Oligomeric and Polymeric Systems with a Cross-conjugated π-Framework[†]

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1. Introduction

1.1. Background

Conjugated organic compounds play a primary role in the development of a new generation of optical and electronic materials. Molecules, oligomers, and polymers with carbon, heteroatomic, or organometallic frameworks have been widely explored as media for electroluminescence, data storage, and nonlinear optics.[1] The most intensely studied conjugated molecules with carbon-rich frameworks feature extended, linearly-conjugated π-systems. There are, however, alternative modes of π-electron communication, including cross conjugation and omniconjugation[2] that can also produce electronically interesting materials.

Cross-conjugated molecules are molecules with "three unsaturated groups, two of which although conjugated to a third unsaturated center are not conjugated to each other".[3] In comparison to linearly-conjugated materials, oligomeric and polymeric compounds with a fully cross-conjugated carbon backbone are relatively unexplored. This is not to say, however, that molecules with a cross-conjugated framework are rare.[4] The situation is, in fact, quite the opposite. Cross conjugation can be found in a wide range of molecules, including such examples as quinones, radialenes, fulvalenes, and fused aromatics. It has only been recently, however, that nonaromatic cross-conjugated frameworks have emerged as a versatile platform for the synthesis of expanded cyclic and acyclic systems. As a result, trends in the structural, physical, and electronic properties of materials with a fully cross-conjugated π-backbone are only now starting to reveal themselves.

1.2. Scope of the Review

This review will focus on the synthesis and study of oligomeric and polymeric systems in which cross conjugation occurs by virtue of an exocyclic methylene (**1**), alkylidene (**2**), or vinylidene (**3**) group(s) present within the structure (Scheme 1). Monomeric species based on substructures **1**–**3**, however, are too numerous to address here and have been reviewed previously, including those derived from tetra-arylethene, di-, tri-, or tetraethynylene (TEE),[5] fulvalenes,[6] and tetrathiafulvalene.[7,8] Also excluded are systems in which cross conjugation derives solely from a particular substitution pattern about an aromatic ring (e.g., **4**–**7**).

Early work on acyclic cross-conjugated systems was reviewed by Hopf in 1984,[9] while cross-conjugated cyclic systems, the radialenes, were reviewed in 1992.[10–12] Our focus will therefore be primarily on work that has appeared after these seminal reviews.

Mojtaba Gholami, born in 1966, is a native of Tehran (Iran). He graduated with a B.Sc. Degree in Applied Chemistry from Azad University in 1990 and an M.Sc. Degree from the University of Otago, Dunedin, New Zealand, in 1998, working under the joint supervision of Professors Brian H. Robinson and Jim Simpson. After two years working in the private sector in Singapore, he moved to Canada in 2001 and joined the group of Professor Rik Tykwinski in 2003 to complete his graduate study. His research interests are focused on the synthesis and characterization of expanded radialenes, radiaannulenes, and derivatives of expanded radialenes.

Rik R. Tykwinski was born in 1965 in Marshall, MN. He completed his B.S. Degree in 1987 at the University of Minnesota—Duluth, where he also developed his interest in organic chemistry, working as an undergraduate researcher with Prof. Ron Caple. With Prof. Peter J. Stang at the University of Utah, he explored the chemistry of alkynyl iodonium salts, receiving his Ph.D. in 1994. Awarded an Office of Naval Research Postdoctoral Fellowship, he moved to ETH Zürich (1994–1997) to work with Prof. François Diederich on the chemistry and materials properties of functionalized tetraethynylethenes. He joined the faculty at the University Alberta in 1997, where he is now Professor of Chemistry. He is currently preoccupied with the development of synthetic methods for assembling conjugated carbon-rich molecules, characterization of their electronic properties, applications of conjugated systems to nonlinear optics, and mountain biking.

2. Acyclic Cross-conjugated Systems

Scheme 2 illustrates the cross-conjugated isomers that arise as the constitutional isomers of their linearly-conjugated analogues: dendralenes, *iso*-polydiacetylenes (*iso*-PDAs), *iso*-polytriacetylenes (*iso*-PTAs), and poly(phenylene-vinylidene) (*iso*-PPV). The obvious difference between the two classes of compounds is that π-electron density in the 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.[3] Nonetheless, evidence of π-electron communication via cross conjugation in such systems is often

Scheme 1
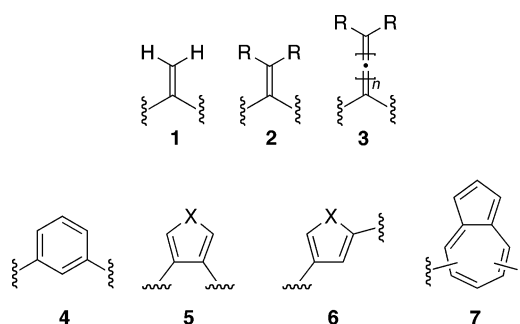
observable and provides for molecular systems of both fundamental and practical importance.

2.1. Cross-conjugated Molecules Based on 1,3-Butadiene

While not yet classified as a dendralene, the inclusion of pendent and/or terminal functionalization onto the 1,3-butadienyl framework provides for molecules with a range of cross-conjugated interactions, as outlined in Scheme 3. Formation of 2,3-diaryl butadienes **8** is fairly common[13–15] and has recently been extended to oligomeric derivatives **9** by Ikeda and co-workers.[15] Halton and co-workers have formed the uniquely substituted **10**.[16] Compounds based on 2,3-diethynyl-1,3-butadienes **11**–**13** are much less common, with or without pendent substitution.[17–20] Hybrids such as **14** have been reported,[21] as have heteroatom derivatives such as the vicinal diimine derivatives **15** and **16**[22] and the dicyano substituted **17**.[19]
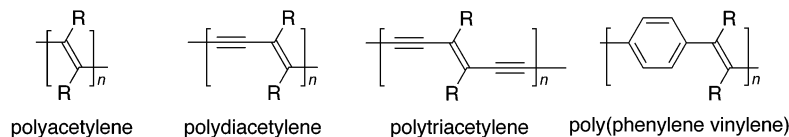
The formation of a 2,3-diethynyl-1,3-butadiene via the Pd-catalyzed dimerization of a cumulene was explored by Suzuki et al., giving a potentially interesting building block **18** for cross-conjugated oligomers and polymers via desilylation and elaboration (Scheme 4). To date, however, only a single example has been reported.[23]

Diederich and co-workers have recently discovered an extremely efficient and versatile route to mono- and oligomeric, donor-substituted 1,1,4,4-tetracyanobutadienes (Scheme 5).[24] The [2+2] cycloaddition between donor-substituted alkynes or diynes and tetracyanoethylene (**19**) followed by an electrocyclic ring opening of the intermediate cyclobutene provides the desired products **20** or **21**. Reaction of di- and triethynylarenes affords oligomeric derivatives **22** and **23**, with the 1,2- and 1,3-analogues of **22** formed as well (not shown). Despite the fact that these chromophores show a substantial twist between the two adjacent dicyanovinyl groups, efficient intramolecular charge-transfer interactions are observed, as documented by X-ray crystallography, electrochemical analysis, UV−vis spectroscopy, and theoretical calculations. Furthermore, substantial third-order nonlinear optical (NLO) responses were determined for several derivatives, as measured by degenerate four wave mixing in solution at 1.5 μm.[25,26]

One cross-conjugated polymer based on 2,3-substitution of butadiene has been reported and was accomplished by Grubbs and Swager using ring opening metathesis of 3,4-diisopropylidenecyclobutene (**24**) with a titanocene catalyst (Scheme 6).[27] The resulting polymer **25** is an air-sensitive white powder that is soluble in a variety of organic solvents ($M_{\mathrm{w}} = 12$−51K, PDI = 2.1). UV spectroscopy showed a single absorption peak at 278 nm, consistent with a framework limited to triene chromophores by a lack of planarity

Scheme 2

Linearly-conjugated oligomers

polyacetylene   polydiacetylene   polytriacetylene   poly(phenylene vinylene)

Cross-conjugated oligomers

dendralenes   *iso*-polydiacetylene   *iso*-polytriacetylene   poly(phenylenevinylidene)
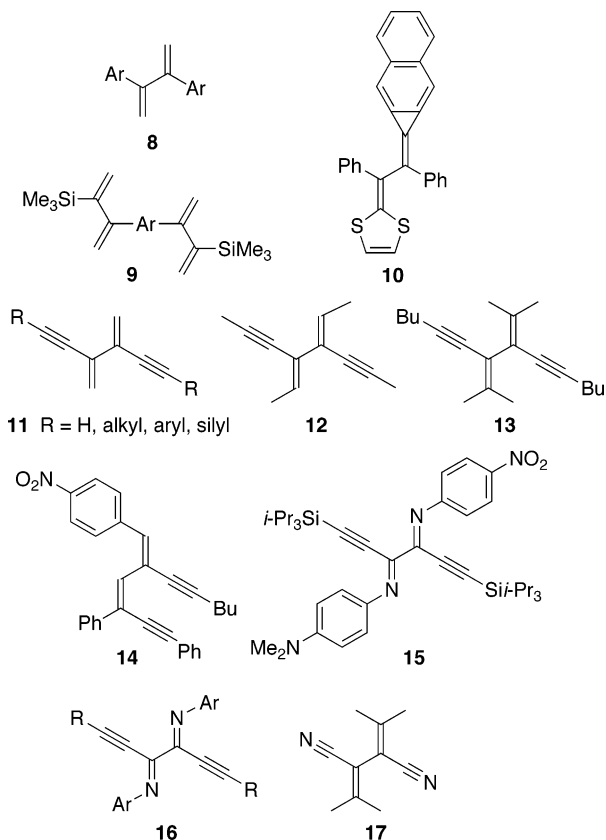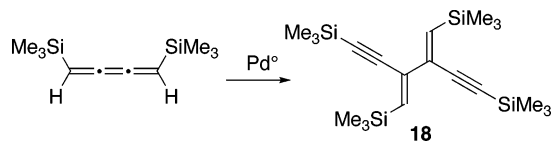   (*iso*-PDA)   (*iso*-PTA)   (*iso*-PPV)

Scheme 3

8

9

10

11 R = H, alkyl, aryl, silyl   12   13

14   15

16   17
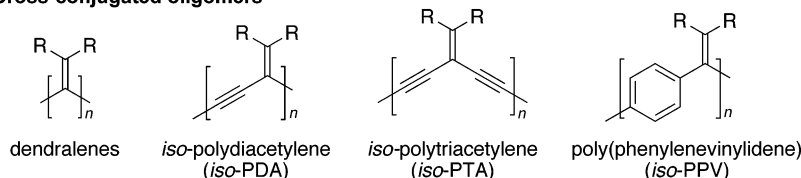
Scheme 4

and the presence of cross-conjugated isopropylidene units. The polymer could be cast into films, and upon doping with iodine became conductive ($10^{-3}-10^{-4}$ S cm^{-1}).

2.2. Dendralenes

The first family of cross-conjugated oligomers is the [*n*]dendralenes, **26(*n*)**, which feature a conjugated skeleton composed of sp^2-hybridized carbon atoms.[28] The first two members of this series, [3]- and [4]dendralene, **26(3)** and **26(4)**, are both thermally labile, which has historically

Scheme 5

19   20

21

23   22

Scheme 6

24   25

Scheme 7

26(3) (87%)

27   26(4)

26(4) (26%)
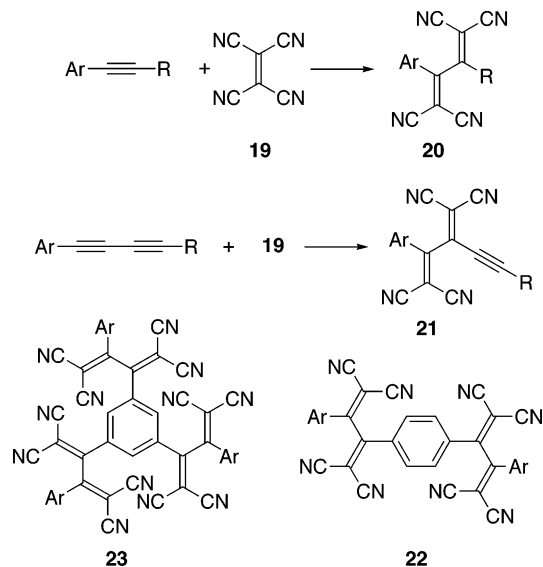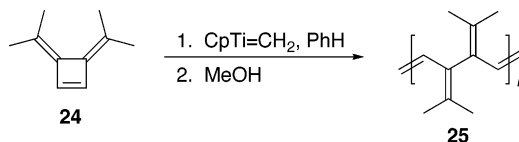
hampered their formation and characterization (Scheme 7).[9] The smallest dendralene, **26(3)**, has been made through the chelatropic extrusion of SO$_2$ from a 3-sulfolene precursor.[29] The parent [4]dendralene was effectively made via fragmentation of a sulfolane precursor **27**,[30] the method used by

Scheme 8

Scheme 9

31
(Bpin = pinacolatoboryl)

X = I, Br

29 R = alkyl, silyl (*n* = 1)
30 R = aryl (*n* = 1, 2)

Scheme 10

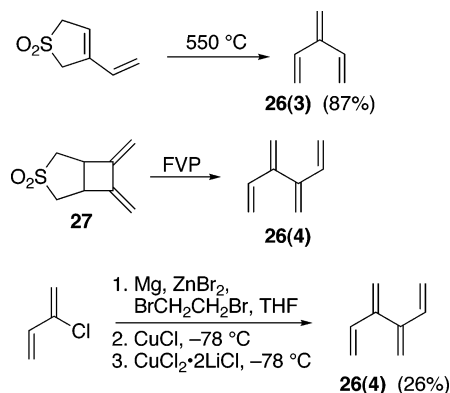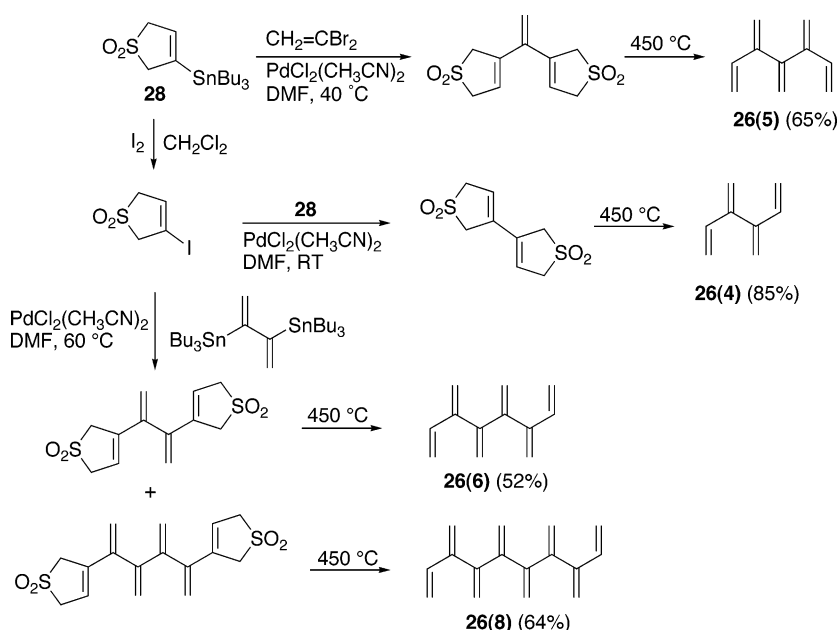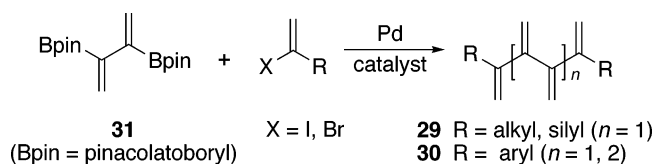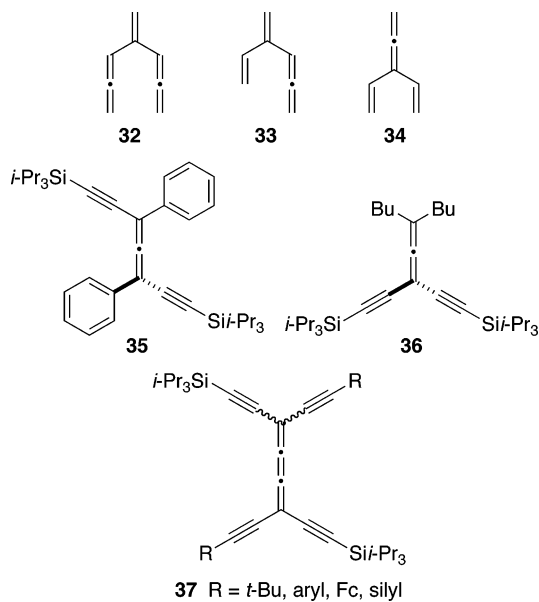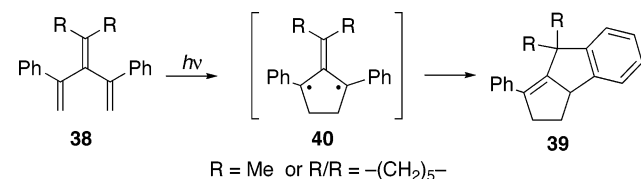**32** **33** **34**

35 **36**

37 R = *t*-Bu, aryl, Fc, silyl

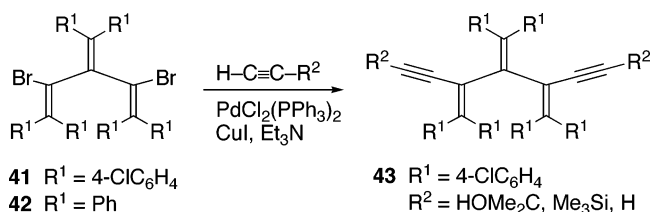**Scheme 11**

38 **40** **39**
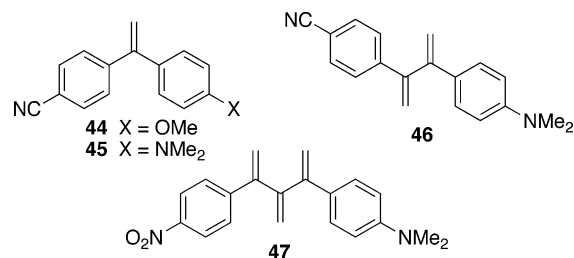
R = Me or R/R = –(CH$_2$)$_5$–

Rankin and co-workers in a recent study of the molecular structure of **26(4)** by electron diffraction and ab initio calculations.[31] A recent synthesis of **26(4)** reported by Sherburn and co-workers used metal-mediated coupling

Scheme 12

41 R^1 = 4-ClC$_6$H$_4$
42 R^1 = Ph

43 R^1 = 4-ClC$_6$H$_4$
R^2 = HOMe$_2$C, Me$_3$Si, H

Scheme 13

44 X = OMe
45 X = NMe$_2$

46

47

followed by elimination, and this route could prepare upward of 10 g of **26(4)** at a time.[32]

The big breakthrough in the synthesis of dendralenes was reported by Sherburn and co-workers in 2000,[33] and it was based on the concept of masking the terminal butadiene moiety as a sulfolene (Scheme 8). The masked precursors were assembled starting from **28** using a sequence of Stille coupling reactions, and the dendralene products were then produced through heating at 450 °C. The dendralenes **26(4)**–**26(6)** and **26(8)** showed rather surprising thermal stability and were fully characterized by ^{1}H and ^{13}C NMR spectroscopy. UV absorption analysis confirmed that conjugation does not increase as a function of length, with λ_{max} values for **26(3)**–**26(6)** and **26(8)** of 232.2, 222.8, 219.8, 220.0, and 220.6 nm, respectively (0.4% CDCl$_3$ in EtOH).

Shimizu and co-workers have recently synthesized dendralenes **29** and **30** based on cross-couplings with the 2,3-diboryl-1,3-butadiene precursor **31** (Scheme 9).[34] Using a variety of vinyl halides, reaction with **31** under Pd-catalysis gave [4]- and [6]dendralenes in 31–63% yield. Adaptation

Scheme 14

48 $R^1 = R^2$ ($n = 0,1$)
49 $R^1 \neq R^2$ ($n = 0,1$)

50

51   **52**
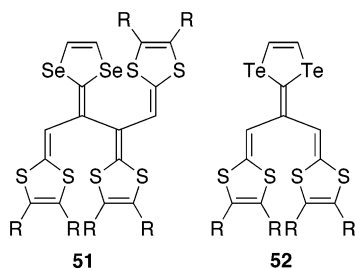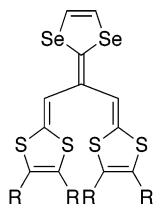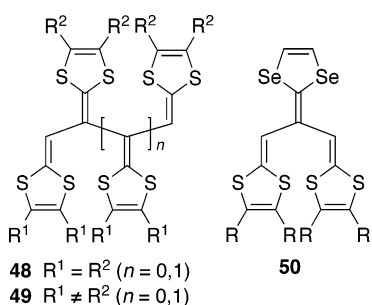
of this protocol also gave two different [5]dendralenes (not shown).

The formation of [3]dendralenes with a wide range of alkyl and aryl substitution patterns has been reported, often assembled for subsequent participation in cycloaddition reactions.[35−41] Of particular note are the allene analogues **32**−**34**, which were reported by Hopf and Lehrich (Scheme 10).[42] More recently, cross-conjugated allenes **35** and **36** have been reported by Diederich and co-workers,[43] as well as a large series of tetraethynylbutatrienes **37**.[44]

The [3]dendralenes **38**, studied by Okada and co-workers, underwent light induced cyclization to give products **39**, presumably via biradical intermediate **40** (Scheme 11).[45]

Iyoda and co-workers constructed [3]dendralenes **41** and **42** for use as precursors to radialenes (Scheme 12). Dibromide **42** was used as a template for derivatization via Sonogashira cross-coupling reactions with terminal alkynes to give [3]dendralenes **43**.[46,47]
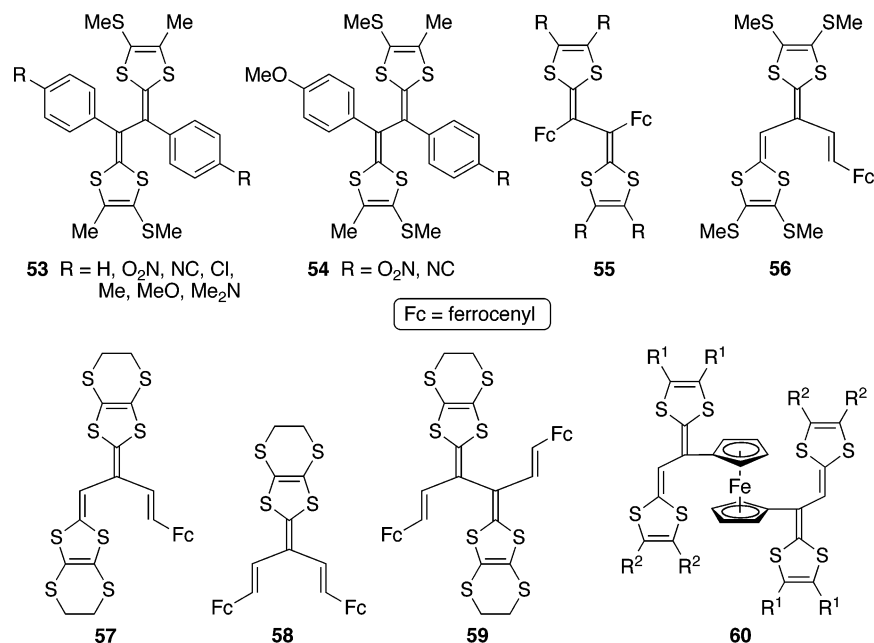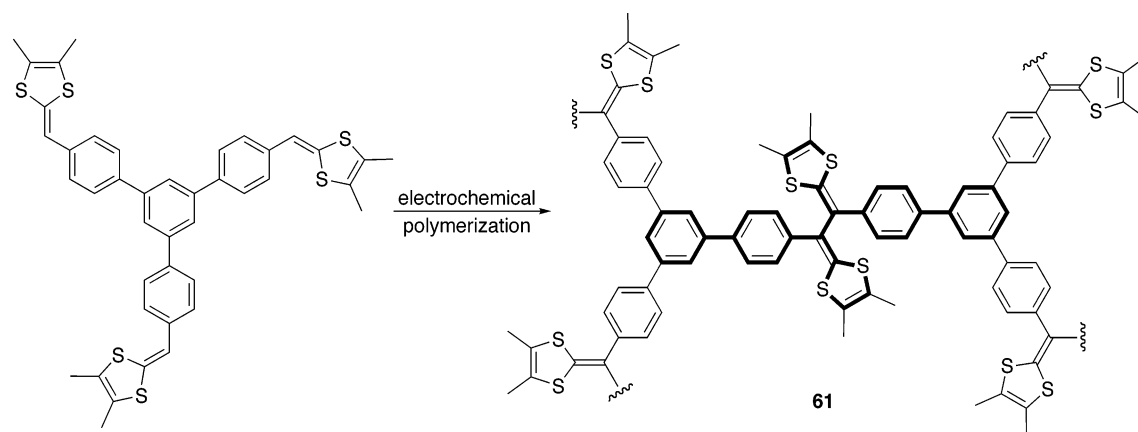
A study of donor−acceptor interactions via a cross-conjugated framework was reported by van Walree and co-workers (Scheme 13).[48] Compounds **44** and **45** both showed strong fluorescence originating from a twisted intramolecular charge-transfer state, indicating photoinduced charge separation through the cross-conjugated framework. UV−vis spectroscopy indicated only modest ground-state donor−acceptor (D−A) coupling. Spectroscopically it was also shown that the introduction of the second bifurcating olefin upon going from **45** to **46** had a relatively small effect on the overall D−A interaction.[49] The D−A [3]dendralene analogue **47** has also recently been reported.[34]

2.3. Extended Tetrathiafulvalenes and Related Systems

Dendralenes and related structures flanked by 1,3-dithioles have been common synthetic targets, being viewed as vinylogous analogues of tetrathiafulvalene (Scheme 14). Numerous reviews have recently documented the synthesis and remarkable redox behavior of such systems, so discussion here will be limited to a description of the major structural motifs that have been achieved.[7,8,50] Yoshida and co-workers reported the 1,3-dithiole-[3]- and [4]dendralenes **48**, and used these acyclic oligomers to better understand the redox properties displayed by the corresponding radialenes.[51] Bryce and co-workers discovered a somewhat shorter synthetic route to derivatives **48**, as well as those with alternating pendent substitution, as in **49**.[52,53] The analogous [3]- and [4]dendralenes in which sulfur has been replaced with more polarizable selenium (**50** and **51**)[54] or tellurium (**52**)[55] atoms have also been reported.

The electrochemical oxidative dimerization of 1,4-dithiafulvenes was used by Lorcy and co-workers to form the extended tetrathiafulvalenes (TTFs) **53** and donor−acceptor analogues **54**. Mechanistic studies concluded that the dimerization rate does not vary appreciable as a function of the substituent (Scheme 15).[56,57] Bryce and co-workers showed that oxidative dimerization of 1,4-dithiafulvenes could also be effected by the presence of acid, providing the ferrocenyl derivatives **55**.[58] The ability of both the ferrocene and 1,4-

Scheme 15

53 R = H, O$_2$N, NC, Cl, Me, MeO, Me$_2$N

54 R = O$_2$N, NC

55   **56**

Fc = ferrocenyl

57   **58**   **59**   **60**

Scheme 16

61

Scheme 17

62 R = Me₃Si (*n* = 1,3-5,7)
63 R = *i*-Pr₃Si (*n* = 1,3-5,7,9)

64 R¹ = Me₃Si, R² = *i*-Pr₃Si, R³ = Me
65 R¹ = R² = *i*-Pr₃Si, R³ = Me
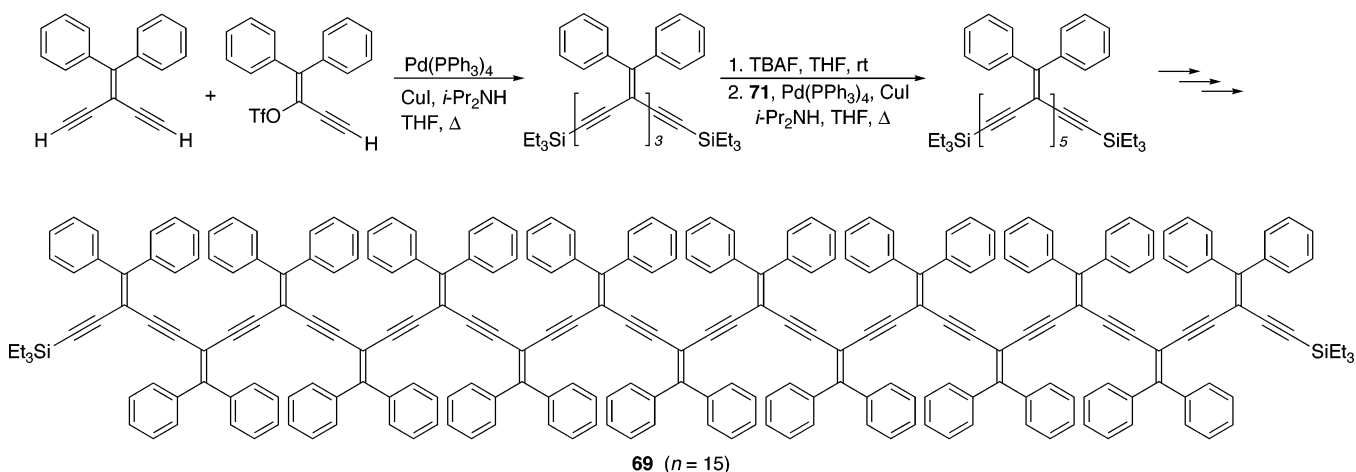**70** R¹ = R² = *i*-Pr₃Si, R³ = Ph

66 R = –(CH₂)₅– (*n* = 1,2)
67 R = Me (*n* = 1,2)

68 (*n* = 1,3,5)

69 (*n* = 1-3,5,7,9,11,13,15)
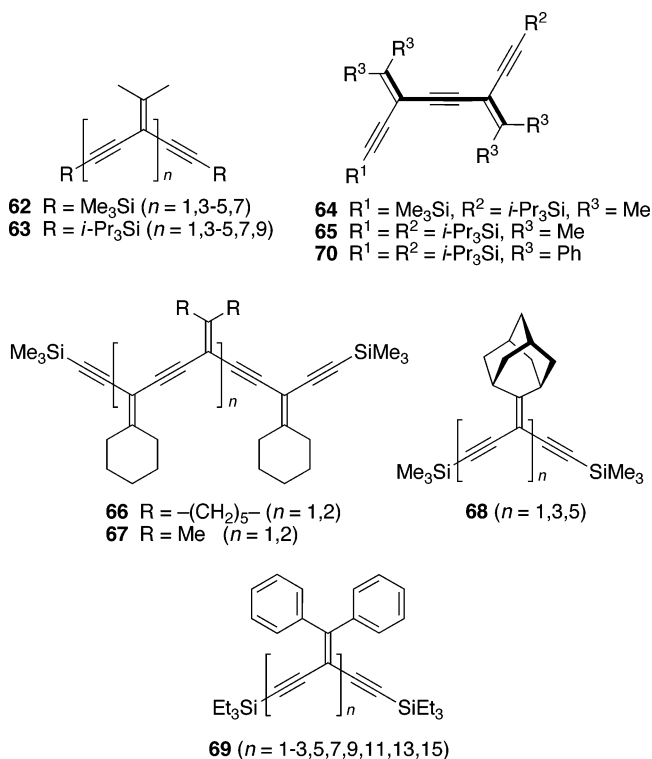
dithiafulvalene to act as electron donors has fostered numerous other examples of dendralenes incorporating both units.

Bryce and co-workers have thoroughly explored this topic through the synthesis of dendralenes terminated with ferrocenyl groups (**56**–**59**) and the subsequent analysis of their electrochemical and electronic absorption characteristics.[53,58] Analogous cross-conjugated systems built around a ferrocene core **60** have also been reported.[58,59]

The two-dimensional polymer **61** based on the cross-conjugated vinylogous TTF subunit was synthesized using electrochemical polymerization (Scheme 16).[60] As a result of the meta-linkages of the aryl rings, the redox activity of the polymer was limited to the segment shown in bold, and upon p-doping the polymer undergoes a significant conformational change in order to planarize the vinylogous TTF units.

2.4. *Iso*-Polydiacetylenes

Insertion of an acetylene group between the intervening olefins of a dendralene skeleton affords the *iso*-polydiacetylenes (*iso*-PDAs, also called expanded dendralenes). While dendralenes had been the object of study for some time, *iso*-PDAs were unknown until quite recently.[61] The first series to be studied, **62** and **63**, were based on an isopropylidene framework as reported by Tykwinski and Zhao in 1999 (Scheme 17).[62] Assessment of the solid-state structure of a trimeric *iso*-PDA (**63**; *n* = 3) showed a completely planar, cross-conjugated framework. The electronic characteristics of the monodisperse oligomers **62** and **63** were analyzed by UV–vis spectroscopy in solution and as thin films.[63] By comparison to the dimeric species, **64** and **65**, which contain

Scheme 18

69 (*n* = 15)

Scheme 19

71 *n* = 1–5
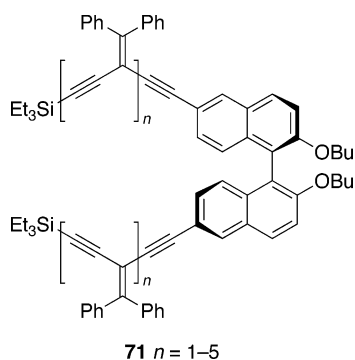
the longest linearly-conjugated segment of each oligomer (shown in bold), this study suggested that π-electron communication is present along the enyne framework of the *iso*-PDAs but quickly reaches saturation by the stage of nonamer (**63**; *n* = 9). The solubility and kinetic stability of both series **62** and **63** were, however, less than ideal.

The use of pendent cyclohexylidene groups (**66**) was explored toward improving solubility, but this resulted in *iso*-PDAs with even lower kinetic stability; the use of alternating isopropylidene and cyclohexylidene (**67**) units faired little better.[64] The adamantylidene series of *iso*-PDAs (**68**) was made, and while kinetic stability was improved versus that of **62**−**67**, solubility remained a serious issue.[63] The most successfully studied *iso*-PDAs have been the perphenylated derivatives **69**. Monodisperse oligomers, ranging from dimer **70** to pentadecamer **69** (*n* = 15), were synthesized using a Pd-catalyzed cross-coupling protocol with a vinyl triflate as the coupling partner, as shown in Scheme 18.[65] The pentadecamer is the longest monodisperse *iso*-PDA oligomer synthesized to date, and it consists of a cross-conjugated enyne backbone composed of 62 sp- and sp^2-hybridized carbons. Structural characteristics determined by X-ray crystallographic analysis for several derivatives demonstrated a nonplanar backbone conformation for the oligomers as a result of steric interactions between neighboring alkylidene phenyl groups. The electronic absorption spectra of the oligomers showed a slight red-shift of the maximum absorption wavelength as the chain length increases from dimer to pentadecamer, a trend that has reached saturation by the stage of nonamer **69** (*n* = 9). Fluorescence spectroscopy confirmed that the pendent phenyl groups

enhanced emission, and the relative emission intensity consistently increased as a function of chain length *n*. Molecular modeling and spectroscopic studies suggest that the longer *iso*-PDA oligomers **69** (*n* > 7) adopt a coiled, helical conformation in solution.[65]

The π-electron-rich framework of cross-conjugated *iso*-PDAs, in combination with their electronic transparency in the visible region of the spectrum, made them interesting candidates as NLO materials, and molecular third-order nonlinearities, *γ,* for the oligomers **69** were measured via the differential optical Kerr effect (DOKE).[66,67] While the nonresonant *γ*-values were modest, the molecular hyperpolarizabilities did show a superlinear increase as a function of the oligomer chain length *n*.

The general synthetic protocol describe for *iso*-PDAs in Scheme 18 has recently been extended to the formation of chiral, monodisperse *iso*-PDAs **71** (Scheme 19), based on a 1,1-binaphthyl core.[68] The optical properties were examined as a function of length, and initial studies suggest that, in acetonitrile as a solvent, a folded structure is possible for the longest soluble derivative, tetramer (*R*)-**71** (*n* = 4).

Scheme 20

72a-c (*n* = 1-3)

73a-c (*n* = 1-3)

74a-c (*n* = 1-3)
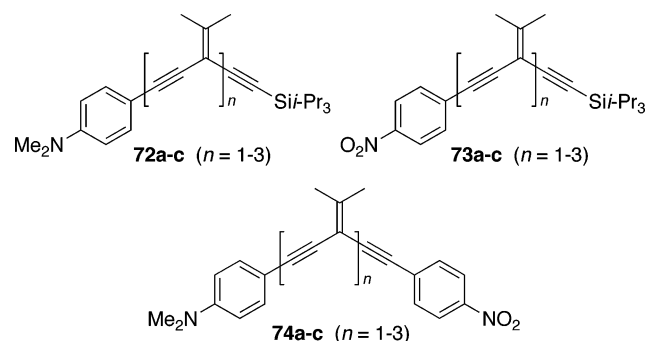
The first series of donor (**72**), acceptor (**73**), and donor−acceptor (**74**) *iso*-PDAs was reported by Tykwinski and Ciulei, and it included monomeric, dimeric, and trimeric species of each class (Scheme 20).[69] Evidence for intramolecular charge-transfer via cross conjugation came from UV−vis spectroscopy, which showed that D−A monomer **74a** has a lower energy absorption tail that extends out beyond 450 nm, whereas **72a** and **73a** were transparent

Scheme 21

75 (*n* = 1-4)

76 (R = Si*i*-Pr$_3$)

82 (*n* = 1-3,4,8)

77 (*n* = 1-4)

78 (*n* = 1-3,5)

79 R = Si*i*-Pr$_3$
80 R = C≡CSi*i*-Pr$_3$
81 R = Bu

Scheme 22

83 R[1] = trialkylsilyl, R[2] = Ph, n = 0,1
84 R[1] = i-Pr$_3$Si, R[2] = Br, n = 0,1

85 X = O$_2$N, or Me$_2$N

86

87

88

89

Scheme 23

90

91

92

93

R = i-Pr$_3$Si, D = 4-Me$_2$NC$_6$H$_4$, A = 4-O$_2$NC$_6$H$_4$
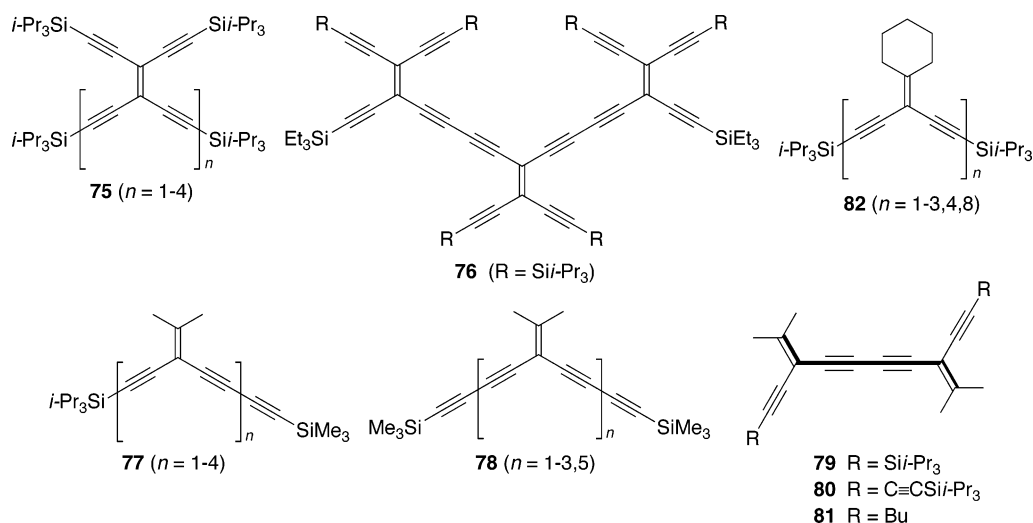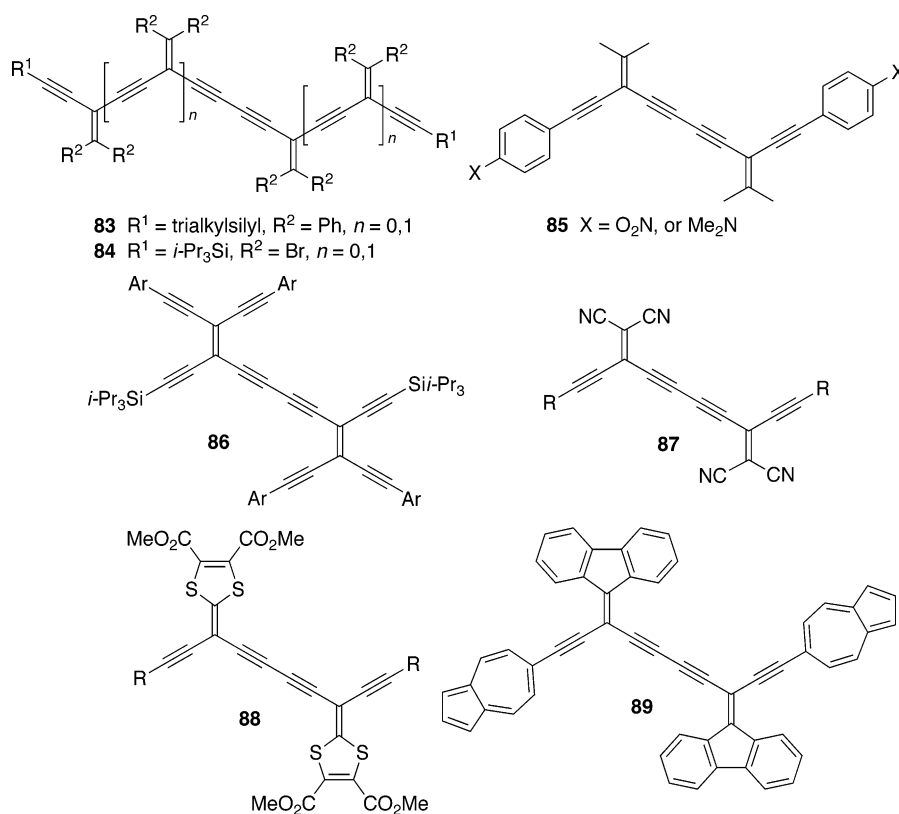
beyond about 425 nm. It was concluded, however, that charge-transfer mediated by the enyne framework was not present in the D−A dimer (**74b**) and trimer (**74c**).

2.5. Polytriacetylenes

2.5.1. Iso-Polytriacetylenes

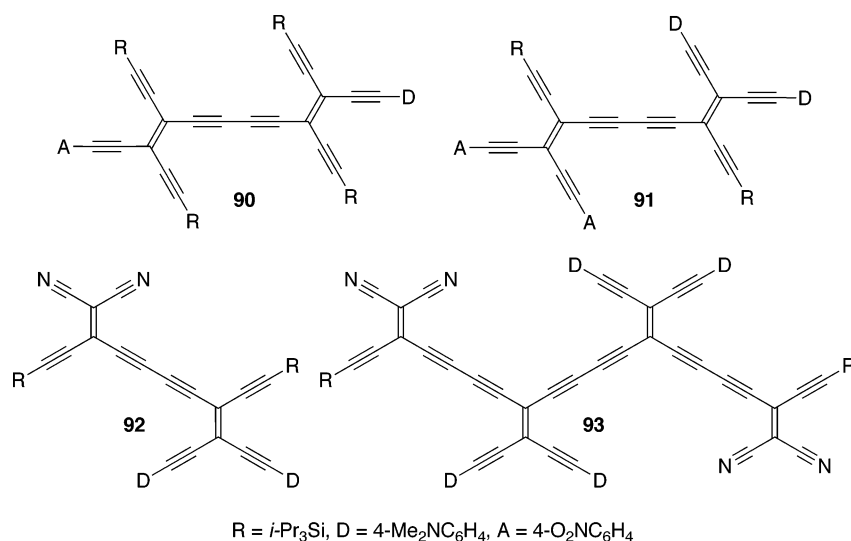Insertion of a diacetylene group between the intervening olefins of the dendralene skeleton affords the next series of cross-conjugated oligomers, the *iso*-polytriacetylenes (*iso*-PTAs). The first members of this series, **75**, were reported by Diederich and co-workers in 1995 and were based on the tetraethynylethene building block (Scheme 21).[70] A one-pot homocoupling procedure was employed, and individual oligomers were then isolated by column chromatography. The *iso*-PTAs **75** were air- and light-stable solids, and even

the longer derivatives (n = 3 and 4) showed melting points above 100 °C. Trimer **76** was reported by the same group, differing only in the terminal silyl groups.

Tykwinski and co-workers reported the synthesis of two series of *iso*-PTAs, with pendent isopropylidene groups, **77** and **78**. The members of both series were assembled using an iterative approach similar to their synthesis of *iso*-PDAs described above (Scheme 18).[71,72] For the purpose of comparison, dimeric species **79−81**[72,73] were also synthesized because they contain the longest linearly-conjugated enyne segment of the *iso*-PTAs oligomers (shown in bold). Unlike the peralkynylated derivatives **75−76**, the longer oligomers for both series **77** and **78** showed much reduced kinetic stability, decomposing over a period of days, even when stored under nitrogen at low temperature. The same kinetic

Table 1. Aryl Bridged Dendralenes

	$\begin{smallmatrix}\xi\\\xi\end{smallmatrix}$ Ar $\begin{smallmatrix}\xi\\\xi\end{smallmatrix}$	R^1 or $R^1 \diagup\!\!\diagdown R^1$	R^2	Reference
94a	$p\text{-}C_6H_4$	Br	$Me_3SiC\equiv C-$	83
94b	$m\text{-}C_6H_4$	Br	$Me_3SiC\equiv C-$	84
94c	$p\text{-}C_6H_4$	Br	2-thienyl	83
94d	(aryl structure)	Br	$Me_3SiC\equiv C-$	85
94e	(aryl structure, OC_8H_{17}, $H_{17}C_8O$)	Br	$t\text{-Bu}$—〈 〉—	83
94f	(thiophene structure)	$MeO_2C \diagup\!\!\diagdown CO_2Me$ (dithiole)	$i\text{-}Pr_3SiC\equiv C-$	86

Scheme 24

95 ($n = 1$–3)

96 R = $H_{21}C_{10}O_2C$

97 R = $t\text{-}BuMe_2Si$
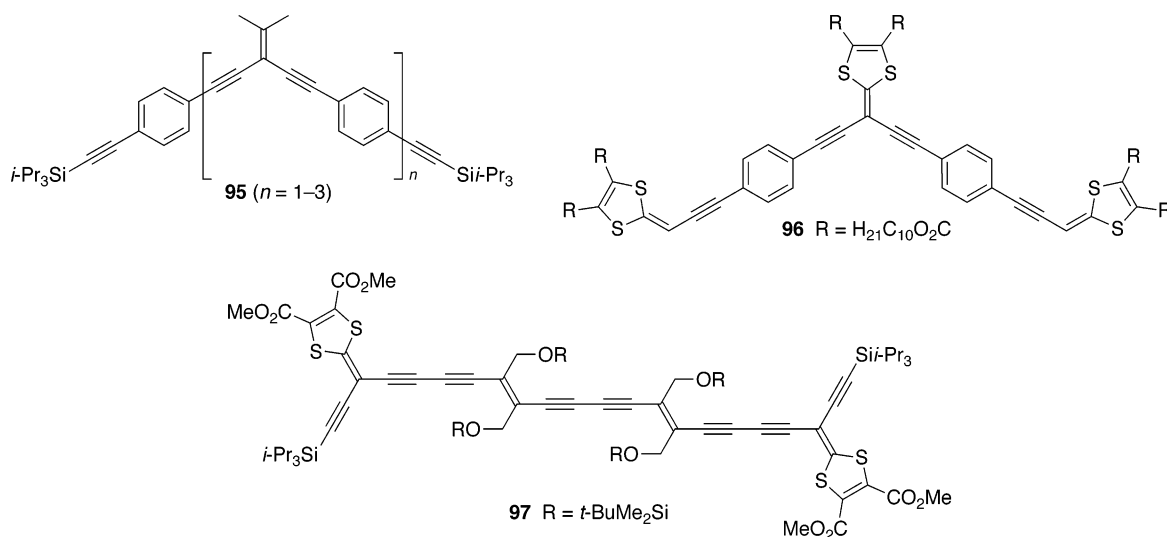
instability was found for *iso*-PTAs based on the cyclohexylidene subunit, **82**, reported by Diederich and co-workers.[74] The octamer **82** ($n = 8$), composed of 40 sp- and sp^2-carbon atoms, represents the longest *iso*-PTA synthesized to date.

The electronic characteristics of all the *iso*-PDA series have been examined by UV–vis spectroscopy. While little evidence for a lowering of the HOMO–LUMO gap was found for either the TEE (**75**)[70] or isopropylidene (**77** and **78**)[72] series, analysis of the cyclohexylidene (**82**) series by three different methods demonstrated a consistent drop in HOMO–LUMO energy as length was increased,[74] suggesting a contribution from cross conjugation to the overall electronic makeup of the molecules. The electronic delocalization of *iso*-PTAs in comparison to linearly-conjugated

PTAs has also been studied theoretically by Lüthi and co-workers.[75,76]

Similar in structure to **79**–**81**, symmetrical dimeric *iso*-PTAs with a range of terminal and pendent functionality have been reported to date, and their structures are summarized in Scheme 22. In nearly all cases, these molecules are readily available via an oxidative homocoupling reaction connecting the two halves via the central bond. Derivatives with pendent phenyl (**83**)[65] and bromo (**84**)[77,78] substituents are known, while those with isopropylidene building blocks (**85**) have been used to look at the electronic effects of terminal donor or acceptor groups via cross conjugation.[79] Using a combination of spectroscopic and electrochemical analyses, Diederich has extensively explored the effects of substituents in the

Scheme 25

98

99 R = aryl
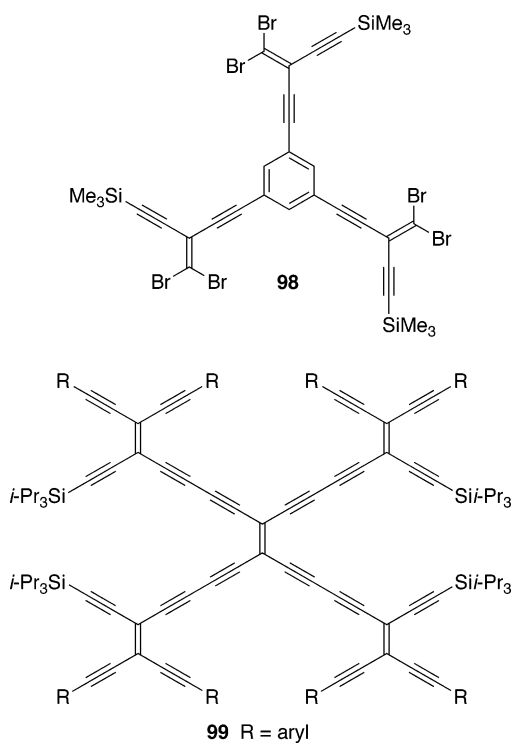
pendent alkylidene positions of TEE dimers **86**, including neutral (aryl, arylethynyl, silyl)[70] as well as donor (p-R$_2$NC$_6$H$_4$) and acceptor (p-O$_2$NC$_6$H$_4$) groups.[80] A similar study by this group looked at cyanoethynylethylene (CEE) **87**.[81] Extended TTF derivatives **88** have been studied, and the interesting azulene-terminated dimer **89** was synthesized by Ito and co-workers.[82]

Unsymmetrical substituted *iso*-PTA dimers are more difficult to synthesize, since homocoupling reactions are either inappropriate or lead to mixtures of products that are typically tedious to separate. Nonetheless, a number of highly functionalized examples are known, including TEE dimers **90** and **91** (Scheme 23)[80] and the extended donor−acceptor systems **92** and **93**.[81] A very thorough experimental and theoretical study of the ground-state properties of **92** and

93, in comparison to smaller analogues, showed that more extensive π-conjugation could lead to molecules with *higher* HOMO−LUMO gaps. This ultimately suggested that, for molecules with strong electron donor/acceptors, evaluation of π-conjugation by UV−vis spectroscopy alone could provide misleading results.[81]
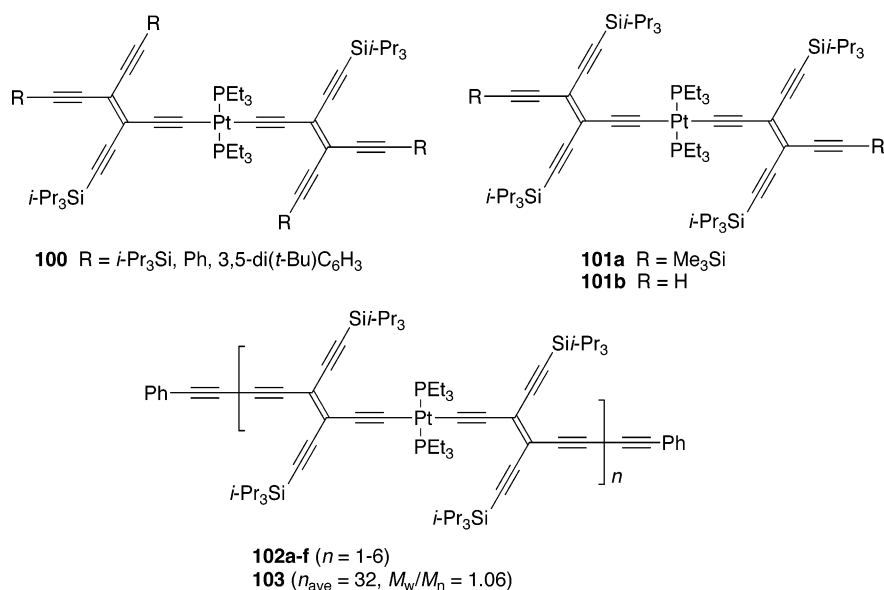
2.5.2. Hybrid Iso-Polytriacetylenes

The *iso*-PTA framework can be linked by an aryl spacer group, affording molecules with the general structure of **94** (Table 1). Several such molecules have been described, including those with dibromoolefinic units, **94a**−**94e**, suitable for further elaboration at the vinylidene group, and those with functionality designed to alter electronic characteristics, such as **94f**.

An oligomeric series **95** based on aryl insertion into an *iso*-PTA framework has been examined, and UV−vis spectroscopic analysis demonstrated that electronic communication along the framework of these oligomers was limited due to the cross-conjugated enyne/arylene structure (Scheme 24).[87] Two extended TTF oligomers have been synthesized, one lined by arylene ethynylene units **96**[88] and the other by a PTA backbone **97**.[86]
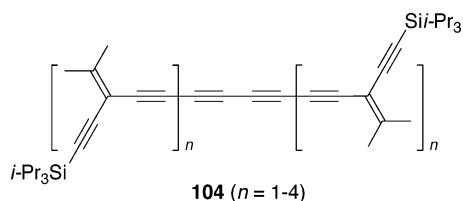
This basic concept has also been directed toward molecules with a two- or three- dimensional structure. A triskelion-shaped, two-dimensional analogue of the dimers **94a**−**b** has been reported (**98**, Scheme 25),[77] while networks based on five TEE units (**99**) have been used as precursors to radiaannulenes (vide infra, Scheme 78).[89]

As an alternative to an aryl spacer, insertion of a transition metal was used by Diederich and co-workers to form σ-acetylide complexes linking TEE building blocks (Scheme 26).[90,91] Dimeric species **100** and **101** were readily formed via reaction of the corresponding terminal acetylene with *trans*-[PtCl$_2$(PEt$_3$)$_2$]. Polymerization of **101b** under Glaser−Hay conditions in the presence of PhC≡CH as an end-capping reagent gave oligomers **102a**−**f**, which could be separated by GPC. Running the same polymerization reaction while waiting 20 min to introduce the end-capping reagent resulted in polymer **103** ($n_{ave} = 32$) as an air-stable red solid that decomposed only above 250 °C. UV−vis absorption and third-order NLO characterization showed that the Pt

Scheme 26

100 R = *i*-Pr$_3$Si, Ph, 3,5-di(*t*-Bu)C$_6$H$_3$

101a R = Me$_3$Si
101b R = H

102a-f (n = 1-6)
103 (n_{ave} = 32, M_w/M_n = 1.06)

Scheme 27

104 (n = 1-4)

centers acted as an insulator toward π-electron delocalization in these oligomers.[91]

The differentially protected *iso*-PTAs series **77** (Scheme 21) were used to form a sequence of hybrid oligoenynes **104** based on a tetrayne core via desilylation and oxidative dimerization under Hay conditions (Scheme 27).[71,72] Overall good yields were achieved for these oligomers (56–78%), despite limited kinetic instability. Octadecayne **104** (n = 4) is composed of a contiguous sequence of 44 sp and sp[2] carbons, and it spans ca. 5.6 nm from silicon atom to silicon atom, based on molecular modeling of the all *s-trans* orientation.

Several dimeric species based on a cross-conjugated tetrayne core have been reported (Scheme 28), including those with pendent dibromoolefins, **105**,[77,78] or dicyanoolefins, **106**,[81] and the extended TTF derivative **107**.[86]

Scheme 28

105 R = *i*-Pr₃Si, Ph

106 Ar = 4-Me₂NC₆H₄

107
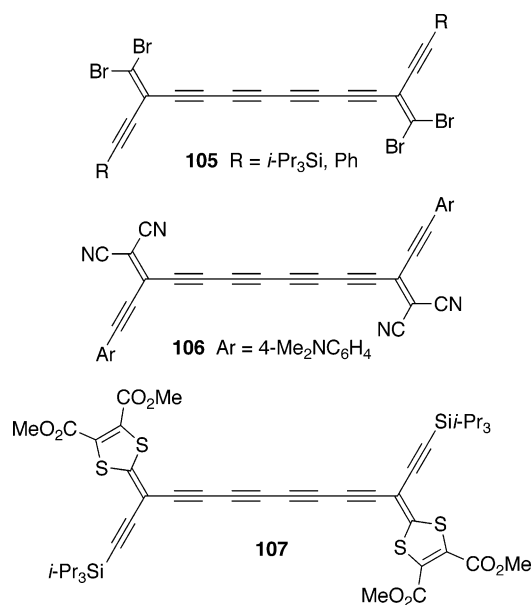
2.5.3. Polytriacetylenes and Polypentaacetylenes

Polytriacetylenes have been studied as advanced materials due to their rigid, conjugated structure and the ability to isolate and characterize monodisperse oligomers. While many of their properties derive from the linearly-conjugated framework, in some cases these properties are augmented through the presence of cross-conjugated pendent functionality. As a result, their structures (**108**–**111**, Scheme 29) are mentioned here, as are those of polypentaacetylenes **112**, while a full account of their syntheses and properties can be found in recent reviews.[1b,5]
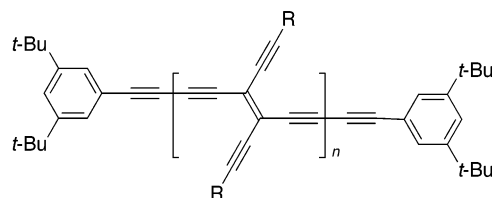
2.6. Poly(phenylenevinylidene)s and Related Systems

Insertion of a phenyl ring into the dendralene structure affords the poly(phenylene-vinylidene)s (*iso*-PPVs). The
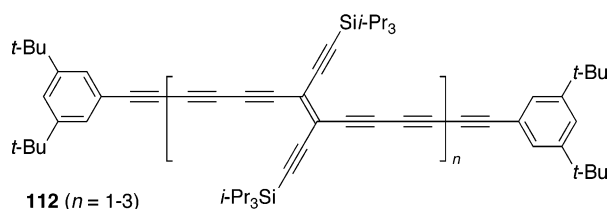
Scheme 29
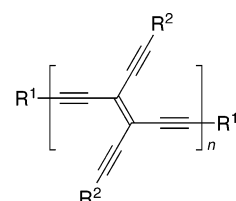
108 R¹ = R² = *i*-Pr₃Si (n = 1-5)
109 R¹ = PhC≡C, R² = *i*-Pr₃Si (n = 1-5)

110 R = *i*-Pr₃Si, (n_ave = 22)
111 R = 4-(C₁₂H₂₅)₂NC₆H₄ (n_ave = 22)

112 (n = 1-3)

Scheme 30

114 → PTSA / PhCH₃ → **113** (n = 1-4)

Scheme 31

116 → 1. BuLi, Et₂O, −78 °C 2. C₆F₆, monoglyme, −20 °C 3. H₃O⁺ → **115** (n = 1-5)

116 → Mg, THF → **117**

Scheme 32

Me₃Si—≡—C₆H₄—Li → Cp₂ZrMeCl / THF, −95 °C → Me₃Si—≡—C₆H₄—ZrCp₂Me **119**

↓ Δ

120 → HCl (conc.) 80% → **118**
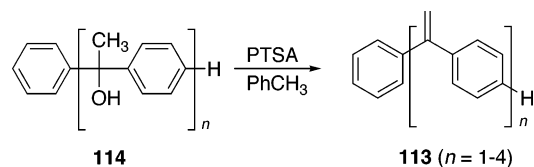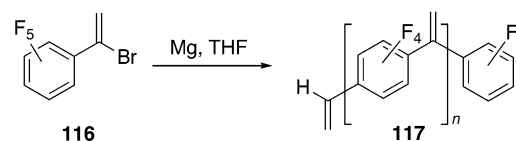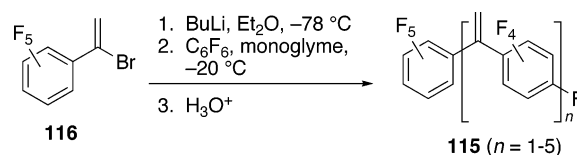
parent monodisperse *iso*-PPV oligomers **113** were recently reported by van Walree and co-workers, via dehydration of the corresponding alcohols **114** (Scheme 30).[92] X-ray crystallographic analysis of the dimer (**113**; n = 2) showed a

Scheme 33

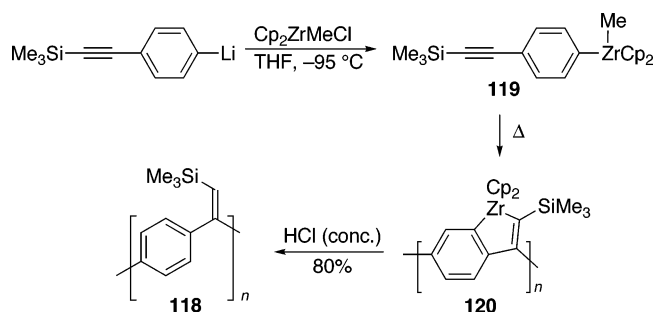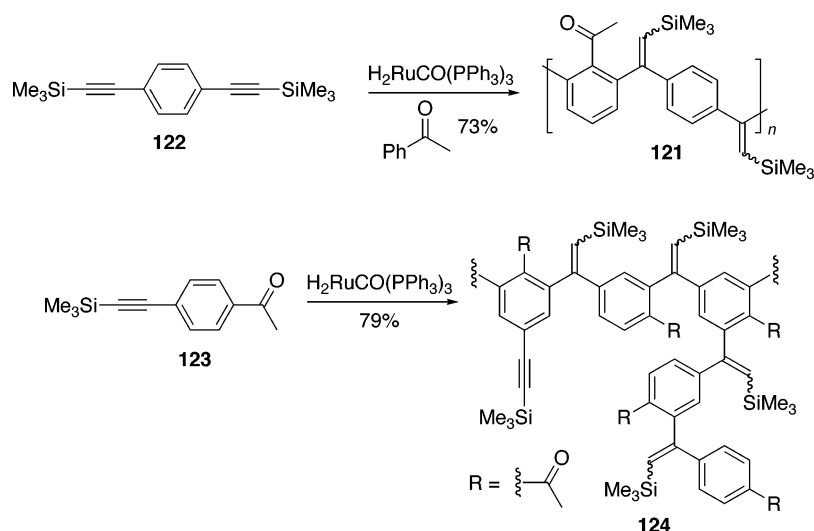nonplanar structure, as expected due to steric interactions between the *ortho*-hydrogens. The extent of conjugation in this series of oligomers was probed by a number of means, including vibrational and absorption spectroscopies, electrochemistry, and theoretical calculations at the AM1 and PPP/SCF levels. While a coherent picture of the extent of π-electron delocalization has not yet emerged, this study suggested that conjugation clearly extends beyond that of the longest linearly-conjugated subunit, divinylbenzene. It was noted as well that UV−vis spectroscopy alone, which suggested saturation of the HOMO−LUMO gap at $n = 2$, was not a good indicator of the extent of π-conjugation.

Brooke and Mawson reported a series of monodisperse *iso*-PPV oligomers **115** based on perfluoroaryl units (Scheme 31).[93] Monomer **116** was oligomerized via lithiation with BuLi at low temperature, and C_6F_6 was added as an end-capping reagent. Following workup, a combination of sublimation and chromatography was used to provide small quantities of each oligomer **115**. Reaction of **116** with Mg in THF provided a pale brown polymer, presumably with the structure **117**. Unfortunately, this polymer was completely insoluble in common organic solvents, rendering characterization impossible. It was reported to be very hydrophobic, and it did not melt at temperatures up to 380 °C.

One of the first *iso*-PPV derivatives to be reported, polymer **118**, came from Tilley and co-workers (Scheme 32).[94] Their synthesis relied on the initial formation of the unstable Zr-complex **119**, which was then thermolyzed at 70 °C to give the organometallic polymer **120**, as an air-sensitive red solid. Reaction of **120** with HCl gave the *iso*-PPV **118** ($M_w/M_n = 2700/1700$) in 80% yield.

A structurally related polymer, **121** ($M_w/M_n = 6560/5712$), was synthesized by Weber and co-workers based on the Ru-

catalyzed copolymerization of acetophenone and diyne **122** (Scheme 33).[95] Polymerization of the acetophenone derivative **123** led to the analogous hyperbranched polymer **124** ($M_w/M_n = 1550/1077$). The *iso*-PPVs **121** and **124** both showed a UV absorption maximum at $\lambda_{max} = 284$ nm and $T_g = 173$ and 113 °C, respectively. When irradiated at 285 nm, polymer **121** showed emission at $\lambda_{em} = 420$ nm, while the emission for **124** was red-shifted slightly to $\lambda_{em} = 450$ nm.

Cross-conjugated oligomers based on a thienyl rather than a phenyl spacer are also known. Oda and co-workers reported the first examples, **125a−d**, incorporating up to four fulvene units (Scheme 34).[96] The oligomers were dark red solids with moderate stability, and UV−vis spectroscopic analysis showed that extending the cross-conjugated framework from **125b** ($\lambda_{max} = 415$ nm) to the tetramer **125d** ($\lambda_{max} = 408$ nm) had little effect on the HOMO−LUMO energy. The oligomers could be reduced by reaction with 3% Na/Hg, and the dimer **125b** and tetramer **125d** gave the corresponding di- and tetraanions, respectively, composed of an oligoacetylene spine with pendent cyclopentadienyl anions (**125b^{2-}** and **125d^{4-}**, respectively).[97]
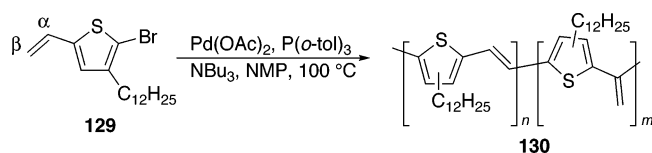
Scheme 34
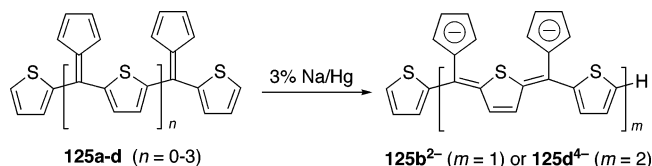
Ohta and Yamashita reported a similar set of oligomers **126** based on thienyl linkers, with pendent 1,3-dithioles (Scheme 35).[98] Doping of these electron-rich systems with
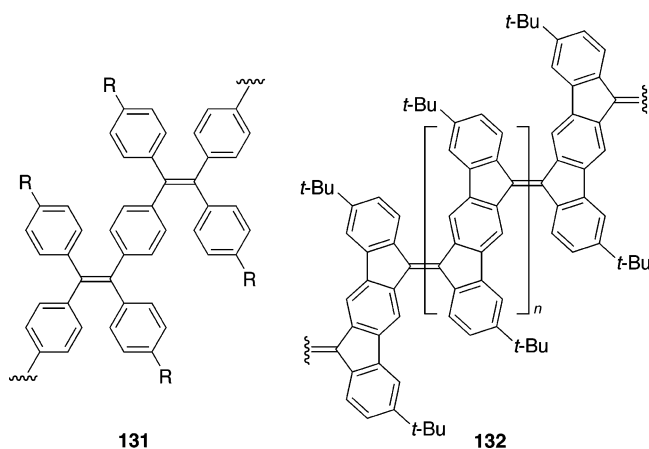
Scheme 35

126 $R_1 = H$ or Me
$R_2 = H$, SMe,
$R_2/R_2 = -SCH_2CH_2S-$
$R_2/R_2 = -(CH=CH)_2-$
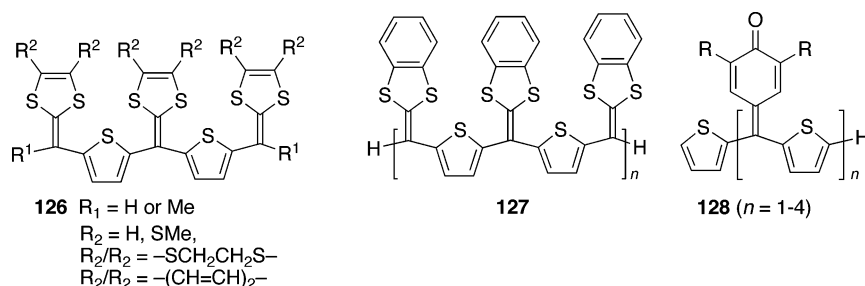
Scheme 36

iodine gave conducting charge-transfer complexes (with conductivities of 10^{-2}–10^{-5} S cm^{-1}), and electrochemical oxidation of one derivative provided the electroactive polymer, **127**. Both the oxidation peak potential (0.85 V vs SCE) and λ_{max} (404 nm) for **127** were higher than those of the monomer (0.58 V vs SCE and 464 nm, respectively), demonstrating inefficient π-delocalization in the polymer. The related series **128** was reported by Oda and co-workers, in this case based on *p*-quinone methide linkers. These oligomers were easily reduced, as demonstrated by CV analyses.[99]

In an attempt to synthesize poly(thienylenevinylenes), Loewe and McCullough utilized the Heck coupling protocol with precursor **129** (Scheme 36).[100] Due to a lack of regioselectivity toward coupling at the α- and β-positions, a regioirregular polymer was recovered, composed of a red portion (31%, M_n = 6.8K, PDI = 1.87 (GPC)) that was soluble in hexanes and a purple portion (25%, M_n = 12.1K, PDI = 1.90 (GPC)) that was insoluble in hexanes but dissolved in methylene chloride. It was determined by ^{1}H NMR spectroscopic analysis that approximately 15% of the cross-coupling events had occurred at the α-vinyl positions rather than the β-position, as desired, leading to the cross-conjugated polymer **130**.

Scheme 37

Based on tetraarylethene segments, the linearly-conjugated diaryl-PPVs **131** do not rigorously fit the criteria of a cross-conjugated polymer as per this review (Scheme 37). Given their interesting structure and that some of their properties derive from communication with the cross-conjugated pendent aryl moieties, they are mentioned here. The parent system (**131**, R = H) was first synthesized by Hörhold et al. as a structurally well-defined polymer, with molecular weights up to 20 000.[101] Since their introduction, diaryl PPVs with a variety of different substituents have been reported and studied for use as NLO and electroluminescent materials.[102,103] Introduction of two additional aryl–aryl bonds provided a related polymer, poly(indenofluorene) (**132**), which was reported by Scherf and co-workers.[104]
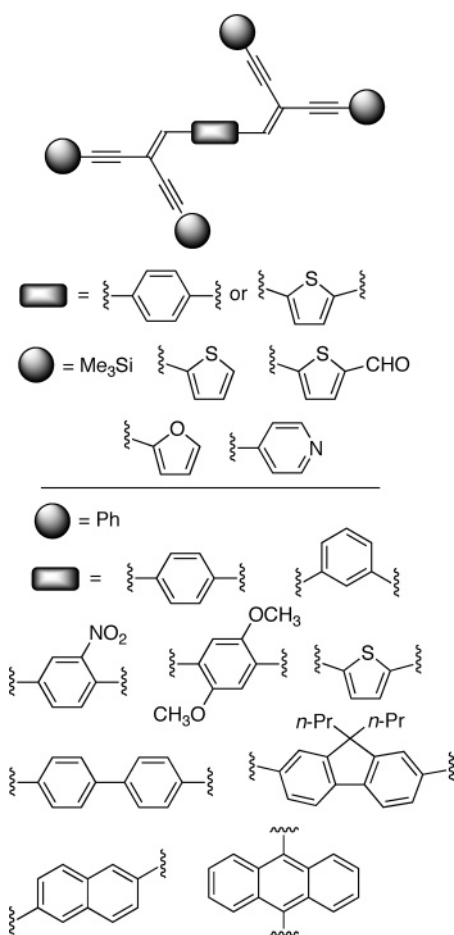
Scheme 38
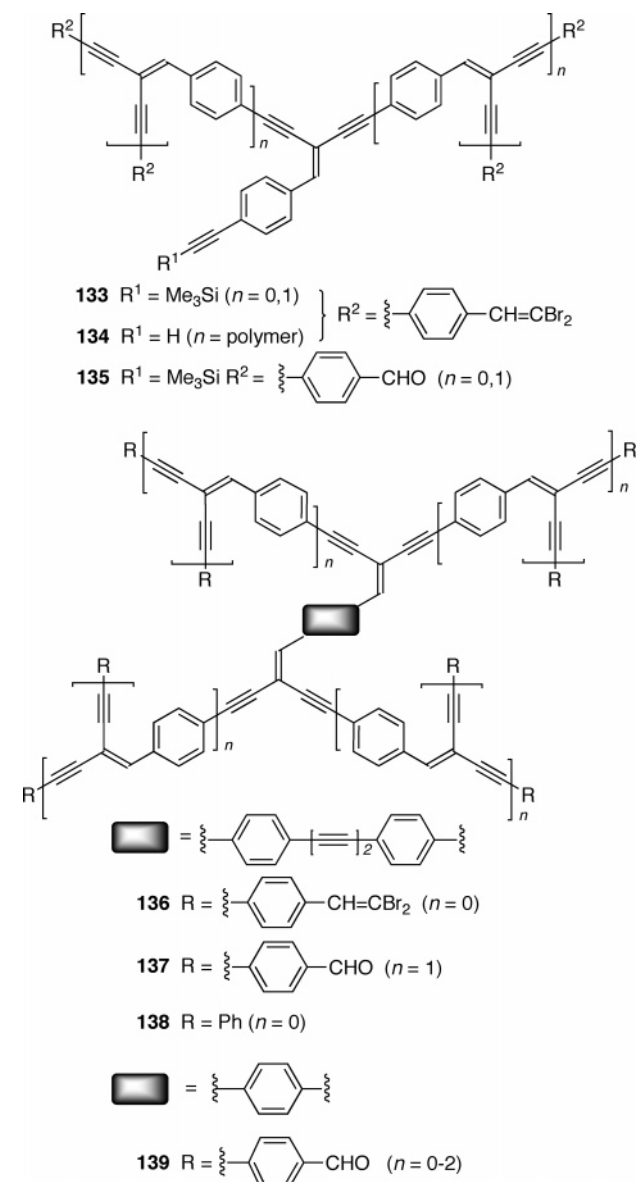
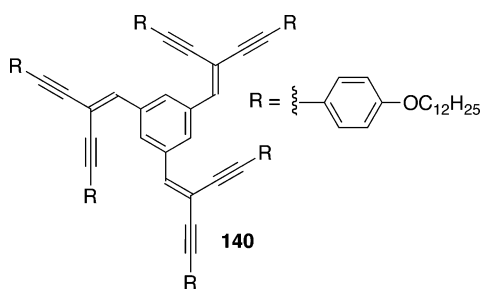## 2.7. Other Aryl-Bridged, Cross-conjugated Systems

An early foray into the formation of cross-conjugated oligomers was reported by Salcedo, Fomine, and co-workers, who explored the properties of hyperbranched dendritic and polymeric structures **133**–**138** derived from *β,β*-dibromo-4-ethynylstyrene and 4-ethynylbenzaldehyde.[105–107] First (*n* = 0) and second (*n* = 1) generation dendrons, **133** and **135**, were synthesized in a stepwise manner, using a combination of Sonogashira cross-coupling and Corey–Fuchs dibromoolefination methods. Hyperbranched polymer **134** was obtained directly from *β,β*-dibromo-4-ethynylstyrene via a Sonogashira reaction (M_w = 70 000, GPC), although spectral evidence suggested that incomplete branching during the polymerization reaction was likely a problem. Dimerization of **133** (*n* = 0) and **135** (*n* = 1) gave the G1 and G2 dendrimers **136** and **137**, respectively, while dimeric **138** was assembled by an alternate route as a model compound.

Kim and Hwang reported the synthesis of three generations of the related cross-conjugated, hyperbranched dendrimers **139** (Scheme 38).[108] All three generations show strong blue/

Scheme 39

Scheme 40

Scheme 41

141 $R^1 = H_{21}C_{10}$, Me
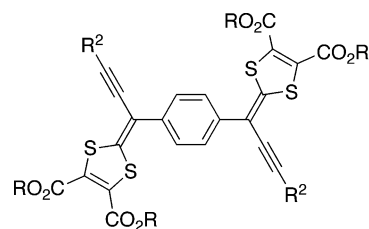R^2 = Ar, *i*-Pr$_3$SiC≡C, PhC≡C

Scheme 42

green emission, and the third generation ($n = 2$) has both the highest extinction coefficient and the highest quantum yield of the three.
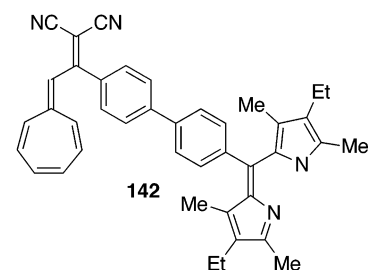
A large number of small molecule structures based on cross-conjugated segments bridged by an aryl moiety have been reported by Kim and co-workers.[109,110] Two different series of dimeric, cross-conjugated enynes were synthesized and characterized primarily with respect to their emission properties (Scheme 39). In one case, a common aryl linker (1,4-phenyl or 2,5-thienyl) was appended with a range of terminal substituents, and in the other case, the terminal phenyl moiety was held consistent while the nature of the linking aryl group was altered. Most of these compounds showed strong emission bands, and both the emission wavelength and quantum yields varied greatly with structure.

A two-dimensional derivative with a similar structure, triskelion-shaped **140**, has been reported by Neckers and co-workers (Scheme 40). Its properties in comparison to a 1-D analogue were investigated, and both showed strong emission in solution.[111]

Nielsen and co-workers have constructed a series of cross-conjugated donor−acceptor chromophores **141** based on a phenylene group that links two redox-active dithiafulvene units (Scheme 41).[88] The optical, third-order nonlinear optical, structural, and redox properties were examined as a function of the various substitution patterns and in comparison to larger systems such as **96** and **97** (Scheme 24). Rurack, Daub, and co-workers have fashioned **142**, which combined the photochromic dihydroazulene/vinylheptafulvene system with the fluorophore boron dipyrromethene in a cross-conjugated skeleton.[112]

Halton reported a series of *iso*-PPV analogues based on extended cyclopropanes with dithiol and cyclopentadiene functionality **143**−**146** (Scheme 42).[16] While neither **144** nor **146** could be isolated easily or in reasonable amounts, sufficient quantities of **145** were produced such that its ability to act as donor in the formation of a charge-transfer salt with DDQ was successfully demonstrated, based on UV−vis spectroscopic analysis.

3. Cyclic Cross-conjugated Systems
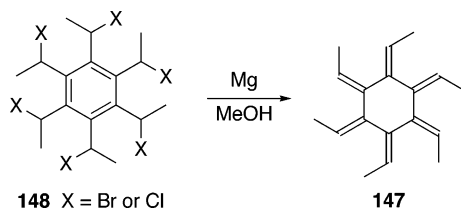
3.1. Radialenes

Radialenes are the cyclic analogues of dendralenes, with a general formula $C_{2n}H_{2n}$ and containing n ring atoms and n exocyclic double bonds (Scheme 43).[113] They are named in a manner similar to that of dendralenes, according to their
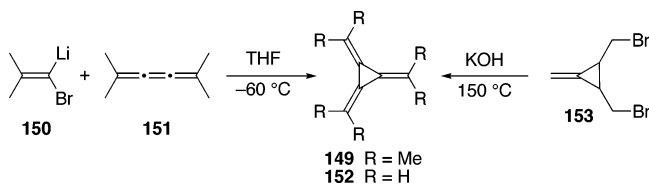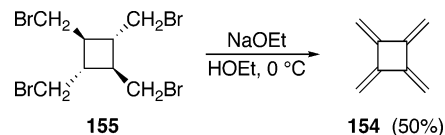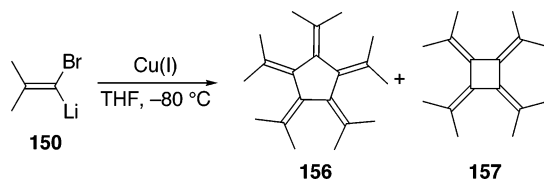
Scheme 43

[3]radialene   [4]radialene   [5]radialene   [6]radialene

Scheme 44

148 X = Br or Cl   **147**

Scheme 45

150   **151**   **149** R = Me   **153**
                              152 R = H

Scheme 46

155   **154** (50%)

Scheme 47

150   **156**   **157**
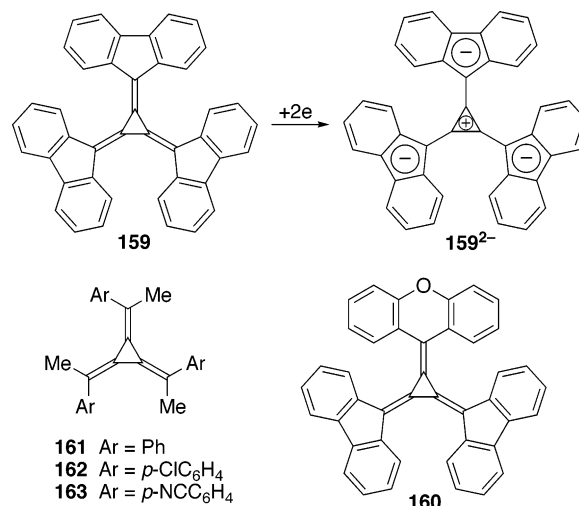
Scheme 48

158

152
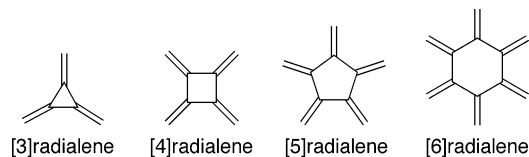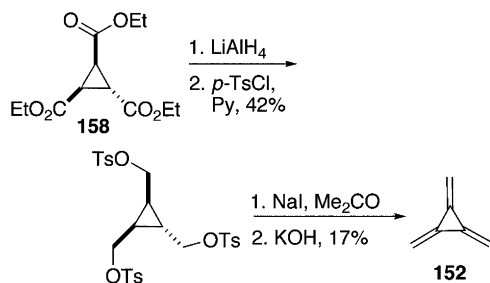
ring size, i.e., [n]radialene.[10] While early syntheses of radialenes have been summarized by Hopf,[10,11] several historical aspects of these unusual compounds are provided here as background.[114]
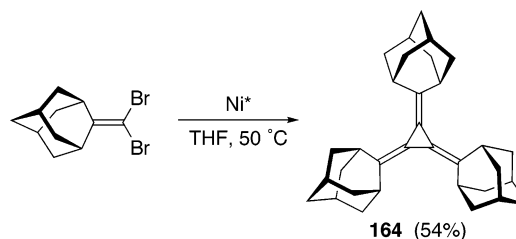
3.1.1. Introduction and Historical Perspectives

Hopff and Wick reported the first member of the radialene family in 1961.[115] This [6]radialene, hexaethylidenecyclo-

Scheme 49

159   **159**$^{2-}$

161 Ar = Ph
162 Ar = p-ClC$_6$H$_4$ **160**
163 Ar = p-NCC$_6$H$_4$
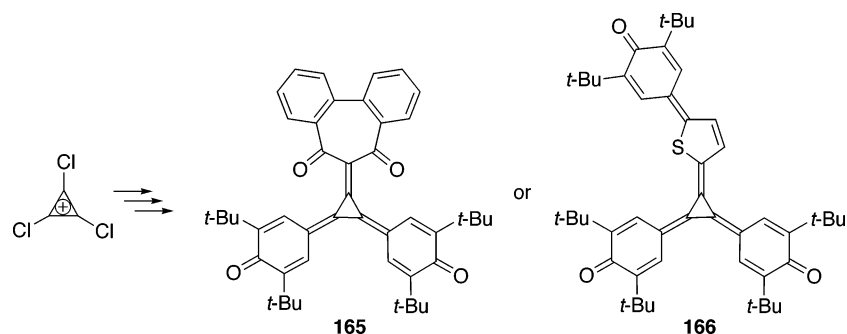
Scheme 50

164 (54%)

hexane **147**, was synthesized as a mixture of diastereomers from the hexahalide **148** via reaction with Mg metal (Scheme 44).

The first [3]radialene, **149**, was synthesized shortly thereafter in 1965 by Köbrich and Heinemann in 2% yield as a colorless solid via the addition of the isopropylidene carbenoid **150** to cumulene **151** (Scheme 45).[116] That same year the parent [3]radialene (**152**) was reported by Dorko,[117,118] prepared in 47% from the dibromocyclopropane derivative **153** when refluxed at 150 °C in the presence of KOH. The lowest energy UV absorption for **149** at λ_{max} = 309.5 nm (in hexanes) was an indication of electronic communication between the three double bonds,[116] while λ_{max} for the parent radialene **152** was found at slightly higher energy, 295 nm (in EtOH).[113]

In 1962, Uhler et al. reported that octaphenyl[4]radialene[119] could be formed from the photochemical dimerization of tetraphenylbutatriene[120] in the solid state. Slightly over a decade later, however, it was shown through X-ray crystallographic analysis that the product of this reaction was not a [4]radialene but rather an isomer, 1,3-bis(diphenylvinylidene)-2,2,4,4-tetraphenylcyclobutane.[121] It was not until 1986 that Iyoda and co-workers would finally succeed in the synthesis of octaphenyl[4]radialene.[122] Griffin and Peterson achieved the first synthesis of a [4]radialene in 1962, the parent [4]radialene **154** (Scheme 46).[123] Their efforts ultimately showed that **154** could be arrived at via a number of different transformations, and the most effective involved the exhaustive elimination of tetrabromide **155** to give **154** in 50% yield.[124]

Completing the series of [n]radialenes, the first [5]radialene, **156**, was synthesized by Iyoda and co-workers in 1986 using the same carbenoid precursor as that used by Köbrich (**150**, Scheme 47).[125] In this case, transmetalation to Cu(I) afforded relatively good yields of both **156** (up to

Scheme 51

Scheme 52
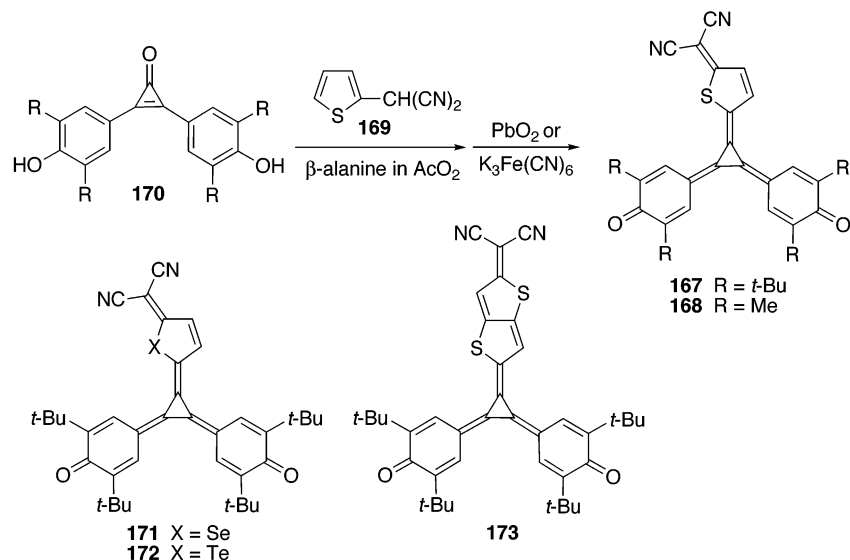
Scheme 53
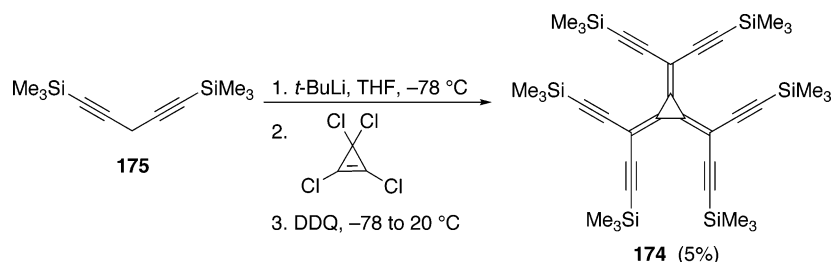
32%) and **157** (up to 30%). X-ray crystallographic analysis showed a half-chair conformation for **156**, as a result of the steric bulk of the isopropylidene methyl groups.

Over the past four decades, the formation of radialenes has come to rely on two major synthetic strategies.[4] The first uses cyclization reactions of precursor olefins to form the radialene core, as in the formation of **149**, **154**, **156**, and **157**. The second follows a route that first sees formation of the cyclic carbon skeleton, followed by the subsequent introduction of the exocyclic olefin groups, as in the synthesis of **147** and **152**. The syntheses and properties of radialenes were detailed by Hopf and Maas in 1992; we therefore focus our attention on major advancements since this time.[10,11,126]

3.1.2. [3]Radialenes

de Meijere and co-workers reported an improved synthesis of the parent [3]radialene **152** based on the development of a large-scale protocol for formation of tricarboxylate precursors such as **158** (Scheme 48).[127] Conversion of **158** to **152**

was then achieved as originally reported by Griffin and co-workers.[118]

Aside from an interest in the parent and alkyl-substituted radialenes, the late 1980s and early 1990s saw the synthesis of a number of more highly functionalized [3]radialene derivatives. Iyoda and co-workers reported the synthesis of **159** and **160** and studied their reduction to the corresponding dianions (Scheme 49).[128,129] The electronic absorptions for dianions **159^{2-}** and **160^{2-}** showed significant hypsochromic shifts (150−250 nm) when compared to those of the neutral molecules. Experimental and theoretical evidence suggested that the charge-separated, symmetric resonance structure shown (**159^{2-}**) makes a relatively large contribution to the stabilization of the dianion; the stable dianion **159^{2-}** remained unchanged in an NMR tube at room temperature for 1 year.

Using the carbenoid route developed by Iyoda for the synthesis of **161**−**163**,[128] Komatsu and co-workers have extended this methodology to the adamantylidene substituted

Scheme 54

a R^1 = R^2 = H
b R^1 = Br, R^2 = H
c R^1 = I, R^2 = H
d R^1 = CO$_2$Me, R^2 = H
e R^1 = CN, R^2 = H
f R^1 = NO$_2$, R^2 = H
g R^1 = H, R^2 = Cl
h R^1 = H, R^2 = Br

Scheme 55

Scheme 56

Scheme 57

Ar = Ph, 4-MeC$_6$H$_4$, 4-MeOC$_6$H$_4$, 4-ClC$_6$H$_4$, 4-PhC$_6$H$_4$, 4-MeO$_2$CC$_6$H$_4$, c-C$_6$H$_{11}$

Scheme 58

Ar = Ph, 4-MeC$_6$H$_4$, 4-t-BuC$_6$H$_4$
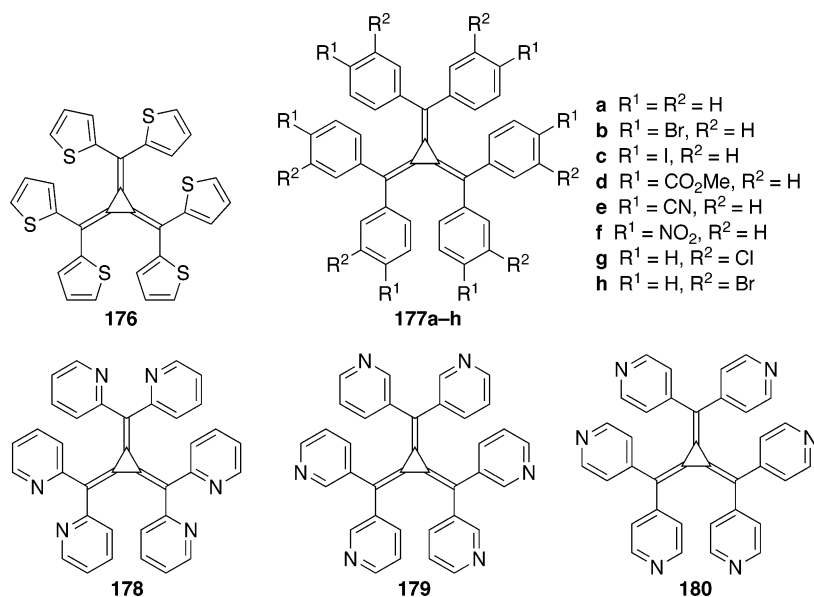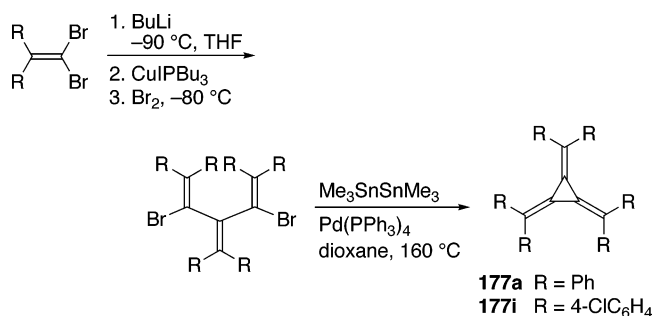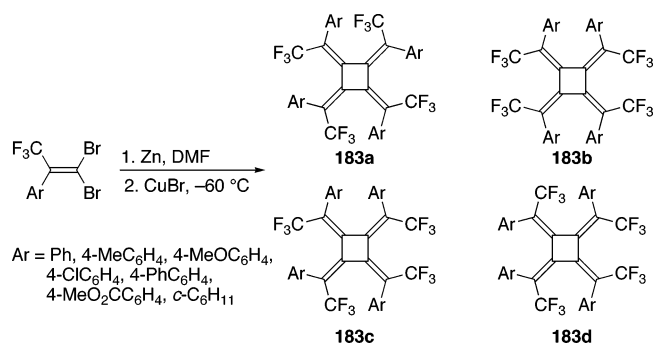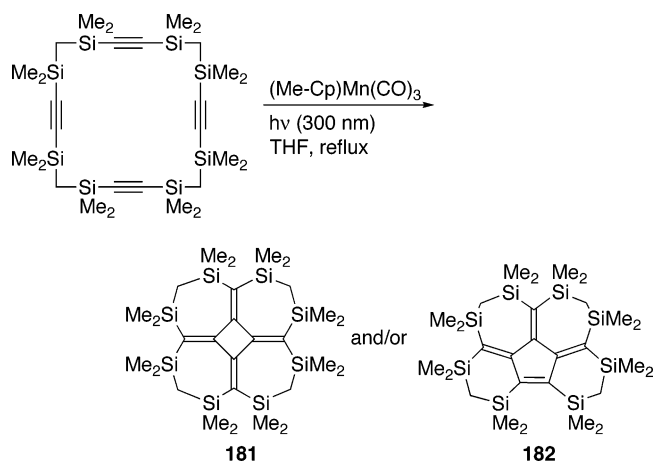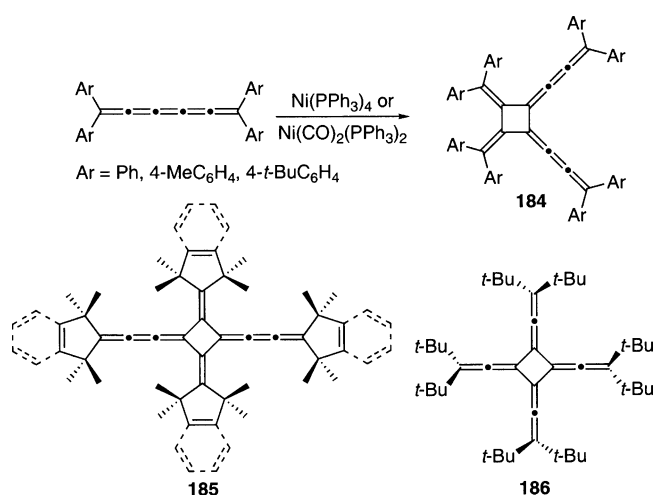
[3]radialene, **164**, using an activated Ni-catalyst (Ni*) (Scheme 50).[130] Electrochemical analysis revealed one irreversible oxidation at 1.15 V vs SCE, and the π-donor ability of **164** was demonstrated through the formation of a charge-transfer complex with tetracyanoethylene (TCNE) in dichloromethane.

Starting from the trichlorocyclopropenium ion, Takahashi and co-workers used West's method[131] to synthesize a number of [3]radialenes based on a bis(benzoquinone) core structure (Scheme 51), including **165** and **166**.[132,133]

The electron-deficient [3]radialenes **167** and **168** were formed in excellent yield using a two-step sequence of condensation of malononitrile derivative **169** with cyclopropenones **170**, followed by oxidation to the radialene structure (Scheme 52).[134] Cyclic voltammetry of **167** and **168** revealed two reversible one-electron reductions, and charge-transfer complexation of **167** with a variety of donors was investigated. The 1:1 complex **167**/TTF showed a substantial conductivity at room temperature (3.1 S cm^{-1}). This same synthetic protocol later afforded the Se and Te analogues **171**−**172**, as well as **173**.[135−138]

Diederich and co-workers synthesized [3]radialene **174** based on Fukunaga's method,[139] starting with pentadiyne **175**

Scheme 59
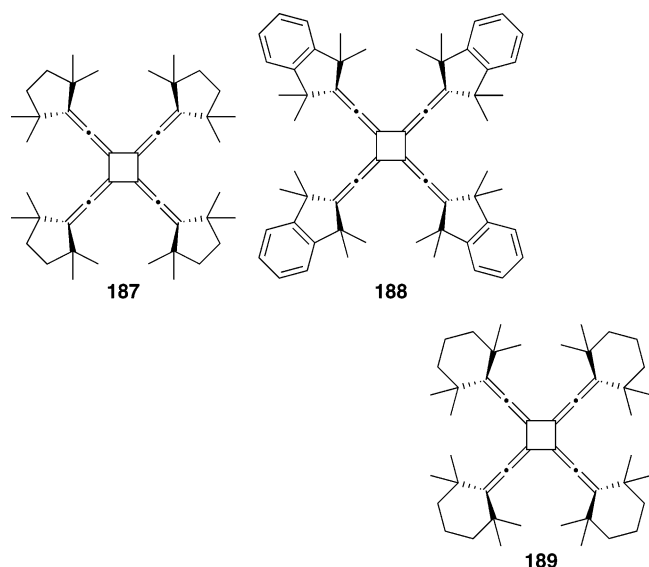
and tetrachlorocyclopropene (Scheme 53).[140] The perethynylated **174** was isolated as a red dark solid ($\lambda = 567$ nm). X-ray crystallographic analysis showed a planar cross-conjugated framework, and the C−C bond lengths of the cyclic fragment showed values from 1.420(5) Å to 1.431(3) Å, which were fairly close to those of the parent [3]radialene **152** and its hexamethyl derivative **149**.[141−143]

Oda and co-workers synthesized [3]radialenes **176** and **177a−h** according to Fukunaga's method (Scheme 54).[144,145] These compounds showed two reversible reductions, and cyclic voltammetry also showed that the reduction potentials increased in the order of **177f** < **177e** < **177d** < **177b**, reflecting the electronic nature of the aryl substituents. X-ray crystallography of **177e** showed the radialene core to be planar and the two phenyl rings on each corner to be twisted with regard to the central core. [3]Radialenes bearing either 2- or 3-pyridyl groups have been made analogously (**178** and **179**), as reported simultaneously by two groups.[146−149] Steel and co-workers were subsequently able to show that reaction of **178** with AgNO₃ and AgPF₆ gave polymeric coordination complexes with an Ag₂L motif that was confirmed by X-ray crystallography. Reaction of **178** with AgBF₄ or [Ru(byp)₂Cl₂], on the other hand, gave discrete coordination complexes.[147−149] The final member of this series of [3]radialenes (**180**) was based on the 4-pyridyl group and was synthesized by Masumoto and co-workers.[150] Upon reaction with silver perchlorate, **180** assembles into a three-dimensional coordination polymer, as characterized by X-ray crystallography, the first such polymer based on the use of a [3]radialene as a bridging ligand.

The hexaaryl radialenes **177a** and **177i** have also been assembled by Iyoda and co-workers via oligomerization of Cu-carbenoids, followed by ring closure (Scheme 55).[47] X-ray crystallography of both species confirmed the planar radialene core and showed that the aryl rings were arranged in a screw-shaped geometry.

3.1.3. [4]Radialenes

Sakurai reported synthesis of the first persilylated [4]radialene **181** via cyclization with an excess of a manganese carbonyl complex in the presence of light (Scheme 56).[151] Conversely, the use of only 1 equiv of the Mn-complex afforded primarily **182**, with only a small amount of **181** observed. X-ray crystallography showed the structure of **181** to be severely puckered from planarity (by 32.5°). Radialene **181** was easily reduced to the corresponding dianion by exposure to Li, Na, or K.[152−154]

In a series of reports, Uno and co-workers reported the synthesis of a diastereomeric series of [4]radialenes **183a−d** based on the coupling of a carbenoid intermediate (Scheme 57).[155,156] Thermal and photochemical isomerization experiments showed that when the all Z-radialenes **183b** were heated in tetralin at 170−200 °C, a mixture of [4]radialenes in a ratio of approximately **183a**:**183b**:**183c**: **183d** = 1:10:5:1 was produced. When the isomeric mixtures were heated in the solid state at the same temperature, however, selective isomerization took place to give the **183b** isomers in >90%. Photochemical irradiation of the isomers **183b** caused isomerization to a mixture of ca. **183a**:**183b**: **183c**:**183d** = 2:2:48:48.

Iyoda and co-workers developed a synthesis of radialenes **184** based on Ni-catalyzed cyclodimerization of [5]cumulenes (hexapentaenes) (Scheme 58).[157] Yields ranged from 13 to 64% dependent on the catalyst and reaction conditions. This protocol has been expanded to include the incorporation

Scheme 60

Scheme 61

Ar = 2,4,6-*t*-Bu₃C₆H₂
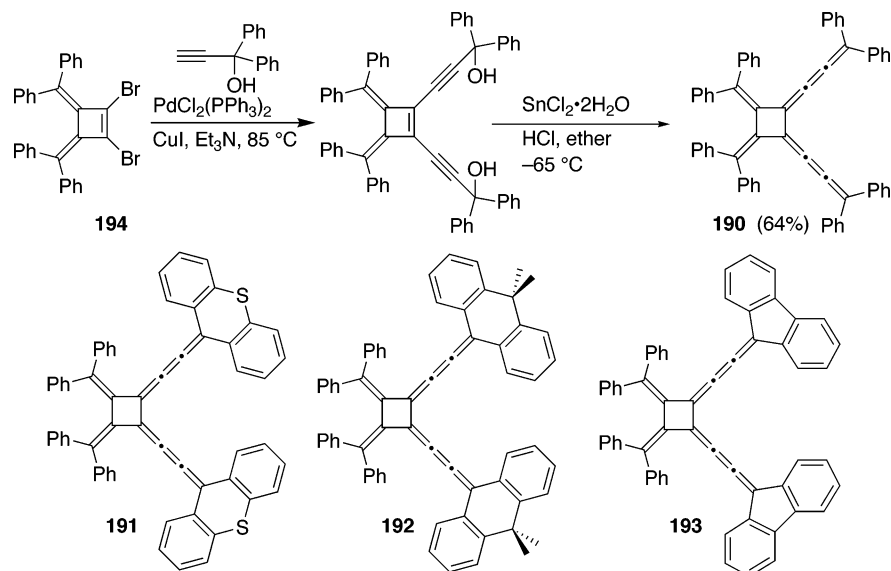
196 (60%)   **195** (21%)
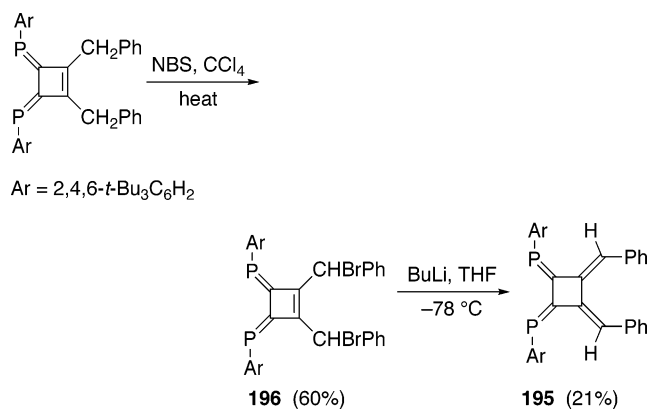
of alkyl substituents, giving **185**−**186**.[158] The outcome of the dimerization reaction depended on the steric requirements of the cumulene. Head to tail dimerization was observed in the formation of **185** (and the benzo-analogue), while the C_4 symmetrical radialene **186** formed when the steric requirements of the substituents were increased even further.

Thermal dimerization of [5]cumulenes was also explored and gave C_4 symmetrical [4]radialenes **187**−**189** in 21−69% yield through regioselective reaction only at the central double bond (Scheme 59). X-ray crystallographic study of **188** showed the radialene core to be perfectly planar, whereas that of **189** was slightly puckered.

A stepwise procedure was devised for [4]radialenes **190**−**193** (Scheme 60).[159] Starting with dibromide **194**, the Pd-catalyzed Sonogashira coupling with various alkynes was followed by reductive dehydroxylation to the radialene, as shown for the phenyl derivative **190**. The radialenes carrying thioxanthracene (**191**) and dihydroanthrancene (**192**) moieties showed a remarkably low rotational barrier about the butatriene bonds ($\Delta G^\ddagger$ = 13.7 and 14.9 kcal/mol, respectively), while this barrier for **193** was measured to be slightly higher ($\Delta G^\ddagger$ = 17.8 kcal/mol) due to reduced steric repulsion in the ground state of this derivative.

Yoshifuji and co-workers reported the synthesis of diphospha[4]radialene **195** via an elimination reaction effected on **196** (Scheme 61).[160] X-ray crystallography of

195 confirmed that the cyclic periphery was nearly planar and established the stereochemistry of the pendent substituents.[161]

3.1.4. [5]Radialenes

The same synthetic process that afforded [4]radialene **181** (Scheme 56) also provided the [5]radialene analogue **197** (Scheme 62).[162−164] X-ray crystallography showed that neutral **197** adopted an envelope conformation. Upon reduction with Li, however, structural analysis of the corresponding tetraanion showed that the 10-carbon radialene core is nearly planar due to the involvement of these atoms in delocalization of the negative charge.

Scheme 62

197
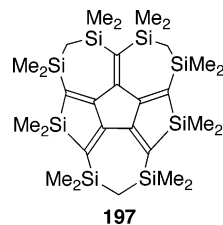
Yoshida and co-workers described the synthesis of a series of [5]radialenes **198**−**200** starting from a common intermediate, radialenone **201** (Scheme 63). Compounds **198**−**200** could be readily oxidized by NOBF₄ or NOPF₆ in CH₃CN to the corresponding tetracations.[165] Cyclic voltammetry of **198** showed a single-wave, four-electron transfer from the potent donor **198**, giving **198**[4+]. This process was explained by aromatic stabilization of the cyclopentadienide ring of the tetracation and rearrangement of the benzodithiol groups to a nonplanar conformation that reduced intramolecular Coulombic repulsion and steric hindrance.

Iyoda and co-workers reported the synthesis of extended [5]radialenones **202** and **203** based on Ni-catalyzed dimerization of [5]cumulenes (Scheme 64), reactions that also gave [4]radialenes, as described earlier (Scheme 58).[158] X-ray analysis of **203** confirmed that it adopted a planar structure in the solid state, and electronic absorption studies revealed that both **202** and **203** showed strong solvatochromism, with λ_{max} shifting to lower energy as a function of increasing

Scheme 63

201

198 R = -(CH=CH)₂- (64%)
199 R = SMe (55%)
200 R = Me (50%)

198[4+]
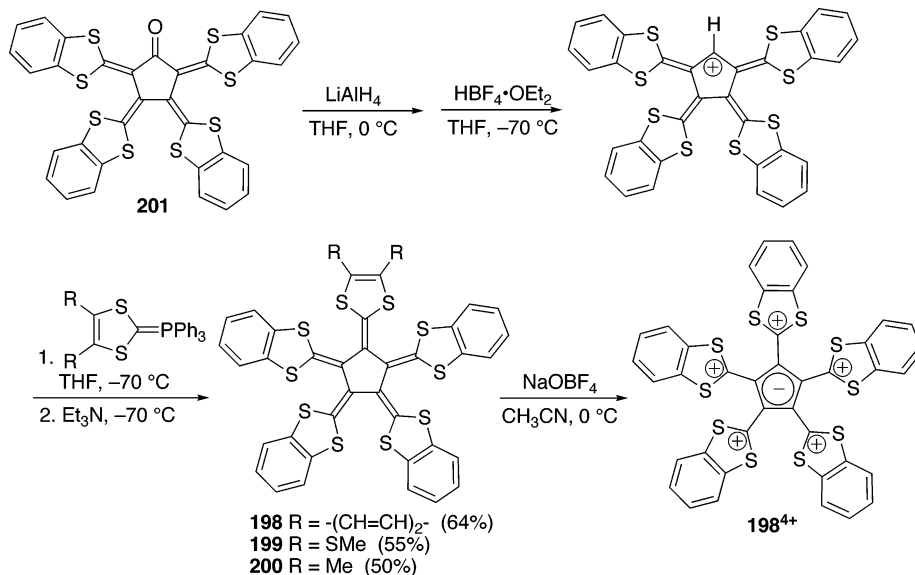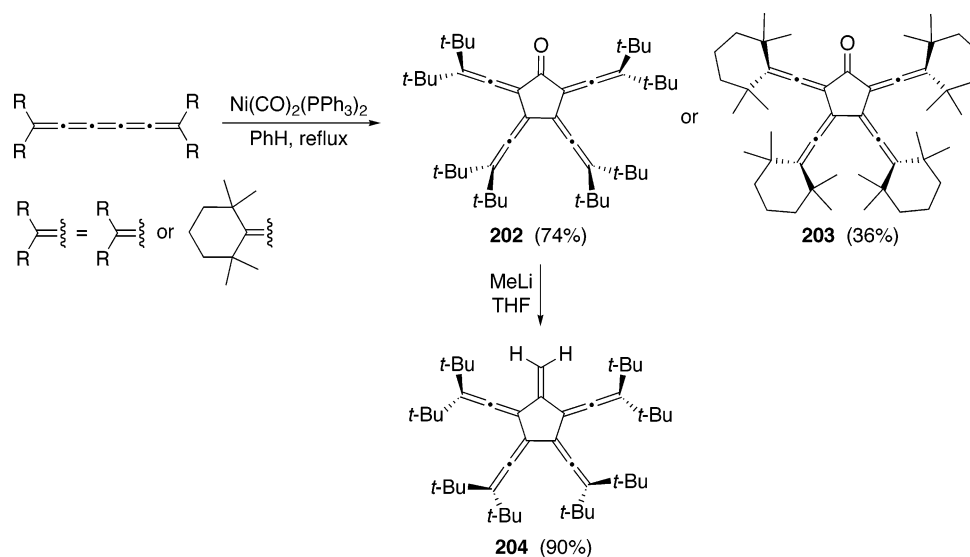
Scheme 64

Scheme 65

Scheme 66

Scheme 67

Radialenes   Expanded radialenes

Hybrid expanded radialenes
◯ = π-linker or metal
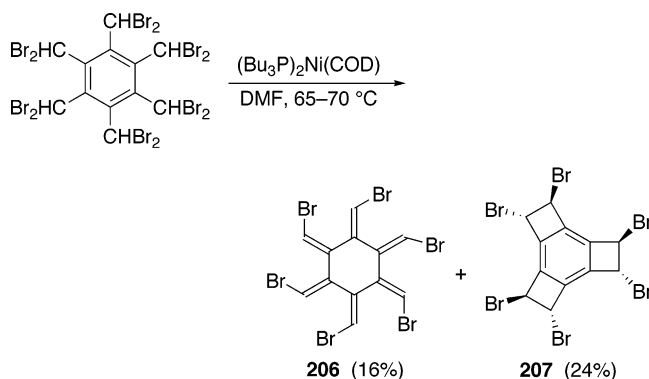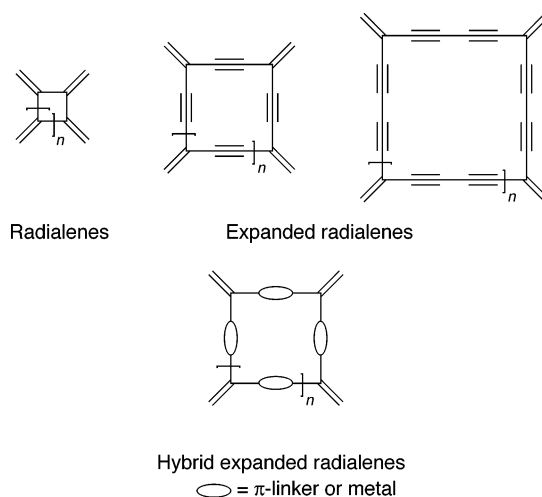
solvent polarity. Radialenone **202** was subsequently converted to [5]radialene **204** through reaction with MeLi.

3.1.5. [6]Radialenes

After over 40 years, the original synthesis of [6]radialene **147** (see Scheme 44) was revisited by Hopf and co-workers.[166] It turned out that the synthesis of **147** produced up to five other diastereomers according to GC/MS analysis, and one of these isomers could be separated using preparative thick layer chromatography (Scheme 65). Analysis by NMR spectroscopy identified the byproduct as most likely *cccaca*-**147** over the other possibilities of *ccccca*-**147** and *ccccaa*-**147**.[167]
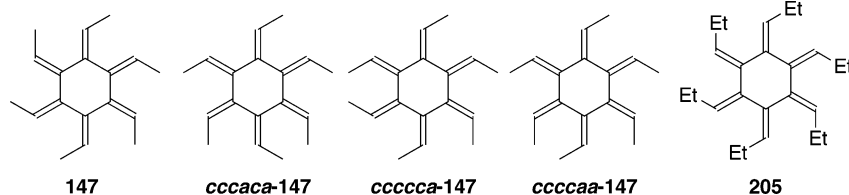
Hopf and co-workers have also recently reported the X-ray crystal structure of [6]radialene **205** (Scheme 65),[168] which revealed this derivative adopted a chair conformation with a structure quite close to that reported for the hexamethyl analogue **147**.[169]

Stanger and co-workers have synthesized the hexabromo[6]radialene **206** and its valence isomer **207** in a 2:3

ratio using a Ni-catalyst (Scheme 66).[170] Heat or radical impurities cleanly transformed **207** into **206**. X-ray single-crystal analysis confirmed that this [6]radialene also adopted a chair conformation, while the core of **207** was planar.

3.2. Expanded Radialenes

"Expanded radialenes" is the general term given to the cyclic compounds that originate by formal insertion of an unsaturated spacer between each pair of exo-methylene fragments in the cyclic framework of a radialene (Scheme 67). This was pioneered through the work of Diederich via the insertion of a diacetylene moiety into the radialene framework,[171] and it has been extended to encompass acetylene linkers, as well as hybrid radialenes with aryl

Scheme 68

Scheme 69

Scheme 70

internal bond angles about the sp-hybridized carbons were significantly bent (157.4°) from the optimum of 180°.

3.2.2. Expanded Radialenes with Diacetylene Spacers

Expanded [4]-, [5]-, and [6]radialenes with diacetylene spacers were the first expanded radialenes to be reported and were introduced by Diederich and co-workers in 1994 (Scheme 71).[5,171,173] The even-numbered members of this series of expanded radialenes (**214a** and **214c**) resulted from oxidative coupling of a TEE dimer **215**.

Scheme 71

moieties, heteroatoms, and transition metals introduced into the radialene core.

3.2.1. Expanded Radialenes with Acetylene Spacers

The first example of an expanded radialene based on insertion of a single acetylene unit into the radialene skeleton was reported in 1999 (Scheme 68).[64] The synthesis of **208** derived from the Sonogashira cross-coupling reaction of *iso*-PDA pentamer **67** with a dibromoolefin. Compound **209** was also formed as a result of oxidative homocoupling of the *iso*-polydiacetylene moiety. A UV−vis spectroscopic comparison between **67** and **208** suggested that virtually the same extent of π-delocalization was present in each of the two molecules; that is, no evidence of macrocyclic cross-conjugation was observed.

A larger cousin of **209**, radialene **210**, was formed as a byproduct during the elongation of *iso*-PDA **211**, likely due to the high dilution conditions used in the reaction that favored an intramolecular reaction (Scheme 69).[63] Expanded radialene **210** could be synthesized deliberately via the oxidative homocoupling of **211** using the Hay catalyst in dry acetone.

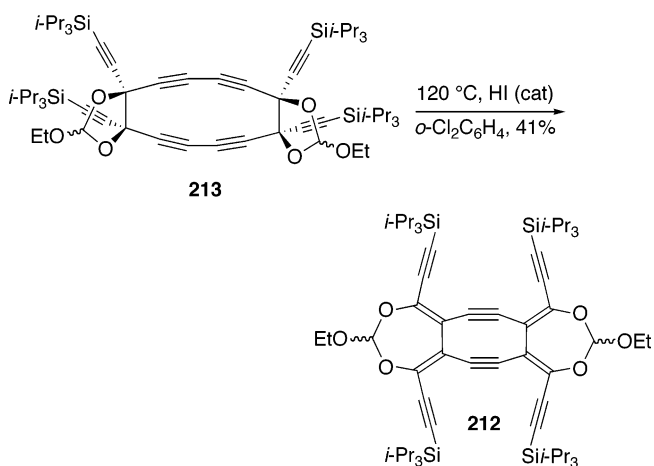Diederich and co-workers synthesized the unique hybrid radialene **212** by heating **213** to 120 °C in *o*-dichlorobenzene in the presence of a catalytic amount of HI (Scheme 70).[172] The highly strained, diastereomeric products were isolated as an inseparable 2:1 mixture that showed surprisingly high kinetic and thermal stability. The structure of **212** could only be elucidated by X-ray analysis, which showed that the

The odd-numbered expanded [5]radialene **214b** (Scheme 72) required a somewhat more elaborate building block, trimeric **216**, which was then combined with dimer **215** under oxidative coupling conditions.

The macrocycles **214a**−**c** were highly stable and yellow in color, despite the high degree of unsaturation. Based on UV−vis absorption analysis and AM1 calculations, there was little evidence for strong macrocyclic cross conjugation, which could be rationalized by the steric repulsion of the

Scheme 72

216

$$\xrightarrow[\text{Py/PhH (3:2)}]{\textbf{215}, \text{Cu(OAc)}_2}$$

214b (15%)

Scheme 73

217a–c (n = 1,3,5)

218a–d (n = 1-4) **219a–c** (n = 1-3)
R = $(C_{12}H_{25})_2$N   R = NC$(4$-$C_6H_4)_2$O$(CH_2)_{11}$O
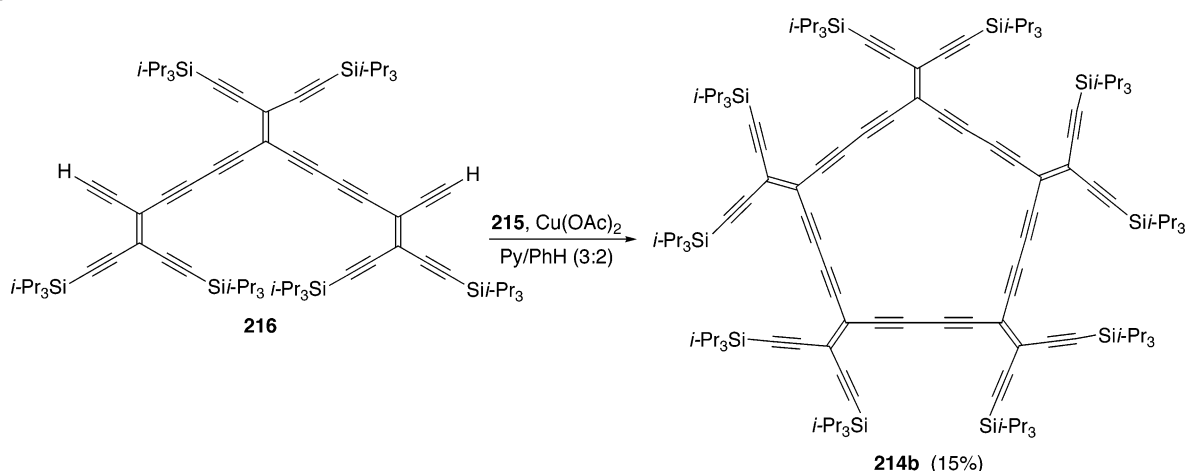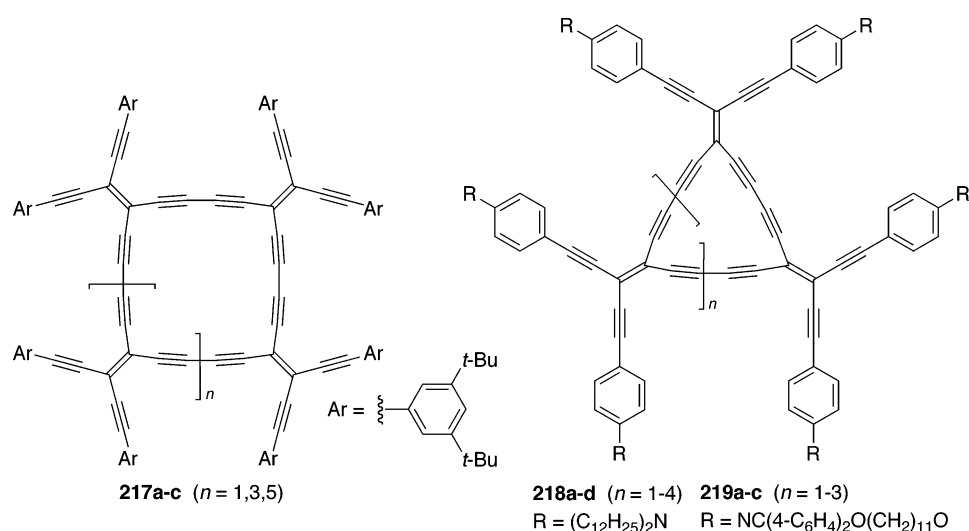
bulky TIPS groups that caused the macrocycles to adopt a nonplanar conformation particularly for hexameric **214c**.

In addition to the bis(*tert*-butyl)aryl radialenes **217a−c** (Scheme 73),[80] the synthesis of donor end-capped expanded radialenes **218** has been reported via oxidative homocoupling reactions of the appropriate TEE precursor.[80,174] Amine-capped expanded radialenes **218a−d** showed low-energy absorptions (λ_{max} = 609−646 nm) consistent with increased macrocyclic cross conjugation in these systems and also showed large third-order nonlinear optical coefficients. The addition of mesogenic groups was accomplished as well, albeit the resulting radialenes **219** did not display good liquid crystalline properties.[80]

Structure−function relationships for radialenes **214**, **217**, and **218** have been thoroughly explored with respect to their cross-conjugated core, particularly by UV−vis spectroscopy and electrochemical analysis.[5,175] These studies confirm the ability of the cyclic radialene core to act as a better electron acceptor than acyclic analogues. Theoretical analysis of similar expanded radialenes has also been reported.[176]

Following the same one-pot approach as established by Diederich, Tobe and co-workers have synthesized expanded radialenes of **220a−d** (as a mixture of diastereomers) via the oxidative coupling of enediyne **221** (Scheme 74).[177] UV−vis spectroscopic analysis of **220a−d** revealed the smallest macrocyclic **220a** (n = 1) showed the lowest energy

Scheme 74

221

$$\xrightarrow[\text{O}_2, \text{Py}]{\text{Cu(OAc)}_2}$$

220a-d (n = 1-4)

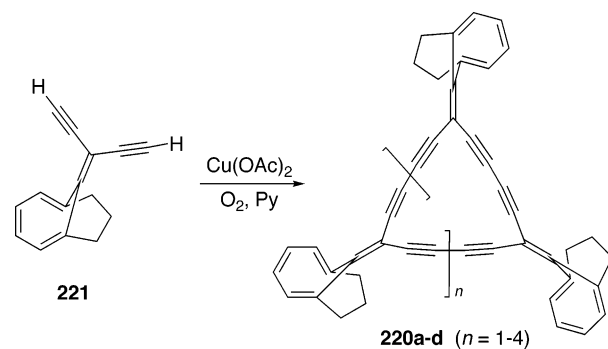absorption (λ_{max} = 344 nm) as well as the smallest molar absorptivity, in agreement with that known for other radialenes of similar structure.[80,174] Expanded radialenes **220a−d** were then used as precursors to the cyclo[n]-carbons.

Zhang and co-workers reported the one-pot synthesis of an expanded 1,3-dithiolane[5]radialene **222** from enediyne **223** in the presence of a Ni-catalyst (Scheme 75).[178] Interesting was the fact that the use of typical Cu-catalyzed homocoupling conditions was ineffective in the case of **223** → **222** and that reaction of dimer **224** (toward formation of the even-numbered analogues n = 0, 2, 4, ...) under the Ni-catalysis conditions was not successful. The UV−vis

Scheme 75

222 (*n* = 1)

Scheme 76

Ar = 4-Cl-C$_6$H$_4$

226 (trace)

227 (23%)

Scheme 77

R^1 = NMe$_2$, R$_2$ = H
R^1 = NMe$_2$, R$_2$ = N(C$_6$H$_{13}$)$_2$
R^1 = NMe$_2$, R$_2$ = NO$_2$
R^1 = NO$_2$, R$_2$ = N(C$_6$H$_{13}$)$_2$

Scheme 78

228 R =   **229** R =

3.2.3. Radiaannulenes
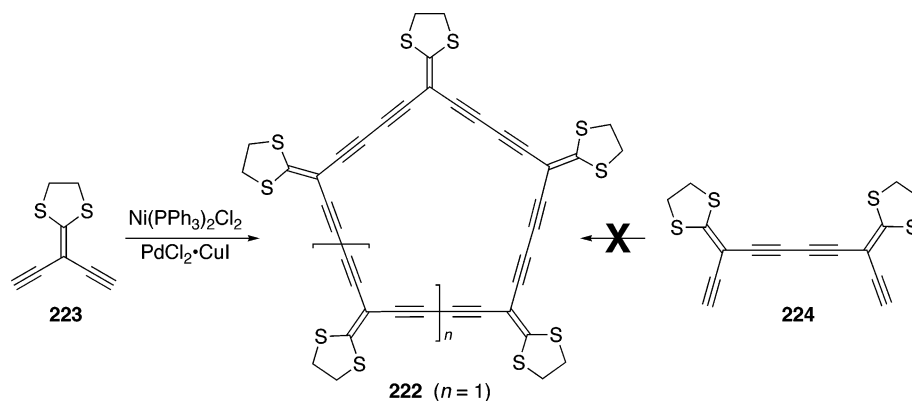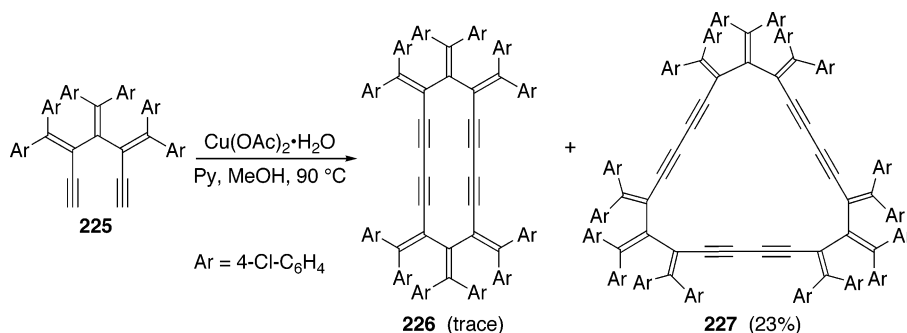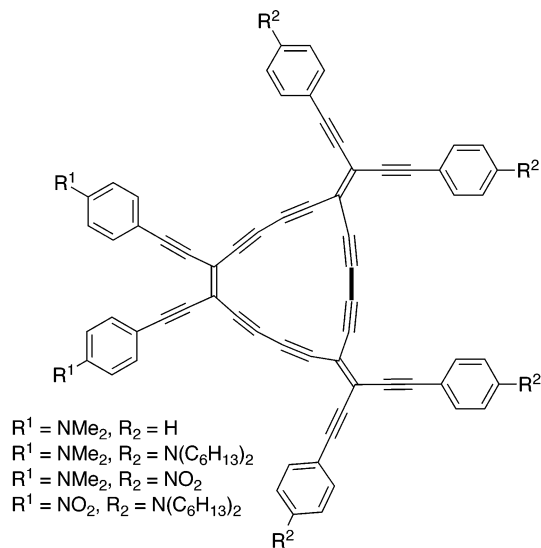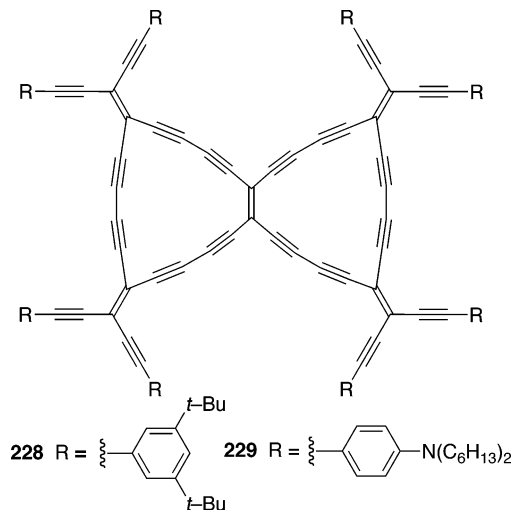
spectrum of **222** (λ_{max} = 443 nm) showed a slight batho-chromic shift relative to that of **224** (λ_{max} = 421 nm). The shift was explained by the presence of macrocyclic cross conjugation, consistent with that reported by Diederich for electron-rich [5]radialene **218c**.[80] X-ray crystallography confirmed the macrocycle **222** adopted a nonplanar, envelope conformation.

Expanded radialenes have been formed based on the oxidative coupling of **225**, giving a mixture of the dimer **226** and trimer **227** (Scheme 76).[46] Whereas **227** could be isolated and characterized, **226** was only detected by MS analysis. Radialene **227** contains a small cavity (2.6 Å) and formed a complex with AgOCOCF$_3$ or AgClO$_4$, as charac-terized by ^{1}H NMR spectroscopy and MALDI TOF-MS analysis.

Diederich and co-workers developed a hybrid series of cross-conjugated macrocycles that married the attributes of traditional annulenes with those of expanded radialenes, christening them radiaannulenes (Scheme 77).[89,179] The first derivatives were formed from the corresponding trimeric TEE precursor via desilylation and intramolecular oxidative coupling to close the cycle at the bond shown in bold. Electrochemical analysis showed that the acetylenic cores of these molecules were powerful electron acceptors, and in combination with peripheral donor and/or acceptor groups, intense intramolecular charge-transfer results.

Bicyclic radiaannulenes **228** and **229** were synthesized from a pentameric TEE precursor (**99**, Scheme 25) via an oxidative homocoupling reaction (Scheme 78).[89,179] Radi-aannulene **228** showed a remarkably low first reduction

Scheme 79

R$_1$ = Me
R$_2$ = SMe

230 **231**

232
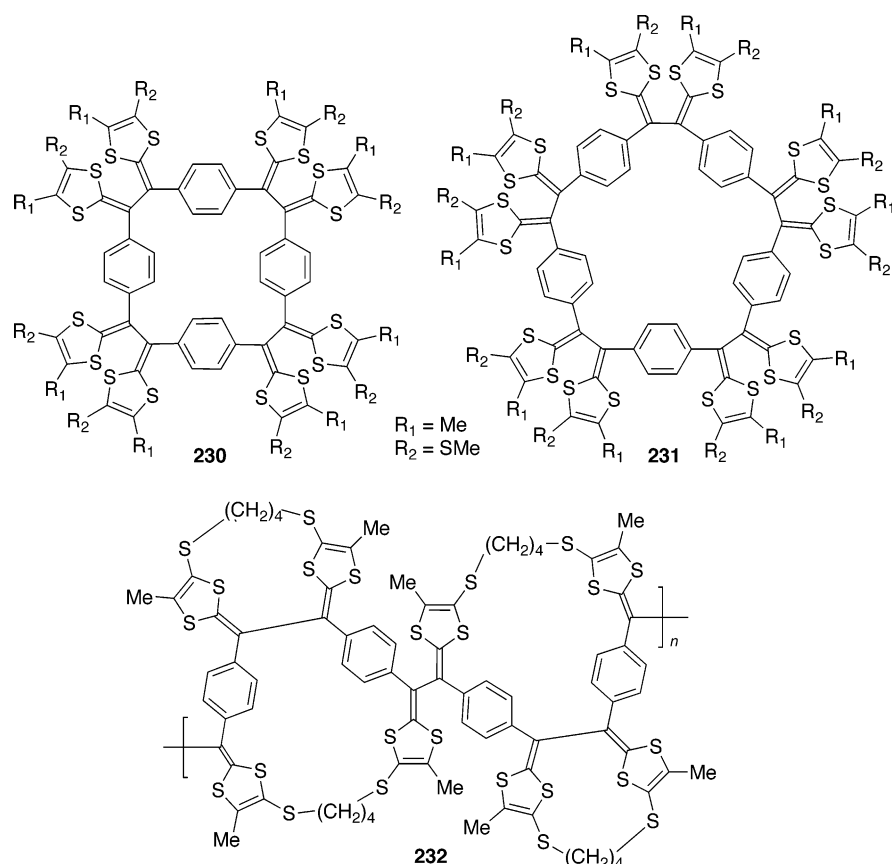
potential at -0.81 V (vs reference to Fc/Fc$^+$), making it a better electron acceptor than even C$_{60}$ (under comparable conditions). The electronic absorption spectrum of **229** confirmed a very strong intramolecular charge transfer with a low-energy end-absorption at 850 nm, the lowest ever reported for a macrocyclic TEE derivative.

3.2.4. Expanded Radialenes with Aryl Spacers

Lorcy and co-workers synthesized cross-conjugated macrocycles **230** and **231** via preparative electrolysis of 1,4-bis-(1,4-dithiafulven-6-yl)benzene (Scheme 79).[180] While formed as an inseparable mixture, the macrocycles could be characterized by ^{1}H NMR spectroscopy. Using an electrochemical oxidative coupling reaction, the synthesis of polymer **232**, which contains cross-conjugated fragments as a part of the macrocyclic skeleton, was also achieved.[181]

3.2.5. Expanded Radialenes with Arylene Vinylene Spacers

The first cross-conjugated macrocycle based on an arylene vinylene spacer, **233**, was synthesized by Kawase and Oda via a McMurry coupling reaction and served as a synthetic precursor to a Fritsch−Buttenberg−Wiechell rearrangement (Scheme 80).[182] Several years later, Märkl and co-workers prepared cross-conjugated macrocycles **234**−**236** based on dithiafulvene subunits with annulene spacers, also using the McMurry coupling.[183] Compound **234** was obtained as a mixture of (*E,E*)- and (*Z,Z*)-isomers that could be converted thermally to the (*E,E*)-isomer.

3.2.6. Expanded Radialenes with Arylene Ethynylene Spacers

Tykwinski and co-workers have synthesized cross-conjugated macrocycles **237**−**240** based on a Cu-catalyzed

Scheme 80

233 **234** X = O
235 X = S

236
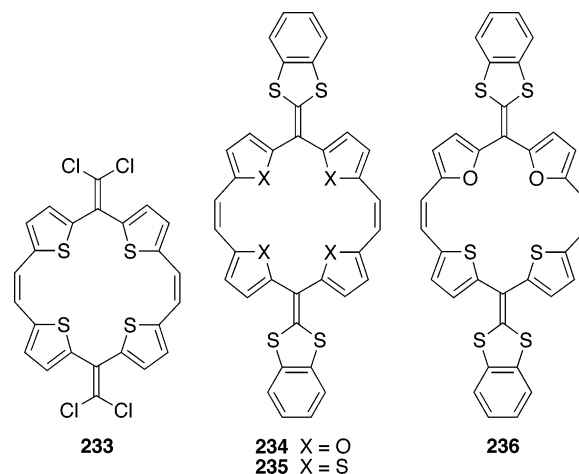
acetylenic dimerization strategy (Scheme 81).[184−186] Their work included an unfunctionalized hydrocarbon skeleton (**237**) and examples in which a pyridyl moiety was oriented endocyclic (**238**) and exocyclic (**239** and **240**) with respect to the macrocyclic core. An X-ray analysis of **238** showed it adopted a nearly planar conformation in the solid state, essentially free of ring strain.[184]

Carbon-rich macrocycles **239** and **240** function as equivalents to 4,4′-bipyridine and participate in self-assembly reactions and metal coordination, such as the axial coordination to Ru-porphyrins in **241** and **242** (Scheme 82).[186,187] Both complexes were characterized by X-ray crystallography that showed a planar macrocyclic framework for **241**, while **242** adopted a chairlike conformation that likely resulted from

Scheme 81

237 X = Y = CH, R = Ph (39%)
238 X = N, Y = CH, R = Ph (62%)
239 X = CH, Y = N, R = Me (not isolated)
240 X = CH, Y = N, R = Ph (52%)

Scheme 82

241 R = Me
242 R = Ph

Scheme 83

243 (86%)

Scheme 84

244a-b (n = 1,2)
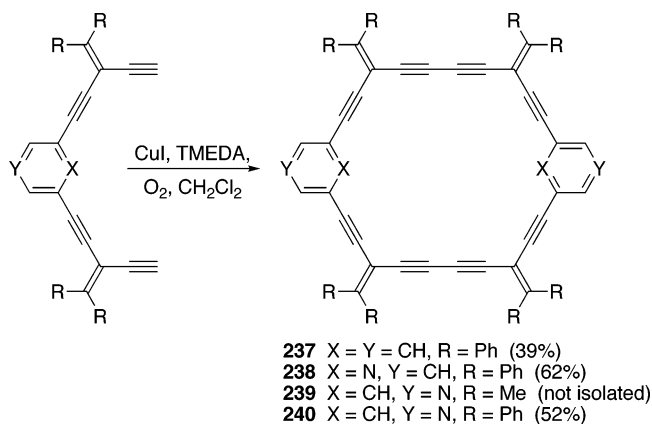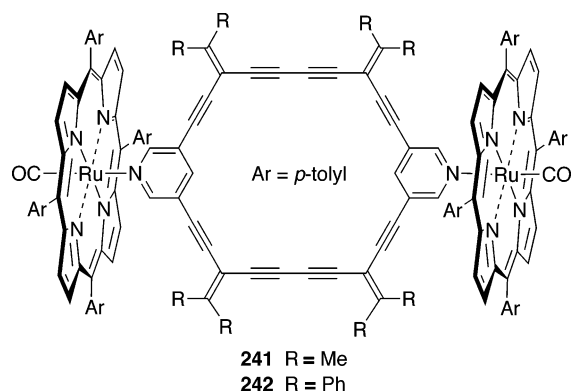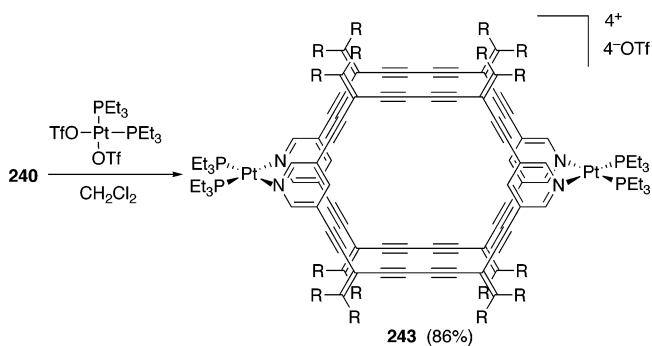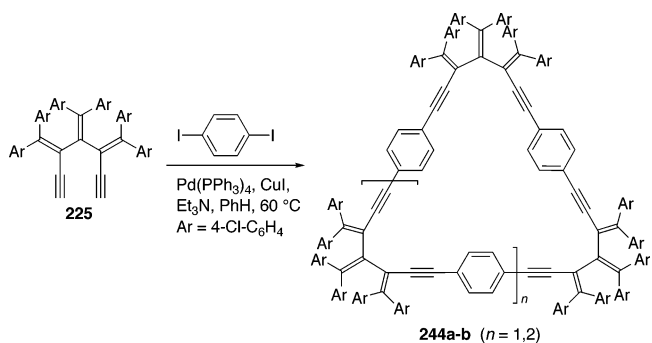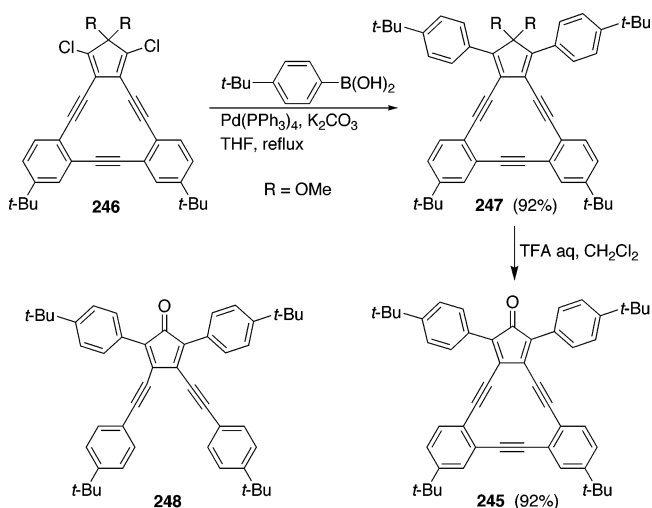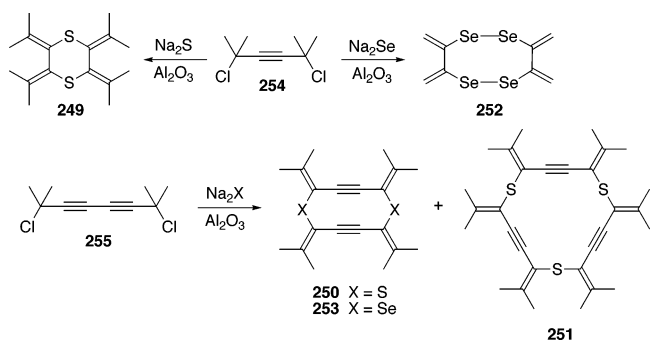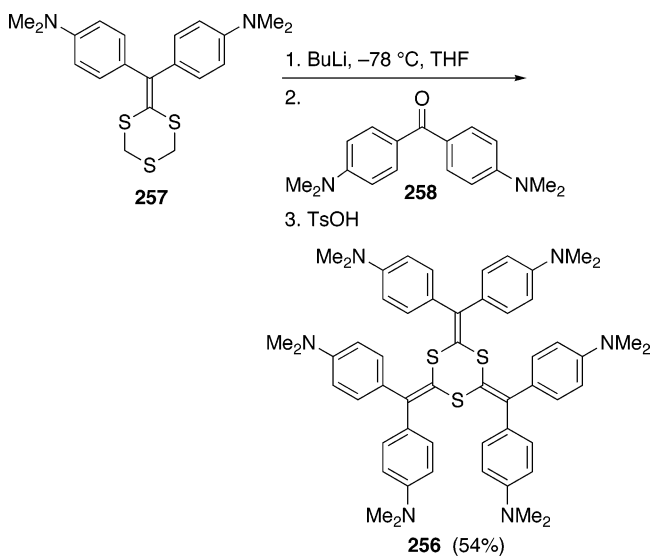
steric repulsion between the diphenyl alkylidene moieties and the exocyclic porphyrin rings.

Reaction of **240** with Pt(PEt₃)₂(OTf)₂ in CH₂Cl₂ gave the assembly **243** (Scheme 83).[188] X-ray crystallographic analysis established that assembly **243** packs such that bidirectional channels were realized, and the incorporation of

Scheme 85

246 → **247** (92%)

R = OMe

248   **245** (92%)

Scheme 86

249 → **252**

255 → **250** X = S / **253** X = Se + **251**

Scheme 87

257

1. BuLi, –78 °C, THF
2. **258**
3. TsOH

256 (54%)

ClCH₂CH₂Cl into the channels demonstrated that the solid was suitable for the selective uptake of small organic guests. The displacement of this solvent and characterization of the resulting pores were explored using hyperpolarized ¹²⁹Xe NMR spectroscopy.[189]

Using the same approach as shown for **226** and **227** (Scheme 76), Iyoda and co-workers synthesized π-extended radialenes **244** using the Sonogashira coupling protocol with *p*-diiodobenzene (Scheme 84).[46] These macrocycles have calculated cavities with free space diameters of 5.4 and 9.1

Scheme 88

259
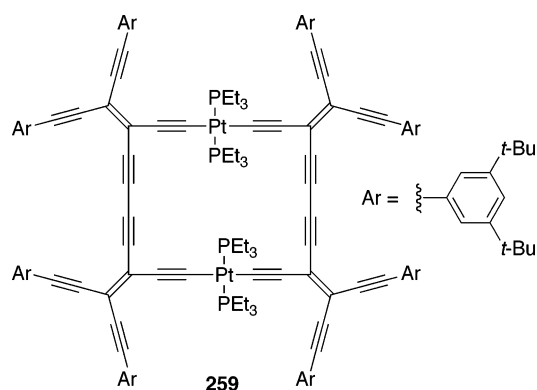
Å, respectively, and hence were too large to form complexes with small cations such as Ag(I).

A sequence of cross-conjugated macrocycles culminating in the cyclopentadienone-annulated hexadehydrodibenzo-[12]annulene **245** was devised by Tobe and co-workers (Scheme 85).[190] Starting with **246**, a Suzuki coupling gave perarylated **247**, and deprotection with TFA gave **245**. Based on spectroscopic characterization and theoretical calculations in comparison to acyclic **248**, it was suggested that compound **245** was weakly aromatic due to the resonance contribution of the 14π-electron [15]annulenone structure.
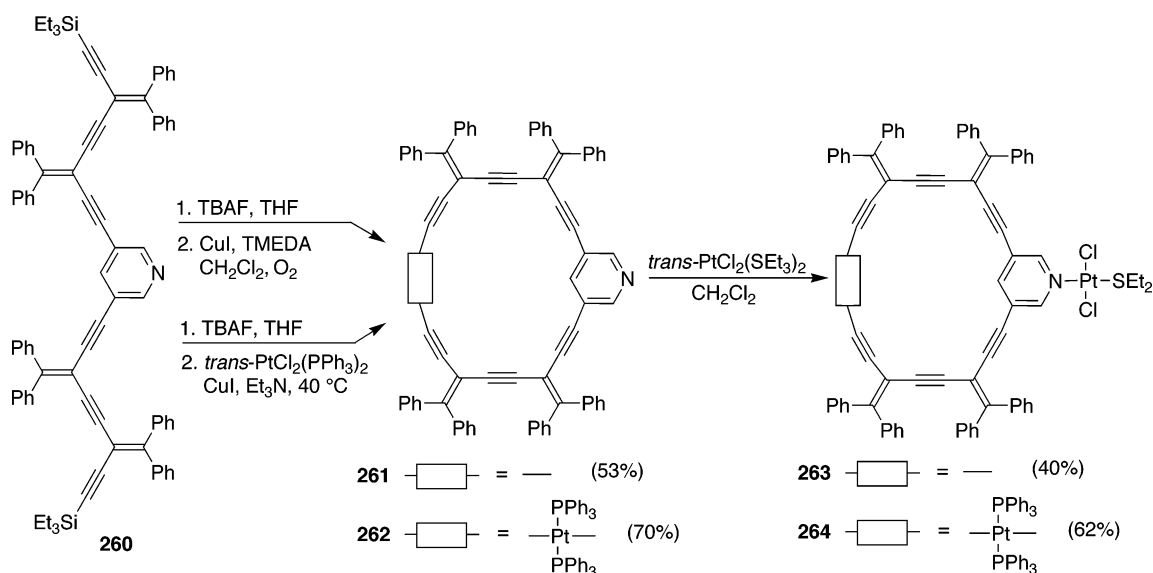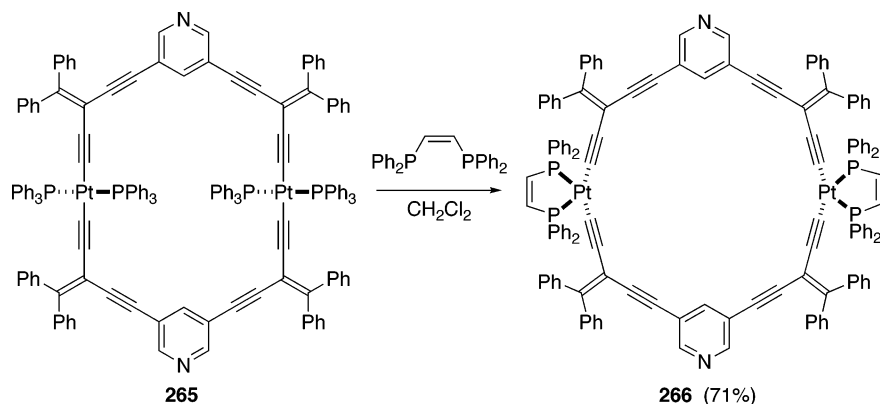
3.2.7. Expanded Radialenes with Heteroatom Spacers

Gleiter and co-workers synthesized thiaradialenes **249–251** and selenaradialenes **252–253** via the reaction of **254** and **255** with Na_2S and Na_2Se, respectively, in the presence of Al_2O_3 (Scheme 86).[19,191] Whereas the reaction of **255** with Na_2S gave an isolable amount of the trimeric **251**, the selenium analogue was not observed during the reaction with Na_2Se.

Suzuki and co-workers reported the synthesis of thiaradialene **256** via lithiation of trithiane **257** and reaction with diaryl ketone **258**, followed by elimination (Scheme 87).[192] Compound **256** is a strong electron donor, and cyclic voltammetry indicated large skeletal changes and/or transannular bonding upon oxidation. An electron-rich radialene analogous to **256** with pendent 1,3-dithiafulvene groups has been studied by Schumaker et al.[193]

3.2.8. Expanded Radialenes with Metal Spacers

The first expanded radialene with a transition metal incorporated into the conjugated framework **259** was synthesized by Diederich and co-workers, based on the readily formed Pt-acetylide linkage (Scheme 88).[90] The electronic absorption spectrum of **259** suggested that the Pt-centers could mediate electron communication, leading to delocalization over the entire π-system.

Using the acyclic precursor **260**, Tykwinski and co-workers synthesized a series of cross-conjugated macrocycles

Scheme 89

Scheme 90

Scheme 91

(S,S)-**267** (73%)

(S,S)/(S,S)-**268**

(S,S)/(S,S)-**269**
(R,R)/(R,R)-**269**
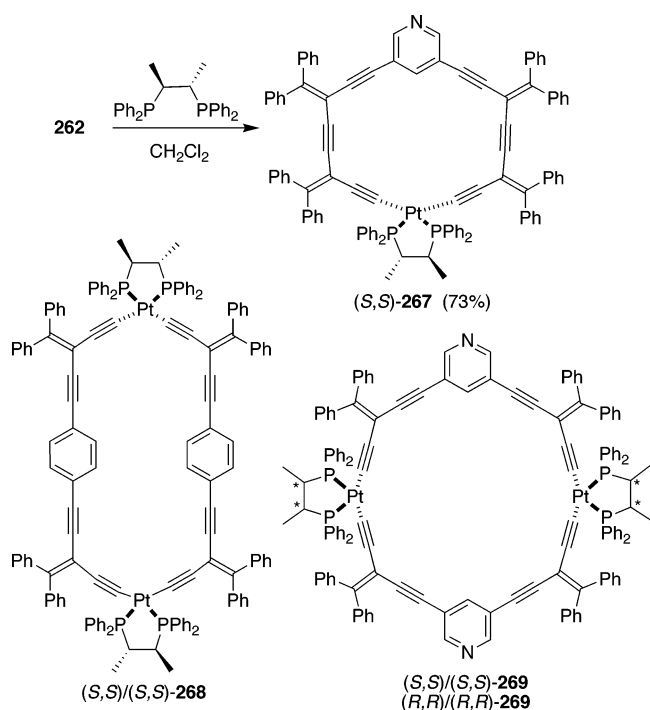
261 and **262**, with and without Pt-acetylide subunits (Scheme 89[194,195] The exocyclic orientation of the pyridine moiety made these systems suitable for metal coordination, as demonstrated by the formation of **263** and **264**. All four systems were characterized spectroscopically and crystallographically.

A similar protocol was used to form **265** (Scheme 90), which could then be subjected to ligand exchange with the bidentate ligand *cis*-bis(diphenylphosphino)ethylene to give **266**. Attempts to effect the analogous ligand exchange with the PEt₃ derivative of **265** were not successful.[195]
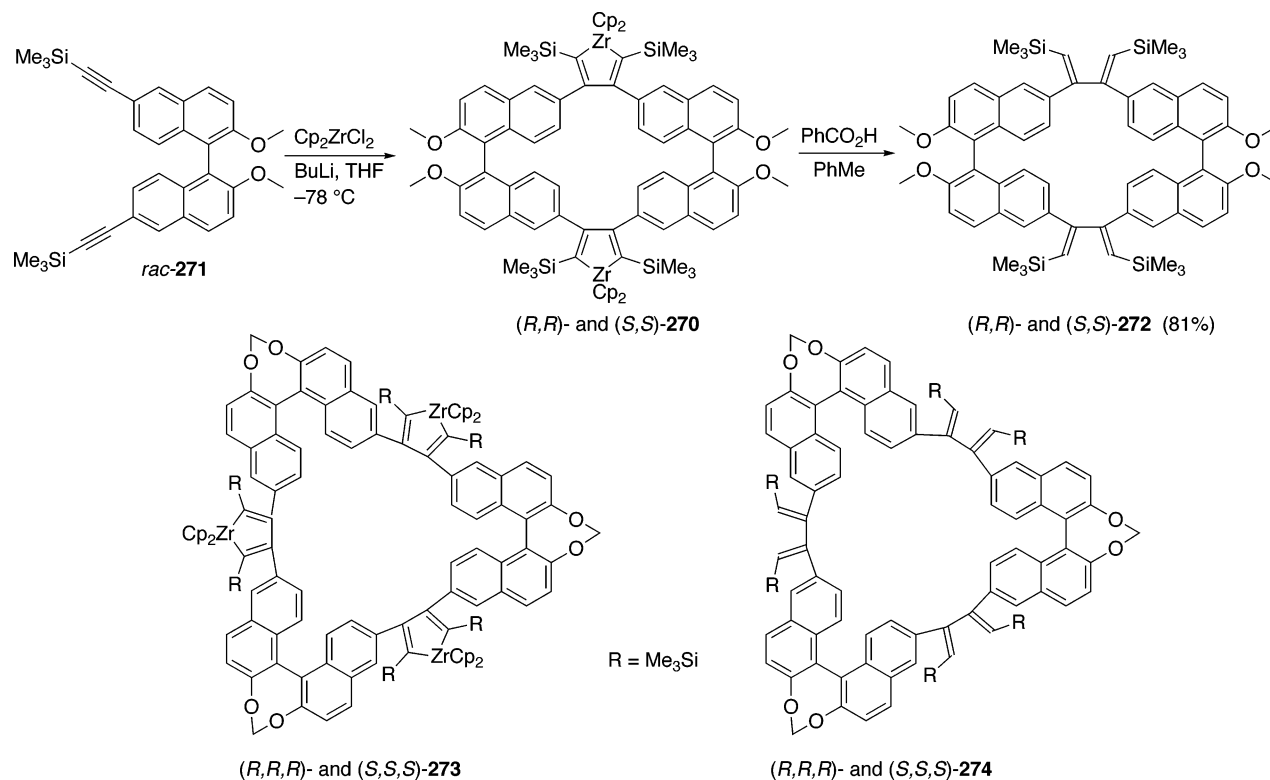
Chiral macrocyclic systems have been studied in the past decade, in particular due to their potential application in areas such as asymmetric catalysis, chemical sensors, and enantioselective guest inclusion.[196] In this regard, Tykwinski and co-workers have expanded on the ligand exchange protocol described in Scheme 90 toward the formation of chiral cross-conjugated macrocycles based on (S,S)-chiraphos and (R,R)-chiraphos ligands (Scheme 91).[197] Starting with, for example, achiral **262**, reaction with (S,S)-chiraphos provides the chiral product (S,S)-**267** in good yield. An analogous reaction afforded (S,S)-**268**, while both enantiomers of **269** were formed using either (S,S)- or (R,R)-chiraphos. Crystallographic analysis of (S,S)-**267** and CD studies of the series of macrocycles demonstrated unambiguously the ability of the chiraphos ligand to efficiently induce chirality in the conjugated molecular framework via the Pt–acetylide complex.

The creation of chiral, metal-containing macrocycles by the direct formation of metal–carbon bonds has been developed by Tilley and Schafer, who reported a diastereoselective synthesis of zirconocene-containing cross-conjugated macrocycles **270** starting from racemic BINOL derivative **271**.[198] Subsequent treatment of **270** with benzoic acid gave the metal-free, cross-conjugated macrocycles **272** (Scheme 92). The authors predicted that a reduction in the allowed dihedral angle between the naphthyl rings could result in the formation of even larger metallamacrocycles, and this premise gave rise to trimers **273** and demetalated derivative **274**. X-ray crystallographic analysis of **273** indicated an average dihedral angle for the naphthyl rings of 60° and confirmed the cyclic structure.

Rosenthal and co-workers synthesized radialene-like fused titanacyclopentadienes **275** and **276** via reaction of **277** or **278** with diphenylbutadiyne (Scheme 93).[199] X-ray crystallographic analysis of **275** confirmed the proposed structure, but insolubility in organic solvents prevented solution-state

Scheme 92

rac-**271**

(R,R)- and (S,S)-**270**

(R,R)- and (S,S)-**272** (81%)

R = Me₃Si

(R,R,R)- and (S,S,S)-**273**

(R,R,R)- and (S,S,S)-**274**

Scheme 93

277 R = H
278 R = Me

275 R = H
276 R = Me

280

279
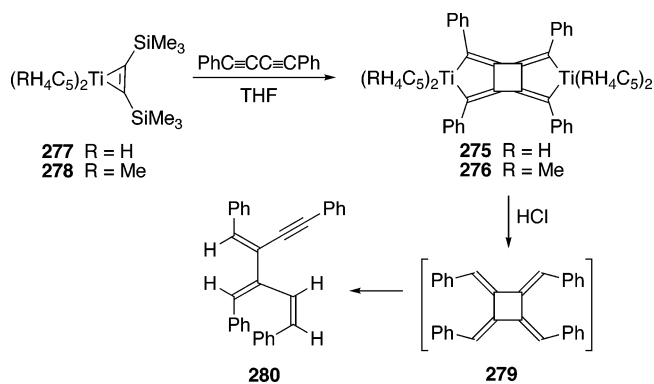
characterization. Reaction of **275** with HCl did not lead to the radialene **279** as expected, but rather to [3]dendralene **280**.

3.2.9. Radialene Substructures

Halton and Dixon reported several cyclic molecules based on cycloproparenes that, while not completely cross-conjugated, do feature a partially cross-conjugated substructure (Scheme 94). The cyclic derivatives **281**−**283** are locked into the *s-cis/s-cis* conformation and show dipole moments (μ = 1.73, 2.91, and 3.51 D, respectively) that are lower than those of the acyclic analogues **284**−**286** (μ = 2.07, 3.38, and 4.23 D, respectively), as measured in benzene. This suggested that the *s-trans/s-cis* conformation achievable by **284**−*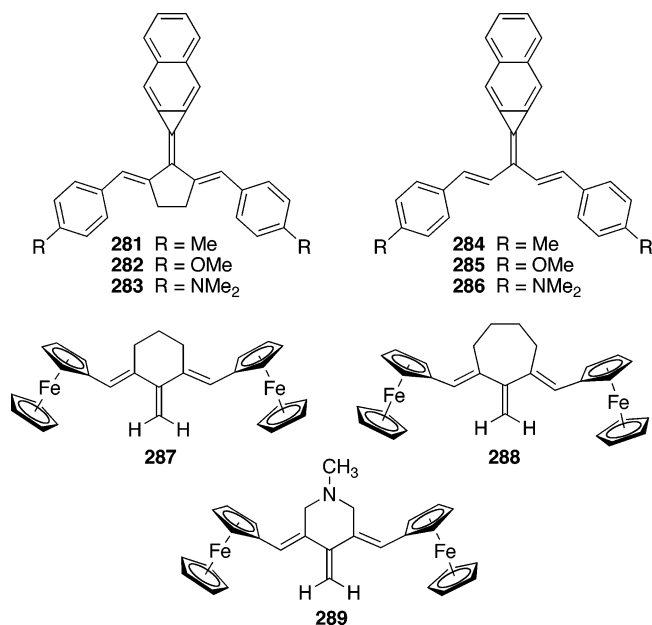*286** provided a significant contribution to the polarity of these molecules.[200] A similar structural motif is shared by ferrocenyl derivatives **287**−**289**, which have been studied by Klimova and co-workers.[201,202]

Scheme 94

281 R = Me
282 R = OMe
283 R = NMe₂

284 R = Me
285 R = OMe
286 R = NMe₂

287

288

289

A desire to explore the effects of ring strain in cross-conjugated macrocycles such as **209** (Scheme 68) led to the synthesis of cyclophanes **290a**−**e** by Tykwinski and Eisler (Scheme 95).[73] Spectroscopic and X-ray crystallographic analyses outlined the resultant changes in the bond orders as ring strain was increased and showed that, for example, correlations between ¹³C NMR shifts, solid-state bond angles,

Scheme 95

290a-e (*n* = 2,3,4,5,7)
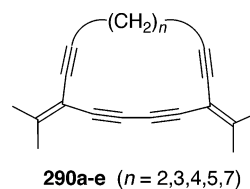
and Raman frequencies were all essentially linear. X-ray crystallography of the most highly strained system, **290a**, showed alkyne angles as small as 155°, making it one of the most strained alkynyl systems characterized to date. UV−vis spectroscopy revealed that ring strain had a surprisingly small effect on the electronic absorption energies of these macrocycles.

4. Conclusions

A little over 20 years ago, Henning Hopf remarked that cross-conjugated dendralenes were a neglected class of highly unsaturated hydrocarbons.[9] At that time, little was known about any members of this family of compounds outside of the smallest, unfunctionalized derivatives, such as [3]- and [4]dendralene. The research efforts of many over the past two decades have certainly brought us a long way toward addressing this situation. Improved synthetic techniques now readily provide access to [5]-, [6]-, and even [8]dendralenes,[33,34] while more highly substituted dendralenes serve as, for example, precursors to radialenes and vinylogous analogues of TTF. Entire new classes of dendralenes, the expanded dendralenes, have been realized, including *iso*-polydiacetylenes,[65] *iso*-polytriacetylenes,[70] poly(phenylenevinylidene)s,[92,94] and numerous hybrid systems. Systematic study of monodisperse oligomers from many of these families has provided a model for predicting the properties of the corresponding cross-conjugated polymers. Recent advances in transition metal catalysis have aided tremendously in the functionalization of cross-conjugated compounds, which has provided for a better understanding of the ability of cross-conjugated frameworks to mediate π-electron communication. Determining the extent of π-conjugation in cross-conjugated molecules has been a particularly challenging and difficult aspect toward evaluating their potential as advanced materials. It is clear, as predicted, that cross-conjugated oligomers show moderated delocalization in comparison to linearly-conjugated analogues. The magnitude of electronic communication in cross-conjugated molecules can vary widely, however, and is often highly dependent on the presence (or absence) of electron donor and/or acceptor functionality, conformation, and steric interactions. Furthermore, several studies, including those of *iso*-polytriacetylenes[81] and poly(phenylenevinylidene)s,[92] have shown that the use of UV−vis spectroscopy to determine π-conjugation can provide misleading results, even though it is often the first and easiest choice of analysis for researchers.

Closing of a dendralene into a cyclic structure gives a radialene, and insertion of a conjugated spacer into the framework of a radialene provides an expanded radialene. As a class of molecules, radialenes originally intrigued chemists due to their unusual topology and aesthetically pleasing structures. Very quickly, however, they became useful building blocks for materials chemists. The incorporation of electron donating groups about a radialene core provides molecules that are powerful electron donors that

can form remarkable polycations.[165] Conversely, incorporation of electron accepting groups on the periphery of radialenes has created strong acceptors that form stable polyanions upon reduction.[128,129,162–164] Electron-deficient radialenes also function well as partners in charge-transfer complexes with electron donors such as TTF, some of which show substantial conductivities.[134] Even with only pendant aryl rings, expanded radialenes with diacetylene spacers are inherently strong electron acceptors, and one expanded radiaannulene derivative is a better acceptor than even C_{60} fullerene.[89,179] The presence of π-electron delocalization due to cross-conjugation has been explored for a number of expanded radialenes, and in the absence of strong electron donors or acceptors, little difference is found between cyclic and acyclic analogues.[5,64,171,173] However, UV−vis spectroscopic analysis of several expanded radialenes substituted with strong electron donors has shown that macrocyclic cross conjugation is a factor in the electronic makeup of these molecules.[80,178]

While it is fair to say that neither dendralenes nor radialenes remain neglected classes of compounds, in many cases, researchers have only begun to unravel the full picture of cross conjugation. It is clear that future efforts toward improved synthetic methods and the latest materials applications will afford molecules that help to clarify this picture. Equally important, however, will be the contributions of those who are simply fascinated by the fundamental properties of these unique molecules and captivated by their structures.

5. Acknowledgments

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