

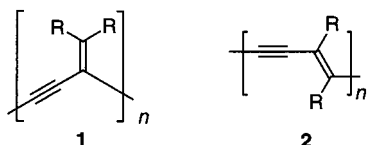
Iterative Synthesis and Properties of Cross-Conjugated *iso*-Polydiacetylene Oligomers

Yuming Zhao and Rik R. Tykwinski*

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

Received September 15, 1998

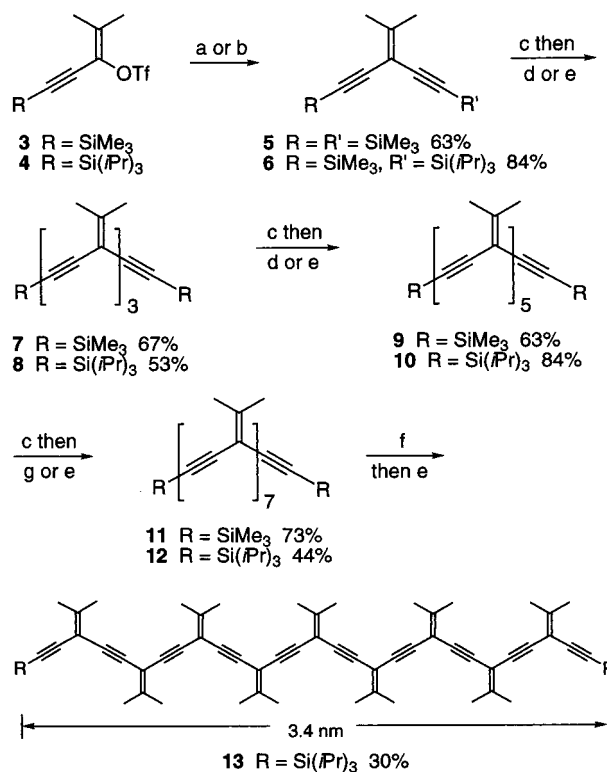
The ability of a conjugated carbon or heteroatom framework to participate in π -electron delocalization is fundamental to the electronic behavior of organic materials,^{1–7} which in turn, is central to their applications as media for electroluminescence,⁸ ferromagnetism,⁹ and nonlinear optics^{2,10} among others. The most intensely studied conjugated molecules have extended, linearly-conjugated π -systems, as found in semiconducting oligomers such as, e.g., polythiophene or polydiacetylene (PDA). Alternative modes of π -electron delocalization, in particular cross conjugation,¹¹ are much less frequently encountered, and the nature of cross-conjugated π -delocalization is thus far less understood.¹² Surprisingly, even oligomers such as **1**, the cross-conjugated constitutional isomers of the ardently studied polydiacetylenes **2**,¹³ are an unrealized class of molecules.



We identified oligomers **1** (*iso*-PDAs) as a class of molecules ideally suited to probe the electronic characteristics of cross conjugation in organic materials. Herein we report the first iterative synthesis and characterization of these enyne oligomers, which span up to 3.4 nm in length for the nonamer. UV-vis spectroscopic analysis shows that electronic communication along the conjugated framework indeed increases as a function of oligomer length, clearly demonstrating a subtle contribution from cross conjugation to the overall π -electron delocalization in *iso*-PDAs.

- (1) *Photonic and Optoelectronic Polymers*; Jenekhe, S. A., Wynne, K. J., Eds.; American Chemical Society: Washington, D.C., 1995.
 (2) Bosshard, C.; Sutter, K.; Prêtre, P.; Hulliger, J.; Flörsheimer, M.; Kaatz, P.; Günter, P. *Organic Nonlinear Optical Materials*; Gordon and Breach: Basel, 1995.
 (3) *Conjugated Polymers and Related Materials: The Interconnection of Chemical and Electronic Structure*; Salaneck, W. R., Lundström, I., Rånby, B., Eds.; Oxford University Press: Oxford, 1993.
 (4) Müller, J. S. *Adv. Mater.* **1993**, *5*, 671–676.
 (5) Roncali, J. *Chem. Rev.* **1997**, *97*, 173–205.
 (6) *Electronic Materials: The Oligomer Approach*; Müllen, K., Wegner, G., Eds.; Wiley-VCH: Weinheim, 1998.
 (7) Moore, J. S. *Acc. Chem. Res.* **1997**, *30*, 402–413.
 (8) Kraft, A.; Grimsdale, A. C.; Holmes, A. B. *Angew. Chem., Int. Ed. Engl.* **1998**, *37*, 402–428.
 (9) Rajca, A. *Chem. Rev.* **1994**, *94*, 871–893.
 (10) Tykwinski, R. R.; Gubler, U.; Martin, R. E.; Diederich, F.; Bosshard, C.; Günter, P. *J. Phys. Chem. B* **1998**, *102*, 4451–4465.
 (11) Trættestad, M.; Hopf, H. *Acta Chem. Scand.* **1994**, *48*, 989–993.
 Phelan, N. F.; Orchin, M. *J. Chem. Educ.* **1968**, *45*, 633–637.
 (12) Cross-conjugated materials, see: Anderson, K. K.; Dougherty, D. A. *Adv. Mater.* **1998**, *10*, 688–692. Shultz, D. A.; Gwaltney, K. P.; Lee, H. *J. Org. Chem.* **1998**, *63*, 4034–4038. Baumgarten, M.; Tyutyulkov, N. *Chem. Eur. J.* **1998**, *4*, 987–989. Lu, H. S. M.; Berson, J. A. *J. Am. Chem. Soc.* **1997**, *119*, 1428–1438. Mao, S. S. H.; Tilley, T. D. *J. Organomet. Chem.* **1996**, *521*, 425–428. Nicoud, J. F.; Serbutoviez, C.; Barrans, Y.; Chasseau, D.; Gautier-Luneau, I.; Ledoux, I.; Zyss, J. *Nonlinear Opt.* **1995**, *9*, 127–141. Hopf, H.; Maas, G. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 931–954.
 (13) *Polydiacetylenes*; Bloor, D., Chance, R. R., Eds.; Martinus Nijhoff: Dordrecht, 1985. Wudl, F.; Bitler, S. P. *J. Am. Chem. Soc.* **1986**, *108*, 4685–4687. Giesa, R.; Klapper, M.; Schulz, R. C. *Makromol. Chem., Macromol. Symp.* **1991**, *44*, 1–10. Giesa, R.; Schulz, R. C. *Polym. Int.* **1994**, *33*, 43–60.

Scheme 1^a



^a Reagents and conditions: (a) trimethylsilylacetylene, Pd(PPh₃)₄, CuI, Et₂NH, DMF, rt, 2h. (b) Triisopropylsilylacetylene, Pd(PPh₃)₄, CuI, Et₂NH, DMF, rt, 2h. (c) K₂CO₃, wet MeOH/THF (1:1), rt, 2h. (d) **3**, Pd(PPh₃)₄, CuI, Et₂NH, DMF, rt, 2h. (e) **4**, Pd(PPh₃)₄, CuI, Et₂NH, DMF, rt. (f) TBAF, wet THF, rt. (g) **3**, Pd(PPh₃)₄, CuI, Et₂NH, THF, rt.

Palladium catalyzed coupling of terminal alkynes with vinyl triflates¹⁴ provides an efficient route to the desired oligomers.¹⁵ Furthermore, these couplings facilitate an iterative chain elongation that significantly simplifies the synthesis. The assembly of the *iso*-PDAs began with the palladium catalyzed cross-coupling of trimethylsilylacetylene and vinyl triflate monomer **3**¹⁴ (Scheme 1). The coupling proceeded rapidly at room temperature in DMF utilizing ca. 5% Pd(PPh₃)₄ catalyst and CuI as a cocatalyst¹⁶ to give diyne **5** in 63% yield.¹⁷ Protodesilylation of **5** gave quantitatively the deprotected diyne that could be used without further purification in the reaction with **3** to afford trimer **7**.¹⁸ Using **7**, iteration of the protodesilylation and coupling sequence gave pentamer **9** in 63% yield. Following protodesilylation of **9**, cross-coupling with **3** was brought about in THF to help solubilize the heptamer product **11**, which ultimately proved to be only sparingly soluble in common organic solvents.

As a result of the low solubility of the TMS end-capped oligomers, the *iso*-PDAs were instead derivatized with triisopropylsilyl (TIPS) groups, which were expected to significantly enhance solubility. Thus, protodesilylation of **5** followed by cross-coupling with TIPS-protected **4** afforded trimer **8**, and similarly,

- (14) Stang, P. J.; Fisk, T. E. *Synthesis* **1979**, 438–440.
 (15) Scott, W. J.; McMurry, J. E. *Acc. Chem. Res.* **1988**, *21*, 47–54. Ritter, K. *Synthesis* **1993**, 735–762.
 (16) Rossi, R.; Carpita, A.; Bellina, F. *Org. Prep. Proc. Int.* **1995**, *27*, 127–160.
 (17) The purity and structure of all new compounds were confirmed by ¹H and ¹³C NMR, IR, UV, MS, and either EA or HRMS (except **13**). Details are provided as Supporting Information.
 (18) For the synthesis of a related molecule, 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.

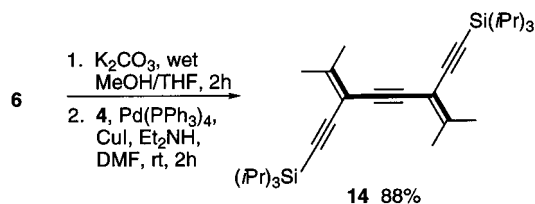


Figure 1. Synthesis of dimer **14**. The longest linearly-conjugated sequence present in any of the *iso*-PDA oligomers is outlined in bold.

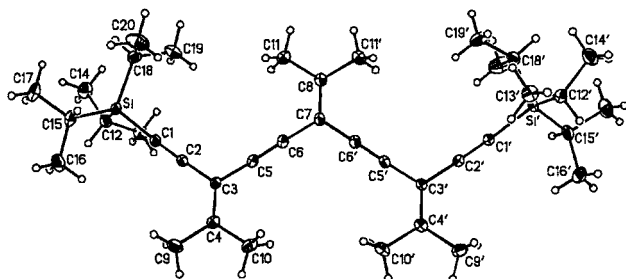


Figure 2. ORTEP drawing (20% probability level) of **8**.

desilylation of **7** followed by cross-coupling with **4** gave pentamer **9**. Pentamer **9** was desilylated and coupled with **4** to afford heptamer **12** as a stable white solid, gratifyingly soluble in most organic solvents. To produce nonamer **13**, heptamer **11** was desilylated with tetrabutylammonium fluoride (TBAF) in a dilute solution of THF. Extraction of this reaction mixture into a large volume of Et_2O , aqueous workup, and coupling of the deprotected heptamer with **4** gave nonamer **13**. The increased solubility of **13** allowed complete spectroscopic characterization of this nanometer-length oligomer that extends ca. 3.4 nm from Si atom to Si atom.¹⁹ For spectroscopic comparison, dimer **14** was also prepared (Figure 1) from the differentially protected enediyne **6** (Scheme 1). Thus, treatment of **6** with K_2CO_3 in THF/MeOH (1:1) gave selective removal of the TMS group, and subsequent cross-coupling with **4** gave dimer **14**.

X-ray analysis of **8** provided insight into the solid-state character of the *iso*-PDA oligomers (Figure 2).²⁰ The C_2 -symmetrical molecule is essentially planar with a maximum deviation from the least-squares plane of the carbon and silicon framework (excluding the *iPr* groups) of 0.126(4) Å. Of the three possible planar geometries, **8** assumes an all-transoid orientation of the olefins with respect to the acetylenic linkers.

The predominant feature of the electronic absorption spectra of the *iso*-PDA oligomers is a steadily increasing molar absorption as the number of enyne monomer units is increased (Figure 3). In the spectrum of dimer **14**, two distinct low-energy absorptions are discernible at 291 and 306 nm, corresponding to cisoid and transoid orientations, respectively, of the two alkenes about the central alkyne.²¹ These absorptions broaden significantly for longer oligomers as a result of increasing rotational degrees of freedom. Already at the stage of the trimer **8**, only the higher energy cisoid absorption is clearly discernible, and for the longer *iso*-PDAs, only one broad, featureless absorption is observed.

(19) Calculations performed on a SGI Indigo² using Macromodel 5.5.

(20) X-ray crystal data for **8**; monoclinic space group $C2/c$ (No. 15), $D_c = 0.998 \text{ g cm}^{-3}$, $Z = 4$, $a = 21.0638(8)$, $b = 15.4221(7)$, $c = 11.8055(5)$ Å, $\beta = 95.757(4)^\circ$, $V = 3815.7(3)$ Å³. Final $R(F) = 0.071$, $wR_2(F^2) = 0.17$ for 182 variables and 2572 data with $F_o^2 \geq -3\sigma(F_o^2)$ (2064 observations [$F_o^2 \geq 2\sigma(F_o^2)$]). Details are provided as Supporting Information.

(21) A cyclic hexameric oligomer, constrained to a cisoid ene-yne-ene orientation, shows only one low energy absorption at 285 nm (ref 22).

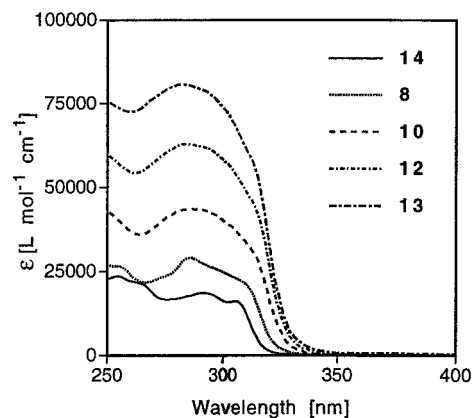


Figure 3. Electronic absorption spectra (ϵ [$L \text{ mol}^{-1} \text{ cm}^{-1}$]) in $CHCl_3$ comparing the effects of oligomer length between **8**, **10**, **12**, **13**, and **14**.

Dimer **14** provides a standard by which the electron contributions from cross conjugation can be examined. The ene-yne-ene segment of **14** (Figure 1, shown in bold) represents the longest linearly-conjugated path present in any of the *iso*-PDA oligomers. In the absence of an effective cross-conjugated π -delocalization mechanism, this six-carbon sequence is expected to dictate the lowest energy electronic absorption band of these oligomers.²³ Clearly evident in Figure 3, however, is a steady red shift in the lowest energy absorption as a function of oligomer length. Dimer **14** has an absorption cutoff at ca. 320 nm, whereas the cutoff value of nonamer **13** has been shifted to ca. 345 nm.²⁴ Clearly, as the number of cross-conjugated enyne segments increases, π -electron delocalization is augmented.²⁵ This effect diminishes with increasing chain length and suggests that saturation of electronic delocalization via cross conjugation has essentially been reached at the stage of the nonamer, i.e., further extending the length of the oligomers is not expected to significantly change the optical gap of the materials.²⁶ These spectra clearly provide evidence of π -electron communication conveyed between cross-conjugated enyne subunits of *iso*-PDA oligomers. Additional investigations to determine the effects of donor/acceptor functionalization on this mode of π -electron delocalization, as well as the formation of polymeric materials, are currently underway.

Acknowledgment. This work was supported by a Gen-Science Endowment from the University of Alberta and by NSERC of Canada. We thank Dr. R. McDonald for the X-ray structural determination of **8** and Professor J. M. Stryker for helpful discussions.

Supporting Information Available: Synthetic procedures and characterization data for **5**, **6**, **8**, **10**, **12**–**14**, and X-ray crystallographic data for compound **8** (11 pages, print/PDF). See any current masthead page for ordering information and Web access instructions.

JA983288P

(22) Eisler, S.; Tykwinski, R. R., manuscript in preparation.

(23) Anthony, J.; Boldi, A. M.; Boudon, C.; Gisselbrecht, J.-P.; Gross, M.; Seiler, P.; Knobler, C. B.; Diederich, F. *Helv. Chim. Acta* **1995**, *78*, 797–817.

(24) Contributions from homoconjugation as measured by UV-vis spectroscopy appear negligible as determined by comparison to a cyclic, hexameric analogue. The more rigid cyclic oligomer, constrained to an orientation nearly optimal for overlap of the in-plane sp-orbitals of the acetylenic units, shows no enhanced π -electron delocalization attributable to homoconjugation (ref 22).

(25) Similar bathochromic shifts as a function of oligomer length were observed in hexane and THF.

(26) Electronic absorptions in UV spectra (from ca. 10^{-5} to 10^{-8} M) as well as the shift and line shape of ¹H NMR resonances (from ca. 10^{-1} to 10^{-3} M) were all consistent suggesting negligible aggregation of the oligomers in chloroform.