

# Synthesis and Photophysical Properties of Biphenyl and Terphenyl Arylene–Ethynylene Macrocycles

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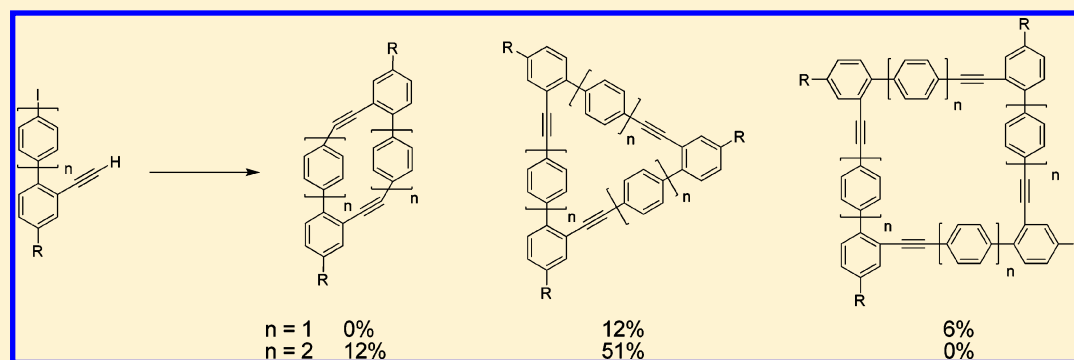
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## S Supporting Information



**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<sup>1</sup> and, in particular, arylene ethynylene macrocycles (AEMs)<sup>2</sup> 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;<sup>3</sup> they often have strong UV absorptions and are often highly fluorescent.<sup>4</sup> Their rigid shape makes them suitable for host–guest interactions.<sup>5</sup> Additionally, these macrocycles have been of interest because their high polarizability makes them desirable as second-order nonlinear optical materials<sup>6</sup> and as materials for organic semiconductors<sup>7</sup> and devices.<sup>8</sup> 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,<sup>9</sup> in the liquid crystalline phase,<sup>10</sup> and in the solid phase<sup>11</sup> through weak van der Waals

interactions. AEMs can aggregate into columnar mesophases as well as vesicles<sup>12</sup> and have the potential to act as model systems for organic nanotubes.<sup>13</sup>

Arylene ethynylene macrocycles are synthetically accessible either by statistical cyclization of a single aryl halide ethynyl monomer<sup>14,15</sup> or by the cyclization of a linear oligomer via a palladium catalyzed cross coupling,<sup>16</sup> 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<sup>17</sup> unless specific macrocycle ring sizes are excluded by ring strain or steric interactions on neighboring monomer units.<sup>18</sup> More recently, alkyne metathesis has proven to be an efficient synthetic method to prepare the arylene

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ethynylene scaffold.<sup>19</sup> 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,<sup>20</sup> *m*-terphenyl,<sup>21</sup> *m*-terpyridinyl,<sup>22</sup> and 11,12-dihydroindolo[2,3-*a*]carbazole<sup>23</sup> (nominal *p*-terphenylenes) and tetram-phenylene<sup>24</sup> 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.

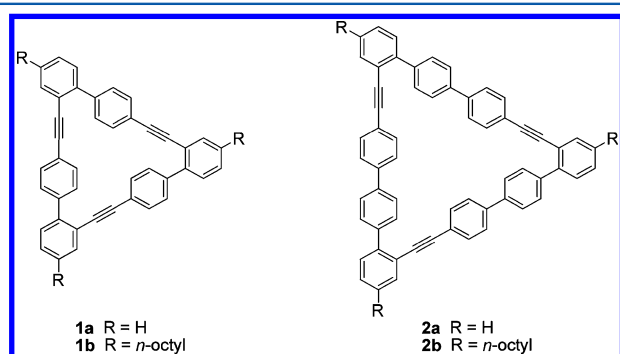


Figure 1. Biphenyl and terphenyl macrocycles.

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.<sup>25</sup> 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.<sup>26</sup>

A similar strain strategy pioneered by Bertozzi and Jasti<sup>27</sup> converts a more highly curved precursor containing  $sp^3$  centers to the all- $sp^2$  nanotube segment. Jasti,<sup>28</sup> Itami,<sup>29</sup> and others<sup>30</sup> have used this route to prepare a variety of  $[n]$ -cycloparaphenylenes, and Jasti<sup>31</sup> and Mullen<sup>32</sup> have recently prepared  $[n]$ cycloparaphenylenes that could in principle give belts of longer length upon oxidative cyclodehydrogenation of pendant phenyl substituents. Bodwell<sup>33</sup> 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.<sup>34</sup> 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

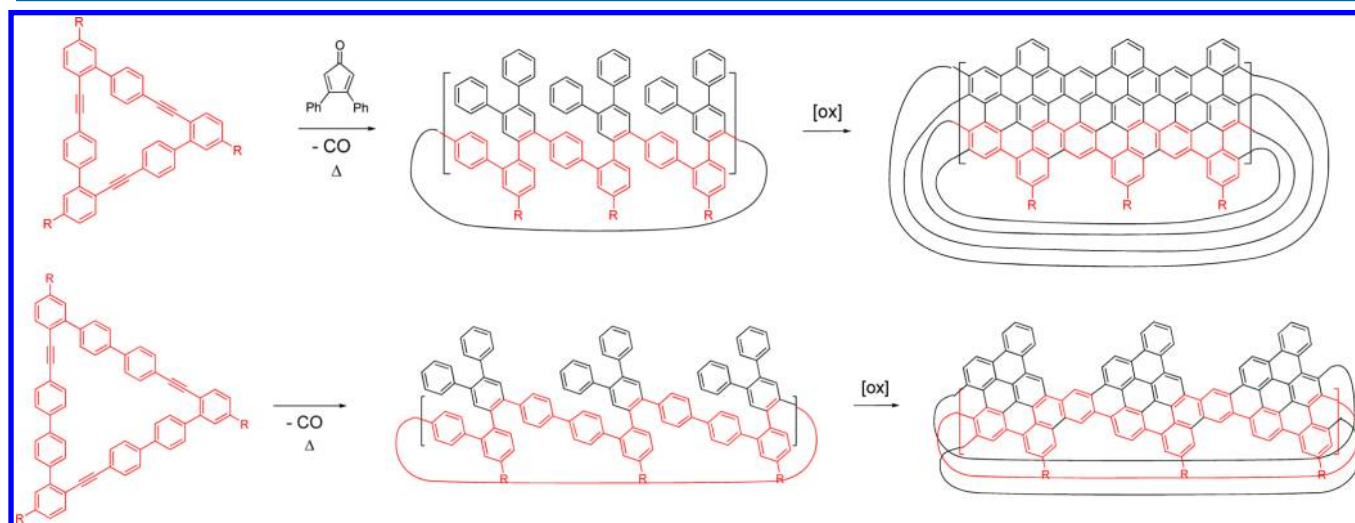
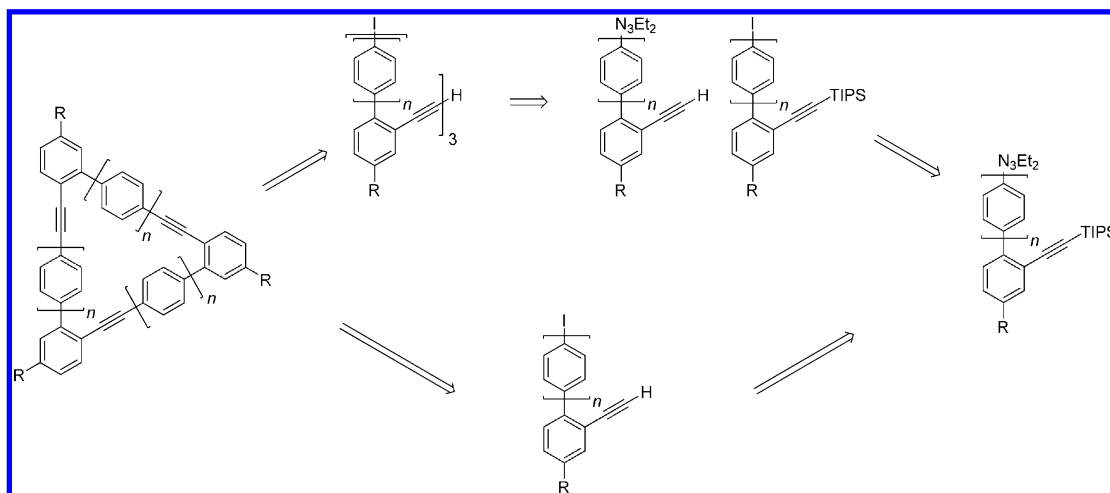
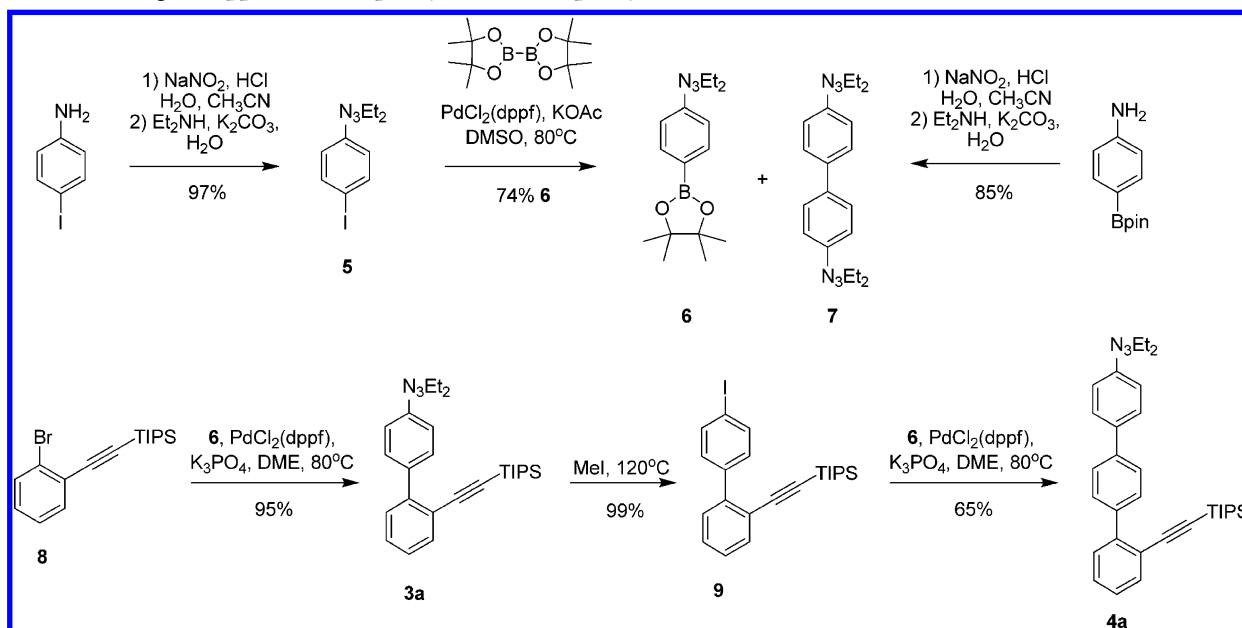


Figure 2. Potential conversion of title macrocycles to nanotube segments.

Scheme 1. Retrosynthetic Analysis



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



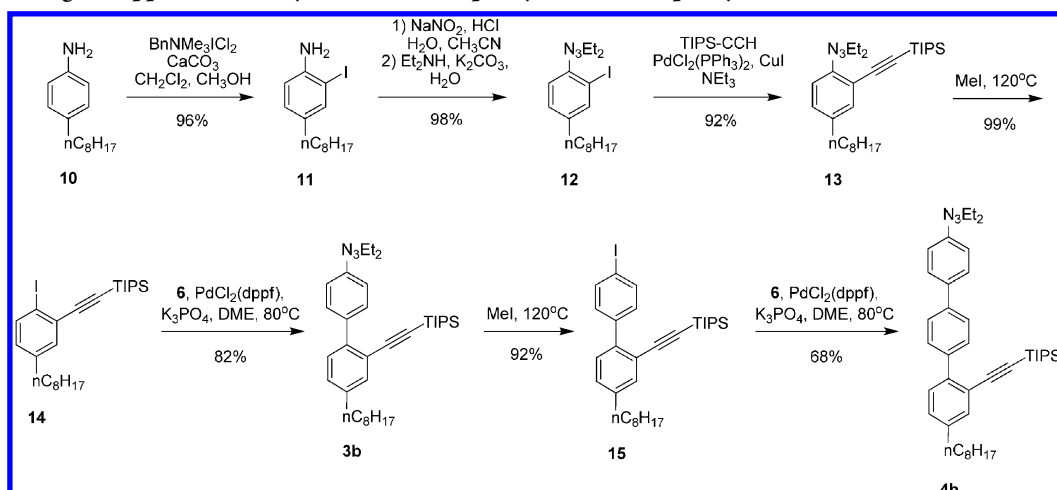
of 3 and 4 are protecting groups that can be removed under orthogonal reaction conditions to give the aryl iodide or terminal alkyne, respectively. A statistical macrocyclization would require both groups to be deprotected to give the AB monomer, while the synthesis of a linear trimer which could be 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(pinacolato)-diboron,  $\text{Cl}_2\text{Pd}(\text{dppf})$ , 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(pinacolato)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  $\text{Cl}_2\text{Pd}(\text{dppf})$  and  $\text{K}_3\text{PO}_4$  in DME to give the biphenyl monomer 3a in 95% yield. It should be noted that other palladium catalysts (notably  $\text{Pd}(\text{PPh}_3)_3$ ), 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

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



the second Suzuki coupling was the result of competitive protodeiodination<sup>35</sup> to give 2-(triisopropylsilyl)ethynyl-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 regioselectivity to give iodoarene 11, which was diazotized and quenched with diethylamine to give 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 protodeiodination product of 14. The concentration of reactants was increased 5-fold in an attempt to make the coupling more competitive with protodeiodination, and the yield of the desired biphenyl 3b was increased to 82%. The careful exclusion of water, a potential source of protons,<sup>36</sup> 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  $\text{Cl}_2\text{Pd}(\text{PPh}_3)_2$  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  $^1\text{H}$  NMR (Figure 3) that matched those in pure samples of 1a obtained by the alternate synthesis described below.

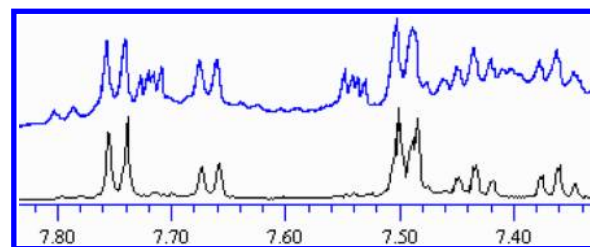
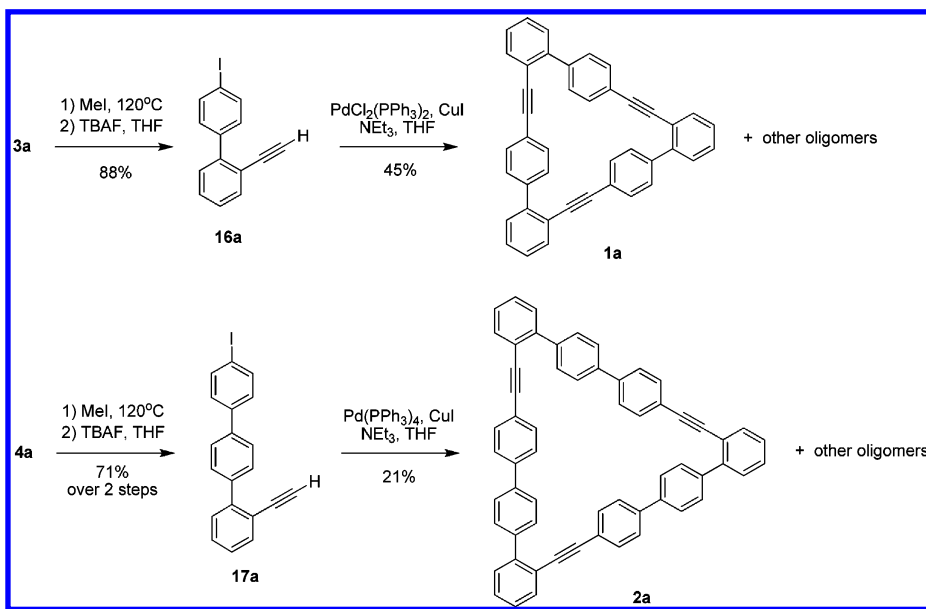


Figure 3. (Top) statistical macrocyclization of 16a. (Bottom) stepwise construction of 1a.

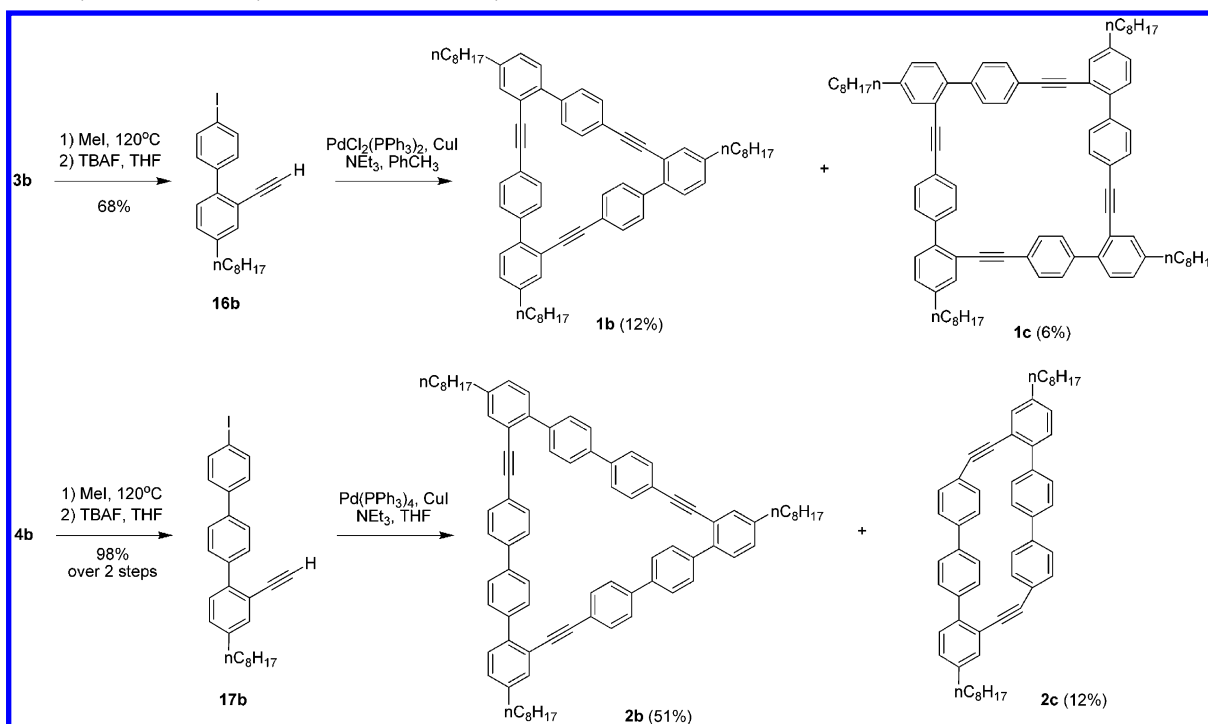
Stephens–Castro coupling of terphenyl monomer 17a at 182 mM and Sonogashira coupling at 155 mM with  $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$  gave only an insoluble yellow product, which had an  $^1\text{H}$  NMR spectrum consistent with a mixture of linear and cyclic oligomers. The Sonogashira coupling of 17a was attempted again, using  $\text{Pd}(\text{PPh}_3)_4$  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

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



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



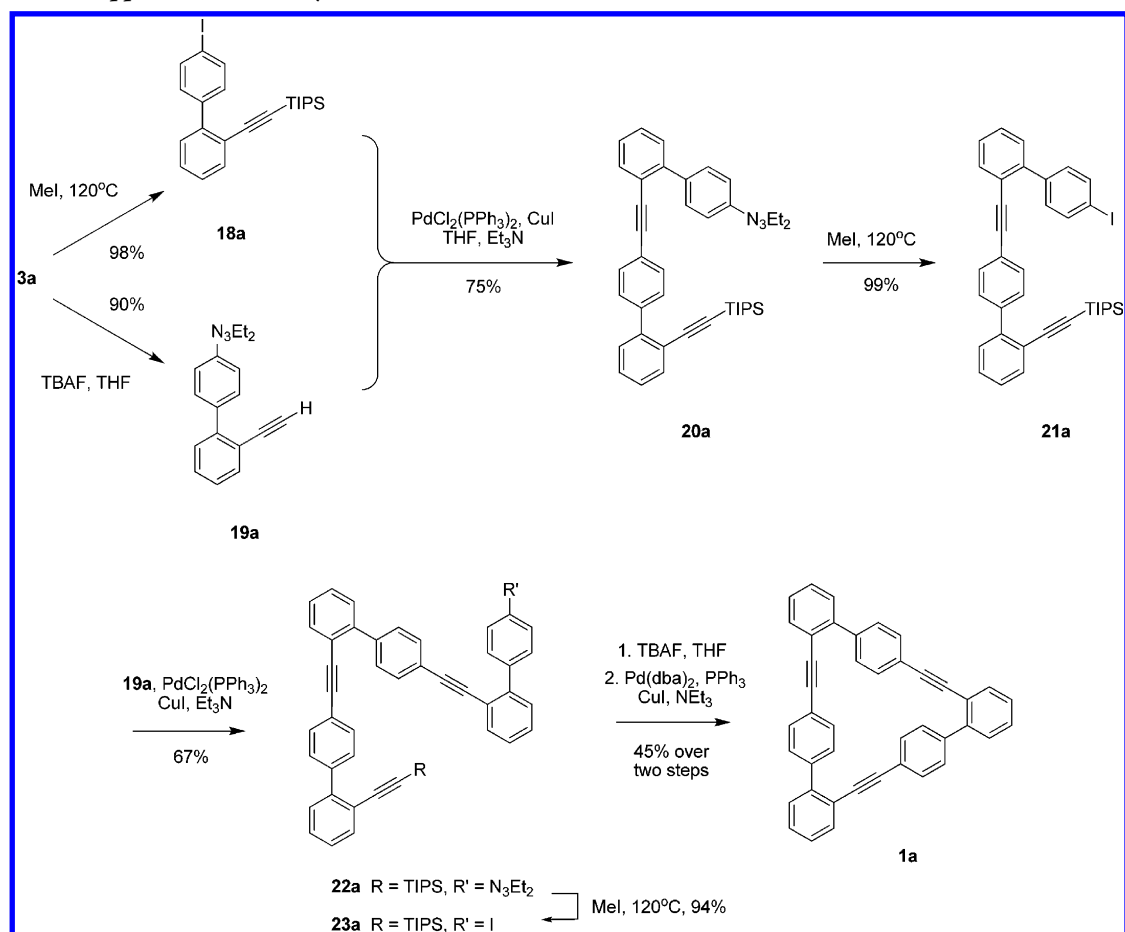
cyclooligomerization of **17b** because of the use of  $\text{Pd}(\text{PPh}_3)_4$  instead of  $\text{PdCl}_2(\text{PPh}_3)_2$ . The isolation of the substituted macrocycles was greatly facilitated by their much higher solubility, attributable to their long alkyl side chains.

**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).



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).

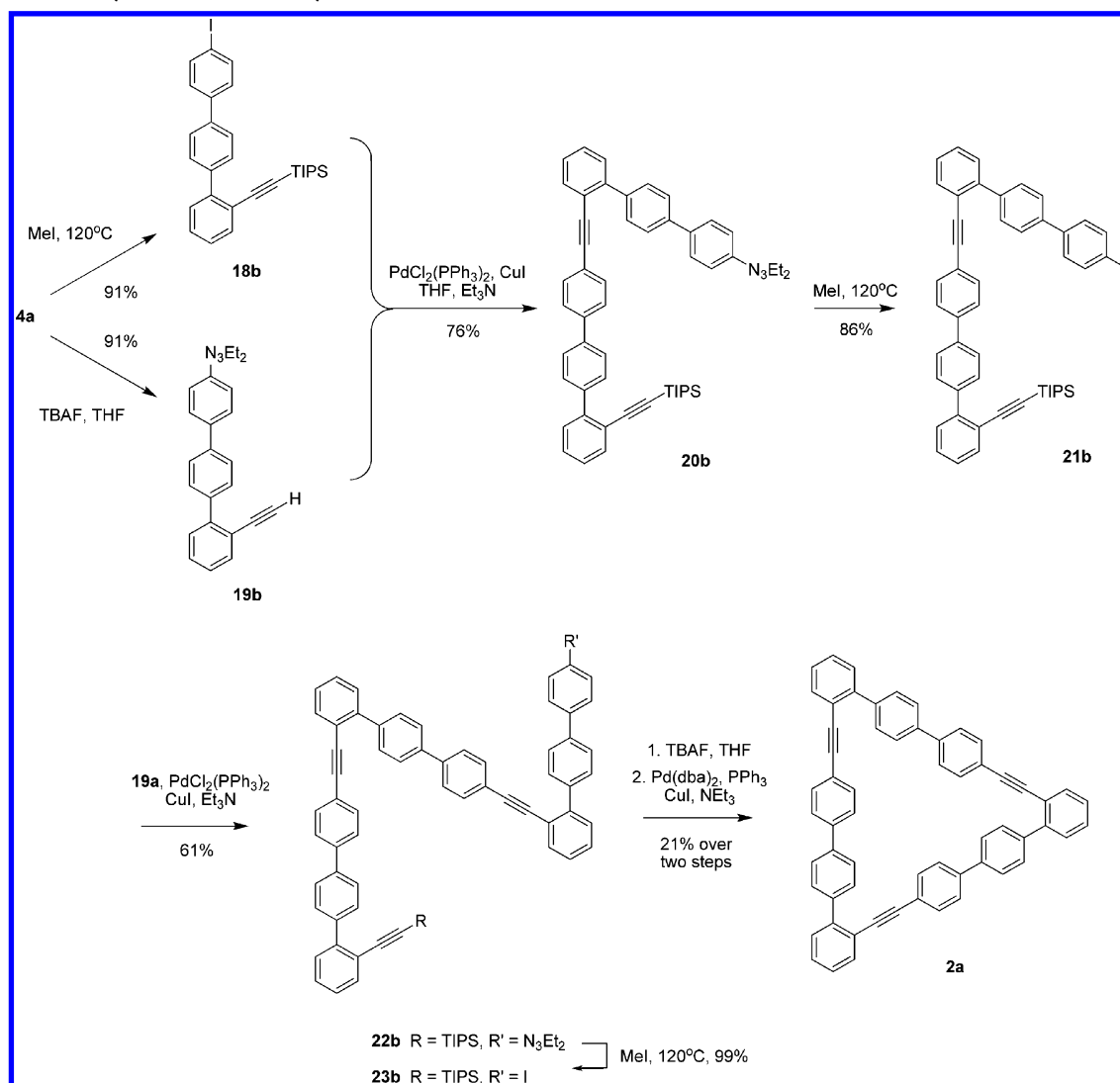
#### Computational Modeling of Cyclooligomer Strain

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.<sup>14</sup> In some of these reports, the cyclo-trimeric and cyclotetrameric products isolated from *o*-iodoethynylenebenzene precursors were relatively unstrained.<sup>15</sup> Other studies have reported the production of strained cyclic dimeric species along with unstrained cyclotrimers and cyclotetramers.<sup>37</sup>

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,<sup>38</sup> 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*<sub>2h</sub> cyclodimer **24c** is much higher in energy than either the *D*<sub>3h</sub> cyclotrimer **24a** or *D*<sub>2d</sub> tetramer **24b**. The incomplete treatment of the closed  $\pi$ -system in the molecular mechanics force field is most likely the source of the difference

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<sub>14</sub>H<sub>8</sub> repeat units in cyclodimer C<sub>2h</sub> **1d** are ~10 kcal/mol higher in energy than those in C<sub>3</sub> **1a**, and the two *para*-substituted rings are predicted to be coplanar with one another, which gives C<sub>2</sub> **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<sub>2</sub> symmetric **2d** forces the two *para*-substituted rings to be nearly coplanar, while being orthogonal to the *ortho*-substituted ring. The C<sub>20</sub>H<sub>12</sub> 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<sub>3</sub> 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<sub>2</sub> symmetric **2e**. The lack of angle strain in the alkyne 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 alkyne 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 alkyne 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

**Table 1. Energies and Geometries of Various Arylene Ethynylene Macrocycles<sup>a</sup>**

	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	-

<sup>a</sup>Energies are in kcal mol<sup>-1</sup> 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

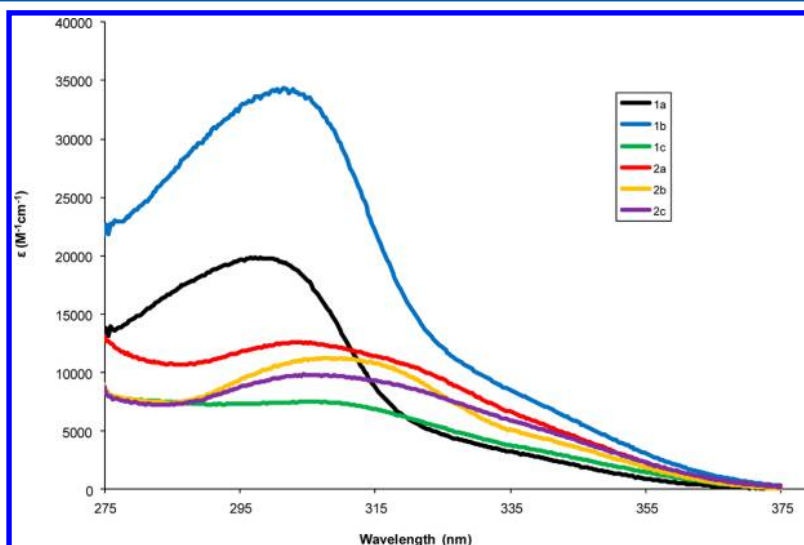
The observation of cyclic dimer **2c** in the macrocyclization of **3b** suggests that the strain calculated per repeat unit is not great enough to prevent the irreversible, kinetic formation of **2c**. The larger strain calculated for the biphenyl dimer **1d** suggests that strain may be playing a role 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 ( $\Phi$ ) of organic molecules.<sup>39</sup> Their poor solubility in some solvents such as pentane limited full comparisons of all of the macrocycles, but in benzene, THF and CHCl<sub>3</sub>, their  $\lambda_{\text{max}}$  and  $\epsilon_{\text{max}}$  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  $\lambda_{\text{max}}$  of biphenylene linear trimer **23a**, 299 nm, does not change appreciably upon cyclization to **1a**, which has a  $\lambda_{\text{max}}$  of 298 nm. Alternatively, the  $\lambda_{\text{max}}$  of terphenylene linear trimer **23b**, 295 nm, is shifted bathochromatically by 8 nm upon cyclization to cyclic trimer **2a** ( $\lambda_{\text{max}}$  = 303 nm). This could arise from an increase in conjugation upon moving from the linear to the cyclic system.<sup>40</sup> 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.



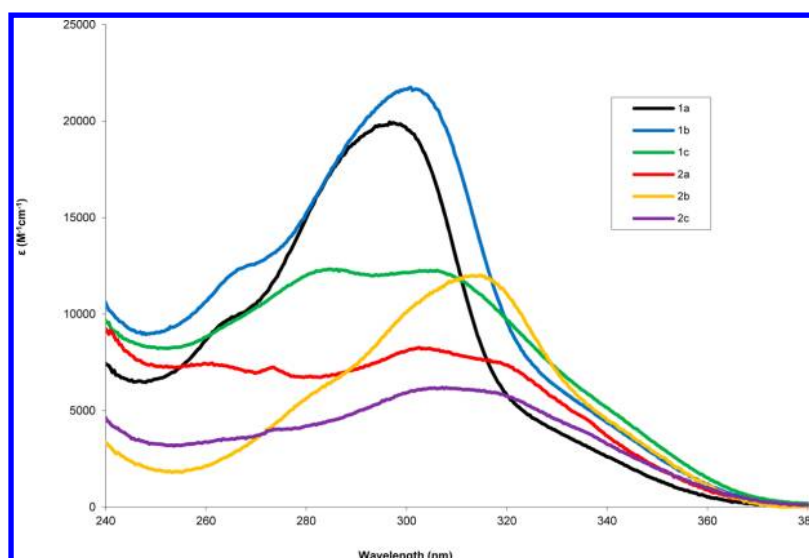


Figure 5. UV-vis absorption spectra of macrocycles in  $\text{CHCl}_3$ .

Table 3.  $\lambda_{\text{max}}$  (nm) and  $\epsilon$  ( $\text{M}^{-1} \text{cm}^{-1}$ ) of *n*-Octyl Terphenyl Cyclodimer and Cyclotrimer

solvent	1a $\lambda_{\text{max}}$ ( $\epsilon$ )	1b $\lambda_{\text{max}}$ ( $\epsilon$ )	1c $\lambda_{\text{max}}$ ( $\epsilon$ )	2a $\lambda_{\text{max}}$ ( $\epsilon$ )	2b $\lambda_{\text{max}}$ ( $\epsilon$ )	2c $\lambda_{\text{max}}$ ( $\epsilon$ )
$n\text{C}_5\text{H}_{12}$		296 (20300)	282 (14700) 301 (14500)		312 (—)	306 (—)
$\text{C}_6\text{H}_6$	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)
$\text{CHCl}_3$	297 (19900)	302 (21700)	285 (12300) 306 (12200)	303 (8200)	315 (12000)	307 (6200)

All of the terphenylene macrocycles **2a–c** exhibit a bathochromic shift in their absorption maxima in  $\text{CHCl}_3$  compared to THF, while no such shift is observed for the biphenylene macrocycles **1a–c**. Just as was observed in benzene, the  $\lambda_{\text{max}}$  of linear trimer **23a**, 298 nm, is very similar to that of cyclic trimer **1a**, 297 nm, while terphenylene linear trimer **23b** has a  $\lambda_{\text{max}}$  of 293, 10 nm blueshifted compared to the cyclic trimer **2a** which has a  $\lambda_{\text{max}}$  of 303 nm. Alkyl substitution again redshifts the  $\lambda_{\text{max}}$  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  $\lambda_{\text{max}}$  observed in the solvents examined. As observed in previous solvents, biphenyl cyclotetramer **1c** exhibits two  $\lambda_{\text{max}}$  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  $\lambda_{\text{max}}$  in pentane, THF and chloroform, it has only a single broad  $\lambda_{\text{max}}$  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  $\sim 47^\circ$  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  $\lambda_{\text{max}}$  compared to **1b** which has a smaller  $\pi$  system. This trend exists in all solvents

tested, although the extent of the shift increases as solvent polarity decreased.  $\text{CHCl}_3$  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 ethynyl systems.<sup>41</sup> 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  $\lambda_{\text{max}}$  at around 300 nm, and tetramer **1c** showed two  $\lambda_{\text{max}}$  one  $\sim 15$  nm shorter and another  $\sim 5$  nm longer wavelength (Table 3). It should be noted that the two-dimensional  $\pi$ -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  $6^\circ$  to near orthogonality,  $87^\circ$ , by removing a single repeat unit to form the terphenyl cyclodimer **2c**. Despite this interruption in the

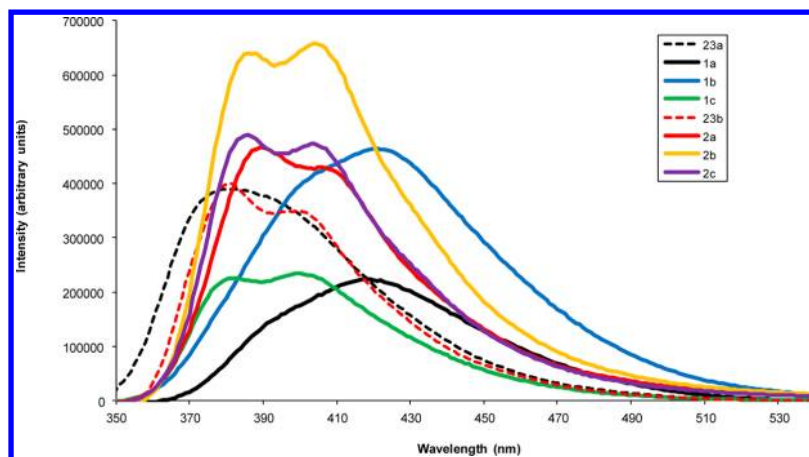


Figure 6. Fluorescence spectra in benzene of macrocycles and linear trimers.

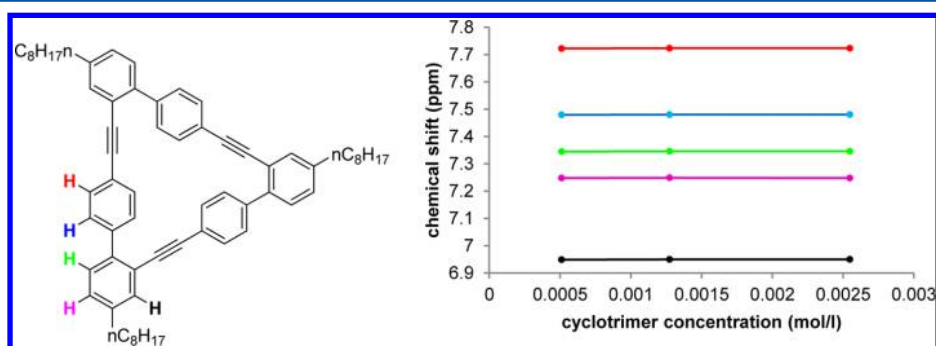


Figure 7. Concentration-dependent NMR chemical shifts of **1b** in  $C_6D_6$ ; fluorescence spectra were observed at 0.066 mM.

cyclic  $\pi$ -network, the UV–vis spectra are similar. This suggests that either  $\pi$ -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).<sup>40</sup>

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  $\lambda_{em}$  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  $\lambda_{em}$  at similar wavelengths to **1c**, at  $\sim$ 390 and  $\sim$ 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  $\sim$ 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 ( $\Phi$ ) in benzene compared to larger arylene ethynylene macrocycles (Table 4).<sup>13</sup> However, these systems do not contain long linear conjugated pathways which has been correlated to high quantum yields.<sup>28</sup> Quantum yields for the biphenyl macrocycles range from 0.02 for **1b** to 0.04 for **1c** while the quantum yields

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

	$\lambda_{\text{abs}}$ (nm)	$\lambda_{\text{em}}$ (nm)	Stokes Shift (nm)	$\Phi$
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).**<sup>42</sup> 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<sub>2</sub> (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<sub>2</sub>CO<sub>3</sub> (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<sub>2</sub>O 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): <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  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); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)  $\delta$  150.9, 137.6, 122.4, 88.9; IR (cm<sup>-1</sup>)

2974, 2933, 2871, 1475, 1420, 1391, 1341, 1238, 1198, 1108, 1093, 1001, 828; MS (CI-isobutane) [MH<sup>+</sup>] 304.6 *m/z*.

**(2-(2-Bromophenyl)ethynyl)triisopropylsilane (8).**<sup>43</sup> A 25 mL round-bottomed flask was charged with 1-bromo-2-iodobenzene (2.697 g, 9.53 mmol, 1.00 equiv), Cl<sub>2</sub>Pd(PPh<sub>3</sub>)<sub>2</sub> (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<sub>3</sub>N. 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<sub>4</sub>Cl (aq). The organic layers were dried over MgSO<sub>4</sub>, 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): <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  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); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)  $\delta$  134.1, 132.6, 129.6, 127.0, 126.0, 125.9, 105.0, 96.4, 18.9, 11.6; IR (cm<sup>-1</sup>) 2943, 2865, 2161, 1464, 1220, 1047, 908, 883, 834, 753, 678; MS (CI-isobutane) [MH<sup>+</sup>] 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<sub>2</sub>Pd-(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<sub>4</sub>Cl (aq), dried over MgSO<sub>4</sub>, 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: <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  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); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)  $\delta$  153.6, 135.5, 119.7, 83.5, 24.8; IR (cm<sup>-1</sup>) 2979, 1602, 1391, 1351, 1320, 1139, 1087, 857, 655; HRMS (ESI) *m/z* calc'd for C<sub>16</sub>H<sub>26</sub>BN<sub>3</sub>O<sub>2</sub>H ([M + H<sup>+</sup>]) 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<sub>2</sub> (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<sub>2</sub>CO<sub>3</sub> (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<sub>2</sub>O. The organics were washed with H<sub>2</sub>O, dried over MgSO<sub>4</sub>, 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: <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  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); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)  $\delta$  153.6, 135.5, 119.7, 83.5, 24.8; IR (cm<sup>-1</sup>) 2979, 1602, 1391, 1351, 1320, 1139, 1087, 857, 655; HRMS (ESI) *m/z* calc'd for C<sub>16</sub>H<sub>26</sub>BN<sub>3</sub>O<sub>2</sub>H ([M + H<sup>+</sup>]) 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<sub>2</sub>(dppf) (0.150 g, 0.184 mmol, 0.03



equiv). The flask was purged with nitrogen, and 50 mL of deoxygenated 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):  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  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);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  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 ( $\text{cm}^{-1}$ ) 2940, 2864, 2151, 1464, 1397, 1330, 1235, 1096, 883, 835, 761, 677; HRMS (ESI)  $m/z$  calcd for  $\text{C}_{27}\text{H}_{39}\text{N}_3\text{SiH}$  ( $[\text{M} + \text{H}^+]$ ) 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):  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  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);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  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 ( $\text{cm}^{-1}$ ) 2940, 2863, 2152, 1469, 1386, 1000, 883, 820, 758, 677; HRMS (EI)  $m/z$  calcd for  $\text{C}_{23}\text{H}_{29}\text{ISi}$  ( $[\text{M}^+]$ ) 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  $\text{H}_2\text{O}$ , and extracted with diethyl ether (3  $\times$  50 mL). The organic layers were combined, dried over  $\text{MgSO}_4$ , 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:  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  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);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  143.1, 139.7, 137.1, 133.9, 131.1, 129.2, 129.0, 127.3, 120.3, 93.6, 80.6; IR (neat,  $\text{cm}^{-1}$ ) 3274, 3061, 1583, 1472; HRMS (ESI)  $m/z$  calcd for  $\text{C}_{14}\text{H}_{10}\text{I}$  ( $[\text{M} + \text{H}^+]$ ) 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),  $\text{Cl}_2\text{Pd}(\text{PPh}_3)_2$  (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  $\text{Et}_3\text{N}$ . The reaction was stirred for 10 days at room temperature before being diluted with  $\text{H}_2\text{O}$  and extracted with  $\text{Et}_2\text{O}$  (3  $\times$  20 mL). The organics were washed over brine, dried over  $\text{MgSO}_4$ , 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  $\text{H}_2\text{O}$ , and extracted with diethyl ether (3  $\times$  50 mL). The organic layers were combined, dried over  $\text{MgSO}_4$ , 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:  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  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);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  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 ( $\text{cm}^{-1}$ ) 3284, 1330, 1229, 837; HRMS (photospray ionization)  $m/z$  calcd for  $\text{C}_{18}\text{H}_{20}\text{N}_3$  ( $[\text{M} + \text{H}^+]$ ) 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  $\text{Cl}_2\text{Pd}(\text{PPh}_3)_2$  (0.020 g, 0.0285 mmol, 0.06 equiv) and flushed with  $\text{N}_2$ . To this 20 mL of deoxygenated THF/ $\text{Et}_3\text{N}$  (1:1 v/v) was added, and the reaction flask was sparged with  $\text{N}_2$  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  $\text{H}_2\text{O}$  and extracted with diethyl ether (3  $\times$  25 mL). The organics were combined, washed with satd  $\text{NH}_4\text{Cl}$ , dried over  $\text{MgSO}_4$ , 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:  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  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);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  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 ( $\text{cm}^{-1}$ ) 2942, 2860, 2356, 1460, 1334, 1229, 830; HRMS (MALDI)  $m/z$  calcd for  $\text{C}_{41}\text{H}_{48}\text{N}_3\text{Si}$  ( $[\text{M} + \text{H}^+]$ ) 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  $\text{N}_2$ . 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  $\text{CH}_2\text{Cl}_2$ , washed with  $\text{H}_2\text{O}$ , dried over  $\text{MgSO}_4$ , 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:  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  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);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  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 ( $\text{cm}^{-1}$ ) 2940, 2865, 2148, 1467, 1000, 756; HRMS (ESI)  $m/z$  calcd for  $\text{C}_{37}\text{H}_{38}\text{ISi}$  ( $[\text{M} + \text{H}^+]$ ) 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),  $\text{Cl}_2\text{Pd}(\text{PPh}_3)_2$  (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  $\text{NH}_4\text{Cl}$  and extracted with EtOAc. The organics were washed with satd  $\text{NH}_4\text{Cl}$ , dried over  $\text{MgSO}_4$ , 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):  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  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);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  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,  $\text{cm}^{-1}$ ): 2932, 2860, 2154, 1473, 1096, 836, 744; HRMS (ESI)  $m/z$  calcd for  $\text{C}_{55}\text{H}_{56}\text{N}_3\text{Si}$  ( $[\text{M} + \text{H}^+]$ ) 786.4244, found 786.4257.

**2-(2-(4-(2-(2-(4-(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): <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) 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); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) 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, 129.3, 129.2, 128.7, 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<sup>-1</sup>) 2802, 2847, 2356, 1726, 1457, 1273, 761; HRMS (ESI) *m/z* calcd for C<sub>51</sub>H<sub>46</sub>ISi ([M + H]<sup>+</sup>) 813.2413, found 813.2406.

**2-(2-(4-(2-(2-(4-(2-(4-iodophenyl)phenyl)ethynyl)phenyl)phenyl)ethynyl)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<sub>2</sub>O. The organics were washed with satd NH<sub>4</sub>Cl (aq), dried over MgSO<sub>4</sub>, 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<sub>3</sub>N and charged in a gastight syringe in a syringe pump. Pd(dba)<sub>2</sub> (0.039 g 0.068 mmol, 1.42 equiv), CuI (0.015 g, 0.079 mmol, 1.71 equiv), and PPh<sub>3</sub> (0.076 g, 0.290 mmol, 6.26 equiv) were dissolved in 11.6 mL of Et<sub>3</sub>N. 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<sub>4</sub>Cl (aq) and extracted with EtOAc. The organic phases were dried over MgSO<sub>4</sub>, filtered, and concentrated in vacuo. The crude material was purified using 15% CH<sub>2</sub>Cl<sub>2</sub> in hexanes to afford 11 mg (45% yield) of the desired macrocycle as a white solid: mp 282–291 °C; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) 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); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) 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<sub>49</sub>H<sub>24</sub> ([M]<sup>+</sup>) 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<sub>3</sub>PO<sub>4</sub> (4.52 g, 21.3 mmol, 5.1 equiv), and PdCl<sub>2</sub>(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); <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) 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); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) 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<sup>-1</sup>) 2940, 2864, 2361, 2151, 1463, 1329, 1233, 1092, 995, 882, 823, 764, 674, 639; HRMS (ESI) *m/z* calcd for C<sub>33</sub>H<sub>43</sub>N<sub>3</sub>SiH ([M + H]<sup>+</sup>) 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); <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) 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); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) 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<sup>-1</sup>) 2939, 2862, 2152, 1473, 1384, 1064, 1000, 882, 837, 812, 578, 662; HRMS (photospray ionization) *m/z* calcd for C<sub>29</sub>H<sub>33</sub>Si ([M]<sup>+</sup>) 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): <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) 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); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) 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<sub>20</sub>H<sub>14</sub>I ([M + H]<sup>+</sup>) 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); <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) 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); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) 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<sup>-1</sup>) 3280, 1471, 1427, 1324, 1233, 1098, 1003, 828, 761, 659, 634; HRMS (APCI) *m/z* calcd for C<sub>24</sub>H<sub>24</sub>N<sub>3</sub> ([M]<sup>+</sup>) 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)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<sub>2</sub>(Ph<sub>3</sub>P)<sub>2</sub> (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**: <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) 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); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) 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<sup>-1</sup>) 3280, 2978, 2932, 2360, 1471, 1427, 1390, 1322, 1233, 1098, 828, 761, 698, 659; HRMS (EI) *m/z* calcd for C<sub>53</sub>H<sub>55</sub>N<sub>3</sub>Si ([M]<sup>+</sup>) 761.4165, found 761.4160.

**2-(2-(4-(4-(2-(2-(4-(4-iodophenyl)phenyl)phenyl)ethynyl)phenyl)phenyl)ethynyl)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





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):  $^1H$  NMR (500 MHz,  $CDCl_3$ )  $\delta$  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,  $CDCl_3$ )  $\delta$  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-octylphenyl)triaz-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  $EtOAc$  ( $3 \times 50$  mL). The combined organic phases were washed with satd  $NH_4Cl$  ( $2 \times 50$  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):  $^1H$  NMR (500 MHz,  $CDCl_3$ )  $\delta$  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,  $CDCl_3$ )  $\delta$  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)ethynylidobenzene (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):  $^1H$  NMR (500 MHz,  $CDCl_3$ )  $\delta$  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,  $CDCl_3$ )  $\delta$  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  $C_{25}H_{41}Si$  ( $[M + H]^+$ ) 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  $Et_2O$  ( $3 \times 30$  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):  $^1H$  NMR (500 MHz,  $CDCl_3$ )  $\delta$  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,  $CDCl_3$ )  $\delta$  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):  $^1H$  NMR (500 MHz,  $CDCl_3$ )  $\delta$  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,  $CDCl_3$ )  $\delta$  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):  $^1H$  NMR ( $CDCl_3$ , 500 MHz)  $\delta$  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)  $\delta$  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  $Et_2O$  ( $3 \times 20$  mL), and the combined organic phases were washed with satd NaCl before being dried over  $MgSO_4$ , filtered, and concentrated in vacuo. Purification required 5X 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:  $^1H$  NMR ( $CDCl_3$ , 500 MHz)  $\delta$  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,  $CDCl_3$ )  $\delta$  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:  $^1H$  NMR ( $CDCl_3$ , 500 MHz)  $\delta$  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,  $CDCl_3$ )  $\delta$  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-octylphenyl)phenyl)triaz-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



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):  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  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);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  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 ( $\text{cm}^{-1}$ ) 2926, 2864, 2146, 1462, 1396, 1352, 1235, 1100, 882, 818, 770, 663; HRMS (ESI)  $m/z$  calcd for  $\text{C}_{37}\text{H}_{49}\text{N}_2\text{Si}$  ( $[\text{M} - (\text{C}_4\text{H}_{10}\text{N})^+]$ ) 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:  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  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);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  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 ( $\text{cm}^{-1}$ ) 2923, 2861, 2363, 2148, 1476, 1382, 1064, 1000, 882, 810, 771, 734, 666; HRMS (EI)  $m/z$  calcd for  $\text{C}_{37}\text{H}_{50}\text{I}$  ( $[\text{M} + \text{H}^+]$ ) 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);  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  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);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  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 ( $\text{cm}^{-1}$ ) 3288, 2922, 2854, 2360, 2340, 1478, 1386, 1000, 895, 808, 788, 731, 657, 611; HRMS (EI)  $m/z$  calcd for  $\text{C}_{28}\text{H}_{29}\text{I}$  ( $[\text{M}^+]$ ) 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  $\text{Pd}(\text{Ph}_3\text{P})_4$  (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:**  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  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,

$\text{CDCl}_3$ )  $\delta$  7.75  $\times$  7.67, 7.60  $\times$  7.41, 7.37  $\times$  7.22, 2.66  $\times$  1.68, 1.68  $\times$  1.38, 1.30  $\times$  0.89; HMQC ( $\text{CDCl}_3$ )  $\delta$  7.75  $\times$  130.0, 7.67  $\times$  126.3, 7.60  $\times$  126.9, 7.51  $\times$  132.6, 7.41  $\times$  131.8, 7.37  $\times$  129.3, 7.22  $\times$  129.0, 2.66  $\times$  35.5, 1.68  $\times$  31.3, 1.36  $\times$  29.4, 1.31  $\times$  22.6, 1.26  $\times$  31.8, 1.22  $\times$  26.7, 1.21  $\times$  33.5, 0.89  $\times$  14.1; MALDI-TOF (DHB matrix)  $[\text{M}^+]$   $m/z$  calcd for  $\text{C}_{56}\text{H}_{56}$  728.4832, found 728.6150.

**2b:**  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  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);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  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 ( $\text{CDCl}_3$ )  $\delta$  7.80  $\times$  130.1, 7.68  $\times$  126.4, 7.64  $\times$  127.1, 7.49  $\times$  131.7, 7.52  $\times$  132.6, 7.42  $\times$  129.2, 7.26  $\times$  129.9, 2.67  $\times$  35.4, 1.69  $\times$  31.3, 1.36  $\times$  29.5, 1.29  $\times$  22.7, 0.89  $\times$  14.1; HMBC ( $\text{CDCl}_3$ , selected peaks)  $\delta$  7.80  $\times$  140.7, 7.80  $\times$  139.3, 7.68  $\times$  140.6, 7.68  $\times$  139.8, 7.64  $\times$  139.3, 7.64  $\times$  122.5, 7.52  $\times$  90.5, 7.52  $\times$  35.4, 7.49  $\times$  140.7, 7.49  $\times$  91.8, 7.42  $\times$  142.1, 7.42  $\times$  139.8, 7.42  $\times$  121.2, 7.26  $\times$  140.6, 2.67  $\times$  129.2, 2.67  $\times$  132.6, 2.67  $\times$  142.1, 2.67  $\times$  31.3, 2.67  $\times$  29.3, 1.69  $\times$  29.3, 1.36  $\times$  29.7, 0.90  $\times$  31.9, 0.90  $\times$  22.7; MALDI-TOF (DHB matrix)  $m/z$  calcd for  $\text{C}_{84}\text{H}_{84}$  ( $[\text{M}^+]$ ) 1092.7, found 1092.7. HRMS (MALDI)  $m/z$  calcd for  $\text{C}_{84}\text{H}_{84}$  ( $[\text{M}^+]$ ) 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  $\text{CHCl}_3$ , **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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