tube equipped with a magnetic stir bar was charged with **34** (14 mg, 12 $\mu$mol), Zn powder (79 g, 1.21 mmol), 1 drop AcOH, and THF (3.0 mL). The mixture was allowed to stir at 30 °C for 15 min. The resulting greenish solid was purified by column chromatography (silica gel, hexanes/$CH_2Cl_2$ 1:1) to provide a mixture of **35** and **35′** as a white powder (8 mg, 59%). FTIR (neat) 3484, 3387, 3060, 2919, 2851, 2609, 2356, 2326, 2220, 1719, 1602, 1504, 1460, 1407, 1384, 1284, 1224, 1180, 1145, 1062, 1045, 1012, 892, 868, 830 $cm^{-1}$; $^1H$ NMR (400 MHz $CDCl_3$) $\delta$ 7.48−7.49 (m, 2H), 7.23 (d, $J$ = 8.1 Hz, 2H), 7.14 (dd, $J_1$ = 8.1 Hz, $J_2$ = 1.6 Hz, 2H), 7.11−7.06 (m, 4H), 6.54−6.51 (m, 2H), 4.00 (m, 6H), 3.81 (br s, 2H), 3.20−1.60 (br m, 44H); $^{13}C$ NMR (100 MHz $CDCl_3$) $\delta$ 154.23, 147.49, 135.54, 133.51, 132.33, 131.16, 126.73, 124.04, 123.97, 122.14, 115.81, 114.65, 113.51, 113.47, 113.40, 110.49, 110.40, 92.15, 92.13, 91.19, 90.96, 90.93, 88.01, 69.69, 69.34, 60.52, 56.65; MALDI-TOF MS (+eV) $m/z$ calcd for $C_{48}H_{63}B_{40}NO_2$ 1118.5, found 1118.9.

**Compound 5.** In a Schlenk tube under nitrogen the aniline nanocar **35** (8 mg, 7 $\mu$mol) was dissolved in $CH_2Cl_2$ (1.0 mL) and $Et_3N$ (0.1 mL). TRITC (3 mg, 7 $\mu$mol) in DMF (1.0 mL) was added dropwise, and the mixture was stirred overnight at rt in the dark. The solvents were then removed by rotary evaporation under reduced pressure. The resulting solid was purified by column chromatography (silica gel, 10% MeOH in $CH_2Cl_2$) to yield a mixture of **5** and **5′** as a purple solid (3.1 mg, 29%). FTIR (neat) 3337, 3060, 2922, 2854, 2612, 2362, 2338, 1711, 1593, 1578, 1504, 1460, 1410, 1381, 1260, 1219, 1180, 1104, 1062, 1045, 1009, 847 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$ 7.95 (br s, 1H), 7.82 (d, $J$ = 8.8 Hz, 1H), 7.74 (d, $J$ = 8.8 Hz, 1H), 7.58 (d, $J$ = 8.9 Hz, 1H), 7.49−7.48 (m, 3H), 7.15−7.05 (m, 5H), 6.98 (d, $J$ = 8.4 Hz, 2H), 6.82 (m, 2H), 6.72 (d, $J$ = 8.6 Hz, 1H), 6.46−6.40 (m, 4H), 4.01 (br s, 6H), 3.00 (br s, 12H), 3.00−1.47 (br m, 43H). The material was not soluble enough for $^{13}C$ analysis. MALDI-TOF MS (+eV) $m/z$ calcd for $C_{73}H_{84}B_{40}N_4O_5S$ 1561.9, found 1562.0.

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**Supporting Information Available:** $^1H$ and $^{13}C$ NMR of new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.