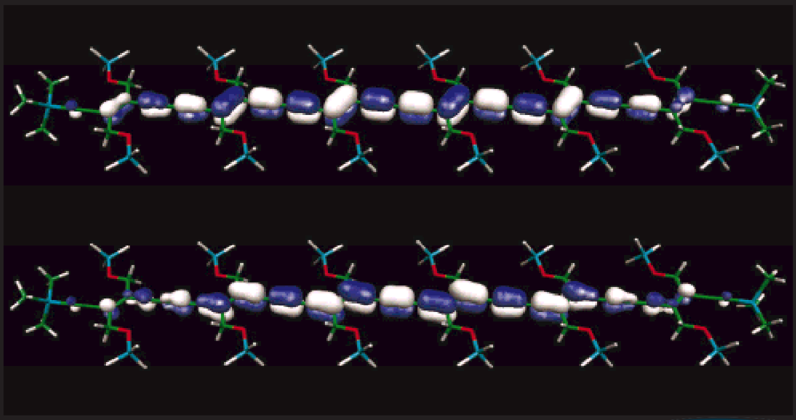
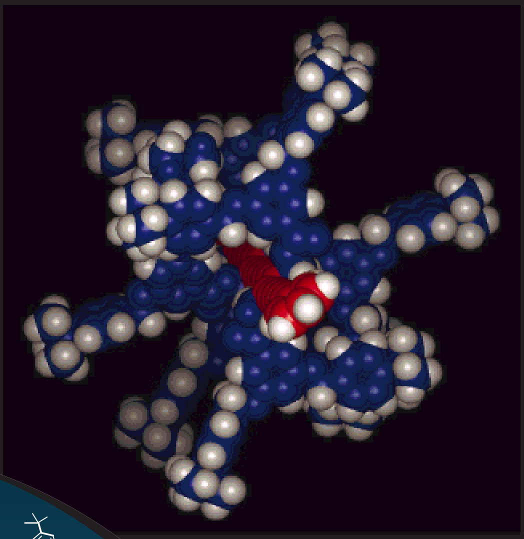
Linear monodisperse π-conjugated oligomers





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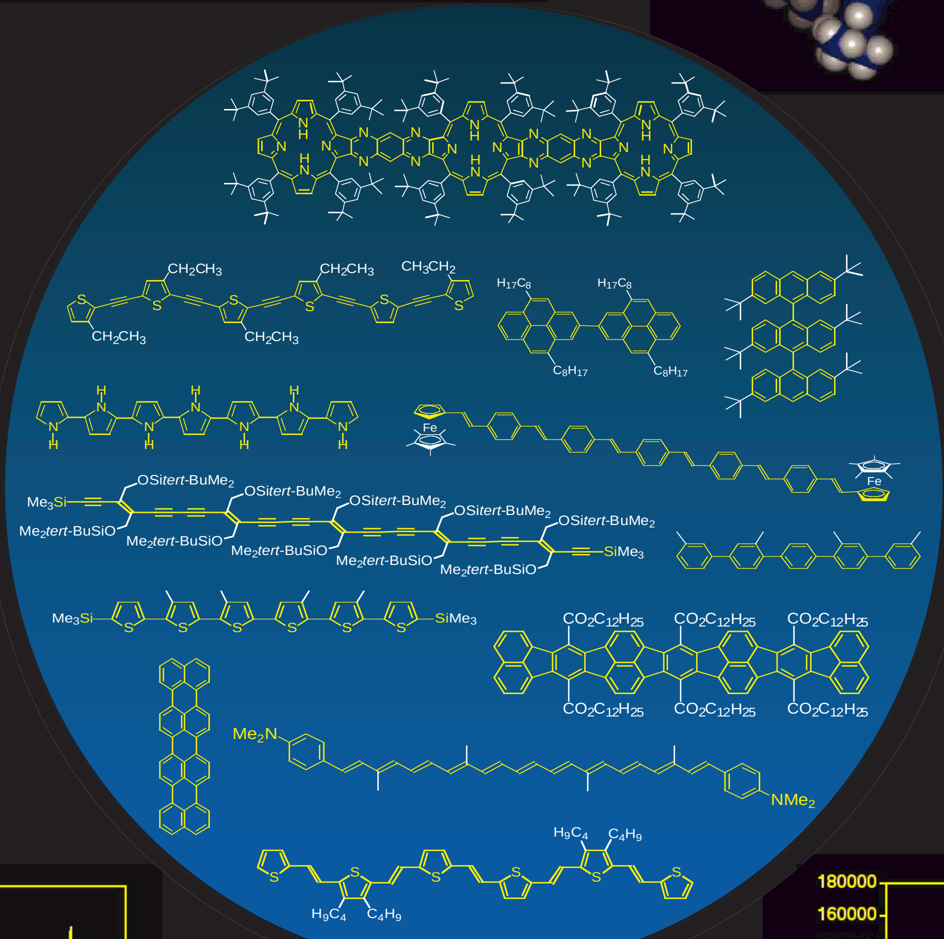

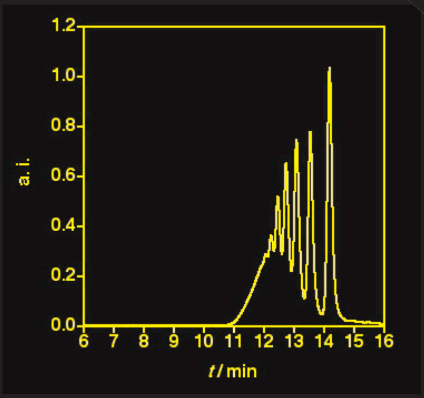

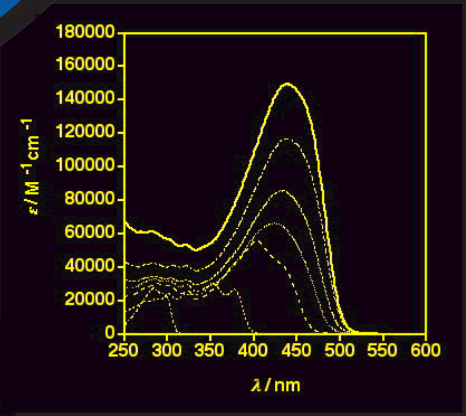

Structure – property relationships

Linear Monodisperse π-Conjugated Oligomers: Model Compounds for Polymers and More

Rainer E. Martin and François Diederich*

Dedicated to Professor Hans-Jürgen Quadbeck-Seeger on the occasion of his 60th birthday

Research on monodisperse π-conjugated oligomers has dramatically expanded during the past decade. It has been fueled by advances in synthetic methodology, such as the development of metal-catalyzed cross-coupling reactions, and by advances in analytical techniques that now allow an accurate characterization of linear π-conjugated molecular rods with lengths exceeding 10 nm. An initial target of this research was the development of structure–property relationships to rationalize the properties of known high molecular weight π-conjugated polymers, which are often poorly soluble and difficult to process, and to predict those of yet unrealized ones. However, in the meantime the study of well-defined monodisperse oligomers has advanced into a strong field of its own right, because of the promising electronic and optical properties of these compounds. Multinanometer-long π-conjugated oligomers are today seen as potential components in future molecular scale electronic devices, and their development has generated some spectacular molecular architecture. In this review, the recent progress achieved in the synthesis and characterization of monodisperse π-conjugated oligomers is illustrated by featuring some of the most predominant systems. The manifold contributions of oligomer systems to today's understanding of polymer properties are discussed with a particular focus on how molecular properties of oligomers converge with increasing chain length to yield those of the infinite polymers.

Keywords: conjugation · molecular wires · oligomers · polymers · structure–property relationships

1. Introduction

During the past decade the number of π-conjugated polymers investigated as advanced materials for electronic and photonic applications has developed rapidly, and has caused an ever increasing interest from both academic and industrial research laboratories. The inherent synthetic flexibility, potential ease of processing, and the possibility of tailoring characteristic properties to accomplish a desired function makes them promising candidates for manifold applications in materials science. Thus, they are used as laser dyes,[1] scintillators,[1] light-emitting diodes,[2] piezoelectric and pyroelectric materials,[3] photoconductors,[4] and are investigated for optical data storage,[5] optical switching and signal processing,[6] as well as in nonlinear optical applications.[7–9]

The direct analytical characterization and physical study of extended π-chain polymers with high molecular weight is often hampered by low solubility. Structural defects also represent a common obstacle towards obtaining sound physical data. Soluble, monodisperse (that is, with the same number of monomer units) oligomers as finite model systems offer the possibility to attain, by extrapolation, specific information concerning the electronic, photonic, thermal, and morphological properties of their corresponding polydisperse high molecular weight analogues.[10, 11] Furthermore, the systematic study of oligomers with precisely defined length, constitution, and conformation allows direct correlation of physical properties with chemical structures, and enables the generation of useful and predictive structure–property relationships. More recently, monodisperse oligomers have also been shown to be useful as model compounds for elucidating the folding properties of polymers.[12] However, limitations to this "oligomeric approach",[13] also exist and not all physical or chemical properties of high molecular weight polymers can be modeled with the corresponding smaller oligomers. For instance, macromolecules differ from smaller analogues both in their solution (for example, high viscosity, diffusion behavior) and solid-state properties (for

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[*] Prof. Dr. F. Diederich, Dr. R. E. Martin[+]
Laboratorium für Organische Chemie, ETH-Zentrum
Universitätstrasse 16, CH-8092 Zürich (Switzerland)
Fax: (+41) 1-632-1109
E-mail: diederich@org.chem.ethz.ch
[+] Current address:
Melville Laboratory for Polymer Synthesis
University of Cambridge, New Museums Site
Pembroke Street, Cambridge CB2 3RA (UK)

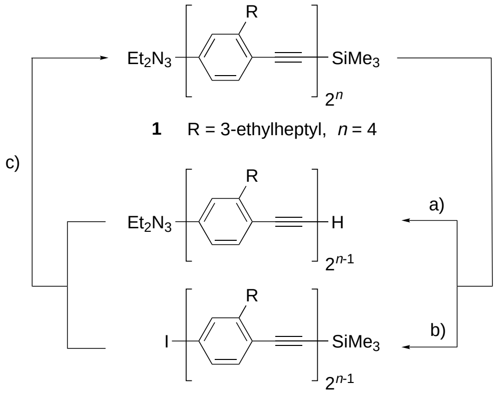
example, amorphous or semicrystalline structures), and such bulk effects are not likely to be reproduced by low molecular counterparts.[14]

A second interest in monodisperse π-conjugated oligomers of defined length and constitution arises from their potential to act as molecular wires in molecular scale electronics[15] and nanotechnological devices. A variety of spectacular molecular architecture has resulted from the efforts aimed at the construction of such wires. With the progress in synthetic organic methodology and the increasing availability of advanced analytical methods for the purification and characterization of very large molecules, monodisperse linear π-conjugated oligomers have recently reached the 10 nm length mark,[16] which is about the current resolution limit for microstructure manufacturing by state-of-the-art lithographic techniques.[17, 18] This achievement in organic synthesis has greatly stimulated the interest in the experimental[19–22] and theoretical[23] study of molecular scale mesoscopic devices. Although the fascinating concept of constructing a molecular computer based purely on organic molecules as an ultimate system[24] in terms of information storage density and speed still remains an impetuously discussed and exceptionally controversial item,[10] it is widely accepted that future nanoelectronic or nanophotonic processes will likely require π-conjugated molecular rods of defined length as key components for ultradense and ultrafast information transportation, processing, and storage.[10, 11, 16]

The emphasis of this review will be to provide an overview of the recent progress made in the synthesis and characterization of well-defined π-conjugated oligomers by looking at some of the most predominant recent systems. It should also illustrate the numerous contributions of monodisperse oligomers to the current understanding of the properties of polymers by relating molecular structures to macroscopic properties. For a more detailed treatment, the reader is referred to an excellent recent multi-author monograph[13] and specialized reviews.[10, 11, 14, 24–27]

2. General Strategies for the Synthesis of Monodisperse Oligomers

Despite much methodological progress, the synthesis and purification of monodisperse oligomers often remains quite tedious. New approaches to the preparation of well-defined π-conjugated oligomers have emerged in recent years.[10, 11] The most elegant and efficient way to prepare long-chain oligomers uses an iterative divergent/convergent binomial strategy,[28] which is illustrated in Scheme 1 for the synthesis of the 12.8 nm long hexadecameric oligo(*p*-phenyleneethynylene) rod **1**, reported by Tour and co-workers (Scheme 1).[29, 30] Three attractive features are combined in this approach: 1) two orthogonal protecting groups ($SiMe_3$ and Et_2N_3) allow the selective deprotection ($C{\equiv}C{-}SiMe_3 \rightarrow C{\equiv}C{-}H$) or activation ($Ar{-}Et_2N_3 \rightarrow Ar{-}I$) in very high yield (steps a and b); 2) the Pd-catalyzed cross-coupling reaction (step c)[31] is selective and high yielding; and 3) the product in this chain elongation step is generally readily separable from by-



Scheme 1. Iterative binomial synthesis of the 12.8 nm long hexadecameric oligo(*p*-phenyleneethynylene) **1**.[29, 30] a) K_2CO_3, MeOH or $n$$Bu_4NF$, THF. b) MeI, 120 °C. c) $[Pd(dba)_2]$, CuI, PPh_3, $HN(i\text{Pr}_2)$/THF, (dba = dibenzylideneacetone).

François Diederich was born in the Grand Duchy of Luxembourg in 1952 and received his PhD in 1979 from the University of Heidelberg. Following postdoctoral studies at the University of California at Los Angeles (UCLA) from 1979 – 1981, he was a research associate at the Max-Planck-Institut für medizinische Forschung in Heidelberg. After his Habilitation in 1985, he joined the faculty of the Department of Chemistry and Biochemistry at UCLA where he advanced to full professor of organic and bioorganic chemistry in 1989. Since April 1992, he has been a professor of organic chemistry at ETH Zürich. He currently serves as a member of the Kuratorium of Angewandte Chemie.

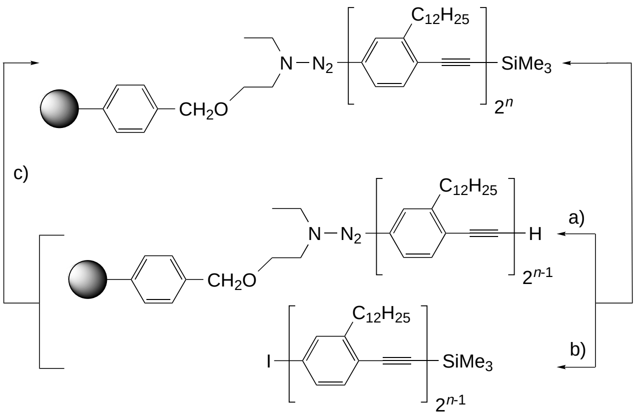
F. Diederich

R. Martin

Rainer Martin, born 1970 in Dornbirn, Austria, studied chemistry at the Eidgenössische Technische Hochschule in Zürich, from where he received his diploma in 1995. He then joined the group of Prof. F. Diederich to work on the synthesis and physical investigation of monodisperse poly(triacetylene) oligomers and obtained his PhD in August 1998. In September 1998, he moved to the Melville Laboratory for Polymer Synthesis, Cambridge UK, where he is currently doing postdoctoral research with Prof. A. Holmes on electroluminescent polymers, supported by a fellowship from the Swiss National Science Foundation.

products and starting materials as a result of large differences in molecular weight.[28] The same iterative strategy was used for the preparation of oligo(α-thiopheneethynylene) derivatives up to a heptadecamer.[16, 32]

The binomial strategy for oligomer preparation is also applicable to protocols for solid-phase synthesis.[30, 33] For this purpose, the starting monomer or oligomer is anchored covalently to an insoluble polymer resin such as poly(chloromethylstyrene) (Merrifield's resin). After orthogonal deprotection/activation (Scheme 2, steps a and b) cross-coupling occurs (step c) to yield the extended resin-bound oligomer, which can again be reactivated for the next coupling step. In the last step, low-weight molecules are removed by filtration and washing the resin and the completed oligomers are then cleaved from the polymer support.



Scheme 2. Binomial oligomer synthesis on a Merrifield resin.[30] a) nBu$_4$NF, THF. b) MeI, 120 °C. c) [Pd(dba)$_2$], CuI, PPh$_3$, NEt$_3$.

The second possible strategy is homo- or heterocoupling of a symmetrical or asymmetrical monomer and eventual addition of an end-capping agent to the oligomerization mixture that will irreversibly block the chain ends to prevent any further reaction towards long-chain polymers. This one-pot approach generally lacks control of oligo-selectivity, and such a statistical polymerization often yields very low amounts of a particular oligomer. Nevertheless, this reaction protocol can be useful if high yielding cross-coupling reactions, which are required in the iterative binomial synthesis, are simply not available or if rapid access to an entire series of monodisperse oligomers is desirable and subsequent chromatographic separations are applicable. Such a strategy has been used in our group and by others for the synthesis, for example, of monodisperse poly(triacetylene) oligomers (see Section 4.3),[34–39] for the synthesis of oligo(pyrrole)s,[40] or for the preparation of linear (1,3-diethynylcyclobutadiene)cyclopentadienylcobalt oligomers.[41]

The practical limit of this method often lies in difficulties encountered during the chromatographic separation (such as by size-exclusion chromatography (SEC)) of oligomers with relatively low differences in molecular weight. This problem can be alleviated by submitting already higher oligomers ("macro-oligomers") to the endcapping oligomerization reaction, to yield oligomers with larger molecular weight differences that are more readily separable.[42]

A general limitation for the construction of larger, well-defined oligomers often arises from the insolubility of π systems with extended π-electron conjugation, which can prevent chromatographic purification and isolation as well as physical characterization. Therefore, the attachment of suitable, solubility-providing side-chains to the repeat units is an essential design criterion in any synthesis planning. Furthermore, appropriate side chains can provide extra stability or modulate the morphological[43] or electronic properties of the targeted oligomers or polymers in a desirable way. A very good example of how side chains can influence the optical properties is provided by poly(alkylthiophene)s. Depending on the number and nature of side chains, the colors of emission in polymer light-emitting devices (LEDs) can be changed from blue to red.[2]

3. The Effective Conjugation Length in π-Conjugated Systems

The knowledge of the number of repeat or monomer units in a π-conjugated oligomer required to furnish size-independent redox, optical, or other properties that correspond to those of the related infinite-chain polymer is of great practical and theoretical interest. For instance, if π-conjugated materials with saturated properties are targeted, intractable high molecular weight polymers could be substituted in specific applications by shorter oligomers that have reached convergence of their physical properties and display better processability. Initially, "conjugation and no end" was thought to be a characteristic property of linearly π-conjugated systems, but soon, however, it turned out that an effective conjugation length (ECL)[44] (or confinement length (CL), delocalization length (DL)[45]) exists even in π-conjugated chain or ladder polymers for which structural defects can be excluded. Although the ECL is a numerical quantity that is not directly accessible by physical measurements, it rapidly evolved into one of the central concepts in the understanding of many properties of π-conjugated polymers.[46] The usefulness of homologous series of oligomers to estimate the ECL experimentally has been widely demonstrated.[42, 46–49]

The fact that π-conjugated polymers exhibit a convergent limit for certain physical properties (such as the longest-wavelength electronic absorption maximum $\lambda_{\max}$ and the optical end absorption (the solution optical "HOMO–LUMO" gap), redox potentials, vibrational frequencies, first and second hyperpolarizabilities) may arise in solution from mutual distortions from planarity of the conjugated backbone, for instance by rotations around single bonds. This results in reduced π overlap, and thus the conjugation exhibits a limited extension. In systems containing aromatic rings as part of the linear π-conjugated backbone, resonance stabilization within these rings is another factor that reduces the mobility of the π electrons. Furthermore, electron–electron correlations, which are often negligible in short π systems, become relevant in molecules that contain large numbers of π electrons.

One of the simplest theoretical models used to describe changes of physical properties as a function of chain length follows the description of a "particle in a box".[50] Since this model contains no correction for electron–electron correlation effects, its validity is restricted to molecules with a limited number of π electrons. However, one-particle models have proved to have significant predicting power at both the qualitative and quantitative levels, although one has to be aware of certain limitations.[51]

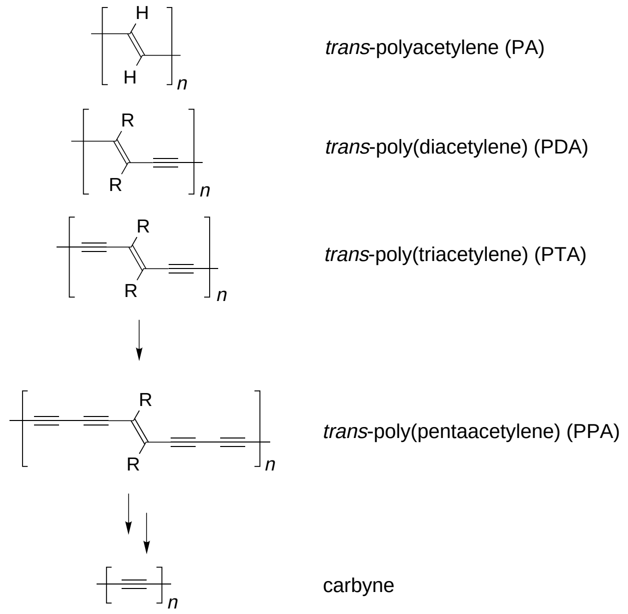
A simple way to evaluate the ECL includes plotting a relevant physical property (such as the longest-wavelength absorption energy $E_{\max}$ or the solution optical gap E_g) against the inverse number of monomer units n^{-1}.[44] Extrapolation to infinite chain length yields n_{ECL}, the number of repeat units in an oligomer at which saturation of a property occurs. Usually, such a linear correlation among a homologous series of smaller oligomers yields only reasonable results in cases where no obvious saturation is observed. In fact, this estimation of convergence values by extrapolation can often only be a rough approximation and sometimes even results in misleading conclusions.[44] However, satisfying results can be obtained in cases where higher oligomers or polydisperse polymers are available that already show saturation of their physical properties. In such cases, the crossing point of the linear regression line obtained from the oligomer series with the horizontal saturation level line for the polymers allows a good estimation of the ECL.[34]

Wenz et al.[52] deduced on the basis of the "free electron gas model" of Kuhn[53] a linear relationship between the longest-wavelength optical absorption energy or the optical band gap E and N, the number of conjugated double and triple bonds per molecule, which was successfully applied to estimate the ECL in a series of poly(diacetylene)[54] and poly(triacetylene)[34] oligomers. Lewis and Calvin formulated a simple, linear relationship between the number of monomer units in the conjugated chain and the square of the wavelength of absorption.[55] This equation, based on the harmonic oscillator model, was demonstrated to give excellent results in the case of polyenes.[55] A modification of this model was later used by Hirayama to describe the position of the longest-wavelength absorption maximum as a function of oligomeric length in polyene derivatives and oligo(*p*-phenylene)s.[56] In cases where physical data for only three oligomers are available, the approximation of Pade has found some significance to estimate the convergence value of the infinitely long chain.[44, 57] Recently, Meier et al. presented an exponential equation, which accurately describes the dependence of electronic absorption and emission data on the number of repeating units n.[44] Contrary to the algorithms presented so far, this approach allows the direct characterization of the overall effect of conjugation and the velocity of oligomeric growth, which serves as a measure of how fast the limit of convergence is actually attained.

4. Survey on Monodisperse π-Conjugated Oligomers

4.1. Oligoenes

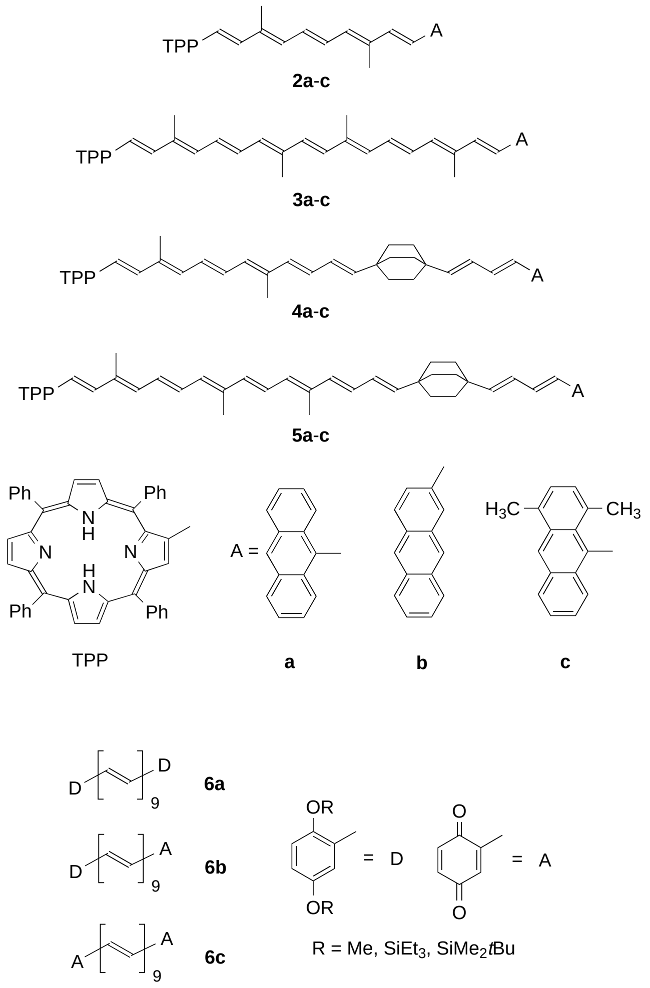
Linear oligoenes may be viewed as structurally well-defined model compounds for polyacetylene (PA), which is the simplest π-conjugated polymer with an all-carbon backbone not composed of aromatic rings (Scheme 3). PA has been widely explored over the last years for its interesting material properties, in particular for its high electrical conductivity (up to 10^5 S cm^{-1}) upon doping.[58–61]



Scheme 3. Progression of linear π-conjugated all-carbon backbones from *trans*-polyacetylene to carbyne.

Oligoene model compounds have played a dominant role in investigating the properties of PA.[62] Unfortunately, unsubstituted PA is an intractable, insoluble, and infusible material and thus several attempts have been made to make PA more processable by using "precursor polymer routes".[26] However, substitution of the ethylenic hydrogen atoms by solubility-providing side chains leads to severe steric interactions and distortion of the π-conjugated backbone out of planarity, and results in a loss of conjugation and widening of the HOMO–LUMO gap. In oligoenes with a carotenoid backbone[63] this effect, known as allylic 1,3-strain,[64] also plays a significant role because of steric interactions between the methyl groups and the adjacent allylic hydrogen atoms.

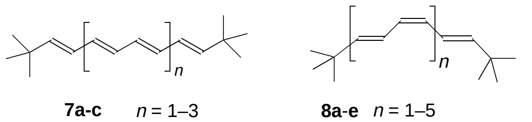
Various oligoenes with terminally functionalized donor (D), acceptor (A), or redox-active groups have been synthesized with the aim of investigating their intramolecular energy and electron transfer properties or exploring their use as molecular wires.[10, 11, 24, 65–68] For instance, Lehn and co-workers demonstrated that *α*,*ω*-bispyridyl oligoenes incorporated into vesicle bilayer membranes function as molecular wires and mediate electron transfer from an external reducing phase to an internal oxidizing phase.[67] Effenberger and Wolf synthesized the carotenoid polyenes **2**–**5** (Scheme 4) with different end groups to study intramolecular energy transfer processes. Interestingly, the interruption of the conjugation by a bicyclo[2.2.2]alkane unit in oligomers **4** and **5** resulted in a modified, but still observable energy transfer as evidenced by fluorescence quantum yield measurements.[63] Duhamel and co-workers prepared the D–D, D–A, and A–A oligoenes **6a**–**c** that lack angular alkyl groups and, therefore, should



Scheme 4. Donor–acceptor substituted oligoenes for intramolecular energy and electron transfer studies.[63, 68]

have a fully planar π-conjugated backbone.[68] Such compounds could have the potential to function as molecular wires.

Müllen and co-workers applied the Stille cross-coupling reaction[31] to the synthesis of the homologous series of stable oligoenes **7a–c** (Scheme 5) and studied their electron transfer behavior by cyclic voltammetry (CV).[62] The formation of $C(sp^2)-C(sp^2)$ single bonds in the cross-coupling reaction was found to provide a versatile alternative to the construction of oligoene backbones by formation of C=C double bonds by the Wittig and analogous reactions.[69] The oligomers **7a–c** are highly redox active, with **7c** displaying seven successive one-electron transfers, which lead from a tetraanion to a trication, that are reversible on the cyclic voltammetric time scale. From the plot of the electrochemical HOMO–LUMO gaps ΔE of **7a–c** against n^{-1} (n = number of double bonds), the ΔE value for PA was extrapolated to 1.7 eV, which is in agreement with the band gap determined experimentally and theoretically for PA itself.[70] A single crystal X-ray structure analysis of hexaene **7b** revealed a packing structure formed by layers of oligoenes with each linear chain being surrounded by six neighboring *tert*-butyl groups which occupy spaces between the layers. The oligomeric arrangement is similar to that of *trans*-PA as determined by X-ray diffraction and lattice packing calculations, which demonstrates the potential of crystalline **7b** to act as a model for bulk *trans*-PA.[71] Furthermore, **7b** and **7c** can serve as models for doped PA, since oligoenes with six to ten or more C=C double bonds are comparable in size to the regions of the PA chain that become charged upon oxidation or reduction.[72]

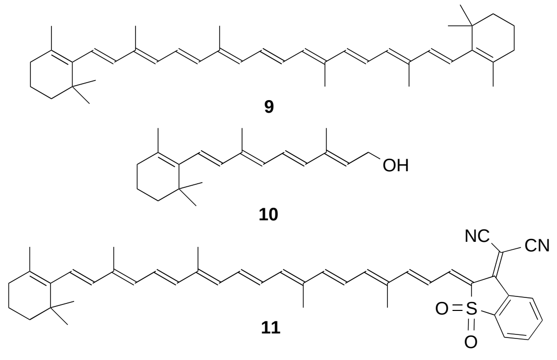


Scheme 5. All-*trans* oligoenes **7a–c** prepared by Stille cross-coupling[62] and *trans(cis,trans)*$_n$ oligoenes **8a–e** obtained by ring-opening metathesis polymerization.[76]

The nature of the electrical conductivity in PA has been the subject of a tremendous amount of experimental and theoretical research and has also been addressed in several publications on oligoene model systems.[73–75] Valence effective Hamiltonian (VEH) calculations on oligomers have been used to compute ionization potentials, optical transition energies, and electron affinities in PA.[48] These have been found to be in remarkably good accordance with experimentally observed values.

An elegant way to synthesize oligoenes with odd and even numbers of C=C double bonds was reported by Knoll and Schrock.[76] Controlled ring-opening metathesis polymerization (ROMP) gave access to polydisperse mixtures of different oligomers endcapped by *tert*-butyl groups, and those having as many as 13 C=C double bonds were subsequently separated by flash chromatography on silica gel under nitrogen at −40 °C. The *trans*(*cis*,*trans*)$_n$ series **8a–e** (Scheme 5) as well as odd and even series of all-*trans* oligomers containing up to nine C=C double bonds were analyzed in more detail by UV/Vis, and ^{1}H and ^{13}C NMR spectroscopy. Oligoenes beyond the 17-mer were found to be rather unstable under the reaction and isolation conditions. Extrapolation by plotting UV/Vis absorption data versus n^{-1} revealed a HOMO–LUMO gap in solution of 1.79–1.80 eV for an infinite all-*trans* PA chain. In a different study, the same oligomers containing 3–13 conjugated double bonds were subjected to ^{60}Co γ-irradiation in Freon matrices. The generated radical cations were then used as model compounds to study the doping process in PA by means of UV/Vis spectroscopy.[73]

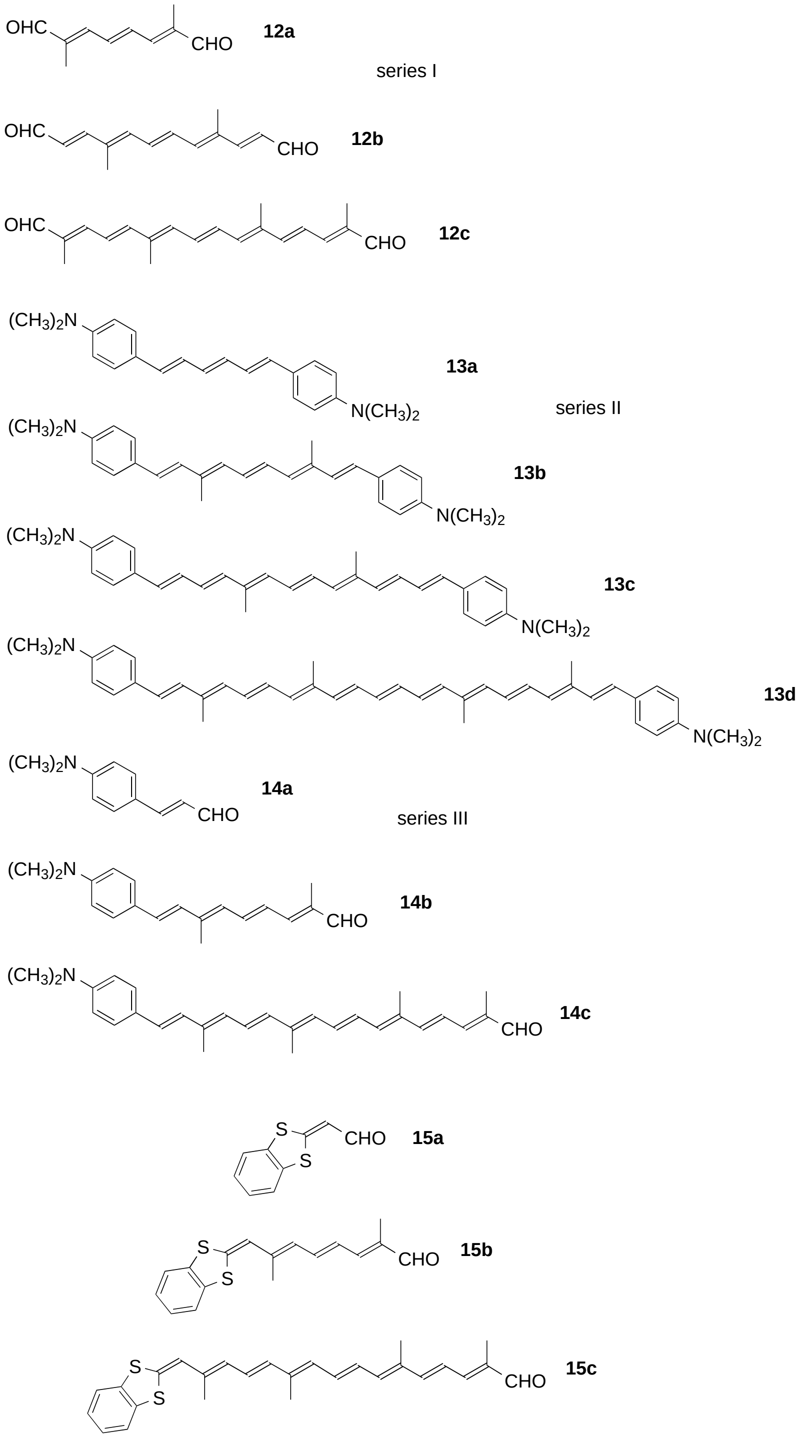
β-Carotene (**9**) and vitamin A (**10**) are naturally occurring polyene oligomers (Scheme 6) and thus were early targets for



Scheme 6. The natural polyenes β-carotene (**9**), vitamin A (**10**), and a carotene derivative (**11**) were investigated for third-order nonlinear optical properties.[77, 78]

studying first (β) and second (γ) hyperpolarizabilities, which characterize the efficiency of molecular second- and third-order nonlinear optical effects. Large molecular third-order optical nonlinearities were measured in polarized carotenoid derivatives such as **11**, which displays a 35-fold enhancement of the second hyperpolarizability (measured at the three-photon resonance) relative to the symmetric parent β-carotene (**9**).[77, 78] The dramatic improvement over β-carotene, which itself has one of the largest third-order nonlinearities known, has been attributed to symmetry breaking and to the large difference in dipole moments between the ground and excited states introduced by the strong terminal acceptor functionality in **11**.

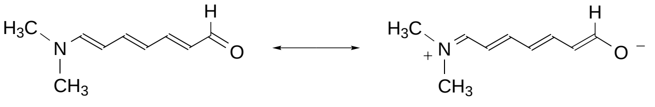
Oligoenes serve as textbook examples for the correlation between various propounded theoretical models (such as the "particle in a box" model) and experimentally observed parameters. A variety of combined experimental and theoretical studies have been undertaken to establish structure–property relationships and design criteria for conjugated organic molecules with enhanced nonlinear optical responses.[79–82] The chain length dependence of the third-order polarizability in three different series of α,ω-oligoenes (Scheme 7) bearing electron-withdrawing (series I: **12a–c**), electron-donating (series II: **13a–d**), or both donor and acceptor end groups (series III: **14a–c**) was studied systematically by Pucetti et al. and revealed the following trends:[83] 1) In each series, the lengthening of the conjugated chain induces hyperchromic and bathochromic shifts in the UV/Vis absorptions and each series obeyed the previously observed[55] linear dependence of the longest-wavelength absorption maximum λ_{max} from the square root of the number of C–C double bonds. 2) Measurements of the first hyperpolarizability β by EFISH (electric field induced second harmonic generation) using a laser excitation wavelength of 1.34 μm and the second hyperpolarizability γ by third harmonic generation (THG) at 1.91 μm showed a sharp increase in the γ values in all three series of compounds with increasing chain length. A nonlinear fit according to the power law relationship $\gamma = kn^a$ of the γ values against the number of monomer units n revealed an exponent of $a = 2.3$ for the bis-acceptor series I (**12a–c**) and 3.0 for the bis-donor series II (**13a–d**). 3) Exceptionally large γ values were observed for the bis-donor-substituted oligoenes **13a–d** and for the D–A series III (**14a-d**). Saturation of the nonlinear optical properties was not observed in any of the three series of compounds.



Scheme 7. Three series of α,ω-substituted oligoenes investigated for nonlinear optical properties.[83, 84]

In a similar study, the asymmetrically substituted α,ω-polyenes **15a–c** (Scheme 7) were investigated using THG and EFISH techniques, and displayed an increase in γ by about two orders of magnitude for **15c** relative to the γ value for **15a**.[84] For a small number of double bonds n, a power law dependence $\gamma = kn^a$ again is suitable to approximate the experimental results, with an exponent a between 3 and 6. For larger values of n, γ becomes linear in n and γn^{-1} approaches a constant value. The saturation of γn^{-1} in long-chain polyenes with very narrow polydispersities obtained by living polymerization techniques has been found by THG measurements (1.9 μm) to occur at approximately 120 C=C double bonds[85] and thus at considerably longer chain lengths than theoretically predicted.[86] Based on comparisons with all other linearly π-conjugated polymers (see below), the accuracy of this exceptionally high ECL for polyenes must be seriously questioned and re-investigation is strongly suggested.

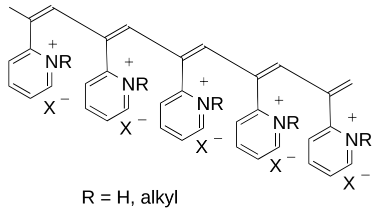
Utilizing D–A substituted oligoenes, specifically polymethine dyes such as **16** (Scheme 8), Marder and co-workers developed a bond length alternation model (BLA, defined as the difference between the average lengths of carbon–carbon single and double bonds in a polymethine chain) from both experimental and theoretical results to relate the magnitude of the second hyperpolarizability γ to the extent of changes in molecular geometry.[87] The γ value could be optimized in either a positive or negative sense for polymethine dyes of a given π-conjugation length by tuning the BLA by chromophoric structure, solvation effects, or an external electric field.[88] These same studies, and others,[89] suggested a strong correlation between linear and nonlinear optical properties (α, β, γ) of conjugated organic molecules and predicted that, as the first hyperpolarizability β is maximized for a given chromophore, the second hyperpolarizability γ should approach zero, which suggests there is a limit to the ability of D–A substitution to increase γ values. More recently, Shu et al. synthesized push–pull oligoenes up to a tetramer in which the π-conjugated backbone is rigidified through incorporation into fused ring structures. This configurational and conformational locking furnished NLO chromophores that possessed significantly enhanced thermal stability.[90] A more detailed overview of the recent experimental and theoretical progress in the field of nonlinear optics dealing with oligomeric and polymeric chromophores can be found in references [8, 91–95].



16 BLA = + 0.06 Å

Scheme 8. Bond length alternation (BLA) in the polymethine dye **16**.[87]

Recently, Blumstein and co-workers reported some interesting developments that potentially promise to eliminate some of the disadvantages associated with classical PA and its doped derivatives.[96] They described a way to make PA more soluble and processable by introducing one or two ionic 2-pyridinium side chains into each repeat unit (Scheme 9).



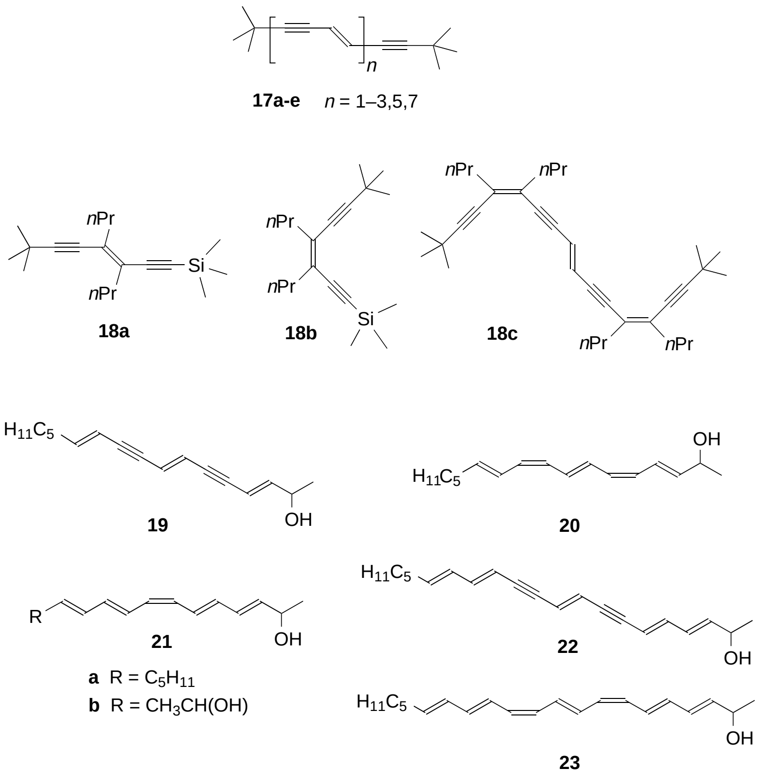
Scheme 9. Schematic representation of polyacetylenes with solubilizing ionic side chains.[96]

The electrostatic repulsion between adjacent monomers apparently favors planarization of the PA backbone and results in significantly extended linear π conjugation relative to uncharged substituted PAs. By using different charged side chains, a wide range of solubilities could be achieved, extending from water to nonpolar solvents. Furthermore, variation in R enabled formation of amphiphilic or mesogenic systems, composites, and blends. The high film-forming potential of the amphiphilic structures makes them excellent candidates for LB (Langmuir–Blodgett) or electrostatic layer-by-layer deposition,[97] and offers considerable potential to process PAs into thin-film architectures for device fabrication. It can be expected that monodisperse oligomeric model systems for these novel PA materials will also be developed in future work.

4.2. Oligoenynes

The second representatives in the progression of linearly π-conjugated nonaromatic all-carbon backbones are poly(diacetylene)s (PDAs, Scheme 3). They represent a unique class of conjugated polymers insofar as PDAs can be obtained as perfect macroscopic single crystals by topochemical solid-state polymerization of suitably pre-arranged and substituted buta-1,3-diynes,[52, 98] a requirement, however, which severely limits their accessibility. PDAs are not conducting upon doping but show large third-order nonlinear coefficients[8, 99] and are considerably more stable than PAs. Oligoenynes have been much less investigated as model compounds for PDA than oligoenes (as models for PA), presumably as a result of the requirement for a topochemically controlled synthesis of the π-conjugated backbone. The first systematic series of *trans*-enyne oligomers dates back to 1986 and was published by Wudl and Bitler.[100] They reported the synthesis of *tert*-butyl endcapped oligomers **17a–e** (Scheme 10) which showed, with increasing chain length, a color change from white (**17a**, **b**) to deep yellow (**17e**), as well as a rapidly decreasing solubility in *n*-hexane or benzene. The *tert*-butyl endcaps were found to be essential for high thermal stability, and the oligomers displayed no particular sensitivity to air and light as it is generally observed in the case of oligoenes. Interestingly, **17d** did not react with iodine over a period of greater than 24 h, which strongly contrasts the behavior of oligoenes with identical chain length. For example, β-carotene (**9**) can be easily doped with I_2 to give IR and Raman spectra similar to those obtained for I_2-doped PA. Additionally, attempts to dope a film of **17d** with sodium naphthalenide and [18]crown-6 in Et_2O were unsuccessful.[100]

In an in-depth study Giesa and Schulz used the oligoenynes **17a–d** and the substituted derivatives **18a–c** (Scheme 10) as model compounds for PDA and investigated their physical properties by UV/Vis, Raman, ^1H NMR, and ^{13}C NMR spectroscopy as a function of chain length and geometry.[54] The ECL in PDAs was calculated to be around $n_{ECL} = 10$ monomer units, with the longest-wavelength electronic absorption energy at infinite chain length being extrapolated as 2.25 eV ($\lambda_{max} = 551$ nm).[54] The construction of the stereodefined oligomers **19–23** (Scheme 10) was reported by



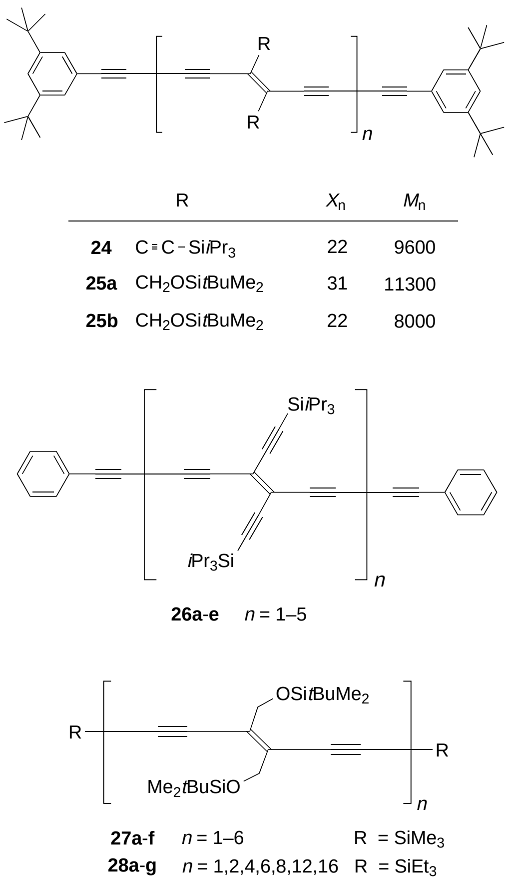
Scheme 10. Oligoenynes as models for poly(diacetylene)s (PDAs).[54, 100, 101]

Crousse et al., who studied the influence of geometry (Z/E) or bond type (C–C double or triple bond) on their physical properties.[101]

With the enhanced synthetic repertoire to form C(sp)–C(sp^2) bonds provided by modern metal-catalyzed cross-coupling reactions[31] we expect a renewed interest in the formation and physical study of oligoenynes as model systems for PDAs in future years.

4.3. Oligoenediynes

The third linear π-conjugated polymer without aromatic repeat units in the series that starts with PA and PDA is poly(triacetylene) (PTA, Scheme 3). Whereas the chemistry and physical properties of PA and PDA oligomers and polymers had been exhaustively investigated for about two decades, much less is known about PTAs, which were reported for the first time in 1994.[36, 102] Despite this late discovery the synthetic accessibility of PTAs and functional derivatives by simple oxidative acetylenic coupling is more versatile than that of PAs and PDAs. Furthermore, the additional acetylenic moiety in each repeat unit of PTAs increases the spacing between laterally appended side chains, which, as a consequence, do not easily undergo intramolecular steric repulsions that cause distortion of the linear π-conjugated backbone from planarity. Similar to PDAs, PTA polymers such as **24** and **25** (Scheme 11) were found not to become conductive upon doping.[102]



	R	X_n	M_n
24	C≡C-Si*i*Pr$_3$	22	9600
25a	CH$_2$OSi*t*BuMe$_2$	31	11300
25b	CH$_2$OSi*t*BuMe$_2$	22	8000

Scheme 11. Poly(triacetylene)s (PTAs) **24** and **25**[102] and oligoenediyne model compounds **26**–**28**.[34, 38, 42]

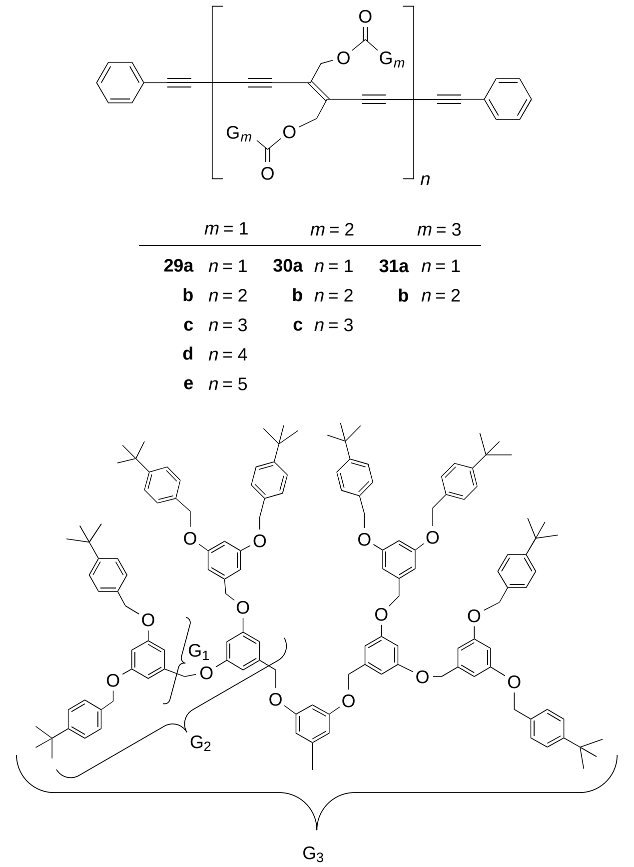
The first series of monodisperse PTA oligomers (oligoenediynes) prepared were the phenylacetylene endcapped compounds **26a**–**e** (Scheme 11) that contained tetraethynylethene (TEE, 3,4-diethynylhex-3-ene-1,5-diyne) repeat units.[36, 38, 102, 103] The highly colored compounds **26a**–**e** extend in length up to about 5 nm and are amazingly kinetically stable, high-melting materials that remain unchanged for months when exposed to air at ambient temperature. The X-ray crystal structure of dimeric **26b** displayed a perfectly planar π-conjugated backbone including the two terminal phenyl rings. The solution optical gap for the series **26a**–**e** extrapolated to infinite chain length was estimated to be $E_g = 2.3$ eV (536 nm), which is comparable to that of many PDAs ($E_g = 2.1$ eV).[36] Electrochemical analysis of these π-conjugated rods revealed interesting redox properties. While none of the oligomers **26a**–**e** could be oxidized below +1.0 V in THF (versus ferrocene/ferrocenium (Fc/Fc$^+$)), which helps to explain their amazingly high stability in air, they were all readily reduced with the number of reversible, one-electron reduction steps corresponding to the number of TEE moieties in each oligomer. Furthermore, the first electron transfer was strongly shifted to less negative potentials with increasing number of monomer units; thus, the first reduction of **26a** occurs at $E^\circ = -1.57$ V (versus Fc/Fc$^+$, in THF +0.1 M Bu_4NPF_6) whereas the first reduction of **26e** is much facilitated and occurs at −1.07 V.[36]

The Me$_3$Si endcapped oligoenediynes **27a**–**f** (Scheme 11) with *trans*-1,2-diethynylethene (DEE, (*E*)-hex-3-en-1,5-diyne) repeat units displayed significantly enhanced solubility and processability relative to the tetraethynylethene oligomers **26a–e** as a consequence of the more flexible Me$_2t$BuSiOCH$_2$ side-chains.[34] These compounds ranged from a 0.96 nm long monomeric to a 4.61 nm long hexameric rod and allowed for a comprehensive investigation of structure–property relationships in PTAs. By extrapolative evaluation of linear optical and nonresonant third-order nonlinear optical data the ECL of PTAs was predicted to lie in the range of seven to ten monomer units, which corresponds to 21 or 30 conjugated double and triple bonds, respectively.[34] Furthermore, a plot of γn^{-1} versus n for the PTA samples **27a–f** revealed an exponential correlation for γ with a fitted exponent $a = 2.5 \pm 0.1$.

For a direct determination of the ECL the Et$_3$Si-endcapped, monodisperse oligomers **28a–g** (Scheme 11) containing $n =$ 1, 2, 4, 6, 8, 12, 16 monomeric units were prepared by a rapid and efficient statistical deprotection–oxidative oligomerization protocol.[42] Longer-chain monomers were used as starting materials for the preparation of the higher oligomers ($n =$ 8, 12, 16) in order to reduce separation problems by SEC (see Section 2). The gap between oligomer and polymer analysis was closed with the completion of this series of PTA oligomers. All compounds up to hexadecamer **28g** featured good solubility in apolar solvents, which allowed a direct determination of the ECL by means of UV/Vis spectroscopy. This study revealed the previously predicted value of $n_{\mathrm{ECL}} =$ 10. Raman scattering studies of oligoenynes **28a–g** in CHCl$_3$ solutions at 20 °C showed an exponential decrease in the frequencies of the C−C triple and double bond stretches $\tilde{\nu}_{(\mathrm{C\equiv C})}$ and $\tilde{\nu}_{(\mathrm{C=C})}$, respectively, with lengthening of the π-conjugated backbone, and plots of $\tilde{\nu}_{(\mathrm{C\equiv C})}$ as a function of n also revealed an ECL of ten monomer units. The hexadecameric PTA rod **28g** with its 16 C−C double and 32 C−C triple bonds and a length of 11.9 nm between the terminal Si atoms is currently the longest linearly fully π-conjugated molecular wire that does not contain aromatic repeat units.

PTA monomers (TEEs and DEEs) and dimers substituted at the terminal alkynes with donor (D; *p*-(dimethylamino)-phenyl) and/or acceptor (A; *p*-nitrophenyl) groups were found to display very high second hyperpolarizabilities γ, which were determined by THG measurements.[92, 104a, b] The second-order nonlinear optical properties of these compounds are also quite appealing.[104c] Also, the photochemical *trans* → *cis* isomerization of such compounds was investigated comprehensively.[105] Their photochemical behavior differs substantially from that of similarly substituted stilbenes and azobenzenes since, in contrast to the latter, both *cis* and *trans* isomers of the D/A-substituted TEEs display fully planar conjugated π chromophores.

PTA oligomers with backbones as in **27a–f** but with lateral dendritic side chains of generations one to three were prepared as insulated molecular wires.[35] Interestingly, the insulating layer created by the dendritic, Fréchet-type wedges[106] protects and stabilizes the central conjugated backbone of the tubular macromolecules **29–31** (Scheme 12) by preventing intermolecular reactions, but does not alter its electronic characteristics as evidenced by UV/Vis measurements. An estimation of the longest-wavelength absorption maximum $E_{\max}$ for an infinitely long polymer chain revealed exactly the same limiting value of 2.57 eV for all three oligomeric series **29–31**.[35] It must be concluded from this result that there is no loss of π conjugation along the PTA backbone in the higher generation compounds despite distortion from planarity as a consequence of steric compression of the bulky dendritic side chains.[107, 108]



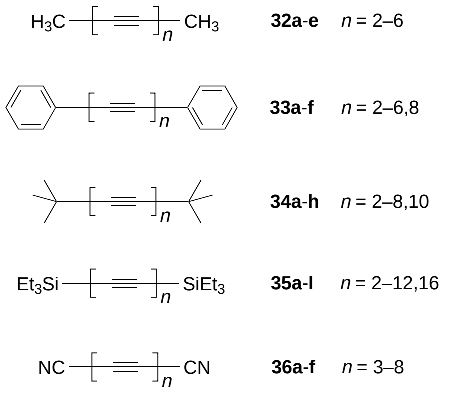
$m = 1$		$m = 2$		$m = 3$	
29a	$n = 1$	**30a**	$n = 1$	**31a**	$n = 1$
b	$n = 2$	**b**	$n = 2$	**b**	$n = 2$
c	$n = 3$	**c**	$n = 3$		
d	$n = 4$				
e	$n = 5$				

Scheme 12. Molecular oligoenediyne wires with lateral dendritic side chains.[35]

4.4. Oligoynes

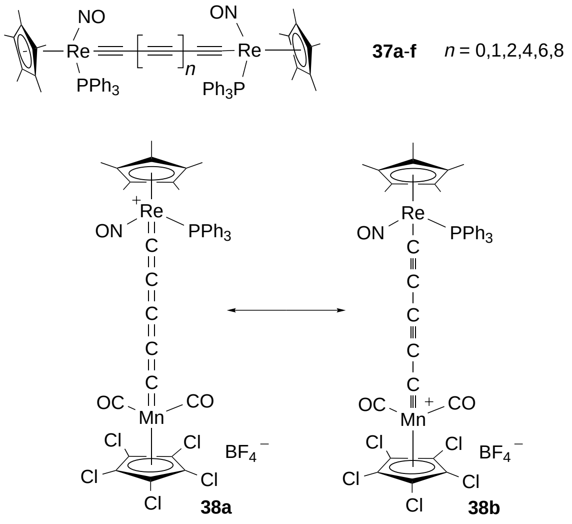
A true challenge in contemporary chemistry is the preparation of infinite one-dimensional carbon allotropes, built exclusively from C≡C units.[103, 109] Such polymers, which have been named as carbyne C_∞ (Scheme 3), have been intensively discussed in the literature[110, 111] yet they remain highly controversial.[112] The inability to attach side chains to carbyne or oligoyne model compounds to provide solubility, stability, or for fine-tuning physical properties is a significant drawback and severely limits the exploration of this class of compounds. Nevertheless, several series of endcapped monodisperse oligoynes such as **32a–e**,[113] **33a–f**,[114] **34a–h**,[111, 115] and **35a–l**[116] (Scheme 13) have been prepared and investigated over the years in order to extrapolate properties of the infinite carbyne polymer.

Hirsch and co-workers reported an extensive investigation of the properties of the rod-shaped α,ω-dicyano oligoynes **36a–f** (Scheme 13) by spectroscopy, electrochemistry, and theoretical calculations.[117] Together with the already known smaller representatives NC−CN, NC−C≡C−CN, and



Scheme 13. Oligoynes as model compounds for the carbon allotrope carbyne (see Scheme 3).[113–117]

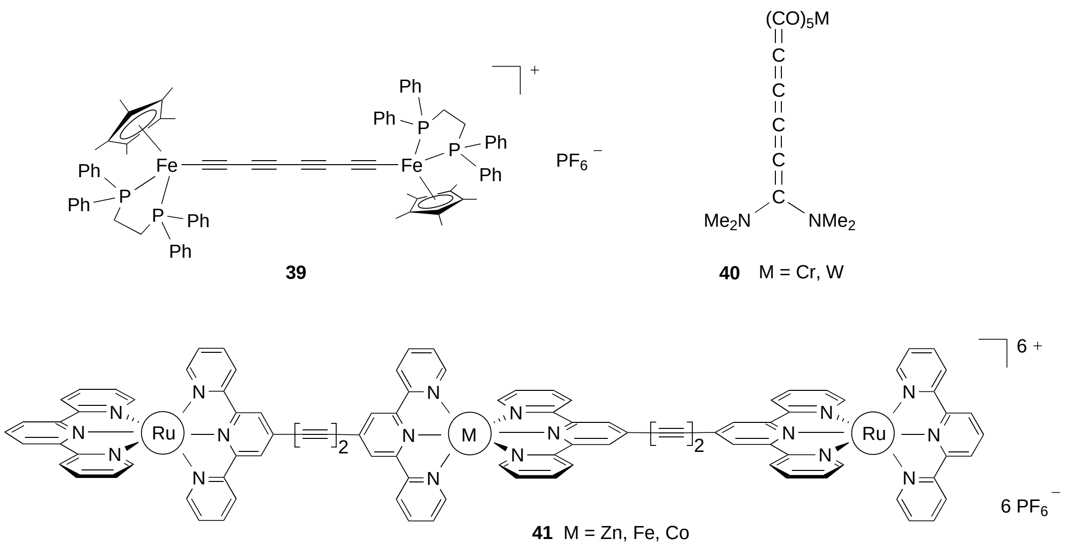
$NC{-}C{\equiv}C{-}C{\equiv}C{-}CN$,[118] oligomers **36a–f** form a continuous homologous series of oligoynes. The preparation of compounds **36a–f** occurred in a truly spectacular way when graphite was vaporized under He in the presence of dicyanogen ($((CN)_2)$) under the conditions of the Krätschmer–Huffman fullerene synthesis. Dicyanogen completely quenches the linear oligoyne intermediates formed at the initial stages of the fullerene synthesis, and the molecular rods **36a–f** are isolated instead of the carbon spheres. Oligoynes with cyano end groups such as HC_nN ($n = 1, 3, 5, 7$) had previously been detected in interstellar space, and the search for such compounds paved the way for the first experimental observation of buckminsterfullerene C_{60}.[119]



Scheme 14. Long oligoynes stabilized by transition metal endcapping groups.[120, 121]

A major advance in the formation of stable long carbyne fragments containing up to ten conjugated C≡C moieties was achieved by endcapping the carbon rods as transition metal complexes. Thus, Gladysz and co-workers prepared the dirhenium μ-oligoynediyl complexes **37a–f** (Scheme 14) by a step-growth approach by employing acetylenic homo- and cross-coupling reactions.[120] The redox-active Re^I end groups undergo reversible oxidations to the Re^{II} state, with a potential separation of the two distinct oxidation events in **37a** of 0.53 V. As the oligoyne spacer between the metal centers, and thus the "resistance" of the bridge increases, the two oxidations start to behave independently and merge to give a single, presumably two-electron, oxidation for **37f**, which represents with its C_{20} chain the longest stable oligoyne reported so far. The oxidation of $Re^I \rightarrow Re^{II}$ becomes thermodynamically less favorable with the lengthening of the C-atom chain in the series **37a–f**, which could reflect the strong electron-withdrawing effect of a chain of sp-hybridized C atoms. The same researchers also reported on the asymmetrically substituted oligomer **38** (Scheme 14) with an odd number of C atoms between the two metal centers.[121] IR measurements on this compound revealed that the cumulenic resonance form **38a** dominates over the alternative acetylenic one (**38b**).

Other monodisperse oligoynes endcapped with metal centers, such as **39**,[122] **40**,[123] and **41**[124] (Scheme 15) have been investigated for the study of intramolecular electron-transfer processes between the metal centers across the bridging carbon fragment. In the thermally stable mixed-valence complex [Fe^{II}-C_8-Fe^{III}] (**39**), the indistinguishable redox states of the two Fe centers suggest that the electron-transfer rate between the termini is very high.[122]

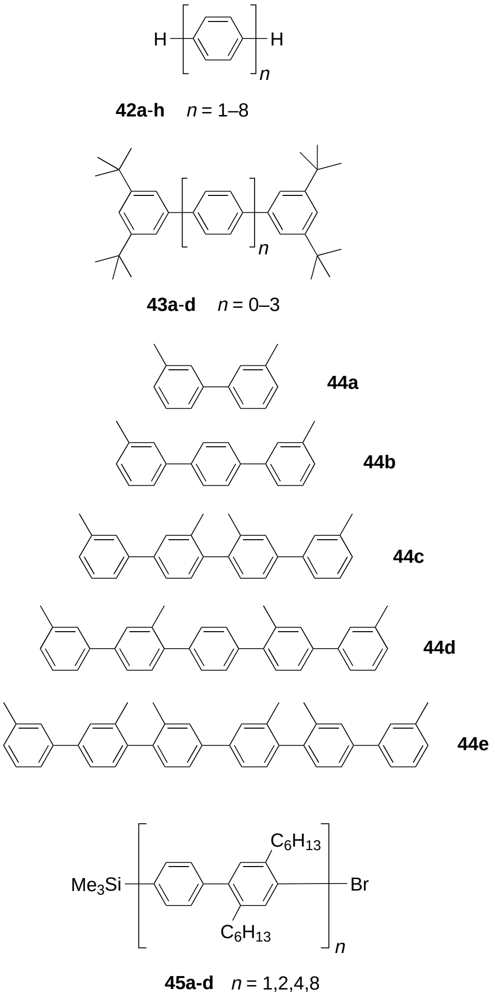


Scheme 15. Oligoynes investigated for intramolecular electron transfer processes.[122–124]

4.5. Oligo(*p*-phenylene)s

Poly(*p*-phenylene) (PPP) has found considerable interest over the last years since it acts as an excellent organic conductor upon doping. Whereas in the neutral form PPP is an insulator and displays conductivities down to 10^{-12} S cm^{-1}, doping with I_2 or AsF_5 raises its conductivity into the metallic region with values around 500 S cm^{-1}.[125, 126] It is therefore not surprising that PPPs have become some of the most widely investigated polymers as documented by several review articles covering all aspects from synthesis to physical properties.[26, 61, 125–128] A second major interest arises from the fact that polymers with a PPP backbone can be used as the active component in blue light-emitting diodes (LEDs).[2, 129–131] In parent oligo- or poly(*p*-phenylene)s, steric interactions between *ortho*-H atoms cause the planes of neighboring aryl rings to adopt dihedral angles up to 23°, which significantly reduces the π-orbital overlap and thus prevents extended π conjugation.[125, 132, 133] The solubility properties of PPP-derived oligomers or polymers are readily enhanced by addition of substituents along the conjugated backbone. However as a severe drawback, replacing the H atoms by any larger group causes even greater dihedral angles between the planes of neighboring rings and results in a disturbance of the π-orbital overlap along the PPP backbone and a reduction in the ECL. Such distortions from planarity of the linear backbone are evidenced by hypsochromic shifts in the UV/Vis spectra.[133] Recently, Schlüter and co-workers described the preparation of PPPs with Fréchet-type dendrons of generations one to three attached to each phenyl group.[107] The resulting cylindrical macromolecules display very high solubilities.

Although unsubstituted oligo- and poly(*p*-phenylene)s often exhibit remarkable thermal stabilities, which makes them attractive candidates for numerous applications that require thermally robust π-conjugated organic materials, their low solubility and intractability has so far precluded any commercial development of this polymer class.[125] In the oligomeric series **42a–h** (Scheme 16), solubility rapidly decreases with increasing chain length,[134, 135] but solubility properties can be slightly enhanced by addition of *tert*-butyl groups to the terminal aryl rings as in the oligomeric series **43a–d** (Scheme 16).[136–138] As expected, the ECLs determined by UV/Vis spectroscopy for both series **42a–h** and **43a–d** were found to be in good agreement and yield $n_{\mathrm{ECL}} = 9$ and $n_{\mathrm{ECL}} = 11$, respectively.[44] The ECL determined from specific refractive index increments of dilute oligo(*p*-phenylene) solutions was found to be around $n_{\mathrm{ECL}} = 6$ phenylene units and thus not too different from UV/Vis derived values.[135] Oligomers of type **42** were also the subject of third-order nonlinear optical investigations by time-resolved degenerate four-wave mixing (DFWM), and revealed $\chi^{(3)}$ values of less than 1.6×10^{-13} esu for both quaterphenyl (**42d**) and quinquephenyl (**42e**), and an increase up to 1.7×10^{-12} esu for octiphenyl (**42h**).[8, 139] Semiempirical calculations involving both singly and doubly excited configurations showed D–A functionalized oligo(*p*-phenylene)s to be much less efficient second and third harmonic generation chromophores than oligoenes or oligoynes of comparable length and substitution.[80] This can be readily rationalized by the higher degree of electron localization in the individual aryl rings of the PPP backbone.



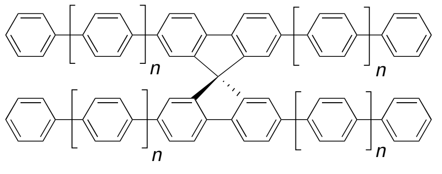
Scheme 16. Oligo(*p*-phenylene)s investigated as model systems for PPP.[134–138, 142, 143, 145]

The evolution of the electronic structure in a series of oligo(*p*-phenylene)s, in comparison with oligoynes and oligo(*p*-phenylenevinylene)s, has been studied by ultraviolet photoelectron spectroscopy and quantum chemical calculations, based upon the valence effective Hamiltonian (VEH) method of Lögdlund et al.[140] The authors found excellent agreement between theory and experiment, which allowed a detailed description of the evolution of the electronic structure in these types of polymers.

Oligo(*p*-phenylene)s have played a dominant role as model compounds for PPP in the study of physical mechanisms related to intra- and interchain charge transport or distribution and stabilization of charges and spins on π-conjugated chains. These mechanisms are of special interest in regard to the potential application of PPP and related conjugated polymers in rechargeable batteries.[128, 136, 141] Oligomers **42c–d**, **43b–d**, and **44b–e** (Scheme 16) were investigated by cyclic voltammetry and the corresponding diamagnetic dianions, obtained by reaction with alkali metals, by NMR spectroscopy.[136, 142] Electrochemical studies of **43b–d** showed an increasingly facilitated first reduction step and a decreasing difference between the first and second reduction potential with increasing chain length. All compounds containing up to four benzene units underwent a two-electron reduction, whereas longer chains are capable of accepting more electrons. Centers of highest charge density are usually the *para* positions, especially on the inner rings. It became evident from NMR experiments that rotation about the C(aryl)–C(aryl) single bonds is significantly retarded in the reduced species. The radical monoanions in both series **43b–d** and **44a–e** were also studied by electronic absorption spectroscopy in THF solutions,[143] and revealed interesting differences between the two oligomer series. In **44a–e** (Scheme 16), the methyl substituents significantly perturb the π conjugation by twisting the phenylene rings out of planarity. This results in the tendency of the radical anions to delocalize the charge in smaller sub-units. Thus, **44c** and **44e** resemble biphenyl radical anions, and **44d** a terphenyl radical anion rather than higher oligo(*p*-phenylene) oligomers with extended π conjugation. The first reduction step in oligo(*p*-phenylene)s causes a geometrical reorientation towards a more planar system, best described by quinoidal resonance structures, to stabilize the monoradical anion. The second electron is then able to delocalize over the entire π system. The ionization potentials, optical transition energies, and electron affinities for **42a–c** and PPP have been calculated by Brédas et al.[48] Oligomers **42c–f** were also shown to be suitable model compounds for PPP in homogeneous photocatalysis processes.[144]

Schlüter and co-workers prepared rigid rods **45a–d** (Scheme 16) in a repetitive sequence with up to 16 phenylene rings and orthogonal functional groups at both termini.[145] Compound **45d** currently represents the longest monodisperse oligo(*p*-phenylene) rod reported so far. The C_6 alkyl chains attached to every second aromatic unit provided solubility in common organic solvents, thereby allowing full spectroscopic characterization of oligomers **45a–d**.

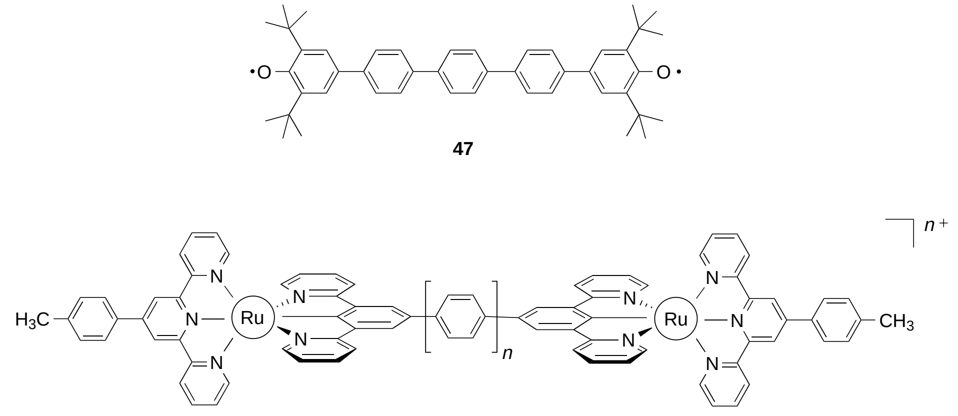
Spiro-linked oligo(*p*-phenylene)s such as **46a–c** (Scheme 17) have been used as blue emitters in electroluminescent applications. They are soluble in common solvents, show glass transition temperatures up to 250°C, and with their high photoluminescence quantum efficiencies in the solid state, represent an alternative to high molecular weight PPP polymers for the construction of LEDs.[146]



46a-c *n* = 1–3

Scheme 17. The spiro-linked oligo(*p*-phenylene)s **46a–c** can be used as blue emittors for electroluminescent applications.[146]

For the diradical **47** (Scheme 18), in which two phenoxyl radicals are connected by a terphenyl spacer, antiferromagnetic coupling between the radical termini is observed.[147] Presumably a quinoidal singlet state is effectively prevented as a consequence of the twisted aryl backbone,.



47

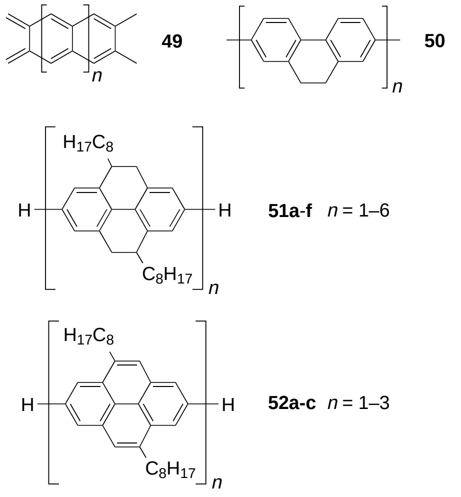
48a-c *n* = 0–2

Scheme 18. The molecular rods **47** and **48a–c** were prepared to investigate electronic coupling mediated by oligo(*p*-phenylene) spacers.[147, 148]

The molecular rods **48a–c** (Scheme 18), which exhibit terminal cyclometalating bipyridylbenzene ligands (for N,C,N coordination) rigidly bridged by short oligo(*p*-phenylene) linkers, display pronounced electronic coupling over distances up to 2 nm in their mixed-valence forms. The much higher electron donor character of the anionic phenyl bridging ligands and the short Ru–C(phenyl) bonds lead to substantially increased metal–metal interactions relative to the analogous systems in which *meta*-terpyridine moieties are chosen for metal ion coordination.[148]

4.6. Strategies to Planarize Oligo- and Poly(*p*-phenylene)s

The planarization of oligo- and poly(*p*-phenylene)s to maximize the extent of conjugation by enhancing π-orbital overlap has been of notable interest for a number of years. One possible approach in pursuing this objective is the connection of adjacent aryl groups by 1,2-annellation rather than linear 1,4-connection as in the case of classical PPP. The resulting linear [*n*]acene oligomers **49** (Scheme 19) differ strikingly in their electronic character from PPPs, as a result of the very different connections between individual six-membered rings in the two classes of compounds. Thus, they feature low band gap energies and are inherently sensitive towards oxidation and dimerization.[149] Nevertheless, they represent an interesting class of compounds from both theoretical and experimental viewpoints.[150] Examples for planarized derivatives, in which the electronic characteristics of the PPP π-electron system are better retained, are oligomers and polymers with 5,6-dihydrophenanthrene-3,8-diyl repeat units (poly(phenanthrene)s, PPT, **50**)[151] or with 4,5,9,10-tetrahydropyrene-2,7-diyl sub-structures (poly(tetra-

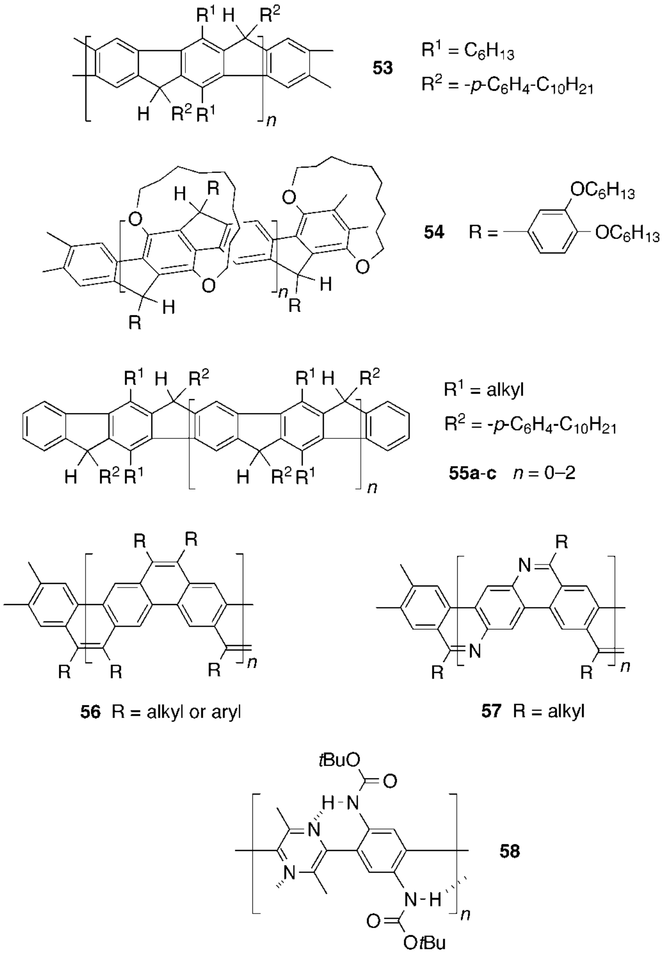


Scheme 19. Linear acenes **49**[149] and planarized PPP models **50**–**52**.[151–154]

hydropyrene)s, PTHP) **51a**–**f** (Scheme 19).[151–153] These systems with their ethane-1,2-diyl bridges between adjacent phenylene rings maintain inherent flexibility and are not fully planarized. Nevertheless, the investigation of the UV/Vis convergence behavior for the series **51a**–**f** revealed an ECL of $n_{\mathrm{ECL}} = 19$ (n = number of phenylene rings in the linear backbone), which is nearly twice as high as those of the parent oligo(*p*-phenylene)s **42a**–**h** (n_{ECL} at $n \approx 7$) and **43a**–**d** (n_{ECL} at $n \approx 11$), respectively.[44]

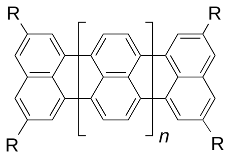
The oligo(pyrene)s **52a**–**c** (Scheme 19) were investigated by Müllen and co-workers as model oligomers for the corresponding infinite polymer and displayed several interesting features.[154] First, the longest-wavelength electronic absorption maxima of **52a**–**c** displayed remarkably close values ($\lambda_{\max}$ [nm] = 344 (**52a**), 350 (**52b**), and 353 (**52c**)) which significantly contrasts with the optical behavior of other oligo(arylene)s. Second, cyclic voltammetry showed that the first reduction potentials E_1 are virtually independent of the number of pyrene units in the rods (**52b**: $E_1 = -2.24$ eV, **52c**: $E_1 = -2.27$ eV). Third, the generation of the dianion **52b**$^{2-}$ did not lead to a diamagnetic state as was observed in the dianions of biphenyl or 1,1′-binaphthyl. All these results provide convincing evidence for the fact that the pyrene moieties are electronically decoupled from each other to a high extent in oligo- and poly(pyrene)s.

The planarization of a classical PPP backbone by the introduction of methylene bridges between the *ortho* positions of adjacent phenylene rings gave raise to the low-band gap polymers **53**[151, 155] and **54** (Scheme 20).[156a] Both polymers exist as mixtures of stereoisomers as a result of the stereogenic bridging centers; additionally, **54** features repeating elements of planar chirality, which increases the number of stereoisomers.[157] These ladder polymers exhibit attractive optoelectronic properties such as extremely small Stoke shifts and are highly electroluminescent when used as the emitter material in light-emitting diodes.[155, 156a, 158] Estimations of the ECL for model compounds **55a**–**c** (Scheme 20) revealed a significantly lower value of $n_{\mathrm{ECL}} = 11-12$ (n = number of phenylene rings in the linear backbone) than that determined for the poly(tetrahydropyrene)s **51a**–**f** ($n_{\mathrm{ECL}} = 19$).[47] The decreased ECL value for oligomers **55a**–**c** relative to **51a**–**f** is surprising and contrasts the expectation that planarization of the π-conjugated backbone should lead to a substantial increase in the ECL as a result of considerably facilitated π-electron delocalization. A series of well-defined poly(fluorene) oligomers up to the decamer was described by Klaerner and Miller.[156b] The UV/Vis-based ECL for this partially rigidified polymer backbone was found to comprise about ten fluorene units. Other examples of fully planarized polymers with a PPP-type backbone are vinylene bridged **56**,[159] imine-bridged **57**,[132, 160] or **58** (Scheme 20), described by Meijer and co-workers, which form ladder-type structures as a result of strong intramolecular hydrogen bonding between the pyrazine-N acceptor centers and the amide N–H donor centers on neighboring rings.[161]



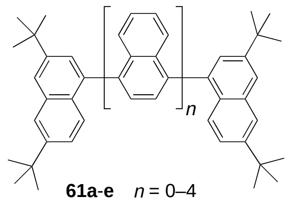
Scheme 20. Planarization of PPP analogues **53**,[151, 155] **54**,[156a] **55a**–**c**,[47] **56**,[159] and **57**[132, 160] by bridging all *ortho*-positions of adjacent phenylene rings in the conjugated backbone. In **58** planarization of the backbone is achieved by intramolecular hydrogen bonding.[161]

The conjugated system **59** (Scheme 21), formally derived by connecting two parallel poly(*p*-phenylene) and *cis*-polyacetylene strands, provides another example of a fully planarized π-conjugated backbone.[162–164] The synthesis of these oligo- and poly(*peri*-naphthalene)s was a long-targeted objective, since theoretical calculations predicted a low-lying HOMO–LUMO band gap, which would give rise to intrinsic conductivity.[165] Various efforts towards their preparation were not

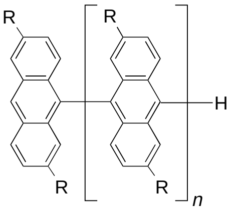


59 R = H

60a-d R = *t*Bu n = 0–3



61a-e n = 0–4



62a-c R = *t*Bu n = 0,2,3

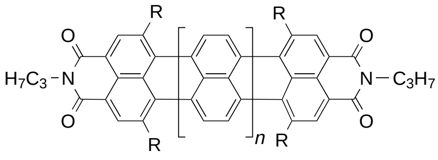
Scheme 21. Conjugation along the planar conjugated backbone of the oligorylenes **60a–d**[162–164] is much more efficient than along the backbone of nonplanar **61a–e**[163] or **62a–c**.[166]

successful as a result of substantial synthetic challenges and their expected extreme insolubility in organic solvents. Some of the solubility problems could be overcome by attaching *tert*-butyl groups and, thus, oligomers **60a–d** (Scheme 21), which have been named oligorylenes, provided a first opportunity for extrapolating experimentally some of the properties of poly(*peri*-naphthylene)s.[162–164] The longest-wavelength electronic absorption maximum λ_{max} in 1,4-dioxane was found to undergo a large increase from 439 (**60a**) to 560 (**60b**) and to 660 nm (**60c**) as a result of the extension of the planar π chromophore.[162]

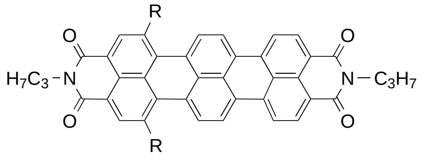
In comparison, the related homologous oligo(1,4-naphthylene) series **61a–e** (Scheme 21) displayed hardly any change in λ_{max} values (CH_2Cl_2) on going from **61a** (293 nm), to **61b** (300 nm), and to **61c** (302 nm). This result reflects the significant steric interactions between adjacent naphthalene units that lead to a ground-state configuration in which neighboring naphthalene moieties adopt a nearly orthogonal orientation.[163] A similar situation was found in the solubilized oligo(9,10-anthrylene)s **62a–c** (Scheme 21), which exhibit a longest-wavelength absorption maximum λ_{max} (CH_2Cl_2) of 402 nm for trimer **62b** and 408 nm for tetramer **62c**.[166]

Further proof for the high rigidity of the conjugated backbones in **60a–d** was obtained by fluorescence spectroscopy in 1,4-dioxane: first by the very small Stoke shifts of 7 nm (**60a**: $\lambda_{em} = 446$ nm), 13 nm (**60b**: $\lambda_{em} = 573$ nm), and 18 nm (**60c**: $\lambda_{em} = 678$ nm) and second by the high fluorescence quantum yields Φ_F of 0.94 for **60a** and 0.70 for **60b**. However, the fluorescence of **60c** was found to be unexpectedly small, with $\Phi_F \approx 0.05$.[162] The optical band gaps ΔE derived from UV/Vis and NIR measurements of the three successive oligomers **60b–60d** were used to extrapolate the band gap of the infinite poly(*peri*-naphthylene) polymer ΔE_∞ to yield 0.98 eV in solution and 0.92 eV in the solid, noncrystalline state. The high redox activity of the oligorylenes **60a–d** is remarkable, and allows in the case of **60d** seven successive fully reversible redox steps (CV) that lead from a tetracation to a trianion. Oligomers **60a–d** were also used to determine the spin-density distribution in oligorylenes as a function of chain length.[167] Study of the radical anions by electron paramagnetic resonance (EPR) and electron-nuclear double resonance (ENDOR) spectroscopy revealed a picture where the positions of the highest spin density are located at the outermost naphthalene units, which is in accordance with theoretical calculations (HMO/McLachlan and Pariser-Parr-Pople (PPP) methods). In contrast, radical anions of other linear π-conjugated systems, such as oligo(*p*-phenylenevinylene)s, show their highest spin densities in the central segments of the conjugated backbone already at small chain length.

The extended planar π systems of oligo(*peri*-naphthylene)s **60a–d** makes them attractive candidates for third-order NLO chromophores. The $\chi^{(3)}$ values from THG measurements at 1.064 μm of **60a–d** increased systematically with the reciprocal of the $S_0 \rightarrow S_1$ excitation energy, the position of the longest-wavelength absorption maximum λ_{max}, and the chain length.[8, 168, 169] The nonresonant $\chi^{(3)}$ value of **60d** was measured to be 80×10^{-12} esu, and the entire oligorylene series **60a–d** afforded a steep power law relationship with an exponent $a = 5.6$. Derivatization of oligorylene oligomers with terminal imide groups yielded the oligorylenimide compounds **63a, b** and **64** (Scheme 22), which represent a promising new class of NIR fluorescence dyes, as they exhibit high molar extinction coefficients, high fluorescence quantum yields, and excellent thermal, chemical, and photochemical stabilities.[170]



63a,b n = 0,2

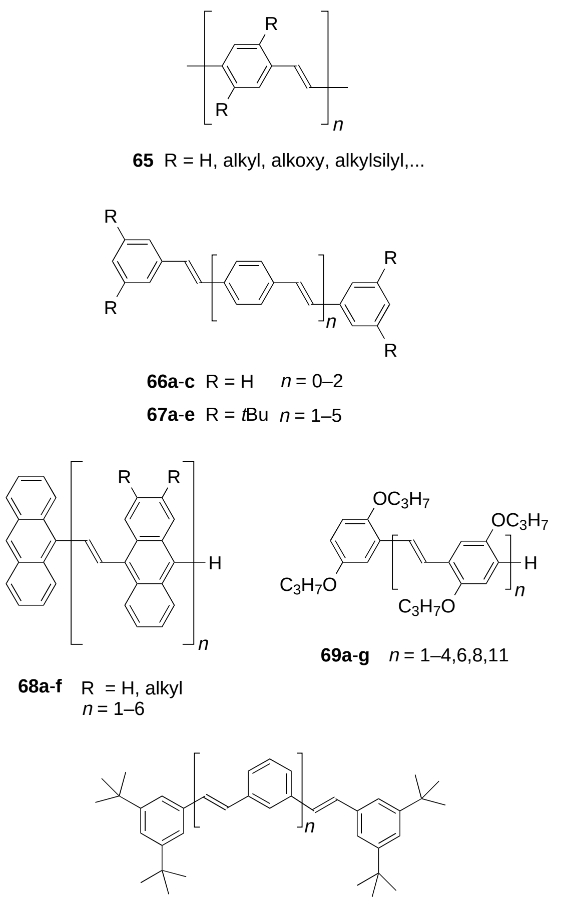


64 R = H, 4-*tert*-butylphenoxy

Scheme 22. Oligorylenimides **63a, b** and **64** represent a promising new class of NIR florescence dyes.[170]

4.7. Oligo(*p*-phenylenevinylene)s

The report of Friend, Holmes, and co-workers[171] in 1990 that light-emitting devices (LEDs) can be constructed from poly(*p*-phenylenevinylene) (PPV, **65**, Scheme 23) films has provided a highly stimulating impetus to the field of π-conjugated organic molecules, and polymers with the PPV backbone are now among the most extensively studied ones.[2, 129] The physical and electronic properties of PPV and its various, differently substituted derivatives have attracted much attention both from experimental and theoretical scientists.[172] Synthetic chemistry has allowed the controlled manipulation of the HOMO–LUMO gap energy in PPV-based polymers, copolymers, and blends, and the manufacture of electroluminescent materials for the construction of



Scheme 23. PPVs[172] and oligomeric model compounds **66**–**70**.[184, 185, 187, 188]

LEDs,[130, 173] with light emissions covering the whole visible spectrum, and light-emitting electrochemical cells (LECs) has come to reality.[174] Even difficult to achieve blue light emitters can be made from PPV polymers with regions of limited conjugation length or from polymers containing short oligomers of the PPV type as side-chain chromophores.[175] In this respect, oligo(*p*-phenylenevinylene) series such as **66a**–**c** or **67a**–**e** (Scheme 23) have helped a great deal in the drive to achieve a basic understanding of the optical properties of PPV polymers. The use of PPVs as emitter materials could also be successfully applied to the fabrication of organic-based lasers.[176–178] More recently, Bazan and co-workers described the synthesis, spectroscopy, and morphology of tetra(stilbenoid)methanes. These compounds combine the advantages of small molecules (for example, high purity and volatility) with those of polymers (for example, amorphous morphology) and may be useful in the design of suitable materials for application in optoelectronics.[177] An orthogonal synthetic approach, using Heck and Horner-Wadsworth-Emmons reactions, was applied by Maddux et al. to the preparation of a series of PPV oligomers, which were designed for the production of novel diblock copolymers.[178] In this elegant, stepwise synthesis, the need for protecting group chemistry was eliminated.

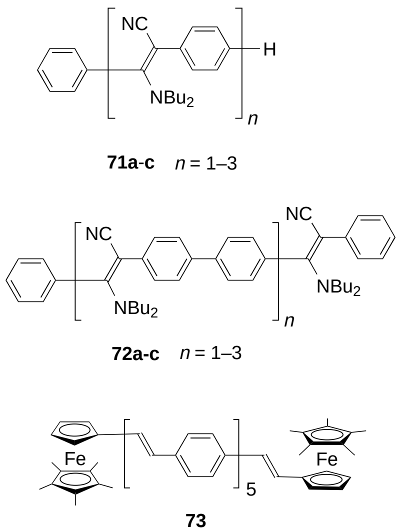
Several groups have studied the photoexcited state behavior of PPVs by utilizing poly(*p*-phenylenevinylene) oligomers of defined length and constitution to obtain structure–property relationships[179] and to gain information about their decay behavior.[180] Recently, Yu and co-workers evaluated in an elegant study the LED performance as a function of conjugation length for partially alkylated hexameric and decameric oligo(*p*-phenylenevinylene)s, which formed uniform films by spin-casting.[181] Whereas UV/Vis, photoluminescence, and electroluminescence spectra showed small shifts for both oligomers, the LED device constructed from the 10-mer displayed a lower turn-on voltage, a smaller operation current, and greater stability than that made from the 6-mer. Furthermore, it has been demonstrated that oligo(*p*-phenylenevinylene)s can be vacuum evaporated to yield high purity thin films that have been studied to gain insight into solid-state structural aspects of π-conjugated materials.[182] Correlated quantum-chemical calculations were of significance in clarifying the effects of intermolecular interactions on the electronic and optical properties of π-conjugated chains.[183]

The ECL for the series **67a**–**e** was estimated from the chain length dependence of the longest-wavelength absorption maximum λ_{max} to be $n_{ECL} = 10$ monomeric units. The good accordance with the value obtained for the oligo(*p*-phenylene)s **43a**–**d** ($n_{ECL} = 11$) is surprising, considering the difference in length of PPV and PPP oligomers with identical numbers of repeat units and the reduced steric hindrance in the PPV relative to the PPP oligomers.[184] Interestingly, the structurally related oligo(9,10-anthrylenevinylene)s **68a**–**f** (Scheme 23),[184] which have an even lower tendency to planarize, revealed exactly the same ECL of $n_{ECL} = 10$ monomer units, but with a much less pronounced convergence behavior than observed for series **67a**–**e**.[44] In the series **69a**–**g** (Scheme 23), with dialkoxy substituted repeat units, saturation of λ_{max} was attained for the longest oligomer **69g** ($n = 11$), which nicely conformed with the experimentally estimated ECL value of about $n_{ECL} = 10$ monomer units found for the unsubstituted series **67a**–**e**.[44, 185] Oligomers similar to **69** were also subjected to a systematic investigation of the photoreactivity and photoconductivity in PPVs with dialkoxy substituted repeat units.[186]

A comparison of the linearly π-conjugated oligomers **67a**–**e** with their *meta*-phenylenes-containing counterparts **70a**–**d** (Scheme 23) revealed several interesting differences. Whereas a bathochromic shift of the λ_{max} values with increasing number of monomer units is observed for the *para*-linked series **67a**–**e**, no chain length dependence of λ_{max} was observed for the constitutional isomers **70a**–**d** or their radical anions obtained upon doping with potassium.[11, 187] The spectra of the monoanions in the *meta*-linked series are fully in accordance with the spectrum of the stilbene monoanion in each case. Furthermore, EPR/ENDOR spectroscopic investigations of **70b**–**d** left no doubt that the spin density in the radical anions is localized in a central stilbene unit.[187, 188]

Optical measurements on oligomers **67a**–**e** provided evidence that a polaronic state within a PPV backbone affects at least about nine to ten styryl units.[143, 189] Detailed studies concerning 1) the redox capacity of **67a**–**e** and several related model PPV oligomers, 2) the charge distribution in the corresponding monoanions, and 3) the structural changes induced by electron transfer were performed by Müllen and co-workers.[45, 57, 141, 190] For instance, all oligomers **67a–e** were found to be effective electron acceptors and the highest negative charge density was localized at the central olefinic bond. While in their neutral state, oligo(*p*-phenylenevinylene)s exhibit rapid rotation about all formal C–C single bonds, ion formation significantly enhances the corresponding rotational barriers and gives rise to detectable stereoisomers.[57, 191]

The donor–acceptor substituted oligo(*p*-phenylenevinylene)s **71a–c** and the expanded analogues **72a–c** (Scheme 24) were prepared by an elegant cation–anion coupling sequence, and targeted NLO chromophores with enhanced hyperpolarizabilities that resulted from large lateral dipole moments.[192] However, the occurrence of configurational and conformational isomerism and Coulombic repulsion between the individual dipoles of each vinylene-bridged donor–acceptor pair prevented their additivity. Therefore, only a modest increase of the molecular dipole (**72a**: $\mu = 6.12$ D; **72c**: $\mu = 9.35$ D) with chain length was measured. Whereas unsubstituted PPV possesses an ECL of about $n = 10$ monomer units, convergence of the longest wavelength absorption maximum $\lambda_{\max}$ was found to occur in **72a–c** after five to six repeat units. Actually, by taking into consideration that a repeat unit in PPV counts three linearly conjugated olefinic and aromatic C–C double bonds and that the corresponding unit in **72a–c** counts five such bonds, convergence of linear optical properties in both systems occurs at around 30 C–C double bonds.



71a-c $n = 1–3$

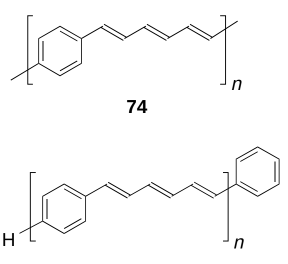
72a-c $n = 1–3$

73

Scheme 24. Functionalized PPV oligomers **71–73**.[192, 193]

In other work, the intramolecular electron transfer along the conjugated π chain of PPV oligomers was investigated. Examples of compounds prepared for such studies are pentameric **73** (Scheme 24) with terminal pentamethylated ferrocene units,[193] or a hexameric PPV oligomer terminated with porphyrin groups.[194]

An expanded version of PPV with the poly(1,4-phenylenehexa-1,3,5-trienylene) (PPHT) backbone **74** (Scheme 25) was proposed by Sonoda and Kaeriyama.[195] Preliminary investigations of the model oligomers **75a–c** showed that PPHT readily undergoes thermally induced *cis–trans* isomerizations under iodine catalysis and displays a significant bathochromic shift of its longest-wavelength absorption maximum relative to PPV.



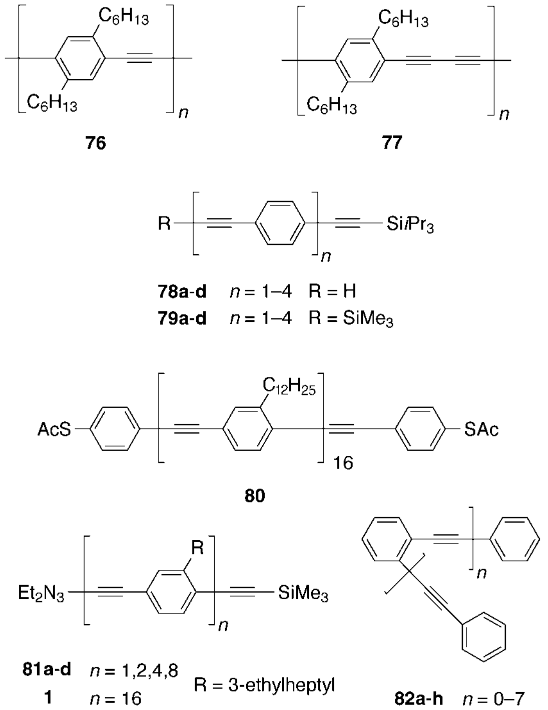
74

75a-c $n = 1–3$

Scheme 25. Expanded PPVs with the poly(1,4-phenylenehexa-1,3,5-trienylene) (PPHT) backbone.[195]

4.8. Oligo(*p*-phenyleneethynylene)s

The tremendous advances in the chemistry and physics of PPV over recent years have stimulated further interest in related types of structures, such as the poly(*p*-phenyleneethynylene) (PPE) polymers **76**, or the poly(*p*-phenylenebutadiynylene)s **77** (Scheme 26).[196] PPEs exhibit large photoluminescence efficiencies both in solution and in the solid state as a consequence of their high degree of rigidity, and their extremely stiff, linear backbone enables maximum orientation,[30, 43, 197-202] which is an important feature for the preparation of oriented films or blends. Their potential as photoluminescence materials in organic polymer-based devices[200] or as fluorescent chemosensors[203] has already been demonstrated. Additionally, various oligo(*p*-phenyleneethynylene) spacers for the modular construction of organo-



76 **77**

78a-d $n = 1–4$ R = H
79a-d $n = 1–4$ R = $SiMe_3$

80

81a-d $n = 1,2,4,8$
1 $n = 16$
R = 3-ethylheptyl

82a-h $n = 0–7$

Scheme 26. Poly(*p*-phenyleneethynylene)s (PPEs, **76**), poly(*p*-phenylenebutadiynylene) **77**,[196] and oligomeric model compounds **78–82** of PPEs.[29, 201, 202, 206, 209] metallic nonlinear optical chromophores[204] or as building blocks for rigid-rod and hyperbranched, dendritic materials have been designed.[205] Furthermore, Moore and co-workers recently demonstrated that poly(*m*-phenyleneethynylene) oligomers spontaneously can adopt a stable helical conformation with a large cavity and thus are valuable tools for studying folding processes in corresponding polymer systems.[12] Oligo(*p*-phenyleneethynylene) series such as **78a–d** and **79a–d** (Scheme 26) should become useful to establish structure–property relationships.[206]

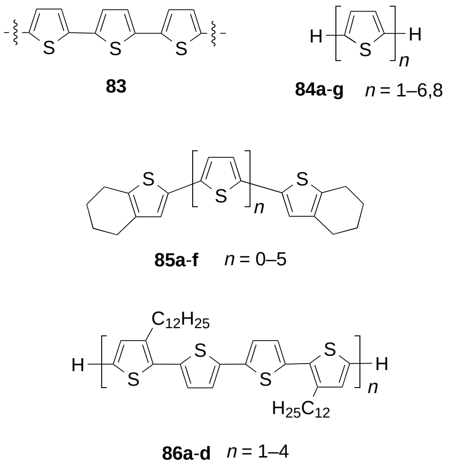
In an attempt to span the lithographically-derived probe gaps between two gold electrodes with a single molecule or with small packets of molecules, Tour and co-workers synthesized the 128 Å long oligo(*p*-phenyleneethynylene) rod **1** (see Section 2).[29, 201] Thioacetyl groups were introduced into **80** (Scheme 26)[201] to generate sites for adhesion to the gold surfaces, which undergo cleavage to the desired thiol end groups[30] under mildly basic conditions.[202] Saturation of the longest-wavelength absorption maximum λ_{max} in the oligomeric series **81a–d** and **1** (Scheme 26) was observed experimentally in the range of $n = 10$ monomer units.[29] An iterative convergent/divergent synthesis for hexyl- and isopentoxy-substituted PEEs was presented by Ziener and Godt.[198] This efficient strategy, which afforded gram quantities of octamer, takes advantage of the selectivity of the Pd-catalyzed alkyne–aryl cross-coupling for aryl iodides over bromides and the possibility for converting an aryl bromide into an iodide by a halogen–metal exchange.

Allara, Tour, Weiss, and co-workers self-assembled a small number of short poly(*p*-phenyleneethynylene) oligomers into an insulating monolayer film of nonconjugated alkylthiols on a gold surface, from which the molecular "wires" protruded by about 7 Å.[207] By searching the surface of the layer with a scanning tunneling microscopy (STM) probe tip, a significantly enhanced current flow was found for the conjugated molecules relative to the insulating monolayer. In a different experimental set-up using the mechanically controllable break junction, Tour and co-workers measured the conductance of a junction containing a single benzene-1,4-dithiol molecule.[208]

A set of conjugated *ortho*-linked oligo(*o*-phenyleneethynylene)s **82a–h** (Scheme 26) were synthesized by Grubbs and Kratz, which showed no tendency for reduction under CV conditions but rather underwent irreversible oxidations in CH_2Cl_2.[209] Single X-ray crystal structure studies of **82c** and **82d** indicated that the compounds adopt a helical structure in the solid state.

4.9. Oligo(α-thiophene)s

Unquestionably, poly- and oligo(α-thiophene)s belong to one of the most carefully studied types of π-conjugated polymers and have received a great deal of attention for both fundamental and practical reasons. Poly(α-thiophene)s (PT, **83**) (Scheme 27) can generally be viewed as a *cis*-PA chain in which the structure is stabilized by the bridging sulfur atom.[210] In comparison to PA, this provides several interesting features such as 1) higher environmental stability, 2) structural versatility that allows for the modulation of electronic and solubility properties by attaching appropriate side groups to the thiophene monomers, and 3) a nondegenerate ground state related to the nonenergetic equivalence of the two limiting mesomeric forms (aromatic and quinoid) of PT. Poly(α-thiophene)s have excellent semiconducting properties when doped,[60, 61, 75] and oligomers exhibit many of the desirable electronic characteristics that have been evident in the long-chain polymers.[211, 212] In addition, it has been shown that poly(α-thiophene)s can be chemically grafted onto glass surfaces to form thin conductive films,[213] are suitable materials for Langmuir–Blodgett LEDs,[214] and, if appropriately functionalized, act as nucleobase-responsive materials.[215]



Scheme 27. Poly(α-thiophene) (**83**) and oligomeric model compounds **84**–**86**.[228, 229, 233]

New developments involve the synthesis of PT co-oligomers and polymers with alternating donor–acceptor repeat units in order to limit the band gap widening that often occurs in fully substituted conjugated polymers.[216] Using such a strategy Zhang and Tour developed new synthetic pathways to low optical band gap poly(α-thiophene)s[217] and to imine-bridged, nearly planar, yet soluble PTs.[218] Oligo(α-thiophenes) in tetrathiafulvalene hybrid systems have also been found to exhibit potent electron donor characteristics,[219] to be attractive building blocks for nonlinear optical materials,[8, 220] and to serve as active components in optical and redox switchable devices.[221] Furthermore, monodisperse oligo(α-thiophene)s and fused derivatives thereof have found growing interest in device applications such as field-effect transistors (FETs),[222] LEDs,[223] photovoltaic cells,[224] and light modulators.[225] Poly- and oligo(α-thiophenes) can be prepared either by chemical[26, 210] or electrochemical[226] methodologies. Recently, the first solid-phase synthesis of oligo(α-thiophene)s on a chloromethylated macroporous resin, by using an alternating sequence of bromination and Stille cross-coupling reactions, was developed by Malenfant and Fréchet.[227]

The second hyperpolarizability γ of the oligo(α-thiophene)s **84a–g** (Scheme 27) was studied as a function of increasing chain length.[228] From these early measurements, the authors concluded that about $n = 9-10$ repeating thiophene units are needed to achieve a respectable $\chi^{(3)}$ value of 10^{-9} esu. The UV/Vis related ECL of oligomers **84a–f** was reported by Meier and co-workers to be around $n_{\mathrm{ECL}} = 17$ monomer units.[44]

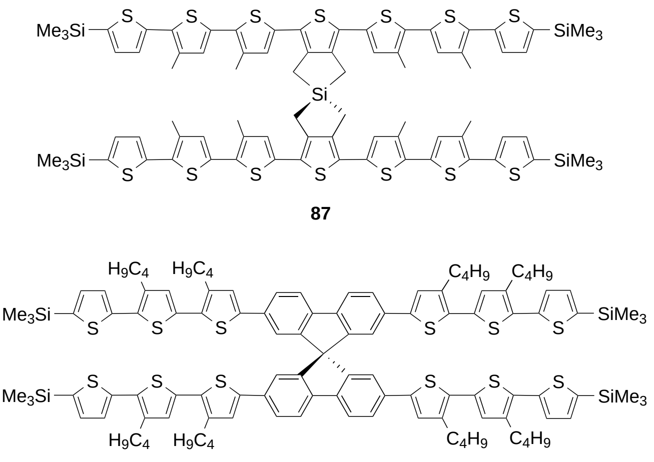
The redox characteristics of oligo(α-thiophene)s **85a–f** (Scheme 27) fused to cycloalkane endcaps to block the reactive α and β positions in the terminal thiophene rings have been studied thoroughly by Bäuerle et al.[229] The first and second oxidation potentials were found to decrease with increasing chain length and to scale linearly with the inverse number of monomer units. This study also showed that the binding energy of the dimer, which is readily formed by oligo(α-thiophene) radical cations, increases with the oligomer chain length. The electronic and optical properties of similar oligo(α-thiophene)s were subject to careful and extensive investigations by several other research groups, who addressed, in particular, questions concerning polaron and bipolaron formation during the charging process.[48, 49, 230–232] A series of oligo(α-thiophene)s bearing Me groups in the β positions of some of the monomeric repeat units and extending to the stage of an octamer was reported by Tour and Wu.[211] From controlled oxidation of these compounds with $FeCl_3$ and subsequent spectroscopic studies, they estimated the delocalization length in PTs for the radical cation (polaron) to be around $n = 12$ monomer units and for the dication (bipolaron) around $n = 10$ monomer units.[49, 231]

The ECL deduced from UV/Vis measurements for the homologous thiophene oligomer series **86a–d** (Scheme 27) was found to be slightly higher ($n_{\mathrm{ECL}} = 20$ monomeric units) than for the oligo(α-thiophene)s **84a–f** ($n_{\mathrm{ECL}} = 17$).[44] Hexadecamers such as **86d** exhibit an end-to-end distance of 64 Å in their extended linear conformation.[233] The longest monodisperse and fully characterized oligo(α-thiophene)s to date are the icosamer (20-mer) and heptacosamer (27-mer) recently reported by Otsubo and co-workers.[234]

Using temperature dependent ^{1}H NMR techniques, LeGoff and co-workers found a barrier to atropisomerization in the ground state in the order of about 8 kcal mol^{-1} for a family of substituted poly(α-thiophene) oligomers, with no significant influence of the length of the oligomer.[235] The barrier to isomerization in the first electronic excited state was determined from fluorescence lifetime measurements to be slightly reduced, with a value of about 5 kcal mol^{-1}. A theoretical study to evaluate the influence of chain length and derivatization on the lowest singlet and triplet states in oligo(α-thiophene)s was performed by Brédas and co-workers.[236]

In an approach to orthogonally fused conducting polymers for molecular electronics, Tour and co-workers prepared the spiro-fused oligo(α-thiophene)s **87** and **88** (Scheme 28).[237] The electronic communication between the two orthogonally arranged heptamer radical cations or the dications in **87** was found to be quite weak.[238] Later, it was shown that the positively charged center (polaron) migration in **87** along the π-conjugated chain has an activation energy barrier of less than 100 cm^{-1}.[239]

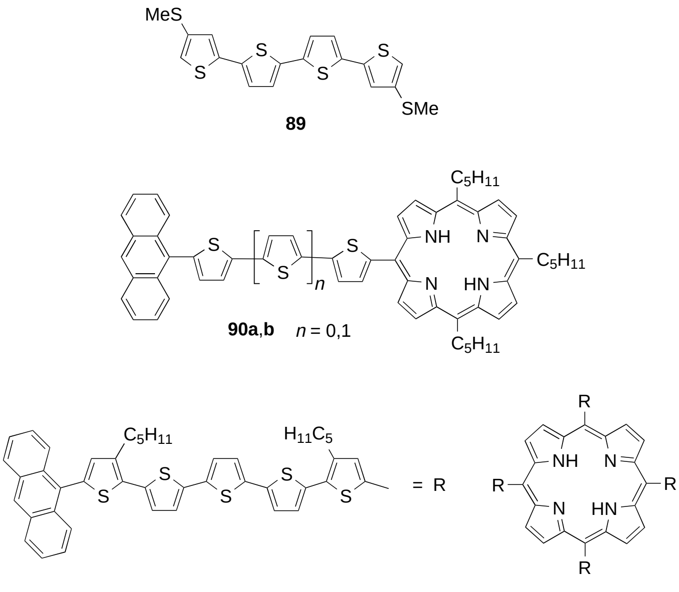
Among functionalized oligo(α-thiophene)s[240] and corresponding (S,S)-dioxides,[241] methylthio derivatives such as **89** (Scheme 29) are of particular interest, since they exhibit high phototoxic activities against nematodes, larvae and eggs of insects, bacteriae, algae, and fungi as a result of their ability to photosensitize the formation of singlet oxygen ($^1O_2$).[242]



87

88

Scheme 28. Spiro-fused dimeric oligo(α-thiophene)s **87** and **88**.[237]



89

90a,b $n = 0,1$

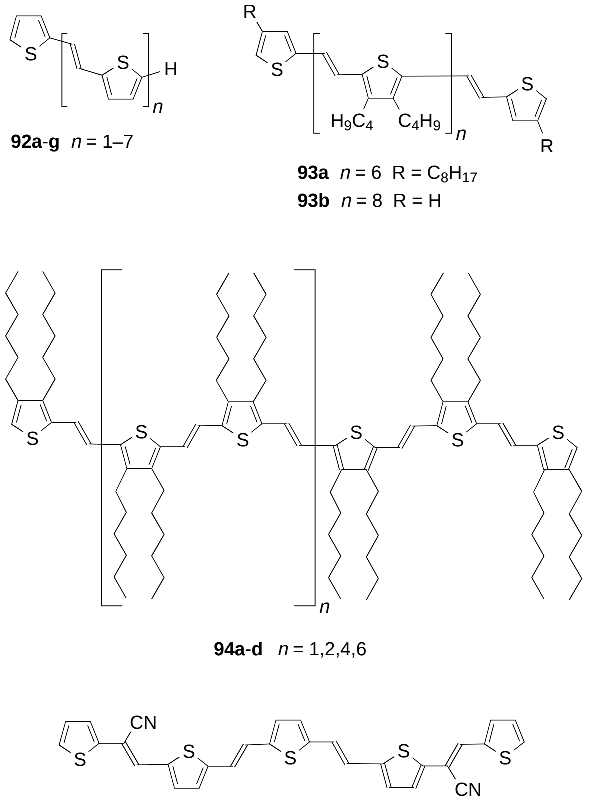
91

Scheme 29. Functionalized oligo(α-thiophene)s with phototoxic (**89**)[242] and electron transfer activity (**90**, **91**).[243, 244]

Oligo(α-thiophene)s have also been used as conjugated linkers between donor–acceptor systems to study intramolecular energy transfer properties, and exhibit several intriguing advantages, when compared to oligoene spacers, such as improved thermal and chemical stabilities, higher fluorescence quantum yields, large degree of π-electron delocalization along the conjugated chain, and the inability to *cis–trans* isomerize.[243] Examples are the anthraceneoligo(thienyl)-porphyrin systems **90a**, **b** (Scheme 29) and the fourfold anthryl quinque(thienyl) substituted porphyrin **91** with its light-harvesting molecular antenna-type architecture.[244]

4.10. Oligo(α-thiophenevinylene)s

Monodisperse oligo(α-thiophenevinylene)s such as the series **92a–g** (Scheme 30) have been synthesized utilizing controlled Wittig-Horner coupling reactions and low-valent



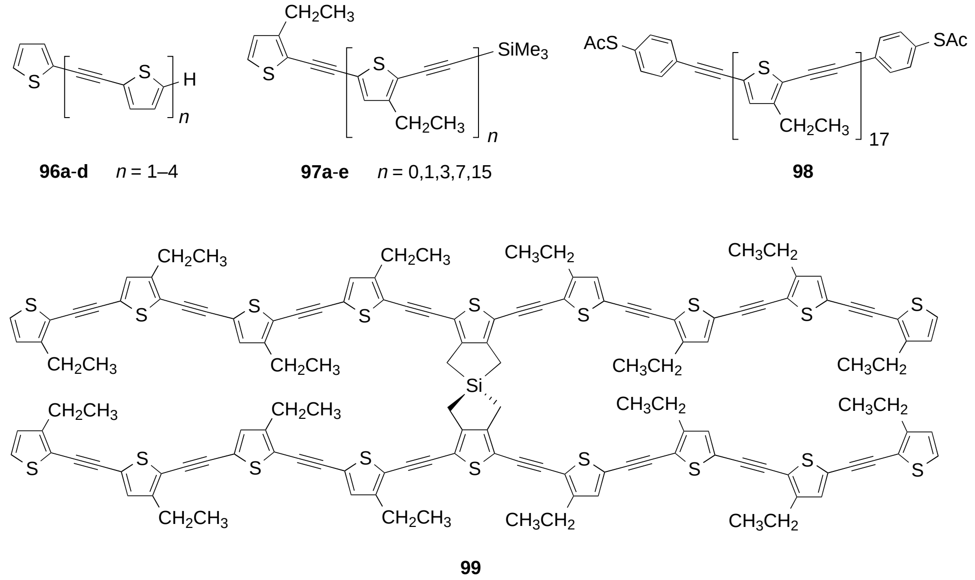
Scheme 30. Monodisperse oligo(α-thiophenevinylene)s **92**–**95**.[245, 247–251]

titanium reagents (McMurry reaction).[245] THG measurements at the fundamental wavelength of 1.064 μm for thin films of **92b** and **92c** revealed values up to $\gamma = 1.65 \times 10^{-33}$ esu, which are larger than theoretically expected because of resonance enhancement.[246] Adding double or triple bonds between the thiophene groups has only a modest effect on the second hyperpolarizability, which has a similar magnitude in oligo(α-thiophene)s and oligo(α-thiophenevinylene)s of comparable chain length.

The estimation of the ECL for the series **92a**–**f** from UV/Vis data revealed convergence at $n_{\mathrm{ECL}} = 14$ repeat units. This is three monomeric units lower than the value reported for the oligo(α-thiophene)s compounds **84a**–**f**, which could be expected given the larger number of conjugated C–C double bonds in the repeat units of oligo(α-thiophenevinylene)s.[44] The poly(α-thienylenevinylene) oligomers **93a**, **b** (Scheme 30) as well as corresponding shorter chain derivatives were prepared by Roncali and co-workers.[247–250] The electrochemical analysis of octamers such as **93b** provided conclusive evidence that dications in such systems are formed directly through a single-step two-electron transfer.[248] The same research group also studied the influence of progressive steric shielding of the π-conjugated backbone on the electrochemical properties by attaching Fréchet-type dendrons to both termini of a thienylene vinylene tetramer.[249] The hexadecamer **94d** of the oligo(α-thienylenevinylene) series **94a**–**d** (Scheme 30) is the longest monodisperse oligo(α-thiophenevinylene) published, and saturation of the effective conjugation was still not observed by UV/Vis spectroscopy.[250] From a comparison of the longest-wavelength absorption maximum of oligomer **94d** with those of hexadecamers containing the same number of carbon atoms or similar dimensions such as the oligo(*p*-phenyleneethynylene) **1** (128 Å, $\lambda_{\max} = 376$ nm in CH_2Cl_2) or a hexadeca(α-thiophene ethynylene) (100 Å, $\lambda_{\max} = 442$ nm in CH_2Cl_2; see Section 4.11), it is apparent that the oligo(α-thiophenevinylene) **94d** (95 Å, $\lambda_{\max} = 601$ nm in CH_2Cl_2) exhibits the largest extended π conjugation. An example of a thiophene-based oligomer with a high electron affinity is the cyano substituted compound **95**.[251]

4.11. Oligo(α-thiopheneethynylene)s

The study of the third-order nonlinear optical properties of the poly(α-thiopheneethynylene) oligomers **96a**–**d** (Scheme 31)[252] by THG measurements revealed γ values up to 2.30×10^{-33} esu for **96d**, and showed no dramatic increase compared to oligo(α-thiophene)s or oligo(α-thiophenevinylene)s of similar length.[246] A preliminary value for the ECL deduced from UV/Vis measurements yielded $n_{\mathrm{ECL}} = 12$ monomer units, which needs re-investigation because of a lack of data points.[44] In the propagation starting with oligo(α-thiophene)s **84a**–**f** and oligo(α-thiophenevinylene)s **92a**–**f**, the oligo(α-thiopheneethynylene)s **96a**–**d** displayed the highest "velocity of convergence" as characterized by the increasing value of the parameter b_i according to Meier et al. (**84a**–**f**: $b_i = 0.352$; **92a**–**f**: $b_i = 0.425$; **96a**–**d**: $b_i = 0.446$).[44]



Scheme 31. Monodisperse oligo(α-thiopheneethynylene)s **96**–**98** and spiro compound **99**.[16, 32, 252–254]

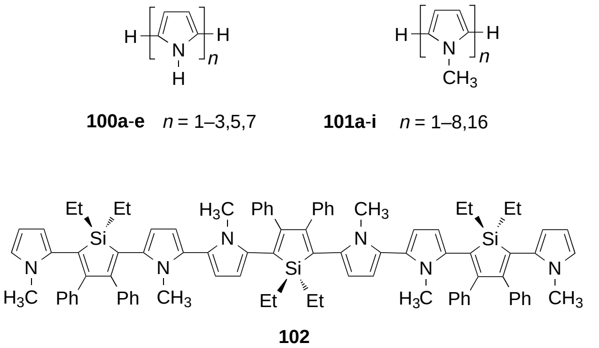
The synthesis of the soluble oligomers **97a–e** (Scheme 31) was described by Tour and co-workers.[16, 32] Recently, the same group also presented the synthesis of the poly(α-thiopheneethynylene) heptadecamer **98** which is 128 Å long and contains acetylthiophenyl groups at the termini. After cleavage of the acetyl groups the resulting terminal thiol functions should allow attachment of the rod to proximal gold probes in order to study its use as a molecular wire in molecular scale electronic devices.[16, 25, 253]

Investigations within the series **97a–e** disclosed important information about the scaling laws that describe the dependence of the second hyperpolarizability on chain length in such types of π-conjugated oligomers.[254] THG measurements in THF solutions of **97a–e** showed a strong increase in γn^{-1} up to octamer **97d** but which tended to level off for hexadecamer **97e**, which demonstrated the effects of saturation. Tour and co-workers also prepared the orthogonally fused system **99** (Scheme 31) as a possible charge-transporting interconnection in molecular-scale electronics.[254]

4.12. A Potpourri of π-Conjugated Oligomers

Substitution of C atoms in oligoenes by N atoms has considerable impact on the resonance energy and thus directly on the lowest-energy absorption maximum λ_{max} and other physical properties.[255] Poly(methineimine) $-(CH{=}N)_n-$ oligomers,[256] for instance, found attention from a theoretical point of view,[257] but as a result of their limited stability they have been much less investigated than their all-carbon counterparts.

Despite the importance of poly(pyrrole) in the field of conducting polymers[61] less experimental work has been devoted to the investigation of poly(pyrrole) oligomers. Although oligo(α-pyrrole)s are quite sensitive to heat and light, two series **100a–e**[258] and the *N*-methyl derivatives **101a–i**[259] (Scheme 32) allowed first estimations of the properties of the corresponding polymers. Whereas for the first oligomer series the ECL was predicted to lie at $n_{ECL} \approx 13$, a value of $n_{ECL} = 7$ was found for **101a–g**, which reflects the increased steric interactions from the *N*-methyl groups in this second series.[44] Recently, Meijer and co-workers presented the first oligo(pyrrole)s functionalized with terminal donor (*p*-methoxyphenyl) and acceptor (*p*-nitrophenyl) groups in the range from monomer to tetramer.[260] Their nonlinear optical properties were studied by hyper-Rayleigh scattering.


100a-e n = 1–3,5,7

101a-i n = 1–8,16

102

Scheme 32. Oligo(pyrrole)s **100a–e** and **101a–i**[258, 259] and (silole pyrrole) co-oligomer **102**.[262]

New developments led to the synthesis of low band gap zwitterionic and planar conjugated poly(pyrrole)s that possess a reversible pH-, solvent-, and ion-dependent absorption ranging from the UV to the NIR spectral region, which makes them attractive for polymer-derived sensor applications.[261] First studies on novel poly(silolepyrrole) co-oligomers such as **102** (Scheme 32) revealed this π-conjugated backbone to be a promising candidate for low-band gap polymers.[262]

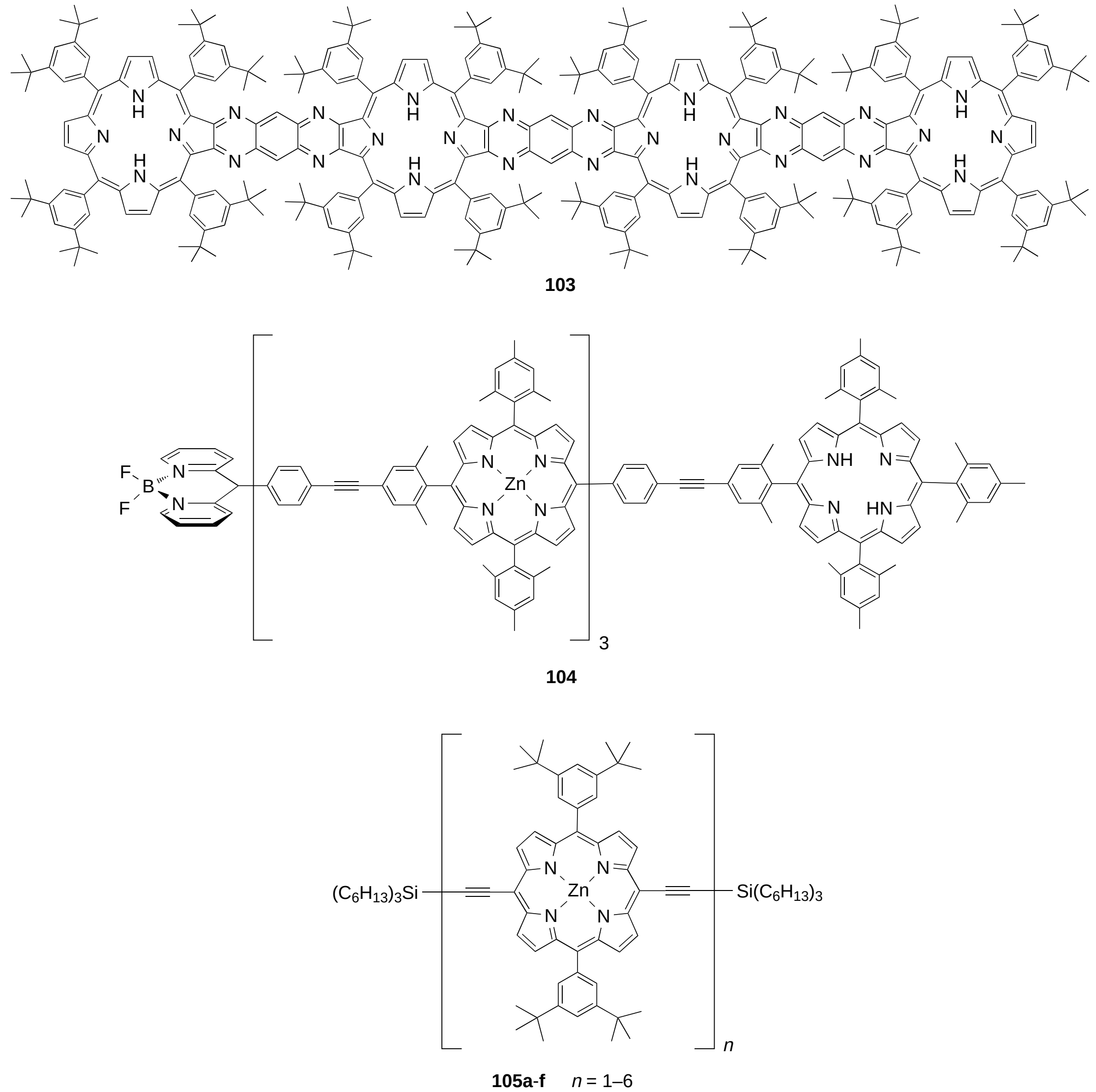
An approach to molecular wires based on linearly conjugated polyporphyrin systems was presented by Crossley and co-workers with the tetrakisporphyrin **103** (Scheme 33), which exhibits an edge-to-edge length of about 56 Å.[263] Other examples are the multichromophoric photonic wire **104** (Scheme 33), studied by Wagner and Lindsey, which showed a remarkably high yield of energy transfer from the boron-dipyridylmethane terminus to the free base porphyrin at the other terminus,[264] the one- and two-dimensional porphyrin oligomers and polymers containing oligothienyl molecular wires explored by Shimidzu et al.,[265] the fascinating windmill-like porphyrin arrays from Osuka and co-workers, which are potent light-harvesting antenna structures,[266] and the porphyrin-poly(triacetylene) co-oligomers studied by Wytko et al.[267]

Recently, Anderson and co-workers presented a series of conjugated buta-1,3-diynediyl-linked porphyrin oligomers **105a–f** (Scheme 33) in the range from monomer to hexamer.[268] From UV/Vis and fluorescence measurements, a HOMO–LUMO energy band gap for the infinitely long polymer of 1.55 eV (from absorption data) and 1.42 eV (from emission data) was extrapolated. The X-ray crystal structure of dimer **105b** revealed a remarkably planar conjugated backbone, which included the entire 56 atoms of the π system (excluding the *meso*-phenyl rings) with a maximum deviation from planarity of ±0.391 Å. The dihedral angle between the two porphyrin planes was found to be near zero in the solid state, although rotation about the buta-1,3-diynediyl linker may freely occur in solution.

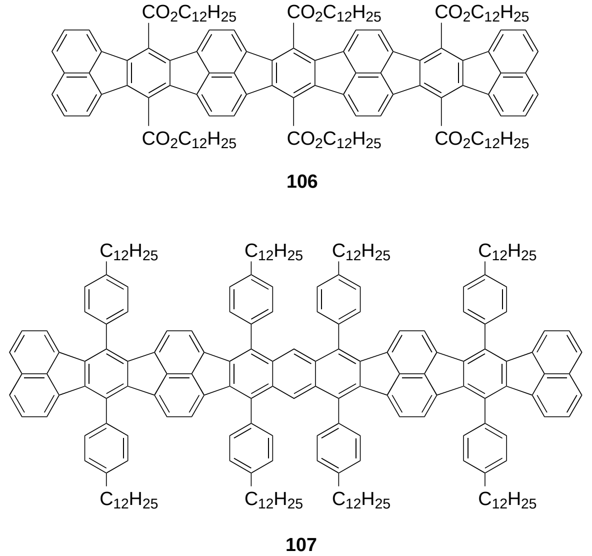
Examples of structurally perfect, fully π-conjugated double-stranded (ladder) oligomers are **106**[269] and **107**[270] synthesized by Schlüter and co-workers (Scheme 34). They have served as model compounds for analogous high molecular weight polymers, that showed conductivities in their doped state up to 0.01 $S\,cm^{-1}$[271] and are interesting materials for their optical nonlinearity, electroluminescence, and photovoltaic properties.[272]

5. Outlook

The preparation and study of monodisperse oligomers to provide structure–property relationships is now well established and provides invaluable information on the properties of infinite, often poorly soluble and intractable polymers. However, monodisperse π-conjugated oligomers are more than just appropriate model compounds for the analogous high molecular weight polymers. Over the past years, they



Scheme 33. Molecular wires with porphyrin units.[263, 264, 268]



Scheme 34. Double-stranded (ladder) oligomers.[269, 270]

have evolved into an independent class of their own, characterized by some spectacular molecular architecture and function, and proved their high potential in several technological applications such as in light-emitting diodes and organic transistors, or as laser dyes and nonlinear optical chromophores. One of the largest challenges fueling the field is certainly the proposed use of single monodisperse oligomers as molecular wires in molecular scale electronic devices. The synthesis of monodisperse π-conjugated oligomers with lengths exceeding 10 nm has brought this interesting prospect closer to reality. Ultimately, it should not be overlooked that the rapid progress in the field of large π-conjugated oligomers has been greatly stimulated by developments in other fields of science. Methods such as scanning tunneling microscopy (STM) or atomic force microscopy (AFM), which allow imaging on a submolecular level, provide entirely new information about the physical behavior of π-conjugated systems. In addition, analytical methods such as matrix-assisted laser-desorption-ionization time-of-flight mass spectrometry (MALDI-TOF MS) made the accurate characterization of large monodisperse oligomers possible for the first time. The developments described in this article have been particularly boosted by modern synthetic methodology, especially by the rich diversity of metal-catalyzed cross-coupling reactions that have been invented in recent years. A large fraction of the multinanometer-scale oligomers described herein and in particular those currently considered for exploitation in molecular-scale electronic devices have been prepared by using cross-coupling reactions in the key steps. Resin-supported solid-phase preparations of oligomers are becoming increasingly efficient. It can also be expected that combinatorial techniques will in the future be applied to the construction of libraries of monodisperse co-oligomers with different repeat units. Efficient and convenient screening of such libraries for desired properties should greatly accelerate the search for technologically useful materials. It is clear that, once the principle of the utilization of π-conjugated oligomers in molecular scale electronic devices has been proved, the field described in this article will push ahead with further explosive growth.

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