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Synthesis of butadiyne-bridged [4$_n$] metacyclophanes having *exo*-annular *t*-butyl groups

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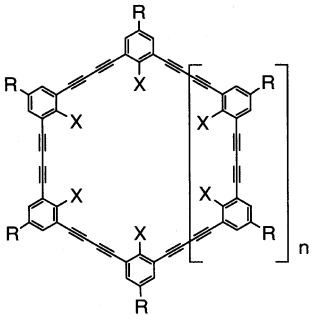
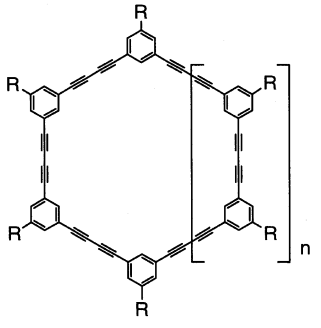
Abstract—Butadiyne-bridged [4$_4$]- and [4$_8$]metacyclophanes having *exo*-annular *t*-butyl groups were prepared by intermolecular Eglinton coupling of the dimeric unit or by intramolecular ring closure of the linear tetramer. Comparison of the ^{1}H and ^{13}C NMR spectra of [4$_4$]metacyclophane with those of [4$_8$]cyclophane and diphenylbutadiyne revealed its prominent geometrical feature due to deformation of the triple bonds from linearity. The [4$_4$]Metacyclophane was converted into [0$_8$]thiophenometacyclophane in good yield by treatment with sodium sulfide.

During the last decade, conformationally rigid and shape-persistent macrocyclic cyclophanes having acetylene linkages have attracted a great deal of interest because of their aggregation behavior,[1] host–guest complexation,[2] electronic properties,[3] strain imposed on the triple bond,[4] and as carbon rich materials such as fullerene precursors[5] and graphite-like motifs.[6] Among them, the acetylene-bridged [2$_n$]metacyclophanes ($n\geq5$),[7] called phenylacetylene macrocycles (PAMs), possessing appropriate *exo*-annular substituents have been reported by Moore and co-workers to exhibit interesting properties owing to their association in solution by π–π stacking as well as solvophobic interactions,[1a,b] organization to porous molecular crystals,[8a] liquid crystals,[1c] and monolayer surfaces.[8b] The parent acetylene-bridged [2$_6$]metacyclophane[9] and the smaller, strained [2$_3$]- and [2$_4$]metacyclophanes were synthesized by other groups.[4a,b] The properties of these macrocycles are critically dependent on the ring size and the nature of the functional groups attached to the periphery as well as interior of the macrocyclic framework. We set up a research program aiming at the development of the chemistry of new macrocyclic structures **1** based on the butadiyne-bridged [4$_n$]metacyclophanes, 'big brothers' of PAMs,[6a,b,10] because we anticipated that the buta-1,3-diyne units would make the properties of the macrocycles different from those of PAMs in the following respects. (i) Since the ring size of the diyne-bridged macrocycles is larger than those of the corresponding PAMs having the same number of aromatic rings, it is possible to introduce guest-binding sites along the interior of the macrocycles. (ii) The electronic properties of the aromatic rings would suffer from stronger perturbation owing to strong electron-withdrawing effect of the buta-1,3-diyne unit. (iii) Topochemically controlled polymerization of the butadiyne units would furnish structurally ordered polydiacetylenes.[11]

In order to optimize the synthetic route to construct the macrocyclic frameworks of butadiyne-bridged [4$_n$]metacyclophanes and to investigate the effect of ring size, particularly in the case of small, strained cyclophanes, on the genuine properties of these macrocycles which are free from aggregation, we investigated the synthesis and properties of the macrocycles **2a**–**4a** having *exo*-annular *t*-butyl group which would ensure their solubility in common organic solvents.[12] In addition, we carried out the transformation of [4$_4$]metacyclophane into [0$_8$]thiophenometacyclophane, a member of another class of interesting macrocycle.[13]



1 n = 0, 1, 2, ...



2a n = 0, R = *t*-Bu; **2b** n = 0, R = H
3a n = 1, R = *t*-Bu; **3b** n = 1, R = H
4a n = 2, R = *t*-Bu; **4b** n = 2, R = H

Keywords: alkynes; coupling reactions; cyclophanes; polyynes; strained compounds; thiophenes.

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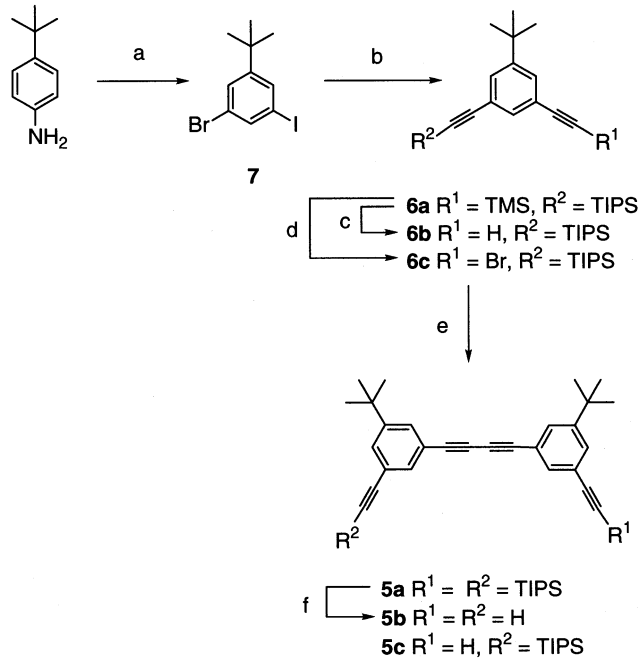
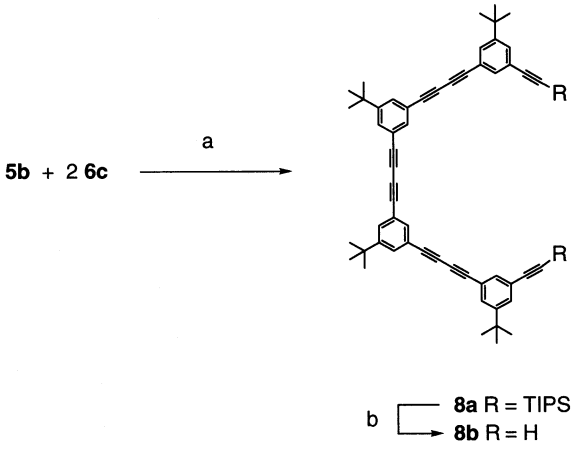


Scheme 1. (a) (i) Ac_2O, benzene, rt, 92%, (ii) Br_2, AcOH, 50°C, (iii) HCl, EtOH, reflux, 89% for two steps, (iv) BTMA·ICl_2, CH_2Cl_2, MeOH, rt, 92%, (v) $NaNO_2$, H_2SO_4, EtOH, benzene, reflux, 69%. (b) (i) (trimethylsilyl)-acetylene, $Pd(PPh_3)_4$, CuI, Et_3N, benzene, 40°C, 98%, (ii) (triisopropyl-silyl)acetylene, $Pd(PPh_3)_4$, CuI, Et_3N, benzene, 60°C, 85%. (c) K_2CO_3, THF, MeOH, 98%. (d) NBS, cat. $AgNO_3$, acetone, rt, 96%. (e) $Cu(OAc)_2$, pyridine, MeOH, rt, 86%. (f) TBAF, THF, rt, 96%.

In general, there are two types of methodologies to construct butadiyne-bridged macrocyclic rings. One is the intermolecular coupling of simple monomer units, 'shotgun synthesis', in which a symmetrical, difunctional monomer is subjected to coupling conditions in the hope that same fraction of the growing chain will cyclize in competition with further chain elongation. In order to reduce the possible number of products, we used dimer **5b** as the substrate of 'shotgun method' to obtain even numbered macrocycles such as tetramer **2a**, hexamer **3a** and octamer **4a**.[14] The other, 'stepwise synthesis', is the intramolecular coupling of appropriately advanced linear oligomers, which can in principle be prepared size-selectively by connecting unsymmetrical monomer units step by step. We examined this method for the preparation of cyclic tetramer.

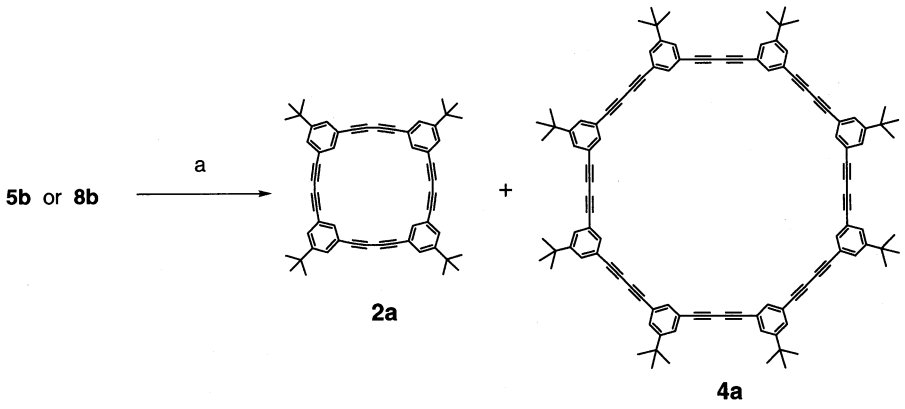


Scheme 2. (a) $Pd_2(dba)_3$·$CHCl_3$, CuI, 1,2,2,6,6,-pentamethylpiperidine, LiI, HMPA, benzene, rt, 30%. (b) TBAF, THF, rt, 99%.

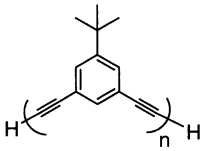
The synthetic route for dimer **5b** is shown in Scheme 1.[15] The key intermediate in this scheme is singly protected monomer unit **6b**. First, bromoiodobenzene **7** was prepared from 4-*t*-butylaniline by: (i) acetylation, (ii) bromination, (iii) deacetylation, (iv) iodination with benzyltrimethylammonium dichloroiodate (BTMA·ICl_2),[16] and (v) deamination in 51% overall yield for five steps. Two successive Pd(0)–Cu(I)–catalyzed coupling of **7** with (trimethylsilyl)-acetylene followed by (triisopropylsilyl)acetylene gave doubly protected monomer unit **6a**. Selective deprotection of the TMS-group with dilute K_2CO_3 solution yielded the key monomer unit **6b**. Eglinton-coupling of **6b** gave dimer **5a** and subsequent removal of the TIPS-group gave the dimer unit **5b**.

For the synthesis of linear tetramer unit, two routes are conceivable: [2+2] homocoupling and [2+1+1] heterocoupling routes. Although singly protected dimer **5c** would be readily prepared by deprotection of doubly protected dimer **5a**, separation of pure **5c** seems to be difficult because **5a**–**5c** would have similar polarity. Accordingly, we chose the [2+1+1] heterocoupling route. In order to synthesize linear tetramer **8a** efficiently, several reaction conditions for the heterocoupling between **5b** and bromoalkyne **6c**, which was obtained by direct bromination[17] of **6b**, were examined using the Pd(0)–Cu(I)-catalyzed coupling method[18] (Scheme 2). The best results were obtained when the reaction was carried out using 1,2,2,6,6-pentamethylpiperidine, lithium chloride, and HMPA as additives in benzene, affording **8a** in 30% yield together with **5c** in 13% yield. Finally, deprotection of **8a** with tetrabutylammonium fluoride (TBAF) gave linear tetramer **8b**.

For the intermolecular coupling of dimer **5b**, three copper-mediated oxidative coupling methods, the Eglinton's,[19] the Breslow's,[20] and the Hay's methods,[21] were examined (Scheme 3). Under high dilution conditions (2.0×10^{-3} M), the Eglinton coupling of **5b** gave cyclic tetramer **2a** and cyclic octamer **4a** in 25% and 13% yields, respectively. However, we were unable to detect the corresponding hexamer **3** under these conditions. At present, we have no explanation for the absence (or very low yield, if any) of hexamer **3**, which is the most thermodynamically stable product as described later. Such anomalous behavior has been frequently observed, however, in the copper-mediated oxidative coupling reactions.[10a,19b,22] Coupling of dimer **5b** according to the Breslow's modification of the Eglinton reaction ($Cu(OAc)_2$ and CuCl) also gave the results similar to those obtained by the Eglinton's method (15% of **2a**, 18% of **4a** and none of **3a**). By contrast, the Hay coupling (CuCl, *N*,*N*,*N*,*N*-tetramethylethylenediamine, acetone, O_2) of **5b** gave only the linear oligomers such as linear dimer **8b** (4%), hexamer **9** (23%), and octamer **10** (22%), but no cyclic compounds were isolated. These results can be attributed to the low solubility of the linear oligomers in acetone in which the linear oligomers precipitated before cyclization. In conclusion: (i) Eglinton coupling was found to be the best method in the present system, and (ii) cyclic hexamer **3a** was not obtained by the shotgun synthesis.



Scheme 3. (a) $Cu(OAc)_2$, pyridine, benzene, rt, or $Cu(OAc)_2$, CuCl, pyridine, rt.



9 n = 6
10 n = 8

The Eglinton coupling of linear tetramer unit **8b** under high dilution conditions gave the same products as those obtained by the coupling of dimer **5b** (Scheme 3). However, the yields of cyclic tetramer **2a** (73%) was remarkably higher than that from the dimer (25%). Cyclic octamer **4a** was also formed in 13%. It turned out that the stepwise intramolecular coupling methodology was efficient in size-selective production of cyclic tetramer **2a**, although the preparation of the open chain precursor **8b** was more laborious.

Since neither of **2a** and **4a** gave crystals suitable for X-ray structure analysis, molecular modeling study was carried out using the AM1 semi-empirical method[23] for the model compounds **2b**–**4b** which do not have the *exo*-annular substituents to simplify calculations. Fig. 1 shows the optimized structures of tetramer **2b** and hexamer **3b**, both which adopt a planar conformation. The heat of formation per diethynylbenzene unit of **2b** is larger than that of **3b** by 9.6 kJ/mol. The difference is due to the strain imposed on the bent butadiyne units of **2b**, though the bent angles (sp^2–sp–sp=173.7°, sp–sp–sp=173.9°) is not very large compared to the reported values for the compounds having highly distorted triple bonds.[10a,22,24] Fig. 2 shows four lowest-energy conformers of octamer **4b**. The difference between the heats of formation of these conformers is within 0.2 kJ/mol, indicating that **4b** is a nonplanar molecule with considerable conformational mobility.

The effect of strain, particularly in the case of tetramer **2a** with slightly deformed butadiyne moieties, and that of

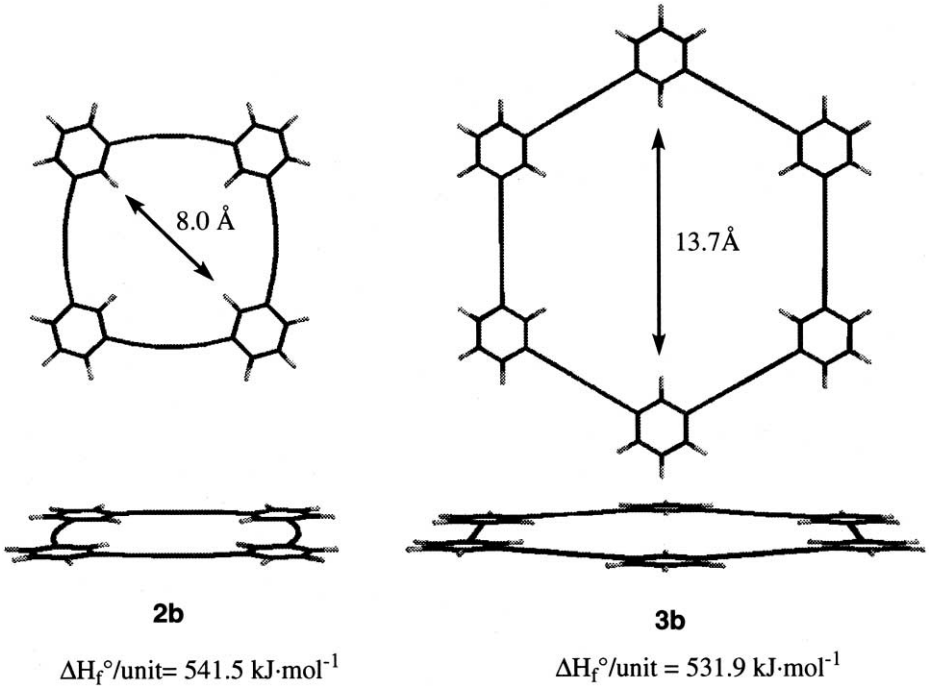


Figure 1. AM1-optimized geometries of tetramer **2b** and hexamer **3b**. $\Delta H_f°$/unit denotes calculated heat of formation per *m*-diethynylbenzene unit.

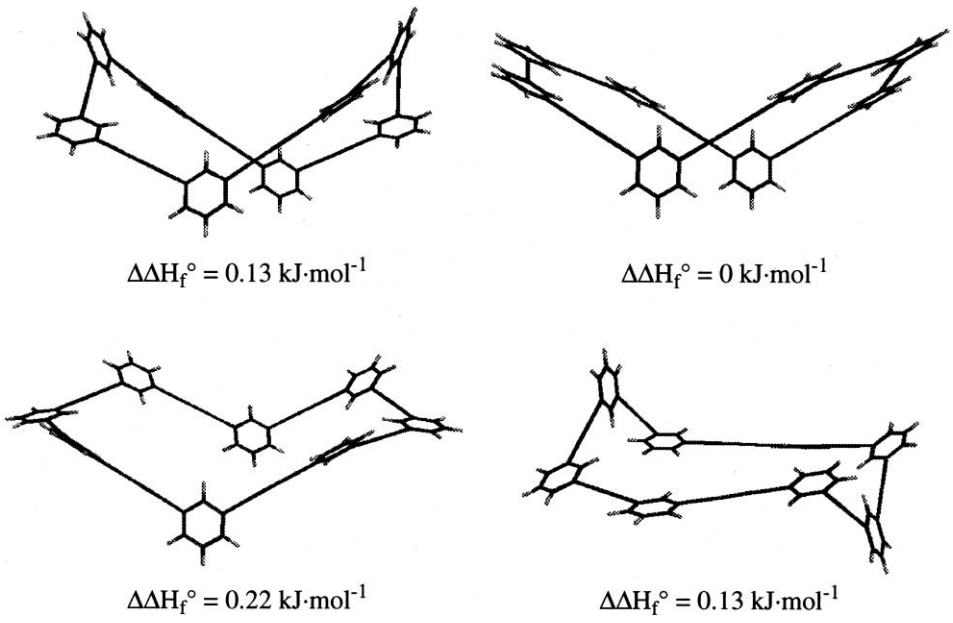


Figure 2. AM1-optimized geometries of octamer **4b**. $\Delta\Delta H_f^\circ$ denotes calculated relative heat of formation.

planarity of the macrocyclic ring would manifest themselves in the electronic spectra of the metacyclophanes. In this respect, the electronic spectra of **2a**, **4a**, and open chain dimer **5b** and tetramer **8b** as a reference are compared. Table 1 lists the wavelengths of the three absorption maxima and their extinction coefficients of these compounds in $CHCl_3$. The spectra were measured in the concentration range of 1.9×10^{-7}–4.6×10^{-5} M, under which conditions no effect of concentration on the spectra was discerned. As shown in Table 1, the longest wavelength absorption maximum of cyclic tetramer **2a** is only marginally shifted to longer wavelength compared to that of acyclic tetramer **8b**, indicating that the conjugation along the entire ring system of **2a** is weak. Although the absorption coefficient of planar **2a** is slightly larger than that of **8b**, the ϵ-value of octamer **4a** is even smaller than that of **2a** and is much smaller than the twice of that of **8a**. This can be ascribed to the nonplanarity of the macrocyclic ring of **4a** which reduces the excitation efficiency of π–π^* transitions.[25]

Table 1. Absorption maxima in UV spectra of cyclophanes **2a** and **4a** and linear oligomers **5b** and **8b** in $CHCl_3$

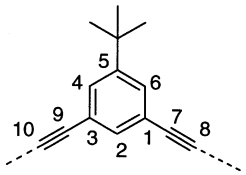
Compound	λ_{max} (ϵ) (nm)		
2a	296 (102000)	316 (195000)	340 (139000)
4a	296 (102000)	315 (141000)	338 (126000)
5b	294 (33300)	312 (43900)	334 (41500)
8b	296 (79600)	315 (108000)	337 (101000)

In contrast to the corresponding macrocycles having *exo*-annular ester groups,[1d,2a] the ^{1}H and ^{13}C NMR chemical shifts of **2a** and **4a** in $CDCl_3$ are not dependent on the concentration, indicating that these do not aggregate in solution. The chemical shifts of **2a** and **4a** listed in Table 2 together with those of the reference compound **5b**, which revealed geometrical characteristics of cyclic tetramer **2a**. Namely, the ^{1}H NMR chemical shift of the *endo*-annular proton H(2) of **2a** appears downfield compared to those of **4a** and **5b**, while that of *exo*-annular proton H(4)/H(6) shifts upfield. This is ascribed to the anisotropic deshielding effect from the neighboring two butadiyne units, because the distance between H(2) and the sp carbon C(7)/C(9) in tetramer **2a** should be shorter than those in octamer **4a** and acyclic **5b**. Similarly, the ^{13}C NMR chemical shifts of C(2) shifts downfield and that of C(4)/C(6) upfield relative to the corresponding chemical shifts of **4a** and **5b**. The chemical shift of the acetylenic carbons of **2a** shifts downfield compared to those of **4a** and **5b**, which is attributed to the bond angle deformation of the triple bonds of **2a** from linearity since such downfield shift was observed for strained cyclic diynes.[25,26]

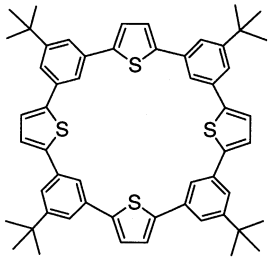
Table 2. ^{1}H and ^{13}C NMR chemical shifts for cyclophanes **2a** and **4a** and dimer **5b**

Compound	^{1}H NMR (ppm)				^{13}C NMR (ppm)			
	H(2)	H(4)/H(6)	C(1)/C(3)	C(2)	C(4)/C(6)	C(5)	C(7)/C(9)	C(8)/C(10)
2a	7.79	7.42	122.2	138.7	128.3	152.1	83.0	75.1
4a	7.55	7.51	121.9	133.3	130.6	152.0	81.1	74.0
5b[a]	7.53	7.51, 7.47	122.3, 121.7	133.0	130.2, 130.1	151.7	81.2	73.9

In $CDCl_3$ at 30°C. The assignment was undertaken based on the DEPT spectra taking into account the usual substituent increment for the chemical shifts.
[a] The signals for the external acetylene carbons appear at δ 83.0 (terminal) and 77.5 (internal).



Finally, tetramer **2a** was transformed into [0_8]thiophenometacyclophane **11**. [0_n]Metacyclophanes and their thiophene analogs are of much interest in view of host–guest chemistry and self-organization.[13] The butadiyne moiety can be converted into thiophene ring by treatment with sodium sulfide,[27] and this method has been applied to the synthesis of structurally interesting cyclic thiophenes.[13d,28] We obtained thiophenometacyclophane **11** by treatment of **2a** with sodium sulfide in THF in the presence of 15-crown-5 in 83% yield. AM1-optimized geometry of **11** suggests that all sulfur atoms are oriented to the cavity because of the steric constraint, indicating that the macrocyclic framework of **11** is shape persistent. However, the distance between the sulfur atoms are too long for binding a metal ion (transannular S–S distance=7.24 Å).



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1. Experimental

1.1. General

^{1}H NMR (400 or 270 MHz) and ^{13}C NMR (100.5 or 67.5 MHz) spectra were recorded on a JEOL JNM-AL-400 or a JEOL JNM-GSX-270 spectrometer at 30°C. IR spectra were recorded as a KBr disk or a neat film on a JASCO FTIR-410 spectrometer. UV spectra were recorded on a Hitachi 220A or a U-3310 spectrometer. EI and FAB mass spectral analyses were performed on a JEOL JMS-DX303HF spectrometer. Elemental analyses were carried out with a Perkin–Elmer 2400II analyzer. Preparative HPLC separation was undertaken with a JAI LC-908 chromatograph using 600 mm×20 mm JAIGEL-1H and 2H GPC columns with $CHCl_3$ as an eluent.

1.1.1. 4-*t*-Butyl-2-bromoaniline. A solution of 4-*t*-butylacetanilide[29] (300 g, 1.57 mol) in acetic acid (1000 mL) was warmed to 45°C and bromine (316 g, 1.98 mol) was added dropwise during 1 h. During the addition, the temperature of the reaction mixture was maintained between 50 and 55°C. After stirring for 21 h at 50°C, the mixture was poured into 10 L of water. To this suspension, $NaHSO_3$ was added until the color of bromine vanished. Resulting pale red solid was collected by filtration, washed with water, and dried under vacuum to give a 510 g of crude, slightly wet, 4-*t*-butyl-2-bromoacetanilide. The crude product was added to 900 mL of EtOH and heated to reflux. After the solid dissolved, conc. HCl (390 mL) was added, and the mixture was stirred for 3 h under reflux. After cooling to room temperature, the solution was neutralized by an addition of 50% aqueous NaOH (400 g) and extracted with ether. The extract was washed with brine and dried over $MgSO_4$. The solvent was concentrated in vacuo to give a dark red oil (362 g). Vacuum distillation (2 mmHg, 108–110°C) afforded 4-*t*-butyl-2-bromoaniline as a colorless oil (320 g, 89%). All physical data agreed with the reported literature values.[15] ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.40 (d, J=2.2 Hz, 1H), 7.13 (dd, J=8.4, 2.2 Hz, 1H), 6.71 (d, J=8.4 Hz, 1H), 3.94 (br, 2H), 1.26 (s, 9H).

1.1.2. 4-*t*-Butyl-2-bromo-6-iodoaniline. To a stirred solution of 4-*t*-butyl-2-bromoaniline (160.0 g, 0.701 mol) in 1000 mL of CH_2Cl_2 and 400 mL of MeOH, 327 g (0.94 mol) of benzyltrimethylammonium dichloroiodate (BTMA·ICl_2),[16] and 122 g (1.22 mol) of calcium carbonate were added, and the mixture was refluxed with stirring for 13 days. After cooling to room temperature, the solvent was removed in vacuo, and the residue was diluted with water. The mixture was extracted with ether, and the extract was washed with 5% aqueous $NaHSO_3$, water, brine, and dried over $MgSO_4$. The solution was concentrated in vacuo to give 250 g of a dark red oil. Vacuum distillation yielded pure 4-*t*-butyl-2-bromo-6-iodoaniline as a red oil (229 g, 92%): bp (0.4 mmHg) 123–125°C; ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.59 (d, J=2.1 Hz, 1H), 7.39 (d, J=2.1 Hz, 1H), 4.40 (br, 2H), 1.23 (s, 9H); ^{13}C NMR (67.5 MHz, $CDCl_3$) δ 143.9 (s), 141.6 (s), 135.3 (d), 130.0 (d), 107.1 (s), 83.3 (s), 33.9 (s), 31.2 (q); IR (neat) 3440, 3340, 2940, 1600, 1460, 1250, 1050, 865, 710 cm^{-1}; HRMS (EI) m/z calcd for $C_{10}H_{13}IBrN$ 352.9257, found 352.9241.

1.1.3. 1-Bromo-3-*t*-butyl-5-iodobenzene (7). To a stirred solution of 99.1 g (0.28 mol) of 4-*t*-butyl-2-bromo-6-iodoaniline in 150 mL of benzene and 450 mL of EtOH, 42 mL of conc. H_2SO_4 was added followed by addition of 42.5 g (0.616 mol) of $NaNO_2$ at 0°C (45 min). The reaction mixture was heated to reflux, and stirred for 1.5 h. After cooling to room temperature, the mixture was diluted with water and was extracted with ether. The extract was washed with water and brine, and dried over $MgSO_4$. Removal of the solvent gave a dark red oil, which was distilled under reduced pressure (102–107°C, 0.6 mmHg) to give a red oil (67.4 g). This red oil was diluted with ether and washed with 5% aqueous $NaHSO_3$, water, and brine, and dried over $MgSO_4$. Removal of the solvent in vacuo gave **7** as a colorless oil (65.5 g, 69%): ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.66 (t, J=1.6 Hz, 1H), 7.62 (t, J=1.6 Hz, 1H), 7.45 (t, J=1.6 Hz, 1H), 1.27 (s, 9H); ^{13}C NMR (67.5 MHz, $CDCl_3$) δ 155.4, 136.7, 133.4, 128.2, 122.8, 94.5, 34.9, 31.0; IR (neat) 2950, 2860, 1570, 1540, 1400, 1255, 850, 720, 680 cm^{-1}; HRMS (EI) m/z calcd for $C_{10}H_{12}IBr$ 339.9147, found 339.9160.

1.1.4. 1-Bromo-3-*t*-butyl-5-[(trimethylsilyl)ethynyl]benzene. To a flask containing 1.44 g (1.29 mmol) of $Pd(PPh_3)_4$ and 490 mg (2.58 mmol) of CuI, a solution of 43.7 g (129 mmol) of **7** in 200 mL of benzene was added, which was followed by 54.0 mL (387 mmol) of Et_3N and 18.2 mL (129 mmol) of (trimethylsilyl)acetylene under a nitrogen atmosphere. The mixture was stirred at 40°C for

5 h and then filtered. The filtrate was concentrated and subjected to column chromatography on silica gel (eluent: hexane) to afford 1-bromo-3-*t*-butyl-5-[(trimethylsilyl)-ethynyl]benzene as a yellow oil (58.4 g, 98%): ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.45 (t, J=1.9 Hz, 1H), 7.43 (t, J=1.9 Hz, 1H), 7.39 (t, J=1.9 Hz, 1H), 1.28 (s, 9H), 0.25 (s, 9H); ^{13}C NMR (67.5 MHz, $CDCl_3$) δ 153.31 (s), 131.81 (d), 129.06 (d), 127.73 (d), 124.54 (s), 121.93 (s), 103.95 (s), 94.97 (s), 34.83 (s), 31.04 (s), −0.09 (q); IR (neat) 2950, 2880, 2150, 1548, 1240, 928, 850, 752, 682 cm^{-1}; HRMS (EI) m/z calcd for $C_{15}H_{21}BrSi$ 308.0596, found 308.0590.

1.1.5. 1-*t*-Butyl-3-[(triisopropylsilyl)ethynyl]-5-[(trimethylsilyl)ethynyl]benzene (6a). Compound **6a** was prepared according to the same procedure as described above using 1-bromo-3-*t*-butyl-5-[(trimethylsilyl)ethynyl]benzene (20.1 g, 65.0 mmol), (triisopropylsilyl)acetylene (17.4 mL, 78.0 mmol), $Pd(PPh_3)_4$ (2.25 g, 1.95 mmol), CuI (742 mg, 3.9 mmol), and Et_3N (54.4 mL, 390 mmol) in 100 mL of benzene. Purification by column chromatography (eluent: hexane) afforded **6a** as a pale yellow oil (22.8 g, 85%): ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.41–7.43 (m, 3H), 1.29 (s, 9H), 1.13 (s, 21H), 0.25 (s, 9H); ^{13}C NMR (67.5 MHz, $CDCl_3$) δ 151.26 (s), 132.81 (d), 129.08 (d), 129.04 (d), 123.46 (s), 123.08 (s), 106.82 (s), 104.86 (s), 93.94 (s), 90.32 (s), 34.59 (s), 31.11 (q), 18.73 (d), 11.46 (q), 0.01 (q); IR (neat) 2940, 2850, 2140, 1570, 1242, 968, 847, 835, 752, 683 cm^{-1}; HRMS (EI) m/z calcd for $C_{26}H_{42}Si_2$ 410.2825, found 410.2805.

1.1.6. 1-*t*-Butyl-3-ethynyl-5-[(triisopropylsilyl)ethynyl]-benzene (6b). To a solution of **6a** (5.0 g, 12 mmol) in THF (20 mL) and MeOH (20 mL), 1 M aqueous K_2CO_3 (0.5 mL) was added under nitrogen and the mixture was stirred at room temperature for 2 h. The reaction was quenched by dilution with water, and the mixture was extracted with hexane. The extract was washed with brine and dried over $MgSO_4$. The solvent was removed in vacuo, and the residue purified with flash chromatography to give **6b** as a pale yellow oil (4.03 g, 98%): ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.40–7.44 (m, 3H), 3.00 (s, 1H), 1.27 (s, 9H), 1.11 (s, 21H); ^{13}C NMR (67.5 MHz, $CDCl_3$) δ 151.44 (s), 132.92 (d), 129.31 (d), 129.25 (d), 123.54 (s), 122.01 (s), 106.64 (s), 90.65 (s), 83.37 (d), 77.07 (s), 34.58 (s), 31.05 (q), 18.69 (d), 11.36 (q); IR (neat) 2950, 2860, 2150, 1580, 1460, 958, 878, 680 cm^{-1}; HRMS (EI) m/z calcd for $C_{23}H_{34}Si$ 338.2430, found 338.2395.

1.1.7. Doubly TIPS-protected dimer 5a. To a solution of $Cu(OAc)_2$ (5.40 g, 29.7 mmol) in pyridine (40 mL) and MeOH (40 mL), a solution of 4.03 g (11.8 mmol) of **6b** in 20 mL of the same solvent was added under a nitrogen atmosphere. The mixture was stirred at room temperature for 7.5 h. Evaporation of the solvent gave a residue, which was acidified with 1N aqueous HCl and extracted with ether. The extract was washed successively with 2N aqueous NaOH, water, and brine and dried over $MgSO_4$. The solvent was evaporated in vacuo, and subsequent purification with flash chromatography (eluent: hexane) gave **5a** as a colorless solid (3.44 g, 86%): mp 157–158°C; ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.49 (t, J=1.7 Hz, 2H), 7.47 (d, J=1.7 Hz, 4H), 1.31 (s, 18H), 1.14 (s, 42H); ^{13}C NMR (67.5 MHz, $CDCl_3$) δ 151.64 (s), 133.23 (d), 129.78 (d), 129.56 (d), 123.72 (s), 121.64 (s), 106.40 (s), 91.05 (s), 81.35 (s), 73.82 (s), 34.67 (s), 31.04 (q), 18.69 (d), 11.36 (q); IR (KBr) 2950, 2850, 2150, 1580, 875, 680, cm^{-1}; HRMS (EI) m/z calcd for $C_{46}H_{66}Si_2$ 674.4703, found 674.4708. Anal. calcd for $C_{46}H_{66}Si_2$: C, 81.83; H, 9.85; Si, 8.32. Found: C, 81.93; H, 10.04.

1.1.8. Dimer 5b. To a solution of **5a** (3.34 g, 5.09 mmol) in 50 mL of THF was added dropwise a solution of TBAF in THF (1.0 M, 12.7 mL, 12.7 mmol) and the mixture was stirred at room temperature for 2.5 h. The mixture was diluted with water and extracted with hexane. The extract was washed with brine and dried over $MgSO_4$. After removal of the solvent, flash chromatography (eluent: hexane) afforded **5b** as a pale yellow solid (1.78 g, 96%): m p 97–98°C; ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.53 (t, J=1.7 Hz, 2H), 7.51 (t, J=1.7 Hz, 2H), 7.46 (t, J=1.7 Hz, 2H), 3.06 (s, 2H), 1.29 (s, 18H); ^{13}C NMR (67.5 MHz, $CDCl_3$) δ 151.74 (s), 132.97 (d), 130.19 (d), 130.05 (d), 122.30 (s), 121.70 (s), 82.98 (d), 81.20 (s), 77.53 (s), 73.92 (s), 34.63 (s), 30.95 (q); IR (KBr) 3280, 2950, 2860, 2170, 2100, 1570, 872, 685 cm^{-1}; MS (EI) m/z 362 (M^+). Anal. Calcd for $C_{28}H_{26}$: C, 92.77; H, 7.23. Found: C, 92.58; H, 7.27.

1.1.9. Mono-brominated monomer 6c. To a solution of 411 mg (1.00 mmol) of **6a** in 7 mL of acetone was added successively 178 mg (1.00 mmol) of NBS and 10 mg (0.06 mmol) of $AgNO_3$. The mixture was stirred at room temperature for 2 h, and after dilution with water, the mixture was extracted with hexane. The extract was washed with brine and dried over $MgSO_4$. Removal of the solvent followed by flash chromatography (eluent: hexane) afforded **6c** as a light yellow oil (399 mg, 96%): ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.43 (t, J=1.6 Hz, 1H), 7.41 (t, J=1.6 Hz, 1H), 7.40 (t, J=1.6 Hz, 1H), 1.29 (s, 9H), 1.13 (s, 21H); ^{13}C NMR (67.5 MHz, $CDCl_3$) δ 151.53 (s), 132.77 (d), 129.25 (d), 129.14 (d), 123.51 (s), 122.47 (s), 106.51 (s), 90.80 (s), 79.81 (s), 49.68 (s), 34.65 (s), 31.05 (q), 18.67 (d), 11.33 (q); IR (neat) 2940, 2860, 2200, 2150, 1580, 875, 690 cm^{-1}; HRMS (EI) m/z calcd for $C_{23}H_{33}SiBr$ 416.1535, found 416.1525.

1.1.10. TIPS-protected linear tetramer 8a. A flask was charged with dimer **5b** (1.09 g, 3.01 mmol), bromide **6c** (3.77 g, 9.03 mmol), $Pd_2(dba)_3{\cdot}CHCl_3$ (187 mg, 0.181 mmol), CuI (28.7 mg, 0.151 mmol), LiI (161 mg, 1.20 mmol), HMPA (0.21 mL, 1.2 mmol), and benzene (20 mL) under nitrogen. After stirring at room temperature for 5 min, 1,2,2,6,6-pentamethylpiperidine (3.05 mL, 16.8 mmol) was added dropwise. After stirring at room temperature for 7 h, the reaction mixture was poured into 1N aqueous HCl and the mixture was extracted with $CHCl_3$. The extract was washed with water and dried over $MgSO_4$. Evaporation of the solvent followed by flash chromatography gave **8a** as a yellow solid (942 mg, 30%). At the same time, 228 mg of **5a**, the dimer of **6c** was also isolated. **8a**: mp 133–134°C; ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.55–7.56 (m, 4H), 7.46–7.51 (m, 8H), 1.36 (s, 36H), 1.14 (s, 42H); ^{13}C NMR (67.5 MHz, $CDCl_3$) δ 152.02 (s), 151.70 (s), 133.25 (d), 133.19 (d), 130.65 (d), 130.60 (d), 129.90 (d), 129.62 (d), 123.71 (s), 122.03 (s), 121.90 (s), 121.48 (s), 106.35 (s), 91.13 (s), 81.63 (s), 81.18 (s), 80.91 (s), 74.14 (s), 74.03 (s), 73.67 (s), 34.79 (s), 34.70 (s), 31.04 (t), 30.99

(t), 18.68 (d), 11.33 (q); IR (KBr) 2950, 2860, 2150, 1570, 870, 680 cm^{-1}; MS (FAB): (relative intensity) *m/z* 1035 (M^++H, 38), 991 (M^+−*i*-Pr, 25). Anal. calcd for $C_{74}H_{90}Si_2$: C, 85.82; H, 8.76; Si, 5.42. Found: C, 85.70; H, 8.87.

1.1.11. Linear tetramer 8b. Compound **8b** was prepared according to same procedure as that for the preparation of **5b** using 882 mg (0.852 mmol) of **8a**, and 2.1 mL (2.1 mmol) of a 1.0 M THF solution of TBAF. Purification by flash chromatography gave linear tetramer **8b** as pale yellow solid (614 mg, 99%): mp 103–104°C; ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.55–7.56 (m, 4H), 7.54 (t, *J*=1.6 Hz, 2H), 7.52 (t, *J*=1.6 Hz, 2H), 7.50 (t, *J*=1.6 Hz, 2H), 7.47 (t, *J*=1.6 Hz, 2H), 3.07 (s, 2H), 1.31 (s, 18H), 1.30 (s, 18H); ^{13}C NMR (67.5 MHz, $CDCl_3$) δ 151.99 (s), 151.81 (s), 133.20 (d), 132.99 (d), 130.60 (d, 2C), 130.27 (d), 130.11 (d), 122.30 (s), 121.95 (s), 121.90 (s), 121.66 (s), 82.98 (d), 81.38 (s), 81.16 (s), 80.99 (s), 77.49 (s), 74.13 (s), 74.09 (s), 73.85 (s), 34.76 (s), 34.68 (s), 30.98 (q), 30.96 (q); IR (KBr) 3280, 2950, 2200, 1570, 872, 694 cm^{-1}; MS (FAB) *m/z* 722 (M^+).

1.2. Cyclization of dimer 5b by the Eglinton's Method

A solution of **5b** (71 mg, 0.20 mmol) in 20 mL of pyridine/benzene (3/2, v/v) was added to a solution of $Cu(OAc)_2$ (715 mg, 3.94 mmol) in 80 mL of the same solvent, which had been deaerated by bubbling nitrogen for 15 min, during a 3 h period at room temperature. The mixture was stirred for 17.5 h and the solvent was removed under reduced pressure. The residue was charged on a column of alumina and eluated with benzene to remove inorganic salts. Purification of the eluate by preparative HPLC afforded cyclic tetramer **2a** (18 mg, 25 %), and cyclic octamer **4a** (9 mg, 13%).

1.2.1. 2a. Dec. at 175°C; ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.79 (t, *J*=1.5 Hz, 4H), 7.42 (d, *J*=1.5 Hz, 8H), 1.31 (s, 36H); ^{13}C NMR (67.5 MHz, $CDCl_3$) δ 152.12 (s), 138.72 (d), 128.33 (d), 122.20 (s), 82.99 (s), 75.13 (s), 34.86 (s), 31.06 (q); IR (KBr) 2950, 2850, 2200, 1565, 1352, 1240, 865, 675 cm^{-1}; UV ($CHCl_3$): λ_{max} (log ϵ) 340 (5.14), 316 (5.29), 296 (5.01), 281 (4.66) nm; MS (FAB) *m/z* (relative intensity) 720 (M^+). Anal. calcd for $C_{56}H_{48}$: C, 93.29; H, 6.71. Found: C, 92.97; H, 6.83.

1.2.2. 4a. Dec. at 180°C; ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.55 (t, *J*=1.5 Hz, 8H), 7.51 (d, *J*=1.5 Hz, 16H), 1.32 (s, 72H); ^{13}C NMR (67.5 MHz, $CDCl_3$) δ 151.98 (s), 133.34 (d), 130.59 (d), 121.91 (s), 81.12 (s), 74.03 (s), 34.77 (s), 30.97 (q); IR (KBr) 2950, 2850, 2200, 1576, 872, 686 cm^{-1}; UV ($CHCl_3$): λ_{max} (log ϵ) 338 (5.10), 315 (5.15), 296 (5.01), 271 (5.07) nm; MS (FAB) *m/z* 1440 (M^+), calcd for $C_{112}H_{96}$ 1441 (M^+).

1.3. Cyclization of dimer 5b by the Breslow's method

To a solution of $Cu(OAc)_2$ (1.43 g, 7.88 mmol) and CuCl (390 mg, 3.94 mmol) in oxygen free pyridine (180 mL), **5b** (71 mg, 0.197 mmol) in the same solvent (20 mL) was added dropwise during 2 h. After stirring at room temperature for 18 h, the solvent was removed under reduced pressure. The green residue was passed through a short plug of alumina (eluent: benzene) to give a pale yellow solid (35 mg), which was purified by a preparative HPLC to yield cyclic tetramer **2a** (11 mg, 15%) and cyclic octamer **4a** (13 mg, 18%).

1.4. Coupling of dimer 5b by the Hay's method: linear tetramer 8b, hexamer 9, and octamer 10

To an oxygen saturated solution of **5b** (710 mg, 1.97 mmol) in acetone (180 mL) was added 0.86 mL of the Hay catalyst (skim of a stirred suspension of 500 mg of CuCl and 250 mL of TMEDA in 9.0 mL of acetone). After stirring at room temperature for 4 h with oxygen bubbling, the solvent was removed under reduced pressure. The green residue was passed through a short plug of alumina to give a yellow solid (723 mg), which was purified by preparative HPLC to yield linear tetramer **8b** (27 mg, 4%), linear hexamer **9** (168 mg, 23%), and linear octamer **10** (154 mg, 22%) each as a pale yellow solid.

1.4.1. Linear hexamer 9. Mp 173–176°C; ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.46–7.56 (m, 18H), 3.07 (s, 2H), 1.31 (s, 36H), 1.30 (s, 18H); ^{13}C NMR (67.5 MHz, $CDCl_3$) δ 151.97 (s), 151.96 (s), 151.77 (s), 133.17 (d), 132.96 (d), 130.60 (d), 130.24 (d), 130.08 (d), 122.27 (s), 121.94 (s), 121.89 (s), 121.64 (s), 82.96 (d), 81.35 (s), 81.13 (s), 80.96 (s), 77.48 (s), 74.11 (s), 74.08 (s), 73.83 (s), 34.74 (s), 34.66 (s), 30.95 (q), 30.94 (q); IR (KBr) 3270, 2948, 2200 1568, 872, 694 cm^{-1}; MS (FAB) *m/z* 1083 (M^+).

1.4.2. Linear octamer 10. Mp 174–176°C; ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.46–7.56 (m, 24H), 3.07 (s, 2H), 1.31 (s, 54H), 1.30 (s, 18H); ^{13}C NMR (67.5 MHz, $CDCl_3$) δ 151.95 (s), 151.94 (s), 151.76 (s), 133.16 (d), 132.95 (d), 130.60 (d), 130.23 (d), 130.06 (d), 122.27 (s), 121.92 (s), 121.88 (s), 121.62 (s), 82.94 (d), 81.34 (s), 81.12 (s), 80.94 (s), 77.47 (s), 74.11 (s), 74.08 (s), 73.82 (s), 34.72 (s), 34.63 (s), 30.92 (q); IR (KBr) 3270, 2948, 2200, 1570, 880, 694 cm^{-1}; MS (FAB) *m/z* 1443 (M^+).

Apparently, some of the ^{13}C NMR signals of **9** and **10** overlap each other, showing much less peaks than those expected.

1.5. Coupling of linear tetramer 8b by the Eglinton's method

Cyclization of tetramer **8a** was carried out as described for the reaction of dimer **5b**, using 300 mg (0.415 mmol) of **8b**, 1.51 g (8.30 mmol) of $Cu(OAc)_2$, and 400 mL of pyridine/benzene (3/2), to give cyclic tetramer **2a** (219 mg, 73%) and cyclic octamer **4a** (36 mg, 12%).

1.5.1. Thiophenometacyclophane (11). To a solution of 59 mg (0.082 mmol) of **2a** in 9 mL of THF, which was warmed to 60°C, was added finely ground $Na_2S{\cdot}9H_2O$ (314 mg, 1.3 mmol) and 15-crown-5 (16 μL, 0.082 mmol). The mixture was heated at reflux under nitrogen for 21 h. After cooling, the solvent was removed under reduced pressure and the residue was directly subjected to flash chromatography to give 58 mg (83%) of **11** as a pale yellow solid: mp >290°C: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (t,

J=1.7 Hz, 4H), 7.68 (d, J=1.5 Hz, 8H), 7.40 (s, 8H), 1.45 (s, 36H); ^{13}C NMR (100.5 MHz, $CDCl_3$) δ 152.36, 143.44, 134.58, 123.45, 121.94, 120.52, 35.08, 31.47; IR (KBr) 2962, 1594, 1434, 865, 793 cm^{-1}; UV λ_{max} (log ϵ) 336 (4.89), 244 (4.63) nm; MS (FAB) m/z 857 (M^++H). Anal. calcd for $C_{56}H_{56}S_4$: C, 78.46; H, 6.58. Found: C, 78.69; H, 6.98.

1.6. Molecular modeling study

Molecular modeling study was carried out using SPARTAN 5.0 software package[30] with a Silicon Graphics O_2 workstation. The geometry optimization was done by the AM1 semi-empirical method.[23] The input geometries for the conformers of octamer **4b** were obtained from the molecular mechanics calculations using the Sybyl force field implemented in SPARTAN.

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