J. Org. Chem. **2002,** *67,* 336−344

Iterative Synthesis and Characterization of Cross-Conjugated Iso-Polydiacetylenes

Yuming Zhao, Katie Campbell, and Rik R. Tykwinski*

Department of Chemistry, University of Alberta, Edmonton AB T6G 2G2, Canada

rik.tykwinski@ualberta.ca

Received May 31, 2001

An iterative synthesis of cross-conjugated iso-polydiacetylenes (iso-PDAs) is reported based on three fundamental building blocks: vinyl triflates **8**, **9**, and **25**. An efficient sequence of palladium-catalyzed cross-coupling reactions of vinyl triflates and terminal alkynes has been employed to extend the chain length of these oligomers. The longest member of the series, nonamer **19**, spans 3.4 nm from Si to Si atom. The stability and solubility of the conjugated oligomers have been evaluated as a function of pendant substitution. Assessment of solid-state structural properties was achieved via X-ray crystallographic analyses of monomer **12** and trimer **14**. The electronic characteristics of the monodisperse oligomers have been fully analyzed by UV−vis spectroscopy in solution and as thin films, and these studies suggest that π-electron communication is present along the enyne framework, but quickly reaches saturation by the stage of nonamer **19**.

Introduction

Conjugated organic molecules are a primary focus of a new generation of optical and electronic materials.[1,2] Monodisperse oligomers[3−5] with carbon, heteroatomic, or organometallic frameworks have been explored as media for electroluminescence,[6] data storage,[7] and nonlinear optics.[8] The most intensely studied conjugated molecules with all-carbon frameworks have extended, linearly conjugated π systems,[4] as found in oligomers and polymers such as polyacetylenes (PAs) **1**,[1b] polydiacetylenes (PDAs) **2**,[9] polytriacetylenes (PTAs) **3**,[4,10] and the one-dimensional carbon allotrope, carbyne **4**.[11] The electronic properties that result from alternative modes of π-electron communication, in particular cross conjugation,[12−14] have been less frequently studied, and the potential utility of materials with a fully cross-conjugated π backbone is not currently known.[15,16]

Chart 1 illustrates the cross-conjugated isomers that arise as the constitutional isomers of the linearly conjugated analogues **1**−**3**: iso-polyacetylenes (iso-PAs) or dendralenes **5**,[12,17] iso-polydiacetylenes (iso-PDAs) **6**,[18]

---

[1] (a) Skotheim, T. A.; Elsenbaumer, R. L.; Reynolds, J. R. *Handbook of Conducting Polymers*, 2nd ed.; Marcel Dekker: New York, 1997. (b) Salaneck, W. R.; Lundström, I.; Rånby, B. *Conjugated Polymers and Related Materials*; Oxford University Press: Oxford, 1993.

[2] Bunz, U. H. F. *Chem. Rev.* **2000**, *100*, 1605−1644.

[3] Wegner, G.; Müllen, K. *Electronic Materials−The Oligomer Approach*; Wiley-VCH: Weinheim, 1998.

[4] Martin, R. E.; Diederich, F. *Angew. Chem., Int. Ed.* **1999**, *38*, 1350−1377.

[5] Huang, S.; Tour, J. M. *J. Am. Chem. Soc.* **1999**, *121*, 4908−4909.

[6] Kraft, A.; Grimsdale, A. C.; Holmes, A. B. *Angew. Chem., Int. Ed.* **1998**, *37*, 402−428.

[7] Feringa, B. L.; Jager, W. F.; de Lange, B. *Tetrahedron* **1993**, *49*, 8267−8310.

[8] (a) Bosshard, C.; Sutter, K.; Prêtre, P.; Hulliger, J.; Flörsheimer, M.; Kaatz, P.; Günter, P. *Organic Nonlinear Optical Materials*; Gordon and Breach: Basel, 1995. (b) Nalwa, H. S. In *Organic Materials for Nonlinear Optics*; Nalwa, H. S., Miyata, S., Eds.; CRC Press: Boca Raton, FL, 1997; pp 611−797. (c) Tykwinski, R. R.; Gubler, U.; Martin, R. E.; Diederich, F.; Bosshard, C.; Günter, P. *J. Phys. Chem. B* **1998**, *102*, 4451−4465. (d) Schulz, M.; Tretiak, S.; Chernyak, V.; Mukamel, S. *J. Am. Chem. Soc.* **2000**, *122*, 452−459.

[9] (a) Giesa, R.; Klapper, M.; Schulz, R. C. *Makromol. Chem., Macromol. Symp.* **1991**, *44*, 1−10. (b) Giesa, R.; Schulz, R. C. *Polym. Int.* **1994**, *33*, 43−60. (c) Bloor, D.; Chance, R. R. *Polydiacetylenes*; Martinus Nijhoff: Dordrecht, 1985. (d) Wudl, F.; Bitler, S. P. *J. Am. Chem. Soc.* **1986**, *108*, 4685−4687.

[10] (a) Martin, R. E.; Gubler, U.; Cornil, J.; Balakina, M.; Boudon, C.; Bosshard, C.; Gisselbrecht, J.-P.; Diederich, F.; Günter, P.; Gross, M.; Bredas, J. L. *Chem.-Eur. J.* **2000**, *6*, 3622−3635. (b) Martin, R. E.; Gubler, U.; Boudon, C.; Bosshard, C.; Gisselbrecht, J.-P.; Günter, P.; Gross, M.; Diederich, F. *Chem.-Eur. J.* **2000**, *6*, 4400−4412. (c) Martin, R. E.; Wytko, J. A.; Diederich, F.; Boudon, C.; Gisselbrecht, J.-P.; Gross, M. *Helv. Chim. Acta* **1999**, *82*, 1470−1485. (d) Martin, R. E.; Mäder, T.; Diederich, F. *Angew. Chem., Int. Ed.* **1999**, *38*, 817−821. (e) Martin, R. E.; Gubler, U.; Boudon, C.; Gramlich, V.; Bosshard, C.; Gisselbrecht, J.-P.; Günter, P.; Gross, M.; Diederich, F. *Chem.-Eur. J.* **1997**, *3*, 1505−1512. (f) Schreiber, M.; Anthony, J.; Diederich, F.; Spahr, M. E.; Nesper, R.; Hubrich, M.; Bommeli, F.; Degiorgi, L.; Wachter, P.; Kaatz, P.; Bosshard, C.; Günter, P.; Colussi, M.; Suter, U. W.; Boudon, C.; Gisselbrecht, J.-P.; Gross, M. *Adv. Mater.* **1994**, *6*, 786−790.

[11] (a) Smith, P. P. K.; Buseck, P. R. *Science* **1982**, *216*, 984−986. (b) Hoffmann, R. *Tetrahedron* **1966**, *22*, 521−538. (c) Dembinski, R.; Bartik, T.; Bartik, B.; Jaeger, M.; Gladysz, J. A. *J. Am. Chem. Soc.* **2000**, *122*, 810−822. (d) Bunz, U. H. F. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 969−971.

[12] Hopf, H. *Classics in Hydrocarbon Synthesis*; Wiley-VCH: Weinheim, 2000; Chapter 11.

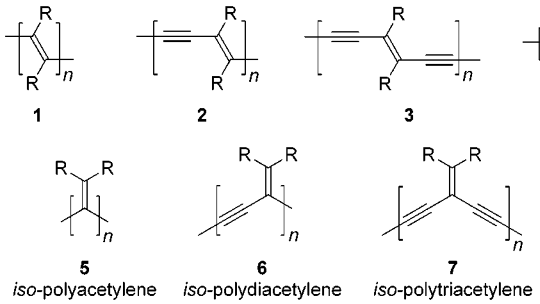
[13] (a) Trætteberg, M.; Hopf, H. *Acta Chem. Scand.* **1994**, *48*, 989−993. (b) Almenningen, A.; Gatial, A.; Grace, D. S. B.; Hopf, H.; Klaeboe, P.; Lehrich, F.; Nielsen, C. J.; Powell, D. L.; Trætteberg, M. *Acta Chem. Scand.* **1988**, *A42*, 634−650.

[14] Phelan, N. F.; Orchin, M. *J. Chem. Educ.* **1968**, *45*, 633−637.

[15] For examples of cross-conjugated molecules, see: (a) Faust, R.; Mitzel, F. *J. Chem. Soc., Perkin Trans. 1* **2000**, 3746−3751. (b) Faust, R.; Göbelt, B.; Weber, C.; Krieger, C.; Gross, M.; Gisselbrecht, J.-P.; Boudon, C. *Eur. J. Org. Chem.* **1999**, *205*, 5−214. (c) Morales-Ríos, M. S.; García-Velgara, M.; Cervantes-Cuevas, H.; Alvarez-Cisneros, C.; Joseph-Nathan, P. *Magn. Reson. Chem.* **2000**, *38*, 172−176. (d) Nicoud, J.-F.; Serbutoviez, C.; Barrans, Y.; Chasseau, D.; Gautier-Luneau, I.; Ledoux, I.; Zyss, J. *J. Nonlinear Opt. Phys. Mater.* **1995**, *9*, 127−141. (e) Shultz, D. A.; Lee, H.; Kumar, R. K.; Gwaltney, K. P. *J. Org. Chem.* **1999**, *64*, 9124−9136. (f) Shultz, D. A.; Gwaltney, K. P.; Lee, H. *J. Org. Chem.* **1998**, *63*, 4034−4038. (g) Wang, H.; Helgeson, R.; Ma, B.; Wudl, F. *J. Org. Chem.* **2000**, *65*, 5862−5867. (h) Yamauchi, J.; Aoyama, T.; Kanemoto, K.; Sasaki, S.; Iyoda, M. *J. Phys. Org. Chem.* **2000**, *13*, 197−202. (i) Maertens, C.; Detrembleur, C.; Dubois, P.; Jérôme, R.; Boutton, C.; Persoons, A.; Kogej, T.; Brédas, J. L. *Chem.-Eur. J.* **1999**, *5*, 369−380. (j) Gleiter, R.; Röckel, H.; Irngartinger, H.; Oeser, T. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1270−1272. (k) Song, Y.; Spencer, L.; Euler, W. B.; Rosen, W. *Org. Lett.* **1999**, *1*, 561−564. (l) Hopf, H.; Theurig, M.; Jones, P. G.; Bubenitschek, P. *Liebigs Ann. Chem.* **1996**, 1301−1311. (m) Diederich, F. *Chem. Commun.* **2001**, 219−227.

10.1021/jo015810n CCC: $22.00

Chart 1



and iso-polytriacetylenes (iso-PTAs) **7**.[19] The obvious difference between the two classes of compounds is that π-electron density in cross-conjugated isomers cannot be readily delocalized along the carbon framework in a manner analogous to that in their linearly conjugated counterparts in accord with classical resonance theory.[14] In a simplistic approach, it may be expected that delocalization could be limited to segments composed of linearly conjugated π orbitals. Using this approach, an infinitely cross-conjugated system could be approximated by the attenuated contributions of these linearly conjugated segments. We thought it inappropriate, however, to ascribe the electronic properties of cross-conjugated molecules on the basis of this simple empirical model that might exclude weak electronic interactions between each cross-conjugated segment.

We thus targeted oligomeric iso-PDAs **6** as a class of molecules ideally suited for probing the subtle electronic characteristics of cross-conjugated organic oligomers.[18a] We anticipated that a series of monodisperse molecules could lead to a better understanding of cross conjugation and structure–property relationships of conjugated enyne polymers. We report the iterative synthesis and detailed characterization of cross-conjugated iso-PDA oligomers **6**.

Results and Discussion

Synthesis. The synthesis of iso-PDA oligomers[18a] is based on palladium-catalyzed cross-coupling reactions between vinyl triflates and terminal alkynes.[20] The parent series of molecules, with only vinylidene subunits in the carbon chain of the backbone (**6**, R = H), represented a desirable target, but were expected to be quite unstable on the basis of the reported synthesis of the parent enediyne of this series.[21] We therefore chose to incorporate an isopropylidene moiety (**6**, R = Me) and envisioned a strategy that included an iterative series of desilylation and cross-coupling steps such that the oligomeric chain lengths could be rapidly increased in a divergent manner from enediynes **10**–**12** (Scheme 1).[22]

The essential vinyl triflate building blocks **8** and **9** were readily obtained through the methods described by Stang et al.[23] Triflates **8** and **9** were cross-coupled with trimethylsilylacetylene (TMSA) or triisopropylsilylacetylene (TIPSA) using $PdCl_2(PPh_3)_2$ catalyst, CuI cocatalyst, and i-Pr_2NH base in THF at ambient temperature to give monomers **10**, **11**, and **12** in yields of 92, 84, and 98%, respectively. Optimization of the cross-coupling conditions of these reactions showed that the choice of catalyst ($PdCl_2(PPh_3)_2$ or $Pd(PPh_3)_4$), base (Et_2NH or i-Pr_2NH), and solvent (THF or DMF) could be altered without significantly affecting the outcome of the coupling reaction.[24] In most cases, the reactions were complete within 2 h as determined by thin layer chromatographic (TLC) analysis.

The first series of oligomers we targeted were end-capped with trimethylsilyl (TMS) groups, as it was anticipated that removal of this group in subsequent iterations would be more facile than the removal of the more robust triisopropylsilyl (TIPS) group. Thus, monomer **10** was protiodesilylated in methanolic K_2CO_3 to give, in essentially quantitative yield, the deprotected terminal diyne that may be used without further purification.[25] The deprotected enediyne was cross-coupled with **8** to afford trimer **13**, which was isolated via flash chromatography as a colorless solid in 92% yield. A subsequent iteration of the protiodesilylation and cross-coupling sequence gave pentamer **15** in 69% yield, as a colorless solid that was still quite soluble in chlorinated organic solvents. Desilylation of **15** followed by cross-coupling in DMF, however, was problematic as both deprotected **15** and heptamer **17** were only sparingly soluble in this solvent. Performing the cross-coupling reaction of desilylated **15** with vinyl triflate **8** with THF

---

(16) For examples of cross-conjugated oligomers and polymers, see: (a) Anderson, K. K.; Dougherty, D. A. *Adv. Mater.* **1998**, *10*, 688–692. (b) Kurata, H.; Hisamitsu, A.; Oda, M. *Tetrahedron Lett.* **1997**, *38*, 8875–8878. (c) Kurata, H.; Kawase, T.; Oda, M. *Chem. Lett.* **1994**, 2219–2222. (d) Xu, B.; Pan, Y.; Zhang, J.; Peng, Z. *Synth. Met.* **2000**, *114*, 337–345. (e) Lu, H. S. M.; Berson, J. A. *J. Am. Chem. Soc.* **1997**, *119*, 1428–1438. (f) Baumgarten, M.; Tyutyulkov, N. *Chem.-Eur. J.* **1998**, *4*, 987–989. (g) Mao, S. S. H.; Tilley, T. D. *J. Organomet. Chem.* **1996**, *521*, 425–426. (h) Londergan, T. M.; You, Y.; Thompson, M. E.; Weber, W. P. *Macromolecules* **1998**, *31*, 2784–2788. (i) Meier, H.; Aust, H. *J. Prakt. Chem.* **1999**, *341*, 466–471. (j) Meier, H.; Aust, H.; Ickenroth, D.; Kolshorn, H. *J. Prakt. Chem.* **1999**, *341*, 529–535. (k) Aust, H.; Ickenroth, D.; Meier, H. *J. Prakt. Chem.* **1999**, *341*, 523–528. (l) Hudson, L. G.; Stevens, M. P. *J. Polym. Sci., Part A: Polym. Chem.* **1995**, *33*, 71–78.

(17) (a) Fielder, S.; Rowan, D. D.; Sherburn, M. S. *Angew. Chem., Int. Ed.* **2000**, *39*, 4331–4333. (b) Bryce, M. R.; Coffin, M. A.; Skabara, P. J.; Moore, A. J.; Batsanov, A. S.; Howard, J. A. K. *Chem.-Eur. J.* **2000**, *6*, 1955–1962. (c) Iyoda, M.; Nakamura, N.; Todaka, M.; Ohtsu, S.; Hara, K.; Kuwatani, Y.; Yoshida, M.; Matsuyama, H.; Sugita, M.; Tachibana, H.; Inoue, H. *Tetrahedron Lett.* **2000**, *41*, 7059–7064. (d) Rajca, A.; Wang, H.; Pink, M.; Rajca, S. *Angew. Chem., Int. Ed.* **2000**, *39*, 4481–4483. (e) Swager, T. M.; Grubbs, R. H. *J. Am. Chem. Soc.* **1987**, *109*, 894–896. (f) Hopf, H. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 948–960.

(18) (a) Zhao, Y.; Tykwinski, R. R. *J. Am. Chem. Soc.* **1999**, *121*, 458–459. (b) Ciulei, S. C.; Tykwinski, R. R. *Org. Lett.* **2000**, *2*, 3607–3610. (c) Eisler, S.; Tykwinski, R. R. *Angew. Chem., Int. Ed.* **1999**, *38*, 1940–1943.

(19) (a) Zhao, Y.; Tykwinski, R. R. *J. Org. Chem.* **2000**, submitted. (b) Zhao, Y. M.; McDonald, R.; Tykwinski, R. R. *Chem. Commun.* **2000**, 77–78. (c) For the synthesis of an iso-PTA dimer to tetramer, see: Boldi, A. M.; Anthony, J.; Gramlich, V.; Knobler, C. B.; Boudon, C.; Gisselbrecht, J.-P.; Gross, M.; Diederich, F. *Helv. Chim. Acta* **1995**, *78*, 779–796.

(20) (a) Diederich, F.; Stang, P. J. *Metal-Catalyzed Cross-Coupling Reactions*; Wiley-VCH: Weinheim, 1997. (b) Lo Sterzo, C. *Synlett* **1999**, 1704–1722. (c) Rossi, R.; Carpita, A.; Bellina, F. *Org. Prep. Proced. Int.* **1995**, *27*, 127–160. (d) Ritter, K. *Synthesis* **1993**, 735–762. (e) Scott, W. J.; McMurry, J. E. *Acc. Chem. Res.* **1988**, *21*, 47–54.

(21) Alberts, A. H. *J. Am. Chem. Soc.* **1989**, *111*, 3093–3094.

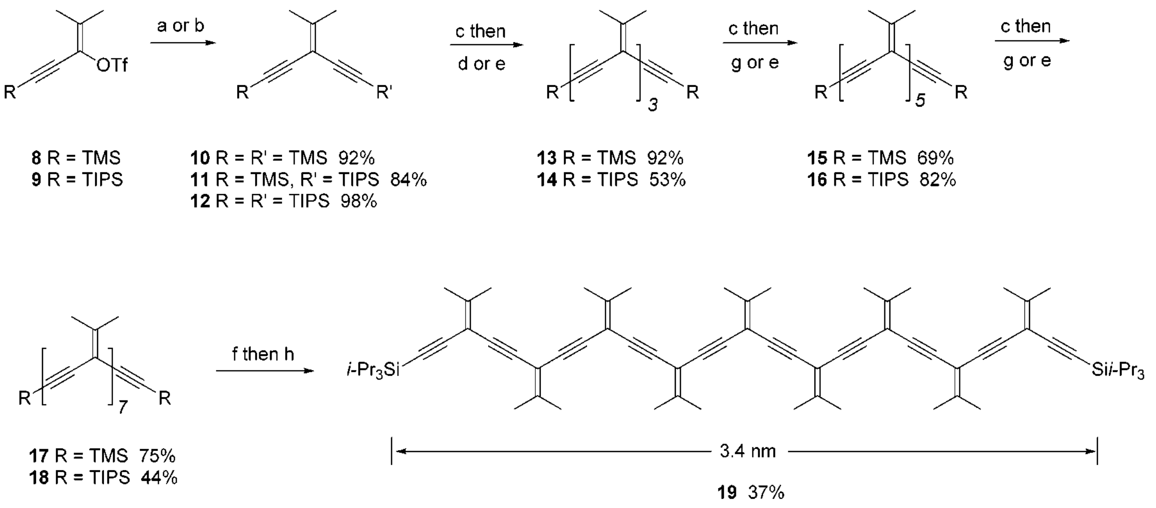
(22) For the discussion of the iterative synthesis of oligomers, see: Feuerbacher, N.; Vögtle, F. *Top. Curr. Chem.* **1998**, *197*, 1–18.

(23) Stang, P. J.; Fisk, T. E. *Synthesis* **1979**, 438–440.

(24) Two commercially available sources of palladium, $Pd(PPh_3)_4$ and $PdCl_2(PPh_3)_2$, were explored as catalysts. Although both worked satisfactorily, results nevertheless showed that $Pd(PPh_3)_4$ often led to slightly better yields, particularly in the preparation of longer oligomers. As $PdCl_2(PPh_3)_2$ is more stable and is easily stored without deterioration, it was routinely used for synthesis of short-chain oligomers, for example, monomers and trimers, whereas $Pd(PPh_3)_4$ was usually employed in the synthesis of longer, more valuable oligomers.

(25) As a result of general instability, desilylated iso-PDAs were carried on, following workup, to the subsequent cross-coupling reaction without additional purification. Yields and purity from desilylation are sufficient to accommodate this procedure.

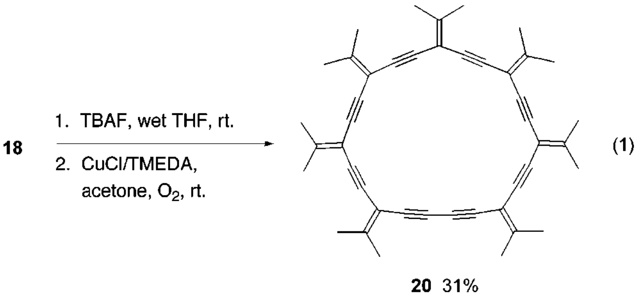
Scheme 1[a]



[a] Reagents and conditions: (a) trimethylsilylacetylene, $PdCl_2(PPh_3)_2$, CuI, i-Pr_2NH, THF, rt. (b) triisopropylacetylene, $PdCl_2(PPh_3)_2$, CuI, i-Pr_2NH, THF, rt. (c) K_2CO_3, wet MeOH/THF (1:1), rt. (d) **8**, $Pd(PPh_3)_4$, CuI, Et_2NH, DMF, rt. (e) **9**, $Pd(PPh_3)_4$, CuI, Et_2NH, DMF, rt. (f) TBAF, wet THF, rt. (g) **8**, $Pd(PPh_3)_4$, CuI, Et_2NH, THF, rt. (h) **9**, $Pd(PPh_3)_4$, CuI, Et_2NH, THF, rt.

as the solvent helped to solubilize the heptamer product **17** such that it could be isolated in 75% yield as a relatively insoluble, colorless solid. We were unable, however, to effect the next iteration with **17** toward the nonameric derivative due to insolubility. Intermolecular aggregation may contribute to this insolubility,[26] although dilution studies (vide infra) monitored by UV−vis spectroscopy as well as NMR data suggest that aggregation is not a major factor.

In the second series of iso-PDAs, the TIPS group was employed as an endcapping group, which was expected to enhance solubility of the products because of increased steric bulk. Using the iterative sequence outlined above, the formation of the TIPS-protected series employed the respective TMS-endcapped precursor due to the more facile removal of this protecting group. Thus, protiodesilylation of enediyne **10** followed directly by cross-coupling with TIPS-protected triflate **9** afforded trimer **14** in 53% yield. Desilylation of TMS-protected trimer **13** followed by cross-coupling with **9** gave pentamer **16** in 82% yield. Desilylation of pentamer **15** and cross-coupling with **9** afforded heptamer **18** as a stable colorless solid in a yield of 44%, which was gratifyingly soluble in most organic solvents. While the increased solubility of **18** circumvented the problems encountered with TMS-protected heptamer **17**, there was no way to enhance the solubility of the deprotected heptamer (vide supra). Thus, toward the formation of nonamer **19**, the best conditions for deprotection of **17** utilized tetrabutylammonium fluoride (TBAF) in a dilute solution of THF, thus avoiding the less solubilizing MeOH used with K_2CO_3. After reaction of **17** with TBAF for ca. 15 min, the reaction mixture was diluted with a large volume of Et_2O, and aqueous workup provided the terminal alkyne. Following concentration of the ethereal solution, and resolvation with a minimal amount of THF, coupling to triflate **9** gave nonamer **19** in 37% yield. The reasonable solubility of **19** allowed for complete spectroscopic characterization of this nanometer-length oligomer, which measures 3.4 nm from Si to Si. The reaction to produce **19** was always accompanied by the formation of macrocycle **20** (see eq 1), the result of copper-catalyzed, oxidative homocoupling of the two terminal alkynes.[27] Prior to this point, competing homocoupling reactions had not been problematic. Two factors likely contributed to its presence in the current case: (1) a greater amount of O_2 (requisite for the homocoupling reaction) due to the increased amount of solvent employed to accommodate desilylated **17**, and (2) higher dilution favoring an intramolecular reaction. To provide sufficient quantities of expanded radialene **20** for characterization, it was synthesized via homocoupling of the deprotected heptamer using Hay catalysis[28] in dry acetone (eq 1). Although the solubility of both the precursor and product complicates this reaction, the cyclic enyne heptamer **20** could be isolated in 31% yield as a rather insoluble colorless solid.



To complete the series of oligomers, and for the purposes of comparison, iso-PDA oligomers with an even number of repeating units were assembled as outlined in Scheme 2. Treatment of differentially protected enediyne **11** with K_2CO_3 in THF/MeOH (1:1) effected selective removal of the TMS group, while leaving the more robust TIPS group unaffected. Following workup, cross-coupling with either vinyl triflate **9** or vinyl triflate **8** gave dimers **21** and **22** in yields of 88 and 81%, respectively.

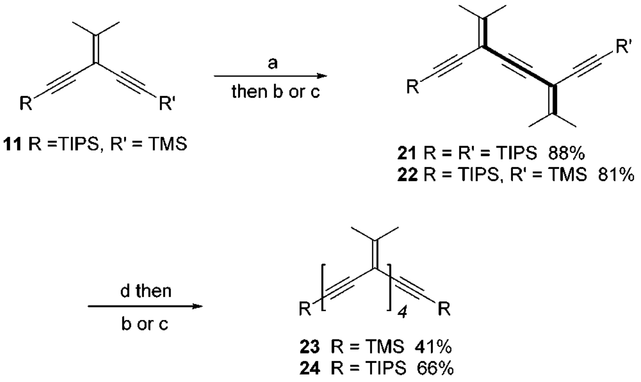
---

(26) (a) Prince, R. B.; Barnes, S. A.; Moore, J. S. *J. Am. Chem. Soc.* **2000**, *122*, 2758−2762. (b) Moore, J. S. *Curr. Opin. Colloid Interface Sci.* **1999**, *4*, 108−116.

(27) Siemsen, P.; Livingston, R. C.; Diederich, F. *Angew. Chem., Int. Ed.* **2000**, *39*, 2633−2657.

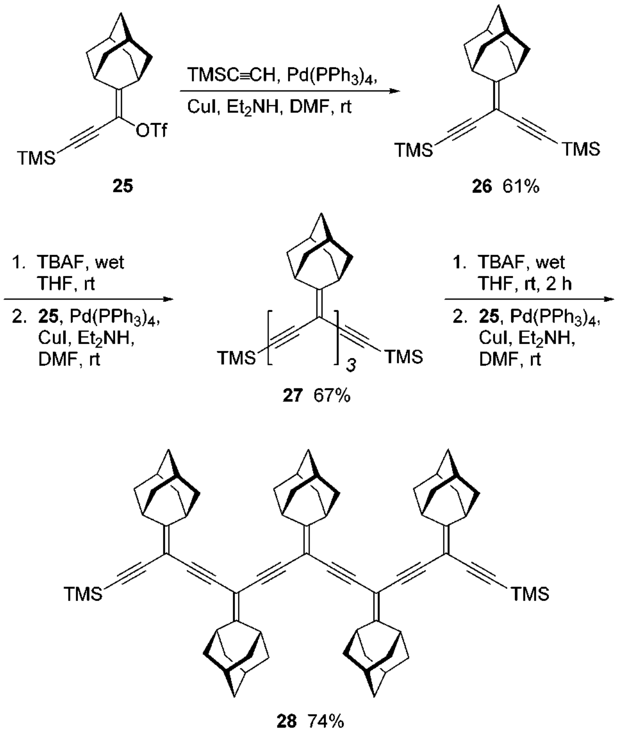
(28) Hay, A. S. *J. Org. Chem.* **1962**, *27*, 3320−3321.

Scheme 2[a]



[a] Reagents and conditions: (a) K_2CO_3, wet MeOH/THF (1:1), rt. (b) **9**, $Pd(PPh_3)_4$, CuI, Et_2NH, DMF, rt. (c) **8**, $Pd(PPh_3)_4$, CuI, Et_2NH, DMF, rt. (d) TBAF, wet THF, rt.

Scheme 3



Protiodesilylation of **21** or **22** in a dilute THF solution using TBAF followed by cross-coupling with **8** or **9** led to tetramers **23** and **24** in yields of 41 and 66%, respectively.

Irrespective of TMS or TIPS protecting groups, the iso-PDA oligomers incorporating the isopropylidene building block show decreasing stability with increasing chain length. For oligomers longer than the pentamer, stability can vary from a couple days to several weeks under refrigeration, as evaluated by TLC and ^1H NMR analysis. Storing the oligomers under an inert gas afforded better stability, but not substantially. Preliminary evidence[29] suggests that an oxygen ene reaction at the isopropylidene moiety is likely the primary decomposition pathway.[30]

In an effort to improve the stability of the iso-PDA derivatives, as well as their solubility, an alternative pendant framework was targeted, with adamantanylidene functionalization as illustrated in Scheme 3. The adamantyl-substituted vinyl triflate **25** was synthesized as previously described.[31] Palladium-catalyzed cross-coupling of this building block with TMSA gave monomer **26** in a yield of 61%.[15f] Desilylation of the adamantyl derivatives always proceeds more efficiently using TBAF in THF rather than methanolic K_2CO_3. Thus, deprotection of **26** using TBAF in THF followed by cross-coupling of the terminal diyne to triflate **25** afforded trimer **27** in 67% yield. The trimer was subsequently deprotected and cross-coupled with an additional 2 equiv of triflate **25** to provide the pentamer **28** in 74% yield. The adamantylidene-substituted iso-PDAs **27** and **28** did indeed show greater long-term stability than the isopropylidene-substituted derivatives and could be stored at ambient conditions for weeks or under refrigeration for months. They were, however, far less soluble than expected. Even at the stage of the pentamer **28**, solubility in organic solvents was already quite limited, which precluded our ability to further elaborate this series. For the molecular mass characterization of trimer **27** and pentamer **28**, electrospray mass spectrometry proved particularly beneficial. Specifically, analysis (positive mode) of a nitromethane solution of **28** with added AgOTf provided a signal at *m*/*z* 1129.6 expected for $[M + Ag]^+$, as silver coordinates to an alkyne unit of the iso-PDA.

Physical Characteristics. The spectroscopic data for the iso-PDA oligomers are consistent with their proposed structures. In the ^{13}C NMR spectra for members of the isopropylidene series, the resonances of the pendant methyl groups are observed in a range of 22−23 ppm. The vinylidene carbons outside of the main chain of the oligomers ($R_2\textit{C}{=}C$) are quite deshielded, resonating in a range of 152−155 ppm for the isopropylidene and 167−169 ppm for the adamantylidene derivatives, respectively. The other vinylidene carbons ($R_2C{=}\textit{C}$) fall into the chemical shift range of the acetylenic carbons, from 88 to 104 ppm. Even at 125 MHz, significant chemical shift degeneracy is observed in the ^{13}C NMR analysis of the longest oligomer, nonamer **19**, for which only 11 of 20 unique sp and sp^2 carbon resonances are discernible. In comparison, all unique sp and sp^2 resonances for the pentameric species **15** and **28** are observed in the expected ranges.

All iso-PDAs show significant thermal stability. For the TMS-endcapped series, trimeric **13** melts at 136 °C, whereas pentameric **15** and heptameric **17** show only decomposition points at 196 and >170 °C, respectively. For TIPS derivatives, dimeric **21**, trimeric **14**, and tetrameric **24** showed well-defined melting points at 65−66, 70−71, and 89−90 °C, respectively. Heptameric **18** and nonameric **19** show only decomposition at 148 and 190 °C, respectively. Although adamantyl derivatives **27** and **28** show greater stability under ambient conditions, their thermal stability is comparable to that of dimethyl-substituted iso-PDAs; adamantyl trimer **27** shows a melting point of 176−178 °C, and pentamer **28** decomposes at 164 °C. These data suggest that, despite their highly unsaturated structure, longer oligomeric or poly-

---

(29) Eisler, S.; Tykwinski, R. R., unpublished results.

(30) (a) Orfanopoulos, M.; Stratakis, M.; Elemes, Y. *Tetrahedron Lett.* **1989**, *30*, 4875−4878. (b) Clennam, E. L.; Chen, X.; Koola, J. J. *J. Am. Chem. Soc.* **1990**, *112*, 5193−5199. (c) Orfanopoulos, M.; Stratakis, M.; Elemes, Y. *J. Am. Chem. Soc.* **1990**, *112*, 6417−6419.

(31) Stang, P. J.; White, M. R.; Maas, G. *Organometallics* **1983**, *2*, 720−725.

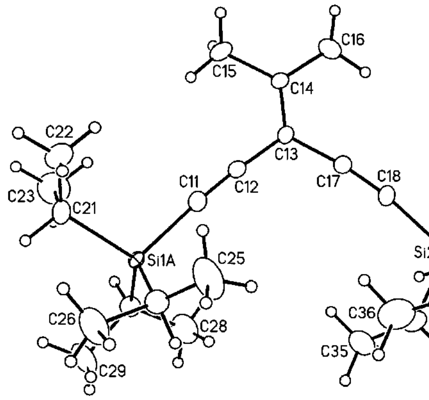


Figure 1. ORTEP drawing (20% probability level) of **12** (molecule A). Selected bond lengths (Å) and angles (°): C(11)−C(12) 1.191(6), C(12)−C(13) 1.440(6), C(13)−C(14) 1.347(6), C(13)−C(17) 1.448(7), C(17)−C(18) 1.215(6); Si(1A)−C(11)−C(12) 173.2(6), C(11)−C(12)−C(13) 176.0(5), C(12)−C(13)−C(14) 124.3(4), C(12)−C(13)−C(17) 112.9(4), C(13)−C(17)−C(18) 172.4(5), Si(2)−C(18)−C(17) 172.7(4).

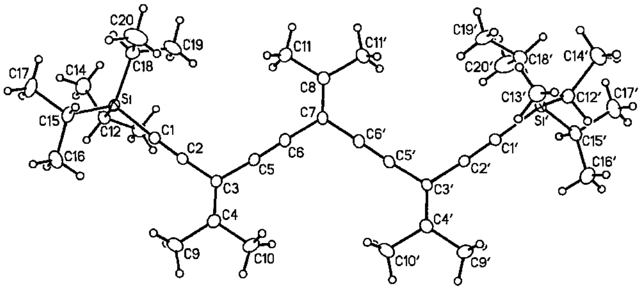
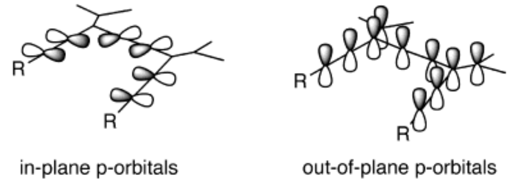


Figure 2. ORTEP drawing (20% probability level) of **14**. Selected bond lengths (Å) and angles (°): C(1)−C(2) 1.206(5), C(2)−C(3) 1.442(5), C(3)−C(4) 1.347(5), C(3)−C(5) 1.435(5), C(5)−C(6) 1.199(5), C(6)−C(7) 1.439(5), C(7)−C(8) 1.349(8); Si−C(1)−C(2) 177.1(3); C(1)−C(2)−C(3) 176.7(4), C(2)−C(3)−C(4) 123.1(3), C(2)−C(3)−C(5) 115.4(3), C(3)−C(5)−C(6) 177.4(4), C(5)−C(6)−C(7) 178.2(4), C(6)−C(7)−C(8) 122.2(2), C(6)−C(7)−C(6′) 115.5(5).

meric iso-PDAs would also be expected to show reasonable thermal stability.

Solid-State Structures. To shed light on the solid-state structural properties of cross-conjugated enynes, single-crystal X-ray analyses of monomer **12** and trimer **14** were performed, and the respective ORTEP plots are found in Figures 1 and 2.[32] Single crystals of **12** were obtained by diffusion of MeOH into a CH_2Cl_2 solution at 4 °C, and the structure was solved at low temperature. Two crystallographically independent molecules were present in the unit cell. Although disorder hampered refinement of the data, the structure of **12** is sufficient for an empirical analysis, as well as a point of comparison to the extended structure of trimer **14**.[33] There are two notable features of the solid-state structure of **12**: (1) the vinylidene angle C(12)−C(13)−C(17) at 112.9(4)° (114.4(4)° for the other independent molecule), which is slightly less than the anticipated angle of 120 °C for an sp^2-hybridized carbon atom, and (2) the Si−C≡C bonds at 173°, which are considerably distorted from linearity, presumably due to crystal packing effects.

Chart 2



in-plane p-orbitals

out-of-plane p-orbitals

Single crystals of **14** were obtained by diffusion of MeOH into a CH_2Cl_2 solution at 4 °C, and the structure was solved at low temperature. The C_{2v} symmetrical structure of **14** is essentially planar with a maximum deviation from the least-squares plane of carbon and silicon framework (excluding the isopropyl groups) of 0.126(4) Å. Of three possible planar geometries, **14** assumes an all-transoid orientation of the olefins with respect to the acetylenic linkers. Unlike their linearly conjugated isomers, polydiacetylenes,[9a,b] no observable reduction in bond length alternation is observed in the iso-PDA trimer. Single bonds of the conjugated framework, for example, C(3)−C(5) and C(6)−C(7) at 1.435(5) and 1.439(5) Å, respectively, are in the range expected for single bonds linking sp and sp^2 carbons. The two C≡C bonds at 1.206(5) and 1.199(5) Å and the two C=C bonds at 1.347(5) and 1.349(5) Å are also in the range expected. Bond lengths for **14** are comparable to those found in monomer **12**. The alkylidene bond angles C(2)−C(3)−C(5) at 115.4(3)° and C(6)−C(7)−C(6′) at 115.5(5)° are also similar to the analogous angle of endiyne **12**.

Electronic Properties. From our perspective, the most interesting feature of the iso-PDA oligomers is their unique cross-conjugated π framework. As demonstrated by the diagrams in Chart 2 for a cisoid iso-PDA dimer, two sets of orthogonal sp orbitals can potentially contribute to electron communication. The out-of-plane p orbitals (right) form the longest π-conjugated segment in an iso-PDA oligomer, and it is anticipated that the lowest-energy electronic absorption would be due to this sequence of sp^2 and sp orbitals. Because of the nature of cross conjugation, the out-of-plane π electrons would be expected to be delocalized across the alkylidene segments only in the lowest-energy π orbital, that is, the fully symmetrical orbital as depicted in Chart 2. The in-plane set of orbitals (left) are essentially isolated, but could allow for a certain amount of overlap between each conjugated segment as a result of homoconjugation.[34]

The UV−vis spectra in $CHCl_3$ of the TIPS-endcapped oligomers ranging from dimer to nonamer are shown in Figure 3. The predominant feature of the electronic absorption behavior of the iso-PDA oligomers is a steadily increasing molar absorptivity as the number of enyne monomer units is increased. In the spectrum of dimer **21**, two distinct, low-energy absorptions are discernible at 291 and 306 nm. These low-energy absorptions are due to the $\pi \rightarrow \pi^*$ transition from HOMO to LUMO. In the cisoid orientation (C_{2v}), the HOMO to LUMO ($A_1 \rightarrow B_1$) and HOMO to LUMO + 1 ($A_1 \rightarrow A_1$) transitions are both symmetry-allowed. However, in the centrally symmetric transoid orientation (C_{2h}), only the HOMO to LUMO ($A_g \rightarrow B_u$) transition is symmetry-allowed, whereas the HOMO to LUMO + 1 ($A_g \rightarrow A_g$) transition is symmetry-forbidden. The low-energy absorption peak at 306 nm is

---

[32] For the X-ray structures of other geminal enediynes, see: (a) ref 15m. (b) Nikas, S.; Rodios, N. A.; Varvoglis, A.; Terzis, A.; Raptopoulou, C. P. *J. Heterocycl. Chem.* **1996**, *33*, 997−999. (c) ref 15e.

[33] For a preliminary report of this structure, see ref 18a.

[34] Eisler, S.; McDonald; Loppnow, G. R.; Tykwinski, R. R. *J. Am. Chem. Soc.* **2000**, *122*, 6917−6928.

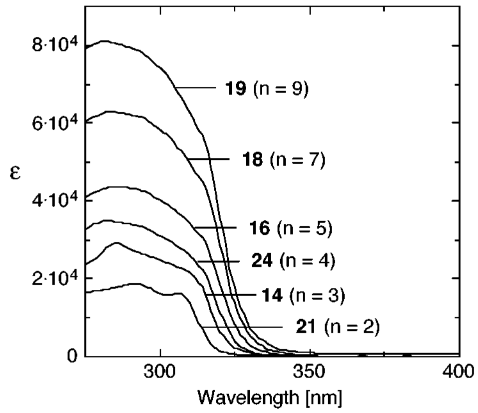
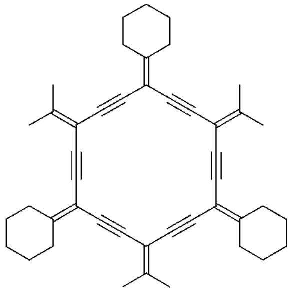


Figure 3. Electronic absorption spectra (ϵ [L M^{-1} cm^{-1}]) in $CHCl_3$ comparing the effects of oligomer length between **14**, **16**, **18**, **19**, **21**, and **24**.

ascribed to the HOMO to LUMO transition in the transoid orientation, whereas the higher-energy absorption peak seen at 291 nm likely corresponds to HOMO to LUMO or a combination of the HOMO to LUMO and HOMO to LUMO + 1 transitions of the cisoid orientation. This assignment is supported by UV−vis analysis of cyclic iso-PDA oligomers (expanded radialenes, e.g., **29**) which are constrained to a cisiod conformation. In the cyclic derivatives such as **29**, the analogous lower-energy absorbance at 305 nm is absent, whereas the higher-energy absorption at 283 nm remains.[18c]



29

Unfortunately, the absence of a second, clear absorption band in the spectrum of **29** makes it impossible to distinguish between the HOMO to LUMO and HOMO to LUMO + 1 transitions in the spectra of either the cyclic or the acyclic iso-PDAs. As one progresses from the dimer **21** to longer oligomers, the absorption bands broaden significantly due to an increasing number of rotational degrees of freedom, and beyond the stage of trimer **14** only one broad, featureless absorption is observed. The spectra of TMS-endcapped iso-PDAs showed similar characteristics.[35]

The framework of dimeric **21** and **22** contains the longest linearly conjugated segment found in any of the iso-PDAs, that is the ene-yne-ene sequence shown in bold (Scheme 2). In the absence of electronic contributions from cross conjugation, the absorbance spectrum of **21** (or **22**) should be representative of the longer iso-PDA oligomers. As can be seen in Figure 3, however, a slight lowering of the cutoff energy for elongated oligomers is observed as one progresses from dimer **21** to nonamer **19**.

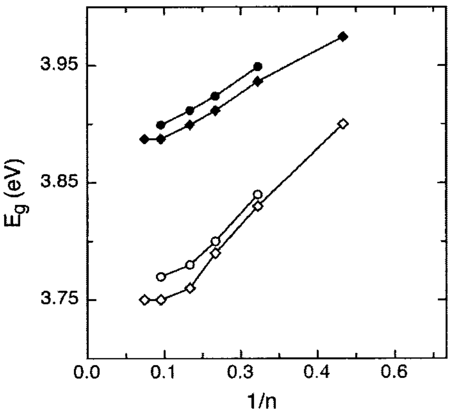


Figure 4. Plot of estimated optical band gap (E_g) versus reciprocal number of monomer units (1/*n*) of TIPS and TMS endcapped iso-PDAs via method A (○, TMS; ◇, TIPS) and method B (●, TMS; ♦, TIPS).

The solution state optical band gap E_g of the iso-PDA oligomers has been approximated by two methods: (a) from the intersection between the tangent passing through the turning point of the shoulder of the lowest-energy absorption band and the *x* axis, and (b) from maximal wavelength at one-half intensity of the maximal absorption.[36] Figure 4 shows that plots of estimated band gap (E_g) versus the reciprocal of monomer unit numbers (1/*n*) are similar for both methods. The band gap values decrease slightly with an increasing monomer unit number (*n*) from dimer to heptamer, eventually reaching a constant at the stage of nonamer. By extrapolation, it is reasonable to suggest that any further extension of the oligomer chain length will not lower E_g; that is, the band gap of a polymer containing an infinite number of monomer units would be the same as that of the nonamer, 3.75 eV (as measured by method A). As this value represents the $\pi \rightarrow \pi^*$ transition, it is clear that π-electron communication along the iso-PDA framework (between adjacent cross-conjugated enyne subunits) quickly reaches saturation by the stage of the nonamer, and transparency should be preserved beyond this energy level.

Changing the pendant functionality of iso-PDAs from isopropylidene to adamantylidene has only a small effect on the overall shape and molar absorptivity of the solution state spectra, albeit there is a pronounced broadening in the spectra of both adamantyl oligomers **27** and **28**.[37] The lower energy cutoff for the adamantyl trimer **27** and pentamer **28**, however, is red shifted by about 10 nm versus that of analogous dimethyl derivatives **14** and **16**, likely the result of the larger alkyl group (i.e., adamantyl vs dimethyl). Unfortunately, the featureless spectra of **27** and **28** made it impossible to tell if a similar red shift was present for specific λ_{max} values.

The influence of solvent polarity on the electronic absorptions for dimeric **21** was investigated via measurement in chloroform, THF, benzene, Et_2O, and hexanes.

---

(35) The UV−vis spectra for **13**, **15**, and **17** are supplied as Supporting Information.

(36) A table of values for Figure 4 is supplied as Supporting Information.

(37) The UV−vis spectra for **27** and **28**, as well as spectra comparing characteristics of **15**, **16**, and **28**, are supplied as Supporting Information.

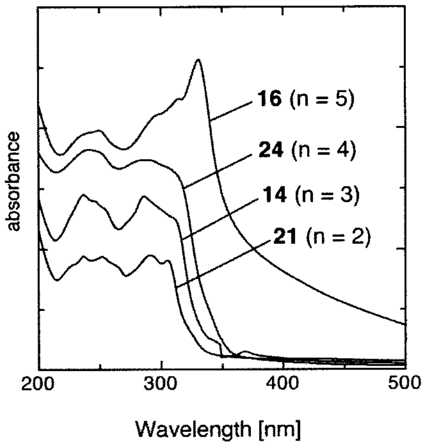


Figure 5. Absorption spectra for thin films of **14**, **16**, **21**, and **24**.

Spectra for **21** acquired in more polar solvents display a maximum absorption peak (λ_{max}) slightly shifted to longer wavelengths. This shift, however, is rather small; it ranges from a minimum value in hexane of 303 nm to a maximum value in THF or $CHCl_3$ of 306 nm. The overall shape and molar absorptivities for the spectra are essentially independent of solvent.[38]

The possible effects of intermolecular aggregation of the iso-PDA pentamer **15** were measured in chloroform at varying concentrations ranging from 10^{-5} to 10^{-8} M. The consistent profiles and molar absorptivity values observed at different concentrations suggest that aggregation is negligible for molecule **15** in chloroform for the concentration range accessible for UV–vis studies.[39] Consistent line shapes and chemical shifts observed in ^1H NMR analyses, regardless of concentration, also support the absence of aggregation in more concentrated solutions of **15**.

The absorption spectra of TIPS-endcapped iso-PDAs as thin films cast from $CHCl_3$ solutions onto quartz slides are shown in Figure 5. The shorter oligomers with $n = 2-4$ (**21**, **14**, and **24**) form reasonably decent films, and the absorption spectra are virtually identical to those measured in $CHCl_3$; that is, no pronounced aggregation band is detected. Films of the longest oligomer to be measured, pentamer **16**, were less well behaved and showed considerable tailing to low energy. The films of **16**, however, reproducibly demonstrated a measurable red shift in the lowest-energy absorption to 331 nm that suggests aggregation may become a factor for longer oligomers.[40] More soluble derivatives with better film-forming characteristics are currently under investigation.

Conclusions

We have described an efficient synthesis for several series of monodisperse cross-conjugated oligomers: the iso-polydiacetylenes. These highly unsaturated materials can be isolated as reasonably stable solids, and all derivatives show substantial thermal stability. Solid-state analyses of two molecules, monomeric **12** and trimeric **14**, show that lengthening of the iso-PDA framework has little effect on bond lengths and angles for these derivatives. UV–vis analysis reveals that the predominant electronic features of the oligomers include a steady broadening of cis and trans absorption bands due to increased rotational degrees of freedom as the chain is increased. A slight lowering of the lower-energy absorption and absorption cutoff energies as a function of chain length is also observed, and these effects reach saturation by the stage of the nonamer.

Experimental Section

General Methods. Reagents and solvents were purchased reagent grade and used without further purification. Compounds **8**[23] and **25**[31] were prepared as previously described. Anhydrous $MgSO_4$ was used as the drying agent after aqueous workup. Evaporation and concentration in vacuo were done at H_2O-aspirator pressure. All reactions were performed in standard glassware under an inert atmosphere of Ar or N_2. A positive pressure of Ar or N_2 was essential to the success of all Pd-catalyzed reactions. Degassing of solvents was accomplished by vigorously bubbling Ar or N_2 through the solution for at least 45 min. Flash chromatography was conducted on silica gel using the eluent system defined in the individual experimental procedures. EIMS were conducted at high resolution with M^+ as the base peak unless otherwise noted in the respective experimental paragraphs. ESI MS analysis was done in nitromethane with added AgOTf.

X-ray crystal data for **12**: monoclinic space group $P\bar{1}$ (No. 2), $D_c = 0.973$ g cm^{-3}, $Z = 4$, $a = 14.440(3)$, $b = 14.464(3)$, $c = 15.314(2)$ Å, $\alpha = 111.702(3)°$, $\beta = 105.415(4)°$, $\gamma = 90.142(3)°$, $V = 2846.6(8)$ Å^3. Final $R(F) = 0.0911$, $wR^2(F^2) = 0.2607$ for 522 variables and 11 521 data with $F_o^2 \geq -3\sigma(F_o^2)$ (3980 observations [$F_o^2 \geq 2\sigma(F_o^2)$]). Details are provided as Supporting Information.

Trifluoromethanesulfonic Acid 2-Methyl-1-triisopropylsilanylethynyl-propenyl Ester (9). Reaction of 4-methyl-1-triisopropylsilanyl-pent-1-yn-3-one[41] with trifluoromethanesulfonic anhydride (4.53 g, 16.1 mmol) and 2,6-di-*tert*-butyl-4-methylpyridine (2.72 g, 13.2 mmol) in CH_2Cl_2 (50 mL) was conducted under Ar for 24 h. The CH_2Cl_2 was removed in vacuo, and the residue was extracted with pentane. The organic solution was washed with 10% HCl, saturated aqueous $NaHCO_3$, and brine. Evaporation followed by flash chromatography (hexane/CH_2Cl_2 2:1) gave **9** (2.72 g, 66%) as a clear light-yellow oil. IR (neat): 2946, 2868, 2150 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 1.99 (s, 3H), 1.90 (s, 3H), 1.07 (m, 21H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 138.1, 126.6, 118.3 (q, $J = 263.4$ Hz), 100.1, 96.2, 21.1, 18.7, 18.5, 11.2. HRMS calcd for $C_{16}H_{27}F_3O_3SSi$ (M^+), 384.1402; found, 384.1404.

General Cross-Coupling Procedure. A mixture of the appropriate trimethylsilyl- or triisopropylsilyl-protected polyyne and K_2CO_3 (ca. 0.2 equiv) or TBAF (2.2 equiv) in wet THF/MeOH (1:1, 20 mL) or THF (20 mL), respectively, was stirred at room temperature for 2 h. Ether and saturated aqueous NH_4Cl were added, and the organic phase was separated, washed with saturated aqueous NH_4Cl (2 × 50 mL), dried, reduced to ca. 1 mL, and added to a degassed solution of vinyl triflate **8**, **9**, or **25** in THF or DMF (20 mL). $Pd(PPh_3)_4$ or $PdCl_2(PPh_3)_2$ (ca. 0.05 equiv) and *i*-Pr_2NH or Et_2NH were sequentially added, the solution was stirred for 5 min, CuI (ca. 0.15 equiv) was added, and the solution was then stirred until TLC analysis no longer showed the presence of the deprotected polyyne starting material. Ether and H_2O were added, and the organic phase was separated, washed with saturated aqueous NH_4Cl (2 × 50 mL), dried, and the solvent was removed in vacuo. Flash column chromatography and/or precipitation from MeOH gave the desired iso-PDA oligomer.

---

[38] The UV–vis spectra for **21** as a function of solvent are supplied as Supporting Information.

[39] The normalized absorption spectra for **15** as a function of concentration are provided as Supporting Information.

[40] Pschirer, N. G.; Bunz, U. H. F. *Macromolecules* **2000**, *33*, 3961–3963. Halkyard, C. E.; Rampey, M. E.; Kloppenburg, L.; Studer-Martinez, S. L.; Bunz, U. H. F. *Macromolecules* **1998**, *31*, 8655–8659.

[41] Helal, C. J.; Magriotis, P. A.; Corey, E. J. *J. Am. Chem. Soc.* **1996**, *118*, 10938–10939.

1-Trimethylsilyl-3-trimethylsilylethynyl-4-methylpent-3-en-1-yne (10). Triflate **8** (0.300 g, 1.00 mmol) was cross-coupled with trimethylsilylacetylene (0.200 g, 2.04 mmol) in degassed THF (20 mL) in the presence of $PdCl_2(PPh_3)_2$ (35 mg, 0.05 mmol), diisopropylamine (3 mL), and CuI (20 mg, 0.11 mmol) for 2 h as described in the general procedure. Flash chromatography (hexane/CH_2Cl_2 5:1) afforded **10** (0.228 g, 92%) as a light-yellow oil. IR (neat): 2960, 2153, 1593 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 1.99 (s, 6H), 0.18 (s, 18H). ^{13}C NMR (75 MHz, $CDCl_3$, APT): δ 156.9, 101.9, 101.5, 96.4, 22.8, 0.0. EIMS *m/z*: 248.1 (M^+, 76), 233.1 ($[M - Me]^+$, 100). HRMS calcd for $C_{14}H_{24}Si_2$ (M^+), 248.1417; found, 248.1417. Anal. Calcd for $C_{14}H_{24}Si_2$: C, 67.66; H, 9.73. Found: C, 67.28; H, 9.88.

1-Triisopropylsilyl-3-trimethylsilylethynyl-4-methylpent-3-en-1-yne (11). Triflate **8** (0.300 g, 1.00 mmol) was cross-coupled with triisopropylsilylacetylene (0.364 g, 2.00 mmol) in degassed DMF (20 mL) in the presence of $Pd(PPh_3)_4$ (58 mg, 0.05 mmol), diethylamine (3 mL), and CuI (29 mg, 0.15 mmol) for 2 h as described in the general procedure. Flash chromatography (hexane/CH_2Cl_2 5:1) afforded **11** (0.280 g, 84%) as a colorless oil. IR (neat): 2959, 2944, 2153, 1464 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 2.01 (s, 3H), 1.99 (s, 3H), 1.07 (s, 21H), 0.17 (s, 9H). ^{13}C NMR (75 MHz, $CDCl_3$, APT): δ 155.6, 103.5, 102.3, 101.9, 96.1, 92.8, 22.7 (2×), 18.7, 11.4, 0.0. EIMS *m/z*: 332.2 (M^+, 24), 289.2 ($[M - i\text{-}Pr]^+$, 100). HRMS calcd for $C_{20}H_{36}Si_2$ (M^+), 332.2356; found, 332.2354. Anal. Calcd for $C_{20}H_{36}Si_2$: C, 72.21; H, 10.91. Found: C, 72.25; H, 10.77.

1-Triisopropylsilyl-3-triisopropylsilylethynyl-4-methylpent-3-en-1-yne (12). Triflate **9** (0.770 g, 2.00 mmol) was cross-coupled with triisopropylsilylacetylene (0.730 g, 4.00 mmol) in degassed THF (40 mL) in the presence of $PdCl_2(PPh_3)_2$ (70 mg, 0.10 mmol), diisopropylamine (6 mL), and CuI (58 mg, 0.30 mmol) for 2 h as described in the general procedure. Flash chromatography (hexane/CH_2Cl_2 5:1) afforded **12** (0.816 g, 98%) as a colorless solid. mp 52.5 °C. UV−vis ($CHCl_3$) λ_{max} (ϵ): 265 (16 500) nm. IR (μscope) 2956, 2941, 2891, 2865, 2151, 1461 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 2.02 (s, 6H), 1.06 (s, 42H). ^{13}C NMR (75 MHz, $CDCl_3$, APT): δ 154.9, 103.8, 102.6, 92.5, 22.7, 18.7, 11.4. EIMS *m/z*: 416.3 (M^+, 63), 373.3 ($[M - i\text{-}Pr]^+$, 100). HRMS calcd for $C_{26}H_{48}Si_2$ (M^+), 416.3295; found, 416.3306. X-ray.

3,9-Bis(trimethylsilylethynyl)-2,10-dimethyl-6-isopropylidene-2,9-undecadiene-4,7-diyne (13). Enediyne **10** (0.146 g, 0.590 mmol) was desilylated with K_2CO_3/MeOH and cross-coupled with triflate **8** (0.360 g, 1.20 mmol) in degassed DMF (20 mL) in the presence of $Pd(PPh_3)_4$ (69 mg, 0.06 mmol), diisopropylamine (3 mL), and CuI (35 mg, 0.18 mmol) for 2 h as described in the general procedure. Flash chromatography (hexane/CH_2Cl_2 5:1) afforded **13** (0.220 g, 92%) as a colorless solid. mp 136 °C. UV−vis ($CHCl_3$) λ_{max} (ϵ): 286 (25 900), 309 (18 000) nm. IR (μscope): 2958, 2907, 2147, 1605 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 1.87 (s, 6H), 1.84 (s, 6H), 1.82 (s, 6H), 0.19 (s, 18H). ^{13}C NMR (75 MHz, $CDCl_3$, APT): 154.6, 152.8, 101.8, 101.7, 95.7, 88.7, 88.0, 22.8, 22.7 (2×), 0.0 (one coincident peak not observed). EIMS *m/z*: 404.2 (M^+, 50), 73.0 (Me_3Si^+, 100). HRMS calcd for $C_{26}H_{36}Si_2$ (M^+), 404.2356; found, 404.2354.

3,9-Bis(triisopropylsilylethynyl)-2,10-dimethyl-6-isopropylidene-2,9-undecadiene-4,7-diyne (14). Enediyne **10** (0.279 g, 1.12 mmol) was desilylated with K_2CO_3/MeOH and cross-coupled with triflate **9** (0.870 g, 2.26 mmol) in degassed DMF (40 mL) in the presence of $Pd(PPh_3)_4$ (0.13 g, 0.11 mmol), diisopropylamine (6 mL), and CuI (63 mg, 0.33 mmol) for 2 h as described in the general procedure. Flash chromatography (hexane/CH_2Cl_2 5:1) followed by precipitation from MeOH gave **14** (0.338 g, 53%) as a colorless solid. mp 70−71 °C. UV−vis ($CHCl_3$) λ_{max} (ϵ): 286 (29 100), 312 (20 200) nm. IR (μscope): 2944, 2864, 2146, 1604 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 2.07 (s, 6H), 2.05 (s, 6H), 2.03 (s, 6H), 1.09 (s, 42H). ^{13}C NMR (75 MHz, $CDCl_3$, APT): δ 153.7, 152.7, 103.8, 102.2, 101.6, 92.2, 88.6, 88.4, 22.8, 22.6 (2×), 18.7, 11.4. EIMS *m/z*: 572.4 (M^+, 73), 157.1 ($i\text{-}Pr_3Si^+$, 100). HRMS calcd for $C_{38}H_{60}Si_2$ (M^+), 572.4233; found, 572.4223. X-ray.

3,15-Bis(trimethylsilylethynyl)-2,16-dimethyl-6,9,12-triisopropylidene-2,15-heptadecadiene-4,7,10,13-tetrayne (15). Trimer **13** (0.171 g, 0.42 mmol) was desilylated with K_2CO_3/MeOH and cross-coupled with triflate **8** (0.255 g, 0.85 mmol) in degassed DMF (20 mL) in the presence of $Pd(PPh_3)_4$ (50 mg, 0.043 mmol), diethylamine (3 mL), and CuI (20 mg, 0.10 mmol) for 2 h as described in the general procedure. Flash chromatography (hexane/CH_2Cl_2 5:1) and subsequent recrystallization from MeOH gave **15** (0.163 g, 69%) as a colorless solid. mp 196 °C (dec). UV−vis ($CHCl_3$) λ_{max} (ϵ): 281 (41 300) nm. IR (μscope): 2958, 2906, 2147, 1605 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 2.02 (s br, 24H), 1.99 (s, 6H), 0.17 (s, 18H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 154.5, 152.6, 152.5, 101.9, 101.8 (2×), 95.8, 94.8, 88.7, 88.4, 88.3, 88.0, 22.8, 22.7 (4×), 0.1. HRMS calcd for $C_{38}H_{48}Si_2$ (M^+), 560.3295; found, 560.3299.

3,15-Bis(triisopropylsilylethynyl)-2,16-dimethyl-6,9,12-triisopropylidene-2,15-heptadecadiene-4,7,10,13-tetrayne (16). Trimer **13** (80 mg, 0.20 mmol) was desilylated with K_2CO_3/MeOH and cross-coupled with triflate **9** (0.152 g, 0.40 mmol) in degassed DMF (20 mL) in the presence of $Pd(PPh_3)_4$ (23 mg, 0.020 mmol), diethylamine (3 mL), and CuI (11 mg, 0.058 mmol) for 2 h as described in the general procedure. Flash chromatography (hexane/CH_2Cl_2 5:1) and recrystallization from MeOH gave **16** (0.120 g, 82%) as a colorless solid. mp 115−116 °C (dec). UV−vis ($CHCl_3$) λ_{max} (ϵ): 286 (43 600) nm. IR (μscope): 2943, 2865, 2147, 1602 cm^{-1}. ^1H NMR (360 MHz, $CDCl_3$): δ 2.03 (s, 6H), 2.01 (s, 18H), 2.00 (s, 6H), 1.08 (s, 42H). ^{13}C NMR (75 MHz, $CDCl_3$, APT): δ 153.8, 152.5, 152.4, 103.8, 102.2, 101.8, 92.2, 88.7, 88.4, 88.3, 22.8, 22.7, 22.6, 18.7, 11.4 (four coincident peaks not observed). HRMS calcd for $C_{50}H_{72}Si_2$ (M^+), 728.5173; found, 728.5164.

3,21-Bis(trimethylsilylethynyl)-2,22-dimethyl-6,9,12,-15,18-pentaisopropylidene-2,21-tricosadiene-4,7,10,13,-16,19-hexayne (17). Pentamer **15** (56 mg, 0.10 mmol) was desilylated with K_2CO_3/MeOH and cross-coupled with triflate **8** (61 mg, 0.20 mmol) in degassed THF (20 mL) in the presence of $Pd(PPh_3)_4$ (23 mg, 0.020 mmol), diethylamine (3 mL), and CuI (11 mg, 0.058 mmol) for 2 h as described in the general procedure. Flash chromatography (hexane/CH_2Cl_2 5:1) and recrystallization from MeOH gave **17** (54 mg, 75%) as a colorless solid. mp > 170 °C (dec). UV−vis ($CHCl_3$) λ_{max} (ϵ): 282 (59 200) nm. IR (μscope): 2959, 2906, 2148, 1606 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 2.02 (s, 36H), 1.99 (s, 6H), 0.17 (s, 18H). HRMS calcd for $C_{50}H_{60}Si_2$ (M^+), 716.4233; found, 716.4236. This oligomer was insufficiently soluble for meaningful ^{13}C NMR analysis.

3,21-Bis(triisopropylsilylethynyl)-2,22-dimethyl-6,9,-12,15,18-pentaisopropylidene-2,21-tricosadiene-4,7,10,-13,16,19-hexayne (18). Pentamer **15** (83 mg, 0.15 mmol) was desilylated with K_2CO_3/MeOH and cross-coupled with triflate **9** (0.114 g, 0.30 mmol) in degassed DMF (20 mL) in the presence of $Pd(PPh_3)_4$ (17 mg, 0.015 mmol), diethylamine (3 mL), and CuI (9 mg, 0.047 mmol) for 2 h as described in the general procedure. Flash chromatography (hexane/CH_2Cl_2 5:1) and recrystallization from MeOH gave **18** (58 mg, 44%) as a colorless solid. mp 148 °C (dec). UV−vis ($CHCl_3$) λ_{max} (ϵ): 284 (62 900) nm. IR (μscope): 2943, 2905, 2146, 1606 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 2.03 (6H), 2.01 (s, 30H), 2.00 (s, 6H), 1.06 (s, 42H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 153.8, 152.5, 152.4, 152.2, 103.8, 102.2, 101.9, 101.8, 92.2, 88.7, 88.4, 22.8, 22.7, 22.6, 18.7, 11.4 (nine coincident peaks not observed). HRMS calcd for $C_{62}H_{84}Si_2$ (M^+), 884.6111; found, 884.6111.

3,27-Bis(triisopropylsilylethynyl)-2,28-dimethyl-6,9,-12,15,18,21,24-heptaisopropylidene-2,27-nonacosadiene-4,7,10,13,16,19,22,25-octayne (19). Heptamer **18** (19 mg, 0.021 mmol) was desilylated with TBAF and cross-coupled with triflate **9** (20 mg, 0.052 mmol) in degassed DMF (20 mL) in the presence of $Pd(PPh_3)_4$ (28 mg, 0.024 mmol), diethylamine (0.6 mL), and CuI (14 mg, 0.073 mmol) for 15 min as described in the general procedure. The crude reaction solid was recrystallized from MeOH to give **19** (8 mg, 37%) as a colorless solid. mp > 190 °C (dec). UV−vis ($CHCl_3$) λ_{max} (ϵ): 283 (80 800) nm. IR (μscope): 2943, 2905, 2146, 1605 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 2.04, (s, 6H), 2.02 (s, 42H), 2.00 (s, 6H), 1.06

(s, 42H). ^{13}C NMR (125.7 MHz, $CDCl_3$): δ 153.8, 152.6, 152.4, 103.8, 102.2, 101.8 (3×), 92.2, 88.7, 88.4, 22.8, 22.7 (2×), 22.6 (2×), 18.7, 11.4 (thirteen coincident peaks not observed). Attempts for MS analyses were unsuccessful.

5,8,11,14,17,20,23-Heptaisopropylidenecyclotricosa-1,3,6,9,12,15,18,21-octayne (20). Heptamer **17** (20 mg, 0.028 mmol) was desilylated with K_2CO_3/MeOH as described in the general procedure and then oxidatively homocoupled in the presence of CuI (16 mg, 0.084 mmol), TMEDA (4.9 mg, 0.042 mmol), and THF (10 mL) under air for 2 h. Flash chromatography (hexane/CH_2Cl_2 5:1) gave **20** (5 mg, 31%) as a colorless solid. mp > 115 °C (dec). UV−vis ($CHCl_3$) λ_{max} (ϵ): 280 (44 400), 336 (6200) nm. ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.07 (s, 12H), 2.04 (m, 30H). ^{13}C NMR (125 MHz, $CDCl_3$, APT): δ 155.1, 152.8, 152.5, 152.4, 102.2, 101.8, 101.7 (2×), 100.7, 88.8, 88.4 (2×), 88.3, 88.2, 87.8, 80.6, 78.8, 22.9, 22.8, 22.7 (five coincident peaks not observed). HRMS calcd for $C_{44}H_{42}$ (M^+), 570.3287; found, 570.3289.

3,6-Bis(triisopropylsilylethynyl)-2,7-dimethyl-2,6-octadiene-4-yne (21). Enediyne **11** (79 mg, 0.24 mmol) was monodesilylated with K_2CO_3/MeOH and cross-coupled with triflate **9** (91 mg, 0.24 mmol) in degassed DMF (20 mL) in the presence of $Pd(PPh_3)_4$ (27 mg, 0.023 mmol), diethylamine (3 mL), and CuI (14 mg, 0.074 mmol) for 2 h as described in the general procedure. Flash chromatography (hexane/CH_2Cl_2 5:1) gave **21** (0.104 g, 88%) as a colorless solid. mp 65−66 °C. UV−vis ($CHCl_3$) λ_{max} (ϵ): 256 (23 400), 291 (18 700), 306 (16 100) nm. IR (μscope): 2943, 2865, 2145, 1463 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.04 (s, 6H), 1.99 (s, 6H), 1.06 (s, 42H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 153.8, 103.7, 102.2, 92.2, 88.6, 22.8, 22.5, 18.7, 11.4. HRMS calcd for $C_{32}H_{54}Si_2$ (M^+), 494.3764; found, 494.3768.

3-(Triisopropylsilylethynyl)-6-(trimethylsilylethynyl)-2,7-dimethyl-2,6-octadiene-4-yne (22). Enediyne **11** (0.140 g, 0.421 mmol) was desilylated with K_2CO_3/MeOH and cross-coupled with triflate **8** (0.127 g, 0.423 mmol) in degassed DMF (20 mL) in the presence of $Pd(PPh_3)_4$ (24 mg, 0.021 mmol), diethylamine (3 mL), and CuI (12 mg, 0.063 mmol) for 40 min as described in the general procedure. Flash chromatography (hexane/CH_2Cl_2 5:1) gave **22** (0.140 g, 81%) as a yellow oil. IR (cast): 2943, 2865, 2149, 1601 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.32 (s, 3H), 2.30 (s, 3H), 2.29 (s, 3H), 2.27 (s, 3H), 1.35 (s, 21H), 0.46 (s, 9H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 154.4, 153.8, 103.8, 102.2, 101.9, 101.8, 95.8, 92.2, 88.8, 88.3, 22.8 (2×), 22.6 (2×), 18.7, 11.4, 0.0. HRMS calcd for $C_{26}H_{42}Si_2$ (M^+), 410.2825; found, 410.2829.

3,12-Bis(trimethylsilylethynyl)-2,13-dimethyl-6,9-diisopropylidene-2,12-tetradecadiene-4,7,10-triyne (23). Dimer **22** (88 mg, 0.21 mmol) was desilylated with TBAF and cross-coupled with triflate **8** (0.128 g, 0.428 mmol) in degassed DMF (20 mL) in the presence of $Pd(PPh_3)_4$ (25 mg, 0.022 mmol), diethylamine (3 mL), and CuI (12 mg, 0.063 mmol) for 40 min as described in the general procedure. Flash chromatography (hexane/CH_2Cl_2 5:1) followed by precipitation from methanol afforded **23** (42 mg, 41%) as a colorless solid. mp 184−184.5 °C. UV−vis ($CHCl_3$) λ_{max} (ϵ): 282 (32 100) nm. IR (cast): 2943, 2865, 2149, 1601 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.02 (s, 12H), 2.01 (s, 6H), 1.99 (s, 6H), 0.17 (s, 18H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 154.5, 152.7, 101.9, 101.8, 95.8, 88.7, 88.3, 88.0, 22.8, 22.7 (2×), 0.0 (two coincident peaks not observed). HRMS calcd for $C_{32}H_{42}Si_2$ (M^+), 482.2825; found, 482.2823.

3,12-Bis(triisopropylsilylethynyl)-2,13-dimethyl-6,9-diisopropylidene-2,12-tetradecadiene-4,7,10-triyne (24). Dimer **21** (50 mg, 0.10 mmol) was desilylated with TBAF and cross-coupled with triflate **9** (78 mg, 0.20 mmol) in degassed DMF (20 mL) in the presence of $Pd(PPh_3)_4$ (12 mg, 0.010 mmol), diethylamine (3 mL), and CuI (6 mg, 0.032 mmol) for 2 h as described in the general procedure. Flash chromatography (hexane/CH_2Cl_2 5:1) gave **24** (43 mg, 66%) as a colorless solid. mp 89−90 °C. UV−vis ($CHCl_3$) λ_{max} (ϵ): 283 (35 000) nm. IR (μscope): 2942, 2865, 2146, 1589 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.08 (s, 6H), 2.05 (s, 12H), 2.03 (s, 6H), 1.09 (s, 42H). ^{13}C NMR (75 MHz, $CDCl_3$, APT): δ 153.7, 152.6, 103.8, 102.2, 101.8, 92.2, 88.6, 88.3, 22.8, 22.7, 22.6 (2×), 18.7, 11.4 (one coincident peak not observed). HRMS calcd for $C_{44}H_{66}Si_2$ (M^+), 650.4703; found, 650.4717.

1,5-Bis(trimethylsilyl)-3-adamantylidene-1,4-pentadiyne (26). Triflate **25** (1.25 g, 3.18 mmol) was cross-coupled with trimethylsilylacetylene (0.92 mL, 6.5 mmol) in degassed DMF (60 mL) in the presence of $Pd(PPh_3)_4$ (0.15 g, 0.13 mmol), diethylamine (9 mL), and CuI (60 mg, 0.32 mmol) for 1.5 h as described in the general procedure. Flash chromatography (hexane/CH_2Cl_2 2:1) afforded **26** (0.641 g, 61%) as a colorless solid. Spectroscopic data were consistent with that reported by Shultz et al.[28]

1,11-Bis(trimethylsilyl)-3,6,9-triadamantylidene-1,4,7,-10-undecatetrayne (27). Enediyne **26** (0.27 g, 0.51 mmol) was desilylated with TBAF and cross-coupled with triflate **25** (0.405 g, 1.03 mmol) in degassed DMF (20 mL) in the presence of $Pd(PPh_3)_4$ (70 mg, 0.061 mmol), diethylamine (3 mL), and CuI (39 mg, 0.20 mmol) for 2 h as described in the general procedure. Flash chromatography (hexane/CH_2Cl_2 8:1) afforded **27** (0.232 g, 67%) as a colorless solid. mp 176−178 °C. UV−vis (CH_2Cl_2) λ_{max} (ϵ): 261 (21 200), 291 (29 900) nm. IR (μscope): 2912, 2850, 2146, 1668 cm^{-1}. ^{1}H NMR (300 MHz, C_6D_6): δ 3.58 (m, 6H), 1.76−1.59 (m, 36H), 0.20 (s, 18H). ^{13}C NMR (125 MHz, C_6D_6): δ 169.0, 168.1, 102.6, 95.8, 95.3, 95.1, 88.6, 87.9, 39.3 (2×), 37.0 (2×), 36.8, 36.7 (2×), 28.3, 28.2, 0.1 (two coincident peaks not observed). ESMS (nitromethane) *m/z*: 681.4 ($[M + H]^+$, 67), 698.4 ($[M + NH_4]^+$, 100), 719.4 ($[M + K]^+$, 29).

1,17-Bis(trimethylsilyl)-3,6,9,12,15-pentaadamantylidene-1,4,7,10,13,16-heptadecahexayne (28). Trimer **27** (96 mg, 0.14 mmol) was desilylated with TBAF and cross-coupled with triflate **25** (0.111 g, 0.283 mmol) in degassed THF (20 mL) in the presence of $Pd(PPh_3)_4$ (20 mg, 0.017 mmol), diethylamine (3 mL), and CuI (10 mg, 0.05 mmol) for 2 h as described in the general procedure. Flash chromatography (hexane/CH_2Cl_2 8:1) afforded **28** (0.11 g, 74%) as a colorless solid. mp 164 °C (dec). UV−vis (CH_2Cl_2) λ_{max} (ϵ): 260 (43 900), 289 (47 700) nm. IR (μscope): 2906, 2849, 2146, 1670 cm^{-1}. ^{1}H NMR (300 MHz, C_6D_6): δ 3.61 (m, 10H), 1.79−1.60 (m, 60H), 0.21 (s, 18H). ^{13}C NMR (125 MHz, C_6D_6, APT): δ 169.0, 167.7, 167.3, 102.6, 95.8, 95.4, 95.2, 88.8, 88.3, 88.2, 87.8, 39.4, 39.3, 37.2, 37.1, 37.0, 36.8 (2×), 36.7, 28.4, 28.3, 0.2 (eight coincident peaks not observed). ESMS (nitromethane, AgOTf added) *m/z*: 1129.6 ($[M + Ag]^+$, 41).

Acknowledgment. Financial support for this work has been provided by the University of Alberta, the Alberta Science, Research, and Technology Authority, and NSERC. We thank Annie Tykwinski for the cover art, and Dr. R. McDonald for the X-ray structural determination of **12** and **14**.

Supporting Information Available: ^{1}H and ^{13}C NMR spectra for all new compounds, UV−vis spectra for compounds **13**, **15**, **17**, **23**, and **27**−**28**, concentration dependent UV−vis analysis for compound **15**, solvent dependent UV−vis analysis for **21**, a table of estimated band gap values, and X-ray crystallographic data for compound **12**. This material is available free of charge via the Internet at http://pubs.acs.org.

JO015810N