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Study of Cross-Conjugated *iso*-Polytriacetylenes and Related Oligoenynes

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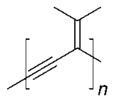
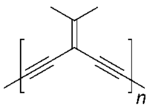
Two series of monodisperse cross-conjugated oligomers based on enyne repeat units have been realized. The first class of molecules, *iso*-polytriacetylenes (*iso*-PTAs, **2**), was divergently synthesized using an iterative sequence of palladium-catalyzed cross-coupling reactions of vinyl triflate **5** with terminal alkynes. The second series of oligoenynes (**17**−**20**) are based on an octatetrayne backbone, and result from homocoupling of the differentially protected *iso*-PTA oligomers **8**−**11**. The longest member of this series, **20**, spans ca. 5.6 nm from Si atom to Si atom and is composed of a contiguous sequence of 44 sp and sp^2 carbons. The lowest energy electronic absorption band for *iso*-PTA dimers in the progression **13** → **9** → **16** is consistently red-shifted as a result of extending the cross-conjugated structure. A similar comparison within each series (i.e., **16**, **6**−**7**, or **17**−**20**), however, suggests little effect on the electronic characteristics of these molecules as oligomer length is increased. The solid-state properties of one derivative, **17**, are also described.

Introduction

As conjugated polymers and oligomers continue to evolve as materials with great potential for electronic and optical applications,[1] we[2] and others[3] have taken an interest in the synthesis and properties of cross-conjugated compounds.[4,5] Cross conjugation has been a sparingly utilized structural motive for the preparation of highly unsaturated oligomers and polymers but presents an interesting and potentially useful alternative to the more prevalent linear conjugation.



1
iso-polydiacetylene



2
iso-polytriacetylene

Cross-conjugated expanded dendralenes such as *iso*-polydiacetylene (**1**)[2a,c,d] and *iso*-polytriacetylene (**2**)[8] are expected to show distinctly different electronic properties in comparison to their linearly conjugated analogues, polydiacetylene[6] and polytriacetylene.[1a,7] Specifically, π-electronic delocalization is not likely to extend along the cross-conjugated carbon backbone to the same extent that it would in the analogous linearly conjugated isomers.[2] Similar modes of moderated π-conjugation have been achieved as a result of steric interactions in molecules such as poly(*p*-phenylenes), in which case distortion from planarity of the conjugated segments limits communication.[9,10] In contrast to poly(*p*-phenylenes), however, both *iso*-PDAs and *iso*-PTAs are fully conjugated compounds that are potentially devoid of steric interactions that might inhibit planarity. This structural attribute could be exploited to generate desirable electronic characteristics such as increased “optical transparency”, which is essential for the use of conjugated organic materials in optical applications in the visible region of the spectrum.[11−13]

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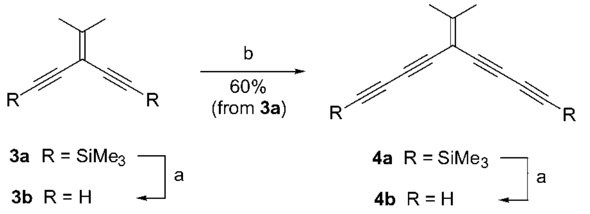
Scheme 1[a]



[a] Reagents and conditions: (a) K_2CO_3, wet MeOH/THF (1:1), rt; (b) Trimethylsilylacetylene, Hay catalyst, O_2, acetone, rt.

We have previously reported the analysis of *iso*-PDA oligomers, and these studies have demonstrated that the electronic properties of these materials are indeed moderated as a result of their cross-conjugated structure.[2a,d] We report herein an extension of our synthetic techniques toward the synthesis of *iso*-polytriacetylene oligomers, as well as a hybrid series of oligo(enynes) that derive directly from *iso*-PTAs **8**−**11**.[2b] We have used the electronic absorption spectra of these derivatives to explore the extent of communication as a function of oligomeric structure and length.

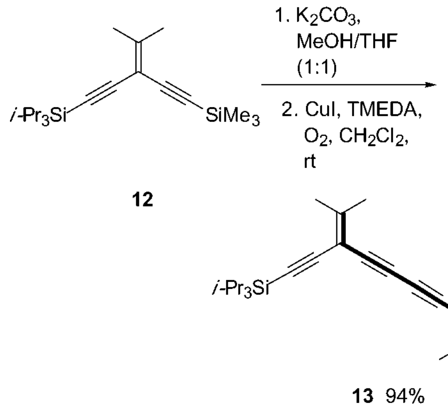
Results and Discussions

Syntheses and Characterization of *iso*-PTAs. Enetetrayne monomer **4a** was prepared to serve as the central core unit for a divergent construction of *iso*-PTAs (Scheme 1). Desilylation of monomer **3a**[2d] with K_2CO_3 in THF/MeOH afforded the terminal enediyne **3b** in essentially quantitative yield, which could be used without additional purification following workup.[14] Oxidative acetylenic coupling[15] of **3b** with an excess of trimethylsilylacetylene using Hay catalyst[16] in dry acetone for 24 h afforded **4a** in 60% yield as a colorless solid. While **4a** is unstable in the solid state, it can be stored for short periods of time in dilute acetone under refrigeration. This reaction also affords a substantial amount of bis(trimethylsilyl)butadiyne, the other product of homocoupling. The two compounds can, however, be separated by column chromatography, and the bis(trimethylsilyl)butadiyne can subsequently be used as starting material for synthesis of vinyl triflate **5**.[17]

Following isolation, monomer **4a** was quickly subjected to protiodesilylation, which proceeds quantitatively to the terminal alkyne **4b**, as judged by TLC analysis. The desilylated enyne **4b** was then taken on directly to the cross-coupling step with 2 equiv of vinyl triflate **5** in dry THF, using $PdCl_2(PPh_3)_2$ catalyst, CuI cocatalyst, and diisopropylamine as the base (Scheme 2). *iso*-PTA trimer **6** was formed in a yield of 93% and isolated as a relatively stable colorless solid. Using trimeric **6**, a second iteration of the protiodesilylation and cross-coupling procedure readily generated *iso*-PTA pentamer **7** in 88% yield. Attempts toward the desilylation of pentamer **7** have resulted in only decomposition of the deprotected derivative, and thus far, all attempts to extend the chain length of this series beyond that of **7** have been unsuccessful.

A complementary series of *iso*-PTA oligomers was synthesized as illustrated in Scheme 3, starting from vinyl triflate **5**. In contrast to the method outlined in Scheme 2, this more laborious approach achieved chain extension by only a single unit per protiodesilylation/cross-coupling iteration. It was expected, however, that the incorporation of the TIPS group would help to alleviate problems with stability and solubility that had plagued advanced stages of the previous approach in Scheme 2. Thus, vinyl triflate **5** was cross-coupled with triisopropylsilylacetylene under standard conditions to afford an enetriyne monomer **8** in 93% yield as a stable colorless solid that melts just above room temperature (mp 30−31 °C). Selective removal of the trimethylsilyl group in monomer **8** with K_2CO_3/MeOH, followed by cross-coupling with 1 equiv of vinyl triflate **5**, gave dimer **9** in 71% yield as a colorless solid. Employing **9**, a repetition of the protiodesilylation and cross-coupling with **5** gave trimer **10** in a yield of 73%, and tetramer **11** was then generated from **10** in 77% yield. Both **10** and **11** were isolated by column chromatography as relatively unstable colorless solids.

The incorporation of the TIPS moiety onto one terminus of the *iso*-PTAs did have the desired result of improving the solubility of these derivatives. Although solubility had been achieved, instability of desilylated derivatives, even with only monodesilylation, persisted. As had been observed in attempts to extend the chain length of pentamer **7**, removal of the TMS protecting group of tetramer **11** and attempted cross-coupling failed to produce isolable yields of the next oligomer in the series.



(1)

For purposes of comparison within the *iso*-PTA series, two dimeric derivatives have also been constructed. The first, dimer **13**, was assembled from monomer **12** via selective removal of the trimethylsilyl group followed by oxidative acetylenic homocoupling. Dimer **13** was isolated as a stable solid in a yield of 94%.

Scheme 4 outlines the synthesis of dimeric **16**. Triisopropylsilylbutadiyne was cross-coupled with vinyl triflate

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(14) As a result of their general instability, desilylated derivatives were carried on, following workup, to the subsequent coupling reaction without additional purification. Yields and purities from desilylation are sufficient to accommodate this tactic.

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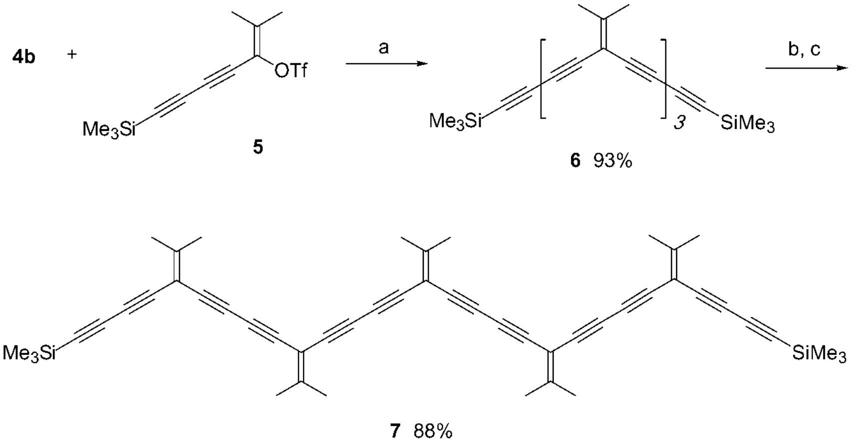
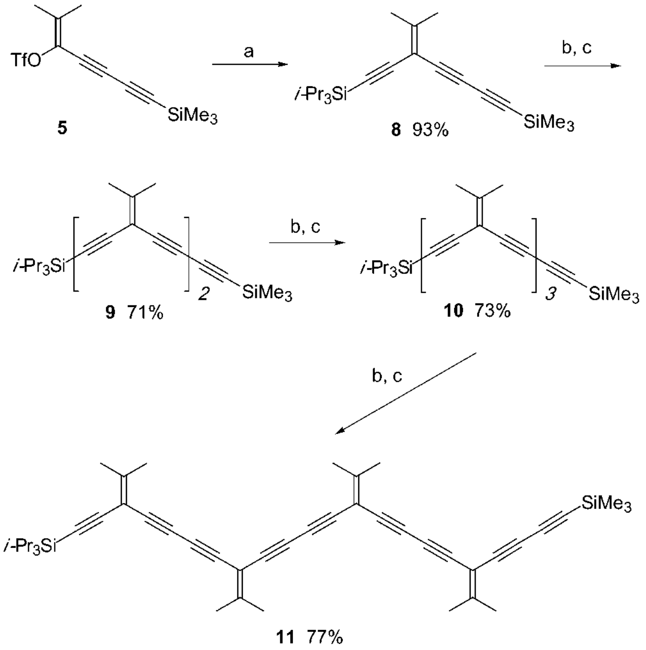
Scheme 2[a]



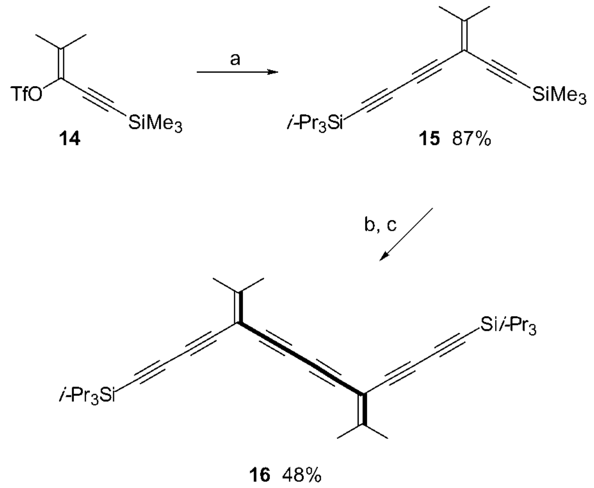
[a] Reagents and conditions: (a) $PdCl_2(PPh_3)_2$, CuI, *i*-Pr_2NH, THF, rt; (b) K_2CO_3, wet MeOH/THF (1:1), rt; (c) **5**, $PdCl_2(PPh_3)_2$, CuI, *i*-Pr_2NH, THF, rt.

Scheme 3[a]



[a] Reagents and conditions: (a) TIPS−C≡CH, $PdCl_2(PPh_3)_2$, CuI, *i*-Pr_2NH, THF, rt; (b) K_2CO_3, wet MeOH/THF (1:1), rt; (c) **5**, $PdCl_2(PPh_3)_2$, CuI, *i*-Pr_2NH, THF, rt.

Scheme 4[a]



[a] Reagents and conditions: (a) TIPS−C≡C−C≡CH, $PdCl_2(PPh_3)_2$, CuI, *i*-Pr_2NH, THF, rt; (b) K_2CO_3, wet MeOH/THF (1:1), rt; (c) CuCl/TMEDA, CH_2Cl_2, O_2, rt.

14[18] using palladium-catalyzed coupling conditions to give triyne **15**. Selective removal of the trimethylsilyl group gave the terminal alkyne, which was carried on directly to oxidative dimerization to give hexayne **16** as a stable colorless solid in 48% yield.

In general, *iso*-PTAs all displayed reasonable thermal stability. For example, monomer **4a** (64−65 °C), dimer **16** (129−130 °C), and trimer **6** (96−98 °C) all show defined melting points, whereas pentamer **7** decomposes at 85 °C. Relative to the shorter oligomers, the kinetic stability of the longer derivatives (e.g., tetramer **11** and pentamer **7**) was quite diminished, and decomposition was observed even when stored under nitrogen at low temperatures.

The stability of all *iso*-PTAs was sufficient for complete spectroscopic characterization, and ^{1}H and ^{13}C NMR analyses are completely consistent with their proposed structures. For example, the ^{13}C NMR spectrum of the longest oligomer, pentamer **7**, demonstrates the polarized nature of vinylidene carbons. The three vinyl carbons external to the oligomer chain (C=*C*Me_2) are significantly deshielded to δ 162−163, whereas the endo-chain vinyl carbons (*C*=CMe_2) are shifted considerably upfield and resonate in the range of the sp-hybridized carbons at δ 100.[19] Considering the similar electronic environment for carbons in an individual enyne repeat unit of the *iso*-PTA oligomers, it is noteworthy that all 20 unique sp- and sp^2-hybridized carbons are distinguishable in the ^{13}C NMR spectrum of **10**, and 25 of 26 such carbons are observed in the spectrum of **11**.

Electron impact mass spectrometric analysis of longer oligomers **7** and **11** was unsuccessful as a result of their high molecular weight. Electrospray ionization, however, proved to be quite useful in confirming their mass. Analysis in the positive mode of MeOH/toluene (3:1) solutions of **7** and **11** with AgOTf added to the solution produced well-resolved signals at *m*/*z* 813.2 and 771.2,

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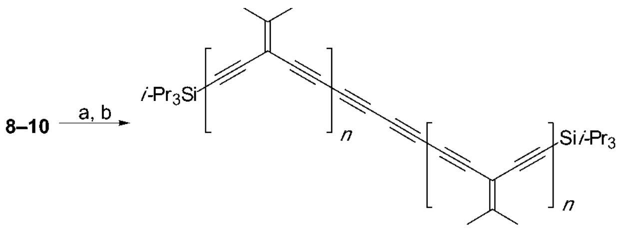
Scheme 5[a]



17 (n = 1) 96%
18 (n = 2) 78%
19 (n = 3) 68%

[a] Reagents and conditions: (a) K_2CO_3, wet MeOH/THF (1:1), rt; (b) CuI/TMEDA, CH_2Cl_2, O_2, rt.

consistent with that expected for $[\mathbf{7} + \mathrm{Ag}]^+$ and $[\mathbf{11} + \mathrm{Ag}]^+$, respectively.

Synthesis and Characterization of Expanded Enynes. Differentially protected enynes **8**−**11** provided the springboard for the realization of a hybrid sequence of oligoenynes based on a tetrayne core, as depicted in Schemes 5 and 6. Synthesis of the parent member of this series began with triyne **8**, which was desilylated with K_2CO_3/MeOH and then dimerized via oxidative acetylenic homocoupling with CuI/TMEDA and oxygen in CH_2Cl_2 to give **17** in a yield of 96% as a pale yellow solid. An analogous sequence of trimethylsilyl removal followed by dimerization was applied to **9** and **10**, giving decayne **18** and tetradecayne **19** as light yellow solids in 78 and 68% yields, respectively. The longest member of this series to be achieved, octadecayne **20**, was obtained from tetrameric **11** in 56% yield (Scheme 6). This molecule is composed of a contiguous sequence of 44 sp and sp^2 carbons, and on the basis of molecular modeling of the all *s*-trans orientation, it spans ca. 5.6 nm from silicon atom to silicon atom.[20]

Whereas enynes **17** and **18** show reasonable solubility, longer oligomers **19** and **20** have only limited solubility in organic solvents. In addition, the environmental stability of the enynes steadily decreased as the conjugated framework was extended from hexayne **17** to octadecayne **20**. Although **20** could be isolated and characterized by ^{1}H NMR, IR, and UV−vis spectroscopies, it was neither sufficiently soluble nor stable for ^{13}C NMR analysis. In the ^{13}C NMR spectra for tetrayne-derived systems **17**−**19**, the most distinguishing features are (1) the sp^2 isopropylidene carbons ($C{=}CMe_2$), which are observed in a range from 160.6 to 167.0 ppm, even more deshielded than those for the *iso*-PTAs (vide supra), (2) the two interior carbons of the tetrayne moiety, shielded to 68.1 and 64.2 ppm, and (3) the fact that resonances of all 28 unique carbons are observable for **19**. ESI MS proved to be invaluable for confirming the formation of the desired oligomers. Analysis of **18**−**20** by ESI in the positive mode with added AgOTf clearly showed signals corresponding to $[\mathrm{M} + \mathrm{Ag}]^+$ at *m/z* 879.3, 1083.4, and 1287.6, respectively.

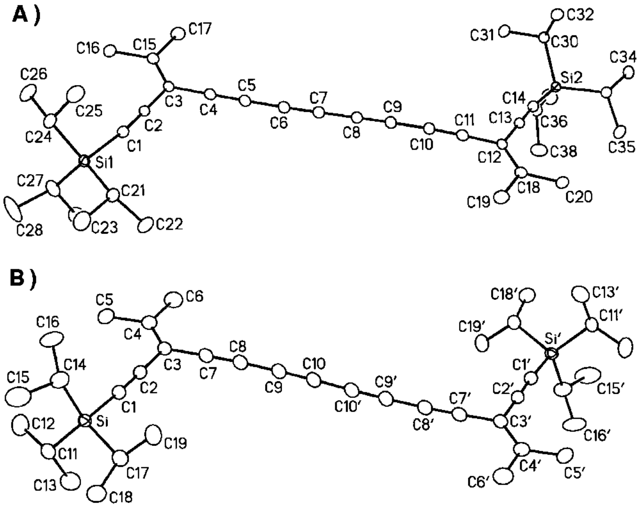


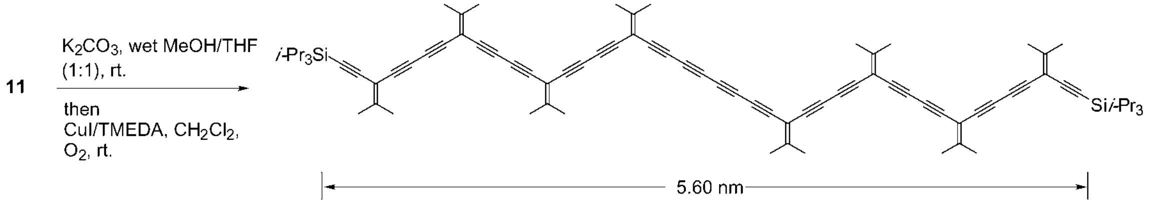
Figure 1. ORTEP drawings (20% probability level) and selected bond lengths (Å) of **17**. (A) Structure 1: C(1)−C(2) 1.204(3), C(4)−C(5) 1.200(3), C(6)−C(7) 1.209(3), C(8)−C(9) 1.203(3), C(10)−C(11) 1.200(3), C(13)−C(14) 1.207(3). (B) Structure 2: C(1)−C(2) 1.203(4), C(7)−C(8) 1.199(4), C(9)−C(10) 1.209(4).

Solid-State Properties of a Cross-Conjugated Tetrayne. Single crystals of compound **17** were obtained by diffusion of MeOH into a CH_2Cl_2 at −20 °C and provided an excellent opportunity to probe the solid-state properties of these highly unsaturated enynes. Surprisingly, under the same crystallization conditions, two different polymorphs of **17** could be obtained. In addition, there appears to be no way to direct which polymorph will result for a given crystallization attempt.

The two geometrically similar solid-state structures adopt *s*-trans orientations with respect to the octatetraynediyl moiety (Figure 1). The overall π-framework is virtually planar in both cases, with maximum deviations of 0.13 and 0.02 Å from a least-squares plane for the 16-carbon conjugated skeletons in structures 1 and 2, respectively. All triple bonds are essentially the same length and comparable to other reported polyynes.[21] The eight tetrayne carbons show only a gradual curvature with bond angles deviating from 180° by less than 3° in all cases.

The major difference between the two structures is the orientation of the individual molecules with respect to each other in the solid state. In the case of structure 1, the molecules are aligned parallel to each other in a manner potentially suitable for topochemical polymerization.[2b,22] In structure 2, neighboring molecules are nearly perpendicular to each other, precluding the possibility of solid-state polymerization. The topochemical

Scheme 6



20 56%

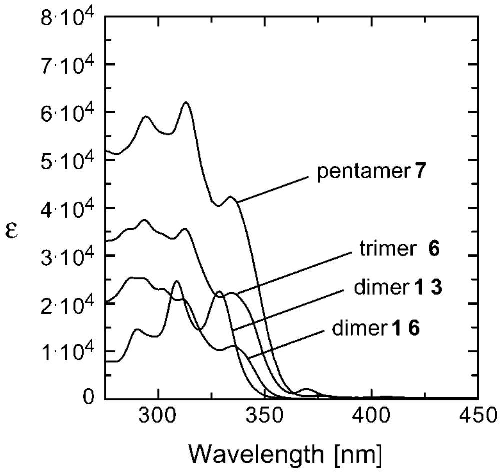


Figure 2. Electronic absorption spectra (ϵ [L M^{-1} cm^{-1}]) in CHCl$_3$ comparing **6**, **7**, **13**, and **16**.

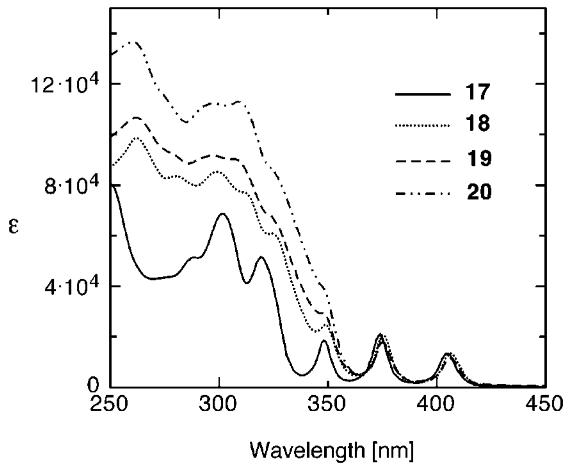


Figure 3. Electronic absorption spectra (ϵ [L M^{-1} cm^{-1}]) in CHCl$_3$ comparing **17**−**20**.

polymerization of **17** and other related cross-conjugated enynes is currently under investigation.

Electronic Characteristics of Cross-Conjugated Oligoenynes. Electronic absorption spectra of cross-conjugated *iso*-PTAs and related oligoenynes were used to survey their π-electronic properties. Dimer **16** provides the basis of comparison with the *iso*-PTA series. It possesses the longest linearly conjugated segment (shown in bold), and contributions via cross conjugation in the longer oligomers would be manifested in a change in λ_{max} values for oligomers **6** and **7** vs **16**. In the progression from dimer **16** to trimer **6** to pentamer **7**, the higher-energy region of the electronic absorption spectra shows a steadily augmenting molar absorptivity. The lower-energy region of the spectra of all three compounds shows two major absorptions of similar energies at 312 and 334 nm.[23] The spectra for this series of *iso*-PTAs, **6**−**7** and **16**, thus suggest that chain length extension is of little consequence to λ_{max} values. This effect is in accord with the previous observations for *iso*-PTAs,[8] but runs contrary to that observed in *iso*-PDAs.[2a,d]

Whereas the spectra of *iso*-PTAs **16**, **6**, and **7** show absorptions of similar energies, a comparison of the three dimeric molecules synthesized in this study, namely, **9**, **13**, and **16**, provides an interesting observation (spectra for the limiting cases, **13** and **16**, are shown in Figure 2). As the terminal functionalities are altered from simply ethynyl to 1,3-butadiynyl in the progression from **13** → **9** → **16**, a steady decrease in both the molar absorptivity and energy of λ_{max} is observed from **13** 329 (22 300) to **9** 332 (13 600) to **16** 335 (11 100) nm.[24] This trend demonstrates the ability to influence the electronic communication in cross-conjugated enynes, albeit to only a small extent as measured by UV−vis spectroscopy.

The spectra of tetrayne-based oligoenynes are shown in Figure 3. As demonstrated for the *iso*-PTAs, the higher-energy region shows a steadily increasing molar absorptivity versus the number of enediyne monomers. The lower-energy region is dominated by the absorption pattern of the tetrayne moiety. Each tetrayne displays three identical absorptions at 405, 374, and 348 nm that are remarkably similar within this series of molecules. Furthermore, these absorptions are found at virtually identical energies for other tetraynes such as 1,8-bis(4-*tert*-butylphenyl)octatetrayne.[2b,24] No obvious energy shift (less than 1 nm) can be observed in the tetrayne absorptions as a result of increasing the cross-conjugated chain length from **17** → **20**. To the contrary, however, the higher energy absorptions resulting from the *iso*-PTA segments of the molecules (ca. 330 nm) show a slight bathochromic shift in the longer oligomers. Thus, with chain elongation, this ultimately results in a merging of the *iso*-PTA absorption with that of the tetrayne moiety at 348 nm, affording a single, nondistinctive shoulder for **20**.

Conclusions

This work has demonstrated an effective synthesis of highly unsaturated, cross-conjugated enynes. The iterative sequence of palladium-catalyzed cross-couplings of terminal alkynes with vinyl triflates is quite effective for the realization of *iso*-PTA oligomers, combining short reaction times with good to excellent yields. Whereas shorter cross-conjugated oligomers are generally soluble and stable, all of the longer oligomers were less robust and only marginally soluble in organic solvents. Ultimately, these factors both prevented chain length extension beyond that found in pentameric *iso*-PTA **7** and tetrayne-based **20**. There is a minimal electronic effect resulting from cross conjugation, although in shorter oligomers such as dimers **9**, **13**, and **16** the effect of the end group (ethynyl vs butadiynyl) is clearly observed.

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[23] We believe that the weak absorbance at ca. 372 nm for compound **6** is due to an impurity resulting from oxidative acetylenic coupling that, to date, we have been unable to separate from the desired oligomer.

[24] These UV−vis spectra are provided as Supporting Information.

Experimental Section

Reagents and solvents were purchased reagent grade and used without further purification. Compounds **5**,[17] **3a**,[2d] 1-triisopropylsilyl-butadiyne,[25] **12**,[2d] and **14**[18] were prepared as described. Anhydrous $MgSO_4$ was used as the drying agent after aqueous workup. Evaporation and concentration in vacuo was done at H_2O-aspirator pressure. All reactions were performed in standard glassware. A positive pressure of argon was essential to the success of all Pd-catalyzed reactions, and oxidative acetylenic couplings were conducted under exposure to air. Degassing of solvents was accomplished by vigorously bubbling argon through the solution for at least 45 min. Column chromatography was performed on silica using the solvent system described.

X-ray crystal data for **17** (structure 1): $C_{38}H_{54}Si_2$, $M = 566.99$, monoclinic space group $P2_1/c$ (No. 14), $D_c = 1.018$ g/cm^3, $Z = 4$, $a = 13.5571(8)$, $b = 7.7132(5)$, $c = 35.616(2)$ Å, $\beta = 96.5990(10)°$, $V = 3699.7(4)$ Å^3, $\mu = 0.118$ mm^{-1}. Final $R(F) = 0.0472$, w$R_2(F^2) = 0.1366$ for 365 variables and 7039 data points with $F_o^2 \geq -3\sigma(F_o^2)$ (4842 observations [$F_o^2 \geq 2\sigma(F_o^2)$]). Full details can be found in ref 2b.

X-ray crystal data for **17** (structure 2): monoclinic space group $P2_1/n$ (an alternative setting of $P2_1/c$ [No. 14]), $D_c = 0.993$ g/cm^3, $Z = 2$, $a = 8.1266(9)$, $b = 12.8068(13)$, $c = 18.6241(19)$ Å, $\beta = 101.987(2)°$, $V = 1896.1(3)$ Å^3, $\mu = 0.115$ mm^{-1}. Final $R(F) = 0.0679$, w$R_2(F^2) = 0.2053$ for 183 variables and 3863 data points with $F_o^2 \geq -3\sigma(F_o^2)$ (2397 observations [$F_o^2 \geq 2\sigma(F_o^2)$]).

General Palladium-Catalyzed Cross-Coupling Procedure. A mixture of the appropriate trimethylsilyl-protected polyyne and K_2CO_3 (ca. 0.2 equiv) in wet THF/MeOH (1:1, 10 mL) was stirred at room temperature for 0.5 h. Ether and saturated aqueous NaCl were added, and the organic phase was separated, washed with saturated aqueous NaCl (2 × 15 mL), dried, reduced to ca. 1 mL, and added to a degassed solution of the appropriate vinyl triflate **5** or **14** (1 equiv) in THF (20 mL). $PdCl_2(PPh_3)_2$ (ca. 0.05 equiv) and diisopropylamine (ca. 3 equiv) were sequentially added, and the solution was stirred for 5 min; CuI (ca. 0.15 equiv) was added and the solution stirred until TLC analysis no longer showed the presence of the deprotected polyyne (generally less than 2 h). Ether and H_2O were added; the organic phase was separated, washed with 10% HCl, saturated aqueous $NaHCO_3$ (25 mL), and saturated aqueous NaCl (25 mL), and dried, and the solvent was removed. Flash column chromatography gave the desired oligomer.

General Copper-Catalyzed Oxidative Acetylenic Coupling Procedure. The appropriate trimethylsilyl-protected oligomer was desilylated in methanolic K_2CO_3 as described above. Following workup, the solution of the deprotected product was reduced to ca. 1 mL and added to CH_2Cl_2 (40 mL). A solution of the catalyst mixture [CuI (50 mg) and TMEDA (75 mg) added to CH_2Cl_2 (2 mL) and stirred until homogeneous] was then added. The mixture was stirred at room temperature under air until TLC analysis no longer showed the deprotected polyyne (generally less than 0.5 h). The reaction solution was concentrated in vacuo to ca. 5 mL and ether added (50 mL). The ethereal solution was consecutively washed with 10% HCl (25 mL), saturated aqueous $NaHCO_3$ (25 mL), and saturated aqueous NaCl (25 mL), and dried, and the solvent was removed. Flash column chromatography and precipitation from MeOH gave the desired homocoupled oligomer.

1,9-Bis(trimethylsilyl)-5-isopropylidene-1,3,6,8-nonatetrayne (4a). Enediyne **3a** (200 mg, 0.805 mmol) was desilylated with K_2CO_3/MeOH to give **3b**, which was directly subjected to oxidative coupling with trimethylsilylacetylene (1.0 g, 10 mmol) using Hay catalyst[16] (4 mL) in dry acetone (100 mL). The mixture was stirred at room temperature under air for 24 h. The solution was extracted with pentane, sequentially washed with 10% HCl (25 mL), saturated $NaHCO_3$ (25 mL), and saturated aqueous NaCl (25 mL), and then dried. Solvent removal and flash chromatography (pentane) afforded **4a** (142 mg, 60%) as a colorless solid. $R_f = 0.5$ (pentane). Mp: 64−65 °C. IR (CH_2Cl_2, cast): 2960, 2901, 2202, 2094, 1588 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.04 (s, 6H), 0.18 (s, 18H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 163.3, 99.7, 91.6, 87.7, 77.0, 72.5, 23.3, −0.4. EI HRMS: calcd for $C_{18}H_{24}Si_2$ (M$^+$), 296.1417; found, 296.1415. Anal. Calcd for $C_{18}H_{24}Si_2$: C, 72.90; H, 8.16. Found: C, 72.61; H, 7.98.

1,19-Bis(trimethylsilyl)-5,10,15-tri(isopropylidene)-1,3,6,8,11,13,16,18-nonadecaoctayne (6). Compound **4a** (30 mg, 0.10 mmol) was desilylated to give **4b**, which was directly cross-coupled with triflate **5** (77 mg, 0.24 mmol) in degassed THF (10 mL) in the presence of $PdCl_2(PPh_3)_2$ (7 mg, 0.01 mmol), diisopropylamine (80 mg, 0.79 mmol), and CuI (4 mg, 0.02 mmol) for 20 min as described in the general procedure. Flash chromatography (hexane/CH_2Cl_2 5:1) afforded **6** (47 mg, 93%) as a light yellow solid. $R_f = 0.8$ (hexane/CH_2Cl_2 5:1). Mp: 96−98 °C. IR ($CHCl_3$, cast): 2960, 2906, 2200, 2096, 1584 cm^{-1}. UV−vis ($CHCl_3$): λ (ϵ) 284 (35 100), 294 (37 400), 312 (35 600), 334 (22 200). ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.06 (s, 9H), 2.05 (s, 9H), 0.18 (s, 18H). ^{13}C NMR (125 MHz, $CDCl_3$, APT): δ 162.5, 162.0, 100.1, 99.9, 91.4, 87.7, 78.1, 78.0, 76.8, 76.5, 76.4, 72.5, 23.3, −0.3 (two coincidental peaks not observed). EI HRMS: calcd for $C_{34}H_{36}Si_2$ (M$^+$), 500.2356; found, 500.2347.

1,29-Bis(trimethylsilyl)-5,10,15,20,25-penta(isopropylidene)-1,3,6,8,11,13,16,18,21,23,26,28-nonacosadodecayne (7). Compound **6** (50 mg, 0.10 mmol) was desilylated and cross-coupled with triflate **5** (65 mg, 0.20 mmol) in degassed THF (10 mL) in the presence of $PdCl_2(PPh_3)_2$ (7 mg, 0.01 mmol), diisopropylamine (80 mg, 0.79 mmol), and CuI (4 mg, 0.02 mmol) for 2 h as described in the general procedure. Flash chromatography (hexane/CH_2Cl_2 5:1) afforded **7** (62 mg, 88%) as a light yellow solid. $R_f = 0.6$ (hexane/CH_2Cl_2 5:1). Mp: 85 °C dec. IR (CH_2Cl_2, cast): 2958, 2923, 2849, 2201, 2095, 1584 cm^{-1}. UV−vis ($CHCl_3$): λ (ϵ) 294 (59 000), 313 (62 000), 334 (42 300). ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.07 (s, 15H), 2.06 (s, 15H), 0.19 (s, 18H). ^{13}C NMR (125 MHz, $CDCl_3$, APT): δ 162.5, 161.6, 100.2, 99.5, 91.4, 87.7, 78.1 (3×), 78.0, 76.8, 76.5, 76.4 (3×), 72.5, 23.4, 23.3, −0.3 (four coincidental peaks not observed). ESI MS (MeOH/toluene 3:1, AgOTf added): 813.2 ([M + Ag]$^+$).

2-Methyl-7-trimethylsilyl-3-triisopropylsilylethynylhepta-2-ene-4,6-diyne (8). Triflate **5** (100 mg, 0.308 mmol) was cross-coupled with triisopropylsilylacetylene (112 mg, 0.616 mmol) in degassed THF (20 mL) in the presence of $PdCl_2(PPh_3)_2$ (11 mg, 0.016 mmol), diisopropylamine (93 mg, 0.92 mmol), and CuI (6 mg, 0.03 mmol) for 0.5 h as described in the general procedure. Flash chromatography (hexane/CH_2Cl_2 2:1) afforded **8** (102 mg, 93%) as a colorless solid. $R_f = 0.8$ (hexane/CH_2Cl_2 2:1). Mp: 30−31 °C. IR (CH_2Cl_2, cast): 2943, 2866, 2202, 2144, 2098, 1587 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.05 (s, 3H), 2.04 (s, 3H), 1.07 (s, 21H), 0.20 (s, 9H). ^{13}C NMR (75 MHz, $CDCl_3$, APT): δ 160.0, 101.9, 101.1, 93.9, 90.6, 88.1, 76.0, 73.9, 23.2, 23.0, 18.7, 11.3, −0.3. EI MS *m/z* (rel intensity): 356 (M$^+$, 46), 313 ([M − *i*-Pr]$^+$, 100). EI HRMS: calcd for $C_{22}H_{36}Si_2$ (M$^+$), 356.2356; found, 356.2357. Anal. Calcd for $C_{22}H_{36}Si_2$: C, 74.08; H, 10.17. Found: C, 74.05; H, 10.41.

2-Methyl-8-isopropylidene-12-trimethylsilyl-3-triisopropylsilylethynyldodeca-2-ene-4,6,9,11-tetrayne (9). Enetriyne **8** (151 mg, 0.423 mmol) was desilylated and cross-coupled with triflate **5** (137 mg, 0.423 mmol) in degassed THF (20 mL) in the presence of $PdCl_2(PPh_3)_2$ (18 mg, 0.026 mmol), diisopropylamine (130 mg, 1.28 mmol), and CuI (6 mg, 0.03 mmol) for 20 min as described in the general procedure. Flash chromatography (hexane/CH_2Cl_2 5:1) afforded **9** (138 mg, 71%) as a pale yellow solid. $R_f = 0.5$ (hexane/CH_2Cl_2 5:1). Mp: 82−83 °C. IR (neat): 2943, 2865, 2202, 2149, 2095, 1581 cm^{-1}. UV−vis ($CHCl_3$): λ (ϵ) 290 (23 900), 310 (21 300), 332 (13 600). ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.06 (s, 9H), 2.04 (s, 3H), 1.07 (s, 21H), 0.18 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 162.3, 159.3, 102.1, 101.4, 100.1, 93.8, 91.4, 87.8, 79.5, 77.4, 76.9, 76.8, 75.5, 72.7, 23.3 (2×), 23.2, 23.0, 18.7, 11.3, −0.4. EI HRMS: calcd for $C_{30}H_{42}Si_2$ (M$^+$), 458.2825; found, 458.2830. Anal. Calcd for $C_{30}H_{42}Si_2$: C, 78.53; H, 9.23. Found: C, 78.89; H, 9.33.

2-Methyl-8,13-di(isopropylidene)-17-trimethylsilyl-3-triisopropylsilylethynyl-heptadeca-2-ene-4,6,9,11,14,16-hexayne (10). Dimer **9** (92 mg, 0.20 mmol) was desilylated and cross-coupled with triflate **5** (65 mg, 0.20 mmol) in degassed THF (20 mL) in the presence of $PdCl_2(PPh_3)_2$ (10 mg, 0.014 mmol), diisopropylamine (60 mg, 0.59 mmol), and CuI (5 mg, 0.02 mmol) for 15 min as described in the general procedure. Flash chromatography (hexane/CH_2Cl_2 2:1) afforded **10** (82 mg, 73%) as a pale yellow solid. $R_f = 0.6$ (hexane/CH_2Cl_2 2:1). Mp 40−44 °C. IR (CH_2Cl_2, cast): 2943, 2865, 2200, 2147, 2096, 1585 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 2.072 (s, 3H), 2.065 (s, 3H), 2.055 (s, 6H), 2.040 (s, 3H), 2.038 (s, 3H), 1.07 (s, 21H) 0.18 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$, APT): δ 162.4, 161.6, 159.0, 102.0, 101.3, 100.3, 100.0, 93.7, 91.4, 87.7, 79.5, 78.3, 77.9, 77.5, 76.8 (2×), 76.6, 76.3, 75.5, 72.5, 23.4, 23.3 (2×), 23.2, 23.0, 18.7, 11.4, −0.3 (one coincident signal not observed). EI HRMS: calcd for $C_{38}H_{48}Si_2$ (M^+), 560.3295; found, 560.3286.

2-Methyl-8,13,18-tri(isopropylidene)-22-trimethylsilyl-3-triisopropylsilylethynyl-docosa-2-ene-4,6,9,11,14,16,19,-21-octayne (11). Timer **10** (67 mg, 0.12 mmol) was desilylated and cross-coupled with triflate **5** (39 mg, 0.12 mmol) in degassed THF (20 mL) in the presence of $PdCl_2(PPh_3)_2$ (4 mg, 0.006 mmol), diisopropylamine (40 mg, 0.40 mmol), and CuI (2 mg, 0.01 mmol) for 15 min as described in the general procedure. Flash chromatography (hexane/CH_2Cl_2 2:1) afforded **11** (61 mg, 77%) as a pale yellow solid. Mp 82−85 °C. $R_f = 0.6$ (hexane/CH_2Cl_2 2:1). IR ($CHCl_3$, cast): 2942, 2865, 2195, 2147, 2097, 1584 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ 2.074 (s, 3H), 2.067 (s, 9H), 2.06 (s, 9H), 2.04 (s, 3H), 1.07 (s, 21H), 0.19 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$, APT): δ 162.5, 162.0, 161.6, 159.0, 102.0, 101.3, 100.3, 100.2, 99.9, 93.7, 91.4, 87.7, 79.4, 78.27, 78.15, 78.05, 78.0, 77.5, 76.8, 76.53, 76.47, 76.37, 76.32, 75.5, 72.5, 23.35, 23.34, 23.32, 23.2, 23.0, 18.7, 11.3, −0.3 (four coincident peaks not observed). ESI MS *m*/*z* (MeOH/toluene 3:1, AgOTf added): 771.2 ([*M* + Ag]$^+$).

3,8-Bis(trimethylsilylethynyl)-2,9-dimethyl-deca-2,8-diene-4,6-diyne (13). The trimethylsilyl group of enediyne **12** (60 mg, 0.18 mmol) was removed with methanolic K_2CO_3 according to the general procedure. Homocoupling as described in general procedure followed by flash chromatography (hexane/CH_2Cl_2 2:1) afforded **13** (44 mg, 94%) as a colorless solid. $R_f = 0.7$ (hexane/CH_2Cl_2 2:1). Mp 117 °C. IR ($CHCl_3$, cast): 2943, 2866, 2150, 2096 cm^{-1}. UV−vis ($CHCl_3$): λ (ϵ) 290 (14 600), 309 (24 600), 329 (22 300). ^1H NMR (300 MHz, $CDCl_3$): δ 2.06 (s, 6H), 2.04 (s, 6H), 1.07 (s, 42H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 158.8, 102.3, 101.5, 93.6, 79.0, 75.9, 23.1, 23.0, 18.7, 11.4. EI HRMS: calcd for $C_{34}H_{54}Si_2$ (M^+), 518.3764; found, 518.3744.

2-Methyl-3-trimethylsilylethynyl-7-triisopropylsilyl-hepta-2-ene-4,6-diyne (15). 1-Triisopropylsilylbuta-1,3-diyne (89 mg, 0.43 mmol)[25] was cross-coupled with triflate **14** (109 mg, 0.363 mmol) in degassed THF (20 mL) in the presence of $PdCl_2(PPh_3)_2$ (12 mg, 0.017 mmol), diisopropylamine (93 mg, 0.92 mmol), and CuI (6 mg, 0.03 mmol) for 2 h as described in the general procedure. Flash chromatography (hexane/CH_2Cl_2 2:1) afforded **15** (113 mg, 87%) as a pale yellow oil. $R_f =$ 0.8 (hexane/CH_2Cl_2 2:1). IR (CH_2Cl_2, cast): 2944, 2866, 2201, 2147, 2095, 1587 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ 2.04 (s, 3H), 2.03 (s, 3H), 1.07(s, 21H), 0.18 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$, APT): δ 160.1, 100.6, 100.2, 97.2, 89.6, 88.0, 76.6, 72.2, 23.1 (2×), 18.6, 11.4, 0.0. EI MS *m*/*z* (rel intensity): 356 (M^+, 50), 313 ([M − *i*-Pr]$^+$, 100). EI HRMS: calcd for $C_{22}H_{36}Si_2$ (M^+), 356.2356; found, 356.2355.

1,14-Bis(trimethylsilyl)-5,10-di(isopropylidene)-1,3,6,8,-11,13-tetradeca-hexayne (16). Enetriyne **15** (70 mg, 0.20 mmol) was selectively protiodesilylated with K_2CO_3 as described in the general procedure and homocoupled in the presence of Hay catalyst[15] under air in CH_2Cl_2 (10 mL) for 4 h. Flash chromatography (hexane/CH_2Cl_2 2:1) afforded **16** (26 mg, 48%) as a pale yellow solid. Mp: 129−130 °C. $R_f = 0.6$ (hexane/CH_2Cl_2 2:1). IR (CH_2Cl_2, cast): 2943, 2865, 2199, 2092 cm^{-1}. UV−vis ($CHCl_3$): λ (ϵ) 289 (25 200), 310 (20 700), 335 (11 100). ^1H NMR (500 MHz, $CDCl_3$): δ 2.08 (s, 6H), 2.06 (s, 6H), 1.07 (s, 42H). ^{13}C NMR (125 MHz, $CDCl_3$, APT): δ 162.4, 100.0, 89.3, 88.7, 78.2, 76.4, 71.2, 23.41, 23.35, 18.6, 11.4 (one coincident peak not observed). EI HRMS: calcd for $C_{38}H_{54}Si_2$ (M^+), 566.3764; found, 566.3753.

3,12-Bis(triisopropylsilylethynyl)-2,13-dimethyl-tetradeca-2,12-diene-4,6,8,10-tetrayne (17). Enetriyne **8** (42 mg, 0.12 mmol) was desilylated and homocoupled in CH_2Cl_2 (20 mL) in the presence of CuI (50 mg, 0.26 mmol), TMEDA (75 mg, 0.65 mmol), and air for 20 min as described in the general procedure. Flash chromatography (hexane/CH_2Cl_2 2:1) afforded **17** (32 mg, 96%) as a yellow solid. $R_f = 0.7$ (hexane/CH_2Cl_2 2:1). Mp: 103−104 °C. IR (μscope): 2943, 2865, 2194, 2143, 1586 cm^{-1}. UV−vis ($CHCl_3$): λ (ϵ) 288 (51400), 300 (67 900), 319 (51 700), 348 (18 600), 374 (20 200), 405 (13 400). ^1H NMR (300 MHz, $CDCl_3$): δ 2.07 (s, 6H), 2.05 (s, 6H), 1.07 (s, 42H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 162.4, 101.2, 100.9, 94.8, 76.3, 75.0, 67.8, 64.1, 23.4, 23.2, 18.7, 11.3. EI HRMS: calcd for $C_{38}H_{54}Si_2$ (M^+), 566.3764; found, 566.3774.

3,22-Bis(triisopropylsilylethynyl)-8,17-di(isopropylidene)-2,23-dimethyl-tetracosa-2,22-diene-4,6,9,11,13,15,-18,20-octayne (18). Dimer **9** (29 mg, 0.063 mmol) was desilylated and homocoupled in CH_2Cl_2 (20 mL) in the presence of CuI (50 mg, 0.26 mmol), TMEDA (75 mg, 0.65 mmol), and air for 0.5 h as described in the general procedure. Flash chromatography (hexane/CH_2Cl_2 2:1) afforded **18** (19 mg, 78%) as a waxy yellow solid. $R_f = 0.4$ (hexane/CH_2Cl_2 2:1). IR (μscope): 2942, 2864, 2200, 2145, 1580 cm^{-1}. UV−vis ($CHCl_3$): λ (ϵ) 262 (98 700), 299 (85 300), 312 (77 100), 324 (61 000), 349 (25 000), 375 (20 900), 406 (13 500). ^1H NMR (300 MHz, CD_2Cl_2): δ 2.11 (s, 12H), 2.09 (s, 6H), 2.06 (s, 6H), 1.10 (s, 42H). ^{13}C NMR (125 MHz, CD_2Cl_2): δ 166.6, 160.8, 102.3, 101.2, 99.7, 94.3, 80.2, 77.5, 77.0, 76.9, 75.4, 74.4, 68.1, 64.2, 23.7, 23.6, 23.3, 23.1, 18.8, 11.7. ESI MS *m*/*z* (MeOH/toluene 3:1, AgOTf added): 879.3 ([M + Ag]$^+$).

3,32-Bis(triisopropylsilylethynyl)-8,13,22,27-tetra(isopropylidene)-2,33-dimethyl-tetratriconta-2,32-diene-4,6,9,-11,14,16,18,20,23,25,28,30-dodecayne (19). Trimer **10** (37 mg, 0.066 mmol) was desilylated and homocoupled in CH_2Cl_2 (20 mL) in the presence of CuI (50 mg, 0.26 mmol), TMEDA (75 mg, 0.65 mmol), and air for 15 min as described in the general procedure. Flash chromatography (hexane/CH_2Cl_2 2:1) afforded **19** (22 mg, 68%) as a light yellow solid. Mp: 85 °C dec. $R_f = 0.2$ (hexane/CH_2Cl_2 2:1). IR (CH_2Cl_2, cast): 2941, 2849, 2195, 2146, 1582 cm^{-1}. UV−vis ($CHCl_3$): λ (ϵ) 262 (107 000), 297 (91 800), 307 (90 300), 324 (67 700), 348 (29 200), 375 (18 100), 406 (11 900). ^1H NMR (400 MHz, $CDCl_3$): δ 2.09 (s, 12H), 2.08 (s, 6H), 2.07 (s, 6H), 2.06 (s, 6H), 2.04 (s, 6H), 1.07 (s, 42H). ^{13}C NMR (100 MHz, $CDCl_3$, APT): δ 165.3, 162.0, 159.2, 102.0, 101.3, 100.3, 99.8, 93.7, 79.5, 78.7, 77.4, 77.2, 77.1, 77.0, 76.9, 76.1, 75.5, 73.7, 68.1, 63.9, 23.5, 23.4, 23.3, 23.2, 23.1, 22.9, 18.8, 11.7. ESI MS *m*/*z* (MeOH/toluene 3:1, AgOTf added): 1083.4 ([M + Ag]$^+$).

3,42-Bis(triisopropylsilylethynyl)-8,13,18,27,32,37-hexa-(isopropylidene)-2,43-dimethyl-tetratetraconta-2,42-di-ene-4,6,9,11,14,16,19,21,23,25,28,30,33,35,38,40-hexadecayne (20). Tetramer **11** (10 mg, 0.015 mmol) was desilylated and homocoupled in CH_2Cl_2 (20 mL) in the presence of CuI (50 mg, 0.26 mmol), TMEDA (75 mg, 0.65 mmol), and air for 15 min as described in the general procedure. Flash chromatography (hexane/CH_2Cl_2 1:1) afforded **20** (5 mg, 56%) as a light yellow solid. Mp: >98 °C dec. $R_f = 0.6$ (hexane/CH_2Cl_2 1:1). IR (μscope): 2942, 2865, 2196, 2145, 1578 cm^{-1}. UV−vis ($CHCl_3$): λ (ϵ) 260 (137 000), 308 (113 000), 375 (18 200), 406 (11 500). ^1H NMR (400 MHz, $CDCl_3$): δ 2.08 (s, 12H), 2.07 (s, 24H), 2.06 (s, 6H), 2.04 (s, 6H), 1.07 (s, 42H). This sample was insufficiently soluble and stable for meaningful ^{13}C NMR analysis. ESI MS *m*/*z* (MeOH/toluene 3:1, AgOTf added): 1287.6 ([M + Ag]$^+$).

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Supporting Information Available: Additional experimental details, ^{1}H and ^{13}C NMR spectra for new compounds, UV–vis spectra for selected oligomers, ESI MS for **20**, and X-ray crystallographic data for **17**. This material is available free of charge via the Internet at http://pubs.acs.org.

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