

Chiral, cross-conjugated isopolydiacetylenes†

Chad A. Lewis and Rik R. Tykwinski*

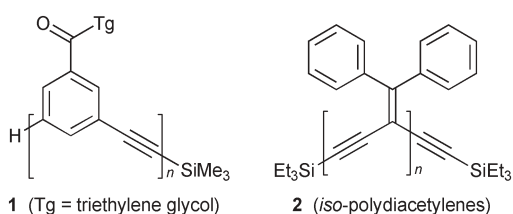
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A series of chiral, monodisperse enyne oligomers (isopolydiacetylenes) based on a 1,1-binaphthyl core has been synthesized and characterized spectroscopically.

The alpha helix is one of the most important architectural units in nature, typified by the secondary structure found in macromolecules such as DNA and keratin. As a structural motif, helicity has been used by chemists as a means of providing an ordered chiral framework, the properties of which can be varied by both structural changes to the backbone itself and functional groups attached laterally to the helix.¹ Helical oligomers and polymers with a conjugated skeleton are a specialized class of materials that combine desirable electronic properties for use as nonlinear optical, optoelectronic, and luminescent materials with a chiral framework that is potentially useful for enantioselective sensing,^{2,3} polarized emission,⁴ or catalysis.⁵ One approach toward conjugated helical molecules is through the design of foldamers, in which secondary bonding interactions ultimately provide for a helical conformation.^{6,7} One of the premier examples of this approach is the oligo(phenylene ethynylene) oligomers (**1**) studied by Moore and coworkers, which have provided a wealth of information about the conformational behavior of nonbiological foldamers.⁶



1 (Tg = triethylene glycol)

2 (iso-polydiacetylenes)

We have recently explored an alternative motif for the formation of conjugated oligomers, that of the isopolydiacetylenes, **2** (iso-PDAs).⁸ Because of their cross-conjugated skeleton, iso-PDAs maintain significant transparency in the visible portion of the spectrum, which is a significant goal in the realization of new nonlinear optical materials.^{9,10} During the course of this study, it was determined that iso-PDAs have the potential to form helical foldamers in solution based on the π -stacking interactions of neighboring phenyl groups in the all cisoid conformation.⁹ Intrigued by this result, we sought to synthesize optically pure iso-PDAs through the incorporation of a 1,1-binaphthyl unit into

the oligomeric framework. The preliminary results of this study are reported herein.

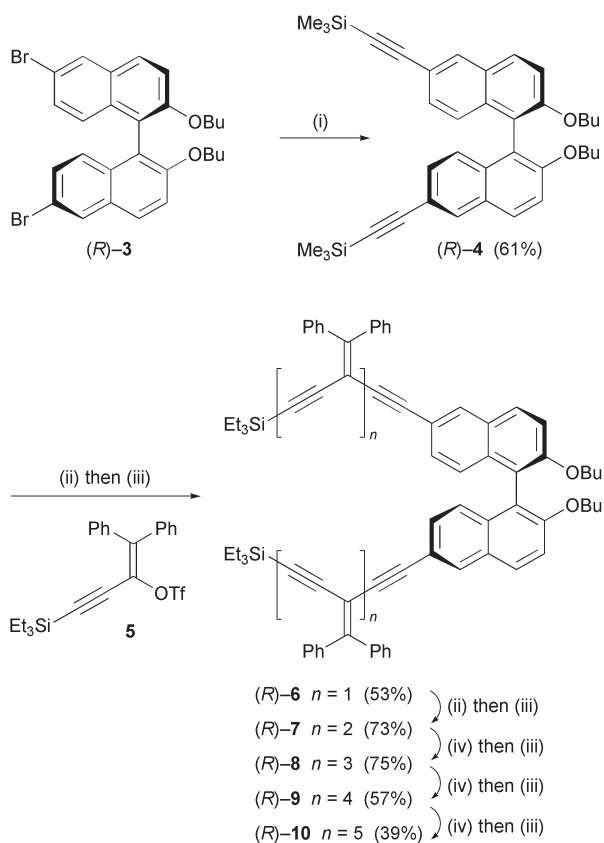
The synthesis of the iso-PDA oligomers is shown in Scheme 1, and began from the known dibromide (*R*)-**3**,¹¹ which could readily be coupled to trimethylsilyl acetylene under Sonogashira conditions to give (*R*)-**4**. Removal of the trimethylsilyl group of (*R*)-**4** with K₂CO₃-MeOH gave the terminal alkyne, which was subjected to cross-coupling with vinyl triflate **5**.⁹ Even at 55 °C, this reaction was sluggish and required two days to reach completion, giving 53% of monomer (*R*)-**6** as a yellow solid following column chromatography. Subjecting (*R*)-**6** to desilylation with K₂CO₃-MeOH provided the terminal alkyne, but this reaction required a surprisingly long reaction time (16 h). Following workup, the desilylated monomer was taken directly on to cross-coupling with **5** using the same conditions as for (*R*)-**6**, giving dimer (*R*)-**7** in reasonable yield. The formation of trimer (*R*)-**8** followed an analogous route, albeit tetrabutylammonium fluoride (TBAF) was used in place of K₂CO₃-MeOH for desilylation to reduce the reaction time. The formation of tetramer (*R*)-**9** and pentamer (*R*)-**10** also proceeded smoothly using this approach, but insolubility of the iso-PDA products became an issue in both cases when purification was attempted by column chromatography. As a result, preparative GPC was employed (Bio-Beads, SX-1, CHCl₃) which gave pure (*R*)-**9** and (*R*)-**10**. All oligomers **6–10** were fully characterized by ¹H and ¹³C NMR spectroscopy and mass spectrometry.†

It is worth noting that the synthesis of **6–8** was typically accompanied by a significant amount of a byproduct that derived from the oxidative homocoupling of the desilylated acetylenic precursor under the Sonogashira reaction conditions.¹² This culminated during the formation of trimer (*R*)-**8**, when up to 15% of (*R,R*)-**11** was isolated pure by column chromatography and could be identified by ¹H NMR spectroscopy and MALDI MS analysis which showed a single strong signal at *m/z* 3142 ([M + H]⁺).

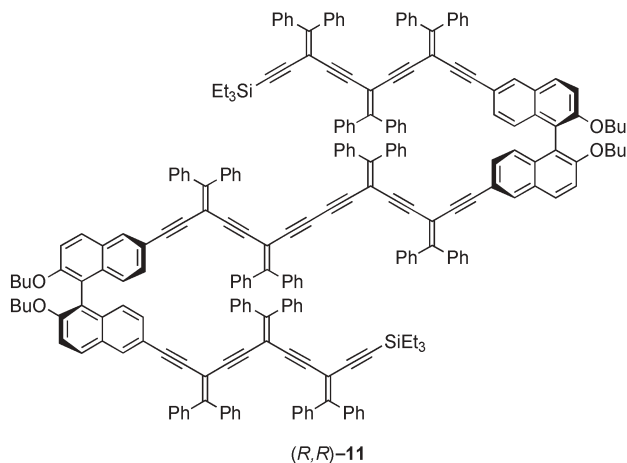
The UV-vis spectra (Fig. 1) for chiral iso-PDA oligomers **6–9** in acetonitrile solution show two distinct absorption bands, one at high energy (*ca.* $\lambda_{\text{max}} = 255$ nm) and a second broader absorption centered at $\lambda_{\text{max}} = 355$ nm.‡ As has been observed for iso-PDA **2**, the HOMO-LUMO gap for **6–9** remains essentially constant, as a result of the cross-conjugated π -framework.⁹ For both absorption bands, ϵ steadily increases *versus* length, which is representative of the increasing number of oligomer units. It is interesting to note the appearance of a higher energy shoulder at *ca.* 325 nm in the trimer (*R*)-**8** and tetramer (*R*)-**9**, a shoulder that is absent when spectra are acquired in chloroform.† Previous work has shown that this higher energy absorption is consistent with the cisoid conformation of the diphenylalkylidene units about the intervening acetylene unit, as would be expected in a helical arrangement.⁹

Department of Chemistry, University of Alberta, Edmonton, AB, Canada. E-mail: rik.tykwinski@ualberta.ca; Fax: +1 780 492 8231; Tel: +1 780 492 5307

† Electronic supplementary information (ESI) available: Experimental details, spectroscopic data, minimized structure of **9**, UV-vis spectra of **6–10** in chloroform, and CD spectra in THF (**6–9**) and chloroform (**6–10**). See DOI: 10.1039/b607630k



Scheme 1 Synthesis of chiral iso-PDAs **6–10**. Reagents and conditions: (i) $\text{Me}_3\text{SiC}\equiv\text{CH}$, $\text{Pd}_2(\text{dba})_3$, CuI , Et_3N , H_3CCN , 55°C . (ii) K_2CO_3 , MeOH-THF . (iii) **5**, $\text{Pd}(\text{PPH}_3)_4$, CuI , THF , $i\text{-Pr}_2\text{NH}$, 55°C . (iv) TBAF , THF .



Molecular mechanics minimization supports this premise, showing that the binaphthyl-based iso-PDA **9** can readily fold into a helix that is stabilized by π -stacking interactions.[†]

CD spectra of the chiral oligomers were acquired in THF,[†] chloroform,[†] and acetonitrile (Fig. 2). In all solvents, the spectra show a bisignate band centered at *ca.* 255 nm, due to the $\pi \rightarrow \pi^*$ absorption of the naphthyl unit. While $\Delta\epsilon$ values measured in THF and chloroform are virtually identical for all the oligomers, the situation is different in acetonitrile (Fig. 2).[‡] As the length of the oligomers increases from $n = 1$ to $n = 3$, the $\Delta\epsilon$ intensity of the positive Cotton effect at 235 nm decreases. At the stage of the

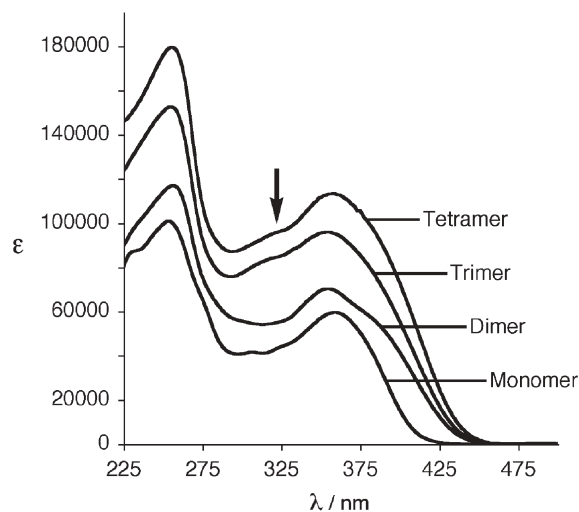


Fig. 1 UV-vis absorption spectra for **6–9** (in NCCH_3); the arrow denotes the higher energy shoulder at *ca.* 325 nm (see text for discussion).

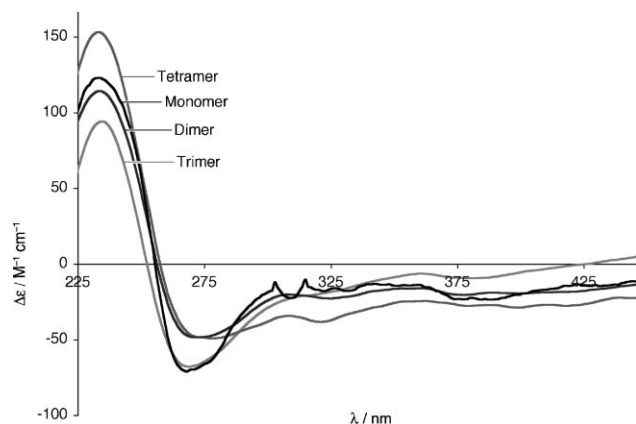


Fig. 2 CD spectra for **6–9** (in NCCH_3).

tetramer (*R*)-**9**, however, $\Delta\epsilon$ shows an increase that would be consistent with attaining a critical chain length at which a more organized structure comes to dominate.¹³ The lower energy region of the CD spectra, including that corresponding to the UV absorption at $\lambda_{\text{max}} = 355$ nm, is unremarkable.

In summary, a series of chiral, monodisperse, iso-PDA oligomers has been synthesized and the optical properties examined as a function of length. Initial studies suggest that with acetonitrile as a solvent, a folded structure is possible for the longest soluble derivative, tetramer (*R*)-**9**. The synthesis of longer and more soluble analogues will now be undertaken to further explore the potential of these cross-conjugated materials.

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Notes and references

[‡] Attempts to measure the UV-vis absorption and circular dichroism spectra for pentamer (*R*)-**10** in CH_3CN resulted in low signal to noise and inconsistent ϵ and $\Delta\epsilon$ values, respectively, because of minimal solubility.

- 1 T. Nakano and Y. Okamoto, *Chem. Rev.*, 2001, **101**, 4013.
- 2 D. T. McQuade, A. E. Pullen and T. M. Swager, *Chem. Rev.*, 2000, **100**, 2537.
- 3 (a) L. Pu, *Chem. Rev.*, 2004, **104**, 1687; (b) L. Pu, in *Acetylene Chemistry: Chemistry, Biology, and Material Science*, ed. F. Diederich, P. J. Stang, and R. R. Tykwinski, Wiley-VCH, Weinheim, Germany, 2005, ch. 11.
- 4 F. J. M. Hoeben, P. Jonkheijm, E. W. Meijer and A. P. H. J. Schenning, *Chem. Rev.*, 2005, **105**, 1491.
- 5 L. Pu and H.-B. Yu, *Chem. Rev.*, 2001, **101**, 757.
- 6 (a) C. R. Ray and J. S. Moore, *Adv. Polym. Sci.*, 2005, **177**, 91; (b) D. J. Hill, M. J. Mio, R. B. Prince, T. S. Hughes and J. S. Moore, *Chem. Rev.*, 2001, **101**, 3893.
- 7 S. H. Gellman, *Acc. Chem. Res.*, 1998, **31**, 173.
- 8 R. R. Tykwinski and Y. Zhao, *Synlett*, 2002, 1939.
- 9 Y. Zhao, A. D. Slepko, C. O. Akoto, R. McDonald, F. A. Hegmann and R. R. Tykwinski, *Chem.–Eur. J.*, 2005, **11**, 321.
- 10 A. D. Slepko, F. A. Hegmann, Y. Zhao, R. R. Tykwinski and K. Kamada, *J. Chem. Phys.*, 2002, **116**, 3834.
- 11 J. C. Ostrowski, R. A. Hudack, Jr., M. R. Robinson, S. Wang and G. C. Bazan, *Chem.–Eur. J.*, 2001, **7**, 4500.
- 12 Glaser/Hay coupling, see: P. Siemsen, R. C. Livingston and F. Diederich, *Angew. Chem., Int. Ed.*, 2000, **39**, 2632.
- 13 M. T. Stone, J. M. Heemstra and J. S. Moore, *Acc. Chem. Res.*, 2006, **39**, 11.



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