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Synthesis and Photophysical Properties of Biphenyl and Terphenyl Arylene−Ethynylene Macrocycles

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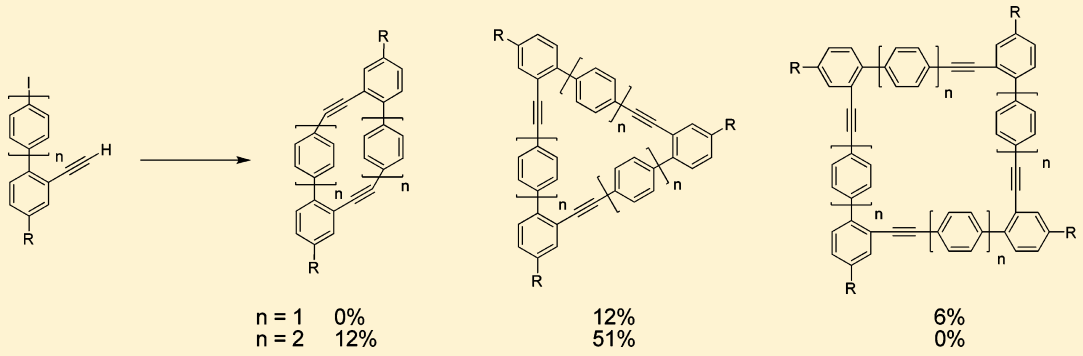
Supporting Information



ABSTRACT: A series of single-walled carbon nanotube precursors, C_{3h}-symmetric cyclotri(ethynylene)(biphenyl-2,4′-diyl) and cyclotri(ethynylene)(*p*-terphenyl-2,4″-diyl), have been prepared by a linear stepwise oligomerization−cyclization route and by statistical intermolecular cyclooligomerization. In addition to producing these members of a novel class of arylene ethynylene macrocycles, **1** and **2**, the latter statistical process produces the smaller cyclic dimer, cyclodi(ethynylene)(*p*-terphenyl-2,4″-diyl) and the larger cyclic tetramer cyclotetra(ethynylene)(biphenyl-2,4′-diyl). These macrocycles display large Stokes shifts in their fluorescence spectra. Their biphenyl or terphenyl connectivity prevents these macrocycles from achieving full planarity in the ground state, and the ethynylene moieties could provide synthetic access to cyclic arylene oligomers and discrete carbon nanotube segments.

INTRODUCTION

Conjugated shape-persistent macrocycles[1] and, in particular, arylene ethynylene macrocycles (AEMs)[2] have received much attention in recent years because advances in synthetic techniques have made them more accessible, and they have potential in many applications. AEMs are relatively thermally, photolytically, and oxidatively stable;[3] they often have strong UV absorptions and are often highly fluorescent.[4] Their rigid shape makes them suitable for host−guest interactions.[5] Additionally, these macrocycles have been of interest because their high polarizability makes them desirable as second-order nonlinear optical materials[6] and as materials for organic semiconductors[7] and devices.[8] Their unique two-dimensional structure could potentially allow these materials to circumvent the trade-off between efficiency and transparency observed in linear systems, and C_3-symmetric systems can be derivatized to give noncentrosymmetric materials. Planar AEMs have been shown to aggregate in solution,[9] in the liquid crystalline phase,[10] and in the solid phase[11] through weak van der Waals interactions. AEMs can aggregate into columnar mesophases as well as vesicles[12] and have the potential to act as model systems for organic nanotubes.[13]

Arylene ethynylene macrocycles are synthetically accessible either by statistical cyclization of a single aryl halide ethynyl monomer[14,15] or by the cyclization of a linear oligomer via a palladium catalyzed cross coupling,[16] in either case at low concentrations. This latter approach requires a linear, stepwise, and often tedious synthesis of the linear oligomer but usually gives a single discrete macrocycle as the sole product. Alternatively, the former methodology employs more synthetically accessible precursors but often yields various cyclic and linear oligomers[17] unless specific macrocycle ring sizes are excluded by ring strain or steric interactions on neighboring monomer units.[18] More recently, alkyne metathesis has proven to be an efficient synthetic method to prepare the arylene

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ethynylene scaffold.[19] Metathesis allows the formation of the thermodynamically most favored product(s) but may not offer the functional group tolerance of the palladium-catalyzed protocols. Derivatization of the monomers should allow the formation of electron-rich and/or electron-poor ring systems and thus the tuning of their physical properties. The incorporation of side chains is often crucial to allow the solubility of the highly rigid macrocycles.

Despite the recent attention given arylene ethynylene macrocycles, the incorporation of biphenyl and terphenyl moieties is rare, and such macrocycles have not been fully explored. The few reported examples of biphenyl or teraryl units include bipyridyl,[20] *m*-terphenyl,[21] *m*-terpyridinyl,[22] and 11,12-dihydroindolo[2,3-*a*]carbazole[23] (nominal *p*-terphenylenes) and tetra*m*-phenylene[24] subunits but no simple biphenyl or *p*-terphenylene containing macrocycles have been reported. The presence of such biphenyl units disrupts the fully planar geometry of the macrocycle and would therefore be expected to attenuate any aggregation via stacking of the planar rings. The deviation from planarity also would affect the conjugation around the macrocycle, and change their electronic properties in comparison to their fully planar analogs. The macrocycles depicted in Figure 1 represent novel classes of arylene ethynylene macrocycles.

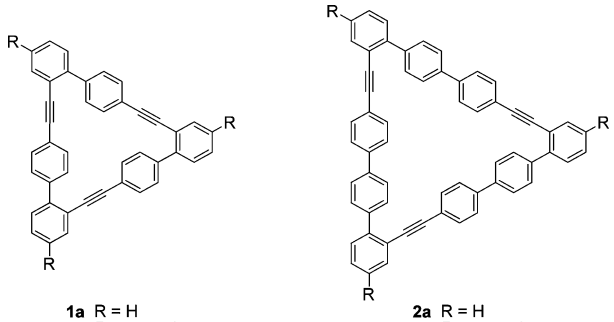

Figure 1. Biphenyl and terphenyl macrocycles.

More significantly, the title C_3 macrocycles offer the possibility to synthesize short segments of single-walled carbon nanotubes. Ethynylene units in shape-persistent macrocycles are usually used as rigid spacers that prevent diaryl steric interactions. However, alkynes are also reactive moieties, and if the alkynes in the title macrocycles can be incorporated into *ortho*-substituted aromatic rings via cycloaddition reactions with cyclopentadienone synthons, the vertices of the triangular macrocycles could be folded out of the plane to form the walls of the nanotube segment.[25] The phenylene rings in such a cycloaddition product are geometrically disposed to produce a fully fused nanotube segment upon oxidative cyclodehydrogenation (Figure 2). This synthetic path toward carbon nanotube segments relies on the title macrocycles as relatively strain-free templates that are elaborated with additional phenyl rings in a stepwise increase of strain until the fused tube is achieved. Alternatively, macrocycles containing cyclopentadienone moieties could be constructed and undergo cycloadditions with diarylalkynes to give similar cyclooligophenylenes.[26]

A similar strain strategy pioneered by Bertozzi and Jasti[27] converts a more highly curved precursor containing sp^3 centers to the all-sp^2 nanotube segment. Jasti,[28] Itami,[29] and others[30] have used this route to prepare a variety of [*n*]-cycloparaphenylenes, and Jasti[31] and Mullen[32] have recently prepared [*n*]cycloparaphenylenes that could in principle give belts of longer length upon oxidative cyclodehydrogenation of pendant phenyl substituents. Bodwell[33] has also prepared highly curved nanotube segments by incorporating polycyclic arenes in cyclophanes. Scott has proposed a slightly different approach that uses bowl-shaped templates upon which the nanotube can be grown.[34] To further our synthetic proposal, the synthesis of C_3-symmetric biphenyl and terphenyl arylene ethynylene macrocycles and their alkyl derivatives, along with their photophysical properties, are described below.

RESULTS AND DISCUSSION

Monomer Synthesis. As discussed above, the construction of cyclooligomers is usually achieved by one of two means: a statistical coupling of simple monomer units or a cyclization of a linear oligomer of appropriate length. The former method involves a shorter synthetic route and was the first one attempted for the construction of the C_3-symmetric macrocycles **1a**, **1b**, **2a**, and **2b**. Since both synthetic approaches require monomers **3a**, **3b**, **4a**, and **4b**, they were prepared first. The diethyltriazene and triisopropylsilyl groups on the termini

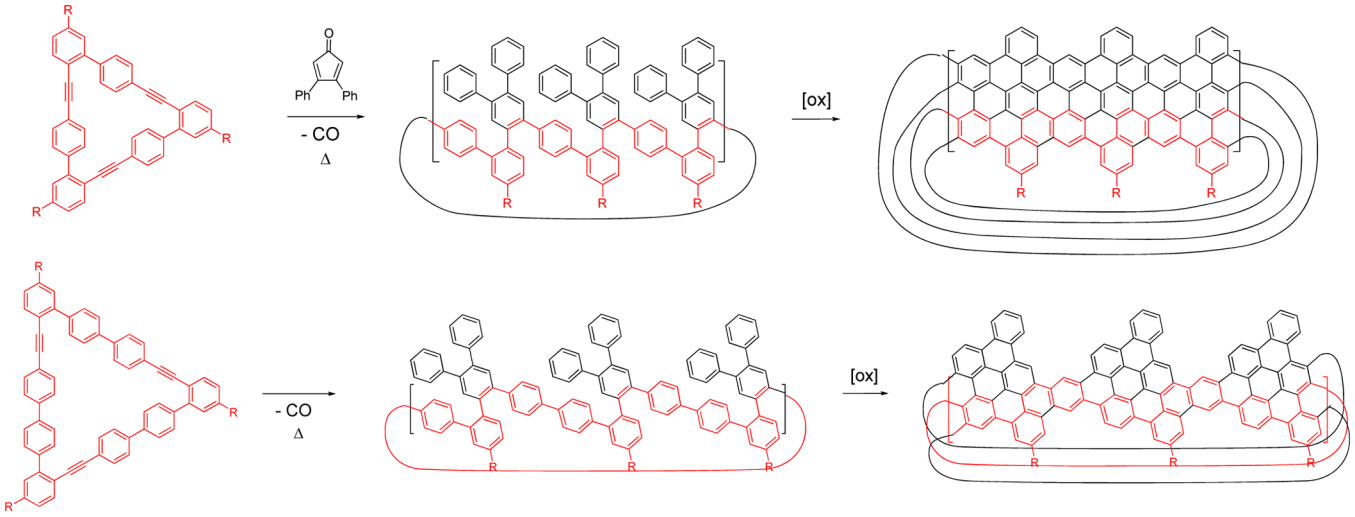

Figure 2. Potential conversion of title macrocycles to nanotube segments.

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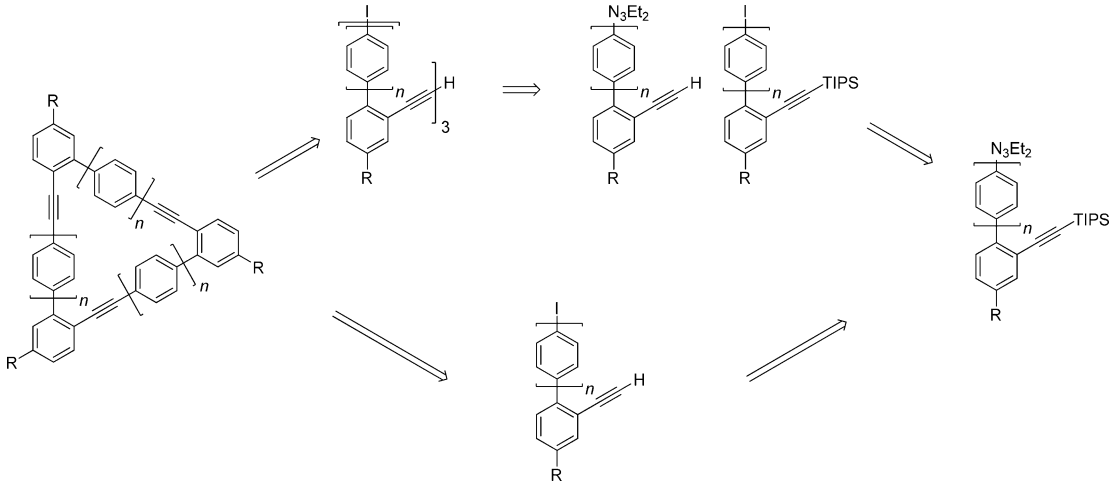
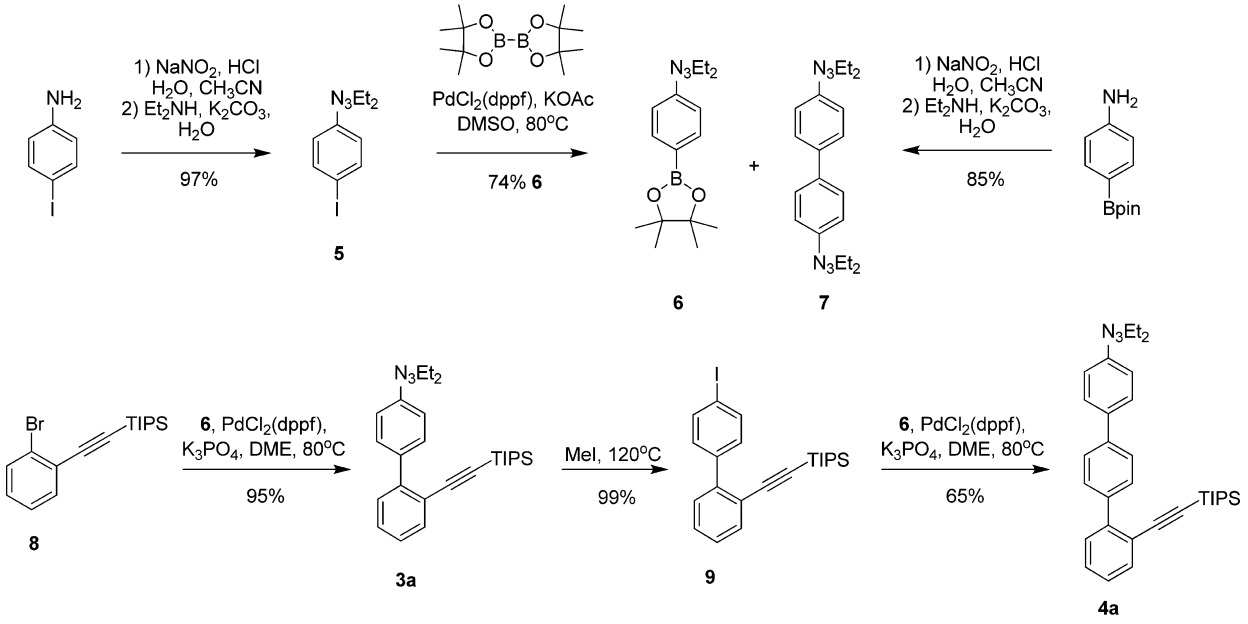
Scheme 1. Retrosynthetic Analysis



Scheme 2. Convergent Approach to Biphenyl 3a and Terphenyl 4a Monomers



of **3** and **4** are protecting groups that can be removed under orthogonal reaction conditions to give the aryl iodide or terminal alkyne, respectively. A statistical macrocyclization would require both groups to be deprotected to give the AB monomer, while the synthesis of a linear trimer which could be subsequently cyclized could be accomplished using a split-pool strategy (Scheme 1).

Compound **3a** was prepared via a convergent approach (Scheme 2). Triazene **5** was prepared in 97% yield by diazotization of 4-iodoaniline followed by quenching with diethylamine. Boronation of **5** with 1.2 equiv of bis(pinacalato)-diboron, $Cl_2Pd(dppf)$, and dry KOAc in DMSO gave **6** in 74% yield. However, this boronation also produced a significant quantity of biphenyl **7** which could only be removed by recrystallization from 2-propanol. In an attempt to minimize the formation of this undesired homodimer, a 3-fold excess of bis(pinacalato)boron was used. No homodimerization was observed, but the excess diboron proved equally difficult to remove during purification. The most effective purification protocol involves recrystallization from 2-propanol to remove the homodimer **7** followed by column chromatography to remove the residual palladium and excess diboron. Alternatively, **6** was prepared by diethylamine addition to the diazotized aminophenylboronic acid pinacol ester in 85% yield. This second protocol not only provided an overall higher yield of the phenylene synthon **6** but also a high enough purity after workup that the crude product could be used in further reactions without further purification, in stark contrast to the first protocol. Alkyne coupling partner **8** was prepared in 99% yield according to literature procedures from 1-bromo-2-iodobenzene and triisopropylsilylacetylene.

Suzuki coupling of the boronate ester **6** and alkyne **8** was performed using $Cl_2Pd(dppf)$ and K_3PO_4 in DME to give the biphenyl monomer **3a** in 95% yield. It should be noted that other palladium catalysts (notably $Pd(PPh_4)_3$), bases, and solvents did not give comparable yields. Terphenyl monomer **4a** was prepared in 65% yield from triazene **3a** by treatment with iodomethane to give **9** followed by a Suzuki coupling with triazene **6**. Despite the more reactive iodide and lack of hindering *ortho* group in **9** compared to **8**, the lower yield for

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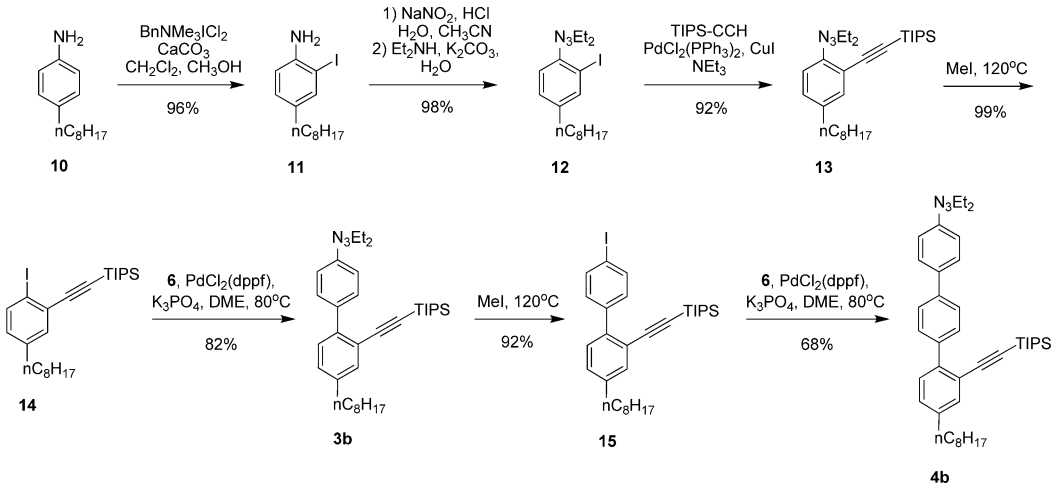
Scheme 3. Convergent Approach to Alkyl-Substituted Biphenyl 3b and Terphenyl 4b Monomers



the second Suzuki coupling was the result of competitive protiodeiodination[35] to give 2-(triisopropylsilylethynyl)-biphenyl. The terphenyl triazene also undergoes photolytic decomposition, especially in the presence of silica gel or Florisil; alumina was used in the chromatography of all terphenyl triazenes described, and little such decomposition was observed on this stationary phase.

Since the macrocycles constructed from **3a** and **4a** were anticipated to have low solubility, alkyl-substituted analogues **3b** and **4b** were also prepared (Scheme 3). Octylaniline **10** was iodinated with an ammonium dichloroiodate with high regiospecificity give iodoarene **11**, which was diazotized and quenched with diethylamine gave triazene **12**. The Sonogashira coupling of **12** with triisopropylsilylacetylene gave **13**, which was then converted to iodoarene **14** in 86% yield over four steps.

As with the unsubstituted analogues, biphenyl monomer **3b** was obtained by Suzuki–Miyaura coupling of **6** and **14**, and terphenyl monomer **4b** was obtained from **3b** by deprotection of the triazene in **3b** with methyl iodide to give iodoarene **15** (in 94% yield) which was then coupled with another equivalent of **6**. Initial attempts to couple **6** and **14** produced very poor yields of **3b** along with significant quantities of (3-octylphenylethynyl)triisopropylsilane, the protiodeiodination product of **14**. The concentration of reactants was increased 5-fold in an attempt to make the coupling more competitive with protiodeiodination, and the yield of the desired biphenyl **3b** was increased to 82%. The careful exclusion of water, a potential source of protons,[36] did not increase the yield of coupled product **3b** appreciably. Additionally, the yield of the Suzuki coupling to produce the terphenyl monomer **4b** was 68%, lower than that for **3b**, presumably for the same reasons discussed above for **3a**.

Statistical Macrocyclization. The doubly deprotected monomeric iodoalkynes **16a** and **17a** were obtained by diethyltriazene removal in methyl iodide followed by fluoride deprotection of the ethynyl protecting groups (Scheme 2) in 88% and 71% yields over two steps, respectively. The instability of terphenyl **17a** required that this free alkyne be utilized immediately after preparation and explains the lower yield of its preparation in comparison to the biphenyl **16a**. Biphenyl monomer **16a** was subjected to Sonogashira reaction conditions using $Cl_2Pd(PPh_3)_2$ at low concentration (18 mM) for 10 days at room temperature to give a product mixture containing a mixture of linear and cyclic oligomers. Poor solubility and similar polarities of the reaction products precluded chromatographic separation or purification, but the presence of **1a** was evident by peaks in the ^{1}H NMR (Figure 3) that matched those in pure samples of **1a** obtained by the alternate synthesis described below.

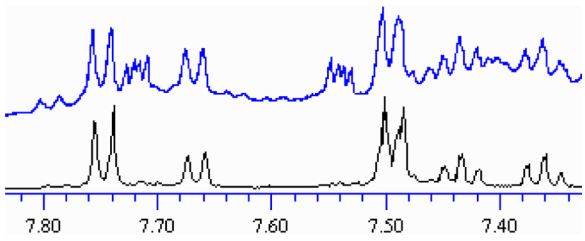


Figure 3. (Top) statistical macrocyclization of **16a**. (Bottom) stepwise construction of **1a**.

Stephens–Castro coupling of terphenyl monomer **17a** at 182 mM and Sonogashira coupling at 155 mM with $Pd(PPh_3)_2Cl_2$ gave only an insoluble yellow product, which had an ^{1}H NMR spectrum consistent with a mixture of linear and cyclic oligomers. The Sonogashira coupling of **17a** was attempted again, using $Pd(PPh_3)_4$ and at lower concentration, 18 mM. After 12 days at room temperature, this reaction yielded a solid that when washed repeatedly with methylene chloride proved to be macrocycle **2a**. The cyclic trimer was isolated in 20% crude yield but could not be separated from an impurity of unknown structure.

Similar protocols were used to convert the alkyl-substituted monomers **3b** and **4b** to cyclooligomers. Double deprotection of **3b** and **4b** to give **16b** and **17b** proceeded as with the unsubstituted analogues in 68% and 98% yields over two steps, respectively. Compound **16b** was subjected to Sonogashira coupling conditions at 28 mM; four fluorescent compounds were identified by TLC, but only two compounds were isolated by five iterations of flash chromatography, the cyclic trimer **1b** in 36% yield, and the cyclic tetramer **1c** in 24%. In an effort to improve the yield of the cyclooligomers, the concentration was lowered to 1.5 mM in the Sonogashira coupling reaction of **17b**. A 51% yield of the cyclic trimer **2b** was recovered by column chromatography as well as cyclic dimer **2c** in 12% yield. The yield of the cyclic trimer may also have been higher in the

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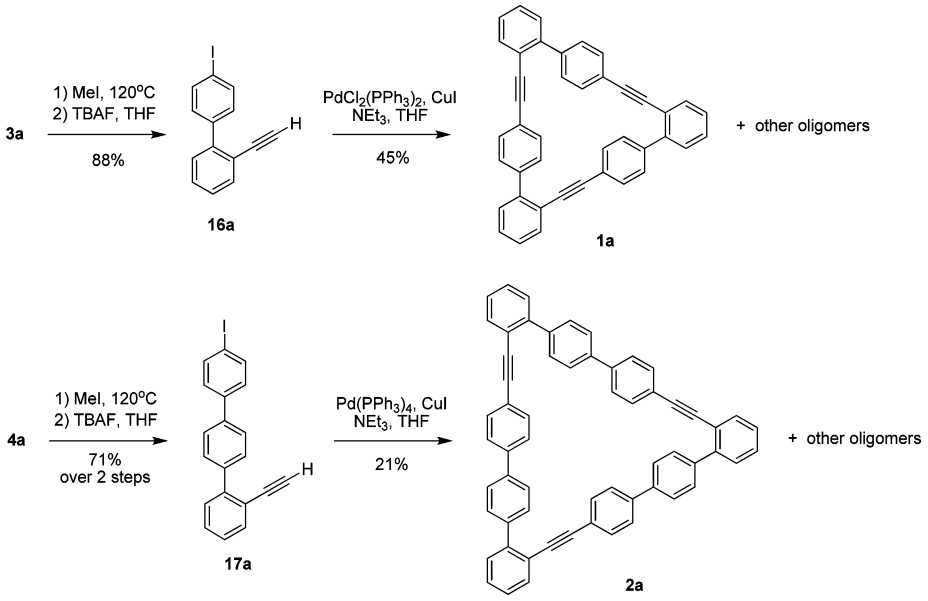
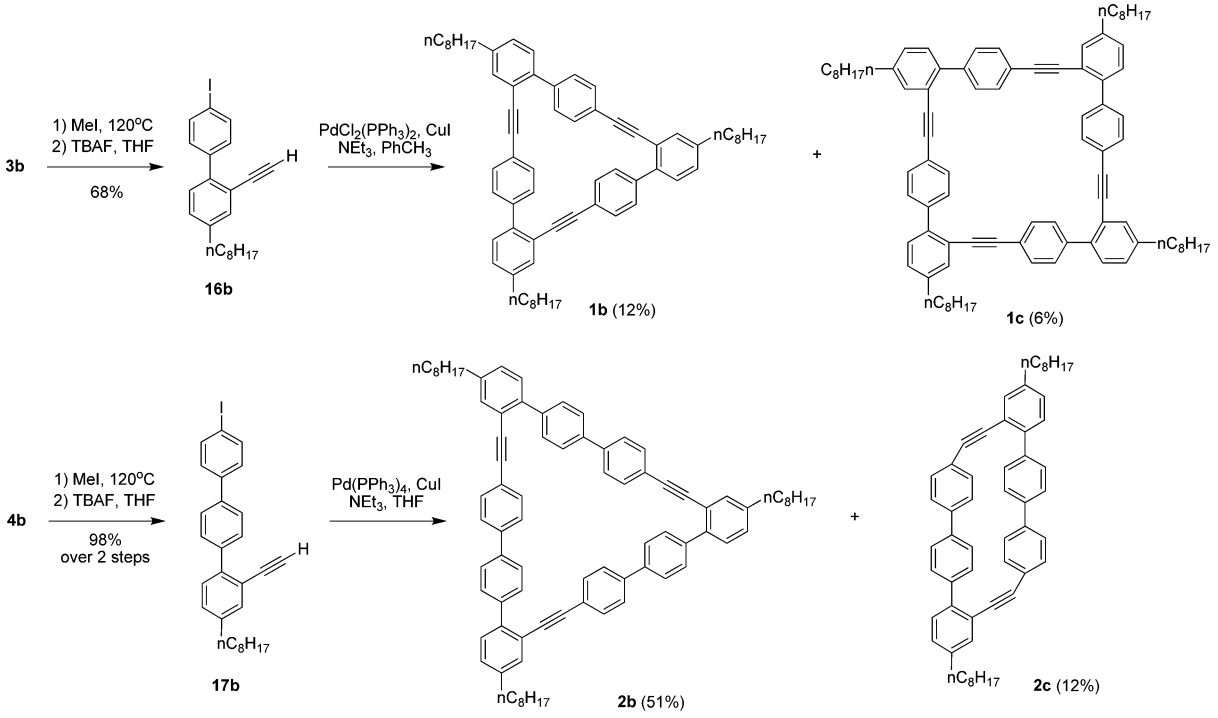
Scheme 4. Cyclization of Unsubstituted and Alkyl-Substituted Free Monomers



Scheme 5. Cyclization of Alkyl-Substituted and Alkyl-Substituted Free Monomers



cyclooligomerization of **17b** because of the use of $Pd(PPh_3)_4$ instead of $PdCl_2(PPh_3)_2$. The isolation of the substituted macrocycles was greatly facilitated by their much higher solubility, attributable to their long alkyl side chains.

Macrocyclization of Linear Oligomers. Analytically pure samples of **1a** and **2a** were obtained by constructing each through a linear, stepwise approach (Schemes 4 and 5, respectively). This split pool approach began with the removal of the diethyltriazene of **3a** to give **18a** in 98% yield and the removal of the ethynyl protecting group of **3a** using TBAF to yield **19a** in 90% yield (Scheme 3). Sonogashira coupling of fragments **18a** and **19a** gave the protected dimer **20a** in 75% yield. Unmasking the aryl iodide by removal of the diethyltriazene was followed by a second coupling with fragment **19a**, which led to the linear trimer **22a** in 67% yield over the two steps. Compound **22a** was then quantitatively converted to the iodide **23a**. Deprotection of **23a** with TBAF gave an iodoarylethyne which was immediately subjected to Sonogashira coupling conditions without purification. The cyclization was performed by slowly adding a solution of the linear trimer iodoarylethyne with a syringe pump to a solution of the catalysts in triethylamine. The final and highest concentration of the linear trimer was 3.7 mM, and after the addition was complete, the reaction was stirred for another 12 h before workup. Column chromatography gave pure **1a** in 45% yield (Scheme 6).

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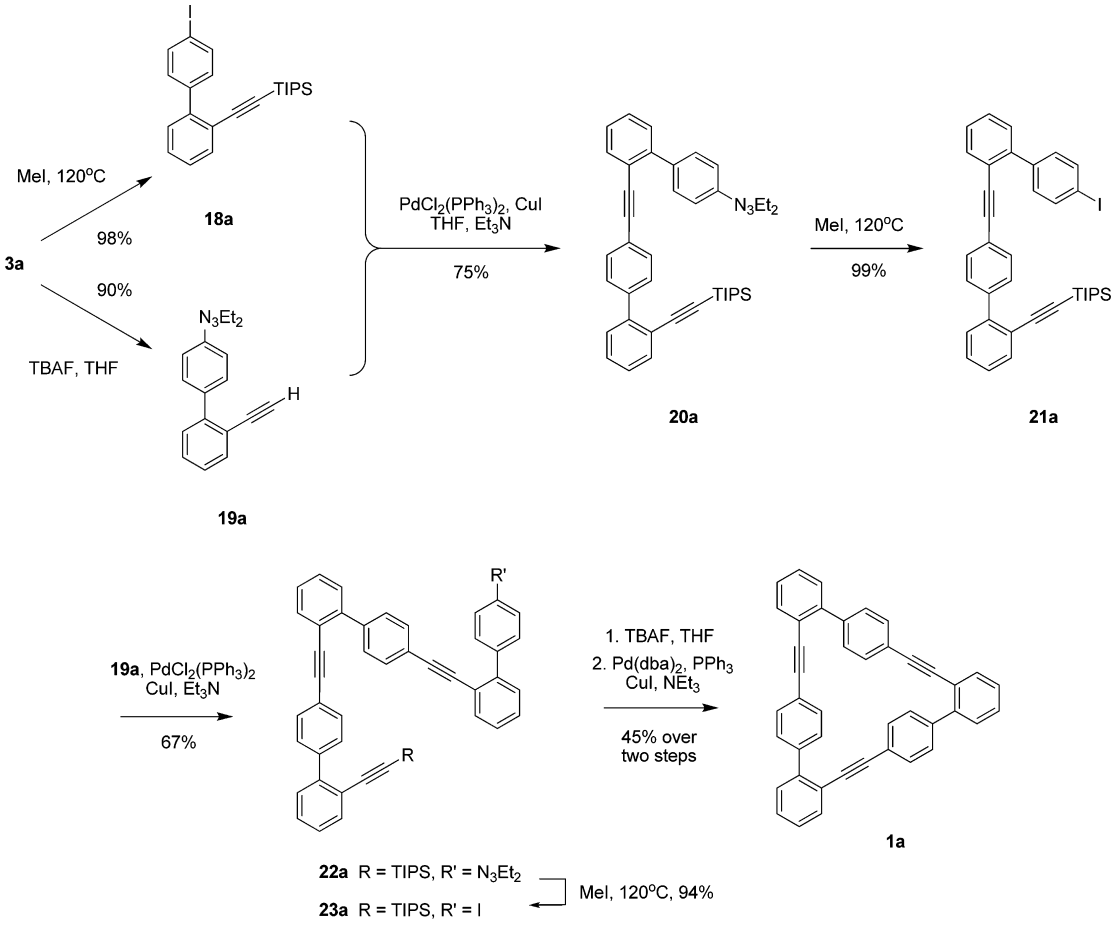
Scheme 6. Linear Approach to Macrocycle 1a



A split-pool approach to the terphenyl macrocycle **2a** also occurred in a similar sequence, but the additional *p*-phenylene unit within the monomer unit contributed to solubility problems (Scheme 4). Both deprotections of **3b** proceeded in 91% yield to give the iodide **18b** and terminal alkyne **19b**, which were coupled under Sonogashira conditions to give dimer **20b** in 76% yield. A significant quantity of unreacted **18b** was also recovered, along with a similar amount of a third organic product which is presumed to be the Hay coupled dialkyne arising from dimerization of **19b**. Conversion of the triazene to the iodide **21b** and Sonogashira coupling with another 1.3 equiv of **19b** gave the trimer **22b** in 52% combined yield. The lower yield compared to the biphenyl system can be attributed to losses during chromatography of the sparingly soluble synthons, and the larger excess of the terminal alkyne was utilized to minimize yield loss due to Hay coupling. Deprotection of the triazene to give iodide **23b** proceeded in quantitative yield. Removal of the TIPS group gave the sparingly soluble iodoarylethyne linear trimer; the loss of the relatively small alkyl groups in the TIPS group significantly lowered its solubility, and its subsequent cyclization was carried out without further chromatographic purification or complete characterization. As with the biphenyl trimer, the cyclization was carried out under high dilution Sonogashira conditions (2.1 mM) achieved using a syringe pump. The product mixture was purified by removing the solvent and centrifugation of the residue slurried with dichloromethane. The insoluble organic products floated on the chlorinated solvent while the inorganic catalysts and byproducts thereof formed a solid pellet. Macrocycle **2b** was thus isolated in 21% yield (Scheme 7).

Computational Modeling of Cyclooligomer Strain. The formation of both linear and cyclic oligomers of various sizes during cyclooligomerization is not unexpected and has been shown to occur in various systems under a wide array of reaction conditions.[14] In some of these reports, the cyclotrimeric and cyclotetrameric products isolated from *o*-iodoethynylenebenzene precursors were relatively unstrained.[15] Other studies have reported the production of strained cyclic dimeric species along with unstrained cyclotrimers and cyclotetramers.[37]

On the basis of the macrocycles described above, the cyclic dimer, cyclic trimer, and cyclotetramer of the 1,2-phenylene, 1,4′-biphenylene, and 1,4″-terphenylene ethynylene macrocycles were computationally modeled. Geometry optimization and single-point energies were calculated at various levels of theory using Gaussian 03,[38] and the alkyl chains were omitted for computational ease. The structures shown are from the B3LYP/6-31G(d) geometry optimization, but the structures for the geometries optimized with every method do not differ appreciably. The energies tabulated in Table 3 are per repeat unit and normalized to the cyclotrimer for each analogous series.

For the *o*-arylene ethynylene cyclooligomers, it is no surprise that the D_{2h} cyclodimer **24c** is much higher in energy than either the D_{3h} cyclotrimer **24a** or D_{2d} tetramer **24b**. The incomplete treatment of the closed π-system in the molecular mechanics force field is most likely the source of the difference

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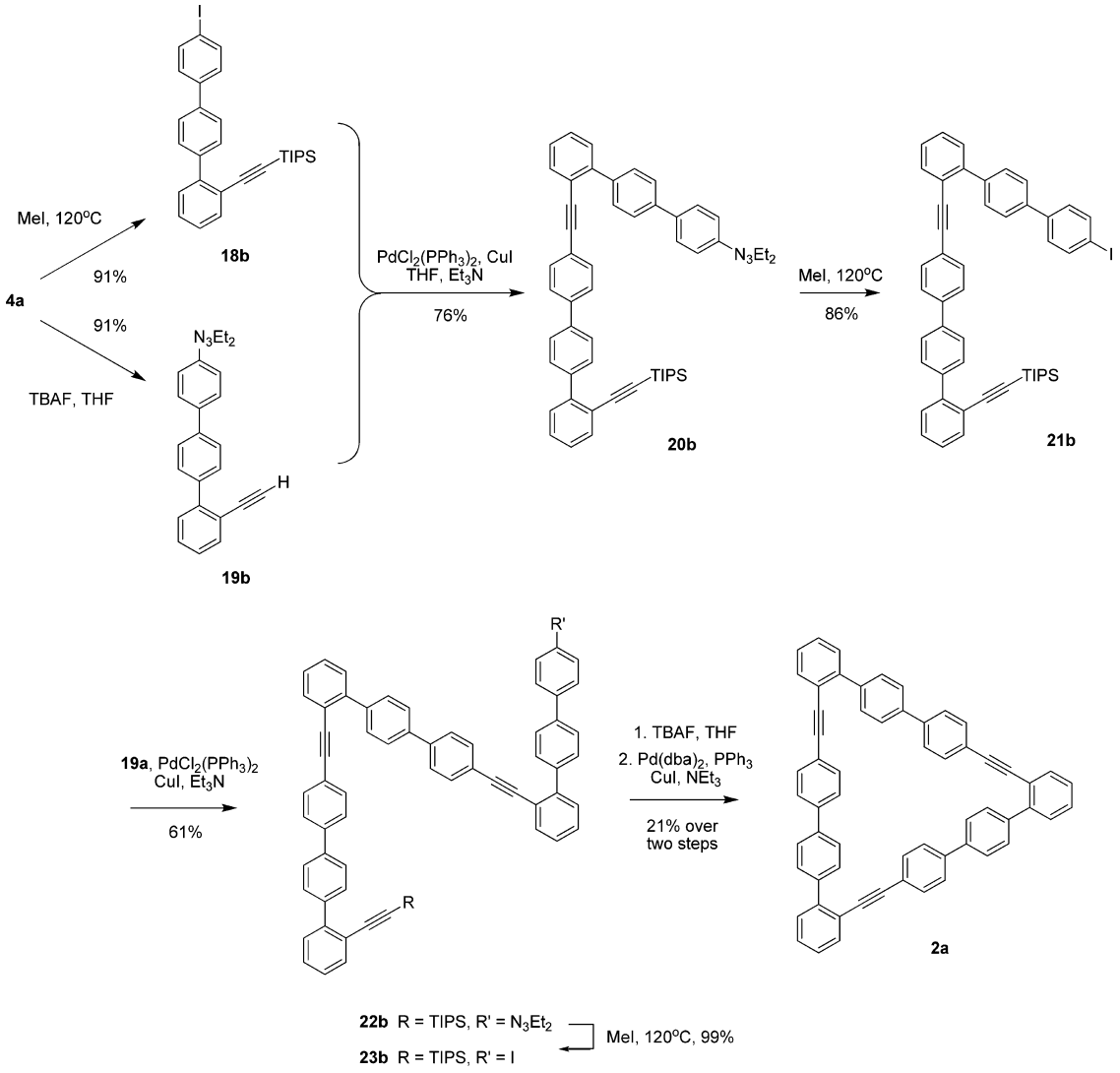
Scheme 7. Linear Synthesis of Macrocycle 2b



in repeat unit strain calculated for the cyclotetramer **24b**; the puckered ring of **24b** is predicted to be as nearly strainless as cyclotrimer **24a** by semiempirical, ab initio, and density functional methods but not by molecular mechanics.

Calculations on the biphenyl cyclooligomers exhibit similar energy trends. The $C_{14}H_8$ repeat units in cyclodimer C_{2h} **1d** are ~10 kcal/mol higher in energy than those in C_3 **1a**, and the two *para*-substituted rings are predicted to be coplanar with one another, which gives C_2 **1d** the appearance of an extended cyclophane. The aryl−aryl dihedral angle decreases from 90° in **1d** to 56° in cyclotrimer **1a**. Cyclic tetramer **1e** shows a similar aryl−aryl dihedral angle (57°) as well as a similar alkyne bond angle to that of the cyclic trimer. These structural similarities, despite the pucker in the cyclotetramer ring, contribute its lack of strain; the cyclotrimer and cyclotetramer are nearly isoenergetic on the basis of each repeat unit.

The constrained cyclic array of the terphenyl dimer C_2 symmetric **2d** forces the two *para*-substituted rings to be nearly coplanar, while being orthogonal to the *ortho*-substituted ring. The $C_{20}H_{12}$ repeat units are calculated to be ~8 kcal/mol more strained in **2d** than in **2a**, a smaller difference than that calculated in the biphenyl macrocycles. The optimized geometry of the cyclotrimer **2a** is C_3 symmetric and features a nearly all-planar system in which only the central *p*-phenylene of the terphenyl unit is twisted out of the plane. As a result, there are three planar diphenylacetylene moieties within **2a**, a structural feature that is shared by the optimized geometry of C_2 symmetric **2e**. The lack of angle strain in the alkykyl moieties in both **2a** and **2e** is a contributing factor making them nearly isoenergetic.

In all cases, the cyclodimers have the highest energy per monomer unit compared to the respective cyclotrimers or cyclotetramers, which in each case are nearly isoenergetic. There is a relationship between the number of *p*-phenylene units in the macrocycle and the relative strain of the cyclodimer; presumably, the angle strain of the alkynyl moieties is shared among additional phenylene units and the overall strain of the repeat unit is reduced. The average sp carbon bond angle is 155.4° in **24c**, 166.5° in **1d**, and 170.0° in **2d**, and it is evident that smaller deviations from the ideal bond angle in the alkynyl carbons is accompanied by a reduction in the strain energy. The structural similarities shared between **1a** and **1e** as well as **2a** and **2e** shown in Table 1 reflect their isoenergetic relationships. There is one close nonbonded C−H interaction present in the biphenyl and terphenyl macrocycles that is as significant in setting the aryl−aryl dihedral as the distance

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Table 1. Energies and Geometries of Various Arylene Ethynylene Macrocycles[a]

									
	24c	**24a**	**24b**	**1d**	**1a**	**1e**	**2d**	**2a**	**2e**
MM2	32.5	0	-4.1	21.3	0	-6.9	15.9	0	13.0
AM1	18.8	0	0.2	9.3	0	-0.4	6.5	0	-0.2
HF/6-31G(d)	17.4	0	0.4	10.7	0	-0.8	8.5	0	-0.1
B3LYP/6-31G(d)	15.0	0	0.7	10.0	0	-0.7	8.2	0	-

[a]Energies are in kcal mol^{-1} per repeat unit of cyclooligomer and are referenced to the cyclic trimer repeat unit energy for each set of cyclooligomers.

between the 2- and 2′-hydrogens; these distances are only significant in the cyclic trimers and tetramers since the cyclic dimer has a near orthogonal biphenyl dihedral angle (Table 2).

Table 2. Structural Features of Various Arylene Ethynylene Macrocycles

	avg sp C bond angle (deg)	H–C (Å)	Ar–C≡C–Ar dihedral angle (deg)	other Ar–Ar dihedral angles (deg)
24c	155.4		0.0	
24a	179.4		0.0	
24b	178.0		60.5	
1d	166.5	3.60	95.0	
1a	**177.8**	**2.72**	**47.6**	
1e	**177.6**	**2.74**	**47.9**	
2d	170.0	3.07	87.4	29.0, 68.3
2a	**177.2**	**2.72**	**6.5**	**39.4, 46.5**
2e	**177.4**	**2.66**	**18.1**	**38.4, 52.8**

The observation of cyclic dimer **2c** in the macrocyclization of **3b** suggests that the strain calculated per repeat unit is not great enough to prevent the irreversible, kinetic formation of **2c**. The larger strain calculated for the biphenyl dimer **1d** suggests that strain may be playing a role in favoring the formation of cyclotrimer **1b** and cyclotetramer **1c** in the macrocyclization of **3a**.

Optical Properties. The absorption and emission spectra of the novel macrocycles described above were recorded in a variety of solvents, since solvent polarity has been shown to affect the absorption and emission wavelength as well as the quantum yields (Φ) of organic molecules.[39] Their poor solubility in some solvents such as pentane limited full comparisons of all of the macrocycles, but in benzene, THF and $CHCl_3$, their λ_{max} and ε_{max} were determined.

Compounds **1a** and **2a** were not sufficiently soluble in pentane to record UV–vis absorption spectra, but the alkyl-substituted cyclooligomers were. Compound **1b** exhibited an absorption maximum at 296 nm, with shoulders near 264 and 330 nm. Cyclotetramer **2b** exhibited two nearly equally intense absorptions at 282 and 301 nm, and these two maxima were observed in other solvents as well. Cyclotrimer and cyclodimer **2b** and **2c** exhibited more similar spectra in pentane, with single dominant absorption maxima at 312 and 306 nm, respectively. It should be noted that accurate molar absorptivities were not obtained for **2b** and **2c** because of the formation of insoluble precipitate during the measurement of the spectra in pentane.

All of the macrocycles were more soluble in benzene, and their absorption spectra are shown in Figure 4. The spectra of linear trimers **23a** and **23b** were also obtained in benzene. The λ_{max} of biphenylene linear trimer **23a**, 299 nm, does not change appreciably upon cyclization to **1a**, which has a λ_{max} of 298 nm. Alternatively, the λ_{max} of terphenylene linear trimer **23b**, 295 nm, is shifted bathochromatically by 8 nm upon cyclization to cyclic trimer **2a** (λ_{max} = 303 nm). This could arise from an increase in conjugation upon moving from the linear to the cyclic system.[40] Both **1b** and **2b** are red-shifted by 5–6 nm compared to their unsubstituted analogs, **1a** and **2a**. Cyclic tetramer **1c** is also red-shifted 6 nm compared to cyclic trimer **1b** and has a much broader and less intense UV absorption band. All of the terphenylene macrocycles also showed broad absorptions, but cyclic dimer **2c** and cyclic trimer **2b** had very similar spectra. The absorption spectra of the macrocycles in THF show similar trends to those seen in the less polar benzene and pentane.

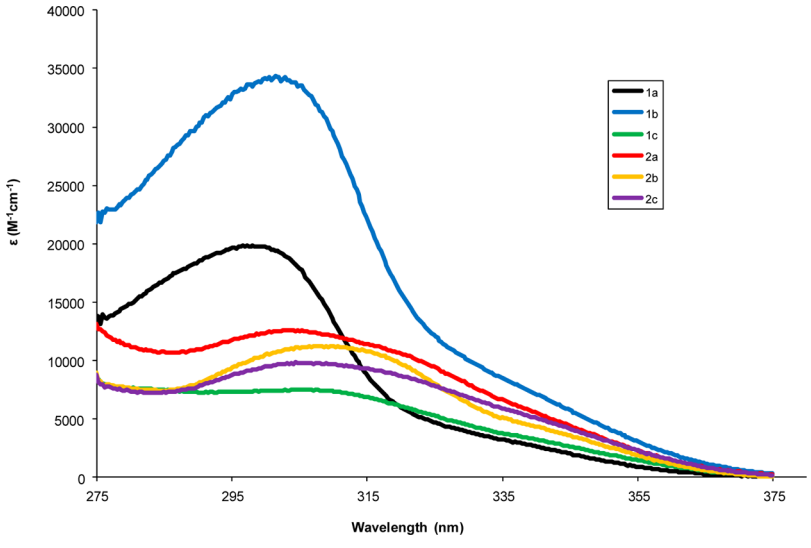

Figure 4. UV–vis absorbance spectra of macrocycles in benzene.

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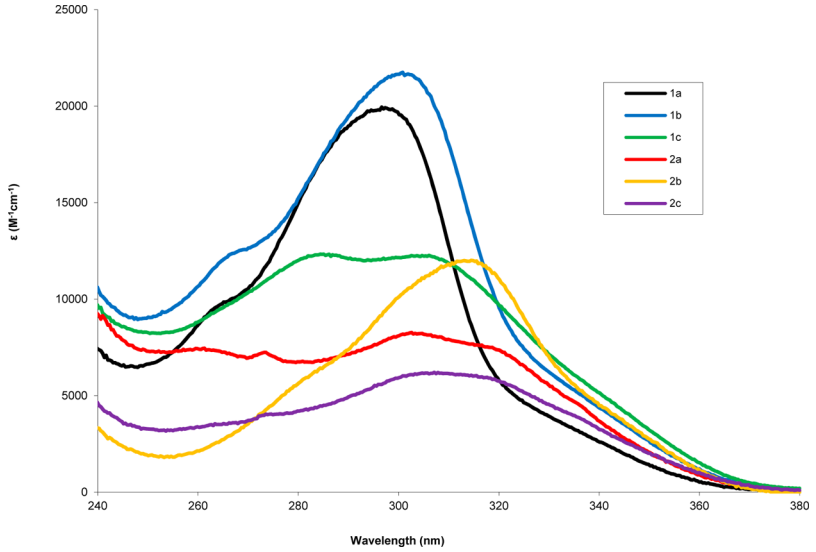

Figure 5. UV−vis absorption spectra of macrocycles in $CHCl_3$.

Table 3. λ_{max} (nm) and ε (M^{-1} cm^{-1}) of *n*-Octyl Terphenyl Cyclodimer and Cyclotrimer

solvent	**1a** λ_{max} (ε)	**1b** λ_{max} (ε)	**1c** λ_{max} (ε)	**2a** λ_{max} (ε)	**2b** λ_{max} (ε)	**2c** λ_{max} (ε)
nC_5H_{12}		296 (20300)	282 (14700) 301 (14500)		312 (−)	306 (−)
C_6H_6	298 (19800)	303 (34100)	309 (7400)	303 (12600)	309 (11200)	307 (9800)
THF	295 (13000)	302 (15800)	285 (7500) 307 (7500)		305 (10900)	305 (4800)
$CHCl_3$	297 (19900)	302 (21700)	285 (12300) 306 (12200)	303 (8200)	315 (12000)	307 (6200)

All of the terphenylene macrocycles **2a−c** exhibit a bathochromatic shift in their absorption maxima in $CHCl_3$ compared to THF, while no such shift is observed for the biphenylene macrocycles **1a−c**. Just as was observed in benzene, the λ_{max} of linear trimer **23a**, 298 nm, is very similar to that of cyclic trimer **1a**, 297 nm, while terphenylene linear trimer **23b** has a λ_{max} of 293, 10 nm blueshifted compared to the cyclic trimer **2a** which has a λ_{max} of 303 nm. Alkyl substitution again redshifts the λ_{max} of cyclic trimers, from 297 nm for **1a** to 302 nm for **1b** and from 303 for **2a** to 315 nm for **2b**, which was the largest λ_{max} observed in the solvents examined. As observed in previous solvents, biphenyl cyclotetramer **1c** exhibits two λ_{max} at 286 and 308 nm, and cyclic dimer **2c** exhibits a broad maximum with a relatively small molar absorptivity (Figure 5).

There is little to no solvent dependence on absorption for macrocycles **1a−c** and **2a−c**. cyclotrimers **1a**, **1b** and **2a** or for cyclotetramer **1c** or cyclodimer **2c**. Only substituted biphenylene cyclotrimer **1b** and terphenylene cyclotrimer **2b** exhibited a significant solvatochromic shifts, and while cyclotetramer **1c** exhibits two nearly identical λ_{max} in pentane, THF and chloroform, it has only a single broad λ_{max} in benzene.

The relationship between the structure of the macrocycle and its absorption spectrum should depend on the extent of conjugation around the macrocyclic ring. The three central *p*-phenylene aromatic rings of the terphenylene moiety in **2b** are ∼47° out of the macrocyclic plane, as are the three *p*-phenylenes in **1b**. It is possible that the conjugation around the macrocyclic ring is not interrupted to a significant extent, thus causing **2b** to exhibit a more red-shifted λ_{max} compared to **1b** which has a smaller π system. This trend exists in all solvents tested, although the extent of the shift increases as solvent polarity decreased. $CHCl_3$ and THF show a shift of 1−2 nm each, while nonpolar solvents benzene and pentane cause a larger red shift of 9 and 18 nm, respectively.

Several groups have examined the varying effects of ring strain on absorption properties of conjugated ethynylic systems.[41] In the case of the biphenylene and terphenylene systems, ring strain is accompanied with perturbation of the aryl−aryl dihedral angles. The structures and energies predicted by the computations described above for cyclic trimer **1a** and cyclic tetramer **1e** suggest that all biphenylene macrocycles synthesized, **1a**, **1b**, and **1c**, are all essentially strain-free. The aryl−aryl dihedral angle is also nearly identical in **1a** and **1e**, and both the planar cyclic trimer and puckered cyclic tetramer differ only in the disposition of the identical biphenylene−ethynylene units; these units are coplanar in the cyclic trimer and are not in the cyclic tetramer. In all solvents examined excepting benzene where the solvent may have partially obscured the spectrum, trimer **1b** showed a single, broad λ_{max} at around 300 nm, and tetramer **1c** showed two λ_{max}, one ∼15 nm shorter and another ∼5 nm longer wavelength (Table 3). It should be noted that the two-dimensional π-network is disrupted in the cyclotetramer by the ring pucker, which may explain the lower molar absorptivities of the cyclic tetramer in each solvent examined. Cyclic dimer **2c** and cyclic trimer **2b** exhibit very similar spectra in benzene and THF, and slightly shifted spectra in pentane and chloroform. Deformation from planarity by the ethynyl-substituted *p*-phenylene ring in the terphenyl cyclotrimer, **2b** is amplified from 6° to near orthongonality, 87°, by removing a single repeat unit to form the terphenyl cyclodimer **2c**. Despite this interruption in the

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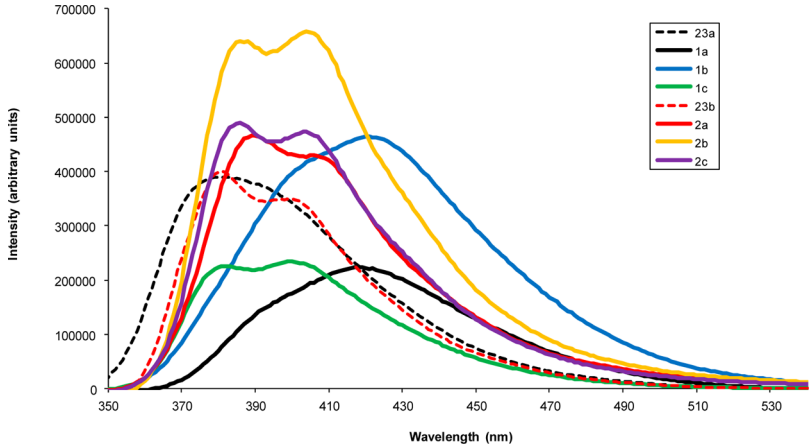

Figure 6. Fluorescence spectra in benzene of macrocycles and linear trimers.

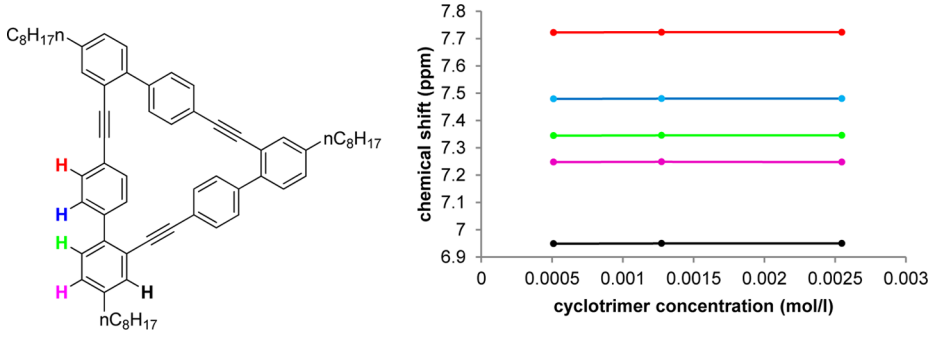

Figure 7. Concentration-dependent NMR chemical shifts of **1b** in C_6D_6; fluorescence spectra were observed at 0.066 mM.

cyclic π-nework, the UV−vis spectra are similar. This suggests that either π-conjugation is not occurring in both systems and absorptions are a result of individual subunits or that delocalization about the macrocycles is not disrupted. In all cases, **2b** exhibits greater molar absorptivity which could be the result of a larger number of absorbing moieties in the cyclic trimer versus the cyclic dimer.

Solutions of all of the macrocycles **1** and **2** as well as the linear trimers **23a** and **23b** are highly fluorescent (Figure 6). The emission properties of these compounds were analyzed in benzene and their fluorescence quantum yields were determined using pyrene as a standard. All macrocycles displayed large Stokes shifts which are indicative of large conjugated arylene ethynylene macrocycles (see Table 4).[40]

The absorbance spectrum of biphenylene linear trimer **23a** and biphenylene cyclic trimer **1a** are very similar, but the single emission maximum exhibited by linear trimer **23a** at 381 nm shifts to 418 nm upon ring closure to form **1a**. No such large shift is observed upon ring closure of terphenylene linear trimer **23b** with an emission maxima of 381 and 399 nm to terphenylene cyclic trimer **2a** with emission maxima of 390 and 406 nm. Comparison of the fluorescence spectra of **1a** to **1b** and **2a** to **2b** indicates that *n*-octyl substitution causes only small shifts in the emission maxima. Cyclic tetramer **1c** displays two λ_{em} at 382 and 401 nm, at much shorter wavelengths than **1a** and **1b**; the puckering of the macrocyclic ring not only affects the absorbance spectrum of 1c, but its emission spectrum. All terphenylene macrocycles emit two λ_{em} at similar wavelengths to 1c, at ∼390 and ∼405 nm. Cyclic dimer **2c** shows similar emission properties to that of the cyclic trimer even though the *p*-phenylenes are orthogonal to the *o*-phenylene. The dihedral angles of the terphenyl moiety do not appear to perturb the optical properties of these systems.

While **1a** and **1b** exhibit Stokes shifts of 120 nm, all of the other macrocycles exhibit Stokes shifts of ∼80 and 100 nm. The larger Stokes shifts for the biphenylene cyclic trimers could indicate a more complete planarization of the macrocycle in **1a** and **1b** than the other macrocycles; extending the conjugation throughout the biphenylene cyclotrimers requires only a single close H−H and a single close C−H contact, while the biphenylene cyclotetramer cannot achieve planarity and greater conjugation without involving a significant amount of angle strain and the terphenylenes would require four close H−H contacts to achieve full planarity and conjugation.

One possible cause for the Stokes shifts observed could be aggregation of the macrocycles in solution, which has been observed for similar structures. To test this hypothesis, we obtained the NMR spectra of solutions of **1b** in benzene at concentrations higher than those used to obtain the fluorescence spectrum of **1b** (Figure 7). If **1b** had been aggregating in the 0.066 mM solution used in the fluorescence experiment, it should be doing so at higher concentrations as well. Since the NMR chemical shifts of all of the aromatic protons in **1b** show no concentration dependence above that concentration, it seems likely that no aggregation would have taken place at the lower concentration.

All macrocycles exhibit fairly low quantum yields (Φ) in benzene compared to larger arylene ethynylene macrocycles (Table 4).[13] However, these systems do not contain long linear conjugated pathways which has been correlated to high quantum yields.[28] Quantum yields for the biphenyl macrocycles range from 0.02 for **1b** to 0.04 for **1c** while the quantum yields

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Table 4. Absorbance and Emission Optical Properties of Macrocycles and Linear Trimers

	λ_{abs} (nm)	λ_{em} (nm)	Stokes Shift (nm)	Φ
23a	300	381	81	
1a	298	418	120	0.03
1b	303	422	119	0.02
1c	309	382	73	0.04
		401	92	
23b	296	381	85	
		399	103	
2a	303	390	87	0.04
		406	103	
2b	309	387	78	0.06
		405	96	
2c	307	387	80	0.05
		405	98	

for terphenyl macrocycles are slightly more efficient ranging 0.04 for both **2a** and **23b** to 0.06 for **2b**.

CONCLUSIONS

In an effort to synthesize precursors of short carbon single-walled nanotubes, cyclic trimers containing biphenylene and *p*-terphenylene ethynylene units were constructed via linear, split-pool approaches to give unsubstituted macrocycles **1a** and **2a**. More soluble alkyl-substituted analogues **1b** and **2b** were also synthesized, utilizing statistical macrocyclizations of monomers made possible by the increased solubility. These statistical macrocyclizations also yielded a cyclotetramer **1c** in the biphenylene system and a cyclodimer **2c** in the *p*-terphenylene system; these alternative cyclooligomers were separable from the cyclotrimers by exhaustive column chromatography. Computational geometry optimizations suggest that the cyclic dimer is not energetically accessible in the statistical macrocyclization of **16b**, while a lesser degree of angle strain in the terphenylene monomer **17b** allows formation of cyclodimer **2c**. All of the macrocycles obtained absorb around 300 nm, but the cyclotrimers **1a** and **1b** exhibit larger Stokes shifts in their fluorescence emission spectra than the other macrocycles observed. Further studies are currently being conducted to determine if multiple cycloadditions can be carried out on the alkynes present in these macrocycles to convert them into arylene cyclooligomers that can be oxidized to make carbon nanobelts.

EXPERIMENTAL SECTION

3,3-Diethyl-1-(4-iodophenyl)triaz-1-ene (5).[42] 4-Iodoaniline (10.004 g, 45.67 mmol, 1.00 equiv) was dissolved in 380 mL of acetonitrile, 160 mL of water, and 16.0 mL of concentrated hydrochloric acid and cooled to 0 °C. A solution of 1.1 equiv of $NaNO_2$ (3.321 g, 48.14 mmol, 1.05 equiv) in 20 mL water was added slowly via syringe and the mixture stirred 45 min at 0 °C. The mixture was transferred to a flask containing K_2CO_3 (21.001 g, 151.9 mmol, 3.32 equiv) and diethylamine (9.5 mL, 91.81 mmol, 2.00 equiv) in 250 mL of H_2O at 0 °C. The reaction was allowed to slowly warm to room temperature and stirred for 2 h before being extracted with diethyl ether. The combined organic layers washed with brine, dried over magnesium sulfate, filtered, and concentrated in vacuo. The crude product was then purified by flash chromatography using 5% diethyl ether in hexanes to afford 13.43 g of the desired product as an orange oil (97% yield): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.61 (d, J = 8.8 Hz, 2H), 7.16 (d, J = 8.8 Hz, 2H), 3.74 (q, J = 7.3, 4H), 1.25 (br t, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 150.9, 137.6, 122.4, 88.9; IR (cm^{-1}) 2974, 2933, 2871, 1475, 1420, 1391, 1341, 1238, 1198, 1108, 1093, 1001, 828; MS (CI-isobutane) [MH^+] 304.6 m/z.

(2-(2-Bromophenyl)ethynyl)triisopropylsilane (8).[43] A 25 mL round-bottomed flask was charged with 1-bromo-2-iodobenzene (2.697 g, 9.53 mmol, 1.00 equiv), $Cl_2Pd(PPh_3)_2$ (0.198 g, 0.282 mmol, 0.03 equiv), CuI (0.051 g, 0.267 mmol, 0.03 equiv), triisopropylsilylethynylene (2.3 mL, 10.25 mmol, 1.07 equiv), and 20 mL of 1:1 THF/Et_3N. The solution was stirred at room temperature for 24 h before being concentrated in vacuo. The crude residue was dissolved in diethyl ether and washed with saturated NH_4Cl (aq). The organic layers were dried over $MgSO_4$, filtered, and concentrated in vacuo. Purification of the crude material by flash column chromatography yielded 3.18 g of the product as a yellow oil (99% yield): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.56 (d, J = 8.2 Hz, 1H), 7.50 (d J = 7.74 Hz, 1H), 7.22 (t, J = 7.74 Hz, 1H), 7.13 (t, J = 7.95 Hz, 1H), 1.13 (br s, 21H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 134.1, 132.6, 129.6, 127.0, 126.0, 125.9, 105.0, 96.4, 18.9, 11.6; IR (cm^{-1}) 2943, 2865, 2161, 1464, 1220, 1047, 908, 883, 834, 753, 678; MS (CI-isobutane) [MH^+] 295.5, 296.4 m/z

3,3-Diethyl-1-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)triaz-1-ene (6). Method A: 1,1-Diethyl-3-(4-iodophenyl)-triazene (1.931 g, 6.370 mmol, 1.00 equiv) was combined with bis(pinacolato)diboron (1.947 g, 7.667 mmol, 1.20 equiv), Cl_2Pd-(dppf) (0.143 g, 0.195 mmol, 0.03 equiv), and KOAc that had been dried under vacuum (1.875 g, 19.11 mmol, 3.00). Deoxygenated DMSO (52 mL) was added, and the reaction was heated to 80 °C and monitored by TLC (5% diethyl ether in hexanes). Upon consumption of triazene starting material, the reaction was diluted with water and extracted with EtOAc. The organic layers were combined, washed with satd NH_4Cl (aq), dried over $MgSO_4$, and concentrated in vacuo. Crude material was purified by flash chromatography using 5% diethyl ether in hexanes as the eluent to afford 1.931 g (74% yield) of the desired product as a white solid, mp 119−120 °C. The product can also be purified by filtration through a silica plug (10% ethyl acetate in hexanes) followed by recrystallization from 2-propanol: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.77 (d, J = 8.3 Hz, 2H), 7.40 (d, J = 8.3 Hz, 2H), 3.77 (q, J = 7.3, 4H), 1.35 (s, 12H), 1.27 (br t, J = 6.8 Hz, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 153.6, 135.5, 119.7, 83.5, 24.8; IR (cm^{-1}) 2979, 1602, 1391, 1351, 1320, 1139, 1087, 857, 655; HRMS (ESI) m/z calc'd for $C_{16}H_{26}BN_3O_2H$ ([M + H^+]) 304.2196, found 304.2194.

3,3-Diethyl-1-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)triaz-1-ene (6). Method B: 6 N HCl (27.10 mL, 162.51 mmol, 8.9 equiv) was added dropwise to a solution of 4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)aniline (4.035 g, 18.42 mmol, 1 equiv) in 62.40 mL of diethyl ether, 48.00 mL of tetrahydrofuran, and 9.60 mL of acetonitrile chilled to −5 °C in an ice−salt bath. A solution of $NaNO_2$ (4.3255 g, 62.69 mmol, 3.5 equiv) in 21.60 mL of water and 9.69 mL of acetonitrile was added dropwise, and the reaction was stirred at −5 °C for 30 min before being slowly transferred via cannula to a flask containing diethylamine (43.45 mL, 419.98 mmol, 23 equiv) and K_2CO_3 (12.640 g, 91.46 mmol, 5 equiv) in 79.20 mL of water and 174.00 mL of acetonitrile at 0 °C. The reaction was stirred for 45 min while being warmed to room temperature before being diluted with satd NaCl and extracted with Et_2O. The organics were washed with H_2O, dried over $MgSO_4$, filtered, and concentrated in vacuo to give a brown crystal. Crude material was purified by extraction with hexanes and concentration in vacuo to afford 4.7567 g (85% yield) of orange crystals: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.77 (d, J = 8.3 Hz, 2H), 7.40 (d, J = 8.3 Hz, 2H), 3.77 (q, J = 7.3, 4H), 1.35 (s, 12H), 1.27 (br t, J = 6.8 Hz, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 153.6, 135.5, 119.7, 83.5, 24.8; IR (cm^{-1}) 2979, 1602, 1391, 1351, 1320, 1139, 1087, 857, 655; HRMS (ESI) m/z calcd for $C_{16}H_{26}BN_3O_2H$ ([M + H^+]) 304.2196, found 304.2194.

3,3-Diethyl-1-(4-(2-(2-triisopropylsilyl)ethynyl)phenyl)-phenyl)triaz-1-ene (3a). (2-Bromophenylethynyl)triisopropylsilane (2.067 g, 6.13 mmol, 1.00 equiv) was added to a flask fitted with a sealed reflux condenser and charged with 3,3-diethyl-1-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)triaz-1-ene (2.787 g, 9.19 mmol, 1.5 equiv), powdered potassium phosphate (tribasic) (6.51 g, 30.65 mmol, 5 equiv), and $PdCl_2$(dppf) (0.150 g, 0.184 mmol, 0.03

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equiv). The flask was purged with nitrogen, and 50 mL of dexoygenated 1,2-dimethoxyethane was added via syringe. The reaction was stirred at reflux for 6−24 h, until TLC indicated completion (some side products run at the same R_f as the bromide, making exact assignment of completion difficult). The reaction mixture was then cooled, and the DME was removed in vacuo. The reaction mixture was then extracted with water and diethyl ether. The combined organic layers were washed with brine, dried over magnesium sulfate, filtered, and concentrated in vacuo. Purification was effected by flash column chromatography over neutral alumina with a mobile phase of 5% diethyl ether in hexanes to obtain 2.66 g of the biphenyl product as an orange oil (95% yield): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.59 (d, J = 8.3 Hz, 3H), 7.43 (d, J = 8.3 Hz, 2H), 7.38 (d, J = 7.8 Hz, 1H), 7.33 (t, J = 7.3 Hz, 1H), 7.23 (t, J = 7.8 Hz, 1H), 3.76 (q, J = 7.3 Hz, 4H), 1.27 (t, J = 7.3 Hz, 6H), 1.03 (s, 21H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 150.48, 144.0, 137.1, 133.9, 129.7, 129.3, 128.4, 126.5, 121.7, 119.9, 106.6, 93.9, 18.6, 11.3; IR (cm^{-1}) 2940, 2864, 2151, 1464, 1397, 1330, 1235, 1096, 883, 835, 761, 677; HRMS (ESI) m/z calcd for $C_{27}H_{39}N_3SiH$ ([M + H$^+$]) 434.2992, found 434.2991.

1-(4-iodophenyl)-2-(2-triisopropylsilyl)ethynylbenzene (9). Compound **3a** (1.855 g, 4.277 mmol, 1.00 equiv) was dissolved in 10 mL of methyl iodide in a sealable reaction flask, degassed, backfilled with nitrogen, sealed, and heated to 125 °C for 44 h. After cooling, the methyl iodide was removed by evaporation and the product purified by flash chromatography over silica with 5% diethyl ether in hexanes to isolate 1.950 g of a yellow oil (99% yield): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.70 (d, J = 8.3 Hz, 2H), 7.59 (d, J = 7.8 Hz, 1H), 7.27−7.37 (m, 5H), 1.01 (s, 21H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 143.1, 140.1, 137.0, 133.7, 131.2, 129.0, 128.5, 127.2, 121.9, 105.9, 94.6, 93.1, 18.5, 11.3; IR (cm^{-1}) 2940, 2863, 2152, 1469, 1386, 1000, 883, 820, 758, 677; HRMS (EI) m/z calcd for $C_{23}H_{29}ISi$ ([M$^+$]) 460.1083, found 460.1091.

2-Ethynyl-1-(4-iodophenyl)benzene (16a). TBAF (1 M) in THF (2.0 mL, 2.00 mmol, 4.35 equiv) was added to a solution of **9** (0.212 g, 0.460 mmol, 1.00 equiv) in 3 mL of THF. The reaction was stirred at room temperature and monitored by TLC. Upon disappearance of starting material, the reaction was concentrated to one-third of its original volume, diluted with 25 mL of H_2O, and extracted with diethyl ether (3 × 50 mL). The organic layers were combined, dried over $MgSO_4$, and concentrated in vacuo. The crude material was purified via flash chromatography using 5% diethyl ether in hexane to afford 0.134 g (96% yield) of a reddish oil: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.78 (d, J = 7.0 Hz, 2H), 7.64 (d, J = 7.5 Hz, 1H), 7.42 (t, J = 6.5 Hz, 1H), 7.37−7.34 (m, 4H), 3.08 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 143.1, 139.7, 137.1, 133.9, 131.1, 129.2, 129.0, 127.3, 120.3, 93.6, 80.6; IR (neat, cm^{-1}) 3274, 3061, 1583,1472; HRMS (ESI) m/z calcd for $C_{14}H_{10}I$ ([M + H$^+$]) 304.9827, found 304.9821.

Attempted Synthesis of Cyclotri(ethynylene)(biphenyl-2,4′-diyl) (1a). 16a (0.060 g, 0.197 mmol, 1.00 equiv), $Cl_2Pd(PPh_3)_2$ (0.007 g, 0.010 mmol, 0.05 equiv), and CuI (0.004 g, 0.020 mmol, 0.11 equiv) were combined and dissolved in 10.6 mL of THF and 0.2 mL of Et_3N. The reaction was stirred for 10 days at room temperature before being diluted with H_2O and extracted with Et_2O (3 × 20 mL). The organics were washed over brine, dried over $MgSO_4$, filtered, and concentrated in vacuo. The crude material was run through a flash column to afford a white solid mixture of cyclic and linear oligomers that resisted further purification.

3,3-Diethyl-1-(4-(2-ethynyl)phenyl)phenyltriaz-1-ene (19a). Compound **3a** (0.655 g, 1.510 mmol, 1 equiv) was dissolved in 5 mL of methanol. A solution of 1 M TBAF in THF (7.6 mL, 7.50 mmol, 4.97 equiv) was added; the reaction was then stirred at room temperature and monitored by TLC. Upon disappearance of starting material, the reaction was concentrated to one-third its original volume, diluted with 50 mL of H_2O, and extracted with diethyl ether (3 × 50 mL). The organic layers were combined, dried over $MgSO_4$, and concentrated in vacuo. The crude material was purified via flash chromatography using 5% diethyl ether in hexane to afford 0.376 g (90% yield) of a yellow oil: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.62 (d, J = 8.0 Hz, 1H), 7.59 (d, J = 8.2 Hz, 2H), 7.50 (d, J = 8.2 Hz, 2H), 7.41−7.40 Hz (m, 2H), 7.30−7.27 (m, 1H), 3.80 (q, J = 7.0 Hz, 4H), 3.06 (s, 1H), 1.30 (t, J = 7.0 Hz, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 150.6, 144.4, 136.9, 133.8, 129.7, 129.5, 128.9, 126.6, 120.3, 119.9, 83.3, 80.0. IR (cm^{-1}) 3284, 1330, 1229, 837; HRMS (photospray ionization) m/z calcd for $C_{18}H_{20}N_3$ ([M + H$^+$]) 278.1657, found 278.1664.

3,3-Diethyl-1-(4-(2-(2-(4-(2-(2-triisopropylsilyl)ethynyl)-phenyl)phenyl)ethynyl)phenyl)phenyltriaz-1-ene (20a). A 50 mL round-bottomed flask was charged with **9** (0.223 g, 0.484 mmol, 1.00 equiv), **19a** (0.180 g, 0.649 mmol, 1.34 equiv), and $Cl_2Pd(PPh_3)_2$ (0.020 g, 0.0285 mmol, 0.06 equiv) and flushed with N_2. To this 20 mL of deoxygenated THF/Et_3N (1:1 v/v) was added, and the reaction flask was sparged with N_2 for 5 min. CuI was added and the reaction stirred at 40 °C for 18 h. Upon completion, the reaction was diluted with 25 mL of H_2O and extracted with diethyl ether (3 × 25 mL). The organics were combined, washed with satd NH_4Cl, dried over $MgSO_4$, and concentrated in vacuo. The crude material was purified via flash chromatography using 5% diethyl ether in hexanes to give 0.226 g (77%) of the desired product as a yellow oil: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.72 (d, J = 8.5 Hz, 2H), 7.70 (d, J = 7.9 Hz, 1H), 7.62 (d, J = 7.8 Hz, 1H), 7.57−7.54 (m, 4H), 7.48 (d, J = 8.0 Hz, 1H), 7.43 (d, J = 7.9 Hz, 2H), 7.40 (d, J = 8.3 Hz, 1H), 7.38−7.27 (m, 4H), 3.82 (q, 7.2 Hz, 4H), 1.31 (t, J = 7.1 Hz, 6H), 1.05 (s, 21H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 150.6, 143.7, 143.5, 140.2, 137.2, 133.8, 133.0 130.9, 129.8, 129.5, 129.2, 129.1, 128.5, 127.1, 126.7, 122.5, 121.8, 121.4, 119.9, 106.0, 94.4, 92.3, 89.8, 18.55, 11.3; IR (cm^{-1}) 2942, 2860, 2356, 1460, 1334, 1229, 830; HRMS (MALDI) m/z calcd for $C_{41}H_{48}N_3Si$ ([M + H$^+$]) 610.3618, found 610.3616.

2-(2-(4-(2-(2-(4-Iodophenyl)phenyl)ethynyl)phenyl)phenyl)-ethynyltriisopropylsilane (21a). Compound **20a** (0.206 g, 0.338 mmol, 1.00 equiv) and 4 mL of MeI were placed in a sealed tube flask under an atmosphere of N_2. The reaction was heated to 125 °C for 18 h before being allowed to cool to room temperature. Excess MeI was allowed to evaporate. The residue was dissolved in 10 mL of CH_2Cl_2, washed with H_2O, dried over $MgSO_4$, and concentrated in vacuo. The crude product was purified via flash chromatography using 5% EtOAc in hexanes as the eluent and afforded 0.202 g (94% yield) of the desired product as a yellow oil: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.81 (d, J = 8.5 Hz, 2H), 7.69 (d, J = 7.7 Hz, 1H), 7.62 (d, J = 7.5 Hz, 1H), 7.59 (d, J = 8.0 Hz, 2H), 7.46 (d, J = 8.0 Hz, 2H), 7.41−7.38 (m, 2H), 7.37−7.35 (m, 5H), 7.32−7.29 (m, 1H) 1.05 (s, 21H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 143.3, 142.5, 140.5, 140.0, 137.0, 133.8, 133.0, 131.3, 130.9, 129.3, 129.2, 128.6, 128.5, 127.4, 127.2, 122.1, 121.8, 121.5, 106.0, 94.5, 93.4, 92.8, 89.1, 18.6, 11.3; IR (cm^{-1}) 2940, 2865, 2148, 1467, 1000, 756; HRMS (ESI) m/z calcd for $C_{37}H_{38}ISi$ ([M + H$^+$]) 637.1787, found 637.1777.

3,3-Diethyl-1-(4-(2-(2-(4-(2-(2-(4-(2-(2-triisopropylsilyl)-ethynyl)phenyl)phenyl)ethynyl)phenyl)phenyl)ethynyl)-phenyl)phenyltriaz-1-ene (22a). Compound **21a** (0.091 g, 0.142 mmol, 1.00 equiv), 3,3-diethyl-1-(2′-ethynylbiphenyl-4-yl)triaz-1-ene (0.035 g, 0.153 mmol, 1.08 equiv), $Cl_2Pd(PPh_3)_2$ (0.005 g, 0.007 mmol, 0.05 equiv), and CuI (0.002 g, 0.010 mmol, 0.07 equiv) were dissolved in 5 mL of deoxygenated THF and 5 mL of deoxygenated triethylamine. The solution was heated to 40 °C overnight before being diluted with satd NH_4Cl and extracted with EtOAc. The organics were washed with satd NH_4Cl, dried over $MgSO_4$, filtered, and concentrated in vacuo. The crude material was purified by flash chromatography using 10% EtOAc in hexanes to afford 0.075 g of the desired product as an off-white waxy solid (67% yield): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.72−7.66 (m, 5H), 7.62 (d, J = 7.5 Hz, 1H), 7.58−7.52 (m, 6H), 7.50−7.28 (m, 8H), 3.77 (q, J = 7.2 Hz, 4H), 1.28 (t, J = 7.2 Hz), 1.02 (s, 21H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 143.7, 143.3, 143.1, 140.4, 140.2, 137.2, 133.8, 133.0, 132.9, 131.0, 130.9, 129.85, 129.4, 129.3, 129.27, 128.18, 128.5, 127.2, 127.0, 126.6, 122.7, 122.2, 121.8, 121.5, 121.4, 119.0, 106.0, 94.4, 92.6, 92.2, 90.2, 89.3, 18.5, 11.2; IR (neat, cm^{-1}): 2932, 2860, 2154, 1473, 1096, 836, 744; HRMS (ESI) m/z calcd for $C_{55}H_{56}N_3Si$ ([M + H$^+$]) 786.4244, found 786.4257.

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2-(2-(4-(2-(2-(4-(2-(2-(4-Iodophenyl)phenyl)ethynyl)phenyl)-phenyl)ethynyl)phenyl)phenyl)ethynyltriisopropylsilane (23a). Compound **22a** (0.039 g, 0.0478 mmol, 1.0 equiv) was sealed in a flask with 1 mL of MeI and heated to 120 °C for 48 h. Excess MeI was allowed to evaporate after the reaction mixture cooled. The crude residue was purified by flash chromatography using 10% EtOAc in hexanes as eluent to afford 0.039 g of the desired product as a light yellow waxy solid (98% yield): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.81 (d, J = 8.0 Hz, 2H), 7.70 −7.67 (m, 4H), 7.61 (d, J = 8.0 Hz, 1H), 7.57 (d, J = 8.5 Hz, 2H), 7.47−7.35 (m, 14H), 7.32−7.27 (m, 1H) 1.05 (s, 21H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 143.3, 142.9, 140.6, 140.5, 140.0, 137.0, 133.8, 133.1, 133.0, 131.2, 130.9, 129.4, 129.4, 129.3, 129.2, 128.7, 128.5, 128.5, 127.4, 127.3, 127.1, 122.3, 122.2, 121.9, 121.6, 121.4, 106.04, 94.4, 93.4, 92.7, 92.6, 89.5, 89.3, 18.5, 11.2; IR (neat, cm^{-1}) 2802, 2847, 2356, 1726, 1457, 1273, 761; HRMS (ESI) m/z calcd for $C_{51}H_{46}ISi$ ([M + H$^+$]) 813.2413, found 813.2406.

2-(2-(4-(2-(2-(4-(2-(2-(4-Iodophenyl)phenyl)ethynyl)phenyl)-phenyl)ethynyl)phenyl)phenyl)ethyne (24a). Compound **23a** (0.039 g, 0.0463 mmol, 1.00 equiv) was dissolved in 0.25 mL of THF before 0.100 mL of 1 M TBAF in THF (0.100 mL, 0.100 mmol, 2.16 equiv) was added. After 5 min, the reaction showed no signs of starting material by TLC and was diluted with Et_2O. The organics were washed with satd NH_4Cl (aq), dried over $MgSO_4$, filtered, and rotovapped. The crude material was purified by flash chromatography using 5% EtOAc in hexanes to afford the desired compound which was used in the following reaction without further characterization.

Cyclotri(ethynylene)(biphenyl-2,4′-diyl) (1a). Compound **24a** (assuming 100% conversion in previous reaction: 0.032 g, 0.0463 mmol, 1.00 equiv) was dissolved in 1 mL of Et_3N and charged in a gastight syringe in a syringe pump. $Pd(dba)_2$ (0.039 g 0.068 mmol, 1.42 equiv), CuI (0.015 g, 0.079 mmol, 1.71 equiv), and PPh_3 (0.076 g, 0.290 mmol, 6.26 equiv) were dissolved in 11.6 mL of Et_3N. The iodoalkyne trimer was added at a rate of 0.1 mL per hour, and the reaction was allowed to stir for an additional 12 h after the addition was complete. The reaction was diluted with sat NH_4Cl (aq) and extracted with EtOAc. The organic phases were dried over $MgSO_4$, filtered, and concentrated in vacuo. The crude material was purified using 15% CH_2Cl_2 in hexanes to afford 11 mg (45% yield) of the desired macrocycle as a white solid: mp 282−291 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.75 (d, J = 8.4 Hz, 6H), 7.67 (d, J = 7.4 Hz, 3H), 7.50−7.48 (m, 9H), 7.45 (t, J = 7.8 Hz, 3H), 7.36 (t, J = 7.4 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 143.7, 140.9, 133.4, 131.5, 130.0, 129.9, 129.5, 128.1, 123.1, 122.2, 93.4, 90.3; HRMS (MALDI) m/z calcd for $C_{42}H_{24}$ ([M$^+$]) 528.1872, found 528.1864.

3,3-Diethyl-1-(4-(4-(2-(2-triisopropylsilyl)ethynyl)phenyl)-phenyl)phenyl)triaz-1-ene (4a). Compound **9** (1.923 g, 4.18 mmol, 1.00 equiv) was added to a flask with **6** (1.90 g, 6.27 mmol, 1.5 equiv), boronate, K_3PO_4 (4.52 g, 21.3 mmol, 5.1 equiv), and $PdCl_2$(dppf) (0.10 g, 0.125 mmol, 0.03 equiv). The flask was purged with nitrogen and 30 mL of deoxygenated DME added. The reaction was refluxed for 20 h and cooled to room temperature, the solvent was removed in vacuo, and the organic products were extracted from water with diethyl ether. The combined organic layers were washed with brine, dried over magnesium sulfate, filtered, and concentrated in vacuo. Purification over neutral alumina with 25% methylene chloride in hexanes afforded 1.38 g of the product as a pale yellow solid: mp 110−111 °C (65% yield);. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.58−7.65 (m, 7H), 7.51 (d, J = 8.3 Hz, 2H), 7.36−4.42 (m, 2H), 7.29 (t, J = 7.3 Hz, 1H), 3.79 (q, J = 7.3 Hz, 4H), 1.29 (t, J = 7.3 Hz, 6H), 1.01 (s, 21H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 150.6, 144.0, 140.0, 139.1, 137.7, 133.7, 129.7, 129.2, 128.4, 127.5, 126.8, 126.4, 122.0, 120.8, 106.4, 94.1, 18.6, 11.3; IR (cm^{-1}) 2940, 2864, 2361, 2151, 1463, 1329, 1233, 1092, 995, 882, 823, 764, 674, 639; HRMS (ESI) m/z calcd for $C_{33}H_{43}N_3SiH$ ([M + H$^+$]) 510.3305, found 510.3309.

1-(4-(4-Iodophenyl)phenyl)-2-(2-triisopropylsilyl)-ethynylbenzene (18b). Compound **4a** (0.096 g, 0.188 mmol, 1 equiv) was dissolved in 2.5 mL of methyl iodide in a sealable reaction flask, degassed, backfilled with nitrogen, sealed, and heated to 125 °C for 40 h. After cooling, the methyl iodide was removed by evaporation and the product purified by flash chromatography over neutral alumina with 50% methylene chloride in hexanes to afford 0.092 mg of the product as a yellow solid: mp 81−83 °C (91% yield); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.77 (d, J = 8.3 Hz, 2H), 7.64 (d, J = 8.3 Hz, 2H), 7.61 (d, J = 7.8 Hz, 1H), 7.54 (d, J = 8.3 Hz, 2H), 7.27−7.38 (m, 5H), 1.00 (s, 21H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 143.7, 140.5, 140.1, 138.9, 137.9, 137.8, 129.9, 128.91, 128.87, 128.5, 127.0, 126.4, 122.0, 106.2, 95.2, 93.0, 18.6, 11.3. IR (cm^{-1}) 2939, 2862, 2152, 1473, 1384, 1064, 1000, 882, 837, 812, 578, 662; HRMS (photospray ionization) m/z calcd for $C_{29}H_{33}SiI$ ([M$^+$]) 536.1396, found 536.1383.

1-(4-(4-Iodophenyl)phenyl)-2-ethynylbenzene (17a). Compound **18b** (0.229 g, 0.427 mmol, 1.00 equiv) was stirred with TBAF (1 M in THF) (5.55 mL, 5.55 mmol, 13 equiv) with 4 mL of THF and 1 mL of methanol for 3 days at room temperature. The solvent was removed in vacuo, and the organic products were extracted from water with methylene chloride. The combined organic layers were dried over magnesium sulfate, filtered, and concentrated to produce 0.127 g of an orange solid (78% yield): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.78 (d, J = 8.6 Hz, 2H), 7.68 (d, J = 8.1 Hz, 2H), 7.61−7.65 (m, 3H), 7.38−7.43 (m, 4H), 7.30−7.34 (m, 1H), 3.08 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 143.7, 140.2, 139.6, 139.1, 137.8, 134.0, 129.7, 129.5, 129.0, 128.9, 127.1, 126.4, 120.3, 93.1, 83.0, 80.4; HRMS (photospray ionization) m/z calcd for $C_{20}H_{14}I$ ([M + H$^+$]) 381.0140, found 381.0151

3,3-Diethyl-1-(4-(4-(2-ethynyl)phenyl)phenyl)phenyl)triaz-1-ene (19b). Compound **4a** (0.240 g, 0.471 mmol, 1.00 equiv) was stirred with TBAF (1 M in THF) (1.41 mL, 1.41 mmol, 3.0 equiv) with 2.0 mL of THF and 6 drops of methanol for 40 h at room temperature. The organic products were extracted from water with methylene chloride, dried over magnesium sulfate, filtered, and concentrated in vacuo. Purification over neutral alumina with 50% methylene chloride in hexanes yielded 0.152 g of 1,1-diethyl-3-(4-(4-(2-ethynyl)phenyl)phenyl)phenyl)triaz-1-ene as an orange solid: mp 117−119 °C (91% yield); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.56−7.68 (m, 7H), 7.51 (d, J = 8.3 Hz, 2H), 7.40 (m, 2H), 7.29 (m, 1H), 3.77 (q, J = 7.3 Hz, 4H), 3.07 (s, 1H), 1.26 (br t, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 150.6, 144.0, 140.1, 138.7, 137.2, 133.9, 129.6, 129.5, 129.0, 127.4, 126.9, 126.8, 126.3, 120.8, 120.3, 83.2, 80.3; IR (cm^{-1}) 3280, 1471, 1427, 1324, 1233, 1098, 1003, 828, 761, 659, 634; HRMS (APCI) m/z calcd for $C_{24}H_{24}N_3$ ([M$^+$]) 354.1970, found 354.1965.

3,3-Diethyl-1-(4-(4-(2-(2-(4-(4-(2-(2-(triisopropylsilyl)-ethynyl)phenyl)phenyl)phenyl)ethynyl)phenyl)phenyl)-phenyl)triaz-1-ene (20b). Compounds **18b** (0.100 g, 0.186 mmol, 1.00 equiv) and **19b** (0.069 g, 0.196 mmol, 1.05 equiv) were dissolved with CuI (0.001 g, 0.0056 mmol, 0.03 equiv) and $PdCl_2(Ph_3P)_2$ (0.006 g, 0.009 mmol, 0.05 equiv) in 0.5 mL of deoxygenated triethylamine and 2.0 mL of deoxygenated THF. The reaction was stirred at room temperature, periodically reloading solvent and palladium catalyst as needed over the course of several days. When TLC failed to show any further conversion, the solvents were removed in vacuo, and the products were extracted from saturated ammonium chloride solution with methylene chloride. The combined organic layers were dried over sodium sulfate, filtered, and concentrated. Flash chromatography over neutral alumina provided 0.108 g (76% yield) of **20b** as a yellow oil as well as 13% recovery of unreacted iodide **18b**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.77 (d, J = 8.3 Hz, 2H), 7.73 (d, J = 8.3 Hz, 2H), 7.51−7.69 (m, 12H), 7.48 (d, J = 7.8 Hz, 1H), 7.33−7.45 (m, 6H), 7.28 (t, J = 7.3 Hz, 1H), 3.78 (q, J = 6.8 Hz, 4H), 1.27 (br t, 6H), 1.00 (s, 21H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 150.7, 143.7, 143.5, 140.1, 139.9, 139.2, 139.1, 137.3, 133.7, 133.0, 131.8, 129.8, 129.7, 129.4, 129.2, 128.8, 128.65, 128.55, 128.4, 127.5, 127.0, 126.9, 126.5, 126.3, 122.3, 120.8, 106.2, 94.2, 92.3, 90.2, 18.5, 11.3; IR (cm^{-1}) 3280, 2978, 2932, 2360, 1471, 1427, 1390, 1322, 1233, 1098, 828, 761, 698, 659; HRMS (EI) m/z calcd for $C_{53}H_{55}N_3Si$ ([M$^+$]) 761.4165, found 761.4160.

2-(2-(4-(4-(2-(2-(4-(4-Iodophenyl)phenyl)phenyl)ethynyl)-phenyl)phenyl)phenyl)ethynyltriisopropylsilane (21b). Compound **20b** (0.096 g, 0.126 mmol, 1.00 equiv) was dissolved in 2.5 mL of methyl iodide in a sealable reaction flask, degassed, backfilled with nitrogen, sealed, and heated to 125 °C for 40 h. After cooling, the methyl iodide was removed by evaporation and the product purified by flash chromatography over silica with 25% methylene chloride in

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hexanes to afford 0.065 mg of a white, crystalline solid: mp 109−112 °C (86% yield); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.78 (m, 4H), 7.51−7.69 (m, 10H), 7.26−746 (m, 10H), 1.01 (s, 21H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 143.7, 143.1, 140.7, 140.3, 140.0, 139.1, 139.0, 137.9, 137.8, 133.7, 133.0, 131.8, 129.9, 129.8, 129.4, 129.2, 128.93, 128.86, 128.5, 127.2, 127.0, 126.9, 126.5, 126.3, 122.2, 122.0, 121.6, 106.3, 94.2, 93.1, 92.4, 90.1, 18.6, 11.3; IR (cm^{-1}) 2939, 2861, 2151, 1473, 1384, 1064, 1000, 882, 813, 758, 664; HRMS m/z calcd for $C_{37}H_{38}ISi$ ([MH^+]) 637.1782, found 637.1777.

3,3-Diethyl-1-(4-(4-(2-(2-(4-(4-(2-(2-(4-(4-(2-(2-(triisopropylsilyl)ethynyl)phenyl)phenyl)phenyl)ethynyl)-phenyl)phenyl)phenyl)ethynyl)phenyl)phenyl)triaz-1-ene (22b). Compound **21b** (0.086 g, 0.109 mmol, 1.00 equiv) was dissolved in 0.5 mL of deoxygenated THF and 0.2 mL of deoxygenated triethylamine with **19b** (0.042 g, 0.120 mmol, 1.10 equiv), $PdCl_2(Ph_3P)_2$ (0.006 g, 0.0087 mmol, 0.08 equiv), and CuI (0.0006 g, 0.0033 mmol, 0.03 equiv). The reaction was stirred at room temperature for 24 h, the solvent was removed in vacuo, and the organic products were extracted from saturated ammonium chloride solution with methylene chloride. The combined organic layers were dried over sodium sulfate, filtered, and concentrated. Four rounds of purification by flash column chromatography over alumina with 40% methylene chloride in hexanes yielded 0.067 g of trimer **22b** as a white, crystalline solid: mp 167−171 °C (61% yield); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.22−7.79 (m, 36H), 3.75 (q, J = 7.3 Hz, 4H), 1.25 (br t, 6H), 1.00 (s, 21H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 150.6, 143.6, 143.4, 143.1, 140.8, 140.6, 140.3, 140.2, 140.1, 139.8, 139.3, 139.1, 139.0, 137.3, 133.6, 133.1, 133.0, 132.9, 131.8, 131.7, 129.8, 129.7, 129.4, 129.1, 128.7, 128.5, 128.4, 127.5, 127.4, 127.1, 127.0, 126.8, 126.4, 126.2, 122.4, 122.3, 122.2, 121.9, 121.5, 120.8, 106.2, 94.1, 92.3, 92.3, 90.3, 90.2, 90.0, 18.5, 11.2; IR (cm^{-1}) 2929, 2862, 1474, 1440, 1343, 1233, 1091, 1003, 882, 821, 760, 665, 553; HRMS (ESI) m/z calcd for $C_{69}H_{57}N_2Si$ ([$M - (C_4H_{10}N)^+$]) 941.4291, found 941.4255.

2-(2-(4-(4-(2-(2-(4-(4-(2-(2-(4-(4-Iodophenyl)phenyl)phenyl)-ethynyl)phenyl)phenyl)phenyl)ethynyl)phenyl)phenyl)-phenyl)ethynyltriisopropylsilane (23b). Compound **22b** (0.067 g, 0.066 mmol, 1.00 equiv) was dissolved in 2.5 mL of methyl iodide in a sealable reaction flask, degassed, backfilled with nitrogen, sealed, and heated to 125 °C for 40 h. After cooling, the methyl iodide was removed by evaporation. The residue was filtered through a silica plug with methylene chloride to provide 0.068 g of the product iodide (99% yield) as a colorless waxy solid, which was reacted without further purification since poor solubility precluded further chromatography: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.78 (d, J = 8.8 Hz, 6H), 7.52−7.70 (m, 15H), 7.35−7.48 (m, 14H), 7.29 (m, 1H), 0.99 (s, 21H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 143.7, 143.1, 140.7, 140.5, 140.3, 139.9, 139.2, 139.1, 139.0, 137.9, 133.7, 133.0, 131.8, 131.7, 129.9, 129.9, 129.8, 129.4, 128.9, 128.6, 127.2, 126.9, 126.8, 126.4, 126.4, 126.3, 122.3, 122.2, 122.0, 121.5, 106.2, 94.1, 93.1, 92.3, 90.1, 18.6, 11.3; IR (cm^{-1}) 2921, 2860, 2360, 2342, 2155, 1473, 1441, 1384, 1000, 822, 814, 761, 667.

Cyclotri(ethynylene)(*p*-terphenyl-2,4″-diyl) (2a). *Method A (Sonogashira Cyclization).* Compound **23b** (0.070 g, 0.067 mmol, 1.00 equiv) was stirred with 4.0 mL of THF, 6 drops of methanol, and TBAF (1 M in THF) (0.20 mL, 0.20 mmol, 3.0 equiv) for 48 h, during which time a precipitate was observed in the reaction. Extraction from water with methylene chloride, drying of the organic layers with magnesium sulfate, filtration, and concentration in vacuo yielded 0.53 g of crude trimer (90% yield), which was used in the next step without further purification or characterization. The crude linear iodoarylethyne trimer was dissolved in 10 mL of deoxygenated THF and placed in a syringe pump. 1.5 equiv of $Pd(dba)_2$ (0.046 g, 0.080 mmol, 1.5 equiv), 1.3 equiv of CuI (0.013 g, 0.068 mmol, 1.3 equiv), and 5.9 equiv of triphenylphosphine (0.082 g, 0.313 mmol, 5.9 equiv) were dissolved in 5.0 mL of deoxygenated triethylamine and 10 mL of deoxygenated THF. The catalyst solution was heated to reflux under nitrogen, and the trimer solution was added at 0.6 mL/h, followed by continued refluxing overnight. The solvents were then removed in vacuo and the organic products extracted from saturated ammonium chloride solution with methylene chloride, washed with water and brine, and concentrated. The solids were then filtered with Whatman quantitative filter paper (1 μm pore size) and washed with methylene chloride; centrifugation in methylene chloride yielded 0.008 g (21% yield) of a colorless solid floating on top of the supernatant. No melting transition was observed below 300 °C: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.81 (d, J = 8.3 Hz, 2H), 7.70 (d, J = 7.8 Hz, 2H), 7.69 (d, J = 6.3 Hz, 1H)7.64 (d, J = 8.3 Hz, 2H), 7.52 (d, J = 7.8 Hz, 1H), 7.49 (d, J = 7.8 Hz, 2H), 7.44 (t, J = 6.8 Hz, 1H), 7.37 (t, J = 7.3 Hz, 1H); ^{1}H NMR (500 MHz, $C_6D_4Cl_2$) δ 7.82 (d, J = 8.0 Hz, 6H), 7.70 (d, J = 7.5 Hz, 3H), 7.67 (d, J = 8.0 Hz, 6H), 7.58 (d, J = 8.5 Hz, 6H), 7.51 (d, J = 8.5 Hz, 6H), 7.47 (d, J = 7.5 Hz, 3H), 7.36 (t, J = 7.3 Hz, 3H), 7.29 (t, J = 7.3 Hz, 3H); COSY (500 MHz, *o*-$C_6D_4Cl_2$) δ 7.82 × 7.67, 7.70 × 7.29, 7.58 × 7.51, 7.47 × 7.36, 7.36 × 7.29; HMQC (500 MHz, *o*-$C_6D_4Cl_2$) δ 7.82 × 130.3, 7.70 × 133.0, 7.68 × 126.6, 7.59 × 127.1, 7.52 × 132.0, 7.47 × 129.5, 7.36 × 128.9, 7.29 × 127.5; HMBC (*o*-500 MHz, $C_6D_4Cl_2$, selected peaks) δ 7.82 × 143.3, 7.82 × 139.5, 7.70 × 143.3, 7.70 × 90.7, 7.68 × 140.4, 7.68 × 139.8, 7.59 × 139.5, 7.59 × 122.6, 7.52 × 140.4, 7.52 × 92.7, 7.47 × 139.8, 7.47 × 121.6, 7.36 × 143.3, 7.29 × 121.6; IR (cm^{-1}) 3056, 3031, 2217, 1922, 1498, 1473, 1442, 1395, 1104, 1004, 819, 758, 733, 703; HRMS (MALDI) m/z calcd for $C_{60}H_{36}$ ([M^+]) 756.2817, found 756.2822.

Method B (Sonogashira Cyclotrimerization). Compound **17a** (0.053 g, 0.139 mmol, 1.00 equiv) was dissolved in 0.8 mL of THF and 0.1 mL of triethylamine (both solvents distilled and deoxygenated) with CuI (0.3 mg, 0.0016 mmol, 0.01 equiv) and $PdCl_2(Ph_3P)_2$ (0.005 g, 0.007 mmol, 0.05 equiv) and stirred at room temperature. The reaction was monitored by TLC and periodically reloaded with catalysts and solvent until TLC failed to indicate a significant change over a 24 h period. The solid precipitate formed was filtered from solution and washed with methylene chloride to yield a solid: ^{1}H NMR (500 MHz, $C_6D_4Cl_2$) δ 7.80 (d), 7.26−7.7.2 (m), 3.07 (s).

Method C (Sonogashira Cyclotrimerization). Compound **17a** (0.053 g, 0.139 mmol, 1.00 equiv) was dissolved in 7.5 mL of THF and 0.1 mL of triethylamine (both solvents were distilled and deoxygenated) with CuI (0.3 mg, 0.0016 mmol, 0.01 equiv) and $Pd(Ph_3P)_4$ (0.005 g, 0.007 mmol, 0.05 equiv) and stirred at room temperature. The reaction was monitored by TLC and periodically reloaded with catalysts and solvent until TLC failed to indicate a significant change over a 24 h period. The solid precipitate formed was filtered from solution and washed with methylene chloride to yield 20% yield of macrocycle **2a** with slight contamination evidenced by: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.78 (d, J = 7.8 Hz), 7.62 (d, J = 7.8 Hz).

2-Iodo-4-*n*-octylaniline (11). $[BnN(CH_3)_3]\cdot ICl_2$ (3.535 g, 10.15 mmol, 1.05 equiv) and $CaCO_3$ (3.141 g, 31.38 mmol, 3.21 equiv) were added to a stirred solution of 4-*n*-octylaniline (1.995 g, 9.72 mmol, 1 equiv) in 80 mL of dry CH_2Cl_2 and 35 mL of anhydrous MeOH. The reaction stirred at room temperature for 2 h prior to being vacuum filtered through a pad of Celite. The filtrate was washed with satd Na_2SO_4 (40 mL) followed by satd NH_4Cl (40 mL). The organics were dried over $MgSO_4$, filtered, and concentrated in vacuo to give a brown oil that was purified by chromatography (10% ethyl acetate in hexane on silica) to give 3.08 g of a brown oil (96% yield). This product was used in subsequent reactions without further purification: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.43 (d, J = 1.9 Hz, 1H), 6.93 (dd, J = 1.9, 8.3 Hz, 1H), 6.65 (d, J = 8.3 Hz, 1H), 3.93 (br s, 2H), 2.44 (t, J = 7.3 Hz, 2H), 1.52 (m, 2H), 1.23−1.31 (m, 10H), 0.88 (t, J = 7.3 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 144.4, 138.4, 134.8, 129.4, 114.6, 84.4, 34.5, 31.8, 31.6, 29.5, 29.4, 29.2, 22.6, 14.0; IR (cm^{-1}) 3407, 3317, 2954, 2916, 2850, 1617, 1496, 1467, 1405, 1306, 1152, 1028, 819, 665; HRMS (MALDI) m/z calcd for $C_{14}H_{22}NI$ ([$M + H]^+$) 332.0870, found 332.0870.

3,3-Diethyl-1-(2-iodo-4-octyl)phenyltriaz-1-ene (12). HCl (1.1 mL, 13.2 mmol, 7.8 equiv) was added dropwise to a solution of **11** (0.558 g, 1.68 mmol, 1 equiv) in 10.0 mL of tetrahydrofuran and 0.6 mL of acetonitrile chilled to −5 °C in an ice−salt bath. A solution of $NaNO_2$ (0.415 g, 6.02 mmol, 3.58 equiv) in 1.8 mL of water and 0.8 mL acetonitrile was added dropwise, and the reaction was stirred at −5 °C for 30 min before being slowly transferred via cannula to a flask

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containing diethylamine (3.5 mL, 42.5 mmol, 25 equiv) and K_2CO_3 (2.32 g, 16.8 mmol, 10 equiv) in 7.0 mL of water at 0 °C. The reaction was stirred for 45 min while warming to room temperature before being diluted with satd NaCl and extracted with Et_2O. The organics were washed with H_2O, dried over $MgSO_4$, filtered, and concentrated in vacuo. Crude material was purified by flash chromatography using hexanes to afford 0.686 g of an orange oil (98% yield): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.66 (d, J = 1.9 Hz, 1H), 7.25 (d, J = 8.6 Hz, 1H), 7.08 (dd, J = 1.9, 8.2 Hz, 1H), 3.78 (q, J = 7.2 Hz, 4H), 2.52 (t, J = 7.5 Hz, 2H), 1.57 (m, 2H), 1.23−1.33 (m, 12H), 0.88 (t, J = 6.4 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 148.3, 141.5, 138.6, 128.8, 117.1, 96.5, 34.9, 31.8, 31.4, 29.4, 29.22, 29.16, 22.6, 14.1; IR (cm^{-1}) 2923, 2853, 1463, 1432, 1389, 1331, 1266, 1234, 1202, 1105; HRMS (MALDI) m/z calcd for $C_{18}H_{30}N_3I$ ([M + H]$^+$) 416.1563, found 416.1558.

3,3-Diethyl-1-(2-(2-triisopropylsilyl)ethynyl-4-octyl)-phenyltriaz-1-ene (13). Compound **12** (0.250 g, 0.602 mmol, 1.00 equiv), (triisopropylsilyl)acetylene (0.21 mL, 0.934 mmol, 1.55 equiv), $Cl_2Pd(PPh_3)_2$ (0.0227 g, 0.0323 mmol, 0.054 equiv), and CuI (0.0039 g, 0.0204 mmol, 0.034 equiv) were combined in a 50 mL round-bottomed flask and purged with N_2. Ten milliliters of deoxygenated THF and 10 mL of deoxygenated Et_3N were added by syringe, and the reaction was stirred at 40 °C for 18 h. The reaction mixture was then diluted with H_2O (50 mL) and extracted with EtOAc (3 × 50 mL). The combined organic phases were washed with satd NH_4Cl (2 × 50 mL), dried over $MgSO_4$, filtered, and concentrated in vacuo. The crude material was purified by flash chromatography using 5% Et_2O in hexanes to give 0.256 g of a brown/orange oil (92% yield): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.34 (d, J = 8.3 Hz, 1H), 7.28 (d, J = 1.9 Hz, 1H), 3.77 (q, J = 7.3 Hz, 4H), 2.53 (t, J = 7.3 Hz, 2H), 1.55−1.60 (m, 2H), 1.22−1.32 (m, 18H), 1.13 (s, 21H), 0.88 (t, J = 6.3 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 150.5, 139.2, 133.5, 129.2, 118.2, 116.5, 105.9, 35.2, 31.9, 31.5, 29.5, 29.2, 22.7, 18.8, 14.1, 11.4; IR (cm^{-1}) 2925, 2862, 2147, 1463, 1398, 1330, 1242, 1201, 1092, 883; HRMS (MALDI) m/z calcd for $C_{29}H_{51}N_3Si$ ([M + H]$^+$) 470.3930, found 470.3917.

4-Octyl-2-(2-triisopropylsilyl)ethynyliodobenzene (14). Compound **13** (0.485 g, 1.032 mmol, 1 equiv) was dissolved in 5 mL of MeI in a sealed tube. The reaction flask was evacuated and backfilled with N_2 before being sealed and heated to 125 °C for 20 h. The reaction was cooled to room temperature before excess MeI was evaporated by N_2 bubbling. The crude residue was purified by flash chromatography using hexanes as eluent to afford 0.51 g of a yellow oil (99% yield): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.70 (d, J = 8.2 Hz, 1H), 7.29 (d, J = 2.1 Hz, 1H), 6.81 (dd, J = 2.1, 8.0 Hz, 1H), 2.51 (t, J = 7.7 Hz, 2H), 1.23−1.31 (m, 10H), 1.16 (s, 21H), 0.88 (t, J = 7.1, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 142.8, 138.4, 133.2, 129.9, 129.8, 108.2, 97.1, 94.6, 31.9, 31.2, 29.4, 29.2, 22.6, 18.7, 14.1, 11.4; IR (cm^{-1}) 2923, 2862, 2366, 2150, 1459, 1394, 1017, 883, 765, 735, 665; HRMS (MALDI) m/z calcd for $C_{25}H_{41}ISi$ ([M + H]$^+$) 497.2100, found 497.2098.

3,3-Diethyl-1-(4-(2-(2-triisopropylsilyl)ethynyl)-4-octylphenyl)phenyltriaz-1-ene (3b). Boronic ester **6** (0.620 g, 2.04 mmol, 2.00 equiv) and **14** (0.508 g, 1.02 mmol, 1.00 equiv) were dissolved in deoxygenated DME and further deoxygenated for 10 min by N_2 bubbling. To this solution were added $Cl_2Pd(dppf)$ (0.061 g, 0.0834 mmol, 0.082 equiv) and dry K_3PO_4 (1.045 g, 4.922 mmol, 4.83 equiv), and the reaction was deoxygenated by N_2 bubbling for an additional 10 min. The reaction was heated to 90 °C for 20 h before being cooled to room temperature and diluted with H_2O. The reaction was extracted with Et_2O (3 × 30 mL), and organics were washed with satd NaCl before being dried over $MgSO_4$, filtered, and concentrated in vacuo. Purification by flash chromatography over neutral alumina with 5% diethyl ether in hexanes gave 0.56 g of a yellow oil (82% yield): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.58 (d, J = 8.3 Hz, 2H), 7.41 (d, J = 8.8 Hz, 3H), 7.29 (d, J = 7.8 Hz, 1H), 7.16 (d, J = 7.8 Hz, 1H), 3.77 (q, J = 7.0 Hz, 4H), 2.60 (t, J = 7.8 Hz, 2H), 1.64 (m, 2H), 1.25−1.38 (m, 16 H), 1.03 (s, 21H), 0.88 (t, J = 6.8 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 150.3, 141.5, 141.3, 137.2, 133.7, 129.8, 129.2, 128.8, 121.5, 119.9, 106.9, 93.2, 35.3, 31.9, 31.4, 29.5, 29.4, 29.3, 22.7, 18.7, 14.1, 11.3; IR (cm^{-1}) 2926, 2862, 2363, 2341, 2146, 1463, 1380, 1234, 1095, 908, 883, 827, 734, 666; HRMS (ESI) m/z calcd for $C_{35}H_{55}N_3SiH$ ([M + H$^+$]) 546.4244, found 546.4235.

4-Octyl-1-(4-iodophenyl)-2-(2-triisopropylsilyl)-ethynylbenzene (15). Compound **3b** (0.349 g, 0.639 mmol, 1.00 equiv) was dissolved in 5 mL of MeI in a sealed tube. The flask was evacuated and purged with N_2 before being sealed and heated to 125 °C for 44 h. The reaction was cooled to room temperature before excess MeI was removed by N_2 bubbling. The crude residue was purified by flash chromatography using 5% Et_2O in hexanes to afford 0.336 g of the desired compound as a colorless oil (92% yield): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.69 (d, J = 8.3 Hz, 2H), 7.39 (s, 1H), 7.30 (d, J = 8.8 Hz, 2H), 7.21 (d, J = 7.8 Hz, 1H), 7.17 (dd, J = 7.8, 1.5 Hz, 1H), 2.60 (t, J = 7.8 Hz, 2H), 1.63 (m, 2H), 1.25−1.37 (m, 10H), 1.01 (s, 21H), 0.88 (t, J = 7.3 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 142.3, 140.5, 140.1, 136.9, 133.5, 131.3, 128.9, 128.8, 106.2, 93.9, 92.8, 35.4, 31.9, 31.4, 29.4, 29.3, 29.2, 22.7, 18.6, 14.1, 11.3; IR (cm^{-1}) 2924, 2861, 2366, 2333, 2145, 1464, 1385, 1000, 883, 816, 667; HRMS (ESI) m/z calcd for $C_{31}H_{45}SiI$ ([M$^+$]) 572.2335, found 572.2344.

4-Octyl-1-(4-iodophenyl)-2-ethynylbenzene (16b). Compound **15** (0.299 g, 0.522 mmol, 1.00 equiv) was dissolved in 2 mL of THF before 0.63 mL of 1 M TBAF (in THF containing 5% H_2O) was added. TLC showed disappearance of starting material within 5 min. The reaction was then concentrated, and the residue was dissolved in Et_2O and washed with satd NH_4Cl. The organic phase was dried over $MgSO_4$, filtered, and concentrated in vacuo. The crude material was purified by flash chromatography using hexanes to afford 0.22 g of a colorless oil (74% yield): ^{1}H NMR: ($CDCl_3$, 500 MHz) δ 7.90 (d, J = 7.0 Hz, 2H), 7.49 (s, 1H), 7.37 (d, J = 7.0 Hz, 2H), 7.28−7.24 (m, 2H), 3.07 (s, 1H), 2.64 (t, J = 7.8 Hz, 2H), 1.68 (m, 2H), 1.25−1.37 (m, 10H), 0.88 (t, J = 7.3 Hz, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 142.3, 140.6, 139.7, 137.1, 133.9, 131.1, 129.4, 129.2, 120.0, 93.4, 83.2, 80.2, 77.1, 35.3, 31.9, 31.2, 29.5, 29.3, 29.2, 22.7, 14.2; IR (neat, cm^{-1}) 3293, 1479.7, 1384, 1007, 814; HRMS (ESI) m/z calcd for $C_{22}H_{25}IH$ ([M + H$^+$]) 417.1071, found 417.1090.

Cyclooligo(ethynylene)(4-octylbiphenyl-2,4′-diyl) (1b, 1c). Compound **16b** (0.031 g, 0.074 mmol, 1.00 equiv) was dissolved in 2.6 mL of 1:1 $PhCH_3/Et_3N$. $Cl_2Pd(PPh_3)_2$ (0.002 g, 0.0028 mmol, 0.038 equiv) and CuI (0.001 g, 0.005 mmol, 0.07 equiv) were added neat. The reaction was stirred at room temperature for 2 h and monitored by TLC (10% EtOAc in hexanes). It was then diluted with H_2O and extracted with Et_2O (3 × 20 mL), and the combined organic phases were washed with satd NaCl before being dried over $MgSO_4$, filtered, and concentrated in vacuo. Purification required 5× silica gel flash columns using 5% CH_2Cl_2 in hexanes to afford 2.5 mg of the cyclotrimer **1b** and 1.2 mg of the cyclotetramer **1c**, both as white waxy solids (12% and 6% yield, respectively).

Cyclic trimer **1b**: ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.73 (d, J = 6.5 Hz, 6H), 7.48 (s, 3H), 7.47 (d, J = 8.0 Hz, 6H), 7.39 (d, J = 8.5 Hz, 3H), 7.23 (d, J = 8.0 Hz, 3H), 2.65 (t, J = 7.7 Hz, 6H), 1.67 (quintet, J = 7.5 Hz, 6H), 1.40−1.26 (m, 30H), 0.89 (t, J = 6.5 Hz, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 140.55, 140.24, 137.32, 132.75, 130.87, 129.42, 129.35, 129.20, 122.35, 121.33, 92.48, 90.02, 35.56, 32.06, 31.46, 29.64, 29.49, 29.42, 22.84, 14.27; HRMS (MALDI) m/z calcd for $C_{66}H_{72}$ ([M$^+$]) 864.5634, found 864.5624.

Cyclic tetramer **1c**: ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.65 (d, J = 8.5 Hz, 6H), 7.49 (d, J = 1.5 Hz, 3H), 7.45 (d, J = 8.5 Hz, 6H), 7.31 (d, J = 8.5 Hz, 3H), 7.20 (dd, J = 8.0 Hz, 1.5 Hz, 3H), 2.64 (t, J = 7.5 Hz, 3H), 1.67 (quintet, J = 7.0 Hz, 6H) 1.40−1.26 (m, 30H), 0.88 (t, J = 7.0 Hz, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 140.56, 137.14, 133.21, 131.40, 129.68, 129.47, 129.25, 122.39, 121.35, 92.20, 89.88, 35.56, 32.05, 31.44, 29.63, 29.52, 29.41, 22.83, 14.27; HRMS (MALDI) m/z calcd for $C_{88}H_{96}$ ([M$^+$]) 1152.75065, found 1152.7470.

3,3-Diethyl-3-(4-(4-(2-(2-triisopropylsilyl)ethynyl-4-octyl)-phenyl)phenyl)phenyltriaz-1-ene (4b). Compound **15** (0.276 g, 0.482 mmol, 1.00 equiv) was added to a round-bottomed flask fitted with a sealed reflux condenser, as were **6** (0.248 g, 0.819 mmol, 1.7 equiv), tribasic potassium phosphate (0.563 g, 2.65 mmol, 5.5 equiv), and $PdCl_2(dppf)$ (0.018 g, 0.022 mmol, 0.045 equiv). The flask was purged with nitrogen and 4.0 mL deoxygenated 1,2-dimethoxyethane

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added. The reaction was heated to reflux for 5 h and cooled to room temperature and the solvent removed under vacuum. The product was extracted from water with ether, and the combined organic layers washed with brine, dried over magnesium sulfate, filtered, and concentrated. Purification by flash column chromatography over neutral alumina with 25% methylene chloride in hexanes afforded 0.204 g of a dark yellow oil (68% yield): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.63 (d, J = 8.4 Hz, 2H), 7.57−7.61 (m, 4H), 7.50 (d, J = 8.8 Hz, 2H), 7.42 (d, J = 1.5 Hz, 1H), 7.31 (d, J = 8.0 Hz, 1H), 7.19 (dd, J = 1.7, 7.7 Hz, 1H), 3.78 (q, J = 7.1 Hz, 4H), 2.61 (t, J = 7.7 Hz, 2H), 1.65 (m, 2H), 1.25−1.38 (m, 16H), 1.01 (s, 21H), 0.89 (t, J = 6.9 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 150.5, 141.7, 141.4, 139.8, 139.1, 137.7, 133.5, 129.6, 129.1, 128.7, 127.3, 126.3, 121.7, 120.7, 106.7, 93.4, 35.4, 31.9, 31.4, 29.5, 29.4, 29.3, 22.6, 18.6, 14.1, 11.3; IR (cm^{-1}) 2926, 2864, 2146, 1462, 1396, 1352, 1235, 1100, 882, 818, 770, 663; HRMS (ESI) m/z calcd for $C_{37}H_{49}N_2Si$ ([M − ($C_4H_{10}N$)$^+$]) 549.3665, found 549.3659.

4-Octyl-1-(4-(4-iodophenyl))phenyl-2-(2-triisopropylsilyl)-ethynylbenzene (4c). Compound **4b** (0.0631 g, 0.101 mmol, 1.00 equiv) was added to 2.5 mL of iodomethane in a flask fitted with a sealable valve and the flask degassed and backfilled with nitrogen. The flask was sealed and the reaction heated to 125 °C for 44 h. After cooling, the methyl iodide was evaporated and the product filtered through a silica plug with 25% dichloromethane in hexanes to afford 0.065 g (quantitative yield) of the iodide as a reddish oil: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.77 (d, J = 8.3 Hz, 2H), 7.64 (d, J = 8.3 Hz, 2H), 7.53 (d, J = 8.3 Hz, 2H), 7.42 (d, J = 1.4 Hz, 1H), 7.33 (d, J = 8.3 Hz, 2H), 7.29 (d, J = 7.8 Hz, 1H), 7.19 (dd, J = 1.4, 7.8 Hz, 1H), 2.60 (t, J = 7.8 Hz, 2H), 1.65 (m, 2H), 1.25−1.39 (m, 10H), 1.00 (s, 21H), 0.89 (t, J = 6.9 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 141.9, 141.1, 140.6, 140.1, 138.6, 137.8, 133.5, 129.8, 129.1, 128.9, 128.8, 126.3, 121.7, 106.6, 93.5, 92.8, 35.3, 31.8, 31.3, 29.4, 29.3, 29.2, 22.6, 18.5, 14.0, 11.3; IR (cm^{-1}) 2923, 2861, 2363, 2148, 1476, 1382, 1064, 1000, 882, 810, 771, 734, 666; HRMS (EI) m/z calcd for $C_{37}H_{50}ISi$ ([M + H$^+$]) 649.2726, found 649.2714.

2-Ethynyl-4-octyl-1-(4-(4-iodophenyl))phenylbenzene (17b). 2-(2-Triisopropylsilyl)ethynyl-4-octyl-4″-iodoterphenyl (0.0519 g, 0.080 mmol, 1.00 equiv) was dissolved in 2 mL of THF with 5 drops of methanol, to which TBAF (1 M in THF) (1.05 mL, 1.05 mmol, 13 equiv) was added. The reaction was stirred overnight at room temperature, and the solvents were evaporated. The crude product was purified by column chromatography over silica with 100% hexanes followed by 25% dichloromethane in hexanes to yield 0.039 g of white crystals: mp 69−71 °C (98% yield); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.76 (d, J = 8.6 Hz, 2H), 7.66 (d, J = 8.6 Hz, 2H), 7.60 (d, J =8.4 Hz, 2H), 7.46 (d, J = 1.7 Hz, 1H), 7.38 (d, J = 8.4 Hz, 2H), 7.31 (d, J = 8.0 Hz, 1H), 7.23 (dd, J = 1.9, 8.0 Hz, 1H), 3.04 (s, 1H), 2.62 (t, J = 7.7 Hz, 2H), 1.65 (m, 2H), 1.25−1.37 (m, 10H), 0.89 (t, J = 7.1 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 142.0, 141.0, 139.6, 138.8, 137.8, 133.8, 129.7, 129.3, 128.9, 126.4, 120.0, 93.0, 83.4, 79.8, 35.3, 31.8, 31.2, 29.4, 29.2, 29.2, 22.6, 14.0; IR (cm^{-1}) 3288, 2922, 2854, 2360, 2340, 1478, 1386, 1000, 895, 808, 788, 731, 657, 611; HRMS (EI) m/z calcd for $C_{28}H_{29}I$ ([M$^+$]) 492.1314, found 492.1312.

Cyclooligo(ethynylene)(4-octyl-*p*-terphenyl-2,4″-diyl) (2b and 2c). Compound **17b** (0.0364 g, 0.074 mmol, 1.00 equiv) was dissolved with CuI (0.0009 g, 0.0047 mmol, 0.06 equiv) and $Pd(Ph_3P)_4$ (0.0243 g, 0.021 mmol, 0.28 equiv) in 40 mL of dry, deoxygenated THF and 10 mL of triethylamine. The reaction was stirred at room temperature under nitrogen for 2 weeks, with periodic reloading of catalyst (only 3 mol % of Pd at a time). When TLC indicated the reaction had gone to completion, the solvents were removed in vacuo, and the reaction was purified over a silica column with 15% dichloromethane in hexanes. Two products were recovered, 3.2 mg of cyclodimer **2c** (12% yield) and 13.8 mg of cyclotrimer **2b** (51% yield), both as colorless waxy solids.

2c: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.75 (d, J = 8.3 Hz, 4H), 7.67 (d, J = 8.3 Hz, 4H), 7.60 (d, J = 8.3 Hz, 4H), 7.51 (d, J = 1.5 Hz, 2H), 7.41 (d, J = 8.3 Hz, 4H), 7.37 (d, J = 7.8 Hz, 2H), 7.22 (dd, J = 7.8, 1.5 Hz, 2H), 2.66 (t, J = 7.8 Hz, 4H), 1.68 (quintet, J = 6.8 Hz, 4H), 1.27−1.41 (m, 20 H), 0.89 (t, J = 6.8 Hz, 6H); COSY (500 MHz, $CDCl_3$) δ 7.75 × 7.67, 7.60 × 7.41, 7.37 × 7.22, 2.66 × 1.68, 1.68 × 1.38, 1.30 × 0.89; HMQC ($CDCl_3$) δ 7.75 × 130.0, 7.67 × 126.3, 7.60 × 126.9, 7.51 × 132.6, 7.41 × 131.8, 7.37 × 129.3, 7.22 × 129.0, 2.66 × 35.5, 1.68 × 31.3, 1.36 × 29.4, 1.31 × 22.6, 1.26 × 31.8, 1.22 × 26.7, 1.21 × 33.5, 0.89 × 14.1; MALDI-TOF (DHB matrix) [M$^+$] m/z calcd for $C_{56}H_{56}$ 728.4832, found 728.6150.

2b: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.80 (d, J = 8.3 Hz, 6H), 7.68 (d, J = 8.3 Hz, 6H), 7.64 (d, J = 7.8 Hz, 6H), 7.52 (s, 3H), 7.49 (d, J = 7.8 Hz, 6H), 7.42 (d, J = 7.8 Hz, 3H), 7.26 (m, 3H), 2.67 (t, J = 7.8 Hz, 6H), 1.69 (quintet, J = 8.3 Hz, 6H), 1.29−1.42 (m, 30H), 0.90 (quintet, J = 8.3 Hz, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 142.1, 140.7, 140.6, 139.8, 139.3, 132.6, 131.7, 130.0, 129.2, 127.1, 126.4, 122.5, 121.2, 91.8, 90.5, 35.4, 31.9, 31.3, 29.7, 29.5, 29.3, 22.7, 14.1; HMQC ($CDCl_3$) δ 7.80 × 130.1, 7.68 × 126.4, 7.64 × 127.1, 7.49 × 131.7, 7.52 × 132.6, 7.42 × 129.2, 7.26 × 129.9, 2.67 × 35.4, 1.69 × 31.3, 1.36 × 29.5, 1.29 × 22.7, 0.89 × 14.1; HMBC ($CDCl_3$, selected peaks) δ 7.80 × 140.7, 7.80 × 139.3, 7.68 × 140.6, 7.68 × 139.8, 7.64 × 139.3, 7.64 × 122.5, 7.52 × 90.5, 7.52 × 35.4, 7.49 × 140.7, 7.49 × 91.8, 7.42 × 142.1, 7.42 × 139.8, 7.42 × 121.2, 7.26 × 140.6, 2.67 × 129.2, 2.67 × 132.6, 2.67 × 142.1, 2.67 × 31.3, 2.67 × 29.3, 1.69 × 29.3, 1.36 × 29.7, 0.90 × 31.9, 0.90 × 22.7; MALDI-TOF (DHB matrix) m/z calcd for $C_{84}H_{84}$ ([M$^+$]) 1092.7, found 1092.7. HRMS (MALDI) m/z calcd for $C_{84}H_{84}$ ([M$^+$]) 1092.6573, found 1092.6612.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Complete ref 21. NMR spectra of novel compounds. Optimized Cartesian coordinates for **1a**,**d**,**e**, **2a**,**d**,**e**, and **24a**−**c**. UV−vis spectra of **1b** and **2b** in pentane, benzene, THF, and $CHCl_3$, **1c** and **2c** in THF and pentane, and **1a** in THF. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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■ REFERENCES

(1) (a) Iyoda, M.; Yamakawa, J.; Rahman, M. J. *Angew. Chem., Int. Ed.* **2011**, *50*, 10522. (b) Höger, S. *Chem.—Eur. J.* **2004**, *10*, 1320. (c) Grave, C.; Schlüter, A. D. *Eur. J. Org. Chem.* **2002**, 3075. (d) Höger, S. *J. Polym. Sci. Part A* **1999**, *37*, 2685.

(2) (a) Gross, D. E.; Zang, L.; Moore, J. S. *Pure Appl. Chem.* **2012**, *84*, 869. (b) Zang, L.; Che, Y.; Moore, J. S. *Acc. Chem. Res.* **2008**, *41*, 1596. (c) Höger, S. High-yield synthesis of shape-persistant phenylene-ethynylene macrocycles. In *Functional Organic Materials*; Mueller, T. J. J., Bunz, U. H. F., Eds.; Wiley: Weinheim, 2007; pp 225−260. (d) Zhao, D.; Moore, J. S. *Chem. Commun.* **2003**, 807.

(3) (a) Youngs, W. J.; Tessier, C. A.; Bradshaw, J. D. *Chem. Rev.* **1999**, *99*, 3153. (b) For an exception, see: Youngs, W. J.; Djebli, A.; Tessier-Youngs, C. A. *Organometallics* **1991**, *10*, 2089.

(4) (a) Takeda, T.; Fix, A. G.; Haley, M. M. *Org. Lett.* **2010**, *12*, 3824. (b) Marsden, J. A.; Miller, J. J.; Shirtcliff, L. D.; Haley, M. M. *J. Am. Chem. Soc.* **2005**, *127*, 2464.

(5) (a) Lei, S.; Tahara, K.; Feng, X.; Furukawa, S.; De Schreyer, F. C.; Müllen, K.; Tobe, Y.; De Feyter, S. *J. Am. Chem. Soc.* **2008**, *130*, 7119. (b) Kawase, T.; Tanaka, K.; Fujiwara, N.; Darabi, H. R.; Oda, M. *Angew. Chem., Int. Ed.* **2003**, *42*, 1624. (c) Kawase, T.; Seirai, H. R.; Darabi, H. R.; Oda, M.; Sarakai, Y.; Tashiro, K. *Angew. Chem., Int. Ed.* **2003**, *42*, 1621.
(6) (a) Spitler, E. L.; Haley, M. M. *Org. Biomol. Chem.* **2008**, *6*, 1569. (b) Zhou, Y.-F.; Feng, S.-Y.; Xie, Z. *Opt. Mat.* **2004**, *24*, 667. (c) Anand, S.; Varnavski, O.; Marsden, J. A.; Haley, M. M.; Schlegel, H. B.; Goodson, T. *J. Phys. Chem. A* **2006**, *110*, 1305.
(7) (a) Zhao, W.; Tang, Q.; Chan, H. S.; Xu, J.; Loa, K. Y.; Miao, Q. *Chem. Commun.* **2008**, 4324. (b) Zang, L.; Che, Y.; Moore, J. S. *Acc. Chem. Res.* **2008**, *41*, 1596.
(8) Luo, J.; Yan, Q.; Zhou, Y.; Li, T.; Zhu, N.; Bai, C.; Cao, Y.; Wang, J.; Pei, J.; Zhao, D. *Chem. Commun.* **2010**, *46*, 5725.
(9) (a) Gielen, J. C.; Ver Heyen, A.; Klyatskaya, S.; Vanderlinden, W.; Höger, S.; Maan, J. C.; De Feyter, S.; Christianen, P. C. M. *J. Am. Chem. Soc.* **2009**, *131*, 14134. (b) Lahiri, S.; Thompson, J. L.; Moore, J. S. *J. Am. Chem. Soc.* **2000**, *122*, 11315. (c) Shetty, A. S.; Zang, J. S.; Moore, J. S. *J. Am. Chem. Soc.* **1996**, *118*, 1019.
(10) (a) Chen, S.; Yan, Q.; Li, T.; Zhao, D. *Org. Lett.* **2010**, *12*, 4784. (b) Seo, S. H.; Jones, T. V.; Seyler, H.; Peters, J. O.; Kim, T. H.; Chang, J. Y.; Tew, G. N. *J. Am. Chem. Soc.* **2006**, *128*, 9264. (c) Mindyuk, O. Y.; Stetzer, M. R.; Heiney, P. A.; Nelson, J. C.; Moore, J. S. *Adv. Mater.* **1998**, *10*, 1363. (d) Zhang, J.; Moore, J. S. *J. Am. Chem. Soc.* **1994**, *116*, 2655.
(11) (a) Xu, L.; Yang, L.; Cao, L.; Li, T.; Chen, S.; Zhao, D.; Lei, S.; Ma, J. *Phys. Chem., Chem. Phys.* **2013**, *15*, 11748. (b) Li, T.; Yue, K.; Yan, Q.; Huang, H.; Wu, H.; Zhu, N.; Zhao, D. *Soft Matter* **2012**, *8*, 2405. (c) Baxter, P. N. W.; Ouahabi, A. A.; Gisselbrecht, J. P.; Brelot, L.; Varnek, A. *J. Org. Chem.* **2012**, *77*, 126. (d) Li, L.; Che, Y.; Gross, D. E.; Huang, H.; Moore, J. S.; Zang, L. *ACS Macro Lett.* **2012**, *1*, 1335−1338. (e) O'Connor, M. J.; Yelle, R. B.; Zakharov, L. N.; Haley, M. M. *J. Org. Chem.* **2008**, *73*, 4424. (f) Müller, P.; Usón, I.; Hensel, V.; Schlüter, A. D.; Sheldrick, G. M. *Helv. Chim. Acta* **2001**, *84*, 778.
(12) Seo, S. H.; Chang, J. Y.; Tew, G. N. *Angew. Chem., Int. Ed.* **2006**, *45*, 7526.
(13) Pasini, D.; Ricci, M. *Curr. Org. Synth.* **2007**, *4*, 59.
(14) Moore, J. S.; Zhang, J. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 922.
(15) Campbell, I. D.; Eglinton, G.; Henderson, W.; Raphael, R. A. *J. Chem. Soc., Chem. Commun.* **1966**, 87.
(16) (a) Kehoe, J. M.; Kiley, J. H.; English, J. J.; Johnson, C. A.; Petersen, R. C.; Haley, M. M. *Org. Lett.* **2000**, *2*, 969. (b) Zhang, J.; Pesak, D. J.; Ludwick, J. L.; Moore, J. S. *J. Am. Chem. Soc.* **1994**, *116*, 4227.
(17) Zhang, W.; Moore, J. S. *Angew. Chem., Int. Ed.* **2006**, *45*, 4416.
(18) (a) Castro, C. E.; Havlin, R.; Honwad, V. K.; Malte, A.; Moje, S. *J. Am. Chem. Soc.* **1969**, *91*, 6464. (b) Chakraborty, M.; Tessier, C. A.; Youngs, W. J. *J. Org. Chem.* **1999**, *64*, 2947.
(19) (a) Johnson, C. A., II; Lu, Y.; Haley, M. M. *Org. Lett.* **2007**, *9*, 3725. (b) Pschirer, N. G.; Zhang, W.; Moore, J. S. *J. Am. Chem. Soc.* **2005**, *127*, 11863. (c) Zhang, W.; Brombosz, S. M.; Mendoza, J. L.; Moore, J. S. *J. Org. Chem.* **2005**, *70*, 10198. (d) Zhang, W.; Moore, J. S. *J. Am. Chem. Soc.* **2004**, *126*, 12796. (e) Vollhardt, K. P. C.; Whitener, G. D. *Synlett* **2003**, 29. (f) Bunz, U. H. F.; Rubin, Y.; Tobe, Y. *Chem. Soc. Rev.* **1999**, *28*, 107. (g) Miljanić, O. Š.; Bunz, U. H. F. *Tetrahedron Lett.* **1999**, *40*, 2481.
(20) (a) Henze, O.; Lentz, D.; Schlüter, A. D. *Chem.—Eur. J.* **2000**, *6*, 2362. (b) Henze, O.; Lentz, D.; Schäfer, A.; Franke, P.; Schlüter, A. D. *Chem.—Eur. J.* **2002**, 357. (c) Opris, D. M.; Franke, P.; Schlüter, A. D. *Eur. J. Org. Chem.* **2005**, 822.
(21) Schafer, L. L.; Nitschke, J. R.; Mao, S. S. H.; Liu, F.-Q.; Harder, G.; Haufe, M.; Tilley, T. D. *Chem.—Eur. J.* **2002**, 74.
(22) Grave, C.; Lentz, D.; Schaefer, A.; Samori, P.; Rabe, J. P.; Franke, P.; Schlueter, A. D. *J. Am. Chem. Soc.* **2003**, *125*, 6907.
(23) (a) Suk, J.-M.; Chae, M. K.; Kim, N.-K.; Kim, U.-I.; Jeong, K.-S. *Pure Appl. Chem.* **2008**, *80*, 599. (b) Kim, N.-K.; Chang, K.-J.; Moon, D.; Lah, M. S.; Jeong, K.-S. *Chem. Commun.* **2007**, *32*, 3401. (c) Chang, K.-J.; Moon, D.; Lah, M. S.; Jeong, K.-S. *Angew. Chem., Int. Ed.* **2005**, *44*, 7926.
(24) Kawase, T.; Daifuku, Y.; Hirao, Y.; Matsumoto, K.; Kurata, H.; Kubo, T. *C. R. Chim.* **2009**, *12*, 403.
(25) (a) Muller, M.; Iyer, V. S.; Kubel, C.; Enkelmann, V.; Müllen, K. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 1607. (b) Brettreich, M.; Bendikov, M.; Chaffins, S.; Perepichka, D. F.; Dautel, O.; Duong, H.; Helgeson, R.; Wudl, F. *Angew. Chem., Int. Ed.* **2002**, *41*, 3688.
(26) (a) Potter, R. G.; Hughes, T. S. *Chem. Commun.* **2007**, 4665. (b) Potter, R. G.; Hughes, T. S. *Org. Lett.* **2007**, *9*, 1187.
(27) Jasti, R.; Bhattacharjee, J.; Neaton, J. B.; Bertozzi, C. R. *J. Am. Chem. Soc.* **2008**, *130*, 17646.
(28) (a) Hirst, E. S.; Jasti, R. *J. Org. Chem.* **2012**, *77*, 10473. (b) Xia, J.; Golder, M. R.; Foster, M. E.; Wong, B. M.; Jasti, R. *J. Am. Chem. Soc.* **2012**, *134*, 19709. (c) Xia, J.; Jasti, R. *Angew. Chem., Int. Ed.* **2012**, *51*, 2474. (d) Sisto, T. J.; Golder, M. R.; Hirst, E. S.; Jasti, R. *J. Am. Chem. Soc.* **2011**, *133*, 15800.
(29) (a) Omachi, H.; Nakayama, T.; Takahashi, E.; Segawa, Y.; Itami, K. *Nat. Chem.* **2013**, *5*, 572. (b) Ishii, Y.; Nakanishi, Y.; Omachi, H.; Matsuura, S.; Matsui, K.; Shinohara, H.; Segawa, Y.; Itami, K. *Chem. Sci.* **2012**, *3*, 2340. (c) Omachi, H.; Segawa, Y.; Itami, K. *Acc. Chem. Res.* **2012**, *45*, 1378. (d) Takab, H.; Omachi, H.; Yamamoto, Y.; Bouffard, J.; Itami, K. *Angew. Chem., Int. Ed.* **2009**, *48*, 6112.
(30) (a) Hitosugi, S.; Yamasaki, T.; Isobe, H. *J. Am. Chem. Soc.* **2012**, *134*, 12442. (b) Kayahara, E.; Sakamoto, Y.; Suzuki, T.; Yamago, S. *Org. Lett.* **2012**, *14*, 3284.
(31) Sisto, T. J.; Tian, X.; Jasti, R. *J. Org. Chem.* **2012**, *77*, 5857.
(32) Nishiuchi, T.; Feng, X.; Enkelmann, V.; Wagner, M.; Muellen, K. *Chem.—Eur. J.* **2012**, *18*, 16621.
(33) (a) Merner, B. L.; Unikela, K. S.; Dawe, L. N.; Thompson, D. W.; Bodwell, G. J. *Chem. Commun.* **2013**, *49*, 5930. (b) Merner, B. L.; Dawe, L. N.; Bodwell, G. J. *Angew. Chem., Int. Ed.* **2009**, *48*, 5487. (c) Yao, T.; Yu, H.; Vermeij, R. J.; Bodwell, G. J. *Pure Appl. Chem.* **2008**, *80*, 533.
(34) (a) Fort, E. H.; Jeffreys, M. S.; Scott, L. T. *Chem. Commun.* **2012**, *48*, 8102. (b) Scott, L. T.; Jackson, E. A.; Zhang, Q.; Steinberg, B. D.; Bancu, M.; Li, B. *J. Am. Chem. Soc.* **2012**, *134*, 107. (c) Fort, E. H.; Scott, L. T. *J. Mater. Chem.* **2011**, *21*, 1373. (d) Fort, E. H.; Scott, L. T. *Angew. Chem., Int. Ed.* **2010**, *49*, 6626. (e) Steinberg, B. D.; Jackson, E. A.; Filatov, A. S.; Wakamiya, A.; Petrukhina, M. A.; Scott, L. T. *J. Am. Chem. Soc.* **2009**, *131*, 10537. (f) Steinberg, B. D.; Scott, L. T. *Angew. Chem., Int. Ed.* **2009**, *48*, 5400. (g) Hill, T. J.; Hughes, R. K.; Scott, L. T. *Tetrahedron* **2008**, *64*, 11360. (h) Jackson, E. A.; Steinberg, B. D.; Bancu, M.; Wakamiya, A.; Scott, L. T. *J. Am. Chem. Soc.* **2007**, *129*, 484.
(35) Liu, Z.; Larock, R. C. *J. Org. Chem.* **2007**, *72*, 223.
(36) Clark, F.; Norman, R.; Thomas, C. B. *J. Chem. Soc., Perkin Trans. 1* **1975**, 121.
(37) Zhou, Q.; Carroll, P. J.; Swager, T. M. *J. Org. Chem.* **1994**, *59*, 1294.
(38) Frisch, M. J. et al. *Gaussian 03*; Gaussian, Inc.: Wallingford, CT, 2004.
(39) Spitler, E. L.; Monson, J. M.; Haley, M. M. *J. Org. Chem.* **2008**, *73*, 2211.
(40) Marsden, J. A.; Haley, M. M. *J. Org. Chem.* **2005**, *70*, 10213.
(41) Tykwinski, R. R. *ChemInform* **2010**, 30. Tykwinski, R. R. *Chem. Commun.* **1999**, 905.
(42) Yamaguchi, Y.; Kobayashi, S.; Amita, N.; Wakamiya, T.; Matsubara, Y.; Sugimoto, K.; Yoshida, Z.-i. *Tetrahedron Lett.* **2002**, *43*, 3277.
(43) Collins, S. K.; Yap, G. P. A.; Fallis, A. G. *Angew. Chem., Int. Ed.* **2000**, *39*, 385.