DOI: 10.1002/anie.201108001

Molecular Materials

Allenes in Molecular Materials

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allenes · chirality · helical structures · macrocycles · molecular materials

Dedicated to Professor Armin de Meijere

This Minireview provides a critical account of the development of allene-containing advanced functional materials, starting with the design and synthesis of stable and enantiopure building blocks. A variety of systems, including shape-persistent macrocycles, foldamers, polymers, charge-transfer chromophores, dendrimers, liquid crystals, and redox-switchable chiral chromophores are discussed from the viewpoint of their syntheses, properties, and potential applications. The goal of this Minireview is to inspire new uses of enantiopure allenes for the rational design of advanced materials.

1. Introduction

Allenes is the common name given to hydrocarbons containing two double bonds from one carbon atom to two others.[1] In 1875, van't Hoff predicted that the substituents of allenes must be placed in two perpendicular planes.[2] A consequence of this 90° twist around the central sp-hybridized carbon atom is that allenes are axially chiral when appropriately substituted (Figure 1). This hypothesis was confirmed experimentally by Maitland and Mills in 1935.[3] Unlike in some other atropisomeric (axially chiral) compounds, the rotational barrier leading to the racemization of allenes is relatively high. For example, the racemization enthalpy $\Delta H^{\ddagger}$ of 1,3-dimethylallene is 45.1 $\mathrm{kcal\,mol^{-1}}$.[4] These characteristics have led to allenes being classified as carbon-rich, shape-persistent, axially chiral scaffolds.

The chemistry of allenes experienced a great advancement in the 20th century, as summarized in the monographs by Schuster and Coppola,[5] and more recently by Krause and Hashmi.[6] Modern synthetic methods allow the construction of allenes with a wide variety of substituents.[7] The reasons for this development are that allenes are useful intermediates in organic synthesis,[8] they are also found in many natural products, and are increasingly being incorporated in pharmaceuticals.[9] In addition, allenes play a central role in hydrocarbon chemistry,[10] and extremely bent allenes are being investigated because of their interesting electronic structure and coordination properties.[11–13] Furthermore, enantiomerically pure allenes have been successfully introduced as chiral ligands for asymmetric catalysis.[14,15]

The fascinating structure of allenes caught the attention of chemists interested in molecular materials. In this Minireview, we offer a critical (rather than exhaustive) account of the progress made in the field of allene-based molecular materials, with a focus on their synthesis and properties. In Section 2 we discuss the development of stable and enantiopure allenic building blocks. Sections 3 and 4 focus on allene-containing macrocycles, oligomers, and polymers, while Section 5 summarizes miscellaneous functional materials, ranging from charge-transfer (CT) chromophores to dendrimers and liquid crystals. We conclude by providing some perspectives and highlighting future challenges in this field.

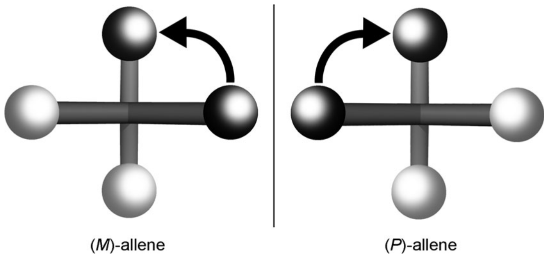

Figure 1. View along the axis of chirality of a chiral allene with two different substituents on each terminal carbon atom. The absolute configuration, using the *P* and *M* descriptors, is assigned by considering the two substituents of highest priority (dark balls) at each terminal carbon atom and looking along the chirality axis to determine the sense of rotation (*P* = clockwise, *M* = anticlockwise) when going from the highest priority substituent at the front to the highest priority substituent at the back.

2. Development of Stable Allenic Building Blocks

The greatest challenge in introducing allenes into advanced functional materials is to control the reactivity of the

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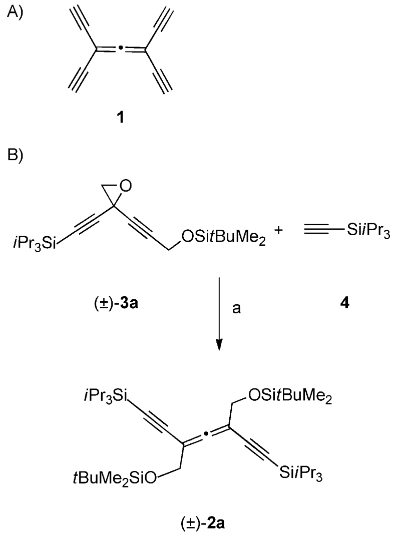
allenic core to produce robust molecular entities. A useful approach has been the development of building blocks where this reactivity is minimized, but functionalization of other sites on the molecule is still possible.

2.1. Development of Ethynylallene Building Blocks

The interest in synthetic approaches to molecular and polymeric carbon allotropes[16] drew attention to tetraethynylallene (**1**; Scheme 1 A), which is a precursor of a theoretical polymeric carbon allotrope.[17] Such a carbon network is predicted to show a negative Poisson's ratio, a rather unusual mechanical property where the material expands laterally and increases its density when stretched.[17]



Scheme 1. A) Elusive tetraethynylallene **1**. B) Synthesis of DEA (±)-**2a**. Reagents and conditions: a) $[Pd(PPh_3)_4]$, CuI, $HNiPr_2$, CH_2Cl_2, 25 °C; then $tBuMe_2SiCl$, imidazole, DMAP, 25 °C, 52%. DMAP = 4-(dimethylamino)pyridine.

In 1988, Alberts and Wynberg reported the isolation of a trimethylsilyl-protected 1,1,3-triethynylallene.[18] However, despite intensive synthetic efforts over the past 20 years, neither **1** nor any substituted derivative has ever been isolated.[19] Indeed, simpler 1,3-diethynylallenes (DEAs) also remained elusive until our research group reported the synthesis of the first stable DEA (±)-**2a**.[20] This DEA was prepared by a regioselective palladium-mediated S_N2'-type reaction, between the bispropargylic precursor (±)-**3a** and triisopropylsilylacetylene (**4**; Scheme 1 B).

The reaction depicted in Scheme 1 B is tolerant of changes in the structure of both the bispropargylic precursor and the terminal alkyne. The leaving group in the bispropargylic precursor can be an epoxide, a carbonate, or a carboxylate,[21] and the best results are obtained with a perfluorobenzoate.[22,23] The substituents of the bispropargylic starting material can be modified as well, in some cases, however, at the cost of a reduced stability of the resultant allene. For example, *n*-butyl and phenyl substituents afford DEAs that decompose easily,[21] and a 1,1-dimethyl-3-butenyl substituent reacts with the allenic core through an allenyl-Cope pathway.[24] Figure 2 summarizes the representative DEAs (±)-**2b–i** that have been prepared from suitable bispropargylic precursors by using a palladium-mediated S_N2'-type reaction.

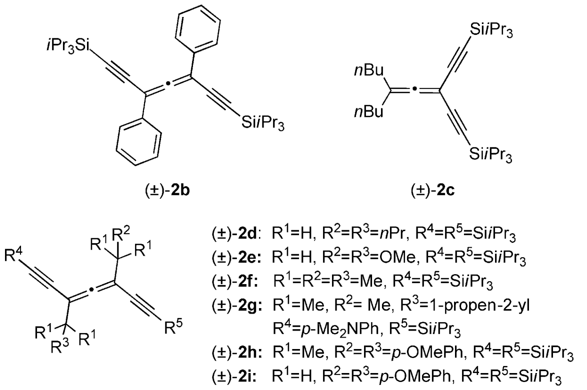


Figure 2. Representative examples of DEAs (±)-**2b–i** that have been prepared by a palladium-mediated S_N2'-type reaction between bispropargylic precursors and terminal alkynes.

2.2. 1,3-Diethynylallenes: Resolution of Enantiomers or Enantioselective Synthesis?

One of the most attractive features of DEAs is their chirality. The first attempt to resolve enantiomers of a DEA was to use HPLC and a chiral stationary phase (CSP). The

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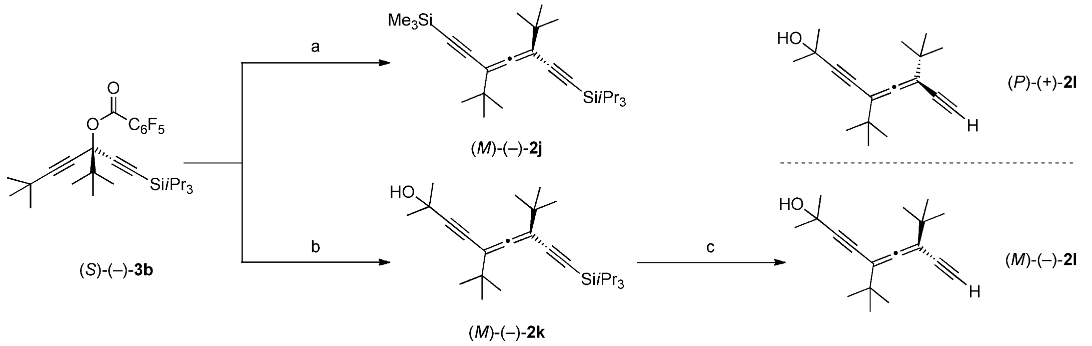
Pablo Rivera-Fuentes was born in 1984 in Mexico City, where he obtained a BSc in chemical engineering from the National Autonomous University of Mexico. He subsequently moved to ETH Zurich, where he obtained a MSc in chemistry under the supervision of Prof. François Diederich. Since 2009, he has been a PhD student in the same group, working on the design and synthesis of enantiopure alleno-acetylenic molecules.



Scheme 2. Enantioselective synthesis of DEAs. Reagents and conditions: a) Trimethylsilylethyne, $[Pd(PPh_3)_2Cl_2]$, CuI, $HNiPr_2$, dichloroethane, 20 °C, 20 h, 90% (e.r. 95:5); b) 2-methyl-3-butyn-2-ol, $[Pd(PPh_3)_2Cl_2]$, CuI, $MeNCy_2$, 1,2-dichloroethane, 30 °C, 96 h, 69% (e.r. 96:4); c) nBu_4NF, wet THF, 20 °C, 1 h, 90%. Cy = Cyclohexyl.

resolution of DEA (±)-**2h** (Figure 2) and other derivatives was attempted under several different conditions, but was unsuccessful.[23] Eventually, it was found to be possible to separate a derivative of (±)-**2h** bearing unprotected alkynes by using HPLC-SMB (SMB = simulated moving bed) techniques.[25] Nevertheless, the possibility of obtaining enantiopure DEAs by stereoselective synthesis was explored.[23,26]

The enantiomerically enriched DEAs (*M*)-(−)-**2j** and (*M*)-(−)-**2k** were prepared by a palladium-mediated S_N2'-type reaction using the optically pure bispropargylic ester (*S*)-(−)-**3b** (Scheme 2). Removal of the $SiiPr_3$ group of (*M*)-(−)-**2k** afforded DEA (*M*)-(−)-**2l**, which can be resolved with an enantiomeric ratio (e.r.) of 100:0 by using HPLC and the CSP Chiralpak IA (the (*P*)-(+)-**2l** enantiomer was obtained in an equivalent manner).[26] The absolute configuration of the product was established by X-ray analysis of a derivative of (*M*)-(−)-**2j**,[26] and later confirmed by comparison of the experimental electronic circular dichroism (ECD) spectrum with that obtained by simulation using time-dependent density functional theory (TD-DFT) calculations.[27]

The CSP Chiralpak IA can also be used to perform preparative separations of racemate (±)-**2l.** Inspired by this result, we developed a four-step high-yielding synthesis of (±)-**2l** starting from commercially available materials,[28] followed by HPLC resolution to give (*P*)-(+)-**2l** and (*M*)-(−)-**2l** in e.r. 100:0. This method is clearly more convenient than the enantioselective synthesis route because both enantiomeric building blocks are obtained in an enantiomerically pure form, and less synthetic operations are involved.

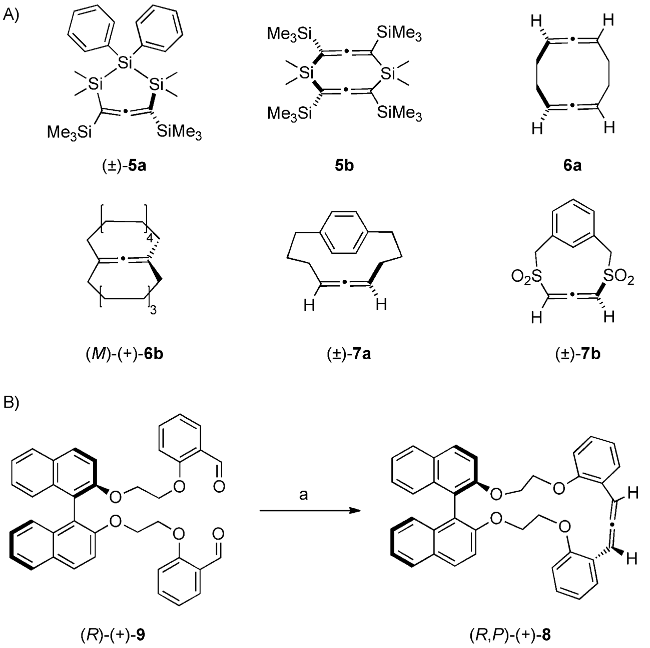
3. Allenophanes and Alleno-Acetylenic Macrocycles

Large cyclic molecules with conjugated backbones and shape-persistent geometries are among the most sought-after structures in chemistry. Comprehensive reviews have been written about their preparation,[29,30] their use as models and precursors of 2D polymers,[31] their "carbomeric" nature,[32] their application in rationally designed advanced materials,[33] and their nanoscopic dimensions.[34,35] Given the popularity of shape-persistent macrocycles, it is not surprising that some of the first allenic molecular materials prepared were macrocyclic structures.

Both historically and conceptually, allenic macrocycles can be divided into allenophanes (allenic macrocycles incorporating aromatic rings in the backbone) and alleno-acetylenic macrocycles (without any rings in the backbone).[36] In the following subsections, we will discuss their development and their fundamentally different properties and applications.

3.1. Allenophanes

Before the concept of allenophane appeared in the literature, there were many reports of allene-containing medium-sized rings and macrocycles. Some representative examples include strained silacycloallenes (±)-**5a** and **5b**,[37,38] *meso*-bisallene **6a**,[39,40] optically active doubly bridged allene (*M*)-(+)-**6b**,[41] paracyclophane (±)-**7a**,[42] and metacyclophane (±)-**7b** (Scheme 3A).[43] An interesting compound is



Scheme 3. A) Early examples of allene-containing medium-sized rings and macrocycles. B) Synthesis of macrocyclic allene (*R*,*P*)-(+)-**8**. Reagents and conditions: a) $[Ti(OiPr)_2Cl_2]$, $(Me_2N)_3P{=}CH_2$, $NaN(SiMe_3)_2$, THF, 25 °C, 10 h. THF = tetrahydrofuran.

macrocyclic allene (*R*,*P*)-(+)-**8**, which was prepared from the dialdehyde (*R*)-(+)-**9** (Scheme 3B).[44] The reaction with enantiopure starting material yields a mixture of diastereoisomers that can be separated by column chromatography, and the absolute configuration of the major isomer (*R*,*P*)-(+)-**8** was established by X-ray analysis. Remarkably, the chiroptical properties of (*R*,*P*)-(+)-**8** resemble those of (*P*)-1,3-diphenylallene, which means that the contribution of the binaphthyl unit is completely overshadowed by the allenic unit.

Krause and co-workers reported the synthesis of the first "true" allenophane **10** in 1999 (Figure 3).[45] The synthesis consisted of a series of Sonogashira-type coupling and copper-mediated S_N2'-type reactions. Since these steps are not stereoselective, **10** was obtained as a complex mixture of stereoisomers, including the chiral (*P*,*P*,*P*,*P*)/(*M*,*M*,*M*,*M*)- (Figure 3) and (*P*,*P*,*P*,*M*)/(*M*,*M*,*M*,*P*)-configured racemates, and the two achiral (*P*,*P*,*M*,*M*) and (*P*,*M*,*P*,*M*) isomers. Attempts to separate these compounds by HPLC failed because of their poor solubility.

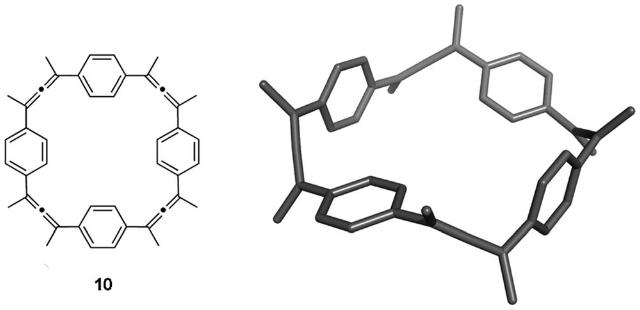

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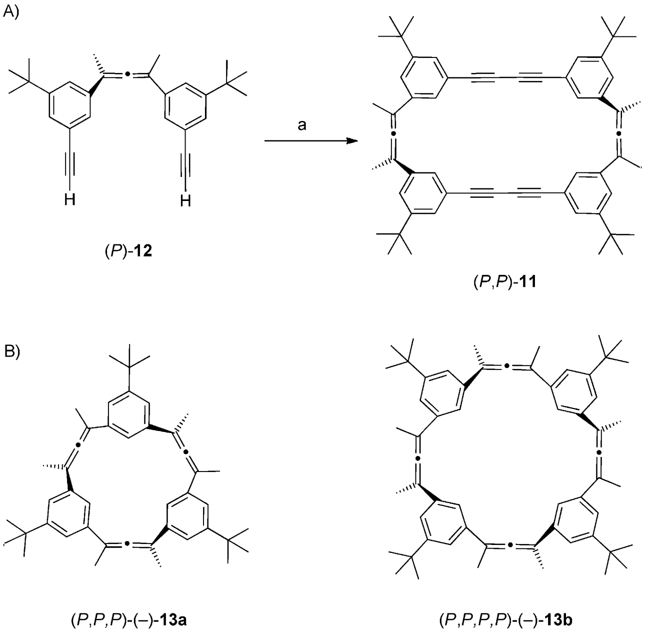
Figure 3. Chemical structure of allenophane **10** and 3D representation of racemate (*P*,*P*,*P*,*P*)/(*M*,*M*,*M*,*M*)-**10**. The 3D structure was optimized at the PM6 level of theory.

The first optically active allenophane (*P*,*P*)-**11** was prepared by Clay and Fallis in 2005.[46] The last step of the synthesis involved the dimerization/macrocyclization of optically enriched (e.r. 92:8) building block (*P*)-**12** (Scheme 4A). The ECD spectrum of (*P*,*P*)-**11** displays intense Cotton effects around 260 nm ($\Delta\varepsilon = +90\,\mathrm{M}^{-1}\,\mathrm{cm}^{-1}$) and 240 nm ($\Delta\varepsilon = -100\,\mathrm{M}^{-1}\,\mathrm{cm}^{-1}$). However, these intensities are essentially the same as those of (*P*)-1,3-diphenylallene,[47] which suggests that the chiroptical properties of allenophanes are not necessarily more intense than those of the constituent allenes.

Leclère and Fallis reported *meta*-allenophanes (*P*,*P*,*P*)-(−)-**13a** and (*P*,*P*,*P*,*P*)-(−)-**13b** (Scheme 4B).[48] Although these allenophanes are very unstable, the ECD spectra were measured, and showed Cotton effects around 260 nm (($\Delta\varepsilon = +20\,\mathrm{M}^{-1}\,\mathrm{cm}^{-1}$) for (*P*,*P*,*P*,*P*)-(−)-**13b** and ($\Delta\varepsilon = +5\,\mathrm{M}^{-1}\,\mathrm{cm}^{-1}$) for (*P*,*P*,*P*)-(−)-**13a**).

Several allenophanes have been synthesized using the DEA building block (±)-**21**. An example is a mixture of allenic anthracenophanes, comprising the (*P*,*P*,*P*,*P*)/(*M*,*M*,*M*,*M*)-**14** (Figure 4) and (*P*,*P*,*P*,*M*)/(*M*,*M*,*M*,*P*)-configured racemates, and achiral (*P*,*M*,*P*,*M*) and (*P*,*P*,*M*,*M*) stereoisomers (not shown).[22] Unlike allenophanes **13**, the allenic anthracenophanes are thermally and chemically fairly stable.



Scheme 4. A) Dimerization/macrocyclization reaction to form allenophane (*P*,*P*)-**11**. Reagents and conditions: a) $\mathrm{Cu(OAc)_2}$, pyridine/$\mathrm{Et_2O}$ 3:1, 20°C, slow addition of (*P*)-**12** over 6 h, 2 h, 40%. B) Trimeric and tetrameric allenophanes (*P*,*P*,*P*)-(−)-**13a** and (*P*,*P*,*P*,*P*)-(−)-**13b**.

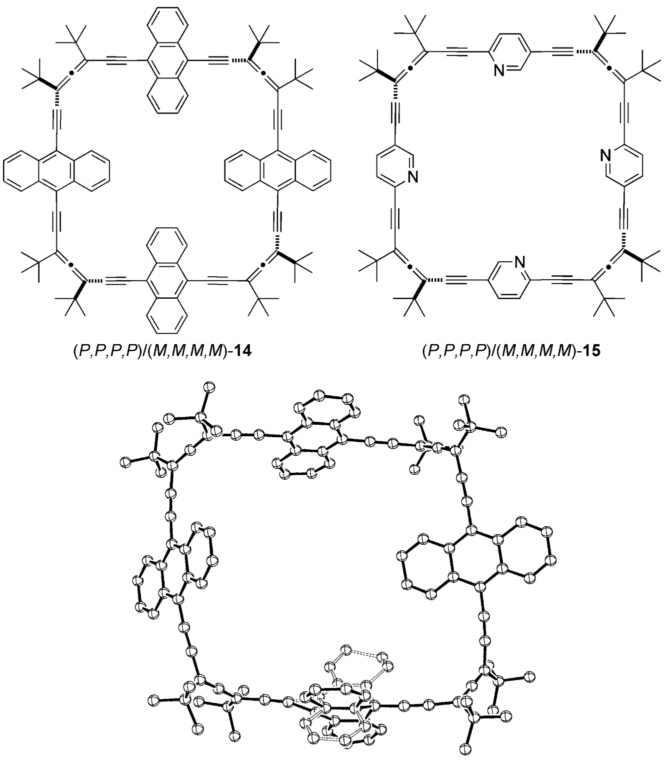


Figure 4. Top: Structures of (*P*,*P*,*P*,*P*)/(*M*,*M*,*M*,*M*)-configured allenophanes **14** and **15**. Bottom: X-ray crystal structure of (*P*,*P*,*P*,*P*)/(*M*,*M*,*M*,*M*)-**14.** Solvent molecules and hydrogen atoms are omitted for clarity; atomic displacement parameters obtained at 220 K are drawn at the 50% probability level.

The two racemates and the two achiral stereoisomers were separated by HPLC, and a crystal of racemate (*P*,*P*,*P*,*P*)/

(*M*,*M*,*M*,*M*)-**14** suitable for X-ray analysis was obtained (Figure 4). Unfortunately, the racemates could not be resolved. Irradiation of any pure diastereoisomer with daylight led to a (photostationary) equilibrium mixture of stereoisomers, resulting from photoisomerization by rotation around the double bonds of the allene moieties. It has been observed that electron donors (such as the anthracene moieties in **14**) can act as intramolecular sensitizers to promote the clean photoracemization of allenes.[26,49,50]

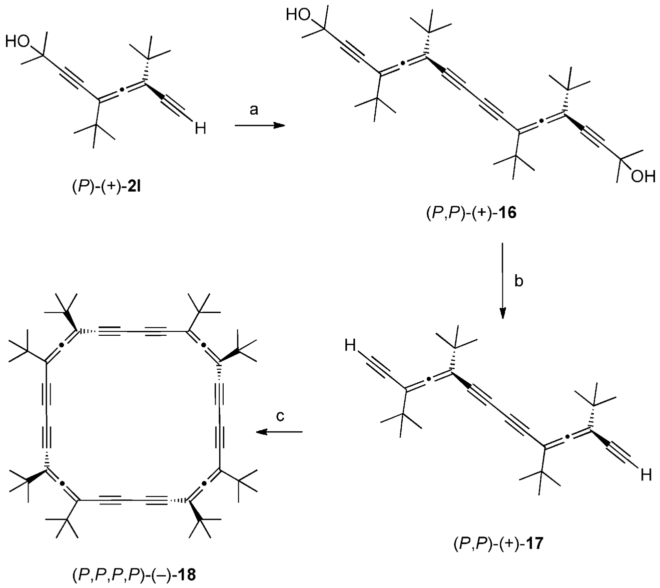
Recently, Cid and co-workers reported the synthesis of a mixture of chiral allenophanes with four pyridine-2,5-diyl spacers in the backbone (**15** in Figure 4).[51] The two racemates and two achiral stereoisomers, as in the case of the anthracenophanes, were separated by HPLC techniques and their structures assigned through their symmetry by using ^{13}C NMR spectroscopy. In addition, racemic (*P*,*P*,*P*,*P*)/(*M*,*M*,*M*,*M*)-**15** could be resolved and their qualitative ECD spectra measured. The racemic mixture of the (*P*,*M*,*M*,*M*)/(*M*,*P*,*P*,*P*) isomer was treated with [Re(CO)$_5$Br] to generate a coordination complex; however, NMR spectroscopy revealed that the metal coordinates to only one of the pyridine moieties and seems to be placed outside of the macrocycle instead of inside the cavity. This study revealed the potential of allenophanes as chiral ligands for coordination chemistry, although ideal combinations of metals and allenophanes are yet to be found.

3.2. Alleno-Acetylenic Macrocycles: Outstanding Chiroptical Properties

Our research group reported in 2005 the first alleno-acetylenic macrocycle without aromatic rings in the backbone.[22] The macrocycle was prepared as a mixture of stereoisomers and HPLC techniques enabled the separation of the two racemates and three achiral diastereoisomers formed. Unfortunately, only one of the racemates could be structurally assigned by NMR spectroscopy, while the other stereoisomers could not be identified. In addition, the racemates could not be resolved.

No information about the chiroptical properties of alleno-acetylenic macrocycles was reported until 2009, when an enantiomerically pure alleno-acetylenic macrocycle was described.[52] Starting from optically pure (*P*)-(+)-**21**, the protected dimer (*P*,*P*)-(+)-**16** was prepared by oxidative homocoupling. A subsequent deprotection gave dimer (*P*,*P*)-(+)-**17**, which was subjected to a one-pot dimerization/cyclization reaction to afford macrocycle (*P*,*P*,*P*,*P*)-(−)-**18** in good yield (Scheme 5). The enantiomer (*M*,*M*,*M*,*M*)-(+)-**18** was prepared in a similar manner starting from enantiopure (*M*)-(−)-**21**.

The D_4-symmetric crown structure of (*P*,*P*,*P*,*P*)-(−)-**18** was first assigned by ^{1}H NMR, ^{13}C NMR, and IR spectroscopy, as well as high-resolution MALDI mass spectrometry,[52] and later confirmed by X-ray analysis (Figure 5).[53] Subsequently, all the stereoisomers of **18** were prepared and isolated, including the enantiopure, twist (*P*,*M*,*M*,*M*)-(+)-**18** and (*M*,*P*,*P*,*P*)-(−)-**18**, the achiral, chair (*P*,*P*,*M*,*M*)-**18**, and boat (*P*,*M*,*P*,*M*)-**18** stereoisomers (Figure 5).[53]



Scheme 5. Synthesis of macrocycle (*P*,*P*,*P*,*P*)-(−)-**18**. Reagents and conditions: a) [Pd(PPh$_3$)$_2$Cl$_2$], CuI, TMEDA, toluene, 50 °C, 24 h, 99%; b) NaOH, toluene, 90 °C, 10 h, 65%; c) CuCl, CuCl$_2$, pyridine, 20 °C, then addition of (*P*,*P*)-(+)-**17** over 20 h, 68%. TMEDA = *N*,*N*,*N*′,*N*′-tetramethylethylenediamine.

The ECD spectra of (*P*,*P*,*P*,*P*)-(−)-**18** and (*M*,*M*,*M*,*M*)-(+)-**18** showed remarkably intense Cotton effects at 253 nm ($\Delta\varepsilon = \pm 790\,\mathrm{M}^{-1}\,\mathrm{cm}^{-1}$). The Cotton effects of (*P*,*P*,*P*,*P*)-(−)-**18** are one order of magnitude greater than those of (*P*,*P*,*P*,*P*)-(−)-**13b** (Scheme 4). This observation is striking, if we consider that the only differences between the two compounds are the (achiral) spacers (butadiyne in **18** and phenyl in **13b**) and the (achiral) substituents on the allenes (*tert*-butyl in **18** and methyl in **13b**). With the aid of TD-DFT calculations, it was found that the origin of the outstanding chiroptical properties of (*P*,*P*,*P*,*P*)-(−)-**18** lies in the topologies of the frontier molecular orbitals,[53] which are radically different in allenophanes.

The synthesis of enantiopure alleno-acetylenic cyclo-oligomers (*P*,*P*,*P*)-(−)-**19**, (*P*,*P*,*P*,*P*)-(−)-**18**, (*P*,*P*,*P*,*P*,*P*)-(+)-**20**, and (*P*,*P*,*P*,*P*,*P*,*P*)-(+)-**21** (and their enantiomers) was performed to establish structure–chiroptical properties relationships (Figure 6).[28] Crystals of racemic (*P*,*P*,*P*)/(*M*,*M*,*M*)-**19** and enantiopure (*M*,*M*,*M*,*M*,*M*,*M*)-(−)-**21** suitable for X-ray analysis were obtained (Figure 6).

The UV/Vis and ECD spectra were measured for these cyclooligomers (Figure 7). While the intensity of the UV/Vis absorptions in the 350–270 nm region increases with the number of DEAs in the macrocycles, the ECD intensity in the same region increases from (*P*,*P*,*P*)-(−)-**19** to (*P*,*P*,*P*,*P*)-(−)-**18**, but decreases from (*P*,*P*,*P*,*P*)-(−)-**18** to larger cyclooligomers.[28] The *g*-factor plot ($g = \Delta\varepsilon/\varepsilon$),[54,55] NMR and Raman spectroscopy, and molecular dynamics calculations showed that conformational flexibility increases in larger cyclooligomers and leads to a decrease in the ECD intensity. Moreover, cyclooligomers (*P*,*P*,*P*,*P*,*P*)-(+)-**20** and (*P*,*P*,*P*,*P*,*P*,*P*)-(+)-**21** adopt conformations that are less symmetric (C_1 and C_2 symmetric, respectively) than (*P*,*P*,*P*)-(−)-

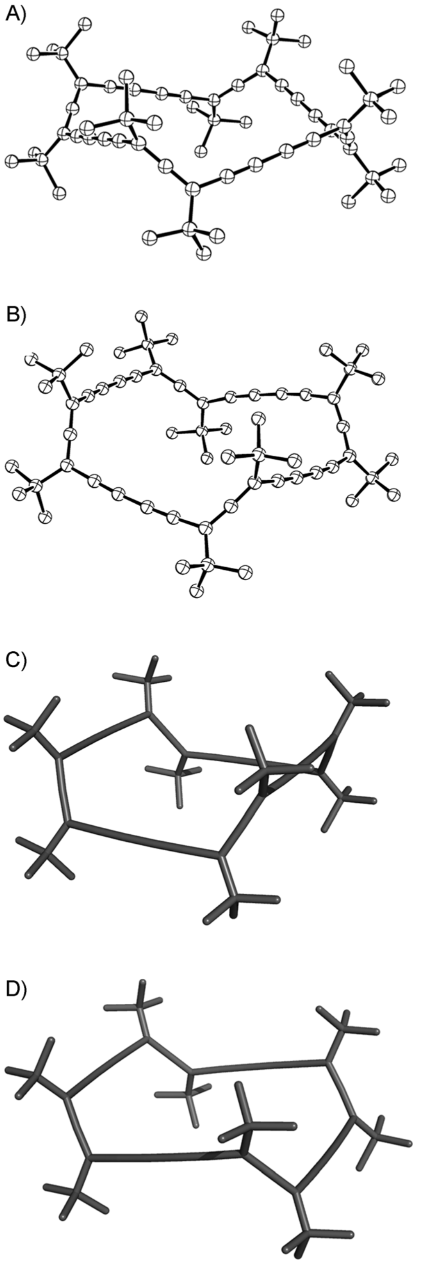


Figure 5. Stereoisomers of **18**. A) (*P*,*P*,*P*,*P*)-(−)-**18**; B) (*M*,*M*,*M*,*P*)-(−)-**18**; C) achiral isomer (*P*,*M*,*P*,*M*)-**18**; D) achiral isomer (*P*,*P*,*M*,*M*)-**18**. The structures of the two chiral macrocycles were obtained by X-ray diffraction of racemic crystals. Solvent molecules and hydrogen atoms are omitted for clarity; atomic displacement parameters obtained at 260 K (for (*P*,*P*,*P*,*P*)/(*M*,*M*,*M*,*M*)-**18**) and 220 K (for (*P*,*P*,*P*,*M*)/(*M*,*M*,*M*,*P*)-**18**) are drawn at the 50% probability level. The structures of the achiral isomers were optimized at the B3LYP/6-31G* level of theory.

19 and (*P*,*P*,*P*,*P*)-(−)-**18** (D_3 and D_4 symmetric, respectively). It was found that the transition dipole moments that give rise to ECD are optimally aligned in molecules with D_n symmetries.[28] This study demonstrated the importance of shape persistency and molecular symmetry in the chiroptical properties of carbon-rich compounds.

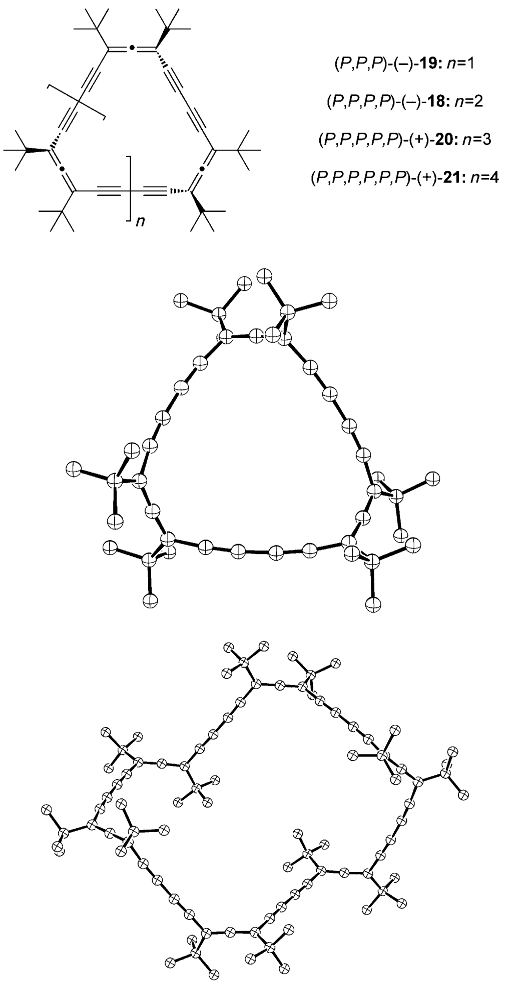


Figure 6. Top: Enantiopure alleno-acetylenic cyclooligomers **18**–**21** obtained by oxidative homocoupling/macrocyclization. Bottom: X-ray crystal structures of racemic (*P*,*P*,*P*)/(*M*,*M*,*M*)-(±)-**19** and enantiopure (*M*,*M*,*M*,*M*,*M*,*M*)-(−)-**21**. Solvent molecules and hydrogen atoms are omitted for clarity; atomic displacement parameters obtained at 100 K are drawn at the 50% probability level.

4. Allene-Containing Oligomers and Polymers

Chiral oligomers and polymers are interesting structures with many applications in sensing, optics, and electronics.[56] The geometry of oligomers and polymers can be controlled by a number of factors, including conformational preferences of the backbone, intrastrand interactions, solvophobic effects, and metal-ion coordination.[57] Chirality can be induced in oligomers and polymers by attaching chiral side chains to the otherwise achiral monomers, by chiral arrangement of an achiral backbone induced by a single chiral unit (sergeant-and-soldiers principle),[58] or by polymerization of chiral monomers.[59] It is clear that the nature of the monomer determines the properties of the oligomer or polymer to a great extent, and innovation in this field relies greatly on the development of novel chiral monomers.

Oligomers and polymers containing allenes in the main chain are extremely rare. A possible reason is that the allene moiety itself participates in many polymerization processes, especially those involving insertion of transition metals,[60]

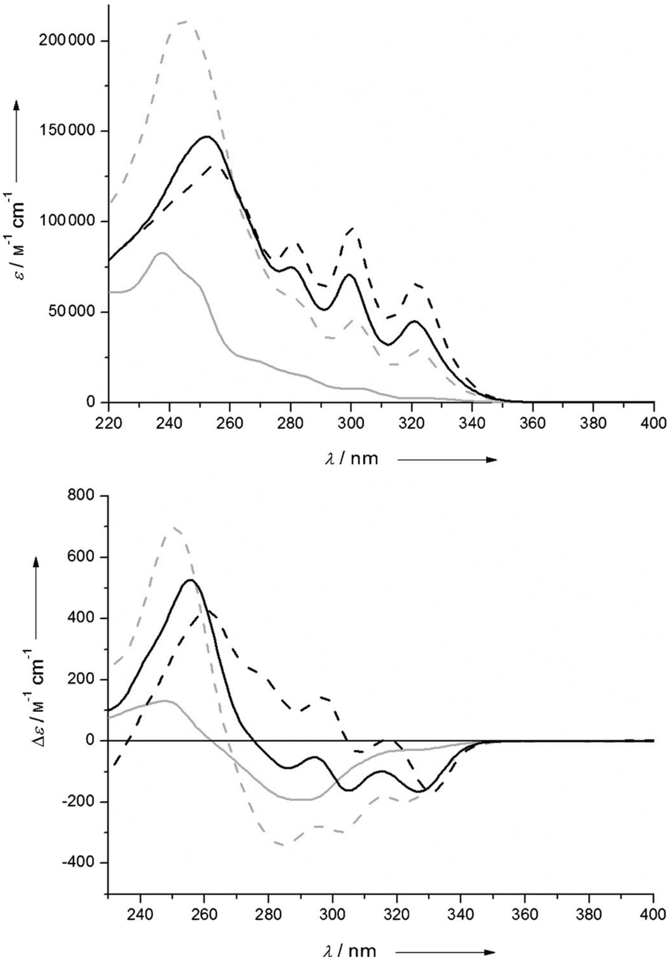
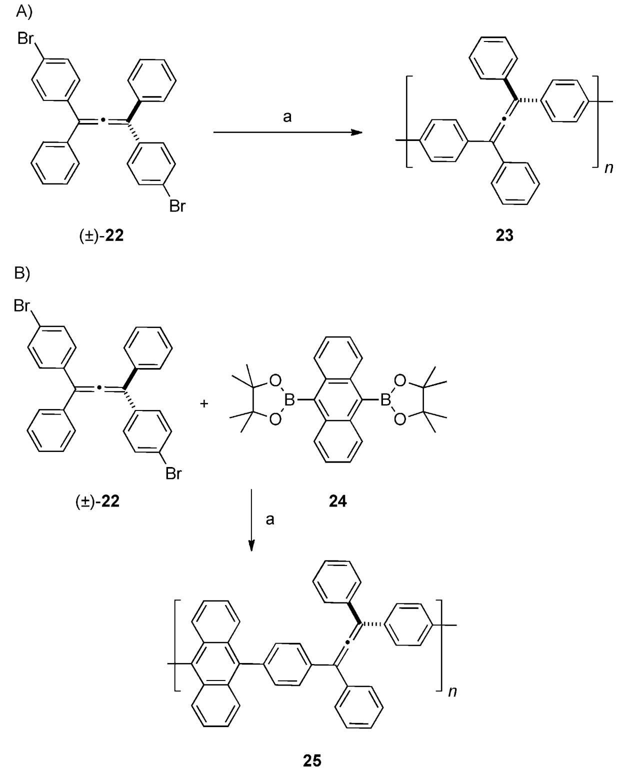


Figure 7. UV/Vis (top) and ECD (bottom) spectra of alleno-acetylenic cyclooligomers in *n*-hexane (10^{-6} M), $T = 25\,°C$: (*P,P,P*)-(−)-**19** (gray solid line), (*P,P,P,P*)-(−)-**18** (gray dashed line), (*P,P,P,P,P*)-(+)-**20** (black solid line), and (*P,P,P,P,P,P*)-(+)-**21** (black dashed line).

and living coordination polymerization.[61] Interestingly, higher cumulenic units were successfully polymerized before the first allene-containing polymer was reported. Some examples include polydisperse oligomers based on hexapentaene[62] and butatriene.[63,64]

The first π-conjugated allene polymer was reported by Kijima et al. in 2002.[65] The synthesis involved the nickel-mediated polymerization of the stable allenic building block (±)-**22** to give compound **23** as a mixture of stereoisomers (Scheme 6 A). This polymer showed high solubility and good processability, but a low average molecular weight (5000 g mol^{-1}) and broad polydispersity. Some other interesting properties of **23** include a strong blue fluorescence in solution upon irradiation with UV light, with a quantum efficiency of 0.29. Protonation with trifluoroacetic acid (TFA) induced a shift in the absorption, from $\lambda_{max} = 310$ nm to $\lambda_{max} = 700$ nm, possibly because of the formation of allylic carbocations,[66] thereby leading to a fully conjugated backbone. This hypothesis is supported by the fact that the conductivity of the polymer increased from 10^{-7} S cm^{-1} to 10^{-3} S cm^{-1} upon exposure of the film to TFA vapor.[65]



Scheme 6. A) Synthesis of polymer **23**. Reagents and conditions: a) [Ni(cod)$_2$], 2,2′-bipyridine, *N,N*-dimethylformamide, 60 °C, 48 h, 84 %. B) Synthesis of polymer **25**. Reagents and conditions: a) [Pd(PPh$_3$)$_4$], NaOH (2 M in H$_2$O), THF, reflux. cod = cyclooctadiene.

A related polymer reported by Hiroki and Kijima was obtained from a Suzuki–Miyaura reaction between 9,10-dibororanylanthracene **24** and (±)-**22** to give compound **25** (Scheme 6 B).[67] This copolymer also showed high solubility and good processability, as well as strong blue fluorescence when irradiated with UV light. The quantum yield was near to 1.0, which is a consequence of the suppression of excimeric radiative processes by the twisted (helical) conformation of **25**. Unfortunately, **25** was prepared from racemic (±)-**22**, which generates a mixture of stereoisomers and the chiroptical properties could not be determined. A potential chiroptical property of enantiopure **25** could be the emission of circularly polarized light.[68]

After the report of the first stable DEA building block in 2001,[20] it was proposed that enantiopure, open-chain oligomers of DEA could fold into helical conformations with a single handedness. In 2007, our research group reported the oligomerization of a racemic DEA.[23] Monodisperse oligomers were obtained as complex mixtures of stereoisomers after gel-permeation chromatography (for related structures, see Figure 8). However, ^{1}H and ^{13}C NMR spectroscopy does not differentiate between the diastereoisomers in a given fraction of monodisperse oligomer: only one set of resonances (as would be expected for a single diastereoisomer) was obtained. Furthermore, separation of the diastereoisomers was unsuccessful. Interestingly, UV/Vis spectroscopy showed only a modest bathochromic shift in the absorption maxima when going from monomeric DEA to monodisperse decamer,

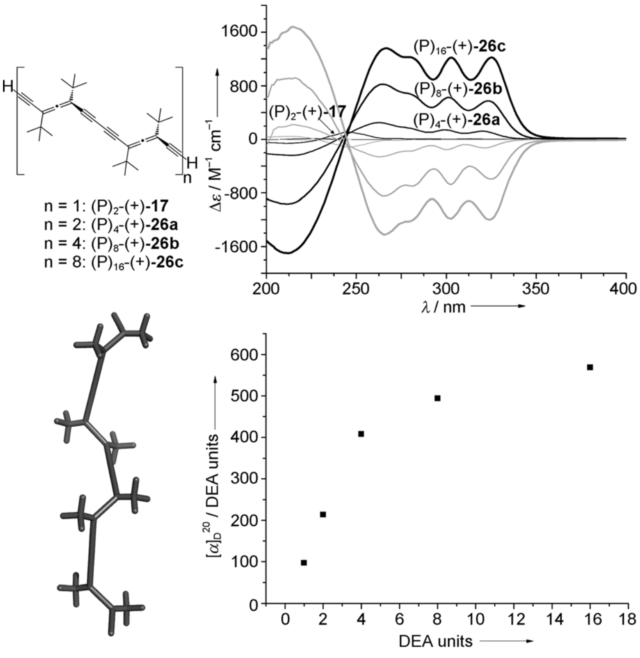


Figure 8. Top left: Structures of monodisperse, enantiopure oligomers **17** and **26 a–c**. Top right: ECD spectra of **17** and **26 a–c** in *n*-hexane, $T = 25\,^\circ$C; black lines = *P*-configured enantiomers, gray lines = *M*-configured enantiomers. Bottom right: Nonlinear increase in the optical rotation $[\alpha]_D^{20}$ in $CHCl_3$, $T = 25\,^\circ$C, as a function of the oligomer length. Bottom left: One structure of $(P)_4$-(+)-**26 a** out of a family of many similar ones with the same helical chirality, proposed by comparison of the calculated and experimental ECD and ORD data.

which reveals the poor electronic communication across the central cumulenic carbon atom of the allene chromophores. This spectral behavior is in sharp contrast with that observed for oligomers with efficiently conjugated π backbones.[69]

In 2010, we reported the synthesis of enantiopure, monodisperse, acyclic alleno-acetylenic oligomers.[70] A strategy of partial deprotection of the terminal alkynes and oxidative homocoupling starting from $(P)_2$-(+)-**16** (see Scheme 5) provided monodisperse tetramer $(P)_4$-(+)-**26 a**, octamer $(P)_8$-(+)-**26 b**, and hexadecamer $(P)_{16}$-(+)-**26 c** (and their corresponding enantiomers). ECD spectroscopy and optical rotation (Figure 8) revealed a nonlinear increase in the intensity of the chiroptical properties as the oligomers grew, thus indicating the formation of an ordered chiral secondary structure. Oligomer $(P)_{16}$-(+)-**26 c** displays a strong Cotton effect around 212 nm ($\Delta\varepsilon = -1690\,\mathrm{M}^{-1}\mathrm{cm}^{-1}$), one of the largest values ever reported.[71] A helical conformation of oligomers **26 a–c** was assigned on the basis of the ECD spectrum and optical rotatory dispersion (ORD), as well as TD-DFT calculations (Figure 8).[70]

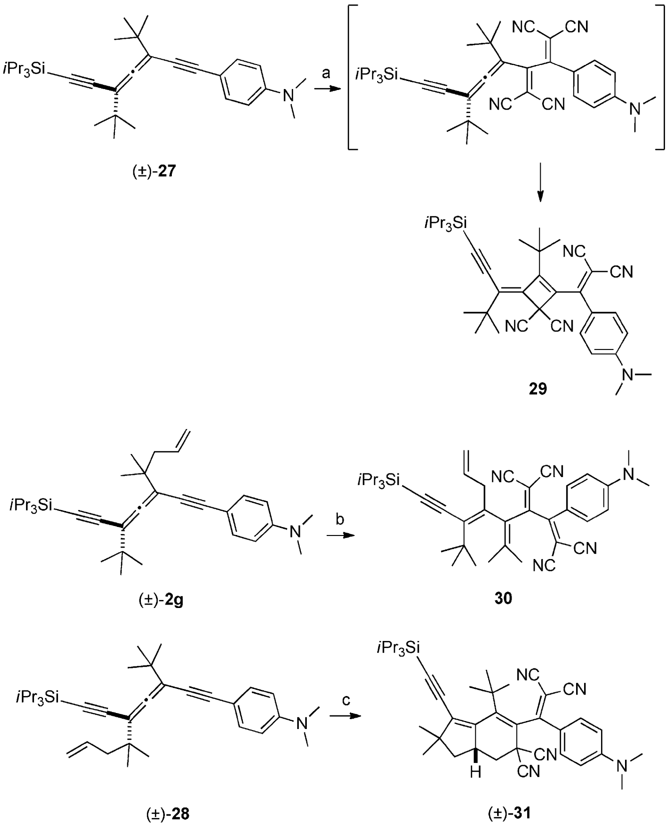
5. Other Allene-Based Molecular Materials

Examples of other exciting applications of chiral chromophores in advanced functional materials are the induction of chirality in metal complexes,[72] chiral sensing,[73] redox-triggered chiral switches,[74] chiral magnets,[75] amplification of chirality in liquid-crystalline phases,[76,77] and nonplanar push-pull chromophores.[78]

Early examples of push-pull allenes are those reported by Saalfrank.[79,80] The reactivity of these allenes was studied in detail, but their optical properties or potential applications were not investigated. Our research group reported the synthesis and optical resolution leading to enantiopure allenic charge-transfer chromophores in 2008.[26] These compounds were obtained using bis(*N*,*N*-dimethylanilino)-substituted DEAs, which reacted with tetracyanoethane (TCNE) in a cascade of formal [2+2] cycloaddition, followed by cycloreversion (CA/CR),[78] to afford allenyltetracyanobutadienes. ECD studies and TD-DFT calculations confirmed that the Cotton effects observed around 500 nm are a consequence of chiral induction from the allene into the sterically crowded tetracyanobutadiene.[27]

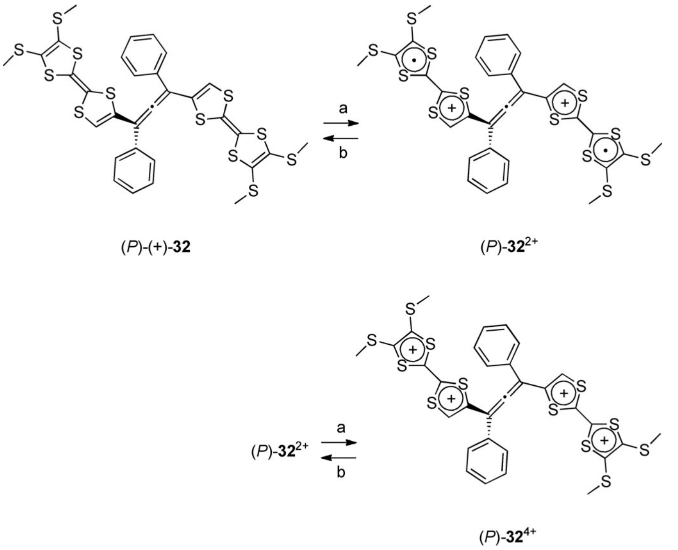
It was also shown that DEAs (±)-**2 g**, (±)-**27**, and (±)-**28** (Scheme 7) react with TCNE to form transient tetracyanobutadienes that further rearrange into complex carbon skeletons through very selective pericyclic reactions. These transformations include 4π electrocyclization (→**29**), allenyl-Cope rearrangement (→**30**), and Diels–Alder reactions (→(±)-**31**; Scheme 7).[24]

Hasegawa, Mazaki et al. recently reported the first redox-switchable, enantiopure, allene-based chromophore.[50] Tetrathiafulvalenylallene (±)-**32** was prepared using a palladium-



Scheme 7. Reactions of substituted DEAs with TCNE. Reagents and conditions: a) TCNE, TFA, 1,2-dichloroethane, 60 °C, 4 h, 60 %; b) TCNE, 1,2-dichloroethane, 90 °C, 1 h, 90 %; c) TCNE, CH_2Cl_2, 25 °C, 30 min, 98 %. TCNE = tetracyanoethylene, TFA = trifluoroacetic acid.

mediated S_N2'-type reaction of a racemic propargylic precursor, and the enantiomers (*P*)-(+)-**32** and (*M*)-(−)-**32** were resolved by preparative HPLC on a CSP. The absolute configuration of these new allene chromophores was assigned by comparing the experimental ECD spectrum with that obtained by TD-DFT simulation. Chemical oxidation of (*P*)-(+)-**32** gave cations (*P*)-$\mathbf{32}^{2+}$ and (*P*)-$\mathbf{32}^{4+}$ (Scheme 8), which exhibit strong absorptions at low energies in the UV/Vis spectra.[50] In addition to electrochromism, enantiopure (*P*)-$\mathbf{32}^{2+}$ and (*M*)-$\mathbf{32}^{2+}$ display mirror-image ECD spectra, with new Cotton effects around 700 nm, while (*P*)-$\mathbf{32}^{4+}$ and (*M*)-$\mathbf{32}^{4+}$ show additional bisignate Cotton effects in the same region of the spectrum.[50]



Scheme 8. Chemical redox switching of (*P*)-(+)-**32**. Reagents and conditions: a) $Fe(ClO_4)_3\cdot 6\,H_2O$, CH_2Cl_2/MeCN, 2 min; b) $H_2NNH_2\cdot H_2O$ (excess), CH_2Cl_2/MeCN.

Modern synthetic methods allow direct connection of electron donors and acceptors to the allene moiety. Some examples include the synthesis of allene-substituted porphyrins by Suzuki–Miyaura cross-coupling[81] and the preparation of cyano-substituted allenes,[82] trifluoromethylallenes,[83] and ferrocenylallenes.[84] These allenic donors and acceptors might exhibit interesting optoelectronic and chiroptical properties, and their functions and applications remain to be explored.

To the best of our knowledge, the only allene-containing dendrimer has been reported by Caminade, Majoral, and coworkers.[85] The allenes were introduced by chemoselective modification of the internal layers of a phosphorus-containing dendrimer. The presence of the allene moiety was confirmed by ^{13}C NMR spectroscopy and X-ray analysis. Although no further investigations have been carried out in this field, substituted allenes might be interesting building blocks for the construction of chiral dendrimers with novel topologies.

Tschierske and co-workers introduced enantiomerically enriched allenyl ethers[86] and acetates[87] into novel ferroelectric liquid crystals. Both classes of compounds exhibit chiral smectic C phases with moderate values of spontaneous polarization. One of the problems encountered was a gradual shift of the phase transition temperatures to lower values, as a result of decomposition of the allene moiety through a Claisen rearrangement.[87] Incorporation of more-stable allene units could improve the performance of these molecules in the induction of chiral liquid-crystalline phases.

6. Conclusions and Perspectives

The development of allene-based molecular materials has grown considerably in the last few years, mainly as a consequence of improved synthetic methods and a deeper understanding of the reactivity of the allenic core. The availability of enantiopure and stable allene building blocks allows access to increasingly complex materials, and also to well-defined molecular entities that can be used for physical-organic studies. Allenes are emerging as shape-persistent chiral chromophores, whose chiral properties are as good as those of benchmark axially chiral scaffolds.

Allenophanes are already being investigated as chiral ligands for metal complexes. Opportunities in this area include the development of ligands for asymmetric catalysis, chiral magnets, chiral sensors, and novel chiral metal-organic frameworks.[72] Alleno-acetylenic macrocycles display very intense and tunable circular dichroism, which has provided information about fundamental questions in the field of chiroptical properties. Acyclic allenic oligomers and polymers fold into helical conformations, and show enhanced optical properties, such as fluorescence emission, and intense chiroptical properties. They hold particular promise for circularly polarized luminescence, molecular recognition, and the formation of chiral supramolecular assemblies.[88,89] Attractive chiroptical properties of allene-based chiral push-pull chromophores and redox-triggered chiroptical switches might lead to future applications in organic molecular electronics.

Interestingly, the initial goal[16] of developing novel carbon allotropes based on allenes still remains. Nevertheless, efforts towards this aim continue, and include the quest for tetraethynylallene **1** and its corresponding polymeric form, the synthesis of shape-persistent alleno-acetylenic helical foldamers by covalently linking their side chains (resembling chiral carbon nanotubes), and the conjugation of DEAs and fullerenes to produce novel molecular carbon allotropes.

We gratefully acknowledge the European Research Council (ERC Advanced Grant No. 246637 "OPTELOMAC") for continuous support of this research. P.R.-F. thanks the Stipendienfonds der Schweizerischen Chemische Industrie (SSCI) for a doctoral fellowship. We thank Dr. Adam Lacy and Dr. Emmanouil Tzirakis (ETH Zurich) for comments on the manuscript.

Received: November 14, 2011

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