Design and Synthesis of a "Molecular Turnstile"

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Abstract: Macrobicycles **1**−**3** have been prepared by palladium-catalyzed double macrocyclization. The planar geometry of this system is such that the *para* axis of the inner ring exactly matches the inner diameter of the macrocycle. Molecular models suggest that the inner ring of **1** should be able to rotate freely about its long axis, acting like the spindle of a turnstile. For large spindle substituents, this rotation will become hindered while for intermediate sized substituents, a pair of energetically equivalent conformational states should rapidly interconvert on an experimentally observable time scale. Substituted derivatives **2** and **3** possess diastereotopic methylene protons which become operationally enantiotopic upon fast rotation. Based on variable-temperature ^{1}H NMR and longitudinal T_1 relaxation experiments, examples of what are believed to be freely rotating **2** and conformationally locked **3** spindles are reported. These molecules represent the first iteration in the development of phenylacetylene macrocycles possessing conformational bistability that may eventually lead to new types of solids or liquid crystals that respond rapidly to external electric fields.

Introduction

The search for functional molecular devices has begun to emerge as an active area of research in organic chemistry, stimulated in part by the imaginative ideas of Feynman over 30 years ago.[1] Recently, several examples that may be considered mechanical molecular devices have been reported including Stoddart's rotaxane based molecular shuttle,[2] Feringa's chiroptical molecular switch,[3] Jørgenson's light activated bianthrone molecules,[4] Kelly's molecular "brake",[5] and Malthête and Collet's conformationally invertable columnar mesophases.[6,7] Despite these and other impressive examples, two formidable obstacles toward the continued development of molecular-based devices present themselves to modern chemistry. These include the development of general schemes for the predictable assembly of multimolecular aggregates in all phases of condensed matter and the fabrication of molecular constituents that exhibit a macroscopically detectable form of bistability.[8] Toward these ends, we are developing a strategy for the programmed assembly of molecular materials that employs structurally well-defined phenylacetylene macrocycles as the basic structural unit.[9−12] In this report, we demonstrate the synthetic feasibility of a functional phenylacetylene construct **1** and provide examples of two achiral derivatives, **2** and **3** (Figure 1a). This new "molecular turnstile" may ultimately exhibit readable bistability and represents our first attempt at a mechanically functional structural unit.

The turnstile architecture consists of a hexa(phenylacetylene) macrocyclic frame and a diethynylarene bridge (Figure 1b). Three elements of symmetry are noteworthy in the basic architecture: a mirror plane perpendicular to the frame along the rotation axis ($\sigma_{\parallel}$), a mirror plane perpendicular to the frame and the spindle axis ($\sigma_{\perp}$), and a mirror plane contained within the plane of the macrocycle (σ_h). The bridging unit should exhibit a well-defined rotational motion about its own axis and act as the "spindle" of a turnstile. Thus, the architecture should exhibit conformational bistability, a term which here describes the double well potential energy surface exhibited by a pair of isoenergetic rotational isomers (Figure 2). Hindrance to rotation about the spindle axis is almost entirely due to steric interactions between groups attached to the spindle and the macrocycle framework (Figure 1c) since the rotational barrier for diphen-

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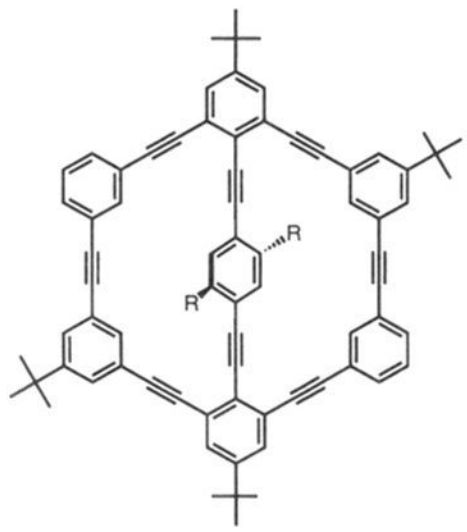
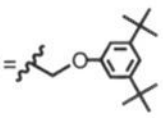
(a)



1 R = H **2** R = CH_2OCH_3 **3** R = 

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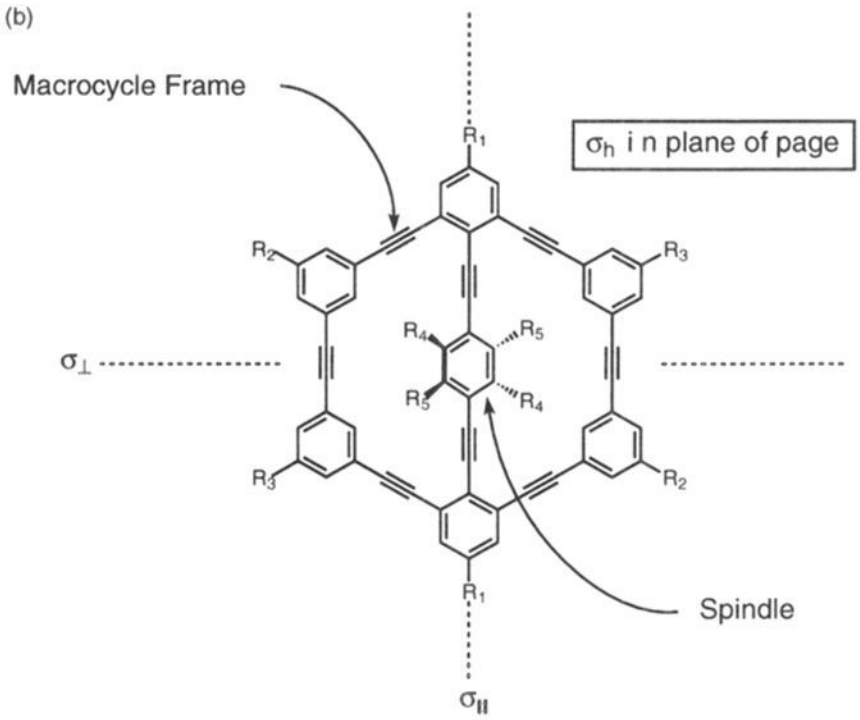

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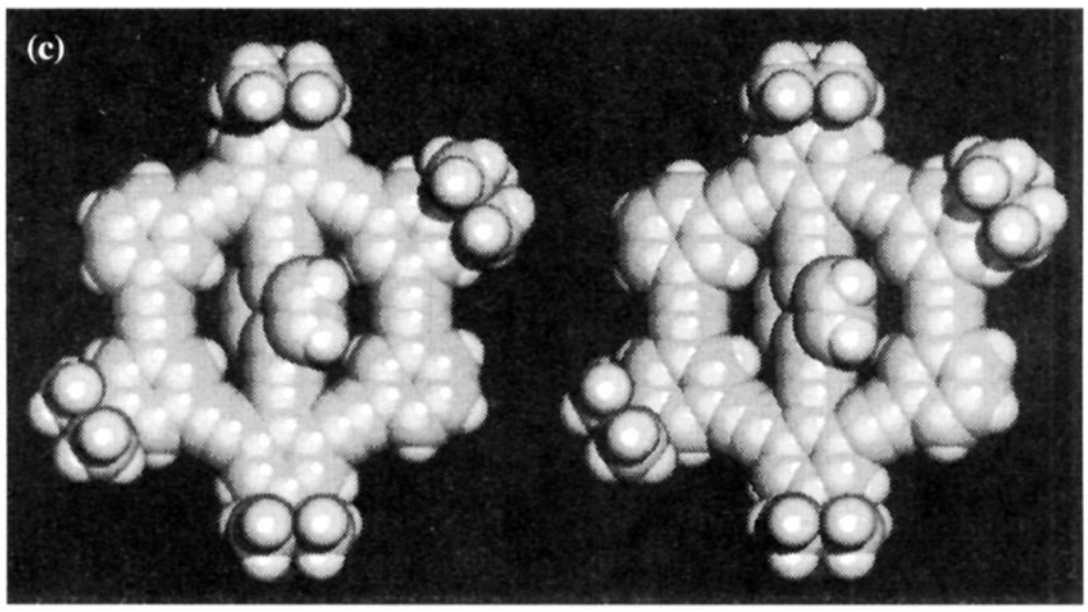

Figure 1. (a) Chemical structure of molecular turnstiles **1**, **2**, and **3**. (b) Generic turnstile architecture and associated symmetry elements $\sigma_{||}$, $\sigma_{\perp}$, and σ_h. (c) Stereoview of a space-filling representation of **1**.

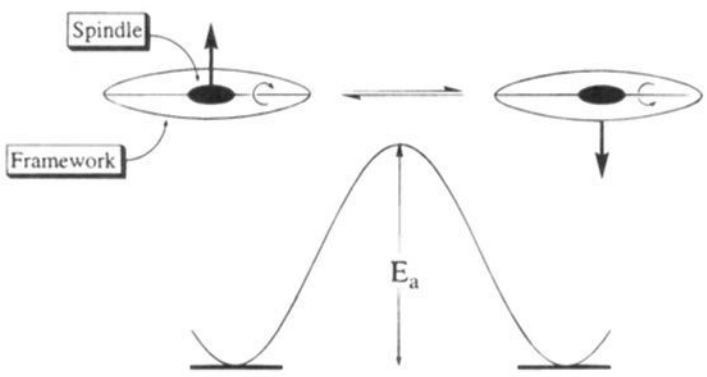

Figure 2. A hypothetical double-well potential energy surface for isoenergetic conformers of the molecular turnstile.

ylacetylene is known to be very small (<1 kcal/mol).[13] Depending on the substitution pattern of the framework and the spindle, two rotomers will be related either as homomers, enantiomers, or diastereomers. Rotational enantiomers are more interesting than homomers or diastereomers since they allow for both polar arrangements of electrical dipoles and true conformational bistability through isoenergetic conformers. In derivatives reported below, *tert*-butyl groups on the phenyl rings adjacent to the spindle junction break both $\sigma_{||}$ and $\sigma_{\perp}$.

Results and Discussion

Synthesis. Two synthetic strategies are considered. The first employs a highly convergent approach through use of common bis-acetylene **9** in which installation of a dihaloarene spindle by palladium-catalyzed coupling to macrocycle **9** affords turnstile **10** (Scheme 1). This general strategy of first assembling the macrocyclic framework followed by spindle connection allows for a straightforward preparation of turnstile derivatives with variation in the spindle unit. Treatment of commercial 2-bromobenzaldehyde (**4**) with (trimethylsilyl)-acetylene under standard palladium-catalyzed coupling conditions readily afforded **5**. Treatment of **5** according to a procedure by Comins[14] afforded **6** via iodine capture of an *ortho*-metalated α-amino alkoxide intermediate followed by protection of the unstable intermediate aldehyde as its cyclic acetal. Elaboration of this functionalized monomer by methods reported previously provided hexamer **7** which was cyclized to give macrocycle **8**.[9c] However, **8** exhibits poor solubility in common organic solvents. This observation in addition to low yields anticipated for the requisite aldehyde to acetylene transformation to form **9** and an unproven final palladium-catalyzed spindle coupling to form **10** suggested another synthetic course.

Strategy two involves initial formation of the spindle portion to form intermediate **18** followed by elaboration and palladium-mediated double cyclization to form the spindle system **19** (Scheme 2). Precedent for this strategy exists as a similar double cyclization reaction is used in the preparation of the macrobicycle illustrated in Figure 1.[9d] While the latter route may appear

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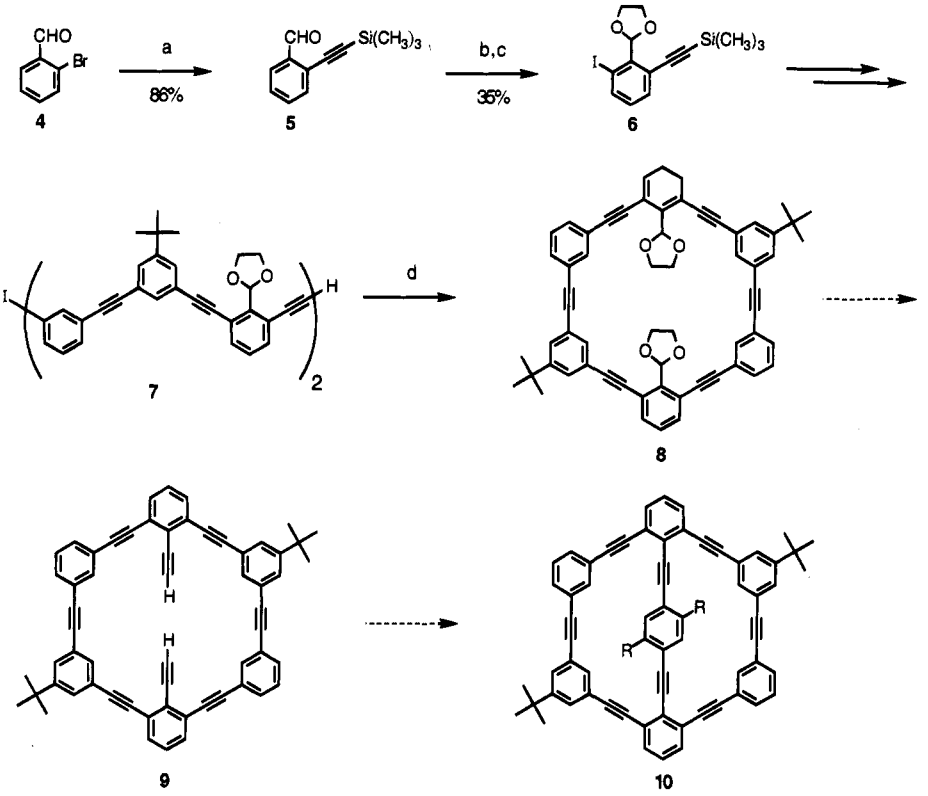
Scheme 1[a]



[a] (a) (Trimethylsilyl)acetylene, $Pd(dba)_2$, CuI, PPh_3, NEt_3, 12 h, 75 °C. (b) *sec*-Butyllithium, *N,N,N'*-trimethylethylenediamine, I_2. (c) Ethylene glycol, PTSA, toluene, 2 h, 110 °C. (d) $Pd(dba)_2$, CuI, PPh_3, NEt_3, 12 h, 75 °C.

more synthetically feasible, it does not allow for the same ease of spindle derivatization found in the former. The second route ultimately proved successful and yields are summarized in Scheme 2.

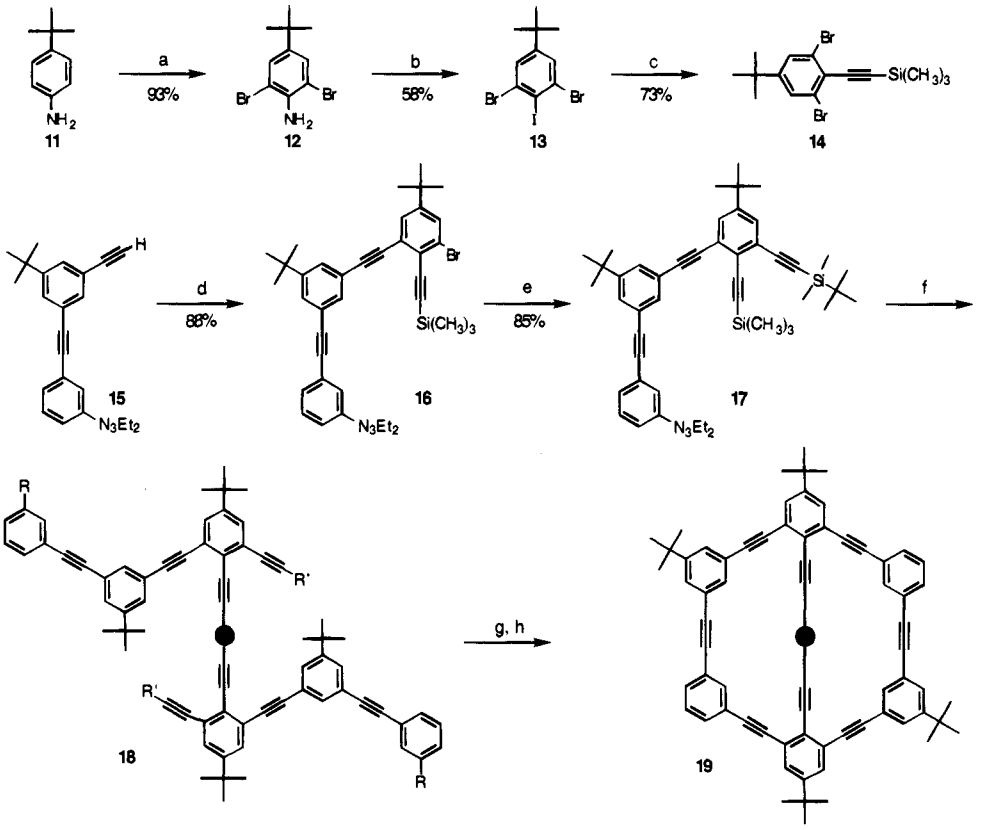
Bromination of commercial *p-tert*-butylaniline (**11**) readily afforded dibromoaniline **12** which was subsequently diazotized in sulfuric and glacial acetic acids and treated with iodine to form **13**. This 1,2,3-trihaloarene derivative **13** proved to be the key intermediate. Palladium-catalyzed coupling with (trimethylsilyl)acetylene is directed to the iodine position by capitalizing on the kinetic lability of palladium insertion into the iodoarene rather than the bromoarene bond. Careful control of stoichiometry and temperature was required to afford compound **14** in good yield. Reaction of a 2.4-fold excess of **14** with the previously reported sequence H−(AC)−N_3Et_2 **15**[9c] affords trimer **16** by taking advantage of the statistical ratio of potentially reactive bromines. The triazene unit serves as a polar group which facilitates separation of **16** by chromatography. Thus approximately 90% of excess **14** is recovered as well as 7−10% of an undesired pentameric linear sequence resulting from reaction of acetylene **15** with both reactive bromine atoms of compound **14**. Coupling of **16** with (*tert*-butyldimethylsilyl)-acetylene then affords trifunctionalized sequence **17** in which the trimethylsilyl protecting group could be selectively removed in the presence of the (*tert*-butyldimethyl)silyl group at room temperature with potassium carbonate in methanol. Subsequent palladium-catalyzed coupling of this deprotected acetylene with dihaloarene spindle precursors **27** and **28** provided linear heptameric sequences of type **18**. Elaboration of heptameric sequences first by treatment with methyl iodide then by treatment with TBAF in wet THF afforded an intermediate bisiodo-bisacetylene which was subjected to pseudo-high-dilution macrocyclization conditions.[9c] Double palladium-catalyzed macrocyclizations provided turnstile derivatives **19** as colorless solids in ca. 50% yields. These yields compare favorably with typical yields obtained for macrocycles lacking a bridging spindle unit of ca. 70%.[9c] Dibromoarene spindles **27** and **28** were prepared in satisfactory yields by treatment of known 1,4-bis(bromomethyl)-2,5-dibromobenzene **26** with appropriate sodium alkoxides (Scheme 3).[15]

Purification of **3** was accomplished by precipitation with methanol from a hot chloroform solution followed by centrifugation. Crystallization of the precipitate from a hot benzene afforded a sample suitable for analysis. Turnstile **3** was characterized by ^1H NMR, high-resolution mass spectrometry, infrared spectroscopy, and elemental analysis. The purified compound revealed only a single, symmetrical peak when analyzed both by HPLC and gel permeation chromatography in chloroform. Single crystals of **3** suitable for X-ray diffraction were grown by slow cooling of a 10% $CH_3CN/CHCl_3$ solution. The resulting crystallographic model confirmed the molecular constitution of the macrocycle framework, but disorder in the (3,5-di-*tert*-butylphenoxy)methyl spindle substituents precluded satisfactory structure refinement.[16] Turnstile **3** was moderately soluble in chloroform, tetrachloroethane, and benzene. The solubility characteristics of **1** and **2**, however, made their purification more difficult as both exhibited very poor solubilities in common organic solvents. This behavior is surprising in light of the good solubility characteristics of similar phenylacetylene macrocycles.[9c] Turnstile **1** was only sparingly soluble in hot bromoform and hot tetrachloroethane and was very sparingly soluble in tetrahydrofuran, diethyl ether, carbon tetrachloride, chloroform, DMSO, DMF, toluene, and benzene. The solubility behavior of turnstile **2** was only slightly improved. Thus, crude precipitates of **1** or **2** from reaction mixtures were washed with diethyl ether, water, and chloroform to remove salts and soluble organics. Continuous soxhlet extraction of

(15) McCoy, R. K.; Karasz, F. E. *Chem. Mater.* **1991**, *3(5)*, 941.

(16) Due to unsatifactory refinement, crystallographic data are not being reported at this time.

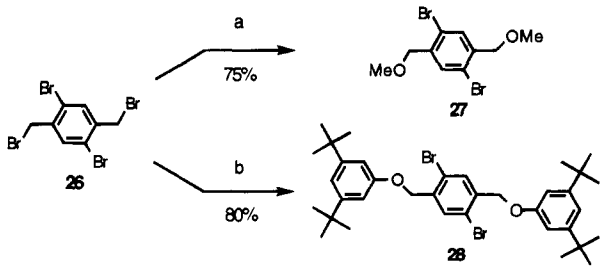
Scheme 2[a]



		R	R'	Yield
g	20	N_3Et_2	TBDMS	90%
h	21	I	TBDMS	98%
	1	Macrocycle	—	35%
g	22	N_3Et_2	TBDMS	46%
h	23	I	TBDMS	70%
	2	Macrocycle	—	50%
g	24	N_3Et_2	TBDMS	54%
h	25	I	TBDMS	79%
	3	Macrocycle	—	50%

[a] (a) Br_2, 1:1 MeOH/CH_2Cl_2, 2 h, rt. (b) $NaNO_2$, H_2SO_4, HOAc, KI, I_2. (c) (Trimethylsilyl)acetylene, $Pd(dba)_2$, CuI, PPh_3, NEt_3, 12 h, 75 °C. (d) 2.4 equiv **14**, $Pd(dba)_2$, CuI, PPh_3, NEt_3, 12 h, 75 °C. (e) *tert*-(Butyldimethylsilyl)acetylene, $Pd(dba)_2$, CuI, PPh_3, NEt_3, 12 h, 75 °C. (f) MeOH, Na_2CO_3, 30 min, rt then spindle (*p*-$C_6H_4I_2$, **27**, or **28**), $Pd(dba)_2$, CuI, PPh_3, NEt_3, 12 h, 75 °C. (g) MeI, 12 h, 120 °C. (h) TBAF, THF then $Pd(dba)_2$, CuI, PPh_3, NEt_3, 12 h, 75 °C.

Scheme 3[a]



[a] (a) NaOMe, THF, 2 h, rt. (b) 3,5-di-*tert*-butylphenol, K_2CO_3, DMF, 12 h, rt.

the remaining residue with hot benzene for extended periods (48 h) provided a solid in the solvent reservoir. Precipitation of **1** from a hot bromoform solution provided a sample for analysis which consistently retained trace amounts of bromine. Crystallization of **2** from a hot tetrachloroethane solution provided a sample which gave a single, symmetrical peak by GPC in $CHCl_3$ and consistently gave a carbon analysis that was 1.5% too low. Low solubility precluded further purification of **1** or **2** by preparative HPLC. Infrared and ^1H NMR spectroscopy, as well as high-resolution mass spectrometry and characterization of all synthetic precursors, support the assigned structure of **2**.

The solubility behavior of the turnstile compounds suggests that the filling of void space present in a typical phenylacetylene macrocycle with the spindle unit makes the solid state more stable. It is interesting to note a strong tendency for crystals of other phenylacetylene macrocycles to include solvent and become brittle and opaque upon exposure to air, presumably due to solvent loss. However, examination of single crystals of turnstile **3** even after 6 months of exposure to the atmosphere, has revealed no such tendency. Differential scanning calorimetry (DSC) measurements indicate a slight lowering of the decomposition temperature from approximately 425 °C in a typical macrocycle to 390 °C for **1** and to 325 °C for **3**. None

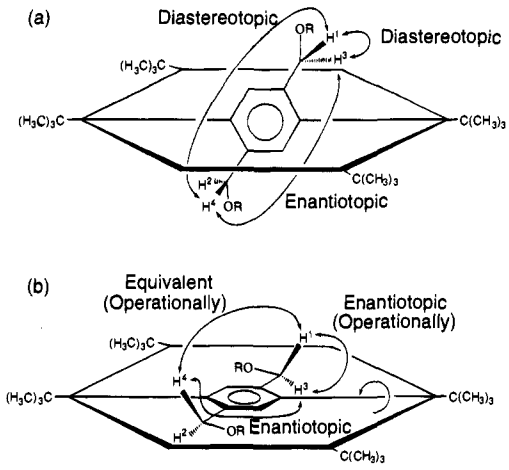


Figure 3. Topic relationships between the spindle methylene protons in the limits of fast and slow rotation. (a) Slow spindle rotation should result in the appearance of H^1 and H^3 as an AB doublet. (b) Fast spindle rotation should result in the appearance of H^2 and H^4 as a singlet.

of the turnstiles exhibit phase transitions below the decomposition temperatures.

Variable-Temperature ^{1}H NMR Studies. Careful examination of structures **2** and **3** shows that while the molecules are achiral and exhibit C_i symmetry, the two spindle methylene protons become diastereotopic in the case of slow spindle rotation on the NMR time scale. These protons should therefore be anisochronous (Figure 3). Hydrogen H^1 is related to H^2 by an improper (S_2) axis of rotation and this pair of protons is enantiotopic by internal comparison. Hydrogens H^3 and H^4 are related in an analogous fashion. According to the terminology employed by Mislow, H^1/H^2 and H^3/H^4 comprise two sets of enantiotopic protons.[17] Hydrogen H^1 cannot be transformed into H^3 by any symmetry operation. Thus, H^1 and H^3 are diastereotopic by internal comparison and comprise a diastereotopic set H^1/H^3 as do H^2/H^4. Restated, H^1/H^2 and H^3/H^4 form two diastereotopic sets of enantiotopic protons (Figure 3a).

Fast rotation about the spindle axis causes H^1 and H^4 to interconvert and become operationally equivalent as do H^2 and H^3. Since H^1 and H^2 are always enantiotopic, H^1 and H^3 become operationally enantiotopic. The term "operationally" is used here to designate that the equivalence or enantiotopicity results from a dynamic process. The easiest way to visualize these relationships is to consider the transition state structure between conformers in which the spindle lies in the plane of the macrocycle (Figure 3b). Since enantiotopic protons are indistinguishable by NMR, the anisochronous NMR signal expected for the methylene protons in the case of slow spindle rotation (an AB doublet) should theoretically collapse to a singlet as spindle rotation becomes fast in the absence of any external chiral agent. However, it should be noted that although H^1/H^3 and H^2/H^4 form diastereotopic sets of protons in the locked case, the magnitude of the chemical shift nonequivalence necessary to observe this difference may be solvent, temperature, and concentration dependent. These factors could result in an apparent singlet although the spindle is actually rotating slowly on the NMR time scale.[18]

Variable-temperature ^{1}H NMR experiments were performed in several different deuterated solvents including DMSO, DMF, benzene, toluene, THF, chloroform, and tetrachloroethane with chloroform providing the largest observable chemical shift difference between methylene signals. The insolubility of **2** made this compound more difficult to study than **3**. Results obtained in chloroform show that spindle methylene protons of turnstile **3** appear as an AB quartet at all temperatures studied (Figure 4). The chemical shift difference of ca. 58 Hz at −65 °C narrows to ca. 25 Hz at the upper temperature limit of 55 °C. The observed AB pattern persists to the high-temperature limit of 150 °C in both DMSO and tetrachloroethane. In contrast, methylene protons of turnstile **2** appear as an AB quartet only at low temperature. A chemical shift difference of ca. 9 Hz is observed at −54 °C, which coalesces to a singlet at a critical temperature of approximately 0 °C (Figure 5). This singlet persists to the upper temperature limit of 85 °C in chloroform (sealed tube). Thus, while the observed signal appears as an AB quartet with a chemical shift difference of ca. 8 Hz at −12 °C and as a singlet at 0 °C, no further multiplicity resulting from the reappearance of an AB pattern associated with temperature-dependent chemical shift is observed even at 85 °C in chloroform.[19] These results are consistent with the idea that turnstile **3** is conformationally locked and cannot undergo spindle rotation while turnstile **2**

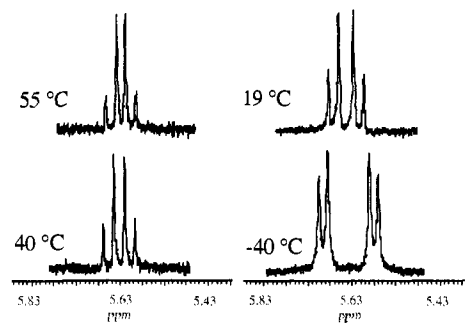


Figure 4. Variable-temperature 500-MHz ^{1}H NMR spectra ($CDCl_3$) of **3** in the region of the spindle methylene resonance at the indicated temperatures.

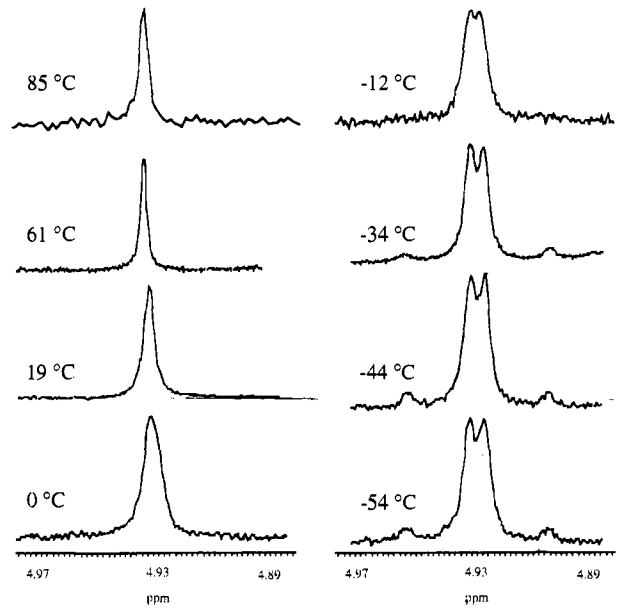


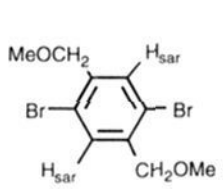
Figure 5. Variable-temperature 500-MHz ^{1}H NMR spectra ($CDCl_3$) of **2** in the region of the spindle methylene resonance at the indicated temperatures.

(17) (a) Mislow, K.; Raban, M. Stereoisomeric Relationships of Groups in Molecules. In *Topics in Stereochemistry*; Allinger, N., Eliel, E., Eds.; Interscience: New York, 1967. (b) Mislow, K.; Siegel, J. *J. Am. Chem. Soc.* **1984**, *106*, 3319. (c) Eliel, E. L.; Wilen, S. H. *Stereochemistry of Organic Compounds*; Wiley: New York, 1994; Chapter 8.

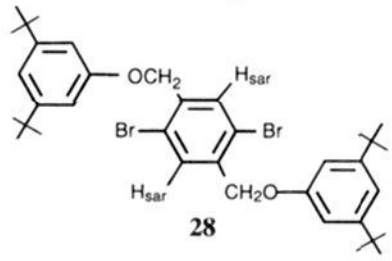
(18) Friebolin, H. *Basic One- and Two-Dimensional NMR Spectroscopy*; VCH: Federal Republic of Germany, 1991; Chapter 11.

(19) The signal also appears as a singlet at all temperatures in tetrachloroethane. This is the only other solvent in which **2** exhibits satisfactory solubility to obtain a low-temperature ^{1}H NMR spectra.

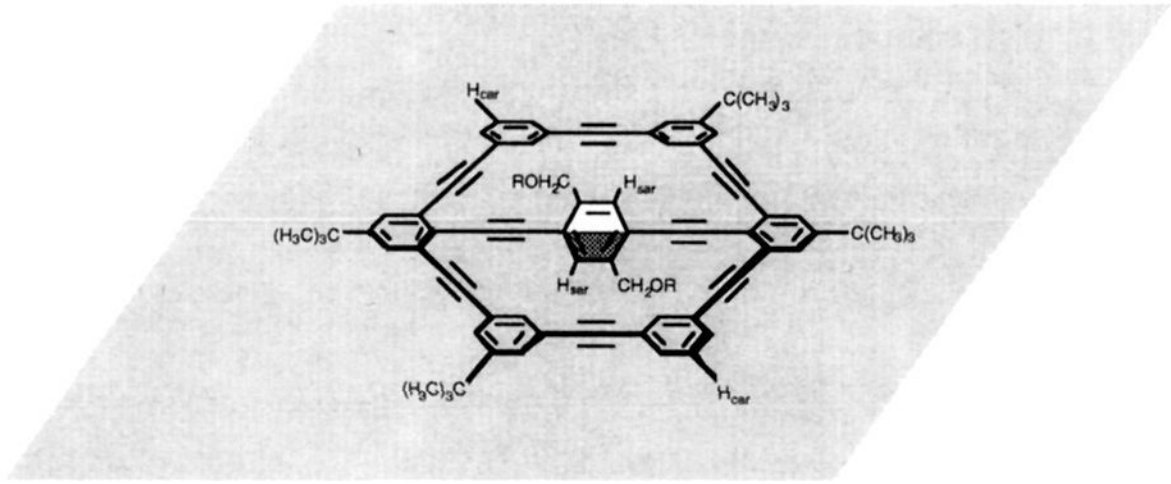
Table 1. Comparison of Longitudinal Relaxation Times (T_1) for Turnstiles **2** and **3** and Spindle Precursors **27** and **28**



27



28



	H_{sar}		CH_2		H_{car}
	T_1[a] (s)	% difference	T_1[a] (s)	% difference	T_1[a] (s)
Dihaloarene **28**	7.39 ± 0.57	-65.8% ± 3.0%	0.96 ± 0.01	-58.0% ± 3.0%	NA
Turnstile **3**	2.53 ± 0.12		0.40 ± 0.01		1.71 ± 0.10
Dihaloarene **27**	19.95 ± 0.97	-83.8% ± 3.0%	3.76 ± 0.20	-72.1% ± 3.0%	NA
Turnstile **2**	3.23 ± 0.39		1.05 ± 0.05		2.00 ± 0.33

[a] Reported values based on five repetitive 500-MHz ^{1}H NMR measurements performed in deoxygenated chloroform at 45 °C.

exhibits rapid spindle rotation on the NMR time scale at room temperature. If rotation is assumed, we estimate the barrier to spindle rotation to be 13.4 kcal/mol for **2** and assign a lower limit for **3** of 20.6 kcal/mol.[20]

Additional evidence for rapid rotation in **2** comes from a comparative study of longitudinal T_1 relaxation times for ^{1}H signals associated with spindle aromatic and methylene signals. Longitudinal relaxation times T_1 were evaluated by the inversion recovery experiment.[21] Measured T_1 values for the aromatic and methylene signals of spindles **27** and **28** become shorter upon incorporation into the turnstile architecture (Table 1). The aromatic signal for **28** is reduced by 66% upon incorporation into turnstile **3** while the corresponding signal of **27** is reduced by 84% upon incorporation into turnstile **2**. Methylene signals are similarly reduced by 58% and 72%, respectively. Based on five repetitive T_1 measurements, a two-tailed student's T-test at the 99% confidence level indicates that a statistically significant reduction of longitudinal relaxation times occurs upon incorporation into turnstile **2**.[22] However, longitudinal relaxation times of an aromatic signal common to both turnstile frames reveal no statistically significant difference in T_1. This suggests an additional relaxation mechanism unique to turnstile **2**. Spindle rotation in **2** could account for these observations.

Two additional explanations for the observed signal coalescence in **2** must be addressed. Temperature-dependent chemical shift could also result in an apparent collapse to a singlet and this is not unreasonable given the fact that the observed chemical shift in turnstile **3** is temperature dependent. The strongest evidence against this explanation is the failure to observe the reappearance in the ^{1}H NMR of an AB pattern on going to higher temperatures. A second explanation involves puckering of the macrocycle framework, the result of a bridging spindle unit that is either too short or too long to keep the macrocycle planar. While a planar turnstile with a locked spindle exhibits C_i symmetry as pictured in Figure 3, a puckered turnstile locked with respect to both spindle rotation and the macrocycle distortion possesses C_1 symmetry. The methylene protons in the C_i structure should exhibit a single AB quartet, while the C_1 structure should exhibit two distinct AB quartets. However, only a single AB quartet is observed in both **2** and **3**, suggestive of structures with C_i symmetry. Chemical shift equivalence in this context does not seem likely since the chemical shift difference of 58 Hz observed in **3** is attributable to framework substituents. Thus, NMR evidence argues against a puckering mechanism. Additional evidence from molecular modeling and X-ray data suggest that the spindle unit fits exactly across the macrocycle cavity.[16]

Turnstile rotation requires two methoxymethyl substituents to pass through the turnstile cavity. It is interesting to consider the shape of the potential energy surface which describes spindle rotation and the nature of the transition state(s) through which the turnstile passes. Figure 1c depicts a space-filling model of the parent turnstile **1** with the macrocyclic framework in a planar conformation. It is apparent from molecular models and molecular mechanics calculations that rotation of the spindle through the framework involves deformation of the macrocycle away from this planar conformation. Elucidation of the spindle

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(22) Bevington, P. R. *Data Reduction and Error Analysis for the Physical Sciences*; McGraw Hill: New York, 1969.

rotation mechanism, however, requires additional experiments. Separation of enantiomeric rotomers from an unsymmetrically substituted spindle derivative followed by observation of a racemization process through optical rotation measurements could conclusively prove that spindle rotation occurs. Kinetic data of such a process could ultimately yield an entropy of activation which may provide further insight into the geometry and degree of order of the transition state.

Conclusion

We have reported the design of a new turnstile architecture exhibiting conformational bistability and have demonstrated its synthetic feasibility. Two achiral derivatives which provide homomeric rotomers are reported. Incorporation of the spindle portion into a phenylacetylene macrocycle appears to stabilize solid state packing as revealed by the low solubility of **1**–**3** in comparison to previously prepared hexaphenylacetylene macrocycles. Variable-temperature NMR as well as longitudinal T_1 relaxation times suggest the spindle of turnstile **2** exhibits dynamic behavior while that in **3** behaves in a fashion consistent with a locked spindle.

A combination of molecular chirality and dipolar order has important implications from the standpoint of designing electroactive materials. Ferroelectric liquid crystals are perhaps the best example where this has been exploited.[23] In light of the demonstrated ability of the phenylacetylene macrocycles to form discotic liquid crystalline phases, one potential use for the turnstile architecture would be as discotic, ferroelectric liquid crystals. A dipole appropriately incorporated on the spindle could allow for its own rotation to be controlled rapidly and reversibly by an external field. If the spindle rotation mechanism is operative, perhaps the turnstile architecture could exhibit unique rotational viscosity properties and ultimately prove advantageous toward reducing the switching times associated with typical ferroelectric liquid crystals.[24]

Experimental Section

General. All solvents and reagents were of reagent quality, purchased commercially, and used without further purification, except as noted below. Dry tetrahydrofuran (THF), benzene, and diethyl ether (Et_2O) were obtained by vacuum transfer from sodium and benzophenone. Dry triethylamine and methyl iodide were obtained by vacuum transfer from calcium hydride and molecular sieves, respectively. (Trimethylsilyl)acetylene was purchased from Farchan Labs, Gainsville, FL, and was vacuum transferred from magnesium sulfate. (*tert*-Butyldimethylsilyl)acetylene was prepared by a literature procedure.[25] 4-*tert*-Butylaniline was obtained commercially from Aldrich. All reactions were carried out under an atmosphere of dry nitrogen through the use of standard Schlenk techniques in glassware which was dried in an oven at 110–120 °C for 12 h prior to use. Analytical thin layer chromatography (TLC) was performed on KIESELGEL F-254 precoated TLC plates. Flash chromatography was performed on Merck 40–63 μm silica gel. Melting points were measured on a Thomas Hoover melting point apparatus and are uncorrected. Nuclear magnetic resonance (NMR) spectra were recorded on a General Electric QE-300 (300 MHz), a Varian Unity (400 MHz), or a General Electric GN500 (500 MHz) spectrometer in the indicated solvent; chemical shifts are expressed in parts per million (δ) using residual solvent protons as an internal standard. Splitting patterns are designated as s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), dd (doublet of doublets); coupling constants are reported in hertz (Hz). Mass spectra were measured by electron ionization (EI, 70 eV) on a Finnigan-MAT 731 spectrometer, field desorption (FD) on a Finnigan-AT CH5 spectrometer, or fast atom bombardment (FAB) on a VG ZAB-SE or a VG 70-VSE spectrometer at the University of Illinois Mass Spectrometry Laboratory. Infrared data were obtained on a Mattson Galaxy Series FTIR 5000 spectrometer. Elemental analyses were performed by either combustion analysis on a Leeman Labs CE440 Elemental Analyzer or classical wet chemical analysis at the University of Illinois Microanalytical Laboratory. Thermogravimetric analyses were performed on a Perkin–Elmer Thermal System VII Thermogravimetric Analyzer and differential scanning calorimetry was performed on a Perkin–Elmer Thermal System VII Differential Scanning Calorimeter. Gas chromatography (GC) was performed on an HP-5890 Series II gas chromatograph equipped with a 12.5 m × 0.2 mm × 0.5 μm HP-1 methylsilicone column and fitted with a flame ionization detector with helium carrier gas at 30 mL/min. Size-exclusion chromatography (SEC) was performed using a Waters 510 HPLC pump, Waters 996 photodiode array detector, and a series of three Waters styragel HR 4E 7.8 × 300 mm columns which were calibrated with narrow molecular weight polystyrene standards. SEC data were obtained in THF at 23 °C. Preparative high-pressure liquid chromatography (HPLC) was performed with a Rainin Dynamax solvent delivery system Model SD-200 using a Microsorb Si-80-120-c5 silica column.

General Acetylene Coupling Procedure A. A sealed flask with a Teflon screw cap was charged with aryl halide (1 equiv), terminal acetylene (1 equiv), bis(dibenzylideneacetone)palladium(0) (0.02 equiv), triphenylphosphine (0.10 equiv), and copper(I) iodide (0.02 equiv) in dry triethylamine. The mixture was evacuated and back-filled with nitrogen three times. When (trimethylsilyl)acetylene was used, it was added to the reaction mixture under nitrogen via syringe after the evacuation/back-fill procedure. The reaction was then stirred under nitrogen at 50–75 °C for 18–24 h and monitored by thin layer or gas chromatography. After the reaction was complete, the mixture was cooled and filtered through a plug of silica. The filtrate was washed with diethyl ether and the combined extracts were washed with water, dried over magnesium sulfate, filtered, and evaporated to provide a crude residue for purification.

General (Trimethylsilyl)acetylene Deprotection Procedure B. The desired (trimethylsilyl)acetylene and a catalytic amount of anhydrous potassium carbonate were stirred in a 1:1 solution of methanol and dichloromethane (1 M) at room temperature under nitrogen. The reaction was monitored by TLC and typically required 2–6 h. The mixture was then diluted with water and extracted with dichloromethane. The organic layer was dried over magnesium sulfate, filtered through a short plug of silica, and evaporated to afford pure terminal acetylene which was used without further purification.

General Methyl Iodide Deprotection Procedure C. A 1 M solution of triazene in methyl iodide was heated in a sealed tube at 115 °C for 6–18 h. After removal of the solvent under reduced pressure, the residue was dissolved in dichloromethane and filtered over a short plug of silica. Removal of the solvent *in vacuo* afforded a crude residue for purification.

General Triazene Formation Procedure D. Arylamine (10.0 mmol) was added to 6 N hydrochloric acid (50 mL). Water and acetonitrile were added as necessary to form a homogeneous solution which was then cooled to 0 °C. Sodium nitrite (11.0 mmol) in water (20 mL) was then added dropwise, keeping the temperature of the solution below 0 °C during the addition. After being stirred for 30 min at 0 °C, the diazonium solution was added slowly to an ice cold mixture of potassium carbonate (15.0 mmol), dialkylamine (15.0 mmol), and water (150 mL). The reaction mixture was extracted with diethyl ether three times. The ether layers were combined and dried over magnesium sulfate. Filtration and evaporation of the solvent afforded a crude residue for purification.

(23) For reports of ferroelectric discotic liquid crystals see: (a) Bock, H.; Helfrich, W. *Liq. Cryst.* **1992**, *12(4)*, 697–703. (b) Bock, H.; Helfrich, W. *Liq. Cryst.* **1995**, *18(5)*, 707–713. (c) Scherowsky, G.; Chen, X. H. *Liq. Cryst.* **1994**, *17(6)*, 803–810.

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(25) Fitzmaurice, N. J.; Jackson, W. R.; Perlmutter, P. *J. Organomet. Chem.* **1985**, *285*, 375–381.

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General Double-Macrocyclization Procedure E. (*tert*-Butyldimethylsilyl)acetylene protected heptamer sequence (0.17 mmol) in wet THF (25 mL) was treated with tetrabutylammonium fluoride (1 M in THF, 2.1 equiv) at room temperature and stirred 5 min. The reaction was monitored by TLC. After dilution with diethyl ether (25 mL) and washing with water, the organic extract was dried over magnesium sulfate and evaporated to provide a crude residue which was separated by flash chromatography in 2% ethyl acetate/hexane. The bisacetylene was immediately dissolved in dry triethylamine (40 mL) and added via syringe pump to a 75 °C solution of bis(dibenzylideneacetone)-palladium(0) (1.5 equiv), triphenylphosphine (6 equiv), and copper(I) iodide (1.4 equiv) in dry triethylamine (50 mL) under positive nitrogen pressure over 16 h. Isolation and purification of the macrocycles was performed as described below.

2-((Trimethylsilyl)ethynyl)benzaldehyde (5). **5** was prepared according to general procedure A. Thus, 2-bromobenzaldehyde (5.00 g, 27.0 mmol) and (trimethylsilyl)acetylene (3.97 g, 40.5 mmol) after purification by Kugelrohr distillation afforded 4.70 g (86%) of product as a colorless solid: mp 50−52 °C; bp 80−100 °C (0.5 mmHg); R_f 0.43 (10% ethyl acetate/hexane); ^{1}H NMR (300 MHz, $CDCl_3$) δ 10.53 (s, 1H), 7.87 (d, J = 12 Hz, 1H), 7.55−7.40 (m, 3H), 0.26 (s, 9H); ^{13}C NMR (300 MHz, $CDCl_3$) δ 191.62, 136.06, 133.56, 133.39, 128.72, 126.75, 126.66, 102.28, 99.99, −0.31; IR (KBr) 2857, 2152, 1698, 868, 838, 765 cm^{-1}; MS (EI) *m/e* calcd for $C_{12}H_{13}OSi$ 201.0733, found 201.0733, 202 (4), 201 (18), 187 (100). Anal. Calcd for $C_{12}H_{14}OSi$: C, 71.24; H, 6.97. Found: C, 71.00; H, 7.04.

2-(2′-Iodo-6′-((trimethylsilyl)ethynyl)phenyl)-1,3-dioxolane (6). **6** was prepared according to a procedure by Comins.[14] To a solution of *N,N,N′*-trimethylethylenediamine (0.66 g, 6.4 mmol) in diethyl ether (25 mL) at −41 °C was added *sec*-butyllithium (3.9 mL, 5.4 mmol) dropwise. 2-((Trimethylsilyl)ethynyl)benzaldeyde **5** (1.00 g, 5.0 mmol) in diethyl ether (5 mL) was then added dropwise and the resulting solution was stirred for 15 min. After a second addition of *sec*-butyllithium (12.0 mL, 17.0 mmol), the reaction was stirred for 12 h in a freezer held at −20 °C. The mixture was then cooled to −78 °C and transferred via cannula to a flask containing a solution of iodine (5.0 g, 19.7 mmol) in THF (25 mL) at −78 °C. After being stirred cold for 0.5 h, this solution was transferred via cannula to a flask containing 10% aqueous sodium bicarbonate (300 mL). The resulting mixture was acidified with 10% aqueous HCl and extracted with diethyl ether. The organic extract was dried over magnesium sulfate, filtered, and evaporated to afford a green liquid which turned black on prolonged standing or heating. This liquid was immediately heated to reflux with ethylene glycol (0.37 g, 6.0 mmol) and a catalytic amount of *p*-toluenesulfonic acid in benzene (100 mL) using a Dean-Stark trap for 0.75 h. The cooled solution was then washed with water (100 mL) and 10% aqueous sodium bicarbonate (100 mL) then dried over magnesium sulfate, filtered, and evaporated. Flash chromatography in 5% ethyl acetate/hexane afforded 0.72 g (35%) of product as a colorless liquid: bp 100−120 °C (0.04 mmHg); R_f 0.38 (10% ethyl acetate/hexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (dd, $J_{3',4'}$ = 8 Hz, $J_{3',5'}$ = 1 Hz, 1H), 7.51 (dd, $J_{4',5'}$ = 8 Hz, 1H), 6.93 (dd, 1H), 6.25 (s, 1H), 4.33−4.30 (m, 2H), 4.09-4.06 (m, 2H), 0.25 (s, 9H); ^{13}C NMR (400 MHz, $CDCl_3$) δ 140.75, 138.19, 134.78, 130.19, 124.69, 106.40, 101.67, 100.35, 96.59, 66.00, −0.13; IR (neat) 2156, 967 cm^{-1}; MS (EI) 371 (6), 329 (35), 313 (59), 245 (100), 73 (44). Anal. Calcd for $C_{14}H_{17}IO_2Si$: C, 45.17; H, 4.60; I, 34.09. Found: C, 45.60; H, 4.74; I, 34.11.

2,6-Dibromo-4-*tert*-butylaniline (12). To a stirred solution of *p-tert*-butylaniline in 1:1 dichloromethane/methanol (200 mL) was added a solution of bromine (66.90 g, 420.0 mmol) in 1:1 dichloromethane/methanol (200 mL) dropwise via pressure addition funnel under nitrogen at room temperature. The mixture was stirred for 2 h and monitored by GC. Evaporation of the solvent afforded a residue which was added to 20% aqueous sodium hydroxide (500 mL). The product was extracted with diethyl ether (1 L) and dried over magnesium sulfate. Filtration and evaporation of the solvent afforded a purple oil which was purified by Kugelrohr distillation to provide 46.0 g (89%) of product as a white solid. All physical data agreed with reported literature values.[25]

1,3-Dibromo-5-*tert*-butyl-2-iodobenzene (13). A solution of *p-tert*-butyl-2,6-dibromoaniline (10.00 g, 33.0 mmol) in glacial acetic acid (100 mL) was added to a solution of sodium nitrite (2.15 g, 35.9 mmol) in concentrated sulfuric acid (20 mL) keeping the internal temperature below 20 °C. The mixture was allowed to stir for 4 h before being added to a solution of potassium iodide (40.00 g, 240.0 mmol) and iodine (8.27 g, 32.6 mmol) in water (70 mL). The resulting dark, viscous mixture was stirred with an overhead stirrer for 12 h then basified with 1.5 L of 15% aqueous sodium hydroxide and extracted with ethyl acetate (500 mL). The extracts were dried over magnesium sulfate, filtered, and evaporated. Simple distillation using a 6 in. Vigreux column of the crude residue afforded 7.90 g (58%) of product as a yellow liquid: bp 125−135 °C (0.06 mmHg); R_f 0.71 (10% ethyl acetate/hexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (s, 2H), 1.28 (s, 9H); ^{13}C NMR (400 MHz, $CDCl_3$) δ 154.36, 130.85, 128.67, 104.99, 34.81, 30.83; IR (neat) 3105, 1571, 1523, 1476 cm^{-1}; MS (EI) 420 (28), 418 (58), 416 (29), 405 (50), 403 (100), 401 (52). Anal. Calcd for $C_{10}H_{11}Br_2I$: C, 28.74; H, 2.65. Found: C, 28.79; H, 2.65.

1,3-Dibromo-5-*tert*-butyl-2-((trimethylsilyl)ethynyl)benzene (14). **14** was prepared according to general coupling procedure A. Thus 1,3-dibromo-5-*tert*-butyl-2-iodobenzene (16.60 g, 40.0 mmol) and (trimethylsilyl)acetylene (3.92 g, 40.0 mmol) after crystallization from 95% ethanol afforded 11.30 g (73%) of product as a yellow solid: mp 67−8 °C; R_f 0.71 (hexane); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.52 (s, 2H), 1.27 (s, 9H), 0.29 (s, 9H); ^{13}C NMR (300 MHz, $CDCl_3$) δ 153.96, 128.57, 126.15, 124.01, 104.03, 101.83, 34.99, 30.85, −0.21; IR (neat) 3105, 2165, 1585, 1250, 858 cm^{-1}; MS (EI) 420 (27), 418 (51), 416 (27), 405 (51), 403 (100), 401 (51). Anal. Calcd for $C_{15}H_{20}Br_2Si$: C, 46.41; H, 5.19. Found: C, 46.43; H, 5.21.

Sequence H−(AC)−N_3Et_2 (15).[27] **15** was prepared according to general coupling procedure A. Thus, 1,3-dibromo-5-*tert*-butylbenzene (32.00 g, 100.7 mmol, 2.5 equiv) and 1,1-diethyl-3-(3-ethynylphenyl)-triazene (11.00 g, 40.3 mmol) after purification by flash chromatography in hexane afforded 20.00 g of unreacted 1,3-dibromo-5-*tert*-butylbenzene and 13.90 g (84%) of product as a yellow oil: bp 180 °C (0.01 mmHg); R_f 0.29 (hexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 (m, 1H), 7.53−7.52 (m, 1H), 7.50−7.48 (m, 2H), 7.44−7.41 (m, 1H), 7.32−7.31 (m, 2H), 3.78 (q, J = 7 Hz, 4H), 1.33 (s, 9H), 1.28 (t, J = 7 Hz, 6H); ^{13}C NMR (400 MHz, $CDCl_3$) δ 153.32, 151.15, 131.28, 128.79, 128.64, 128.07, 127.44, 124.84, 123.32, 123.04, 121.98, 121.16, 90.39, 87.78, 34.84, 31.03; IR (neat) 3064, 2212, 1740, 1620, 1400, 1100 cm^{-1}; MS (EI) *m/e* calcd for $C_{22}H_{26}N_3Br^+$ 411.1313, found 411.1310; 413 (7), 411 (7), 313 (98), 311 (100). Anal. Calcd for $C_{22}H_{26}N_3Br$: C, 64.08; H, 6.36; N, 10.19; Br, 19.38. Found: C, 64.00; H, 6.35; N, 10.19; Br, 19.26. Treatment of this compound according to general procedure A with (trimethylsilyl)acetylene followed by deprotection according to general procedure B afforded sequence H−(AC)−N_3Et_2 (**15**).

Sequence 16. **16** was prepared according to general procedure A and required the deprotection of sequence TMS−(AC)−N_3Et_2. Thus, TMS−(AC)−N_3Et_2 (6.00 g, 14.0 mmol) was treated according to general procedure B and the resulting terminal acetylene **15** was coupled with **14** (13.00 g, 34.0 mmol, 2.4 equiv) according to general procedure A. Flash chromatography in hexane afforded unreacted **14** (6.00 g) and 8.20 g (88%) of product **16** as a colorless solid: mp 97−100 °C dec; R_f 0.60 (10% ethyl acetate/hexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62−7.61 (m, 2H), 7.57−7.56 (m, 2H), 7.55−7.54 (m, 1H), 7.50 (d, J = 2 Hz, 1H), 7.43−7.40 (m, 1H), 7.32−7.30 (m, 2H), 3.78 (q, J = 7 Hz, 4H), 1.36 (s, 9H), 1.32 (s, 9H), 1.28 (t, J = 7 Hz, 6H), 0.33 (s, 9H); ^{13}C NMR (400 MHz, $CDCl_3$) δ 152.59, 151.52, 151.15, 132.31, 129.58, 128.94, 128.77, 128.33, 128.07, 127.76, 127.22, 125.71, 124.52, 123.40, 123.33, 123.27, 122.85, 121.08, 103.24, 101.81, 93.22, 89.84, 88.39, 88.08, 34.88, 34.72, 31.05, 30.89, 0.00; IR (KBr) 2168, 2217, 1588, 1478, 1467, 1452, 1434, 1247, 1236, 860, 843 cm^{-1}; MS (EI) 665 (25), 663 (22), 72 (100), 73 (100). Anal. Calcd for $C_{39}H_{46}BrN_3Si$: C, 70.46; H, 6.97; N, 6.32. Found: C, 70.55; H, 6.99; N, 6.34.

Sequence 17. **17** was prepared according to general coupling procedure A. Thus, **16** (8.20 g, 12.0 mmol) and (*tert*-butyldimethylsilyl)acetylene (2.40 g, 17.3 mmol) after flash chromatography in 5% ethyl acetate/hexane afforded 7.60 g (85%) of product as a viscous oil which solidified on standing. An analytical sample was prepared by

(27) This constitutes an improved synthetic procedure of the previously reported synthesis in ref 9c.

preparative HPLC in 2% ethyl acetate/hexane: mp 76−80 °C dec; R_f 0.65 (10% ethyl acetate/hexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63−7.62 (m, 2H), 7.55−7.54 (m, 2H), 7.53 (d, J = 2 Hz, 1H), 7.46 (d, J = 2 Hz, 1H), 7.42−7.40 (m, 1H), 7.34−7.29 (m, 2H), 3.78 (q, J = 7 Hz, 4H), 1.36 (s, 9H), 1.32 (s, 9H), 1.31−1.26 (m, 6H), 1.05 (s, 9H), 0.31 (s, 9H), 0.24 (s, 6H); ^{13}C NMR (400 MHz, $CDCl_3$) δ 151.47, 151.15, 151.00, 132.31, 129.56, 129.12, 128.77, 128.77, 128.39, 128.08, 126.32, 125.72, 125.03, 123.38, 123.29, 123.27, 123.04, 121.05, 104.04, 102.27, 101.93, 96.34, 92.60, 89.77, 88.46, 88.26, 34.72, 34.70, 31.12, 30.90, 26.29, 16.70, 0.18, −4.49; IR (KBr) 2221, 2162, 1585, 1470, 1465, 1405, 1401, 1249, 1237, 860, 841 cm^{-1}; MS (EI) 726 (3), 725 (7.18), 724 (16), 723 (26), 567 (100). Anal. Calcd for $C_{47}H_{61}N_3Si$: C, 77.95; H, 8.49; N, 5.80. Found: C, 77.78; H, 8.53; N, 6.13.

Sequence 20. **20** was prepared according to general procedure A and required prior deprotection of **17** according to general procedure B. Thus, **17** (2.63 g, 4.0 mmol) and 1,4-diiodobenzene (0.61 g, 1.9 mmol, 0.46 equiv) after flash chromatography in 5% ethyl acetate/hexane yielded 2.50 g (90% based on acetylene) as a colorless solid: mp 128−30 °C dec; R_f 0.43 (10% ethyl acetate/hexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62−7.60 (m, 4H), 7.59−7.56 (m, 6H), 7.54−7.52 (m, 6H), 7.38−7.35 (m, 2H), 7.31-7.28 (m, 4H), 3.75 (q, J = 7 Hz, 8H), 1.36 (s, 18H), 1.28 (s, 18H), 1.26 (t, J = 7 Hz, 12H), 1.01 (s, 18H), 0.23 (s, 12H); ^{13}C NMR (400 MHz, $CDCl_3$) δ 151.55, 151.55, 151.07, 131.67, 131.60, 129.54, 129.08, 128.99, 128.83, 128.64, 128.36, 128.17, 125.89, 125.53, 125.20, 123.43, 123.26, 123.23, 122:90, 121.02, 104.08, 96.70, 96.53, 93.05, 89.86, 89.24, 88.46, 88.20, 34.76, 34.61, 31.02, 30.93, 26.16, 16.72, −4.50; IR (KBr) 2216, 2164, 1584, 1464, 1452, 1436, 1423, 1405, 1247, 1235, 837, 825 cm^{-1}; MS (FAB) 1377 (M + H)$^+$. Anal. Calcd for $C_{94}H_{108}N_6Si_2$: C, 81.93; H, 7.90; N, 6.10. Found: C, 81.91; H, 7.92; N, 6.13.

Sequence 21. **21** was prepared according to general procedure C. Thus, **20** (2.50 g, 1.8 mmol) after flash chromatography in 10% ethyl acetate/hexane afforded 2.30 g (98%) of product as a colorless solid: mp 135−140 °C dec; R_f 0.39 (hexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87−7.85 (m, 2H), 7.60−7.42 (m, 18H), 7.04−7.00 (m, 2H), 1.36 (s, 18H), 1.29 (s, 18H), 1.00 (s, 18H), 0.22 (s, 12H); ^{13}C NMR (400 MHz, $CDCl_3$) δ 151.69, 151.15, 140.03, 137.22, 131.91, 131.62, 130.75, 129.96, 129.62, 129.00, 128.94, 128.90, 125.87, 125.55, 125.31, 125.02, 123.45, 123.08, 122.79, 104.07, 96.79, 96.53, 93.66, 92.92, 90.23, 89.37, 88.52, 87.70, 34.80, 34.66, 31.03, 30.95, 26.18, 16.73, −4.49; IR (KBr) 2224, 2153, 1550, 1512, 1471, 1249, 837, 826 cm^{-1}; MS (FAB) *m/e* calcd for $C_{86}H_{88}Si_2I_2^+$ 1430.4510, found 1430.4514; 1431 (M + H)$^+$.

Turnstile 1. **1** was prepared according to general double-macrocyclization procedure E. The final cyclization reaction mixture which utilized hexamer sequence **21** (0.30 g, 0.21 mmol) was filtered through Celite which was washed with diethyl ether (200 mL), chloroform (200 mL), water (200 mL), and finally diethyl ether (200 mL). The Celite mixture was transferred to a soxhlet extractor and continuously extracted with hot benzene under nitrogen for 48 h during which time a precipitate formed in the solvent reservoir flask. Removal of the solvent *in vacuo* afforded 70 mg (35%) of product as a colorless solid. Precipitation from hot bromoform afforded a sample for analysis: mp 385−390 °C dec; R_f 0.77 (75% $CHCl_3$/hexane); IR (KBr) 2035, 1610, 1435, 1097 cm^{-1}; MS (FD) *m/e* calcd for $C_{74}H_{58}^+$ 946.4556, found 946.4538. Anal. Calcd for $C_{74}H_{58}$·(0.03$CHBr_3$): C, 93.12; H, 6.13; Br, 0.75. Found: C, 93.18; H, 6.02; Br, 0.56.

1,4-Dibromo-2,5-bis(methoxymethyl)benzene (27). A solution of 1,4-bis(bromomethyl)-2,5-dibromobenzene (**26**)[15] (2.00 g, 4.7 mmol) in THF (20 mL) was added over 1 h to sodium methoxide in THF (20 mL, 1.0 M) at room temperature and stirred for 2 h. The reaction was poured into water (100 mL), extracted with diethyl ether (150 mL), dried over magnesium sulfate, filtered, and evaporated. Crystallization from 95% ethanol afforded 1.15 g (75%) of product as a colorless solid: mp 71−2 °C dec; R_f 0.65 (10% ethyl acetate/hexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (s, 4H), 4.46 (s, 4H), 3.47 (s, 6H); ^{13}C NMR (400 MHz, $CDCl_3$) δ 138.27, 132.07, 121.07, 73.01, 58.71; IR (KBr) 3100, 1478, 1450, 1200, 1112, 1056 cm^{-1}; MS (EI) 326 (36), 324 (72), 322 (36), 245 (94), 243 (100). Anal. Calcd for $C_{10}H_{12}Br_2O_2$: C, 37.07; H, 3.73; Br, 49.32. Found: C, 37.33; H, 3.89; Br, 49.37.

Sequence 22. **22** was prepared according to general procedure A and required prior deprotection of **17** according to general procedure B. Thus, **17** (1.80 g, 2.8 mmol) and **27** (0.41 g, 1.3 mmol) after flash chromatography in 10% ethyl acetate/hexane afforded 0.84 g (46%) of product as a colorless solid: mp 125−8 °C dec; R_f 0.30 (10% ethyl acetate/hexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (s, 1H), 7.61−7.60 (m, 1H), 7.58−7.57 (m, 2H), 7.53−7.52 (m, 1H), 7.51−7.49 (m, 2H), 7.39−7.36 (m, 1H), 7.31−7.27 (m, 1H), 4.72 (s, 2H), 3.74 (q, J = 7 Hz, 4H), 3.17 (s, 3H), 1.35 (s, 9H), 1.29−1.24 (m, 15H), 0.98 (s, 9H), 0.21 (s, 6H); ^{13}C NMR (400 MHz, $CDCl_3$) δ 151.61, 151.13, 151.07, 139.22, 131.80, 130.86, 129.78, 129.59, 129.06, 128.80, 128.80, 128.16, 125.79, 125.59, 124.88, 123.39, 123.30, 123.30, 122.86, 121.67, 121.03, 104.06, 96.96, 94.33, 92.91, 92.73, 89.84, 88.48, 88.36, 71.73, 58.03, 34.76, 34.65, 31.01, 30.94, 26.13, 16.73, −4.63; IR (KBr) 2216, 2153, 1584, 1478, 1466, 1453, 1435, 1248, 1236, 839, 825 cm^{-1}; MS (FD) 1464 (M$^+$). Anal. Calcd for $C_{98}H_{116}N_6Si_2O_2$: C, 80.28; H, 7.97; N, 5.73. Found: C, 79.99; H, 7.98; N, 5.68.

Sequence 23. **23** was prepared according to general procedure C. Thus, **22** (0.58 g, 0.4 mmol) after flash chromatography in 5% ethyl acetate/hexane afforded 0.42 g (70%) of product as a colorless solid: mp 138−145 °C dec; R_f 0.62 (10% ethyl acetate/hexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89−7.88 (m, 1H), 7.74 (s, 1H), 7.63−7.60 (m, 1H), 7.58−7.49 (m, 5H), 7.47−7.44 (m, 1H), 7.07−7.04 (m, 1H), 4.72 (s, 2H), 3.17 (s, 3H), 1.36 (s, 9H), 1.28 (s, 9H), 0.98 (s, 9H), 0.21 (s, 6H); ^{13}C NMR (400 MHz, $CDCl_3$) δ 151.71, 151.13, 140.08, 139.17, 137.24, 131.91, 130.85, 130.71, 129.90, 129.85, 129.50, 129.17, 128.98, 125.75, 125.52, 125.07, 124.93, 122.99, 122.71, 121.67, 104.04, 96.98, 94.30, 93.68, 92.95, 92.57, 90.28, 88.57, 87.65, 71.72, 58.02, 34.77, 34.67, 31.10, 30.94, 26.13, 16.73, −4.62; IR (KBr) 2225, 2152, 1588, 1471, 1262, 839, 826 cm^{-1}; MS (FAB) *m/e* calcd for $C_{90}H_{96}O_2Si_2I_2^+$ 1518.5043, found 1518.5038; 1519 (M + H)$^+$.

Turnstile 2. **2** was prepared according to general double-macrocyclization procedure E. The final cyclization reaction mixture which utilized hexamer sequence **23** (0.20 g, 0.13 mmol) was filtered through Celite and washed with diethyl ether (200 mL), chloroform (200 mL), water (200 mL), and finally diethyl ether (200 mL). The Celite mixture was transferred to a soxhlet extractor and continuously extracted with benzene under nitrogen for 48 h during which time a colorless precipitate formed in the solvent reservoir flask. Removal of the solvent *in vacuo* afforded 67 mg (50%) of product as a colorless solid: R_f 0.69 (75% $CHCl_3$/hexane); ^{1}H NMR (500 MHz, 19 °C, $CDCl_3$) δ 8.06 (s, 2H), 7.64 (m, 4H), 7.62−7.60 (m, 4H), 7.58−7.53 (m, 6H), 7.48−7.47 (m, 2H), 7.39−7.36 (m, 2H), 4.94 (s, 4H), 3.36 (s, 6H), 1.40 (s, 18H), 1.39 (s, 18H); IR (KBr) 2963, 2216, 1595, 1582, 1477, 1428 cm^{-1}; HRMS (EI) *m/e* calcd for $C_{78}H_{66}O_2^+$ 1034.5064, found 1034.5063. Anal. Calcd for $C_{78}H_{66}O_2$: C, 90.26; H, 7.43. Found: C, 88.80; H, 7.33.

1,4-Dibromo-2,5-bis((3,5-di-*tert*-butylphenoxy)methyl)benzene (28). A solution of 1,4-bis(bromomethyl)-2,5-dibromobenzene (**26**, 2.00 g, 4.7 mmol) in DMF (20 mL) was added over 1 h to a room temperature solution of 3,5-di-*tert*-butylphenol (2.46 g, 12.0 mmol) and sodium hydride (0.25 g, 10.4 mmol) in DMF (125 mL) and stirred for 12 h. After evaporation of the solvent, the crude residue was dissolved in dichloromethane (200 mL), washed with aqueous 15% sodium hydroxide (300 mL) and brine (100 mL), dried over magnesium sulfate, filtered, and evaporated. Separation by flash chromatography in 25% chloroform/hexane afforded 2.50 g (80%) of product as a colorless solid. A sample was crystallized from 95% ethanol for analysis: mp 235−237 °C; R_f 0.62 (10% ethyl acetate/hexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (s, 2H), 7.11 (t, J = 2 Hz, 2H), 6.88 (d, J = 2 Hz, 4H), 5.12 (s, 4H), 1.35 (s, 36H); ^{13}C NMR (400 MHz, $CDCl_3$) δ 157.81, 152.37, 137.82, 132.57, 121.18, 115.73, 109.29, 68.60, 35.02, 31.43; IR (KBr) 1592, 1428, 1300, 1217, 1203, 1065, 1049 cm^{-1}; MS (EI) 674 (16), 672 (30), 670 (15), 57 (100). Anal. Calcd for $C_{36}H_{48}Br_2O_2$: C, 64.29; H, 7.19; Br, 23.76. Found: C, 64.22; H, 7.30; Br, 23.68.

Sequence 24. **24** was prepared according to general procedure A and required prior deprotection of **17** according to general procedure B. Thus, **17** (2.03 g, 3.1 mmol) and **28** (1.00 g, 1.5 mmol) after flash chromatography in 10% ethyl acetate/hexane afforded 1.47 g (54%) of product as a colorless solid: mp 125−8 °C dec; R_f 0.35 (10% ethyl acetate/hexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (s, 2H), 7.59−7.58 (m, 2H), 7.56 (d, J = 2 Hz, 2H), 7.51 (d, J = 2 Hz, 2H), 7.47 (dd, J = 1 Hz, 2H), 7.43 (dd, J = 1 Hz, 2H), 7.38 (dd, J = 1 Hz, 2H), 7.36 (m, 2H), 7.30−7.25 (m, 4H), 6.91 (t, J = 2 Hz, 2H), 6.78 (d, J = 2 Hz, 4H), 5.43 (s, 4H), 3.76 (q, J = 7 Hz, 8H), 1.36 (s, 18H), 1.27 (t,

J = 7 Hz, 12H), 1.21 (s, 36H), 1.16 (s, 18H), 0.95 (s, 18H), 0.17 (s, 12H); ^{13}C NMR (400 MHz, $CDCl_3$) δ 157.97, 151.62, 151.46, 151.24, 151.07, 138.93, 131.79, 130.48, 129.53, 129.40, 129.05, 128.77, 128.56, 128.41, 128.18, 125.88, 125.64, 124.91, 123.41, 123.25, 122.58, 121.67, 120.93, 114.88, 109.38, 104.01, 97.09, 93.89, 93.84, 93.07, 89.70, 88.59, 88.42, 67.20, 34.82, 34.78, 34.50, 31.52, 30.94, 30.89, 26.11, 16.66, −4.56; IR (KBr) 2219, 2160, 1591, 1479, 1466, 1463, 1451, 1247, 1236, 839, 825 cm^{-1}; MS (FD) 1813 (M^+). Anal. Calcd for $C_{124}H_{152}N_6O_2Si_2$: C, 82.07; H, 8.44; N, 4.63. Found: C, 82.00; H, 8.46; N, 4.64.

Sequence 25. 25 was prepared according to general procedure C. Thus, **24** (1.47 g, 0.8 mmol) after flash chromatography in 5% ethyl acetate/hexane afforded 1.20 g (79%) of product as a colorless solid: mp 130−135 °C dec; R_f 0.65 (10% ethyl acetate/hexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (s, 2H), 7.86−7.85 (m, 2H), 7.61−7.60 (m, 2H), 7.59−7.39 (m, 12H), 7.06−7.02 (m, 2H), 6.91 (t, J = 2 Hz, 2H), 6.78 (d, J = 2 Hz, 4H), 5.43 (s, 4H), 1.37 (s, 18H), 1.21 (s, 36H), 1.18 (s, 18H), 0.95 (s, 18H), 0.17 (s, 12H); ^{13}C NMR (400 MHz, $CDCl_3$) δ 157.98, 151.64, 151.55, 151.31, 140.05, 138.90, 137.14, 131.95, 130.71, 130.56, 130.54, 129.90, 129.62, 129.31, 128.95, 127.48, 125.82, 125.68, 125.18, 124.99, 122.74, 122.63, 121.69, 114.91, 109.36, 103.98, 97.18, 93.89, 93.65, 92.92, 90.41, 88.67, 87.58, 67.23, 34.82, 34.80, 34.53, 31.37, 30.95, 30.90, 26.12, 16.67, −4.56; IR (KBr) 2174, 1590, 1471, 1249, 825 cm^{-1}; MS (FAB) *m/e* calcd for $C_{116}H_{132}O_2Si_2I_2^+$ 1866.7855, found 1866.7843; 1867 $(M + H)^+$.

Turnstile 3. 3 was prepared according to general double-macrocyclization procedure E. The final cyclization reaction utilized hexamer sequence **25** (0.25 g, 0.13 mmol). The crude mixture was filtered through Celite. Removal of the solvent provided a residue which was dissolved in chloroform (10 mL), precipitated with methanol (500 mL), and collected by centrifugation. Crystallization from hot benzene provided 93 mg (50%) of product as a colorless solid: mp 325−330 °C dec; R_f 0.80 (75% $CHCl_3$/hexane); ^{1}H NMR (500 MHz, 19 °C, $CDCl_3$) δ 8.31 (s, 2H), 7.69 (m, 2H), 7.62 (m, 2H), 7.60−7.59 (m, 4H), 7.56−7.54 (m, 2H), 7.53-7.52 (m, 2H), 7.50−7.47 (m, 4H), 7.37−7.32 (m, 2H), 6.84 (t, J = 2 Hz, 2H), 6.74 (d, J = 2 Hz, 4H), 5.66 (d, J = 11 Hz, 2H), 5.61 (d, J = 11 Hz, 2H), 1.41 (s, 18H), 1.39 (s, 18H), 1.10 (s, 36H); IR (KBr) 3094, 2224, 1592, 1478, 1466, 1448, 1428 cm^{-1}; HRMS (EI) *m/e* calcd for $C_{104}H_{102}O_2^+$ 1382.7873, found 1382.7880; MS (EI) 1383 (20), 1177 (25), 766 (65), 613 (60), 460 (50), 154 (100). Anal. Calcd for $C_{104}H_{102}O_2$: C, 90.26; H, 7.43. Found: C, 89.97; H, 7.34.

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Supporting Information Available: All reported ^{1}H and ^{13}C NMR spectra for new compounds, selected variable-temperature ^{1}H NMR and tabular summaries for compounds **2** and **3**, COSY NMR for **2** and **3**, and tabular summary of T_1 data (28 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

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