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# Expanded radialenes: Modular synthesis and properties of cross-conjugated enyne macrocycles\*

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Abstract: During the past two decades, shape-persistent conjugated macrocycles with a broad spectrum of attributes and topologies have been synthesized. This includes macrocycles with remarkable electronic, optical, and supramolecular properties, as well as intriguing frameworks. Expanded radialenes are a class of conjugated shape-persistent macrocycles that arise from the formal insertion of acetylene units into a radialene framework. A related class of macrocycles, the expanded radiaannulenes, contains both endo- and exocyclic vinylene and vinylidene segments, respectively, and accordingly exhibits properties intermediate between radialenes and annulenes. Enyne building blocks have been developed that are suitable for forming a macrocyclic framework through a step-wise sequence of Pd-catalyzed cross-coupling reactions. This "building-block" approach allows us to explore a range of molecular architectures that will ultimately provide for an understanding of  $\pi$ -delocalization in these compounds. The synthesis and structural characterization of the first members of this new class of expanded radialenes are described.

Keywords: macrocycles; cross-conjugation; polydiacetylene; palladium coupling; oligomers.

# INTRODUCTION

Organic oligomers and polymers composed of enyne repeat units, such as polydiacetylene (PDA) [1] and polytriacetylene (PTA, Fig. 1) [2,3] are well known in the realm of organic materials. These carbon-rich and linearly conjugated compounds show a wealth of interesting electronic and optical properties, including very respectable third-order nonlinear optical responses [4–7]. Less well known are the constitutional isomers of PDA and PTA, in which the enyne framework is cross-conjugated, compounds that have come to be known as *iso*-polydiacetylene (*iso*-PDA) and *iso*-polytriacetylene (*iso*-PTA) [8,9].

During the past decade, we and others have worked toward building an understanding of the characteristics of cross-conjugated materials, often through the synthesis of defined length oligomers [9]. The assembly and study of such classes of molecules differing only in the number of repeat units, the

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Fig. 1 General chemical structures of linear- and cross-conjugated enyne oligomers.

so-called oligomer approach [10], allows one to evaluate the properties expected for the corresponding polymers, without entertaining the often difficult tasks of polymer synthesis and purification.

The study of *iso*-PTAs was initiated in the mid-1990s through the efforts of Diederich and coworkers as part of their program concerning the use of tetraethynylethene (TEE) as a key component in the assembly of carbon-rich compounds [11]. As demonstrated by their synthesis of **1**, *iso*-PTAs can be readily achieved through Cu-catalyzed oxidative homocoupling of judiciously chosen monomer units (eq. 1) [12].



While TEE-based *iso*-PTAs **1** were found to be robust molecules, subsequent derivatives with pendent cyclohexylidene[13] or isopropylidene groups (e.g., **2–3**) [14,15] showed quite limited stability under ambient conditions. Following their synthesis, the electronic characteristics of each series of *iso*-PTA oligomers has been evaluated by a number of methods, including UV/vis spectroscopy. These analyses showed almost no lowering of the highest occupied molecular orbital/lowest unoccupied molecular orbital (HOMO/LUMO) gap for either the TEE (**1**) or isopropylidene (**3**) series. Conversely, the cyclohexylidene (**2**) series demonstrated a consistent drop in the HOMO/LUMO energy gap as oligomer length was increased [13], suggesting a contribution from cross-conjugation to the overall electronic makeup of the molecules. It is worth noting that electronic delocalization in PTAs and *iso*-PTAs has been compared and contrasted in theoretical studies published by Lüthi and coworkers [16,17].



The most obvious route toward the synthesis of *iso*-PDAs requires the formation of an electrophilic coupling partner for elaboration via acetylenic coupling using, for example, the Sonogashira reaction (Fig. 2) [18,19]. For several reasons, vinyl triflates were chosen for the current work, including: (a) the physical properties could be varied as a function of the appended R-groups; (b) silyl protection of the alkyne provides synthetic flexibility; (c) vinyl triflates are well established as coupling partners in Sonogashira reactions; and (d) the desired triflates should be readily accessible from the corresponding ketones via reaction with base and triflic anhydride.



Fig. 2 Retrosynthetic analysis of iso-PDA monomer.

## **SYNTHESIS**

The first series of *iso*-PDA oligomers targeted were end-capped with trimethylsilyl groups, since removal of this group in subsequent iterations would be easier than removal of the more robust triisopropylsilyl group. Thus, monomer **4a** was desilylated in methanolic  $K_2CO_3$  to give the deprotected terminal diyne (Scheme 1), which could be used without further purification. Cross-coupling of this enediyne with **6a** gave trimer **4b**, and an iterative sequence of desilylation and Sonogashira couplings then completed the series through heptamer **4d**. At this point, insolubility of the product thwarted efforts to extend further this protocol to the formation of **4e** [20,21]. The second series of oligomers, **5b–e**, then used the triisopropylsilyl group in an attempt to increase solubility of the *iso*-PDAs. Using triflate



Scheme 1 Synthesis of the first iso-PDA oligomers.

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**6b** and an analogous approach of sequential desilylation and Sonogashira couplings as was developed for the formation of **4b–4d**, the triisopropylsilyl end-capped series culminated in the formation of the *iso*-PDA nonamer **5e**. While **5b–e** showed enhanced solubility vs. the series **4**, attempts to desilylate **5e** resulted in an essentially insoluble product and prevented any further elaboration. Somewhat surprising was the rather limited stability of the products, which slowly decomposed over a period of weeks, even when kept under refrigeration and nitrogen protection. Nevertheless, this series of monodisperse oligomers provided an opportunity to explore the electronic aspects of cross-conjugation, and UV/vis spectroscopy suggested that  $\pi$ -electron communication is present along the enyne framework of the *iso*-PDAs, but quickly reaches saturation by the stage of nonamer [21]. Structurally, X-ray crystallographic analysis of the trimer **5b** showed a completely planar, cross-conjugated framework that was devoid of steric interactions between the pendent isopropylidene methyl groups [21].

With the successful synthesis of the acyclic *iso*-PDAs, attention was quickly turned to the possible formation of the corresponding cyclic derivatives, expanded radialenes **7** (Fig. 3). The most basic structure in this general class of compounds is that of the radialenes **8**, which consist of a series of exocyclic olefins linked into a cyclic structure [9,22–24]. Upon the formal insertion of an acetylene unit into the radialene skeleton, a process deemed carbomerization by Chauvin and coworkers [25,26], one arrives to the expanded radialenes **7**. A second iteration of the carbomerization process brings one to the next higher homolog, expanded radialenes **9**. Radialenes **8** have been known for quite some time, and they continue to be the topic of both theoretical and synthetic study, as shown recently, for example, by the work of Chauvin and Iyoda, respectively [26,27]. Expanded radialenes **9** are a much younger class of molecules, only introduced in the mid-1990s by Diederich and coworkers [5,28,29], while examples of the intermediate family **7** were, at the time of our initial work, unknown.



Fig. 3 Radialenes and expanded radialenes.

The first member of the enyne radialenes 7 to be targeted synthetically was 10. This structure was developed with an alternating pattern of pendent cyclohexylidene and isopropylidene units, which were designed to increase solubility vs. the parent *iso*-PDAs that contained only isopropylidene units (Scheme 2) [30]. Vinyl triflate 11 [31] provided a potential means to this end, and reaction with the isopropylidene enediyne gave trimeric 12. A sequence of desilylation and Sonogashira coupling with triflate 6a then gave pentamer 14. A final desilylation and cyclization step with the dibromoolefin 13 gave radialene 10, although the yield was quite disappointing. It was quickly discovered that the stability of both the product 10 and precursor 14 was considerably less than expected under ambient conditions. To date, empirical evidence suggests that an oxygen ene reaction at the peripheral allylic positions is the likely culprit [32], a situation exasperated by the axial protons of the cyclohexylidene units, which are perfectly situated for such a transformation.



Scheme 2 Synthesis of the first iso-PDA-based expanded radialene 10.

The challenge thus became to replace the offending alkylidene segments with components that would provide more stable products. A brief foray into the use of pendent adamantylidene groups was conducted [21]. The synthesis of radialene **15** (Scheme 3) from trimer **16** and dibromoolefin **17** demonstrated that the removal of allylic protons could indeed provide a stable expanded radialene, albeit one that was nearly insoluble in organic solvents [33].



Scheme 3 Synthesis of adamantylidene radialene 15.

Thus, attention was turned to the use of a diphenyl alkylidene building block, which was successfully implemented in the formation of *iso*-PDA oligomers **18–21** using the same stepwise elongation established for the earlier derivatives (Scheme 4). The only real adjustment to the general protocol as described in Scheme 1 was the stronger reaction conditions required with the use of the diphenyl vinyl triflate (reflux), presumably due to steric interactions with the ortho protons during the cross-coupling. Nevertheless, this process was equally successful for either the *t*-butyldimethylsilane (TBDMS)-or TES-protected alkynes, with both showing excellent solubility and stability under normal handling and purification. The dimer through the pentamer of the TBDMS series would provide the immediate precursors to the desired radialenes, and in addition to these shorter oligomers, *iso*-PDAs as long as the pentadecamer **22** could be formed via this process [34]. The entire TES series of oligomers was thoroughly evaluated in terms of their structural, electronic absorption and emission, and film-forming char-



Scheme 4 Synthesis of perphenylated iso-PDA oligomers.

acteristics. Of particular significance, the third-order nonlinear optical characteristics were evaluated via the differential optical Kerr effect (DOKE) method and showed a superlinear increase in  $\gamma$ -values as a function of length [34,35]. It was ultimately concluded that this superlinear increase likely derived from a folding of the longer oligomers into a helical structure rather than from extension of the cross-conjugated skeleton.

Single crystals of **19a** were analyzed by X-ray crystallography and showed that in the solid state, the cross-conjugated framework of **19a** does not assume a planar conformation as a result of steric interactions between the phenyl groups of neighboring alkylidene units (Fig. 4) [34]. More specifically, **19a** shows a pseudo-*cis*-*trans* orientation rather than an all *s*-*trans* orientation, and to date this is the only *iso*-PDA that displays a solid-state cisoid orientation for neighboring alkylidene groups. The intra-molecular distance between H(55) and H(56) to phenyl plane 4 (C61, C62, C63, C64, C65, C66) is observed at 3.20 and 3.37 Å, respectively, and the angle between the two phenyl planes is 79°. This orientation suggests  $\pi$ -stacking of the "face to edge" type that stabilizes the pseudo-*cis* orientation in the solid state.



Fig. 4 ORTEP drawing of iso-PDA trimer 19a.

#### Expanded radialenes

Thus, with oligomers **18–21** in hand, the stage was set for the formation of expanded radialenes with a periphery decorated with phenyl groups. Subjecting pentameric **21b** to desilylation with tetrabutylammonium fluoride (TBAF) gave **23**, and attempted ring closure onto dibromoolefin **24** consistently gave hybrid radialene **25** as the major product (eq. 2), while only a trace of desired hexameric macrocycle, [6]radialene **26**, could be found. Gratifyingly, the products **25** and **26** were both quite stable to chromatography, air, and water as predicted from analysis of oligomeric precursors [36].



The situation was, however, quite different when the analogous procedure was applied to tetrameric **20** (eq. 3). In this case, following desilylation and cross-coupling with **24**, the desired radialene **27** was isolated in a reasonable yield as a light yellow crystalline solid.



Likewise, the reaction beginning with trimeric oligomer **19b** was also quite successful, leading to the desired [4]radialene **28** in an excellent yield (eq. 4). This radialene, in particular, showed impressive thermal stability, decomposing only above 300 °C. Radialene **28** is also remarkably crystalline, easily affording single crystals suitable for X-ray diffraction (vide infra).



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The final radialene in the series, [3] radialene **29**, was expected to be the most difficult to produce, but this turned out not to be the case (eq. 5). Simple PM3 modeling suggested that the alkynyl bond angles in **29** should be less than 160°, which would likely present a significant energy barrier to the final cross-coupling event to close the [3] radialene skeleton. To our knowledge, the ability of a Sonogashira reaction to accommodate this level of strain was unprecedented. Nonetheless, desilylation of **18b** followed by cross-coupling under the now standard conditions led to a reasonable yield of a product that showed spectroscopic data consistent with the proposed structure of **29**. In particular, a strong base peak was observed in the EI/MS analysis at m/z 606.2354, as expected for  $C_{48}H_{30}$ . The <sup>13</sup>C NMR spectrum was also quite convincing and showed the expected seven signals of this highly symmetrical molecule, with those of the vinyl fragment at  $\delta$  146.2 and 107.2 and that of the six equivalent alkynyl carbons at  $\delta$  92.5.



The prospect of forming carbon-rich, cross-conjugated bis-expanded radialenes and radiaannulenes [37,38] in a one-pot process was then explored through the reaction of the corresponding enyne precursor with tetrabromoethene (**30**). For example, trimeric *iso*-PDA **19b** was desilylated and reacted with **30** under conditions analogous to those for the synthesis of radialenes **27–29** (eq. 6). In addition to a substantial amount of baseline material, column chromatographic purification of the crude reaction mixture produced an orange solid as the major product. Subsequent analysis of this material by matrix-assisted laser desorption/mass spectrometry (MALDI/MS) showed a signal at *m/z* 1285.5 consistent with the expected formula  $C_{102}H_{60}$  for **31** and/or **32**. The <sup>13</sup>C NMR spectroscopic analysis of this material showed that more than one product was likely present, but provided little clue as to which might have formed preferentially. All subsequent attempts to separate the products have been unsuccessful, although high-performance liquid chromatography (HPLC) analysis showed a ca. 2:1 ratio of products. X-ray crystallography (vide infra) ultimately confirmed the bis-radialene **31** was the predominant component in this solid, while expanded radiaannulene **32** was the minor.



Desilylation of dimeric *iso*-PDA **18b** followed by Sonogashira coupling with **30** gave a dark redpurple solid (eq. 7). Subsequent MALDI/MS analysis showed a signal at m/z 880.2, which was consistent with the molecular formula of  $C_{70}H_{40}$  expected for **33** as well as the corresponding bis-radialene (not shown). The solid showed very limited solubility in common organic solvents, a fact that made purification a challenging process, although preparative thin-layer chromatography (TLC) separation ultimately provided a pure product in 18 % yield. <sup>13</sup>C NMR spectroscopic analysis of this solid indicated that a single product had been formed, and 13 resonances (out of 14 expected) were identified, consistent with the structure of **33**. The constitution of the product **33** was ultimately confirmed by X-ray crystallography (vide infra).



### SOLID-STATE STRUCTURES

Single crystals of the three expanded radialenes **27–29** could be obtained, but unfortunately only those of the [5]- and [4]radialenes **27** and **28** were suitable for X-ray analysis. The structure of **27** is not planar (Fig. 5), and its cyclic core resembles an envelope conformation presumably due to steric demands

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of the 10 pendent phenyl rings. In contrast, the centrosymmetric structure of **28** (Fig. 6) displays a planar cyclic core, with peripheral phenyl groups twisted from this plane in order to facilitate  $\pi$ - $\pi$  stacking interactions between the parallel rings. This analysis also sheds light on the difficulty encountered in the formation of [6]radialene **26**, where the significant steric crowding from the 12 pendent Ph-rings would hinder the radialene from achieving the approximately planar conformation necessary for ring closure. In contrast, the structure of [4]radialene **28** seems to balance strain and steric factors, resulting in excellent yields of this structure as well as other derivatives with this basic skeleton [39].



Fig. 5 ORTEP drawing of radialene 27 (20 % probability level), edge on view showing envelope conformation. Selected bond angles (deg): C(2)-C(1)-C(15) 171.6(2), C(1)-C(2)-C(3) 172.5(2), C(2)-C(3)-C(4) 112.71(17), C(3)-C(4)-C(5) 177.4(2), C(4)-C(5)-C(6) 170.97(19), C(5)-C(6)-C(7) 111.65(15), C(6)-C(7)-C(8) 172.3(2), C(7)-C(8)-C(9) 171.54(19), C(8)-C(9)-C(10) 111.90(16), C(9)-C(10)-C(11) 173.23(19), C(10)-C(11)-C(12) 175.9(2), C(11)-C(12)-C(13) 113.47(17), C(12)-C(13)-C(14) 176.4(2), C(13)-C(14)-C(15) 175.5(2), C(1)-C(15)-C(14) 113.07(16).



**Fig. 6** ORTEP drawings of radialene **28** (20 % probability level). (a) Top view and (b) side view. Selected bond angles (deg): C(2)–C(1)–C(7') 168.23(14), C(1)–C(2)–C(3) 166.65(14), C(2)–C(3)–C(5) 110.40(12), C(3)–C(5)–C(6) 172.20(15), C(5)–C(6)–C(7) 171.30(15), C(1')–C(7)–C(6) 110.40(11).

Comparing the structures of **27** and **28** provides a gauge of the increased strain found in the smaller [4]radialene **28**. All bond lengths for the two structures fall within a similar range. Bond angles within the macrocyclic core, however, differ quite dramatically. For the [4]radialene **28**, the acetylenic bond angles range from 166.7° to 172.2° with an average of 169.6°, while those for [5]radialene **27** vary from 171.0 to 177.4° with an average of 173.7°. The endocyclic alkylidene bond angles are also a good

indication of ring strain, and both unique angles of **28** are  $110.4^{\circ}$ , while those of **27** range from 111.7 to  $113.5^{\circ}$  with an average of  $112.6^{\circ}$ .

After a significant amount of trial and error, crystals of expanded radiaannulene **33** were obtained from a mixture of THF and pentane that had been cooled to 4–5 °C. Crystallographic analysis reveals that the conjugated, cyclic core of this molecule is essentially planar (Fig. 7). The endocyclic alkylidene bond angles at C(7)–C(8)–C(10) at 105.7(3)° and C(3)–C(4)–C(6) at 106.9(3)° are noticeably smaller than those found for either **27** or **28**, providing evidence of the strained macrocyclic framework. The alkyne bonds are also substantially reduced from optimal values, and range from 158.1(3)° to 173.6(4)° with an average value of 164.6°.



Fig. 7 ORTEP drawings of radialene 33 (20 % probability level). Selected bond angles, C(1')-C(1)-C(1)-119.7(4), C(2)-C(1)-C(11') 122.3(3), C(1')-C(1)-C(2) 118.0(4), C(1)-C(2)-C(3) 171.0(4), C(2)-C(3)-C(4) 164.2(4), C(3)-C(4)-C(6) 106.9(3), C(4)-C(6)-C(7) 158.1(3), C(6)-C(7)-C(8) 159.6(3), C(7)-C(8)-C(10) 105.7(3), C(8)-C(10)-C(11) 161.1(4), C(1')-C(11-C(10)) 173.6(4).

Expanded bisradialene **31** and radiaannulene **32** cocrystallized from CHCl<sub>3</sub> and depending on the initial sample, various ratios of the two molecules are observed as cocrystallites in the solid state. In the structure shown in Fig. 8a, a ratio for **31**:**32** of 2:1 is observed. The structures of **31** and **32** are remarkably similar, and they form a disordered crystal in which the geometric properties of the central TEE core allow for the spatial arrangement of the remaining atoms to be shared by both molecules. Unlike expanded radiaannulene **33**, neither **31** nor **32** are planar. Both structures assume a stretched chair conformation as shown in Fig. 8b for radiaannulene **32**. The structure of molecule **31** shares many similarities to that of [4]radialene **28**, for instance, alkynyl bond angles that average 167.6° (range: 160.4 to 172.7°). Expanded radiaannulene **32** is the next higher analog of **33**, and consequently shows substantially less ring strain than **33** with an average bond angle of 172.3° (range: 165.5 to 178.9°) and internal alkylidene bond angles that vary between 110–111°. Based on a comparison of bond angles for structures **31** and **32**, the bis-radialene is clearly the more strained of the two.



**Fig. 8** ORTEP drawing (20 % probability level) illustrating (a) the structure and disorder of the cocrystallite formed from bisradialene **31** and expanded radiaannulene **32**, and (b) the stretched chair conformation of expanded radiaannulene **32** (only ipso carbons of pendent phenyl rings are shown). Selected bond angles (deg): C(1A')–C(1A)–C(2A) 124.2(7), C(1A')–C(1A)–C(12A) 124.2(7), C(2A)–C(1A)–C(12A) 111.7(6), C(1A)–C(2A)–C(3) 172.6(9), C(2A)–C(3)–C(4) 160.4(6), C(1A)–C(12A)–C(11) 172.7(9), C(1B')–C(1B)–C(2B) 121.3(14), C(1B')–C(1B)–C(12B') 121.3(14), C(2B)–C(1B)–C(12B') 117.2(12), C(1B)–C(2B)–C(3) 174.6(19), C(2B)–C(3)–C(4) 175.2(10), C(1B')–C(12B)–C(11) 178.9(16), C(10)–C(11)–C(12B) 175.8(9), C(3)–C(4)–C(5) 109.8(3), C(4)–C(5)–C(6) 170.3(3), C(5)–C(6)–C(7) 167.1(3), C(6)–C(7)–C(8) 109.9(3), C(7)–C(8)–C(9) 165.4(3), C(8)–C(9)–C(10) 171.3(3), C(9)–C(10)–C(11) 110.9(3), C(10)–C(11)–C(12A) 160.6(5).

## **UV/VIS SPECTROSCOPIC ANALYSIS**

The absorption spectra of expanded radialenes 27–29 are shown in Fig. 9. The spectra of 28 and 27 show a single absorption in the UV region at similar energies of  $\lambda_{max} = 377$  nm ( $\varepsilon = 99$  300) and  $\lambda_{max} = 374$  nm ( $\varepsilon = 51$  300), respectively. This absorption mirrors closely that of acyclic *iso*-PDA oligomers such as 18–21, which show  $\lambda_{max}$  in a narrow range of 373–377 nm [34]. For [4]radialene 28, a shoulder absorption is visible at ca. 420 nm with a much weaker intensity. The major difference between radialenes 27 and 28 is the lower molar absorptivity for 27, which may arise from its more flexible and



Fig. 9 Electronic absorption spectra of radialenes 27-29 in THF.

nonplanar structure. Conversely, [3] radialene **29** shows two major absorptions centered at  $\lambda_{max} = 364$  ( $\varepsilon = 105\ 300$ ) and 415 nm ( $\varepsilon = 107\ 500$ ). The origin of the lower energy absorption has not yet been determined, but it may be the result of an augmentation of the shoulder signal observed for **28** resulting from decreased conformational flexibility in the more strained structure of **29**. Alternatively, it might arise from the influence of macrocyclic cross-conjugation. A similar observation has been made previously to account for the red shift in  $\lambda_{max}$  observed for trimeric derivatives of larger expanded radialenes, **9** [2,40]. The latter argument is bolstered through a comparison of  $\lambda_{max}$  for **27–29** to that of the acyclic precursors **18–21** ( $\lambda_{max} = 374\ nm$ ) [34,41]. Including the pendent phenyl rings, the longest linearly conjugated segment in **18–21** is identical to that of **27–29** (shown in bold for **29**, Fig. 9) [42].

The high-energy region of the UV/vis spectrum of expanded radiaannulene 33 (Fig. 10) shows a profile similar to that of radialenes 27–29 at  $\lambda_{max} = 381$  nm ( $\varepsilon = 63\,000$ ) resulting from the common Ph-ene-yne-ene-Ph segment (shown in bold, compound 29, Fig. 9). The low-energy region is, however, quite disparate from 27–29 and shows two additional absorptions at  $\lambda_{max} = 534$  ( $\varepsilon = 19500$ ) and 572  $(\varepsilon = 31700)$  nm that signify a substantial lowering of the HOMO/LUMO gap. It is unlikely that this lowering of the HOMO/LUMO gap derives simply from an extension of the linearly conjugated segment of 33 (shown in **bold** for 33), since the oligodiacetylene 34, studied by Giesa and workers, shows  $\lambda_{\text{max}}$  = 418 nm. Thus,  $\lambda_{\text{max}}$  for 34 is over 100 nm higher in energy than that of expanded radiaannulene 33, in spite of the fact that 34 contains a significantly longer linear conjugated segment [43]. It seems clear that the constrained, cross-conjugated framework of 33 plays a role in the electronic makeup of this expanded radiaannulene. Unfortunately, isomers 31/32 could not be separated to allow individual analysis of each isomer by UV/vis spectroscopy. Nevertheless, an empirical comparison of the absorption characteristic of isomers 31/32 to that of 33 is informative. The mixture 31/32 shows the same highenergy absorption at 387 nm as found for 33, as well as a broad low-energy absorption centered at 509 nm. Thus, **31/32** also exhibits unique electronic characteristics resulting from their macrocyclic structure.



Fig. 10 Electronic absorption spectra of expanded radiaannulene 33 and mixture of 31/32 in THF.

## **ELECTROCHEMISTRY**

The cyclic voltammetric analysis of 27–29 and 33 was done in  $CH_2Cl_2$  containing 0.1 M of  $NBu_4PF_6$ and with a 3-mm-diameter glassy carbon disk as the working electrode (Fig. 11). Ferrocene was added at the end of the experiments and used as an internal reference for the measured potentials. Quite surprisingly, expanded radialenes 27-29 showed comparable redox behavior despite the varied sizes of their cross-conjugated, macrocyclic frameworks (Table 1). The three radialenes 27-29 show two reduction steps, the initial event is reversible at about -2.0 V vs Fc<sup>+</sup>/Fc and the second is a less well defined event at ca. -2.2 V vs Fc<sup>+</sup>/Fc. A single, one-electron, reversible oxidation step at about 0.8 V was also found. Thus, no significant lowering of the electrochemical HOMO/LUMO gap was observed for the three radialenes as might have been expected on the basis of the UV/vis analysis. It is worth noting that Diederich and coworkers described the same trend for derivatives of larger expanded radialenes 9, where similar redox potentials were observed irrespective of macrocycle size (n = 0-3) [44]. The smaller radialenes 27-29 were considerably more difficult to reduce than any of the reported radialenes 9 [40,44]. The difficult reduction of compound 29 might lead one to suggest that a one-electron reduction should lead to an antiaromatic molecule, as predicted by Chauvin and coworkers for a [3]radialene analog of **29** (i.e., 7 n = 0,  $R = C \equiv CH$ ). At this point, however, such a conclusion is likely premature. In contrast to 27–29, radiaannulene 33 was both easier to reduce and to oxidize, with two reversible one-electron reductions at -1.36 V and -1.71 V vs Fc<sup>+</sup>/Fc and a reversible one-electron oxidation at 0.68 V vs Fc<sup>+</sup>/Fc.



Fig. 11 Cyclic voltammetry of expanded radialenes 27–29 and expanded radiaannulene 33 in  $CH_2Cl_2 + 0.1 \text{ M}$   $NBu_4PF_6$  (Fc<sup>+</sup>/Fc as reference, scan rate 100 mV/s).

**Table 1** Peak and half-wave potentials of the first reduction and oxidationsteps of expanded radialenes 27–29 and expanded radiaannulene 33.

Compound	$Ep_c red_1$	$Ep_a red_1$	$E_{1/2} \operatorname{red}_1$	$Ep_a ox_1$	$Ep_c ox_1$	$E_{1/2}  \mathrm{ox}_1$
27	-1.99	-1.92	-1.96	0.82	0.75	0.79
28	-1.98	-1.91	-1.94	0.81	0.75	0.78
29	-1.98	-1.92	-1.96	0.83	0.76	0.80
33	-1.40	-1.33	-1.36	0.71	0.64	0.68

## Expanded radialenes

# CONCLUSIONS

Based on previous work on the study of cross-conjugated *iso*-PDAs, the synthesis of a new class of stable expanded radialenes and radiaannulenes has recently been achieved by the current study. This work has shown that macrocycles with an incredibly strained enyne framework can be attained through Sonogashira cross-coupling reactions. The cross-conjugated products are remarkably stable under normal laboratory conditions, including extended exposure to air and water. UV/vis spectroscopy shows that the electronic characteristics of the expanded radialenes are related to their macrocyclic, cross-conjugated framework: the more strained the structure, the more interesting the electronic properties. Cyclic voltammetry shows that the reduction and oxidation potentials for the three radialenes **27–29** do not vary appreciably, while those of expanded radiaannulene **33** agree with the lowered HOMO/LUMO gap observed in the UV/vis spectrum. A study of the fundamental structure–property relationships for these compounds and related analogs is currently underway.

# **EXPERIMENTAL**

Adamantylidene [4]radialene 15. A mixture of the *iso*-PDA trimer 16 [21] (0.140 g, 0.206 mmol), Pd(PPh<sub>3</sub>)<sub>4</sub> (0.0235 g, 0.0203 mmol), CuI (0.0069 g, 0.0362 mmol), piperidine (0.5 mL), dibromide 17 (0.0629 g, 0.206 mmol) in THF (20 mL) was put under an inert atmosphere of N<sub>2</sub> and degassed using approximately 10 freeze/pump/thaw cycles. TBAF (1 M in THF, 0.2 mL, 0.2 mmol) was added, and the mixture was stirred at ambient temperature. The reaction was allowed to stir for 11 days at which point starting material was no longer observed by TLC (silica gel, hexanes/CH<sub>2</sub>Cl<sub>2</sub> 5:1) analysis. The reaction was quenched with satd. aq. NH<sub>4</sub>Cl (20 mL) and Et<sub>2</sub>O (20 mL), the organic phase separated, washed with satd. aq. NH<sub>4</sub>Cl (2 × 20 mL), dried (MgSO<sub>4</sub>), and the solvent removed *in vacuo*. Purification by column chromatography (silica gel, hexanes/CH<sub>2</sub>Cl<sub>2</sub> 5:1) provided [4]-radialene 15 (0.040 g, 30 %) as an off-white solid: mp 220 °C (decomp);  $R_{\rm f} = 0.49$  (hexanes/CH<sub>2</sub>Cl<sub>2</sub> 2:1); IR (C<sub>6</sub>D<sub>6</sub> cast) 2916, 2279, 1724, 1616 cm<sup>-1</sup>; <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, 300 MHz)  $\delta$  3.38 (bs, 8H), 1.72–1.62 (m, 48H); <sup>13</sup>C NMR (C<sub>6</sub>D<sub>6</sub>, 125 MHz)  $\delta$  160.6, 96.5, 95.5, 39.3, 37.2, 36.9, 28.3; UV/vis (CHCl<sub>3</sub>)  $\lambda_{\rm max}$  ( $\varepsilon$ ) 283 (64 500), 296 (91 000), 290 (16 500) nm; EI HRMS *m/z* calcd. for C<sub>52</sub>H<sub>56</sub> (M<sup>+</sup>) 680.4382, found 680.4378.

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# REFERENCES

- 1. D. Bloor, R. R. Chance. Polydiacetylenes, Martinus Nijhoff, Dordrecht (1985).
- 2. M. B. Nielsen, F. Diederich. Chem. Rev. 105, 1837 (2005).
- 3. R. E. Martin, F. Diederich. Angew. Chem., Int. Ed. 38, 1350 (1999).
- 4. S. Concilio, I. Biaggio, P. Günter, S. P. Piotto, M. J. Edelmann, J. M. Raimundo, F. Diederich. J. *Opt. Soc. Am. B* 20, 1656 (2003).

- M. Schreiber, R. R. Tykwinski, F. Diederich, R. Spreiter, U. Gubler, C. Bosshard, I. Poberaj, P. Gunter, C. Boudon, J. P. Gisselbrecht, M. Gross, U. Jonas, H. Ringsdorf. *Adv. Mater.* 9, 339 (1997).
- R. E. Martin, U. Gubler, C. Boudon, V. Gramlich, C. Bosshard, J.-P. Gisselbrecht, P. Günter, M. Gross, F. Diederich. *Chem. – Eur. J.* 3, 1505 (1997).
- R. E. Martin, J. A. Wytko, F. Diederich, C. Boudon, J.-P. Gisselbrecht, M. Gross. *Helv. Chim.* Acta 82, 1470 (1999).
- 8. R. R. Tykwinski, Y. Zhao. Synlett 1939 (2002).
- 9. M. Gholami, R. R. Tykwinski. Chem. Rev. 106, 4997 (2006).
- 10. K. Müllen, G. Wegner (Eds.). *Electronic Materials—the Oligomer Approach*, Wiley-VCH, Weinheim (1998).
- A. M. Boldi, J. Anthony, V. Gramlich, C. B. Knobler, C. Boudon, J.-P. Gisselbrecht, M. Gross, F. Diederich. *Helv. Chim. Acta* 78, 779 (1995).
- 12. P. Siemsen, R. C. Livingston, F. Diederich. Angew. Chem., Int. Ed. 39, 2633 (2000).
- 13. E. Bürri, F. Diederich, M. B. Nielsen. Helv. Chim. Acta 85, 2169 (2001).
- 14. Y. Zhao, R. McDonald, R. R. Tykwinski. J. Org. Chem. 67, 2805 (2002).
- 15. Y. Zhao, R. McDonald, R. R. Tykwinski. Chem. Commun. 77 (2000).
- 16. M. Bruschi, M. G. Giuffreda, H. P. Lüthi. ChemPhysChem 6, 511 (2005).
- 17. M. Bruschi, M. G. Giuffreda, H. P. Lüthi. Chem.-Eur. J. 8, 4216 (2002).
- 18. R. R. Tykwinski. Angew. Chem., Int. Ed. 42, 1566 (2003).
- 19. K. Sonogashira, Y. Tohda, N. Hagihara. Tetrahedron Lett. 4467 (1975).
- 20. Y. Zhao, R. R. Tykwinski, J. Am. Chem. Soc. 121, 458 (1999).
- 21. Y. Zhao, K. Campbell, R. R. Tykwinski. J. Org. Chem. 67, 336 (2002).
- 22. H. Hopf, G. Maas. Angew. Chem., Int. Ed. Engl. 31, 931 (1992).
- G. Maas, H. Hopf. In Synthesis and Transformation of Radialenes, Vol. 1, Z. Rappoport (Ed.), pp. 927–977, John Wiley, Chichester (1997).
- 24. F. Geneste, A. Moradpour. Org. Prep. Proc. Int. 31, 509 (1999).
- 25. R. Chauvin. Tetrahedron Lett. 36, 397 (1995).
- 26. C. Lepetit, M. B. Nielsen, F. Diederich, R. Chauvin. Chem.-Eur. J. 9, 5056 (2003).
- 27. Y. Kuwatani, G. Yamamoto, M. Oda, M. Iyoda. Bull. Chem. Soc. Jpn. 78, 2188 (2005).
- J. Anthony, A. M. Boldi, C. Boudon, J.-P. Gisselbrecht, M. Gross, P. Seiler, C. B. Knobler, F. Diederich. *Helv. Chim. Acta* 78, 797 (1995).
- 29. A. M. Boldi, F. Diederich. Angew. Chem., Int. Ed. Engl. 33, 468 (1994).
- 30. S. Eisler, R. R. Tykwinski. Angew. Chem., Int. Ed. 38, 1940 (1999).
- 31. P. J. Stang, T. E. Fisk. Synthesis 438 (1979).
- 32. M. Orfanopoulos, M. Stratakis, Y. Elemes. J. Am. Chem. Soc. 112, 6417 (1990).
- 33. S. Eisler. Ph.D. thesis, University of Alberta (2003).
- Y. Zhao, A. D. Slepkov, C. O. Akoto, R. McDonald, F. A. Hegmann, R. R. Tykwinski. *Chem. Eur. J.* 11, 321 (2005).
- (a) A. D. Slepkov, F. A. Hegmann, Y. Zhao, R. R. Tykwinski, K. Kamada. J. Chem. Phys. 116, 3834 (2002);
  (b) A. D. Slepkov, F. A. Hegmann, K. Kamada, Y. Zhao, R. R. Tykwinski. J. Opt. A, Pure Appl. Opt. 4, S207 (2002).
- M. Gholami, F. Melin, R. McDonald, M. J. Ferguson, L. Echegoyen, R. R. Tykwinski. Angew. Chem., Int. Ed. 46, 9081 (2007).
- F. Mitzel, C. Boudon, J.-P. Gisselbrecht, P. Seiler, M. Gross, F. Diederich. *Chem. Commun.* 1634 (2003).
- F. Mitzel, C. Boudon, J. P. Gisselbrecht, P. Seiler, M. Gross, F. Diederich. *Helv. Chim. Acta* 87, 1130 (2004).
- 39. M. Gholami, R.R. Tykwinski. Unpublished results.

- M. B. Nielsen, M. Schreiber, Y. G. Baek, P. Seiler, S. Lecomte, C. Boudon, R. R. Tykwinski, J.-P. Gisselbrecht, V. Gramlich, P. J. Skinner, C. Bosshard, P. Günter, M. Gross, F. Diederich. *Chem.-Eur. J.* 7, 3263 (2001).
- 41. C. A. Lewis, R. R. Tykwinski. Chem. Commun. 3625 (2006).
- It is possible that molecular symmetry and the associated selection rules also contribute to the differences observed in the electronic transitions of 27–29, as has recently been outlined for cyclic oligothiophenes, see: A. Bhaskar, G. Ramakrishna, K. Hagedorn, O. Varnavski, E. Mena-Osteritz, P. Bäuerle, T. Goodson III. *J. Phys. Chem. B* 111, 2946 (2007).
- 43. R. Giesa, R. C. Schulz. Polym. Int. 33, 43 (1994).
- 44. J.-P. Gisselbrecht, N. N. P. Moonen, C. Boudon, M. B. Nielsen, F. Diederich, M. Gross. *Eur. J. Org. Chem.* 2959 (2004).