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Synthesis of Well-Defined Tower-Shaped 1,3,5-Trisubstituted Adamantanes Incorporating a Macrocyclic Trilactam Ring System

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We describe the synthesis of two novel well-defined tower-shaped 1,3,5-trisubstituted adamantanes **30** and **33** that incorporate a macrocyclic trilactam ring system. Each nanoscale molecule has a broad tripodal base consisting of three identical sulfur-containing termini as the tripod feet, 4-acetylsulfanylmethylphenyl units in the case of **30** and 3,5-bis(acetylsulfanylmethyl)phenyl units in the case of **33**. The sulfur atoms are designed to bind the molecules trivalently to the apex of a gold-coated commercial AFM tip through formation of three S−Au bonds. The rigid adamantane-derived head unit with a single hydrogen atom at the apex is designed to scan the sample. Molecules **30** and **33** are synthesized from 1,3,5-triethynyladamantane by a series of Sonogashira coupling reactions involving terminal alkynes and aryl iodides. A macrocyclic trilactam unit is included for added rigidity. We demonstrate that molecule **30** is sufficiently large and rigid to be visualized by a conventional AFM tip. These nanoscale molecules may also find application as chemically well-defined nanoscale objects for calibration of AFM tips.

Introduction

Tapered nanoscale molecules are potentially useful as single-molecule atomic force microscopy (AFM) tips for imaging both biological[1] and nonbiological surfaces.[2] Examples of such molecules include the tripodal[3] oligophenylene silanes described by Cai et al.[4] and the caltrop-shaped tetrasubstituted silanes described by Yao and Tour.[5] About the same time we described the synthesis of a prototypic tower-shaped molecule **1** (Chart 1) as an inroad to a series of single molecule tips for AFM applications.[6,7] Subsequently, a series of tetrahedrally shaped molecules was completed including 1,3,5,7-symmetrically substituted tetraphenyladamantane **2** and the symmetrically substituted tetraphenylmethane **3**.[8] Most recently, the synthesis of several related, tetrahedrally shaped tripodal adamantane-based molecules **4** and **5** was completed. One terminus was differentiated as an ester group while the other three termini contain sulfur atoms for eventual binding to a gold-coated commercial AFM tip.[9] We also demonstrated that **3**[8] and **4**[9] ($n = 2$) are sufficiently large and rigid to be imaged by a conventional AFM tip. Herein, we describe the synthesis of two nanoscale molecules **30** and **33**, which are much larger versions of **1** and rationally designed to have a more optimal aspect ratio when eventually attached to a commercial AFM tip.

Results and Discussion

Molecular Design. Ideally, potential tip molecules should be mechanically rigid and conformationally well defined and include functional groups suitable for chemical attachment to the apex of a commercial tip. The base of the molecular tip should be broad and the tip height should be such that adjacent tip molecules bound to the convex surface do not interfere with imaging by the apical molecule (Figure 1). If the base of the tip molecule is too small, then covering the commercial tip with tip molecules only increases the radius of curvature of the molecular tip.

Each of the target molecules consists of four units. The first unit is a rigid, trisubstituted adamantane head unit with a single hydrogen atom at the apex and designed to probe the sample. The second unit is the body consisting of three rodlike phenylene−ethynylene units linked

(1) *Atomic Force Microscopy in Cell Biology*; Jena, B. P., Horber, H. J. K., Eds.; Vol. 68, Methods in Cell Biology; 2002.

(2) Nanoscience and Technology. In *Noncontact Atomic Force Microscopy*; Morita, S., Wiesendanger, R., Meyer, E., Eds.; Springer-Verlag: New York, 2002

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(4) (a) Deng, X.; Mayeux, A.; Cai, C. *J. Org. Chem.* **2002**, *67*, 5279. (b) Deng, X.; Cai, C. *Tetrahedron Lett.* **2003**, *44*, 815.

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10.1021/jo035640+ CCC: $27.50
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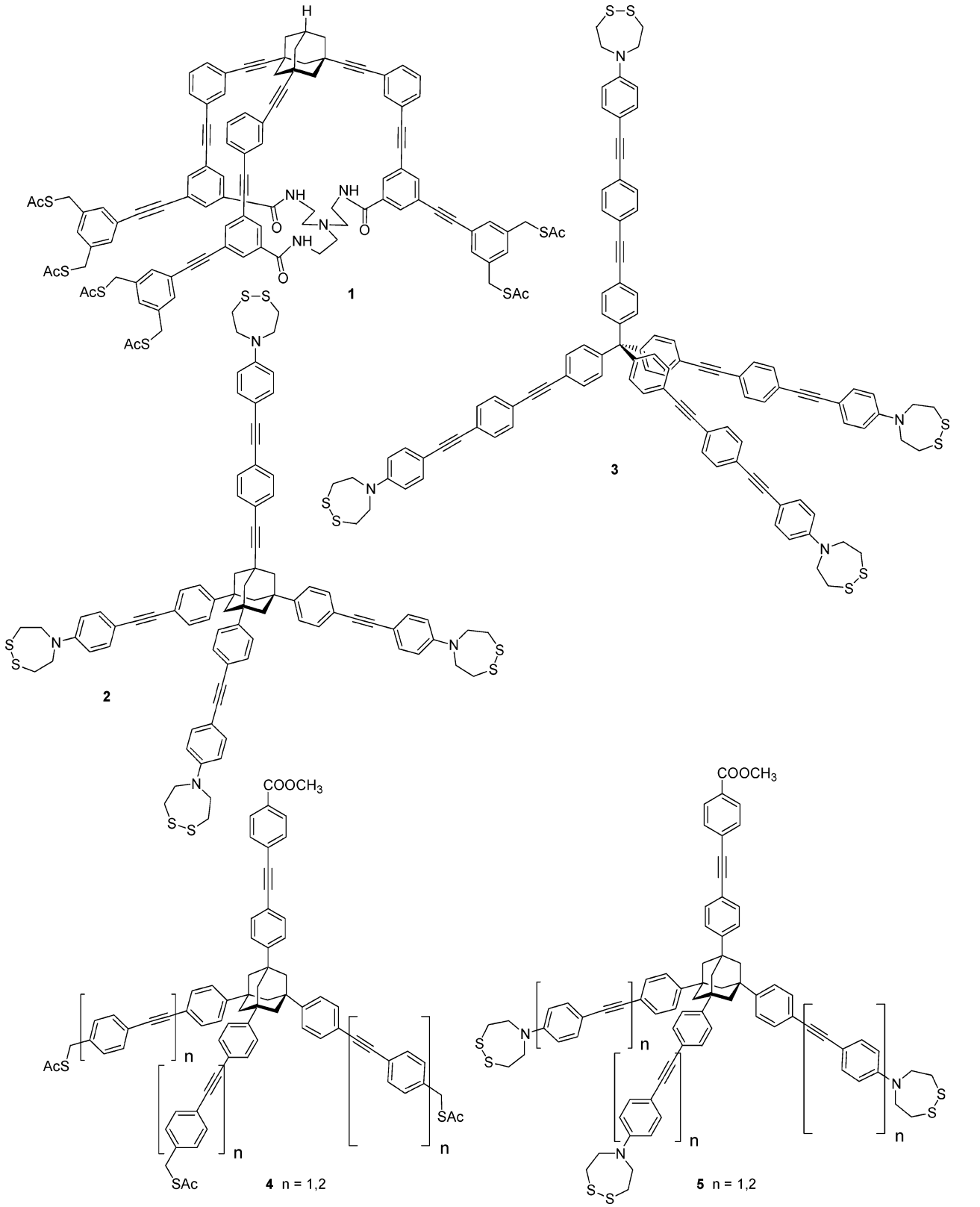
CHART 1



together to form a rigidifying cage-like macrocycle consisting of three 44-membered rings. The third unit is the three legs, which radiate downward and outward from the body and contribute to the height and width of the molecule. Three identical, sulfur-containing termini constitute the fourth unit, which serves as the feet of the tripod. Given the high affinity that thiols,[10] disulfides,[10] or thiolacetates[11] display toward gold, we included S

(10) The question of binding of disulfides and thiols to the gold surface is complicated by thermodynamic stability of disulfide ring and monolayer formation kinetics. See the discussion in: Schlenoff, J. B.; Li, M.; Ly, H. *J. Am. Chem. Soc.* **1995**, *117*, 12528.

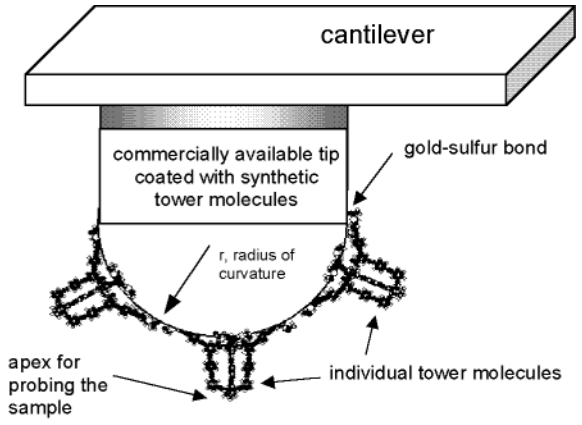
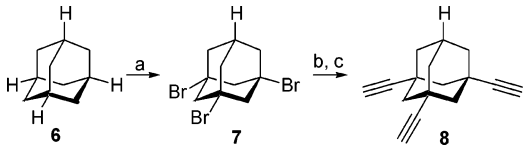


FIGURE 1. Schematic diagram of a commercial AFM tip modified by attachment of tower-shaped molecules.

SCHEME 1[a]

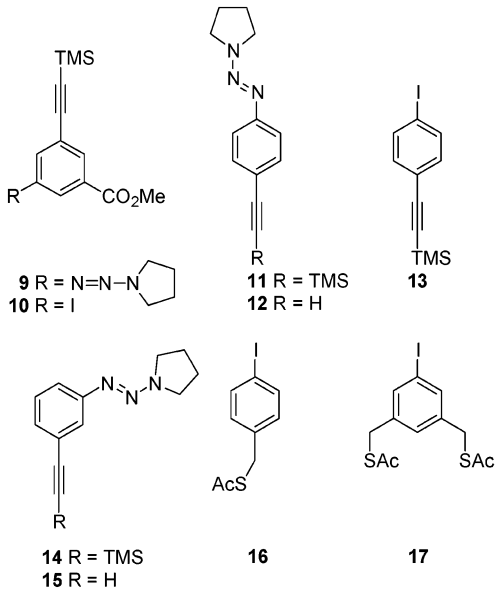


[a] Reagents and conditions: (a) Br_2, Fe; (b) vinyl bromide, $AlCl_3$; (c) *t*-BuOH, *t*-BuOK, heat.

atoms in the feet to anchor the molecular tip to a thin film of gold placed on a conventional AFM tip.[12] Thus, a 4-(acetylsulfanylmethy)phenyl unit and a 3,5-bis(acetylsulfanylmethyl)phenyl unit were chosen as the feet of molecules **30** and **33**, respectively, for eventual anchoring to conventional gold-coated AFM tip. Hydrolysis to the corresponding more air-sensitive thiol groups remains a possibility. The spacing of the trivalent tripodal tip molecules may be modulated either by varying the concentration of tip molecules in the application solution and/or by including an appropriate concentration of competing monovalent short-chain thiol molecules, which can "fill in" the monolayer on the gold surface.

Synthesis of Monomers. We adapted the elegant convergent, stepwise synthesis of oligo(4-phenylene ethynylenes) used by Moore[13,14] and others[15] for the synthesis of our nanoscale, tower-shaped molecules. Triethynyladamantane **8** (Scheme 1) was chosen as the head unit owing to its rigid nature, well-defined geometry, and anticipated reactivity in the Sonogashira coupling reaction. Adamantane **8** was prepared from adamantane generally along the lines of Malik and co-workers.[16] 1,3,5-Tribromoadamantane was prepared as described by

CHART 2. Monomer Building Blocks



Delimarskii and coauthors[17] rather than the route used by Stetter and Wulff[18] or by Malik et al.[16]

The synthesis of monomers **9**,[13] **10**,[13] **11**,[13] **13**,[19,20] **14**,[13] and **15**[13] (Chart 2) followed the protocol of Moore and coworkers.[13] We elected to use iodoanilines instead of bromoanilines for our Sonogashira coupling reactions in view of the reported superior reactivity of aryl iodides.[21,22] In our hands, pyrrolidinyl diazene **11** gave a better yield of iodide **13** than did the corresponding *N*,*N*-diethyl derivative used by Moore.[19] In general, pyrrolidinyl diazenes were used throughout our work. Monomer **12** was prepared by treatment of **11** with K_2CO_3 in MeOH/CH_2Cl_2. Foot units **16**[9,23] and **17**[7] were prepared as previously described by us.[7,9]

Synthesis of the Macrocyclic Trilactam 26. Alkyne **19** was synthesized by a cross-coupling reaction between monomers **13** and **15** to give **18**, which was deprotected with K_2CO_3 in MeOH/CH_2Cl_2 (Scheme 2). Alkyne **19** was next cross-coupled with iodide **10** to give diazene **20**, which was heated in *n*-BuI to give iodide **21**. Triester **23** was synthesized by coupling iodide **21** with 1,3,5-triethynyladamantane **8**. A small amount of diyne **22** was obtained as a byproduct arising by a Glaser-type[24,25] oxidative homocoupling reaction and identified by NMR and MS. The TMS protecting groups in **23** were then removed by *n*-Bu_4NF to afford trialkyne **24**. Alkaline hydrolysis of **24** gave triacid **25**. Treatment of **25** with

(11) Kim, S.; Park, S.-K.; Park, C.; Jeon, I. C. *J. Vac. Sci. Technol. B* **1996**, 14, 1318.
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(24) (a) Ziener, U.; Godt, A. *J. Org. Chem.* **1997**, *62*, 6137. (b) Xu, Z.; Moore, J. S. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 246. (c) Wager, R. W.; Johnson, T. E.; Li, F.; Lindsey, J. S. *J. Org. Chem.* **1995**, *60*, 5266.
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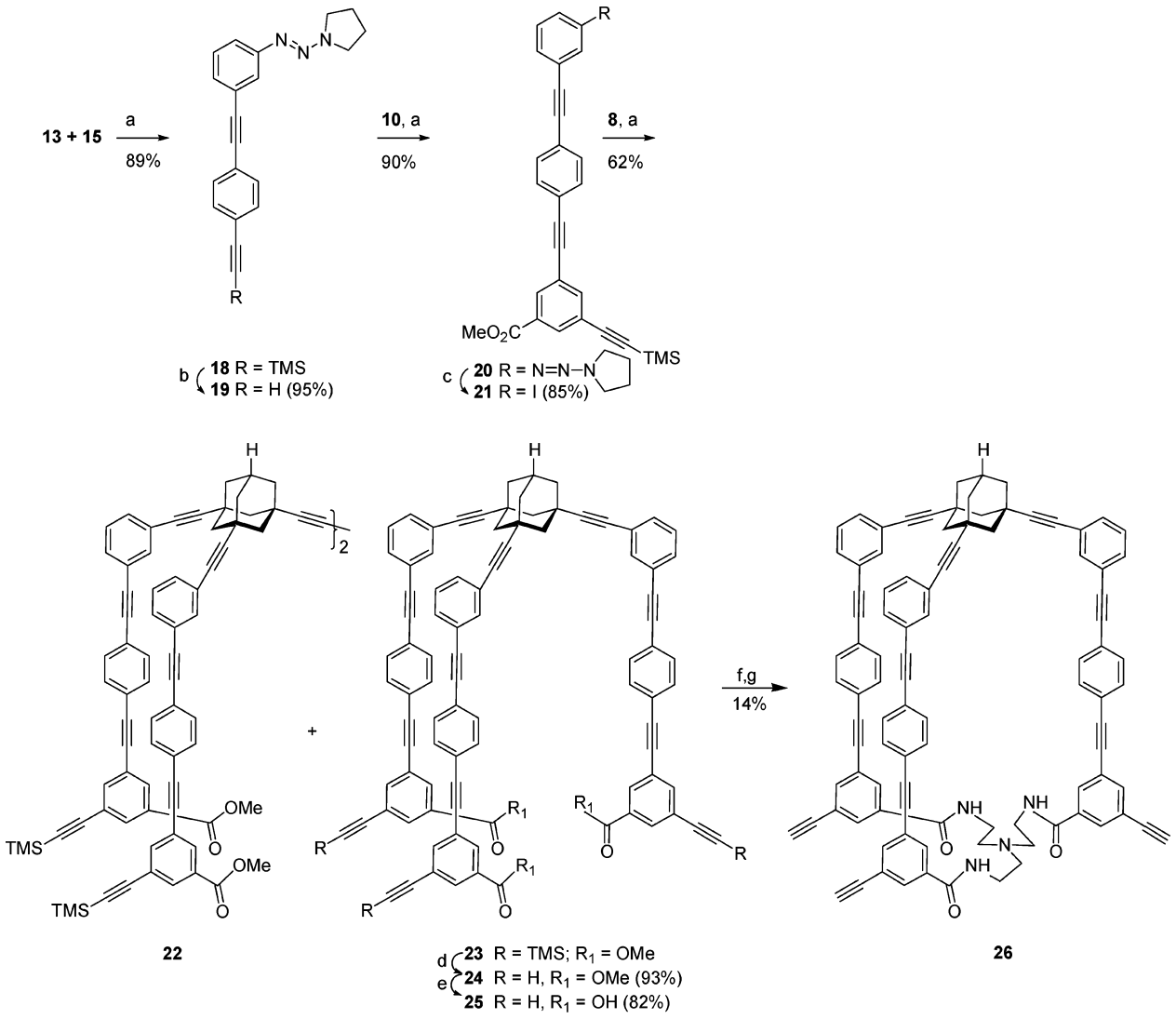
SCHEME 2[a]



[a] Reagents and conditions: (a) $Pd(PPh_3)_2Cl_2$, CuI, NEt_3/THF; (b) K_2CO_3, CH_2Cl_2, MeOH; (c) *n*-BuI, heat; (d) *n*-Bu_4NF, THF; (e) NaOH, EtOH, H_2O, $CHCl_3$; (f) oxalyl chloride, DMF, benzene; (g) tris(2-aminoethyl)amine, chlorobenzene, DMA, high-dilution conditions.

oxalyl chloride in DMF and benzene cleanly gave the corresponding trichloride, which was allowed to react with tris(2-aminoethyl)amine employing high dilution conditions[26] to successfully give the triply bridged macrocycle **26** in 14% yield. The structure of macrocycle **26** was confirmed by ^{1}H (Figure 2) and ^{13}C NMR, FAB MS (Figure 3), and elemental analysis. The main byproduct in the tricondensation reaction was a solid substance of low solubility, which was probably a mixture of amide oligomers formed by intermolecular reactions between partially reacted intermediates in the macrocyclization reaction.

Synthesis of Well-Defined Tower-Shaped Nanoscale Molecules 30 and 33. The "feet" **29** of tower **30** were synthesized as follows. Iodide **16** was coupled with TMSA under Sonogashira conditions to give TMS derivative **27**,[23] which was deprotected with Bu_4NF to give alkyne **28**[23] (Scheme 3). Alkyne **28** was allowed to react with an excess of 1,4-diiodobenzene in the presence of $Pd(PPh_3)_2Cl_2$ and CuI as catalysts giving iodide **29**. Target molecule **30** was obtained in 15% yield after a rather difficult column chromatography following the coupling of an excess of **29** with macrocycle **26** under Sonogashira reaction conditions. The low yield likely was a result of competing Glaser-type oxidative homocoupling reactions of the tri(terminal alkynyl) macrocycle **26** to the corresponding diyne or higher oligoynes despite efforts to exclude oxygen from the reaction. The structure of tower **30** was confirmed by 500 MHz 1- and 2-D ^{1}H NMR, ^{13}C NMR, and FAB MS (calculated and found for M + 2, *m*/*e* 2126.2).

The UV−visible spectrum of **30** in CH_2Cl_2 showed an absorption maximum at 328 nm (Figure 4 top). The molecule is also fluorescent (Figure 4 bottom). The excitation spectrum (dashed line) was taken with the emission wavelength set at 372 nm while the emission spectrum (solid line) was obtained when the excitation was set at 328 nm.

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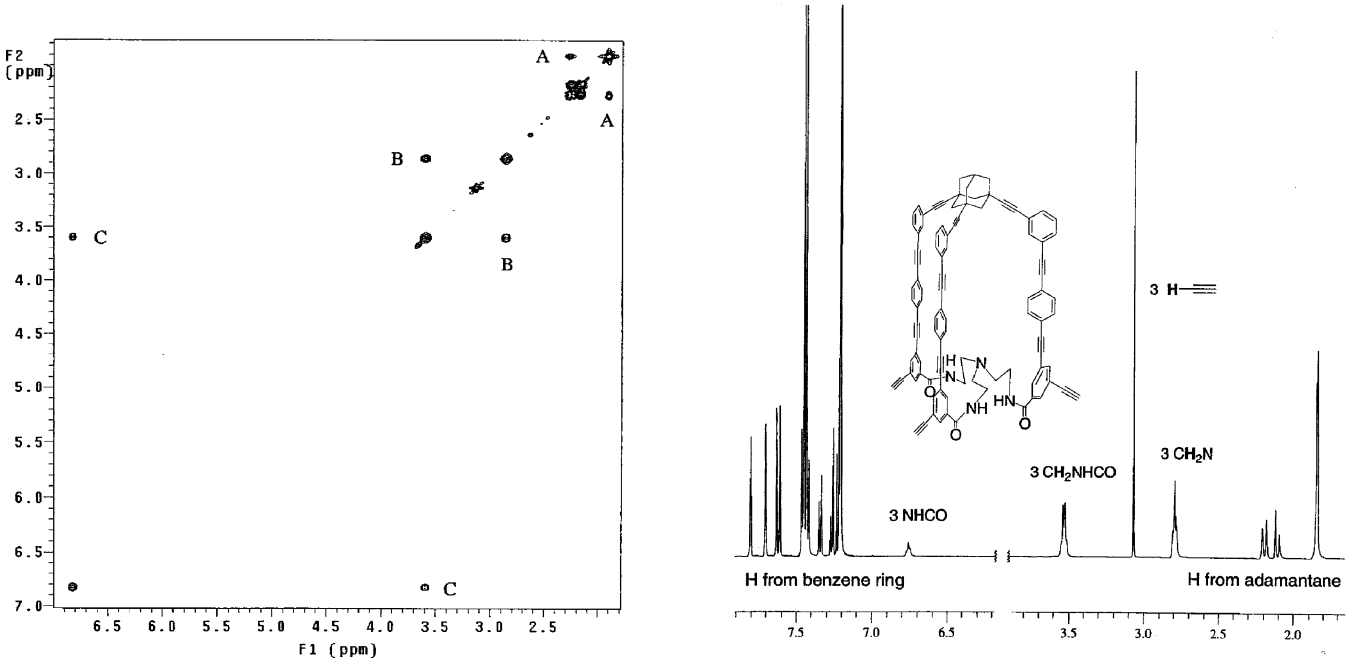


FIGURE 2. Portion of the 500-MHz NMR spectrum of macrocycle **26** in $CDCl_3$. Left: COSY spectrum confirming connectivity in the amide region of the macrocycle. The spectrum shows that the NH proton at δ 6.8 is coupled to the adjacent CH_2 at δ 3.6 (cross-peaks C), which in turn is coupled to the adjacent CH_2 at δ 2.8 (cross-peaks B). Geminal coupling of the CH_2 protons (δ 2.1 and 2.2) at the 2-, 4-, and 6-positions of the adamantane is apparent (cross-peaks A). Right: 1-D proton spectrum.

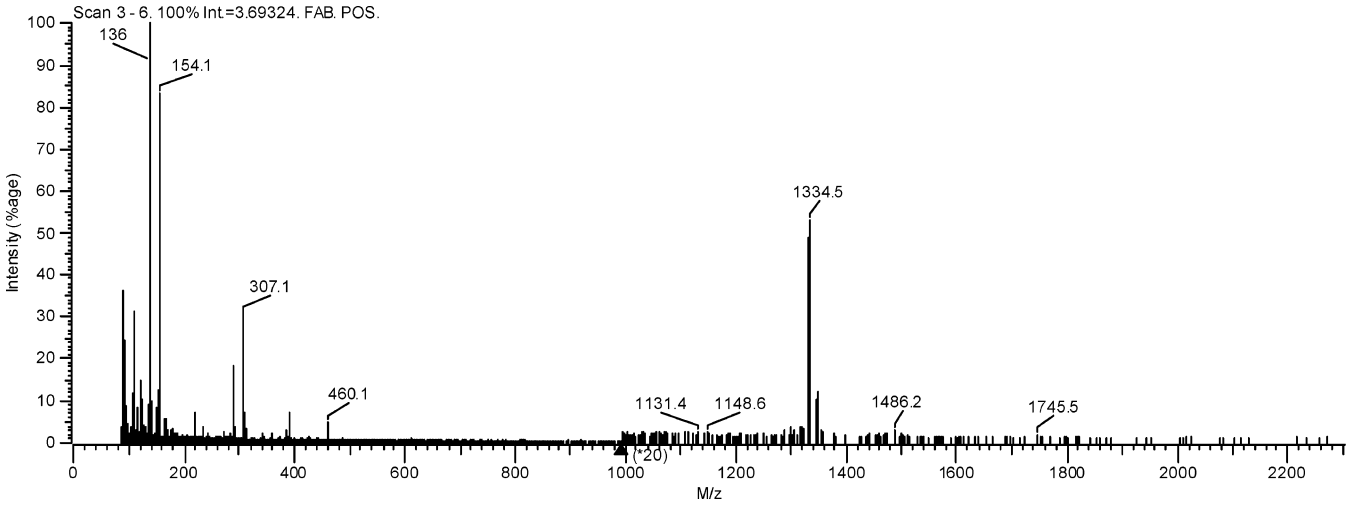


FIGURE 3. FAB MS of macrocycle **26**. The calculated value for *m/e* (M + 2) is 1334.5.

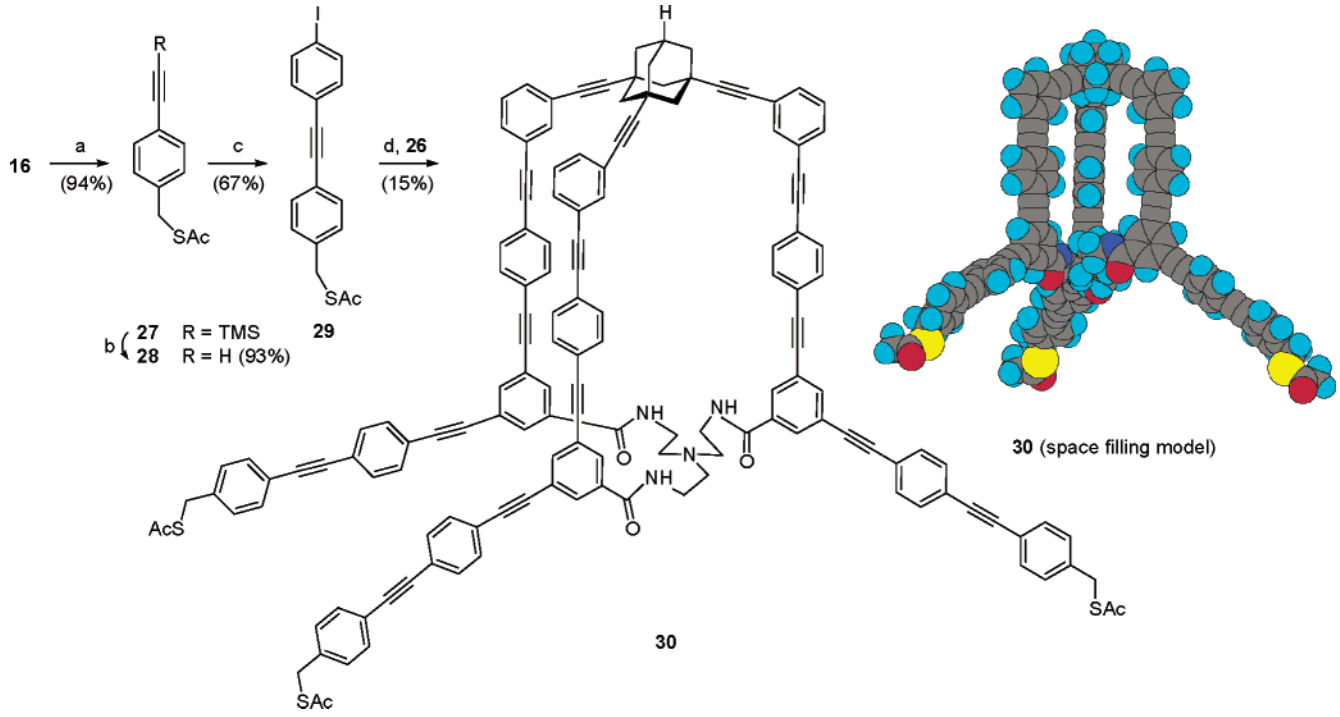
Tower-shaped molecule **33** was synthesized as follows (Scheme 4). Foot unit **17** was coupled to diazene **12** giving diazene **31**. Reaction of **31** with hot *n*-BuI gave iodide **32**. Excess **32** was then allowed to react with macrocycle **26** under Sonogashira conditions to give **33**.

Visualization of Individual Molecules of 30 with Use of a Conventional AFM Tip. CH_2Cl_2 solutions of **30** (0.25 and 1.0 μM) were spin-coated onto a freshly cleaved mica surface and then imaged by AFM in tapping mode with use of a conventional AFM tip. Individual molecules of **30** are easily visualized (Figure 5). Comparing panels A and B in Figure 5, it is seen that the images of **30** are concentration dependent. The height of the dots is uniform and equal to 0.55 ± 0.15 nm (error limits calculated at 80−85% confidence level) for both images. The height determined by AFM is lower than the calculated height based on molecular modeling. This is consistent with similar differences for DNA[27] and C_{60}[28] and may be due to molecular deformation caused by the AFM tip. As a control, a CH_2Cl_2 solution of leg/foot segment **34**[9] (0.25 μM) was similarly spin- coated onto the mica surface and examined by AFM (Figure 5C). Since molecules of alkyne **34** are much smaller than those of **30** and can lay flat on the surface, they cannot be distinguished from the mica surface itself by AFM.

In summary, two rigid, tower-shaped, tripodal nanoscale molecules **30** and **33** designed for AFM applications have been synthesized and characterized. Molecules **30**

(27) Rivetti, C.; Guthold, M.; Bustamante, C. *J. Mol. Biol.* **1996**, *264*, 919−932.
(28) Kobayashi, K.; Yamada, H.; Horiuchi, T.; Matsushige, K. *Appl. Surf. Sci.* **1999**, *140*, 281.

SCHEME 3[a]



[a] Reagents and conditions: (a) TMSA, $Pd(PPh_3)_2Cl_2$, CuI, NEt_3/THF; (b) *n*-Bu_4NF, THF; (c) $Pd(PPh_3)_2Cl_2$, CuI, NEt_3/THF, excess 1,4-diiodobenzene; (d) $Pd(PPh_3)_2Cl_2$, CuI, NEt_3/THF.

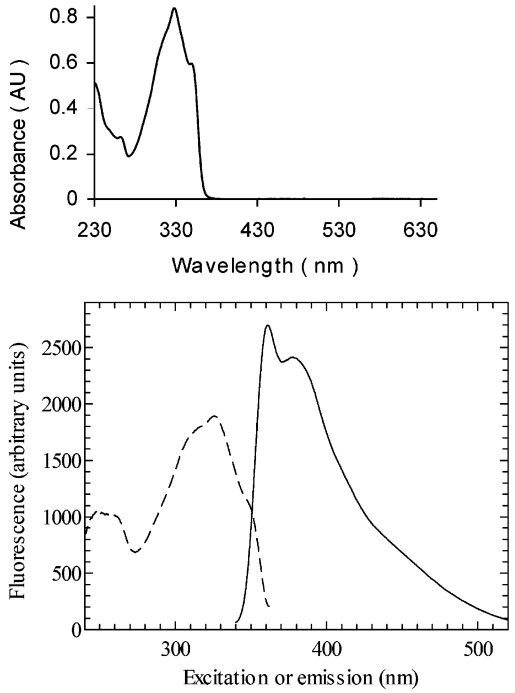


FIGURE 4. Top: UV−visible spectrum of **30** (4 nM in CH_2Cl_2). Bottom: Excitation and emission spectra of molecule **30** (0.25 μM in CH_2Cl_2). The excitation spectrum (dashed line) was taken with an emission wavelength of 372 nm and excitation was at 328 nm for the emission spectrum (solid line). The same sample of **30** was used for both spectra. Uncorrected spectra were acquired at 25 °C with 5 and 10 nm excitation and emission slit widths, respectively, using a 10 mm path quartz cuvette.

and **33** are much larger versions of the prototypic molecule **1** and have a more optimal aspect ratio, important for eventual attachment to a commercial AFM tip. The modular nature of the synthetic route allows for independent variation of each unit. We also demonstrate that molecule **30** is of sufficient size and rigidity that it can be visualized by AFM with use of a conventional tip. These nanoscale molecules may also find application as chemically well-defined, nanoscale objects for the calibration of AFM tips.

Experimental Section

3-Iodo-5-trimethylsilanylethynylbenzoic Acid Methyl Ester (10). 3-(Pyrrolidin-1-ylazo)-5-trimethylsilanylethynylbenzoic acid methyl ester (**9**, 500 mg, 1.51 mmol)[13] was dissolved in *n*-BuI (5 mL). The solution was refluxed for 24 h. The solvent was evaporated in vacuo and the residue was purified by chromatography on silica gel with 1:19 EtOAc/hexanes as the eluent to give iodide **10** (465 mg, 86%) as a yellow solid: mp 65−67 °C; ^{1}H NMR δ 0.25 (s, 9H), 3.92 (s, 3H), 7.97 (t, J = 1.65 Hz, 6H), 8.07 (t, J = 1.35 Hz, 1H), 8.30 (t, J = 1.65 Hz, 1H); ^{13}C NMR δ −0.27, 52.48, 93.11, 97.10, 102.01, 125.33, 131.66, 132.16, 138.15, 144.26, 164.84; MS calcd for $C_{13}H_{16}IO_2Si$ (M + 1) 359.0, found 359.0. Anal. Calcd for $C_{13}H_{15}IO_2Si$: C, 43.58; H, 4.22. Found: C, 43.55; H, 4.09.

(4-Ethynylphenyl)pyrrolidin-1-yldiazene (12). TMS protected alkyne **11** (1.35 g, 5.00 mmol) was dissolved in CH_2Cl_2 (15 mL). The solution was diluted with MeOH (15 mL) and powdered K_2CO_3 (0.40 g) was added. The suspension was stirred for 3 h at room temperature and then evaporated. The residue was purified by chromatography on silica gel with 2:8 EtOAc/hexanes as the eluent to give diazene **12** (0.86 g, 88%) as yellow crystals, which were pure by TLC and NMR: mp 93−95 °C (lit.[30] mp 90 °C); ^{1}H NMR δ 2.03 (t, J = 6.8 Hz, 4H), 3.07 (s, 1H), 3.80 (br s, 4H), 7.36 (dt, J_1 = 2.0 Hz, J_2 = 8.7 Hz, 2H), 7.45 (dt, J_1 = 2.0 Hz, J_2 = 8.4 Hz, 2H); ^{13}C NMR δ 23.74, 76.69, 84.17, 118.19, 120.22, 132.85, 151.63; MS calcd for

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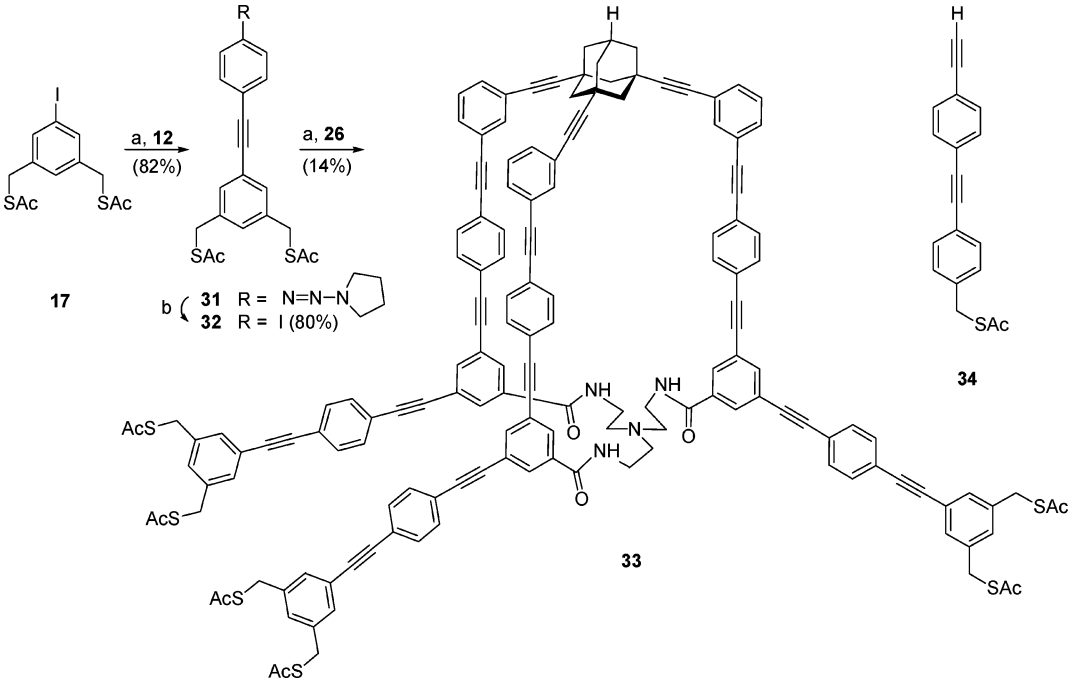
SCHEME 4[a]



[a] Reagents and conditions: (a) $Pd(PPh_3)_2Cl_2$, CuI, NEt_3/THF; (b) *n*-BuI, reflux.

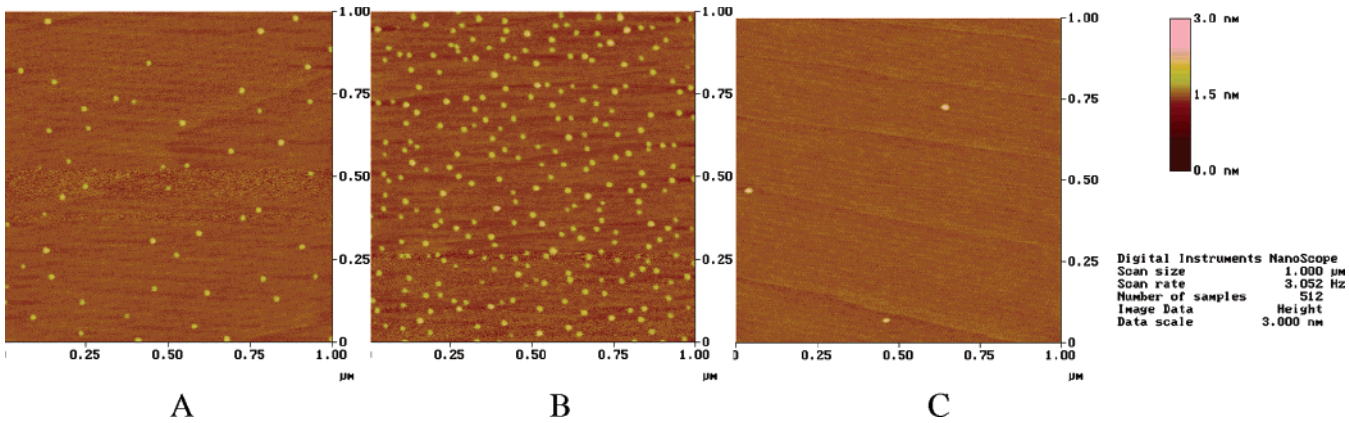


FIGURE 5. AFM images (1.00 × 1.00 μm) of freshly cleaved mica after spin-coating with the following: (A) 0.25 μM solution of **30** in CH_2Cl_2; (B) 1.00 μM solution of **30** in CH_2Cl_2; and (C) 0.25 μM solution of leg/foot segment **34**[9] (Scheme 4). Note the dependence of **30** image density on concentration (A vs B). Nanoscale features such as those seen in C are occasionally seen on certain regions of the surface when imaging freshly cleaved mica and may represent mica particulates produced as the result of the cleavage.[8,29]

$C_{12}H_{14}N_3$ (M + 1) 200.1, found 200.1. Anal. Calcd for $C_{12}H_{13}N_3$: C, 72.33; H, 6.58; N, 21.09. Found: C, 72.15; H, 6.67; N, 21.15.

3-(Ethynylphenyl)pyrrolidin-1-yldiazene (15). To a solution of pyrrolidin-1-yl(4-trimethylsilanylethynylphenyl)-diazene (**14**, 500 mg, 1.84 mmol)[13] in THF (6 mL) was added a 1 M solution of *n*-Bu_4NF in THF (2.00 mL, 2.00 mmol) with stirring at −20 °C. After 30 min the mixture was diluted with water (30 mL) and extracted with CH_2Cl_2 (2 × 20 mL). The combined extract was evaporated and the residue was purified by chromatography on silica gel with 1:1 hexanes/CH_2Cl_2 as the eluent to give diazene **15** (348 mg, 95%) as light yellow crystals, which were pure by TLC and NMR: mp 60−62 °C; ^{1}H NMR δ 1.98 (t, J = 6.8 Hz, 4H), 3.01 (s, 1H), 3.75 (br s, 4H), 7.21−7.24 (m, 2H), 7.35−7.38 (m, 2H), 7.53 (s, 1H); ^{13}C NMR δ 23.73, 76.56, 83.91, 121.25, 122.38, 123.81, 128.63, 128.75, 151.31; MS calcd for $C_{12}H_{14}N_3$ (M + 1) 200.1, found 200.2.

(30) Godt, A. *J. Org. Chem.* **1997**, *62*, 7471.

Pyrrolidin-1-yl[3-(4-trimethylsilanylethynylphenylethynyl)phenyl]diazene (18). A mixture of iodide **13** (5.00 g, 16.7 mmol), alkyne **15** (3.08 g, 15.3 mmol), $Pd(PPh_3)_2Cl_2$ (0.54 g, 0.77 mmol), and CuI (0.30 g, 0.15 mmol) in Et_3N (15 mL) and THF (65 mL) was heated with stirring at 60 °C for 2 h and then at room temperature for 20 h. The reaction mixture was filtered and the solids were washed with ether (50 mL). The combined filtrate and wash were evaporated to dryness. The residue was purified by chromatography on silica gel with 1:9 EtOAc/hexanes as the eluent to give **18** (5.1 g, 89%) as colorless crystals, which were pure by TLC and NMR: mp 140−142 °C; ^{1}H NMR δ 0.25 (s, 9H), 2.01 (t, J = 6.5 Hz, 4H), 3.78 (br s, 4H), 7.24−7.31 (m, 2H), 7.37−7.43 (m, 5H), 7.58 (br s, 1H); ^{13}C NMR δ −0.10, 23.75, 88.51, 91.69, 96.09, 104.67, 121.13, 122.68, 123.16, 123.28, 123.52, 128.14, 128.85, 131.36, 131.82, 151.36; MS calcd for $C_{23}H_{26}N_3Si$ (M + 1) 372.2, found 372.2.

[3-(4-Ethynylphenylethnyl)phenyl]pyrrolidin-1-yldiazene (19). Powdered K_2CO_3 (0.500 g, 3.62 mmol) was added to a stirred solution of silyl derivative **18** (1.5 g, 4.0 mmol) in

CH_2Cl_2 (20 mL) and MeOH (40 mL) at room temperature. After 2 h the solvent was removed and the residue was purified by chromatography over a short column of silica gel. Elution with 1:10 ether/hexane gave alkyne **19** (3.81 g, 95%) as colorless crystals, which were pure by TLC and NMR: mp 126−127 °C; ^{1}H NMR δ 2.03 (t, J = 6.6 Hz, 4H), 3.17 (s, 1H), 3.80 (br s, 4H), 7.27−7.33 (m, 2H), 7.38−7.42 (m, 1H), 7.47 (s, 4H), 7.60 (d, J = 1.2 Hz, 1H); ^{13}C NMR δ 23.77, 78.79, 83.30, 88.33, 91.78, 121.18, 121.65, 123.18, 123.22, 123.94, 128.18, 128.87, 131.45, 132.01, 151.39; MS calcd for $C_{20}H_{18}N_3$ (M + 1) 300.1, found 300.1. Anal. Calcd for $C_{20}H_{17}N_3$: C, 80.24; H, 5.72; N, 14.04. Found: C, 80.13; H, 5.52; N, 13.88.

3-{4-[3-(Pyrrolidin-1-ylazo)phenylethynyl]phenylethynyl}-5-trimethylsilanylethynylbenzoic Acid Methyl Ester (20). A thick-walled reaction tube was charged with iodide **10** (301 mg, 0.840 mmol), alkyne **19** (277 mg, 0.942 mmol), $Pd(PPh_3)_2Cl_2$ (29.5 mg, 0.042 mmol), CuI (16 mg, 0.084 mmol), THF (10 mL), and Et_3N (5 mL). The suspension was flushed with N_2, capped, and then heated at 50−60 °C for 12 h. The mixture was filtered and the residue was washed with CH_2Cl_2 (20 mL). The combined filtrate and wash were evaporated to dryness. The residue was chromatographed with 1:1 CH_2Cl_2/hexanes as the eluent to afford diazene **20** as a colorless glass (400 mg, 90%), which was pure by TLC and NMR: mp 137−139 °C; ^{1}H NMR δ 0.26 (s, 9H), 2.04 (t, J = 6.75 Hz, 4H), 3.81 (br s, 4H), 3.94 (s, 3H), 7.31 (m, 2H), 7.40 (m, 1H), 7.50 (d, J = 1.8 Hz, 4H), 7.60 (d, J = 1.2 Hz, 1H), 7.80 (t, J = 1.7 Hz, 1H), 8.13 (t, J = 1.7 Hz, 1H); ^{13}C NMR δ −0.30, 23.62, 52.27, 88.39, 89.09, 90.52, 91.91, 96.13, 102.87, 121.06, 122.04, 123.10, 123.64, 123.70, 123.86, 128.03, 128.74, 130.54, 131.45, 132.17, 132.39, 138.38, 151.27, 165.44; MS calcd for $C_{33}H_{32}N_3O_2Si$ (M + 1) 530.2, found 530.2. Anal. Calcd for $C_{33}H_{31}N_3O_2Si \cdot {}^1/_2H_2O$: C, 73.58; H, 5.99; N, 7.80. Found: C, 73.80; H, 5.80; N 7.63.

3-[4-(3-Iodophenylethynyl)phenylethynyl]-5-trimethylsilanylethynylbenzoic Acid Methyl Ester (21). Diazene **20** (300 mg, 0.566 mmol) was dissolved in *n*-BuI (6 mL) and then heated at 135−145 °C for 12 h. The mixture was evaporated to dryness. The residue was purified by chromatography with 1:4 CH_2Cl_2/hexanes as the eluent to afford iodide **21** (268 mg, 85%) as a viscous colorless oil, which was pure by TLC and NMR: ^{1}H NMR δ 0.26 (s, 9H), 3.94 (s, 3H), 7.10 (t, J = 7.8 Hz, 1H), 7.48 (m, 1H), 7.50 (s, 4H), 7.68 (m, 1H), 7.80 (t, J = 1.5 Hz, 1H), 7.90 (t, J = 1.5 Hz, 1H), 8.08 (t, J = 1.7 Hz, 1H), 8.13 (t, J = 1.7 Hz, 1H); ^{13}C NMR δ −0.21, 52.45, 89.47, 89.66, 90.21, 90.37, 93.71, 96.31, 102.88, 122.73, 123.04, 123.72, 124.04, 125.00, 129.87, 130.69, 131.64, 132.35, 132.65, 137.47, 138.58, 140.13, 165.67; MS calcd for $C_{29}H_{22}IO_2Si$ (M − 1) 557.05, found 557.0. Anal. Calcd for $C_{29}H_{23}IO_2Si$: C, 62.37; H, 4.15. Found: C, 62.49; H, 4.11.

1,3,5-Tris-{2-[3-({[4-(3-methoxycarbonyl-5-trimethylsilanylethynylphenyl)ethynyl]phenyl}ethynyl)phenyl]ethynyl}adamantane (23). A thick-walled reaction tube was charged with iodide **21** (508 mg, 0.910 mmol), triethynyladamantane **8** (51 mg, 0.245 mmol), $Pd(PPh_3)_2Cl_2$ (26 mg, 0.037 mmol), CuI (14 mg, 0.074 mmol), Et_3N (5 mL), and THF (10 mL). The mixture was flushed with N_2 and sealed with a Teflon screwcap. The mixture was heated with stirring at 55−60 °C for 24 h. The suspension was filtered and the residue was washed with ether (20 mL) and CH_2Cl_2 (20 mL). The combined filtrate and wash were evaporated to dryness. The residue was purified by chromatography with 3:7 CH_2Cl_2/hexanes as the eluent to give crude triester **23**, which was further purified by chromatography. Elution with 20:79.5:0.5 CH_2Cl_2/hexanes/CH_3OH gave ester **23** (230 mg, 62%) as colorless crystals, which were pure by TLC and NMR: mp 154−156 °C; ^{1}H NMR δ 0.26 (s, 27H), 1.93 (br s, 6H), 2.16 (br, 7H), 3.91 (s, 9H), 7.28 (dd, J = 7.8, 7.8 Hz, 1H), 7.38 (d, J = 7.8 Hz, 1H), 7.44 (d, J = 7.8 Hz, 1H), 7.50 (s, 4H), 7.62 (s, 1H), 7.78 (s, 1H), 8.07 (s, 1H), 8.10 (s, 1H); ^{13}C NMR δ −0.15, 28.21, 30.72, 40.64, 46.49, 52.40, 79.42, 89.42, 90.51, 90.82, 96.31, 102.98, 122.54, 123.15, 123.41, 123.79, 124.00, 124.05, 128.36, 130.72, 130.81, 131.61, 131.64, 132.33, 132.60, 134.76, 138.56, 165.60; MS calcd for $C_{103}H_{84}O_6Si_3$ (M + 2) 1500.5, found 1500.5. Anal. Calcd for $C_{103}H_{82}O_6Si_3 \cdot 2H_2O$: C, 80.54; H, 5.64. Found: C, 80.76; H, 5.37. Continued elution gave **22** (33 mg, 6%) as a white solid: ^{1}H NMR δ 0.26 (s, 36H), 1.85−1.92 (m, 12H), 2.06−2.15 (m, 12H), 2.21 (m, 2H), 3.93 (s, 12H), 7.28 (t, J = 7.5 Hz, 4H), 7.35 (d, J = 7.8 Hz, 4H), 7.44 (d, J = 7.5 Hz, 4H), 7.50 (s, 16H), 7.57 (s, 4H), 7.79 (t, J = 1.7 Hz, 4H), 8.08 (t, J = 1.4 Hz, 4H), 8.12 (t, J = 1.5 Hz, 4H); FAB MS, calcd for $C_{148}H_{121}O_8Si_4$ (M + 3), 2137.8, found 2137.8.

1,3,5-Tris-{2-[3-({[4-(3-methoxycarbonyl-5-ethynylphenyl)ethynyl]phenyl}ethynyl)phenyl]ethynyl}adamantane (24). A 1 M solution of Bu_4NF (0.600 mL, 0.600 mmol) in THF was added dropwise to a stirred solution of TMS derivative **23** (220 mg, 0.147 mmol) in THF (10 mL) at −20 °C and then the solution was stirred for 2 h. The solvent was removed and the residue was dissolved in CH_2Cl_2 (30 mL) and washed with water (20 mL) and brine (2 × 30 mL). The organic layer was dried over anhydrous Na_2SO_4 and evaporated to dryness. The residue was purified by chromatography with 3:7 CH_2Cl_2/hexanes as the eluent to give triester **24** (174 mg, 93%) as white crystals, which were pure by TLC and NMR: mp 119−122 °C; ^{1}H NMR δ 1.93 (br s, 6H), 2.16 (s, 6H), 2.25 (m, 1H), 3.16 (s, 3H), 3.94 (s, 9H), 7.29 (t, J = 7.8 Hz, 3H), 7.38 (dt, J_1 = 7.8 Hz, J_2 = 1.4 Hz, 3H), 7.44 (dt, J_1 = 7.5 Hz, J_2 = 1.5 Hz, 3H), 7.51 (s, 12H), 7.60 (m, 3H), 7.80 (t, J_1 = 1.5 Hz, 3H), 8.10 (t, J = 1.5 Hz, 3H), 8.15 (t, J = 1.5 Hz, 3H); ^{13}C NMR δ 28.09, 30.66, 40.55, 46.40, 52.48, 78.84, 79.81, 81.70, 89.18, 89.33, 90.62, 90.78, 96.27, 122.40, 122.98, 123.06, 123.42, 123.89, 123.93, 128.37, 130.80, 131.60, 131.64, 132.72, 132.75, 134.74, 138.69, 165.53; MS calcd for $C_{94}H_{57}O_6$ (M − 1) 1281.4, found 1281.4. Anal. Calcd for $C_{94}H_{58}O_6 \cdot 2H_2O$: C, 85.56; H, 4.74. Found: C, 85.51; H, 4.45.

1,3,5-Tris-{2-[3-({[4-(3-carboxy-5-ethynylphenyl)ethynyl]phenyl}ethynyl)phenyl]ethynyl}adamantane (25). A solution of 25% aqueous NaOH (0.30 mL, 1.9 mmol) was added to a solution of triester **24** (168 mg, 0.131 mmol) in $CHCl_3$ (2.5 mL) and ethanol (3 mL). The mixture was stirred at room temperature for 2 h and then an additional portion of ethanol (5 mL), $CHCl_3$ (0.8 mL), water (1.8 mL), and 25% aqueous NaOH (0.5 mL) was added to make the reaction mixture homogeneous. The solution was stirred for an additional 2 h at room temperature and then evaporated to dryness. The residue was treated with water (8 mL) and the suspension was acidified with 1 M HCl. The mixture was extracted with ether (3 × 10 mL) and the combined extracts were washed with brine and dried over Na_2SO_4. Removal of the solvent gave triacid **25** (133 mg, 82%) as a light yellow solid, which was pure by TLC and NMR: dec ∼160−200 °C (PHB, yellow to brown solid); ^{1}H NMR (300 MHz, DMSO-d_6) δ 1.91 (br s, 6H), 2.12 (br s, 6H), 2.20 (m, 1H), 4.43 (s, 3H), 7.45 (s, 6H), 7.56−7.64 (m, 18H), 7.90 (s, 3H), 7.96 (s, 3H), 8.06 (s, 3H); ^{13}C NMR (125 MHz, DMSO-d_6) δ 27.49, 30.12, 45.62, 79.37, 81.49, 82.60, 89.35, 89.43, 90.38, 90.58, 96.66, 121.99, 122.46, 122.65, 122.87, 123.18, 123.43, 129.17, 130.92, 131.69, 131.85, 132.08, 132.16, 132.30, 134.11, 137.77, 165.65; MS calcd for $C_{91}H_{52}O_6$ (M) 1240.4, found 1240.4. Anal. Calcd for $C_{91}H_{52}O_6 \cdot 2H_2O$: C, 85.56, H, 4.42. Found: C, 85.19; H, 4.04.

Macrocyclic Trilactam 26. Oxalyl chloride (1 mL) was added dropwise to a stirred solution of triacid **25** (200 mg, 0.161 mmol) in dry benzene (10 mL). Two drops of DMF were added and the mixture was stirred at room temperature for 24 h. Evaporation of the volatiles gave crude triacid chloride, which was dissolved in chlorobenzene (10 mL) and DMA (400 μL) and placed in a syringe. A second syringe was filled with tris(2-aminoethyl)amine (46 μL, 0.314 mmol) dissolved in chlorobenzene (10 mL). The contents of the two syringes were simultaneously added dropwise at a rate of 1 mL/h to vigorously stirred chlorobenzene (150 mL) at room temperature in a 250-mL three-necked flask under a N_2 atmosphere with the aid of a syringe pump. Additions were complete after 10 h and the reaction mixture was allowed to stir at room temperature

for another 10 h. The cloudy reaction mixture was filtered through a glass filter to give a clear colorless solution, which was concentrated to dryness. The residue was purified by chromatography with 5:95 $CH_3OH/CHCl_3$ as the eluent to give crude **26**. Further purification by radial chromatography on silica gel with 4:96 $CH_3OH/CHCl_3$ as the eluent gave macrocycle **26** (13 mg, 14%) as a white solid, which was pure by NMR and TLC: dec ~218 °C (PHB, yellow solid); ^{1}H NMR (500 MHz) δ 1.91 (br s, 6H), 2.16 (d, J = 13 Hz, 3H), 2.25 (d, J = 13 Hz, 3H), 2.24−2.27 (m, 1H), 2.86 (br t, 6H), 3.13 (s, 3H), 3.60 (br q, 6H), 6.82 (t, 3H, disappeared after D_2O exchange), 7.28 (t, J = 8.0 Hz, 3H), 7.33 (d, J = 8.0 Hz, 3H), 7.40 (d, J = 7.5 Hz, 3H), 7.49 (d, J = 8.0 Hz, 6H), 7.52 (d, J = 8.5 Hz, 6H), 7.67 (s, 3H), 7.69 (s, 3H), 7.77 (s, 3H), 7.86 (s, 3H); ^{13}C NMR δ 27.98, 30.98, 38.19, 39.38, 47.67, 53.96, 77.20, 78.96, 80.41, 81.88, 89.50, 89.59, 90.64, 90.94, 96.83, 122.54, 123.05, 123.14, 123.42, 123.80, 123.94, 128.43, 129.87, 130.18, 130.55, 131.61, 131.65, 134.87, 137.04, 137.60, 166.56; FAB MS calcd for $C_{97}H_{66}N_4O_3$ (M + 2) 1334.5, found 1334.5. Anal. Calcd for $C_{97}H_{64}N_4O_3 \cdot 2H_2O$: C, 85.06; H, 5.00; N, 4.09. Found: C, 85.29; H, 4.68; N, 3.79.

Thioacetic Acid *S*-[4-(4-Iodophenylethynyl)benzyl] Ester (29). A mixture of thioester **28** (300 mg, 1.58 mmol), 1,4-diiodobenzene (2.00 g, 6.32 mmol), $Pd(PPh_3)_2Cl_2$ (55 mg, 0.079 mmol), CuI (30 mg, 0.16 mmol), Et_3N (8 mL), and THF (8 mL) in a thick-walled reaction tube was flushed with N_2 and sealed with a Teflon screwcap. The mixture was heated with stirring at 50−60 °C for 20 h. The suspension was filtered and the residue was washed with CH_2Cl_2 (30 mL). The combined filtrate and wash were evaporated to dryness. The residue was purified by chromatography with 3:7 CH_2Cl_2/hexanes as the eluent to give iodide **29** (410 mg, 67%) as yellow crystals, which were pure by NMR and TLC: mp 120−122 °C; ^{1}H NMR δ 2.38 (s, 3H), 4.13 (s, 2H), 7.25 (d, J = 8.4 Hz, 2H), 7.29 (d, J = 8.4 Hz, 2H), 7.46 (d, J = 8.4 Hz, 2H), 7.69 (d, J = 8.4 Hz, 2H); ^{13}C NMR δ 30.28, 33.17, 88.65, 90.45, 94.12, 121.75, 122.62, 128.85, 131.74, 133.01, 137.43, 138.16, 194.81; MS calcd for $C_{17}H_{13}IOSNa$ (M + Na) 415.0, found 415.0. Anal. Calcd for $C_{17}H_{13}IOS$: C, 52.05; H, 3.34. Found: C, 52.18; H, 3.06.

Tower-Shaped Molecule 30. A thick-walled reaction tube was charged with macrocyclic trilactam **26** (16.0 mg, 0.0120 mmol), iodide **29** (18.8 mg, 0.0480 mmol), $Pd(PPh_3)_2Cl_2$ (1.3 mg, 0.0018 mmol), CuI (0.7 mg, 0.004 mmol), THF (12 mL), and Et_3N (12 mL). The mixture was flushed with N_2 and sealed with a Teflon screwcap. The mixture was heated at 50−60 °C for 20 h and then allowed to stir at room temperature for 24 h. The suspension was filtered and the residue was washed with CH_2Cl_2 (20 mL) and Et_2O (10 mL). The combined filtrate and wash were evaporated to dryness. The residue was purified by chromatography. Elution with CH_2Cl_2 followed by 3:97 $MeOH/CH_2Cl_2$ gave crude **30**, which was further purified by radial chromatography (1 mm disk). Elution with 1:50 $CH_3OH/CHCl_3$ gave molecule **30** (4.5 mg, 15%) as light yellow crystals, which were pure by NMR and TLC: ^{1}H NMR (500 MHz) δ 1.90 (br s, 6H), 2.16 (d, J = 14 Hz, 3H), 2.25 (d, J = 13 Hz, 3H), 2.23−2.26 (m, 1H), 2.36 (s, 9H), 2.86 (br t, 6H), 3.62 (br q, 6H), 4.11 (s, 6H), 7.00 (m, 3H, disappeared after D_2O exchange), 7.24−7.56 (m, 42H), 7.65−7.69 (m, 12H), 7.89 (s, 3H); ^{13}C NMR (125 MHz) δ 27.98, 30.33, 30.99, 33.27, 38.07, 38.38, 47.74, 53.61, 80.44, 89.34, 89.62, 89.70, 90.46, 90.74, 90.89, 91.15, 96.85 (overlap of an alkynyl carbon), 121.95, 122.46, 122.65, 123.17, 123.36, 123.74, 123.95, 124.02, 128.44, 128.54, 128.88, 129.25, 129.92, 130.15, 131.49, 131.61, 131.87, 132.04, 132.11, 132.92, 135.02, 136.93, 137.02, 138.12, 166.86, 194.87; UV/vis (CH_2Cl_2) λ_{max} = 328 nm; FAB MS calcd for $C_{148}H_{102}N_4O_6S_3$ (M + 2) 2126.7, found 2126.7.

***N*-Pyrrolidino{4-[3,5-bis(acetylsulfanymethyl)-phenylethynyl]phenyl}diazene (31).** A thick-walled reaction tube was charged with iodide **17** (226 mg, 0.595 mmol), alkyne **12** (129 mg, 0.648 mmol), $Pd(PPh_3)_2Cl_2$ (21 mg, 0.030 mmol), CuI (11 mg, 0.058 mmol), Et_3N (2 mL), and THF (10 mL). The mixture was flushed with N_2 and sealed with a Teflon screwcap. The mixture was heated with stirring at 55−60 °C for 18 h. The suspension was filtered and the filtrate was evaporated to dryness. The residue was purified by chromatography with 3:7 CH_2Cl_2/hexanes as the eluent to give diazene **31** (221 mg, 82%) as white crystals, which were pure by TLC and NMR: mp 90−92 °C; ^{1}H NMR δ 2.04 (t, J = 6.75 Hz, 4H), 2.37 (s, 6H), 3.81 (br s, 4H), 4.07 (s, 4H), 7.14 (m, 1H), 7.32 (d, J = 1.5 Hz, 2H), 7.39 (d, J = 8.7 Hz, 2H), 7.47 (d, J = 9.0 Hz, 2H); ^{13}C NMR δ 23.75, 30.32, 32.86, 88.50, 90.47, 119.11, 120.28, 124.25, 128.89, 130.65, 132.37, 138.25, 151.28, 194.86; MS calcd for $C_{24}H_{26}N_3O_2S_2$ (M + 1) 452.14, found 452.2. Anal. Calcd for $C_{24}H_{25}N_3O_2S_2$: C, 63.83; H, 5.58; N, 9.30. Found: C, 63.82; H, 5.48; N 9.14.

4-[3,5-Bis(acetylsulfanymethyl)phenylethynyl]-iodobenzene (32). A solution of diazene **31** (200 mg, 0.443 mmol) in *n*-BuI (8 mL) was heated at 120 °C for 48 h. The solvent was removed and the residue was purified by chromatography with 3:7 CH_2Cl_2/hexane as the eluent to give diazene **32** (171 mg, 80%) as white crystals, which were pure by TLC and NMR: mp 120−121.5 °C; ^{1}H NMR δ 2.37 (s, 6H), 4.07 (s, 4H), 7.17 (s, 1H), 7.23 (d, J = 8.4 Hz, 2H), 7.33 (d, J = 1.5 Hz, 2H), 7.69 (d, J = 8.4 Hz, 2H); ^{13}C NMR δ 30.28, 32.79, 88.83, 90.10, 94.28, 122.49, 123.56, 129.41, 130.73, 133.05, 137.49, 138.45, 194.68; MS calcd for $C_{20}H_{17}IO_2S_2Na$ (M + Na) 503.0, found 503.0. Anal. Calcd for $C_{20}H_{17}IO_2S_2$: C, 50.00; H, 3.57. Found: C, 49.95; H 3.49.

Tower-Shaped Molecule 33. A mixture of macrocyclic trilactam **26** (96.1 mg, 0.0721 mmol), iodide **32** (111 mg, 0.2307 mmol), $Pd(PPh_3)_2Cl_2$ (5.4 mg, 0.0077 mmol), and CuI (4.4 mg, 0.0231 mmol) in a solution of Et_3N (8 mL) and THF (6 mL) was heated at 115 °C for 8 h. The solvent was evaporated and the residue was purified by chromatography over a short column of silica gel. Elution with 3:97 $MeOH/CHCl_3$ gave crude **33**, which was further purified by radial chromatography (2 mm disk). Elution with 1:50 $MeOH/CHCl_3$ gave **33** (24.2 mg, 14%) as an off-white solid, which was pure by NMR and TLC: ^{1}H NMR δ 1.91 (br s, 6H), 2.17 (d, J = 12 Hz, 3H), 2.26 (d, J = 12 Hz, 3H), 2.24−2.28 (m, 1H), 2.37 (s, 18H), 2.89 (br, 6H), 3.64 (br, 6H), 4.07 (s, 12H), 6.96 (br s, 3H), 7.18 (s, 3H), 7.25−7.52 (m, 45H), 7.68 (s, 3H), 7.72 (m, 3H), 7.94 (br s, 3H); FAB MS calcd for $C_{157}H_{112}N_4O_9S_6$ (M) 2389, found 2389.

Atomic Force Microscopy Experiments. AFM measurements were carried out with a Nanoscope IIIa Multimode AFM (Digital Instruments, Santa Barbara, CA), using a 10 μm scanner. Tapping mode AFM (TM AFM) scans were performed in air with NANO*SENSORS* silicon cantilevers/tips: type NCH, cantilever resonance frequency f_0 = 289−332 kHz and force constant 24.0−37.0 N/m.

The instrument was operated at frequencies slightly lower than the natural resonance frequency in air. All data were recorded in height mode. Set point values were chosen so that the interaction of the tip and sample provided a good compromise between stability and resolution, without damaging the tip or the sample. Scan rates ranged from 1 to 3 Hz. Images were taken at a 512 × 512-pixel resolution to increase the detail in the images. All TM AFM studies were carried out on freshly cleaved muscovite mica, grade V-4 (Structure Probe, Inc.).

Sample Preparation. Spectroscopic grade solvents were used for sample preparation. Molecule **30** on mica: One drop of a 0.25 or 1.0 μM solution of **30** in CH_2Cl_2 was spin-coated onto freshly cleaved mica (cleaved with Scotch tape) for 15−20 s under ambient conditions at a speed of 2000 rpm. Scanning of the sample by AFM began immediately after completion of the spin-coating step. A control image was recorded under similar conditions by spin-coating a 0.25 μM solution of leg/foot segment **34** onto freshly cleaved mica. In this case only the mica surface was visible.

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Supporting Information Available: General experimental details and spectral and analytical data for **8**, **11**, **13**, **16**, **17**, **27**, **28**; ^{1}H NMR (300 MHz) spectra for **8**, **10**−**13**, **15**−**25**, **27**−**29**, **31**−**33**; ^{1}H NMR (500 MHz) spectra for **26** and **30**; ^{13}C NMR (75 MHz) spectra for **8**, **10**−**13**, **15**−**21**, **23**, **24**, **26**−**29**, **31**, and **32**; ^{13}C NMR (125 MHz) spectra for **25**, **26**, and **30**; 2D NMR (500 MHz) spectra for **26** and **30**; FAB MS for **22**, **26**, and **30**. This material is available free of charge via the Internet at http://pubs.acs.org.

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