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Synthesis and Properties of Molecular Rods. 2. Zig-Zag Rods

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1. Introduction

Molecular rods are of considerable importance for nanoscience and nanotechnology. They have been used as elementary functional building blocks for the construction of supramolecular assemblies and giant molecules, in investigations of long-range interactions such as charge and energy transfer, as models for specialty polymers with interesting optical and electrical properties, and for other purposes. The Michl research group became interested in the subject in connection with a research project in the area of molecular construction kits (molecular "Tinkertoys"[1]), prompted by the first isolation of the rodlike [*n*]-staffanes and the recognition of their potential in nanotechnology.[2]

After working in the area for a decade, we decided to write a review article covering all rodlike molecules of interest that have been synthesized and characterized as pure individual compounds. We reviewed the chemistry of [*n*]staffanes thoroughly,[3,4] and in 1999, we published what was to be a general review on molecular rods.[5] However, the original intent to cover all rod classes was modified when we realized that after the mid-eighties, interest in molecular rods and the number of publications about them skyrocketed. The coverage was therefore confined to simple axial rods, i.e., covalent structures built from axial modules linked by single bonds or by sharing terminal atoms, and we stated that other types of molecular rods will be covered in a sequel.

At present, we offer Part 2 of the sequence, the scope of whose comprehensive coverage is confined to simple zig-zag rods, built formally by linking the

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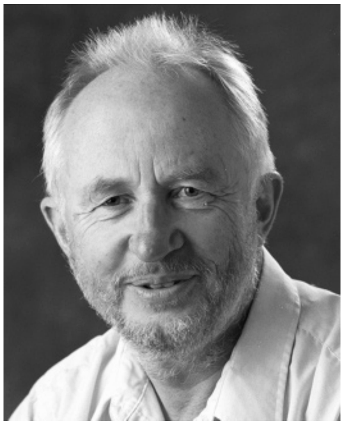


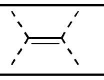
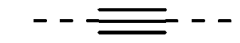
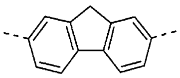
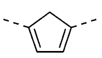
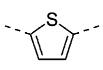
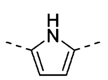
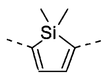
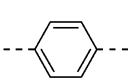
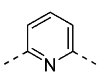
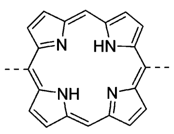
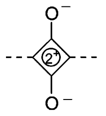
Josef Michl was born in 1939 in Prague, Czechoslovakia. He received his M.S. in Chemistry in 1971 under V. Horák and P. Zuman at Charles University, Prague, and his Ph.D. iin 1965 under R. Zahradník at the Czechoslovak Academy of Sciences, also in Prague. He left Czechoslovakia in 1968. He did postdoctoral work with R. S. Becker at the University of Houston, with M. J. S. Dewar at the University of Texas at Austin, with J. Linderberg at Aarhus University, Denmark, and with F. E. Harris at the University of Utah, where he stayed and became a full professor in 1975 and served as chairman in 1979–1984. In 1986–1990 he held the M. K. Collie-Welch Regents Chair in Chemistry at the University of Texas at Austin, and he subsequently moved to the University of Colorado at Boulder. He is a member of the National Academy of Sciences, the American Academy of Arts and Sciences, the Czech Learned Society, and the International Academy of Quantum Molecular Science. Dr. Michl's current research interests are the development of a molecular-size “Tinkertoy” construction set for the assembly of giant molecules and surface-mounted molecular rotors, photophysics and photochemistry, chemistry of silicon, fluorine, and boron, preparation and study of reactive organic and organometallic molecules, and use of quantum chemical and experimental methods for better understanding of molecular electronic structure. He has been the Editor of *Chemical Reviews* since 1984.

modules listed in Table 1, and, rarely, a few others. The linking is accomplished with single bonds or, in a few cases, by the sharing of terminal atoms. Note that some of these modules are axial and were already used in Part 1;[5] they are now needed again, since a combination of some zig-zag and some axial modules produces a zig-zag rod. Deciding which modules to include and which ones to delete was admittedly somewhat arbitrary, and the zig-zag rods of a few of the classes that we cover are quite flexible. The current plan is to complement this second part in due course by a third one, whose coverage is to be confined to simple ladder rods. In the meantime, Part 1[5] is already quite obsolete and due for an update.

According to the nomenclature that we proposed,[5] all three types of structures, axial, zig-zag, and ladder, belong to the category of “simple rods”. “Linked rods”, which consist of two or more simple rods axially connected by weaker bonds (metal–ligand or metal–metal), would call for yet another separate review. In addition to nomenclature and definitions of what does and what does not qualify for a molecular rod in our usage of the term, the opening sections of Part 1[5] provide a brief historical introduction and references to previous reviews, as well as various generalities, dealing with subjects such as rod mechanical properties, structural considerations, various kinds of uses the rods can be put to, and difficulties with solubility, separation, and characterization, etc. These will not be repeated here.

As in Part 1,[5] we attempt to present a comprehensive description of modern synthetic approaches along with selected representative information on rod structure and properties, especially terminal functionalization, solubility, and transmission of electronic effects. The organization is similar to that adopted in Part 1[5] and is based on the constituent modules and the links between them. The main difference between the contents of the two reviews has to do with the nature of the modules from which the rods are built. Whereas an axial rod consists of modules possessing opposed collinear terminal bonds, in a zig-zag rod, the opposed terminal bonds are only approximately collinear, as is apparent from the structures shown in Table 1. As a result, unlike axial rods, whose equilibrium geometry is linear, the zig-zag rods considered presently are not exactly linear even under the best of circumstances.

Table 1. Characteristics of Axial and Bent Modules Used for Zig-Zag Molecular Rods

Module	Length d[a] / Å	Module Width[b] / Å	Corresponding Hydrocarbon	IP[c] / eV	EA[d] / eV	E_{exc}[e] / 10^3 cm^{-1}	Sections
	1.30-1.34[f]	3.4	ethene **[*n*]1**	10.5138[g]	-1.78[h]	~62[i]	2, 8.3, 8.4, 9.1-9.18
	2.66	3.4	ethyne	11.41[j]	-2.6[h]	~45[i]	9.1-9.3, 9.7.1, 9.8, 10.1-10.5, 10.9. 10.10, 10.12, 11.1-11.3
	7.855[k]	7.9 3.4	fluorene **[*n*]31**	7.95[l] 7.78[m]	~2[n]	33[o]	3, 9.8, 9.19, 10.5
	3.236[p]	5.5 3.4	cyclopentadiene	8.58[q]	-1.09[r]	42[s]	4.5.1, 8.3, 9.12, 10.2-10.4, 10.6
	3.880[t]	5.5 3.4	thiophene **[*n*]36**	8.87[u]	0.9-1.1[v]	43[w]	4, 8.1, 8.2, 8.4, 10.1, 10.8, 10.9, 10.11, 10.12
	3.164[x]	5.5 3.4	pyrrole **[*n*]107**	8.22[y]	2.39, 2.00[z]	49[r]	5, 9.16
	4.15[aa]	6.4 4.2	silole **[*n*]110**	8.9[bb]	-0.06[r]	43[cc]	6, 8.1, 10.10
	4.31	6.7 3.4	*p*-benzene	9.2438[dd]	-0.7[ee] -1.15[h]	~39[i]	4.5.2, 9.4, 9.7.3, 9.8-9.10, 9.12-9.17, 9.19, 10.3, 10.4, 10.6-10.10, 11.1, 11.3, 11.4
	3.72[ff]	6.7 3.4	pyridine	9.34[gg]	-0.62[hh]	~39[i,ii]	7, 9.6, 9.7.4, 9.11, 9.15, 9.18, 10.4, 10.11-10.13, 11.2, 11.3
	8.35	11.4 3.4	porphyrin	6.6[jj]		~16[i]	4.4,9.7
	~3.4	~7.3	squaraine			~39[kk]	9.13

[a] The length of the vector starting at a module terminal atom, crossing the module, and ending at the terminal atom of the adjacent module (module length plus one single CC bond), averaged from crystallographic data (Cambridge Database). The contribution to actual rod length is obtained by multiplication with cosine of the angle between this vector and the rod axis (Figure 2). [b] van der Waals module width including contributions from the hydrogen atoms, in two perpendicular directions, averaged from crystallographic data (Cambridge Database). [c] First ionization potential. [d] Electron affinity. [e] The lowest singlet excitation energy. [f] Depends on rod length. [g] Williams, B. A.; Cool, T. A. *J. Am. Chem. Soc.* **1995**, *99*, 14247. [h] Jordan, K. D.; Burrow, P. D. *Acc. Chem. Res.* **1978**, *11*, 341. [i] Perkampus, H.-H. *UV–Vis Atlas of Organic Compounds*; VCH: New York, 1992. [j] Plessis, P.; Marmet, P. *Int. J. Mass Spectrom. Ion Processes* **1986**, *70*, 23. [k] Gerkin, R. E.; Lundstedt, A. P.; Reppart, W. J. *Acta Crystallogr.* **1984**, *C40*, 1892. [l] Dynes, J. J.; Baudais, F. L.; Boyd, R. K. *Can. J. Chem.* **1985**, *63*, 1292. [m] Fukuzumi, S.; Ohkubo, K.; Imahori, H.; Guldi, D. M. *Chem. Eur. J.* **2003**, *9*, 1585. [n] Gas phase, radical EA, obtained using the difference in measured value of acidity and estimated bond energy. McMahon, T. B.; Kebarle, P. *J. Am. Chem. Soc.* **1976**, *98*, 3399. [o] McGowan, W. M.; Hilinski, E. F. *J. Am. Chem. Soc.* **1995**, *117*, 9019. [p] Liebling G.; Marsh, R. E. *Acta Crystallogr.* **1965**, *19*, 202. [q] Kiselev, V. D.; Kashaeva, E. A.; Konovalov, A. I. *Tetrahedron* **1999**, *55*, 1153. [r] Gas phase calculations. Faustov, V. I.; Egrow, M. P.; Nefedov, O. M.; Molin, Y. N. *Phys. Chem. Chem. Phys.* **2000**, *2*, 4293. [s] Wolfenden, R.; Liang, Y.-L.; Matthews, M; Williams, R. *J. Am. Chem. Soc.* **1987**, *109*, 463. [t] Pelletier, M.; Brisse, F. *Acta Crystallogr.* **1994**, *C50*, 1942. [u] Hsu, C.-W.; Liao, C.-L.; Ma, Z.-X.; Ng, C. Y. *J. Phys. Chem.* **1995**, *99*, 1760. [v] Gas phase experimental and calculations. Jones, D.; Guerra, M.; Favaretto, L.; Modeli, A.; Fabrizio, M.; Distefano, G. *J. Phys. Chem.* **1990**, *94*, 5761. [w] Melo, J. S.; Elisei, F.; Gartner, C.; Aloisi, G. G.; Becker, R. S. *J. Phys. Chem. A* **2000**, *104*, 6907. [x] Goddard, R; Heinemaann, O.; Krüger, C. *Acta Crystallogr.* **1997**, *C53*, 1846. [y] Nyulasi, L.; Toth, T.; Zsombok, G.; Csonka, G.; Reffy, J. *J. Mol. Struct.* **1990**, *218*, 201. [z] Gas phase experimental and calculations. Dewar, M. J. S.; Rzepa, H. S. *J. Am. Chem. Soc.* **1978**, *100*, 784. [aa] From 1,1-dimethyl-2,3,4,5-tetraphenyl-1-silacyclopentadiene. Parkanyi, L. *J. Organomet. Chem.* **1981**, *216*, 9. [bb] Delaere, D.; Nguyen, M. T.; Vanquickenborne, L. G. *Phys. Chem. Chem. Phys.* **2002**, *4*, 1522. [cc] Benkeser, R. A.; Grossman, R. F.; Stanton, G. M. *J. Am. Chem. Soc.* **1962**, *84*, 4727. [dd] Nemeth, G. I.; Selzle, H. L.; Schlag, E. W. *Chem. Phys. Lett.* **1993**, *215*, 151. [ee] Ruoff, R. S.; Kadish, K. M.; Boulas, P.; Chen, E. C. M. *J. Phys. Chem.* **1995**, *99*, 8843. [ff] Merritt, L. L.; Schroeder E. *Acta Crystallogr.* **1956**, *9*, 801. [gg] Arimura, M.; Yoshikawa, Y. *Mass. Spectrosc. (Tokyo)* **1994**, *32*, 375. [hh] Nenner, I.; Schulz, G. J. *J. Chem. Phys.* **1975**, *62*, 1747. [ii] Lowest B–B* transition. [jj] Dupuis, P.; Roberge, R.; Sandorfy, C. *Chem. Phys. Lett.* **1980**, *75*, 434. [kk] Value for the squarate anion $C_4O_4^{2-}$.

One might ask why anyone would want to use them. The main reason for their popularity clearly is their much better synthetic accessibility, but at times, lower rigidity may also actually be desirable.

Under realistic laboratory conditions, the difference in the linearity of the axial and the zig-zag rods is smaller than might appear at first sight, since at room temperature and in solution and most solids even at a very low temperature, axial rods will usually deviate from their strictly linear equilibrium geometry to a smaller or larger degree as well. Perhaps a more significant consequence of the deviation from collinearity of the single bonds at the termini of the modules (or vectorial sums of such bonds if the moduli share terminal atoms) becomes apparent when rotation around these bonds or conformational flexibility about the terminal atoms is contemplated.

In axial rods, rotation of one module relative to another has no effect on the linearity of the rod, whereas in zig-zag rods, it does. Several conformers of a zig-zag rod are then possible, and for longer rods, their number is huge. For a long enough zig-zag rod, the most curved conformer will ultimately even be able to close into a ring structure with essentially no strain. At equilibrium, many conformers will typically be present to a significant degree, and the sample is inhomogeneous. The rate of conformer interconversion will usually be somewhat limited by a loss of conjugation at severely twisted geometries but will still be quite fast. Concepts such as a through-space end-to-end distance then may become somewhat ill-defined. These complications seem to be sometimes ignored by the users of rigid molecular rods of any kind, but they should not be.

1.1. Conjugation

Almost all of the zig-zag rods covered presently contain a conjugated π-electron system. An issue that comes up repeatedly in the present review is the nature of π conjugation, and because it is somewhat ambiguous and was not discussed in Part 1,[5] we shall consider it briefly first.

The term π electron conjugation, as currently used by chemists for carbon-based molecules, has two distinct meanings. One ("structural conjugation") carries information about molecular structure: An atom belongs to a conjugated system if its bonding environment is such that it can offer to the π-electron system a valence p orbital (or a hybrid with much p character) whose axis is more or less parallel to the axes of other such atomic orbitals that are in the system. An orbital can be offered for conjugation only if it is not already used in σ-bond formation to another atom; if it is so used, it can still be offered for hyperconjugation, which we do not discuss here.

An illustration may be helpful. In the structural sense, every carbon atom in a planar *meta*- or *para*-polyphenylene is conjugated with each of its two- or three-carbon neighbors and all of the carbon p orbitals whose axes are perpendicular to the molecular plane form one conjugated π-system. This is equally true in the meta and the para isomer of any oligophenylene, and the overall number of $2p_z$ atomic orbitals participating in the π-conjugated system is exactly the same in *m*-quaterphenyl and in *p*-quaterphenyl. It is possible to break structural conjugation at a bond between two carbon atoms partially, by stretching or slightly twisting the bond, or fully, by twisting it all the way to orthogonality. In the simplest Hückel description, this is described by weakening the resonance integral between the corresponding $2p_z$ orbitals accordingly, until at perpendicular twist the integral is zero. Barring this, all of the carbons are in conjugation, and the strength of coupling between all pairs of neighboring $2p_z$ orbitals is comparable, with small variations due to bond length inequality. This is reflected in the molecular orbital (MO) description of the π system, in that an MO can in principle have a nonvanishing amplitude on any of the conjugated carbon p orbitals, and in the valence bond description, in that a resonance structure can in principle have a double bond on any of the carbon−carbon bonds. In practice, some MOs will be very strongly delocalized while others may be mostly localized in one or another region of the conjugated system.

The other and more common meaning of the term π-electron conjugation ("effective conjugation") refers to the effect on molecular properties offered by additional delocalization opportunities that the electron finds in an enlarged π system: two π systems are conjugated if the fact that they were joined into a single π system modified those of their properties that depend on π electrons, such as the ionization potential, electron affinity, and electronic excitation energies. If the two subsystems are connected by a bond at which structural conjugation is absent, e.g., because it is twisted, there will be no effective conjugation between them either. However, even if they are connected by a bond that is perfectly structurally conjugated, there still need not be any effective conjugation between them; that is, their important π-electron-dependent properties may remain essentially unaffected by their union. This always happens when the system becomes excessively long and the critical length at which it occurs is referred to as the effective conjugation length. In strictly linearly conjugated systems with comparable resonance integrals throughout, this length is not reached until many repeat units are present, but in cross-conjugated π systems, and those containing rings, it can be reached already at very small sizes, even if the molecules are perfectly planar and all resonance integrals are comparable in size.

What dictates the conjugation length, and how can a structurally conjugated system fail to be effectively conjugated throughout? At least two important factors are involved. The first is purely electronic and applies even if all processes involved are "vertical", i.e., occur without any change in the equilibrium geometry of the molecules. The second involves vibronic coupling and applies because in reality an oxidized, reduced, or excited form of a molecule inevitably has an at least slightly different equilibrium geometry than the starting species.

Even before we consider the purely electronic factors, we need to recognize that the difference between the extent of structural and effective con-

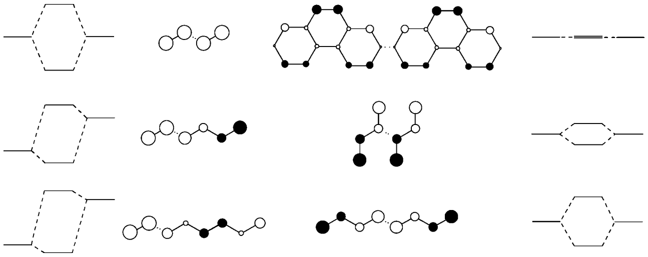


Figure 1. Hückel MO energies: A schematic representation of first-order perturbation theory approximation to HOMO−HOMO interactions (interaction sites are connected with dotted lines). Orbital coefficients are proportional to circle radii, and their signs are indicated by color. Left: the union of ethylene with each of three oligoenes. Right: the union of two phenanthrenes and the cross-conjugating and conjugating union of two butadienes.

jugation depends on the properties chosen for judging the latter. Typically, these are the redox properties of the molecule and the energy and nature of its lowest electronic excitation. In terms of MO theory, these properties are primarily dictated by the frontier MOs. If the energies of these orbitals are not affected much when another repeat unit is added, the measured properties will not be either. The system will be declared effectively nonconjugated, even if it is structurally perfectly conjugated and even if many of its MOs are perfectly delocalized, as long as the properties chosen for monitoring do not depend much on those MOs whose energies were not affected by the union. The way in which structural conjugation is reflected in effective conjugation therefore depends on the property monitored. Two subsystems in a structurally conjugated π-system may be effectively conjugated when judged by the reduction potentials and not effectively conjugated when judged by the oxidation potentials, etc.

The factors that dictate the energies of the frontier MOs as a function of size of a linear system are most easily appreciated by considering a regular sequence of π-conjugated oligomers converging to an infinite polymer, as described by simple Hückel theory. Theoretical studies of the band structure of infinitely long π-conjugated linear polymers started half a century ago[6,7] and represent a vast area of the literature today, well beyond the scope of this review. Here, we merely note that as the number of elementary repeating units in an oligomer increases, the energies of its MOs gradually converge to those of the bands in the polymer. We use first-order perturbation theory at the Hückel level to offer some insight into the effectiveness of conjugation as a function of structure. The change of the energy of an orbital, say the highest occupied molecular orbital (HOMO), upon union with an additional unit is dictated by the effective resonance integral between the oligomer and the new unit, and this can be approximated as the product of the resonance integral connecting the two with the amplitudes (coefficients) of the HOMO in the oligomer and of the HOMO of the unit that is being added (Figure 1). The increase in the HOMO energy will become smaller as the oligomer grows in length and ultimately negligible, as convergence is reached. The reason for this is not a change in the newly added resonance integral but a gradual decrease in the amplitude of the oligomer HOMO at its terminal site as the molecule grows in size (the amplitudes scale approximately as $1/\sqrt{n}$, where n is the number of units in the oligomer).

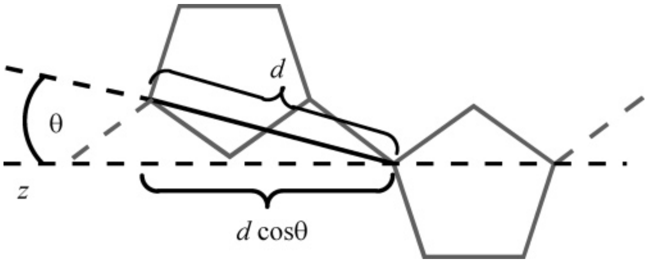


Figure 2. Illustration of the relation of module length d to its rod length increment $d\cos\theta$. The rod axis is labeled z.

When the perturbation of the oligomer HOMO energy by the addition of a new unit becomes smaller than its perturbation by assorted defects, such as variation in the structure of the environment, variation of nuclear geometries due to accidental irregularities or to vibrations, etc., the effective conjugation length has been reached. This will happen sooner if the effective resonance integral between the oligomer and the new unit is small. This integral will be small either because structural conjugation is poor and the resonance integral itself is small (a twisted or a very long bond) or even if structural conjugation is strong, when the amplitude of the oligomer HOMO at its terminal site and/or the amplitude of the HOMO of the added unit at its point of attachment is zero or small. Similar considerations apply to other orbitals, such as the lowest unoccupied molecular orbital (LUMO).

For instance, linking a series of pyrene units through their positions 2 and 7, where the HOMO and the LUMO of pyrene each have a node, produces an effective conjugation length of one unit, when judged by the ease of reduction or oxidation or by the energy of the HOMO−LUMO excitation (L_a band) even if the system is perfectly planar. As shown in Figure 1, this will be nearly true as well when linking a series of phenanthrene units through their positions 2 and 7, which are very close to a node in HOMO and LUMO, and somewhat true when connecting a series of butadienes through their positions 2 and 3, where HOMO and LUMO have relatively small coefficients. Such a union is ineffective and leads to a much shorter effective conjugation length than the union of butadienes through positions 1 and 4, where the amplitude of these orbitals is large. Similarly, the position of the long wavelength maximum and the vertical ionization potential and electron affinity of biphenyl will be affected greatly when its size is quadrupled to p-octiphenyl and hardly at all if it is quadrupled to m-octiphenyl, and this can be understood upon inspection of the Hückel orbitals of biphenyl.

When the change of molecular equilibrium geometries during a redox or excitation process is considered as well, the situation becomes more complicated. This will be the case when the extent of conjugation is not judged by the shift of the most intense absorption peak (vertical transition) but by the position of the zero−zero transition or by the energy of fluorescence from a vibrationally relaxed excited state. Then, one has to do with the "size of the exciton". It will also be the case when one deals with adiabatic ionization potentials or electron affinities and with equilibrium redox processes at an electrode or in solution and, thus, with the "size of the polaron". A detailed discussion is beyond the scope of this review. Briefly, the effective conjugation length will be determined by a competition between the energy saving that can be attained by geometrical distortion to a new equilibrium geometry (the "site distortion energy") and the energy saving that is attainable upon delocalization, which is maximized when the geometry is not distorted at all and was discussed above (stabilization by half the "exciton bandwidth" in the case of electronic excitation). The ratio of the site distortion energy to the exciton band half-width is called the exciton−phonon coupling constant in classical exciton theory of infinite one-dimensional chains, elaborated by physicists half a century ago, and more recently adapted to finite systems that exhibit the effects of quantum confinement (the less than infinite length of the oligomer chain effectively reduces the half-width of the exciton band).[8] The larger the coupling constant, the shorter the effective conjugation length will be. When the constant is much less than unity, the exciton spreads over many modules of the polymer (a "large radius self-trapped exciton"). When the constant exceeds a value in the vicinity of unity, the exciton collapses onto essentially a single site (a "small diameter self-trapped exciton"). The situation is similar for polarons.

In the following, we use the term conjugation in the sense of effective conjugation, and the property monitored typically is the lowest energy electronic excitation.

2. Oligoenes

These compounds comprise the prototypes of linear π conjugation as well as cross-conjugation. They have received an enormous amount of attention over the years, and here, we can only cover some aspects particularly relevant to molecular rod chemistry. We also point out the existence of rods based on nonconjugated oligoenes.

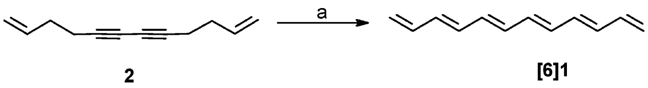
2.1. Conjugated Oligoenes

All-trans oligoenes ([***n***]**1**) represent the simplest example of zig-zag rods. Neither the single bonds connecting the ethene units nor the units themselves are collinear with the axis of the oligomer. Nevertheless, oligoenes maintain some rigidity and overall axiality because of the highly restricted rotation around the double bonds and somewhat constrained rotation around the single bonds, due to π-conjugation through the backbone of the oligomer.

2.1.1. Synthesis

Numerous methods of classical organic synthesis have been developed for the formation of single and double bonds, and these can be used for the preparation of oligoenes. Their discussion is beyond the scope of the present review.[9] Oligoenes are included presently only if they are constructed as intended building blocks for nanoscale architectures and not otherwise; for example, if they were synthesized as a part of a natural product.

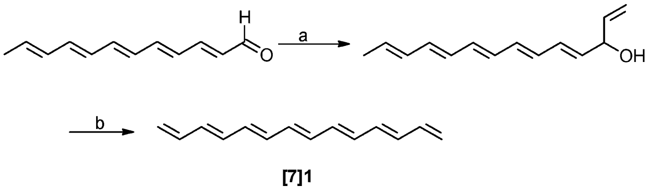
Scheme 1[a]



[a] Conditions and reagents: (a) KO*t*-Bu, HO*t*-Bu.

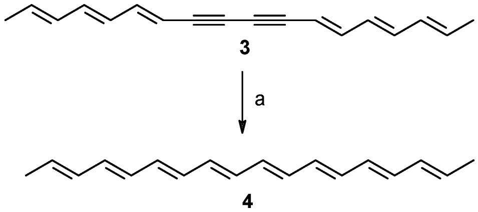
Some of the methods are illustrated in the following examples of preparation of the longer parent oligoenes. The hexaene [**6**]**1** (Scheme 1) was obtained by a prototropic rearrangement of the butadiyne **2**.[10] Self-condensation of crotonaldehyde yielded an aldehyde that was converted into the heptaene [**7**]**1** (Scheme 2).[11] Hydrogenation of a butadiyne precursor **3**, obtained by a double Wittig reaction, afforded the octaene **4** terminated with two methyl groups (Scheme 3).[12] Aten and Hoijtink[13] synthesized a series of α,ω-diphenyloligoenes [***n***]**5** up to the hexamer [**6**]**5**,[14] and Roncali's group[15] reported work on 1,6-diphenylhexatriene [**3**]**5** (Chart 1).

Scheme 2[a]



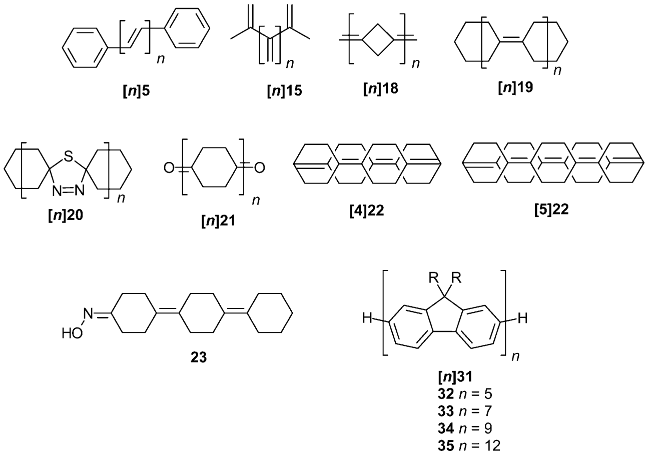
[a] Conditions and reagents: (a) THF, $CH_2 = CHMgBr$. (b) HCl, $CHCl_3$.

Scheme 3[a]



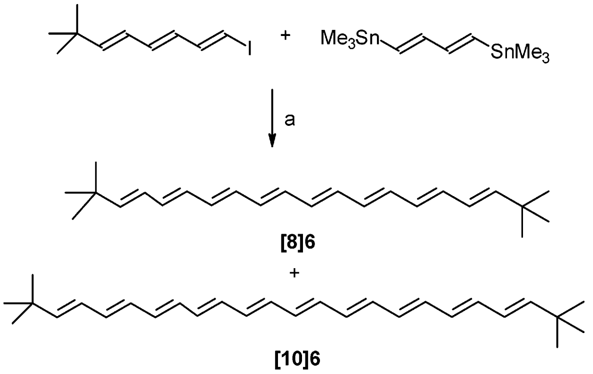
[a] Conditions and reagents: (a) H_2, Lindlar Pt catalyst.

Chart 1



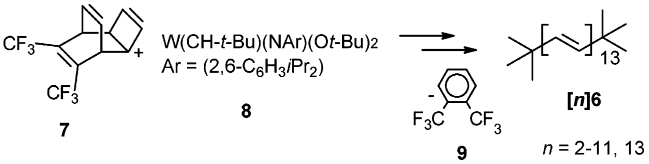
Many transition metal-catalyzed reactions have also been utilized for the synthesis of oligoenes. α,ω-Di-*tert*-butyl-substituted oligoenes ([***n***]**6**) up to the decaene [**10**]**6** have been obtained by Müllen's group using Stille coupling between vinyltin compounds and vinyl halides (Scheme 4).^{16,17} Ring-opening metathesis oligomerization of the cyclobutene derivatives **7** on a tungsten catalyst **8** with subsequent extrusion of the aromatic auxiliary moiety **9** provided a mixture of oligoenes containing cis double bonds and terminal *tert*-butyl groups (Scheme 5).^{18} Isomerization and chromatographic separation yielded all-*trans* oligoenes up to the tridecaene [**13**]**6**.^{18} Oligomerization of 3−13 equiv of acetylene on the same catalyst **8** in the presence of 5 equiv of quinuclidine yielded mixtures of predominantly all-trans oligoenes [***n***]**6** (Scheme 6).^{19} Other ring-opening polymerization reactions have been reported to yield polyacetylenes, but they were not used to prepare oligoenes.^{20,21}

Scheme 4^{a}

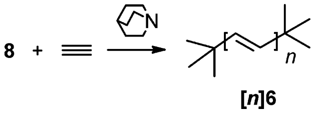


^{a} Conditions and reagents: (a) $PdCl_2(CH_3CN)_2$, DMF. Reprinted with permission from ref 16. Copyright 1995 Wiley-VCH.

Scheme 5

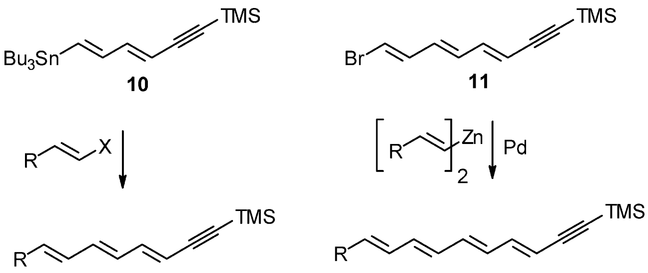


Scheme 6

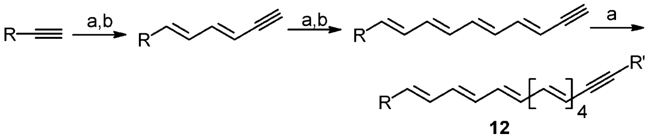


Lipshutz et al.^{22,23} developed the precursors **10** and **11** for rapid construction of tetra-, penta-, and hexaene backbones (Scheme 7). The tin-containing dienyne **10** couples to vinyl bromides or vinyl iodides, while the bromo-terminated trienyne **11** is extended by reaction with vinyl- or dienylzinc reagents. Both precursors contain a trimethylsilyl-protected terminal acetylene group, which is ultimately converted into a terminally substituted *trans*-olefin unit. A very elegant, selective, and general method for the preparation of all-*trans*-oligoenes was recently reported by Zeng and Negishi (Scheme 8).^{24} On the basis of the hydrozirconation/palladium-catalyzed cross-coupling of terminal alkynes with a four-carbon synthon, an iterative methodology yielded oligomers up to the heptamer **12** in high yield. Oligomers with an even number of double bonds were prepared by hydrozirconation of different terminal alkynes and subsequent coupling with (*E*)-bromo-4-trimethylsilyl-1-buten-3-yne (**13**). The terminal alkyne was regenerated by desilylation allowing for an iteration of the procedure up to the tetraenynes (Scheme 8). The odd series (trienynes and pentaenynes) was obtained by insertion of a hydrozirconation-iodinolysis-Pd-catalyzed ethynylation step with HC/CZnBr prior to the four-carbon elongation. Babudri et al.^{25} synthesized symmetrical polyenes using homocoupling of substituted unsaturated silanes (Scheme 9).

Scheme 7

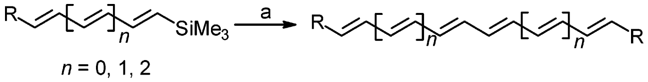


Scheme 8^{a}



^{a} Conditions and reagents: (a) (1) $HZrCp_2Cl$, THF; (2) (*E*)-$BrCH{=}CHCCSiMe_3$ (**13**), $PdCl_2(PPh_3)_2$, DIBAH, $ZnCl_2$, THF. (b) K_2CO_3, MeOH.

Scheme 9^{a}



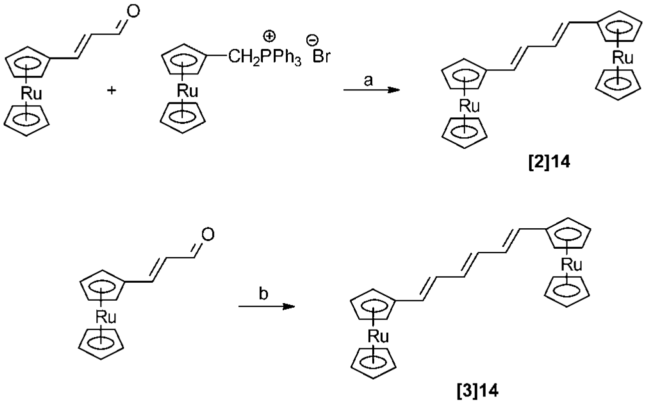
^{a} Conditions and reagents: (a) $PdCl_2$, $CuCl_2$, LiCl.

Very recently, Sato's group^{26} synthesized a series of ruthenocene-capped polyenes [***n***]**14** up to the hexatriene by applying Wittig reaction conditions to 3-ruthenocenyl-2-propenals and ruthenocenylemethylphosphonium salts, as well as by Mukaiyama coupling of the respective propenals (Scheme 10). The binuclear ruthenocene derivatives [***n***]**14** undergo a chemically reversible two-electron redox process, and both the neutral and the oxidized species are air stable.

2.1.2. Properties

Like many other zig-zag rods, all-trans polyenes [***n***]**1** are only rod-shaped in their all-*s*-trans conformation. Although this is generally the most stable, at room temperature, conformations with one or more *s*-cis links are also populated, and the problem becomes more severe as the polyene becomes longer.

Scheme 10[a]



[a] Conditions and reagents: (a) LDA. (b) $TiCl_4$, Zn.

The shorter oligoenes are stable thermally. UV and visible light, however, may cause trans−cis isomerization around one or more of the double bonds and ruin the axiality of the rod altogether. As a rule, push−pull oligoenes with a donor group on one end and an acceptor group on the other are less prone to such isomerization. Long oligoenes are unstable unless terminated with aromatic or bulky substituents.

Bond length alternation in oligoenes [***n***]**1** is smaller than that in oligoynes, and oligoenes are better conductors of charge. Terminal substitution of the oligoene with conjugating polar substituents affects bond length alternation and the extent of conjugation[27] and, through these, many other physical and chemical properties of the oligomers. In push−pull oligoenes, bond length alternates the least when both the donor and the acceptor are of medium strength. Both the combination of very weak donors and acceptors and the combination of very strong donors and acceptors promote localization of bonds in the ground state.[27] Maximum conductivity of the oligoene chain is achieved at the cyanine limit when the system has a net charge and two resonance structures contribute equally or almost equally to the ground state. At infinite length, the band gap of such oligoenes and bond length alternation are caused only by the Peierls distortion.[28]

Müllen and co-workers[17] reported the first reduction potentials of three long polyenes (Chart 1), the tetraene [**4**]**6**(−3 V vs Fc^+/Fc), hexaene [**6**]**6** (−2.7 V), and octaene [**8**]**6** (−2.5 V), and confirmed a linear relation to $1/n$, where n is the number of multiple bonds. The values published[13] for the tetrameric (−2.2 V) and hexameric (−2.0 V) α,ω-diphenyloligoenes [***n***]**5** (Chart 1) are less negative, but a direct comparison is impossible due to the use of different solvents (THF and DMF, respectively). However, both graphs extrapolate to a similar limit around −1.9 V, a value that is in agreement with the results (between −1.3 and −1.4 V vs SCE) obtained by Jozefiak et al.[29] for longer polyacetylene derivatives prepared by ring-opening metathesis polymerization of substituted cyclooctatetraenes. Roncali and co-workers[15] reported an absorption maximum at 370 nm and a first oxidation potential of +1.18 vs Ag/AgCl in CH_2Cl_2 for 1,6-diphenylhexatriene [**3**]**5**. Many electrochemical studies on carotenoid systems have been reported[30−32] in the series of relatively stable $\alpha,\alpha,\omega,\omega$-tetra-*tert*-butyl-substituted oligoenes; photoelectron spectra have been measured for compounds with 3−5 and 7 conjugated double bonds in the molecule, and UV−visible absorption spectra for all compounds with 3−13 double bonds.[33]

2.2. Cross-Conjugated Oligoenes (Dendralenes)

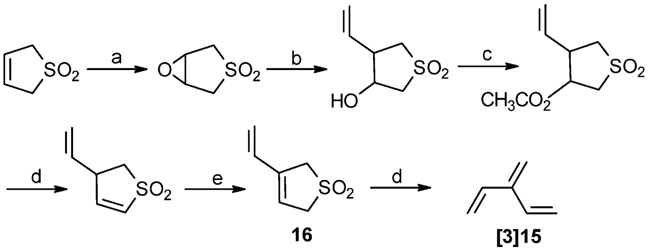
Cross-conjugation is a very intriguing phenomenon that has received comparatively little attention. The term is used for molecular structures that are structurally conjugated but in which effective conjugation extends from any one double bond only to it neighbors on each side, and a regular sequence of alternating single and double bonds does not extend farther, as in [***n***]**15** (Chart 1). Only very recently, systematic syntheses of cross-conjugated oligomers have allowed a more thorough investigation of the underlying governing principles and their consequences.

Dendralenes [***n***]**15** (Chart 1) are acyclic polyenes in which maximum unsaturation and maximum cross-conjugation are combined. Despite early interest in dendralenes dating to the beginning of the last century, very little work has been reported on this structurally interesting and synthetically challenging class of compounds.

2.2.1. Synthesis

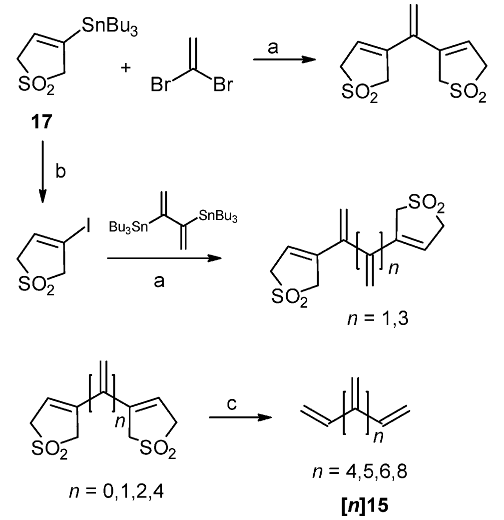
At least in case of the parent, 3-methylene-1,4-pentadiene, or [3]dendralene [**3**]**15**, several synthetic pathways have been explored. All of them were tedious, multistep routes that mostly involve thermal reactions (eliminations and pericyclic processes) in the last step, rendering them rather impractical for large-scale preparative syntheses. Because of its efficiency, the cheletropic decomposition of the sulfolene derivative **16** developed by Cadogan et al.[34] needs to be mentioned as the most feasible approach (Scheme 11). Interest in the second homologue was mainly restricted to mechanistic studies resulting in highly imaginative but rather complicated synthetic solutions. Higher homologues were encountered only in theoretical studies until Fielder et al.[35] developed a general synthetic pathway for [n]dendralenes [***n***]**15** (Scheme 12). The key to their accomplishment was the masking of the dendralene π-system at both ends with sulfolene rings. Starting from the stannylated sulfolene **17**, relatively mild Stille cross-coupling reactions were used to build up the oligomers. The free dendralenes up to [8]dendralene [**8**]**15** were ultimately produced by thermal decomposition of the sulfolene rings under loss of SO_2 at 450 °C.

Scheme 11[a]



[a] Conditions and reagents: (a) HCO_3H, H_2O. (b) $CH_2{=}CHMgBr$, THF. (c) $CH_3COCl{-}NEt_3$, THF. (d) FVP. (e) DBU, THF.

Scheme 12[a]



[a] Conditions and reagents: (a) $PdCl_2(CH_3CN)_2$, DMF. (b) I_2, CH_2Cl_2. (c) 450 °C.

2.2.2. Properties

Dendralenes [***n***]**15** (Chart 1) are reactive compounds that tend to polymerize. [**3**]Dendralene is a very volatile solid that dimerizes quickly. From a synthetic point of view, dendralenes are very useful building blocks for Diels–Alder addition reactions, which can lead to extended ring systems. Interestingly, they probably do not exist in coplanar conformations but contain butadiene fragments that are twisted relative to each other. Their observed UV absorption maxima are similar to those of 1,3-dienes, and the conjugation length is only two double bonds. The longer homologues[35] are crystalline and stable compounds when masked. Although the free dendralenes are more sensitive and polymerize slowly in solution, they are stable enough to have been fully characterized by standard spectroscopic and analytical tools.

2.3. Nonconjugated Oligoenes

In oligomeric cyclobuta-1,3-diylidenes (**18**) and cyclohexa-1,4-diylidenes (**19**), puckered aliphatic cycles are linked by double bonds (Chart 1). Rigidity is moderate and is provided by the conformational stability of the puckered rings, which is presumably higher for the six-membered rings in **19**.

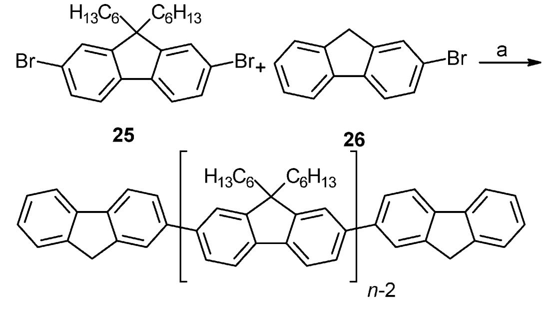
2.3.1. Synthesis

The dimer [**2**]**18** and the trimer [**3**]**18** result from transition metal-catalyzed rearrangement of [1.1.1]-propellane.[36] Oligomers [**2**]**19**–[**5**]**19** (Chart 1) have been prepared by the group of Jenneskens by nitrogen extrusion from the corresponding thiadiazoline precursors [**2**]**20**–[**5**]**20** (Barton–Kellogg olefin synthesis, Chart 1).[37] The same method was used earlier by Vögtle et al.[38] and McMurry et al.[39–41] to prepare the terminal diones [**4**]**21** and [**5**]**21**, respectively (Chart 1).

2.3.2. Properties

The oligomers are stable to air and organic solvents.[37] Their thermal stability increases with length.[37] The higher oligomers of **18** and **19** are marginally soluble in common solvents, but introduction of alkoxy substituents at the termini improves their solubility markedly. The expected all-trans conformation has been confirmed by an X-ray study of a hexyl-substituted [**3**]**19**.[37] The terminal diones [**4**]**21** and [**5**]**21** cyclize under McMurry coupling conditions into the ring compounds [**4**]**22**[38] and [**5**]**22**,[39,40] respectively, in extremely low yields (Chart 1). Clearly, these rods are relatively flexible.

Scheme 13[a]



[***n***]**24**

[a] Conditions and reagents: (a) $Ni(COD)_2$, COD, bipyridine, toluene/DMF, 80 °C.

No evidence for any chemical instability of oligomers **19** has been reported. Excess 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) dehydrogenates oligo(cyclohex-1,4-ylidene)s into the corresponding oligo-*p*-phenylenes.[20] It is noteworthy that an oxime group in the terminal position of **23** (Chart 1) affects the chemical shift of the carbon located 7 Å away along the rod.[42]

3. Oligofluorenes

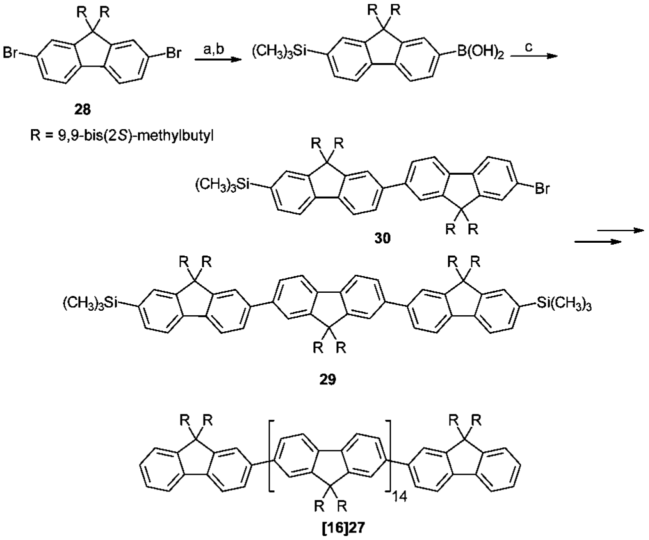
Polyfluorenes are related to the oligo-*p*-phenylenes covered in Part 1.[5] Their aromatic rings are forced into pairwise coplanarity by the presence of bridging methylene groups in five-membered rings, and this enhances conjugation. The price that is paid for this advantage is the loss of axiality, and for this reason, oligofluorenes were not included in Part 1.[5] Oligomers in which planarization is enforced throughout, and not only between every other pair of aromatic rings, are classified as ladder rods, and we plan to cover them in the next installment of this series of reviews.

Polyfluorenes have been prepared through several routes and have been reviewed recently.[43,44] They exhibit very high thermal and chemical stabilities. Because of their high photoluminescence quantum yields, they have been investigated for use in organic LEDs. Their potential for liquid crystal mediated alignment renders them prime candidates for electroluminescence. Here, we focus on well-defined oligomers.

3.1. Synthesis

In an effort to determine the effective conjugation length of polyfluorenes, Klaerner and Miller[45] used Ni-promoted Yamamoto polymerization to prepare a mixture of well-defined fluorene oligomers [***n***]**24** (Scheme 13). 9,9-Di-*n*-hexyl-2,7-dibromofluorene (**25**) was polymerized in the presence of end-capping

Scheme 14[a]



[a] Conditions and reagents: (a) (1) BuLi; (2) $ClSi(CH_3)_3$. (b) (1) BuLi; (2) $(iPrO)_3B$; (3) H_2O. (c) Compound **28**, $Pd(PPh_3)_4$, Na_2CO_3 for **29**, and excess **28** for **30**.

2-bromofluorene (**26**) to control the molecular weight. Relative ratios of **25** and **26** between 3:1 and 1:1 were found to enhance the formation of the oligomeric fraction and HPLC was utilized to separate and purify oligomers ranging from the trimer to the decamer.

The first series of monodisperse chiral oligofluorenes [***n***]**27** was recently reported by Geng et al.[46] following a divergent/convergent approach (Scheme 14). The main building block, 2,7-dibromo-(9,9-bis-(2*S*-methylbutyl)fluorene (**28**), was monolithiated to introduce a trimethylsilyl protecting group, and the second bromo substituent was subsequently converted to a boronic acid. Applying Suzuki conditions, the resulting unsymmetrically substituted fluorene was coupled with **28** to obtain the trimer **29**. Using an excess of **28**, elongation by one fluorene unit to **30** was accomplished while preserving the unsymmetrical substitution pattern. Subsequently, either the terminal protecting group was replaced with iodine to generate a building block with enhanced selectivity in the Suzuki reaction or the bromine was converted to a boronic ester, both of them capable of chain extension at either terminal group.[46] Monofunctional end-capping modules were built up in a similar fashion starting from 2-bromo-(9,9-bis(2*S*-methylbutyl)fluorene by unilateral growth. Mixing and matching various combinations of these building blocks, Chen's group[47] assembled a complete series of oligomers up to the hexadecamer [**16**]**27**. Furthermore, a set of nonamers with a varying extent of pendant chirality was produced by simply changing the substitution pattern of alkyl chains in the 9-position. The divergent−convergent methodology was very recently utilized to synthesize the first series of monodisperse nematic oligofluorenes **31** (Chart 1).[48] Penta- **32**, hepta- **33**, and nonafluorenes **34** carrying various alkyl group substitution patterns in position 9 were assembled using Suzuki coupling, while the Yamamoto coupling reaction was used to prepare the dodecafluorene **35**.

3.2. Properties

The oligofluorenes [***n***]**24** and [***n***]**27** were all isolated as white powders with high thermal and chemical stabilities.[46] The influence of the chain length and substitution patterns on the morphology and optical properties on the system [***n***]**27** was investigated. With increasing chain length, the oligomers switch first from being amorphous to exhibiting cholesteric mesomorphism with varying degrees of morphological stability against crystallization and ultimately become crystalline materials.[46] Phase transition temperatures increase concurrently. The chiroptical activity of the compounds in neat films was shown to be predominantly attributable to cholesteric stacking of the rodlike molecules. Circularly polarized OLEDs built with nonafluorene films exhibited very high luminescence yields.[49,50]

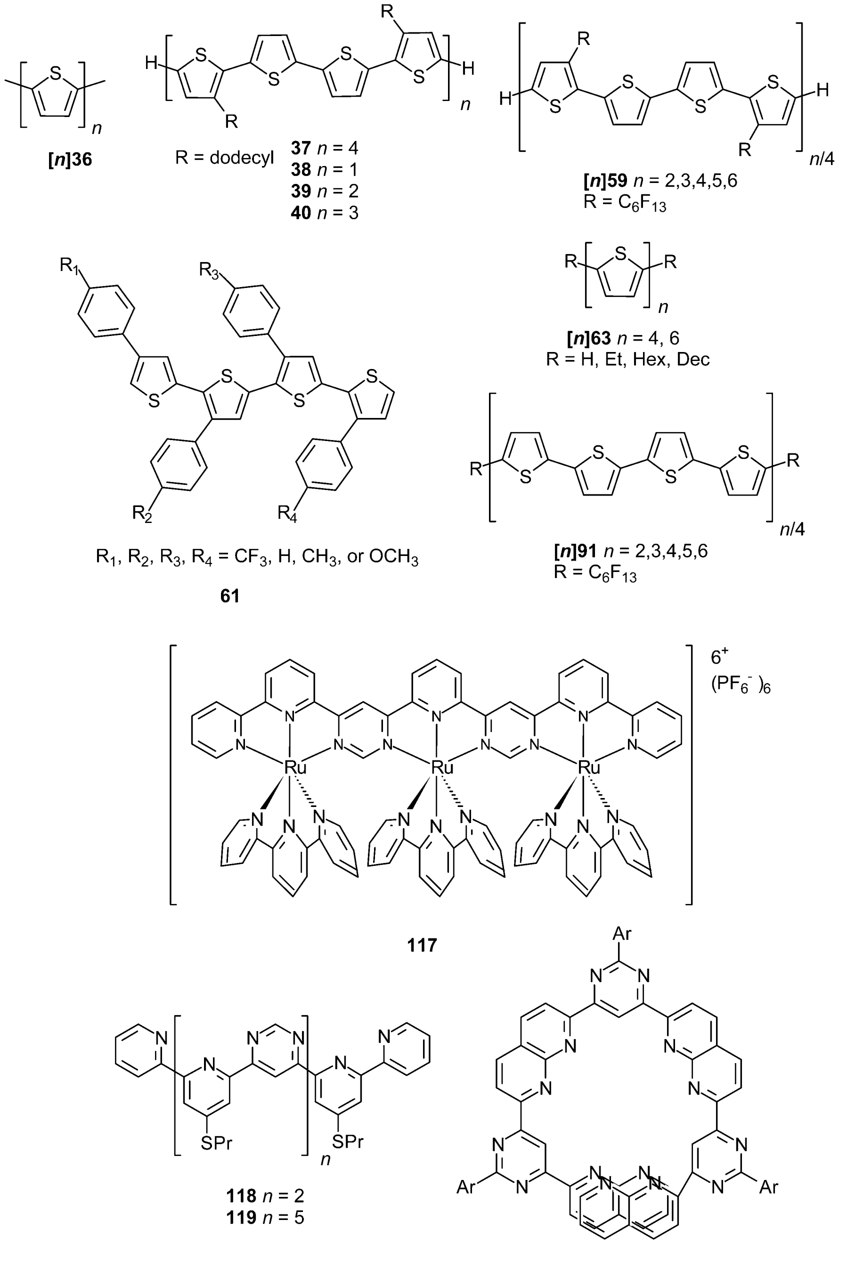
The optical properties of the oligofluorenes [***n***]**24** were studied systematically.[45] While the UV−visible spectra display continuously red-shifted absorption maxima up to the decamer [**10**]**24**, reaching a value of 384 nm [the value for poly(9,9-dihexyl-2,7-fluorene) is 388 nm], the fluorescence emission spectra did not change significantly beyond the hexamer. Analysis of the absorption energy as a function of oligomer length led the authors to estimate the effective conjugation length[51] as about 12 consecutive fluorene units, representing a total of 24 aromatic rings.[45]

The effect of chain length and pendant group structure on the thermotropic and optical properties of the monodisperse nematic oligofluorenes [***n***]**31** was analyzed systematically.[48] Both the pendant group structure and the chain length had an important impact on the glass transition temperature, which was as high as 150 °C for optimized parameters, while the temperature of the nematic to isotropic transition (T_c), determined by polarized optical spectroscopy, was shown to be mostly a function of the length of the backbone. Co-oligomers with branched pendant groups formed superior glassy nematics. The resulting glassy nematic films were characterized by quantum yields of up to 60% for blue photoluminescence emission. The films were stable and showed good processability.[48]

4. Oligothiophenes

Oligothiophenes [***n***]**36**[52−54] (Chart 2) are also analogous to oligo-*p*-phenylenes, but their five-membered aromatic rings are more electron-rich and easier to oxidize. The ortho hydrogens of neighboring units are less likely to clash, and it is easier to attain complete planarity through the conjugated system. This combination of properties combines to confer quite distinctive properties on oligothiophenes, but one of the consequences is the loss of axiality. They have been known for over 60 years. Conjugation between thiophene rings provides significant rigidity in homooligomers and is one of the strongest among the zigzag rods. Advantages of oligothiophenes as molecular rods include cheap precursors, high thermal and photochemical stabilities, and a well-developed set of methods for preparation and handling. Much work has been reported on the synthesis of monodisperse,

Chart 2

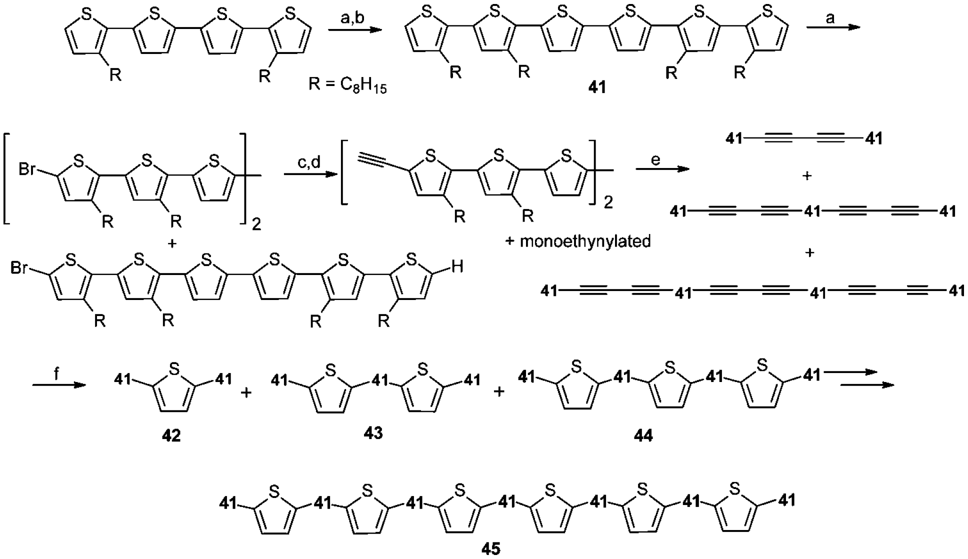


regioregular head-to-tail coupled bi- and terthiophenes, which we will not comprehensively review here. The chemistry of oligothiophenes and polythiophenes has been extensively reviewed elsewhere,[55−60] and presently, we focus on the more recent efforts to prepare long monodisperse oligomers.

4.1. Synthesis

Thiophenes are the most common precursors for oligothiophenes [***n***]**36**. Individual unsubstituted oligomers up to $n = 10$ have been reported.[61] The original method of coupling of 2-halo- or 2,5-dihalothiophenes with copper bronze at elevated temperatures gave poor yields.[62] More recently, the enhanced acidity of the thiophene hydrogens in positions 2 and 5 has been used to prepare the corresponding anions by treatment with n-BuLi, and these can be oxidatively coupled with $CuCl_2$.[57,59,63] Oligothiophenes with only one α-hydrogen available can be oxidatively coupled with $FeCl_3$ in chloroform.[64] The first unsymmetrical coupling of oligothiophenes was achieved by repetitive thiophenylation of a borane reagent followed by oxidation with I_2.[65] Modern methods of unsymmetric coupling include the Kumada,[57,59,63] Suzuki,[66] and Stille[66] reactions. Oligothiophenes may also be prepared by formation of a thiophene ring from 1,4-diketones[64,67,68] or butadiynes[69−71] attached to one or more thiophene groups. In general, the synthesis of monodisperse, and especially isomerically pure, material is notoriously difficult and low yields and tedious purification procedures are common. In the monomers and in the short oligomers, reactions in β positions, undesirable for linear chain extension, are practically negligible as compared to reactions in α positions. Unfortunately, reactions in β positions gain importance in long oligomers. A

Scheme 15[a]



[a] Conditions and reagents: (a) NBS, DMF, CS_2. (b) $NiCl_2$(dppp), ether, benzene, THF, 3-(octyl)thienylmagnesium bromide. (c) Trimethylsilylacetylene, $Pd(PPh_3)_4$, CuI, Et_3N, 70 °C. (d) KOH, benzene-MeOH. (e) $Cu(OAc)_2$, pyridine, 40 °C. (f) Na_2S, H_2O, KOH, dioxane, reflux.

complete blocking of those sites in the building blocks therefore not only improves the solubility of the longer rods but also prevents the formation of branched side products.

4.2. Properties

Oligothiophenes [***n***]**36** with no α-hydrogens are highly stable toward very strong oxidants and acids. Extrapolation studies for poly(3-octylthiophene) and poly(3-decylthiophene) doped with $FeCl_3$ predicted perfect stability for 10−100 years.[72] Polythiophene films are stable toward UV−visible light under argon atmosphere[73] but degrade upon irradiation in solution containing dissolved molecular oxygen.[74]

Unsubstituted oligothiophenes [***n***]**36** up to $n = 5$ are sparingly soluble in common organic solvents under ambient conditions. For solubility of longer oligomers, either one methyl group per thiophene unit[66] or one dodecyl group per every three thiophene units[75] is sufficient. The solubility can also be significantly increased by β substitution with phenyl groups or introduction of spirofluorenyl bridges. Unsubstituted oligomers are planar in the solid state.[76]

4.3. Organic Peripheral Substitution

4.3.1. Synthesis

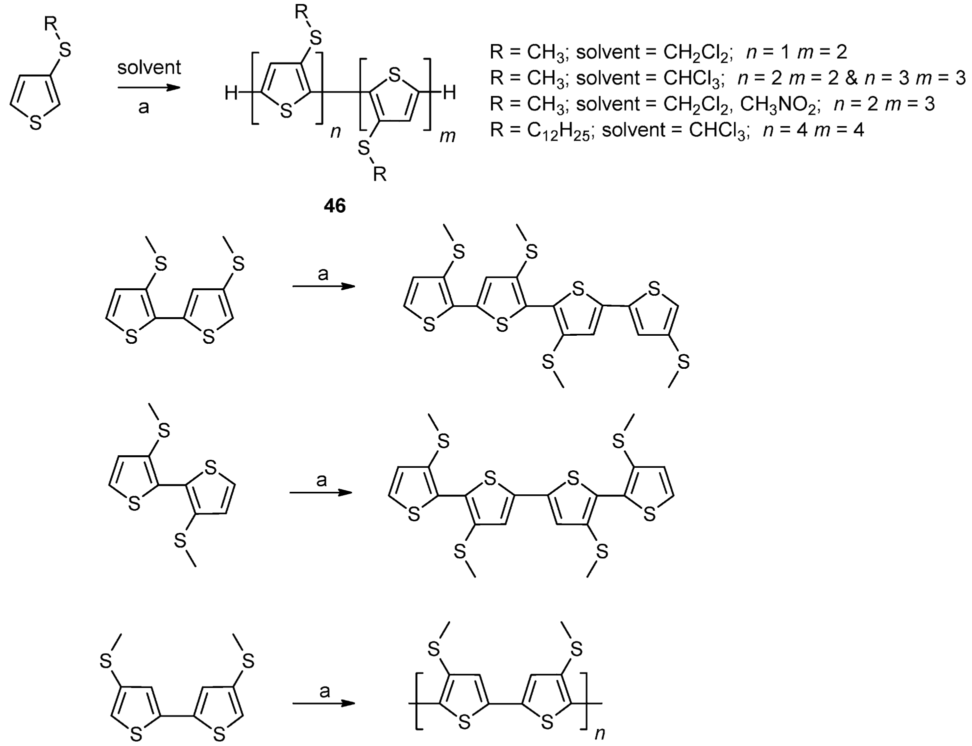
For the synthesis of longer rods, substitution with solubilizing groups in the β positions is necessary. Bäuerle and his group[63] have devised a synthetic scheme to produce a dodecyl-substituted oligomeric series up to the sedicithiophene **37** (Chart 2), spanning 64 Å when extended. 2-Bromo-3-dodecylthiophene was converted to its Grignard reagent and coupled with one-half equivalent of 5,5′-dibromo-2,2′-bithiophene under Ni catalysis in order to obtain 3,3‴-didodecylquaterthiophene **38** in good yield. After lithiation, oxidative dimerization under Cu mediation first led to a mixture of oligomers, from which the tetradodecyloctithiophene **39** and hexadodecyldodecithiophene **40** could be separated by repeated chromatography in a modest and a poor yield, respectively (Chart 2). The sedicithiophene **37** was prepared by similar oxidative coupling of the octithiophene **39** in respectable yield. However, the compounds are inhomogeneous because there is less than one alkyl chain per thiophene unit.

Extremely long rods consisting of tetraoctyl-substituted sexithiophene building blocks bridged by single thiophene modules were reported by the group of Otsubo.[77] The key intermediate, the hexamer **41**, was obtained from a dioctyl-substituted quaterthiophene via bromination and subsequent Ni-catalyzed cross-coupling with the appropriate Grignard reagent (Scheme 15). Compound **41** was selectively mono- or dibrominated, ethynylated, and extended via oxidative Eglington coupling, resulting in a mixture of mainly three butadiyne bridged oligomers. After separation by GPC, treatment with sodium sulfide afforded the tridecamer **42**, the icosamer **43**, and the heptacosamer **44**, spanning 10.8 nm. Repetition of the procedure led to the 48-mer **45**.[78]

Barbarella and co-workers[79] discovered that regioregular oligo(3-(alkylthio)thiophene)s **46** can be prepared from 3-(alkylthio)thiophenes in one step by treatment with ferric chloride (Scheme 16). The products are characterized by one central head-to-head linkage and a variable number of lateral head-to-tail connections. The length of the primarily formed oligomer depends both on the solvent and on the length of the alkyl chain in the monomer. Under the same conditions, it is possible to dimerize the corresponding head-to-tail and head-to-head bithiophenes, while the tail-to-tail compound polymerizes.

Regioregular head-to-tail coupled oligo(3-octylthiophene)s **47** up to the hexamer [**6**]**47** were reported by Bidan et al.[80] who used a chlorine substituent to selectively protect one α position in the monomer (Scheme 17). The free α position was iodinated, and the resulting α-iodochlorothiophene was coupled with

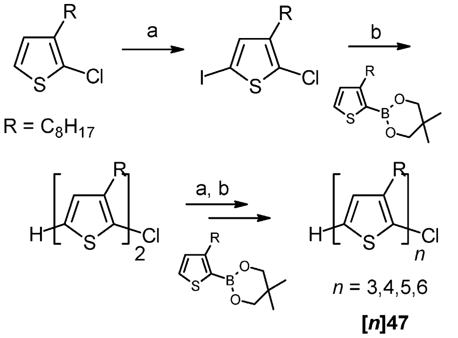
Scheme 16[a]



R = CH_3; solvent = CH_2Cl_2; $n = 1$ $m = 2$
R = CH_3; solvent = $CHCl_3$; $n = 2$ $m = 2$ & $n = 3$ $m = 3$
R = CH_3; solvent = CH_2Cl_2, CH_3NO_2; $n = 2$ $m = 3$
R = $C_{12}H_{25}$; solvent = $CHCl_3$; $n = 4$ $m = 4$

[a] Conditions and reagents: (a) 4 $FeCl_3$.

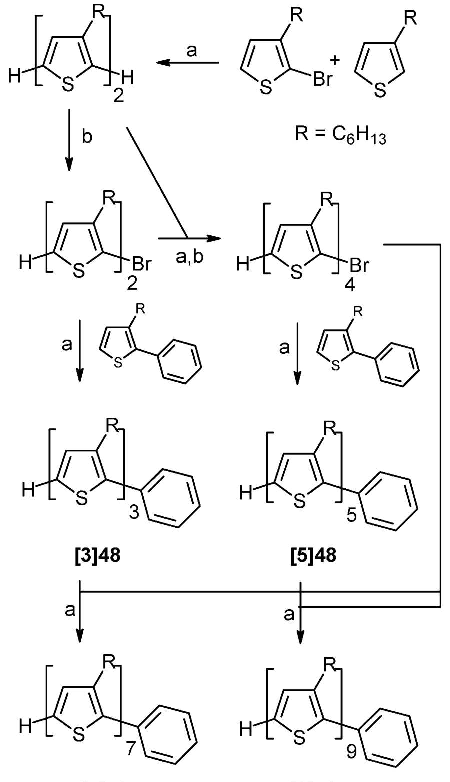
Scheme 17[a]



[a] Conditions and reagents: (a) I_2, $Hg(OAc)_2$. (b) $Pd(PPh_3)_4$, $NaHCO_3(aq)$.

a thiopheneboronate ester in the stepwise buildup of the oligomers. The syntheses of similar phenyl-capped oligo(3-hexylthiophene)s [***n***]**48** up to the nonamer were published by Li et al.,[81] who applied Negishi type coupling conditions between brominated 3-hexylthiophene units and organozinc derivatives (Scheme 18). In addition, these authors utilized this methodology to construct a series of oligothiophenes with nonlinear optical chromophores. As the key building block, they developed 5-trimethylsilyl-3′,4-(di(2″-ethylhexyl)-2,2′-bithiophene (**49**), which allows the controlled nonsymmetrical elongation of rods in both directions (Scheme 19). Thus, two complementary oligothiophenes, one terminated with a siloxyphenyl group and the other bearing a NLO chromophore, were constructed in a stepwise manner and finally cross-coupled to yield the octithiophene [8]**50** and decithiophene [10]**50** (Scheme 20).[82]

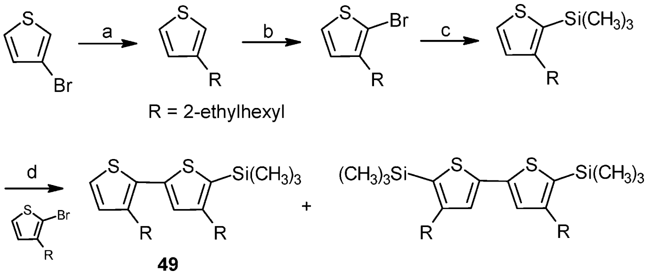
Scheme 18[a]



[a] Conditions and reagents: (a) BuLi, TMEDA, $ZnCl_2$, $Pd(PPh_3)_4$. (b) NBS.

To improve solubility and tune electronic properties, substitution patterns other than alkyl chains in the β positions were explored as well. Mitschke and Bäuerle[83] synthesized a pentamer **51** with phenyl substitution on the central thiophene module and the corresponding rod **52** with a central benzo[*c*]thiophene unit, as well as a spirofluorenyl-bridged hexamer **53**

Scheme 19[a]

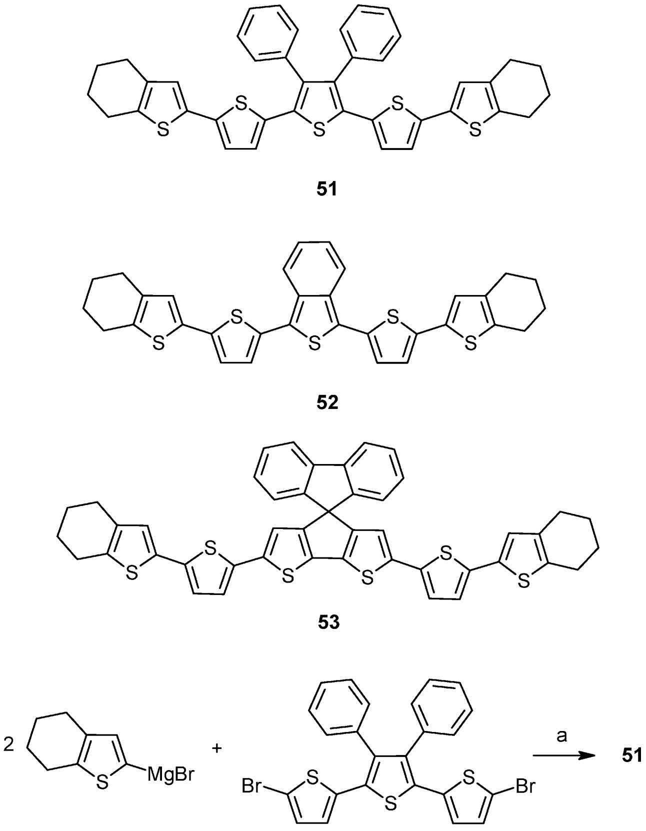


[a] Conditions and reagents: (a) $PdCl_2(dppf)$, CH_2Cl_2, ether, RMgBr. (b) NBS, $CHCl_3$, AcOH. (c) (1) BuLi, ether; (2) $(CH_3)_3SiCl$. (d) (1) BuLi, THF, TMEDA; (2) $ZnCl_2$, THF; (3) $Pd(PPh_3)_4$.

(Scheme 21). The synthesis was accomplished by bromination of the central thiophene building blocks and subsequent nickel-catalyzed cross-coupling with the Grignard reagent of 2-bromo-4,5,6,7-tetrahydrobenzo[*b*]thiophene. Komatsu's group[84] chose the annelated bicyclo[2.2.2]octene cage as a solubilizing group and constructed rods [***n***]**54** up to the hexamer with these modules (Scheme 22). The building block **55** was synthesized in three steps from bicyclo[2.2.2]-octane-2,3-dione in moderate yield and subsequently elongated by selective lithiation and transition metal-catalyzed cross-coupling reactions. An oxidative coupling of the terthiophene **56** with $NO^+SbF_6^-$ was carried out to prepare the hexamer [**6**]**54** in high yield.

Also recently, Otsubo and co-workers[85-87] have carried the synthesis of monodisperse oligothiophenes to a new level. They reported the synthesis of an oligomeric series up to the extraordinarily long 96-mer [**96**]**57**, carrying 2,2-bis(butoxymethyl)-1,3-propanediyl groups in order to block all β sites (Schemes 23 and 24). The key building block **58** was prepared in four steps from 2,5-dibromo-3,4-bis(bromomethyl)-thiophene and selectively converted to its mono- and dibromo derivatives. These units were cross-coupled under Stille conditions to produce the hexamer [**6**]**57** in high yield (Scheme 23). Repetitive oxidative coupling of the dimerized product after intermediate preparative GPC separation of the reaction mixture produced the following series of [***n***]**57** oligomers: first the 12-mer, 18-mer, and 24-mer; then the 24-mer, 36-mer, and 48-mer; and finally, the 48-mer, 72-mer, and 96-mer, albeit in decreasing yields (Scheme 24).[87]

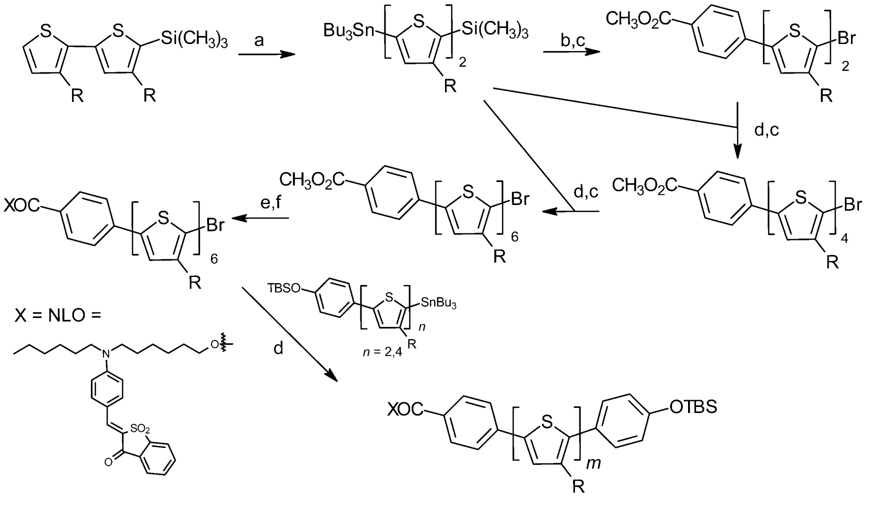
Scheme 21[a]



[a] Conditions and reagents: $NiCl_2(dppp)$, ether, toluene.

Very recently, Fachetti et al.[88] have reported a series of regiochemically pure β,β'-diperfluorohexyl-substituted oligothiophenes [***n***]**59** up to the hexamer

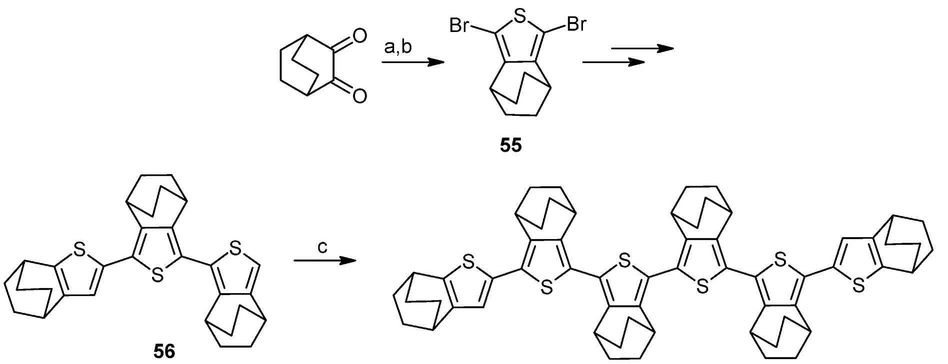
Scheme 20[a]



[8]50 $m = 8$
[10]50 $m = 10$

[a] Conditions and reagents: (a) (1) BuLi, THF, TMEDA; (2) Bu_3SnCl. (b) Methyl *p*-iodobenzoate, $PdCl_2(PPh_3)_2$, PPh_3, toluene. (c) NBS, $CHCl_3$, AcOH. (d) $Pd(PPh_3)_3$, toluene. (e) NaOH, THF, EtOH, H_2O, X = OH. (f) THF, DEAD, PPh_3, X = NLO.

Scheme 22[a]



[a] Conditions and reagents: (a) (1) $CH_3O_2CCH_2SCH_2CO_2CH_3$, KO*t*-Bu, THF; (2) NaOH, H_2O. (b) Br_2, H_2O. (c) (1) $NO^+SbF_6^-$, CH_2Cl_2; (2) $(C_2H_5)_4N^+I^-$.

in order to compare their properties to alkyl functionalized counterparts (Chart 2).

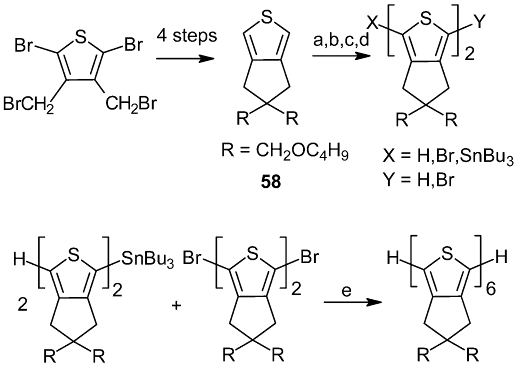
Fazio et al.[89] published a synthetic route to mono-, bis-, and terthiophenes [***n***]**60** containing alternating3,4-bis[methoxycarbonyl)methyl]substituted modules. They utilized an oxidative dicarbonylation of dipropynyl sulfides (Scheme 25). The rods were extended by double bromination and Stille coupling with 2-(tributylstannyl)thiophene to form the respective pentathiophene [**5**]**60**.

A stepwise solid phase synthesis was used by Briehn et al.[90,91] to create a combinatorial library of quater(3-arylthiophene)s **61** in which the *p*-substituent (R = CF_3, H, CH_3, OCH_3) on the benzene spacer was varied systematically in order to derive structure–property relationships (Chart 2).

4.3.2. Properties

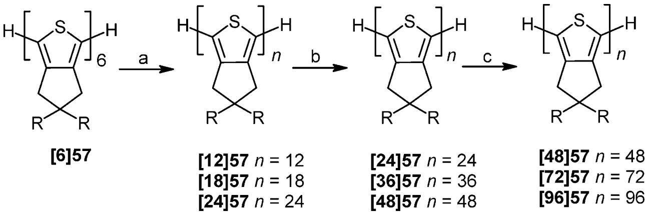
The dodecyl-substituted compounds of Bäuerle, such as **37** (Chart 2), are very stable materials with melting points that increase with increasing rod length but remain below 100 °C. Unsubstituted oligothiophenes of comparable chain length melt at much higher temperatures. The long alkyl side chain markedly improves solubility. All purified rods are soluble in hexane and aromatic and chlorinated hydrocarbons. UV–visible spectroscopy showed a red shift of the longest wavelength $\pi-\pi^*$ transition, as well as an increase in the transition probability, with increasing chain length. The first oxidation potentials

Scheme 23[a]



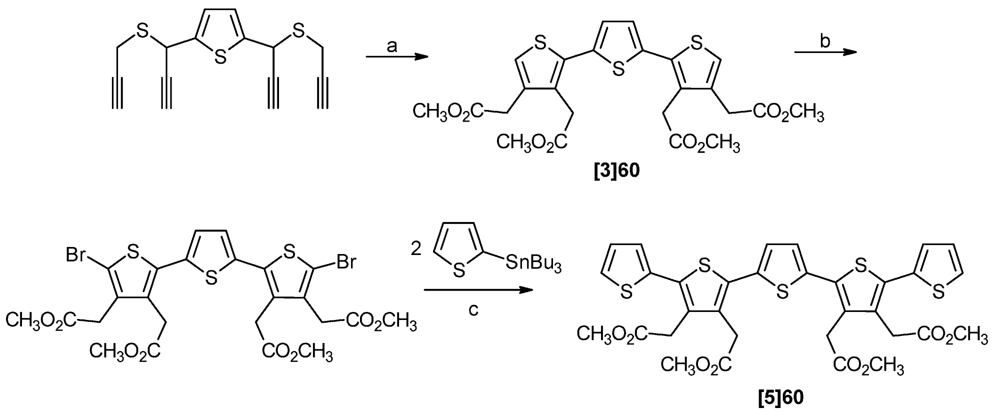
[a] Conditions and reagents: (a) *n*-BuLi, THF, $Fe(acac)_3$. (b) One equiv NBS, DMF–CS_2, X = Br, Y = H. (c) *n*-BuLi, THF, $SnBu_3Cl$, X = $SnBu_3$, Y = H. (d) Two equiv NBS, DMF–CS_2, X = Br, Y = Br. (e) $Pd(PPh_3)_4$, xylene.

Scheme 24[a]



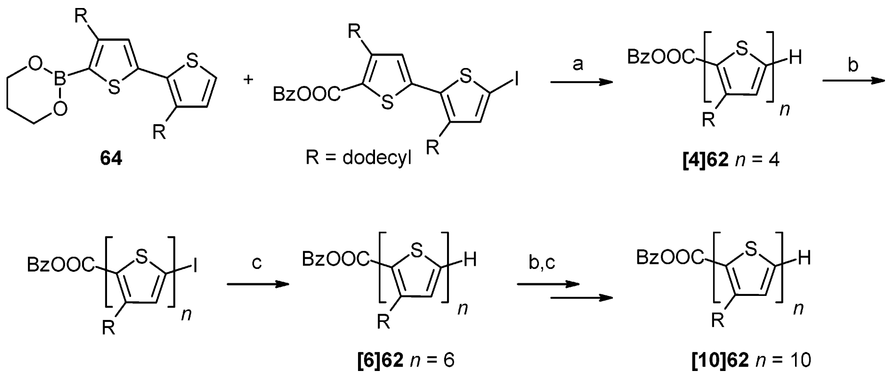
[a] Conditions and reagents: (a) $Fe(ClO_4)_3$, $CHCl_3$, CH_3CN. (b) 1.5 equiv $Fe(ClO_4)_3$, $CHCl_3$, CH_3CN. (c) Two equiv $Fe(ClO_4)_3$, $CHCl_3$, CH_3CN.

Scheme 25[a]



[a] Conditions and reagents: (a) (1) CO, CH_3OH, O_2, PdI_2, KI; (2) Et_3N. (b) NBS, DMF. (c) $Pd(PPh_3)_4$, DMF.

Scheme 26[a]



[a] Conditions and reagents: (a) CsF, $Pd(PPh_3)_3$. (b) I_2, $Hg(C_5H_{11}CO_2)_2$. (c) Compound **64**, CsF, $Pd(PPh_3)_3$.

measured by cyclic voltammetry shift cathodically from the quaterthiophene to the sedecithiophene, indicating an improved stabilization of the radical cation. The oxidation potential of **37** (0.12 V vs ferrocene) is significantly less positive than those of polythiophenes (0.3−0.35 V vs ferrocene) confirming that the parent polymer consists of molecules with an average of 8−10 chemically linked monomer units. STM images recorded for the homologous series reveal an unexpected supramolecular arrangement of the longer oligomers, which line up for coupling at the α positions.

Unsubstituted oligomers are planar in the solid state. Substituents along the backbone cause thiophene rings to twist out of planarity,[76] but in the case of monosubstituted oligothiophenes, the twist is very modest. For the trimer [**3**]**54** with annelated bicyclo[2.2.2]octanes (Scheme 22), Komatsu's group[92] showed that the thiophene rings are rotated around the inter-ring C−C bonds in the crystal with dihedral angles of −149 and 34°, and no π stacking is observed. In general, oligothiophenes are more strongly twisted in solution.[93,94]

A detailed ^{1}H and ^{13}C NMR study of regioregular head-to-tail oligo(octylthiophene)s has been published showing the linear dependence of proton chemical shifts on the reciprocal number of thiophene units in several deuterated solvents.[95]

A comprehensive evaluation of photophysical and energy transfer properties of the parent oligothiophenes **36** up to the heptamer (Chart 2) was performed by Becker et al.[96] Several groups have reported that the longest wavelength absorption band corresponding to the $\pi-\pi^*$ transition is red-shifted with increasing chain length and increases in absorption intensity. There is, however, a significant disagreement in the literature about the onset of the saturation point. The analysis of the dodecyl-substituted compounds of Bäuerle reveals that for a regioregular, head-to-tail coupled series **37**−**40** (Chart 2) the onset of saturation of the conjugation is already evident starting with the octamer. Wynberg and coworkers concluded from their studies that the effective conjugation length is reached at around 11 repeat units.[97] Otsubo's series of octyl-substituted oligomers including the heptacosamer (27-mer) **44** (Scheme 15) displays no further shift in the absorption and emission spectra going from the 20-mer to the 27-mer. However, in Otsubo's latest study, the 2,2-bis(butoxymethyl)-1,3-propanediyl-protected series displays continuous red shifts of the absorption maximum up to the 96-mer [**96**]**57** (Scheme 24).[87] As noted in the Concluding Remarks (section 12), this does not mean that the conjugation length limit has not yet been reached.

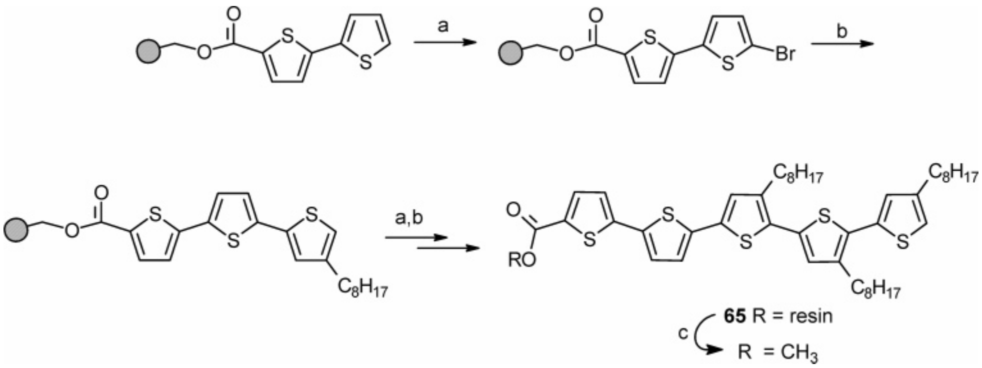
In several studies, cyclic voltammetry revealed the expected gradual shift of the redox potential to more cathodic values with increasing length of the chain. This relationship was found to be linear for up to six repeating units. Simultaneously, the number of stable redox states increases and the potential difference between neighboring redox states decreases. For example, Bäuerle found the existence of four reversible one-electron redox processes for the decamer [**10**]**62** (Scheme 26).[98] Wakamiya et al. reported that for the bicyclo[2.2.2]octene annelated oligomers with three ([**3**]**54**), four ([**4**]**54**), and six ([**6**]**54**) units, both a stable radical cation and a dication exist (Scheme 22).[99]

Extended conjugation provides doped oligothiophene rods with excellent conductance.[55] However, a look at the conductivities of thin films made from Otsubo's systems **41**−**45** (Scheme 15) provides a complicated picture.[85] While the conductivity of the hexamer is relatively low, a marked increase by 1 or 2 orders of magnitude is observed upon going to the 13-mer **42**. From the 13-mer **42** to the 27-mer **44**, a gradual increase is observed. These sharp discontinuities appear to be due to the interplay between interchain and intrachain charge hopping and the effects of solid structure and suggest a change in the limiting step of the conduction mechanism.[85]

Mitschke et al.[100] showed that the connection pattern of aromatic substituents to the β positions has a distinct effect on the physical properties of the system (Scheme 21). While phenyl substituents as in **51** cause only slight disturbances compared to the parent oligothiophenes, benzo[*c*]annulation as in **52** strongly affects the electronic structure and leads to a red shift of both absorption and fluorescence. The planarization of bithiophene units by introduction of spirofluorenyl bridges as in **53** increases the effective conjugation in the rod as is evidenced by a small bathochromic shift of emission and absorption and lower oxidation potentials.[100]

The fluorocarbon-substituted oligothiophenes [***n***]-**59** (Chart 2) show superior thermal stability and have generally higher emission quantum efficiencies

Scheme 27[a]



[a] Conditions and reagents: (a) NBS, DMF. (b) 2-(Trimethylstannyl)-4-octylthiophene, $PdCl_2(PPh_3)_2$, DMF. (c) (1) NaOMe, THF, reflux; (2) CH_3I, 18-C-6, reflux.

compared to their alkyl-functionalized analogues, both in solution and in the solid state. These properties have an important impact for the application of such materials as semiconductors in thin film transistors.[101]

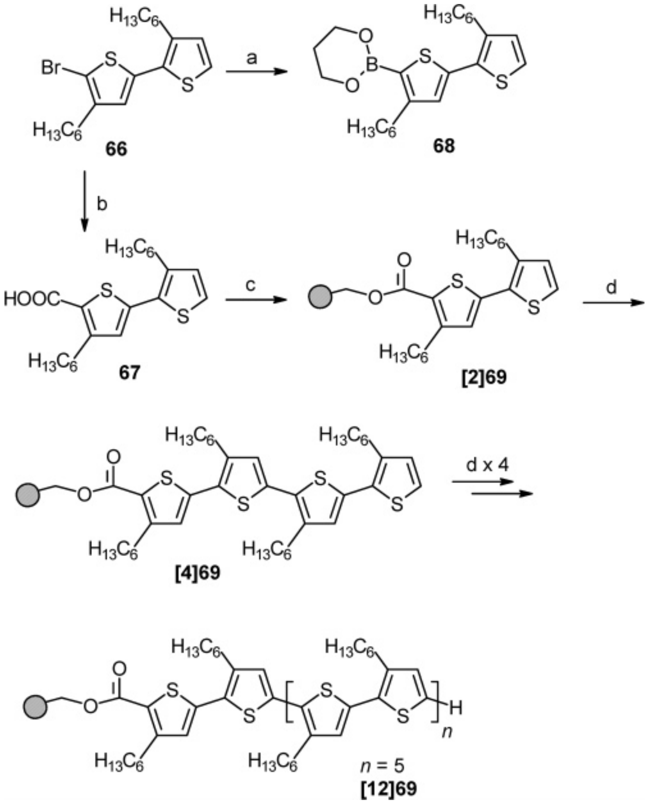
4.4. Organic Terminal Substitution

4.4.1. Synthesis

Halik et al.[102] synthesized a series of α,α-N-alkyl-substituted oligothiophenes [***n***]**63** (Chart 2) with 4−6 thiophene units and with alkyl side chains ranging from decyl to no alkyl units on each terminus, using Kumada cross-coupling and oxidative coupling conditions. Bäuerle and his group developed a strategy to protect one reactive α position of a 3-dodecylthiophene by employing a terminal benzyl ester group.[98] A highly selective iodination with iodine/mercuric caproate was combined with a Suzuki coupling with boronate ester **64** for the stepwise elongation protocol, and a series of regioregular head-to-tail oligo(3-dodecylthiophene)s [***n***]**62** up to the decamer [**10**]**62** were prepared (Scheme 26).

Malenfant and Fréchet[103] developed the first solid phase synthesis of asymmetric oligothiophenes on a Merrifield type chloromethylated resin, which allows the stepwise elongation of the chain in excellent yield and purity without lengthy chromatographic separations typical of the oligomers prepared in solution (Scheme 27). 2,2′-Bithiophene-5-carboxylic acid is bound to a resin, brominated with NBS, and coupled with 2-(trimethylstannyl)-4-octylthiophene under Pd catalysis. Repetition of these steps yielded the quinquethiophene **65**. Cleavage of the rods off the resin is easily accomplished at any stage affording a rod with a functional group for further modification. More recently, Bäuerle's group[104,105] reported a similar solid phase synthesis of isomerically pure head-to-tail coupled oligo(3-hexylthiophene)s up to the dodecamer (Scheme 28). Isomerically pure 5-bromo-3′,4-dihexyl-2,2′-bithiophene (**66**) was prepared as the key building block for the synthesis in three steps from 3-hexylthiophene and further modified to the carboxylic acid **67** and the boronic ester **68**. The carboxylic acid **67** was attached to the resin, iodinated in the α position, and coupled with **68** to form the next higher homologue, [**4**]**69**. Repetition of the procedure allowed the stepwise extension by two thiophene modules, culminating in the preparation of dodeca(3-hexylthiophene) [**12**]**69** in 12 steps and 15% overall yield after efficient detachment from the resin and subsequent decarboxylation of the methyl ester.

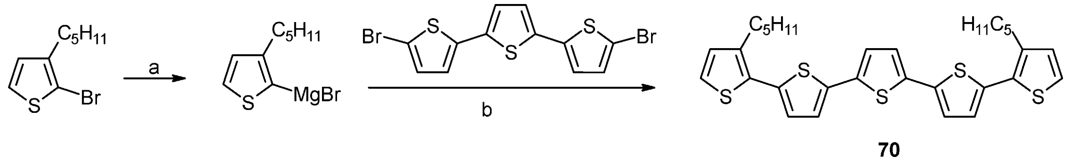
Scheme 28[a]



[a] Conditions and reagents: (a) (1) Mg; (2) trimethyleneborate; (3) BF_3. (b) (1) Mg; (2) CO_2. (c) Cs_2CO_3, chloromethylated polystyrene resin. (d) (1) I_2, $Hg(C_8H_{11}CO_2)_2$; (2) CsF, $Pd(PPh_3)_3$, **68**.

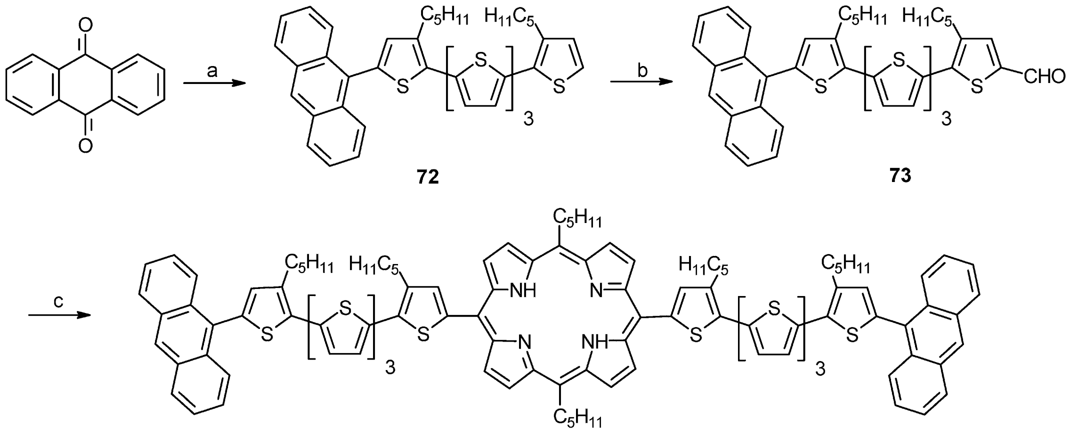
Effenberger's group[106−108] has reported the synthesis of a large number of terminally mono- and disubstituted oligothiophenes for studying intramolecular energy[109,110] and electron transfer[111] processes and the formation of monolayers on graphite.[108] 3,3-Dipentyl-α-quinquethiophene **70** was assembled in a stepwise manner as the central bridging unit (Scheme 29).[106,110] For the preparation of donor−acceptor dyads, such as **71**, compound **70** was monolithiated and treated with anthrone to form the 9-anthryl-substituted dipentylquinquethiophene **72**.

Scheme 29[a]



[a] Conditions and reagents: (a) Mg, ether. (b) $NiCl_2$(dppp), ether, benzene.

Scheme 30[a]

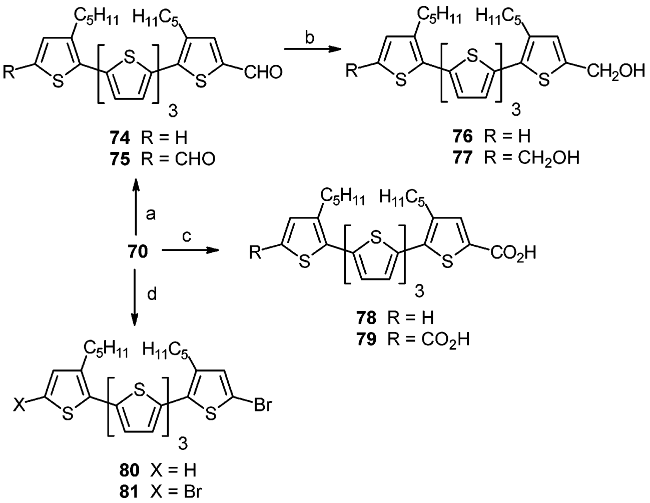


[a] Conditions and reagents: (a) (1) Compound **70**, BuLi; (2) HCl, CH_3OH, toluene. (b) $POCl_3$, DMF, CH_2Cl_2. (c) (1) Pyrrole, hexanal, TFA, CH_2Cl_2; (2) *p*-Chloranil.

Vilsmeier–Haack formylation produced the aldehyde **73**, which was converted to the desired dyad **71** by condensation with pyrrole and hexanal following Lindsey's protocol[112] (Scheme 30). More recently, again starting from **70**, the aldehyde **74** and dialdehyde **75** were selectively prepared by Vilsmeier–Haack formylation in high yields and reduced to the respective alcohols **76** and **77**. Selective lithiation of **70** followed by treatment with carbon dioxide produced the mono- **78** and dicarboxylic **79** acids in moderate to good yields. Bromination with NBS yielded a mixture of mono- and dibrominated products **80** and **81**, which were separated by column chromatography (Scheme 31).[108] Another porphyrin-capped series of oligomers [***n***]**82**, including the quaterthiophene [**4**]**82**, octithiophene [**8**]**82**, and dodecithiophene [**12**]**82**, carrying a fullerene unit at the opposite end, was published by Ikemoto et al.[113] (Scheme 32).

Otsubo's group[114–116] assembled tripod-shaped conjugated thiols [***n***]**83** via a coupling reaction between 5-tributylstannyloligothiophenes [***n***]**84** and 4-bromophenyltris(4*S*-acetylthiomethylphenyl)methane (**85**) in the presence of $Pd(PPh_3)_4$ for the construction of self-assembled monolayers on gold (Scheme 33). 9,9-Diarylfluorene-capped oligothiophenes [***n***]**86** up to the tetramer were prepared by Wong et al.[117] using Suzuki type coupling conditions (Scheme 34). Mann's group[118] recently reported tricyanovinyl (TCV)-substituted oligothiophenes [***n***]**87** with up to six rings. The TCV group was introduced[119] via double lithiation and trapping of the dianion with tetracyanoethylene in moderate yields (Scheme 35). Very recently, Bong et al.[120] described the synthesis of the first isocyanide-functionalized oligothiophenes [***n***]**88** up to the 7.0 nm long heptadecamer [**17**]**88** and studied their chemisorption to platinum surfaces. The regioregularly alkylated rods [***n***]**88** were constructed starting from the terminal phenyl formamide **89** by repetitive coupling with the stannylated quaterthiophene **90** under Stille conditions. At the end of the reaction sequence, dehydration of the formamide yielded the isocyanide functionality (Scheme 36).

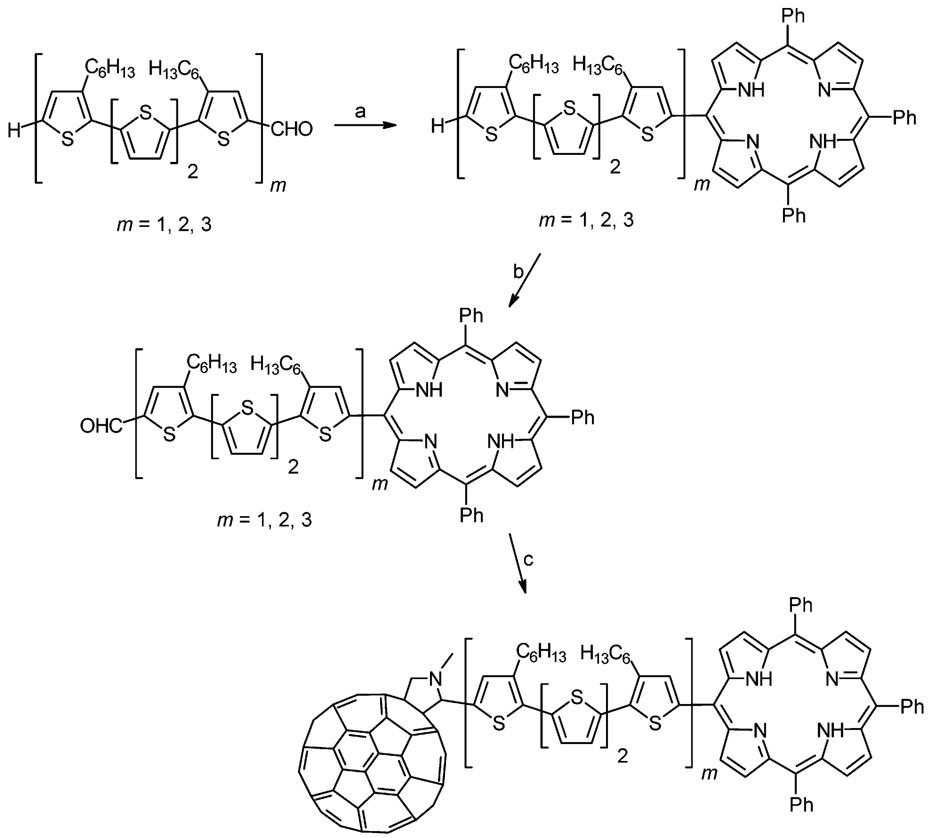
Scheme 31[a]



[a] Conditions and reagents: (a) $POCl_3$, DMF. (b) $NaBH_4$, THF. (c) (1) BuLi; (2) CO_2; (3) HCl. (d) NBS, DMF. Reprinted with permission from ref 108. Copyright 1999 Wiley-VCH.

Very recently, the group of Marks[88,121] has reported a series of α,ω-diperfluorohexyl-substituted oligothiophenes [***n***]**91** up to the hexamer (Chart 2). The synthesis was achieved using a stepwise construction of the thiophene backbone via thienyl–thienyl coupling reactions according to Stille.

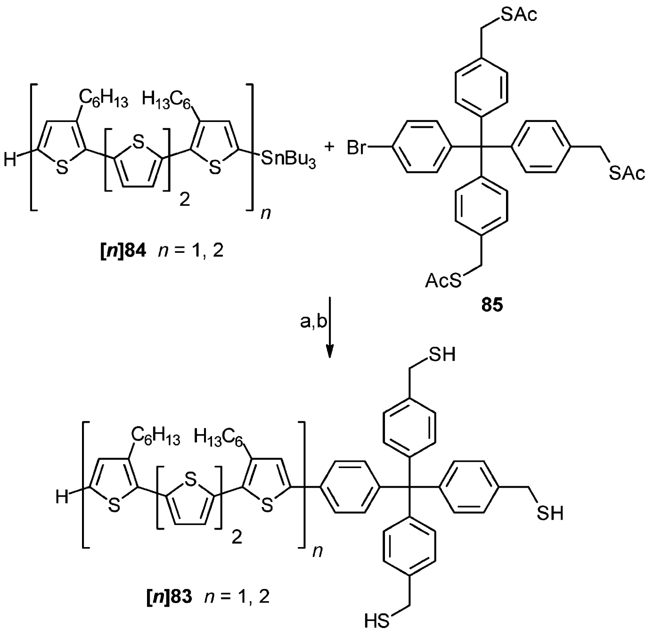
Scheme 32[a]



[4]82 *m* = 1
[8]82 *m* = 2
[12]82 *m* = 3

[a] Conditions and reagents: (a) (1) Pyrrole, benzaldehyde, TFA, CH_2Cl_2; (2) *p*-chloranil; (3) K_2CO_3. (b) $POCl_3$, DMF. (c) C_{60}, *N*-methylglycine, toluene.

Scheme 33[a]



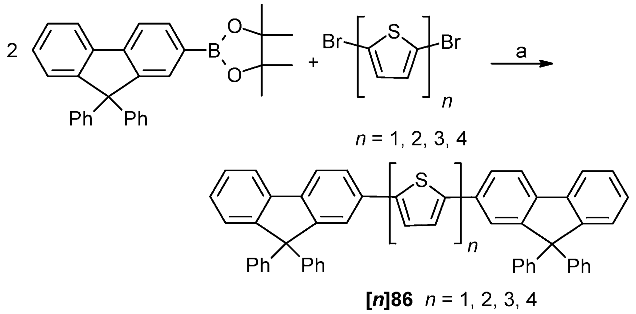
[*n*]84 *n* = 1, 2

85

[*n*]83 *n* = 1, 2

[a] Conditions and reagents: (a) $Pd(PPh_3)_4$, toluene. (b) KOH, CH_3OH.

Scheme 34[a]



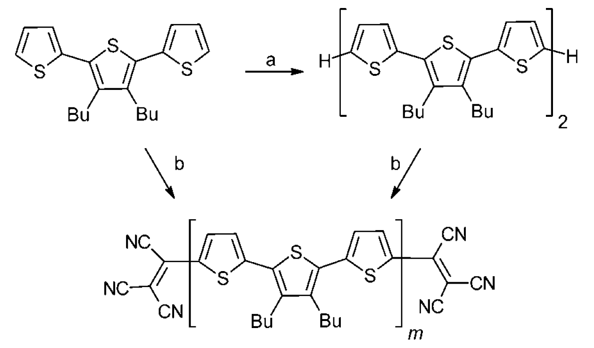
[*n*]86 *n* = 1, 2, 3, 4

[a] Conditions and reagents: (a) $Pd(PPh_3)_4$, $P(t\text{-}Bu)_3$, K_3PO_4, 1,4-dioxane.

4.4.2. Properties

The introduction of various organic terminal groups has been shown to affect the properties of oligothiophenes significantly. Oligothiophenes with phenyl and biphenyl termini[122] exhibit intriguing electroluminescent behavior.[123] Terminal diarylamino functionalities were shown to serve as efficient emitters[124,125] and hole-transporting materials. In Effenberger's anthryloligothienylporphyrin **71**, the individual subunits interact only weakly. Selective excitation of the anthracene donor in **71** leads to quantitative intramolecular energy transfer to the emitting porphyrin acceptor.[110] For the porphyrin-oligothiophene-fullerene dyads [***n***]**82**, efficient electronic coupling between the donor and the acceptor and a weak distance dependence were found.[113] The bulky diarylfluorene groups in [***n***]**86** markedly improve the morphological and thermal stability of the systems.[117] By varying the length of the oligothiophene spacer

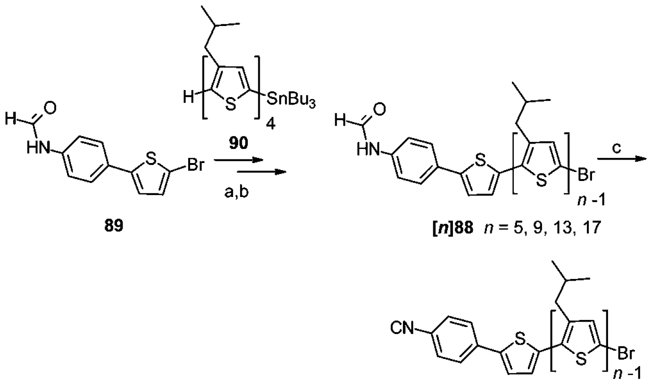
Scheme 35[a]



[n]87 *m* = 1, 2

[a] Conditions and reagents: (a) (1) BuLi; (2) Fe(acac)$_3$. (b) (1) BuLi; (2) TCNE.

Scheme 36[a]



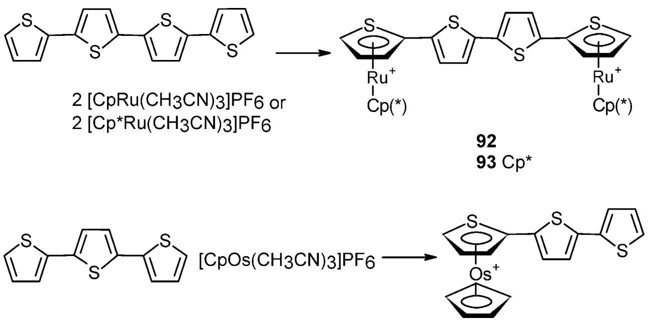
[a] Conditions and reagents: (a) Pd(PPh$_3$)$_4$, toluene. (b) NBS, CH$_3$Cl. (c) Tf$_2$O, DIEA, CH$_2$Cl$_2$.

in series [***n***]**86**, the fluorescent color of the materials could be tuned between emission wavelengths of 420 and 525 nm. The systems exhibit interesting reversible redox behavior.[117]

A structure determination on a single crystal obtained for [**3**]**87** confirmed the near planarity of the backbone, in which a transoid orientation of the sulfur atoms in adjacent thiophene rings is adopted.[118] The TCV-capped oligomers [***n***]**87** are characterized by dramatically lowered optical and electrochemical band gaps as compared to the parent oligothiophenes. The sexithiophene [**6**]**87** shows reversible redox processes.[118]

All of the fluoroalkyl end-capped oligothiophenes [***n***]**91** (Chart 2) show excellent thermal stability and volatility. Remarkably, they behave as n type semiconductors, unlike other oligothiophenes, which are p type semiconductors. This behavior apparently has more to do with injection barrier characteristics than with bulk transport properties. Compound [**6**]**91** exhibits a smectic liquid crystalline phase. The effect of the fluoroalkyl substituents on the optical absorption spectra is negligible, but the emission quantum efficiencies are found to be significantly enhanced as compared to other oligothiophenes. In the solid state, close $\pi-\pi$ intermolecular interactions between the thiophene units are observed, while the fluorocarbon chains segregate into lamellar structures.[88] In fluorocarbon-substituted oligothiophene films, very high solid state optical emission efficiencies were measured.[121]

Scheme 37



4.5. Organometallic Terminal Substitution

4.5.1. Thiophene/Cyclopentadienyl Complex

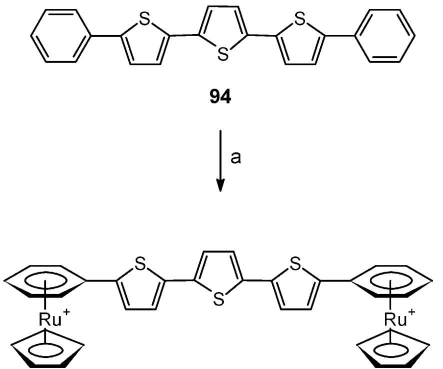
Synthesis. In an effort to adjust the properties of thiophenes, Graf and Mann[126−128] synthesized oligothiophenes π-complexed to CpRu$^+$ **92** or Cp*Ru$^+$ **93** substituents at the termini (Scheme 37).[128] The metal (Os or Ru), the ancillary ligand (Cp or Cp*), the length of the oligothiophene (1−4 rings), and the substituents on the ring were systematically varied. The synthesis was achieved by allowing the appropriate oligothiophene to react with with a PF$_6^-$ salt of CpRu(CH$_3$CN)$_3^+$ or Cp*Ru(CH$_3$CN)$_3^+$.

Properties. The species containing Ru, such as **92** and **93**, are moderately stable in air and noncoordinating solvents but are unstable in coordinating solvents, such as acetone. The Os complexes are much more kinetically stable than the Ru analogues. The electronic influence exerted by the metal also extends to the first uncomplexed thiophene unit. Not surprisingly given the charges in the molecules, the hole generated upon oxidation appears to reside in the uncomplexed thiophene units, while the electron added upon reduction is found localized in the end-capping sandwich units.

4.5.2. Thiophene/Benzene

Synthesis. Oligothiophene rods **94** consisting of up to three units and terminated by a phenyl at each end were prepared and treated with [CpRu(CH$_3$CN)$_3$]-PF$_6$ to form complexes **95** (Scheme 38).[127]

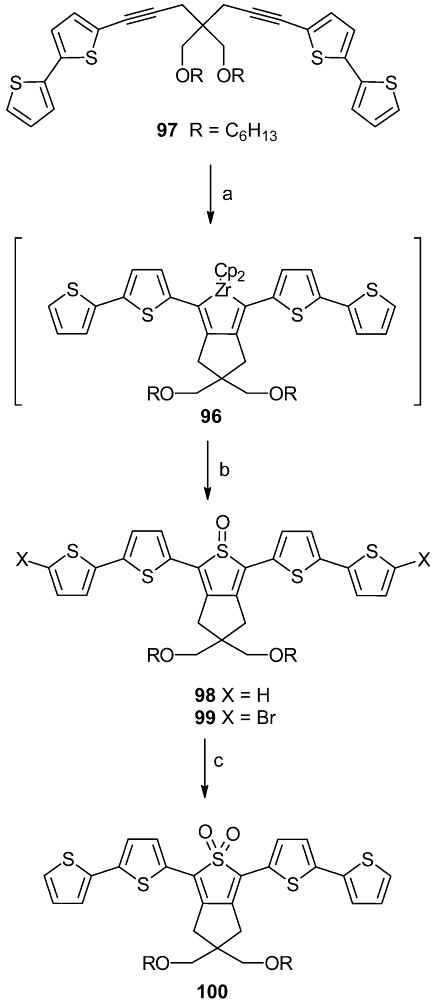
Scheme 38[a]



95

[a] Conditions and reagents: (a) 2[CpRu(CH$_3$CN)$_3$]PF$_6$.

Scheme 39[a]



[a] Conditions and reagents: (a) Cp_2Zr. (b) SO_2. (c) *m*-CPBA.

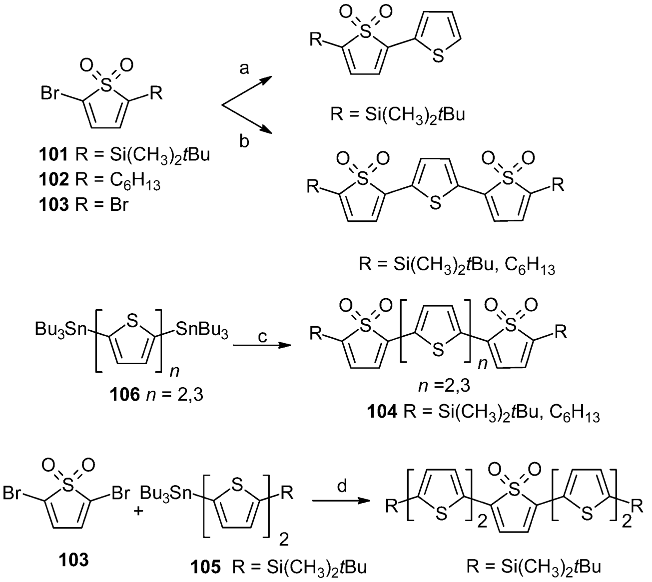
Properties. The complexes **95** are very stable to air in the solid state and in both coordinating and noncoordinating solvents. However, the solubility of the longer homologues in common organic solvents is low. The electronic effect of the metal complexation extends over the complexed ring to the nearest neighbor to a small degree. The complexes exhibit two reversible electrode processes.

4.6. Thiophene-1-Oxides

4.6.1. Synthesis

Jiang and Tilley[129] reported a versatile, high-yield methodology for the synthesis of mixed thiophene-thiophene-1-oxide oligomers in two steps via the zirconocene coupling of alkynes (Scheme 39). For example, the metallacycle **96** was prepared in situ from 4,4-bis(hexyloxymethyl)-1,7-bis(thiophenyl)-1,6-heptadiyne (**97**) and zirconocene and immediately treated with gaseous SO_2 to yield the mixed pentamer **98**. The reaction conditions tolerate the presence of bromoaryl functionalities, and compounds such as the dibromo derivative **99** were prepared as well. These would in principle allow further extension of the rods or incorporation into block co-oligomers.

Scheme 40[a]



[a] Conditions and reagents: (a) $Pd(AsPh_3)_4$, 2-thienylstannane (**105**). (b) $Pd(AsPh_3)_4$, **106**. (c) $Pd(AsPh_3)_4$, **101** or **102**. (d) $Pd(AsPh_3)_4$.

4.6.2. Properties

All reported mixed thiophene-thiophene-1-oxide oligomers have been described as stable at room temperature in air over at least several weeks. The absorption maxima are red-shifted compared to both the corresponding thiophene-1,1-dioxides and thiophenes. An oxidation with *m*-chloroperbenzoic acid to the respective thiophene-1,1-dioxides **100** was demonstrated (Scheme 39).

4.7. Thiophene-1,1-Dioxides

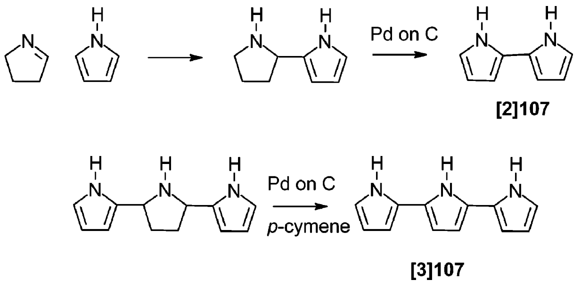
4.7.1. Synthesis

While alkylated oligothiophenes can in principle be oxidized to thiophene-1,1-dioxides by treatment with peroxides, the reaction becomes more difficult with increasing chain length and leads to statistical mixtures of partially oxidized compounds that are difficult to separate. Barbarella et al.[130,131] have developed a synthetic methodology for selective insertion of thiophene-1,1-dioxide moieties into the backbone of bi-, ter-, quater-, and quinquethiophenes (Scheme 40). Using 2-(dimethyl-*tert*-butylsilyl)-5-bromothiophene-1,1-dioxide (**101**), the corresponding 2-(*n*-hexyl) derivative **102**, and 2,4-dibromothiophene-1,1-dioxide (**103**) as modules, they built a large number of dimers, trimers, tetramers, and pentamers, such as **104**, containing from one to three thiophene-1,1-dioxide units in a controlled pattern, by Stille coupling with the appropriate thienylstannanes **105** and thienylbisstannanes **106**. Brominated thiophene-1,1-dioxides are significantly more reactive toward thienylstannanes than the corresponding thienyl bromides and can be coupled under much milder conditions.[131]

4.7.2. Properties

Incorporation of a thiophene-1,1-dioxide unit into an oligothiophene backbone causes a large red shift

Scheme 41



of the longest wavelength peaks and increases the electron affinity of the molecular rod to such an extent that a transformation into an n type (electron transporting) wire becomes feasible.[131] The regioselective insertion shown by Barbarella[130,131] allows a continuous modulation of the electronic and redox properties of the system, which can thus gradually pass from an easily oxidized oligothiophene to an easily reduced oligothiophene-1,1-dioxide.

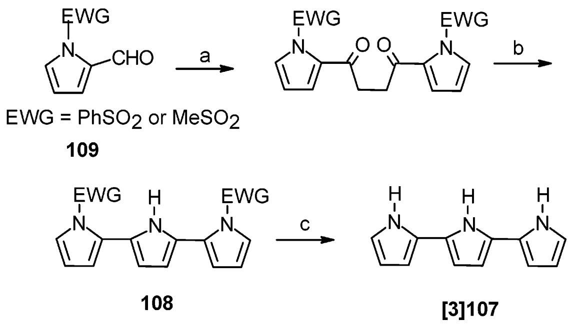
5. Oligopyrroles

The five-membered pyrrole ring is even easier to oxidize than the thiophene ring, and oligopyrroles are quite sensitive to air. As in thiophenes, the valence angles dictated by their five-membered rings are conducive to complete planarity at the expense of strict axiality.

5.1. Synthesis

The synthesis of the simplest oligopyrroles [***n***]**107**, the dimer [**2**]**107**, and the trimer [**3**]**107**, was accomplished for the first time by the groups of Rapoport[132−134] and Johnson[135−137] (Scheme 41). The procedures used were based on the Vilsmeyer condensation with subsequent dehydrogenation of the intermediates. In an elegant method reported by Merrill and LeGoff, a terpyrrole module **108** is formed starting from 2-formylpyrrole **109** (Scheme 42). Compound **108** is then deprotected to give [**3**]**107**.[138]

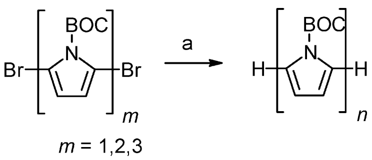
Scheme 42[a]



[a] Conditions and reagents: (a) Thiazolium salt catalyst, NaOAc, divinyl sulfone, EtOH, reflux. (b) NH_4OAc, Ac_2O, $C_2H_5CO_2H$, ultrasound followed by reflux. (c) NaOH, MeOH, reflux.

Modern methods of preparation of oligopyrroles and *N*-substituted oligopyrroles are based on transition metal-catalyzed couplings, similar to those useful for preparation of other oligomers of aromatic cycles. Versions of the Ullmann reaction (Scheme 43),[139−141] coupling of 2-lithiopyrroles with $CuCl_2$, $CoCl_2$, and $NiCl_2$,[142] Suzuki coupling,[143−145] and Stille coupling[143,146−148] have been developed for the appropriate pyrrole precursors. Individual oligomers with up to 48 pyrrole units have been prepared using the Stille reaction.[146]

Scheme 43[a]



[a] Conditions and reagents: (a) Cu, DMF.

5.2. Properties

Unprotected oligopyrroles [***n***]**107** oxidize readily in contact with atmospheric oxygen.[149] They are prepared from the *N*-BOC-substituted oligomers by heating under inert atmosphere or in a vacuum at180−190 °C.[141,150,151] The deprotection is not complete for the oligomers [***n***]**107** with $n > 6$.[141,148] X-ray diffraction of a single crystal of the pentapyrrole dimethylated in the terminal α positions[147] and analysis of Raman and IR spectra of [***n***]**107**[152,153] suggest that the torsion angle between the pyrrole rings is close to 0°, which allows for an extended delocalization through the oligomer backbone. This delocalization extends over 7−9 adjacent pyrrole rings[152] and leads to a very high conductivity of doped oligopyrroles and polypyrroles.[154] Substitution of the pyrrole rings causes a twist of the adjacent pyrrole rings (70° in the case of the *N*-BOC substituents[147]) but does not disrupt conjugation between the rings completely.[155]

6. Oligosiloles

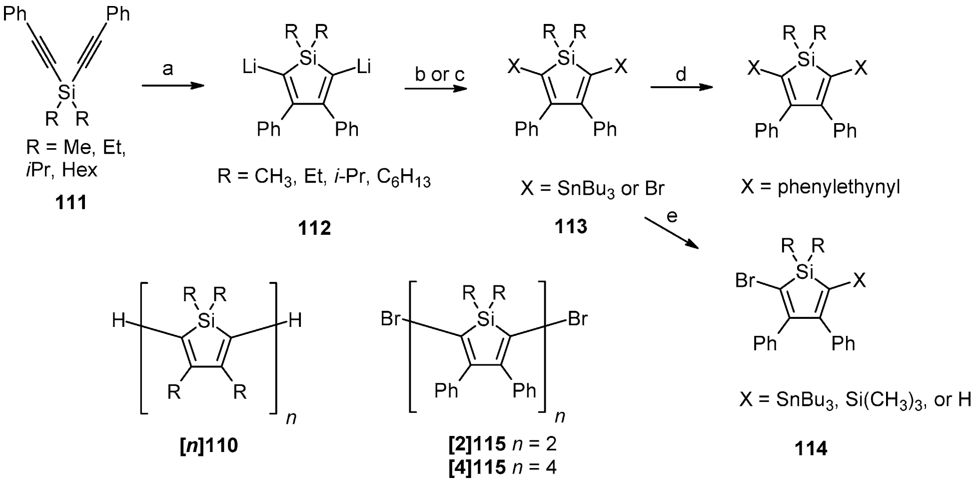
Unlike thiophene and pyrrole, 5-silacyclopenta-1,3-diene (silole) does not possess cyclic conjugation and the parent is even much less stable than cyclopentadiene.[156] However, hyperconjugation through the π-electron-withdrawing SiH_2 or SiR_2 group distinguishes its properties quite clearly from those of cyclopentadiene, whose CH_2 group is π-electron donating, and from butadiene itself.

Oligomers and polymers [***n***]**110** (Table 1 and Scheme 44) consisting of silole modules have been the focus of recent synthetic efforts because theoretical investigations have predicted interesting characteristics such as small band gaps for coplanar polysilols and a nonplanar structure in the most stable conformation. Useful properties such as conductivity, thermochromism, and nonlinear optical behavior were expected. However, the synthesis of polysiloles has long been elusive because the preparation of polymerizable monomers with appropriate functional groups such as Li, Br, and SnR_3 by conventional methods failed.[157]

6.1. Synthesis

Tamao et al.[158] reported the first synthesis of oligosiloles [***n***]**110** up to the tetramer applying a new intramolecular reductive cyclization of diethynylsi-

Scheme 44[a]



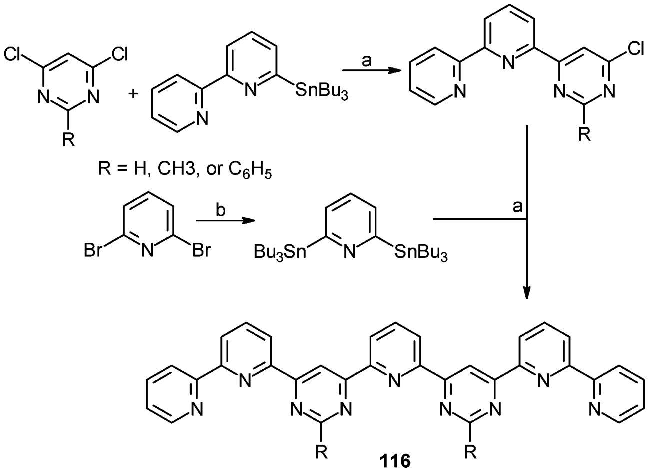
[a] Conditions and reagents: (a) Lithium naphthalide, THF. (b) $SnBu_3Cl$. (c) Br_2. (d) (Phenylethynyl)trimethylstannane (2 equiv), $PdCl_2(PPh_3)_2$ (5 mol %), THF, reflux. (e) BuLi, ether, −78 °C, then $SnBu_3Cl$ (X = $SnBu_3$), $Si(CH_3)_3Cl$ [X = $Si(CH_3)_3$], or H_2O (X = H).

lanes to obtain 2,5-disubstituted silole derivatives (Scheme 44). Thus, treatment of bis(phenylethynyl)dialkylsilane (**111**) with a reducing agent such as lithium naphthalide yielded exclusively 2,5-dilithiosilole (**112**).[158] The cyclization proceeds via the bis(anion radical) solely in an endo−endo mode, similar to the Bergman cyclization of enediynes.[159] 2,5-Dilithiosiloles were trapped with various electrophiles, such as tri-*n*-butylstannyl chloride or bromine, to produce the corresponding 2,5-difunctional siloles **113**. The dibromosilole was utilized in palladium-catalyzed cross-coupling reactions or selectively monolithiated to obtain unsymmetrical functional siloles **114** (Scheme 44).[158] Furthermore, the monolithiated silole was effectively dimerized in a two-step oxidative coupling via a higher order cyanocuprate. Repetition of the sequence with resulting 5,5′-dibromo-2,2′-bisilole ([**2**]**115**) led to the dibromoquatersilole [**4**]**115** (Scheme 44), albeit in considerably lower yield. An extension of the methodology to higher homologues appears feasible, but ultimate success crucially depends on the effective monolithiation of each higher oligomer. Direct cross-coupling reactions with various reagents failed, most likely due to steric constraints.[158]

6.2. Properties

The reported dibromooligosiloles [***n***]**115** are not very air and light stable and gradually decompose under ambient conditions.[158] Like other molecular rods composed of five-membered rings, oligosiloles are not strictly axial. The X-ray crystal structures of the bisiloles show a highly nonplanar arrangement between two silole rings with torsion angles of ∼63°. Despite the twisted conformation, the UV−visible absorption spectra of the bisiloles display unusually long wavelength absorption maxima near 400 nm, higher than those of bithiophene, bifuran, and bicyclopentadiene. There is a large bathochromic shift of 90 nm from the monosilole to the bisilole but a considerably lower red shift of only 26 nm from the dibromobisilole [**2**]**115** to the dibromoquatersilole [**4**]**115**.[158]

Scheme 45[a]



[a] Conditions and reagents: (a) $PdCl_2(PPh_3)_2$, DMF. (b) (1) BuLi; (2) Bu_3SnCl, THF.

7. Oligoazabenzenes

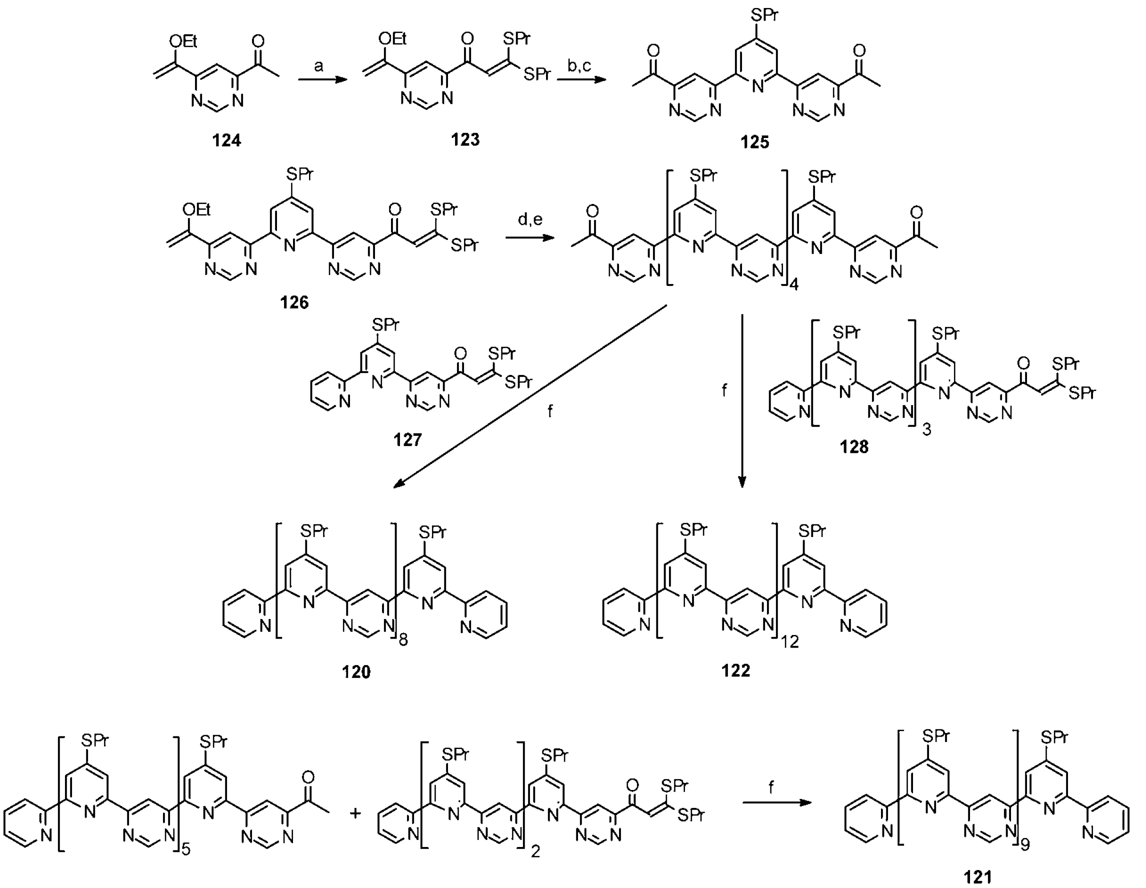
7.1. Pyridine/Pyrimidine

The use of pyridines and similar azabenzenes instead of one or more benzene rings in oligophenylene molecular rods has been especially popular, since the lone pairs of their nitrogen atoms can be used for the binding of metal atoms. Aza analogues of oligo-*p*-phenylenes are (nearly) axial and were covered in Part 1.[5] Here, we deal with aza analogues of oligo-*m*-phenylenes.

7.1.1. Synthesis

On the basis of alternating pyridine and pyrimidine units, oligotridentate ligands **116** with up to seven aromatic rings were synthesized by Lehn and collaborators[160] via Stille coupling (Scheme 45). The framework was functionalized in the periphery by the introduction of phenyl and methyl groups. The terpyridine-like sites are designed to align upon complexation to a metal, thus forming rigid organometallic arrays such as the complex with ruthenium(II) **117** (Chart 2).[161,162]

Scheme 46[a]



[a] Conditions and reagents: (a) NaH, CS_2, PrI, DMSO (68%). (b) KO*t*-Bu, **124**, THF, then NH_4OAc, AcOH. (c) HCl(aq), acetone (36%, two steps). (d) KO*t*-Bu, **125**, THF, then NH_4OAc, AcOH. (e) HCl(aq), acetone (25%, two steps). (f) KO*t*-Bu, THF, then NH_4OAc, AcOH (34% for **120**, 7% for **121**, and 5% for **122**).

Bassani et al.[163] published alternating pyridine−pyrimidine co-oligomers comprising seven (**118**) and 13 (**119**) modules (Chart 2). Later, three even longer mixed pyridine−pyrimidine zig-zag rods with 19 (**120**), 21 (**121**), and 27 (**122**) heterocyclic rings along the backbone were prepared by Ohkita et al. (Scheme 46),[164] all based on the repetitive Potts synthesis of 2,6-disubstituted pyridines.[165] For the shorter members in the series, a construction in which two halves were coupled in the final step proved feasible. Because of the helical structure of the longer species, a sequence based on the repetitive 2-fold reaction of a bifunctional central unit with a larger and a smaller subunit became necessary to produce **121**, formed in a very low yield. For the synthesis of compounds **120** and **122**, a very efficient new route was developed in which the rod was built from a bifunctional central unit by stepwise extension in both directions (Scheme 46). The α-oxoketene dithioacetal **123** was prepared from **124** and coupled with another molecule of **124** to yield the bifunctional central building block **125**, which was then elongated by 2-fold condensation with **126**. Finally, the resulting diketone was coupled with an extended Michael acceptor, either **127** or **128**, to obtain **120** and **122** in very respectable yields.

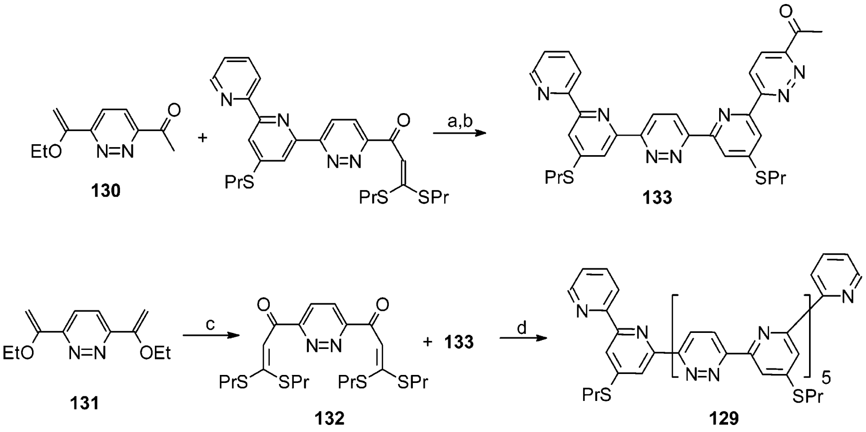
7.1.2. Properties

The rods **120**, **121**, and **122** were all isolated as white powders after column chromatography. They are well soluble only in chloroform and slightly in THF and dichloromethane.[164] Structure determination by single crystal X-ray diffraction showed that the linear strands self-organize to form chiral helical channels in the solid state. On the basis of chemical shifts and distinct NOE effects, ^{1}H NMR spectral data revealed characteristic features of helical conformations in solution, and this was confirmed by electronic spectra. Absorption maxima (289 nm) and edges (365 nm) are similar for all zig-zag rods. However, the optical absorption intensity per heterocyclic unit is reduced with increasing chain length (hypochromism), reflecting the helical ordering and stacking of the chromophores. The emission spectra of all compounds with at least 13 heterocyclic ring units showed a characteristic fluorescence emission between 520 and 550 nm.[164] The large Stokes shift was attributed to intramolecular pyridine excimer-like emission arising from overlapping pyridine moieties in the helix, also observed in the poly(pyridine-2,5-diyl).[166] In contrast, the shorter strands are unable to form a helical turn and have only a simple, pyridine-like emission at 400 nm. The longest rod **122** could be considered a coiled molecular wire of up to 90 Å length in its extended conformation.[164]

7.2. Pyridine/Pyrazine

Alternating pyridine−pyridazine zig-zag rods were also reported by the Lehn group.[167,168]

Scheme 47[a]



[a] Conditions and reagents: (a) (1) NaH, THF/DMSO (3/1); (2) NH_4OAc, AcOH, reflux (33%). (b) Acetone/2 N HCl (9/1) (97%). (c) NaH, CS_2, *n*-PrI, DMSO. (d) (1) NaH, THF/DMSO (6/1); (2) NH_4OAc, AcOH, reflux (19%).

7.2.1. Synthesis

The preparation of an alternating pyridine−pyridazine co-oligomer **129** consisting of 13 modules was accomplished, again relying on the Potts methodology for the construction of 2,6-disubstituted pyridines and on tin-mediated cross-coupling reactions (Scheme 47). Starting from 3-acetyl-6-(1-ethoxyvinyl)-pyridazine (**130**) and 3,6-bis-(1-ethoxyvinyl)pyridazine (**131**) as the key building blocks, the oligoheterocyclic rod **129** was assembled in a convergent route in which the bis-Michael acceptor **132** was extended at both termini by treatment with the single ketone group carrying pentamer **133** in the final step. Similar pyrimidine−naphthyridine co-oligomers **134** (Chart 2) were synthesized in a convergent way from 2-aryl-4,6-dichloropyrimidine following the Friedländer methodology.[169]

7.2.2. Properties

The tridecimer **129** (Scheme 47) was isolated as an air and temperature stable white solid that can be dissolved in chloroform but not in most other organic solvents. In solution, the compound is twisted into a helix in which 12 heterocyclic rings form a turn resulting in an outside diameter of 25 Å and an inside cavity of 8 Å. The pyrimidine−naphthyridine co-oligomers **134** (Chart 2) show self-associative behavior that is strongly influenced by cationic additives.

Other oligoheterocyclic molecular strands based on pyridine−pyrimidine hydrazone[170] and oligopyridine−dicarboxamide[171−173] sequences that show secondary helical structures were prepared in the Lehn group. They will not be reviewed here in detail because they fulfill our admittedly rather arbitrary criterion of backbone rigidity to an apparently even smaller degree.

8. Co-oligomers

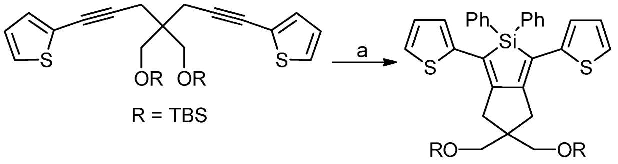
A large number of combinations of the zig-zag modules considered so far are possible, and only a few of them have been examined in any detail.

8.1. Thiophene/Silole

8.1.1. 2:1 Co-oligomer

Synthesis. The first syntheses of co-oligomers consisting of a thiophene-silole-thiophene sequence as a repeating unit were reported by Tamao et al.[174] The trimeric building block **135** was synthesized by nickel-catalyzed intramolecular cyclization of the symmetrical thiophene-terminated diyne **136** with diphenyltrimethyldisilane (Scheme 48). Selective mono- and dibromination yielded compounds **137** and **138**, which were successfully cross-coupled with various organometallic 2-thienyl derivatives to produce the pentamer **139** (Scheme 49). Alternatively, lithiation and transmetalation of **137** and **138** followed by Stille type cross-coupling reactions were utilized to prepare the hexamer **140** and nonamer **141** containing two and three silole modules, respectively. All reactions proceeded in moderate to good yields.

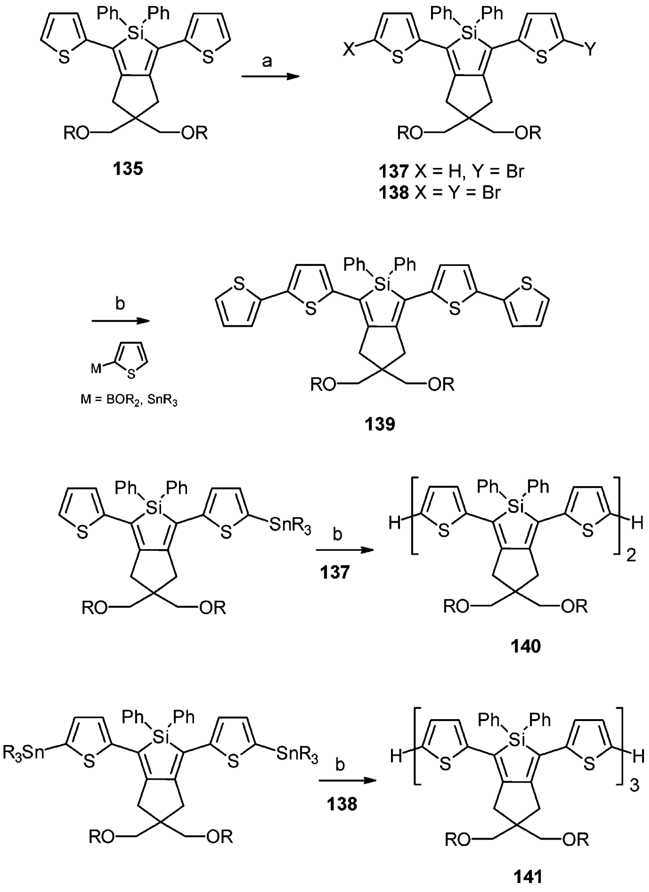
Scheme 48[a]



[a] Conditions and reagents: (a) $Ni(acac)_2$, PEt_3, DIBAH, $HPh_2SiSi(CH_3)_3$.

Properties. All thiophene−silole co-oligomers are air stable colored solids and dissolve well in common organic solvents, even up to the nonamer **141**.[174] An X-ray structure of the trimer **135** revealed a highly planar conformation with only ∼10° twists between the outer thiophene rings and the central silole unit. The co-oligomers show interesting electronic properties due to the interaction of the electron deficient silole rings with the electron-rich thiophene moieties. The UV−visible absorption spectra show large red shifts, from 416 nm in the trimer **135** to 473 nm for the pentamer **139**. The values of the absorption maxima are roughly 60 nm red-shifted from those of the homooligomeric thiophene arrays of comparable lengths. Most notably, the hexameric co-oligomer **141**

Scheme 49[a]



[a] Conditions and reagents: (a) NBS, DMF. (b) $PdCl_2(PPh_3)_2$, THF.

is characterized by a lower energy absorption maximum (505 nm) than the thiophene homooligomer with 11 units.[174] These special optical properties can be rationalized by the occurrence of an intramolecular charge transfer from the thiophene to the silole rings.

8.1.2. 1:1 Co-oligomer

Synthesis. The first alternating 1:1 silole and thiophene co-oligomers consisting of up to seven modules were reported by Tamao and co-workers[175] employing nickel-catalyzed intramolecular cyclizations of the respective thiophene-1,6-heptadiyne precursors with hydrosilanes. The direct route via cross-coupling reactions as shown for the preparation of thiophene homooligomers failed due to difficulties in introducing appropriate substituents in the 2 and 5 positions of the silole ring by conventional methods. Therefore, 4,4-bis[(*tert*-butyldimethylsiloxy)methyl]-1,6-heptadiyne (**142**) was sequentially cross-coupled under Pd/Cu catalysis with 2,5-dibromothiophene and 2-bromothiophene in moderate yields to obtain the tetrayne precursor **143** or treated with 2 equiv of the monobrominated trimer **137** to produce the symmetrical diyne **144** (Scheme 50).[175] Both **143** and **144** were finally converted to the desired rods [***n***]**145** by nickel(0)-promoted intramolecular cyclization in low to moderate yield.[175]

Properties. Oligomer [**2**]**145** was isolated as red crystals, and compound [**3**]**145** was isolated as a golden brown powder. Both are air stable and dissolve well in chlorinated hydrocarbons and THF but little in hexane.[175] The data obtained from the absorption spectra confirmed the tendencies observed with the 1:2 co-oligomers discussed above. The bathochromic shift increases with total chain length and with increasing relative silol content. Thus, rods [**2**]**145** and [**3**]**145** possess longer wavelength absorption maxima at 524 and 582 nm, respectively, than their homooligomeric thiophene and also 1:2 co-oligomeric counterparts of comparable length. However, it was also found in the study of the corresponding polymers that electrical conductivity appears to change in the opposite direction, even though an exact comparison was difficult due to different average polymeric chain lengths.[175]

8.2. Thiophene/Thiazole

8.2.1. Synthesis

Ng and Yu[176] recently prepared a regioregular, head-to-tail co-oligomer **146** consisting of a tetrameric oligo(3-alkylthiophene) as donor unit and a tetrameric oligo(4-alkylthiazole) as the acceptor block. A hydrophobic long alkyl chain was attached to the alkylthiazole modules, while the alkylthiophenes were fitted with a hydrophilic MEEM chain (MEEM = methoxyethoxyethoxymethyl) in order to obtain a surfactant-like amphiphilic behavior. The synthesis followed a convergent approach. First, the two homooligomeric chains were formed in a stepwise fashion (Scheme 51) and then, the monoiodinated alkylthiophene **147** was cross-coupled with the monotributylstannylated thiazole **148** under Stille conditions. The amphiphilic diblock oligomer **146** was ultimately isolated after in situ desilylation.[176]

Very similar chemistry was used to obtain the shorter diblock co-oligomers **149** consisting of two methyl-substituted thiophene and thiazole units with two differently protected thiol end groups (Scheme 52).[177]

8.2.2. Properties

Compounds **146** and **149** are air stable solids. The diblock rods exhibit a molecular p−n junction, and a rectifying effect was observed.[176] Sequential deprotection of the thiol groups in compound **149** enabled its controlled assembly between two gold electrodes. The rectification direction could be controlled by changing the orientation of the diode molecules between the electrodes.[177]

8.3. Ethene/Cyclopentadienyl Complex

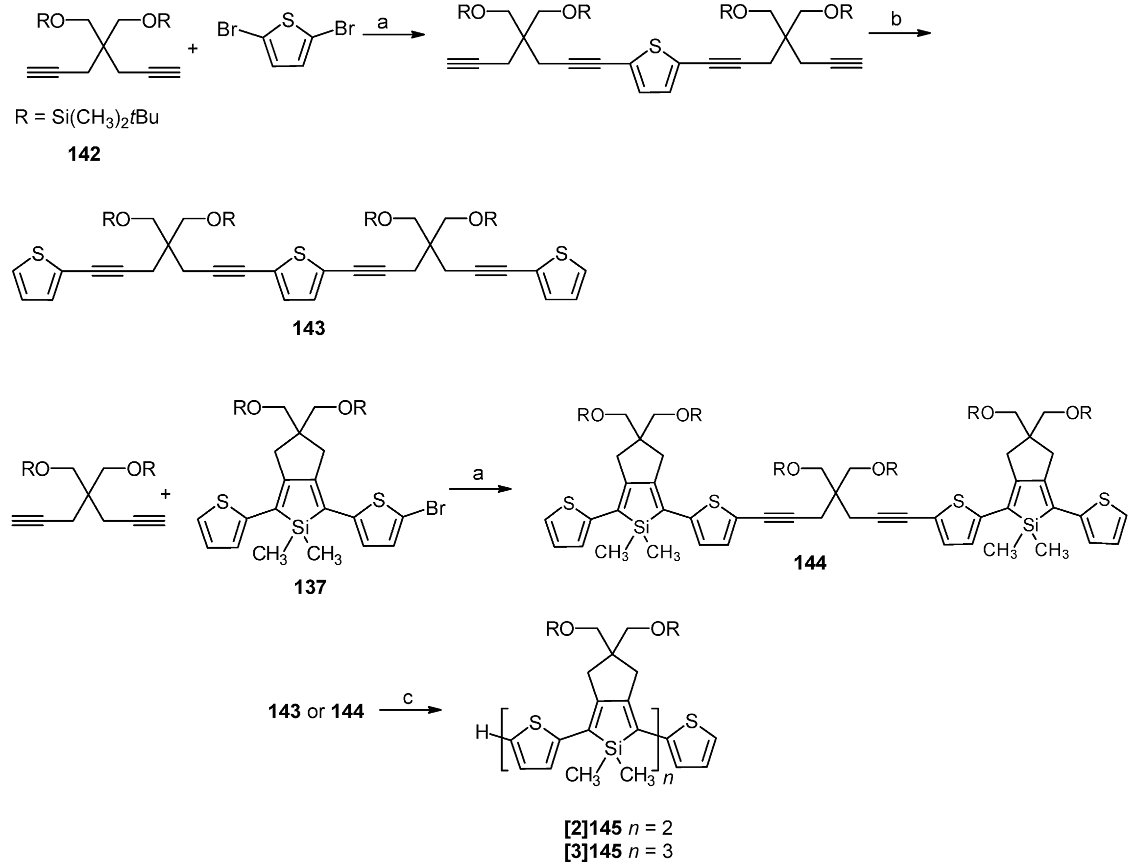
8.3.1. Synthesis

Ferrocene-terminated polyenes with up to five double bonds were first reported by Schlögl and Egger.[178] More recently, the groups of Launay and Spangler[179] synthesized a series of diferrocenylpolyenes [***n***]**150** with up to six conjugated double bonds, using reactions outlined in Scheme 53. Higher homologues remained inaccessible due to low solubility.

8.3.2. Properties

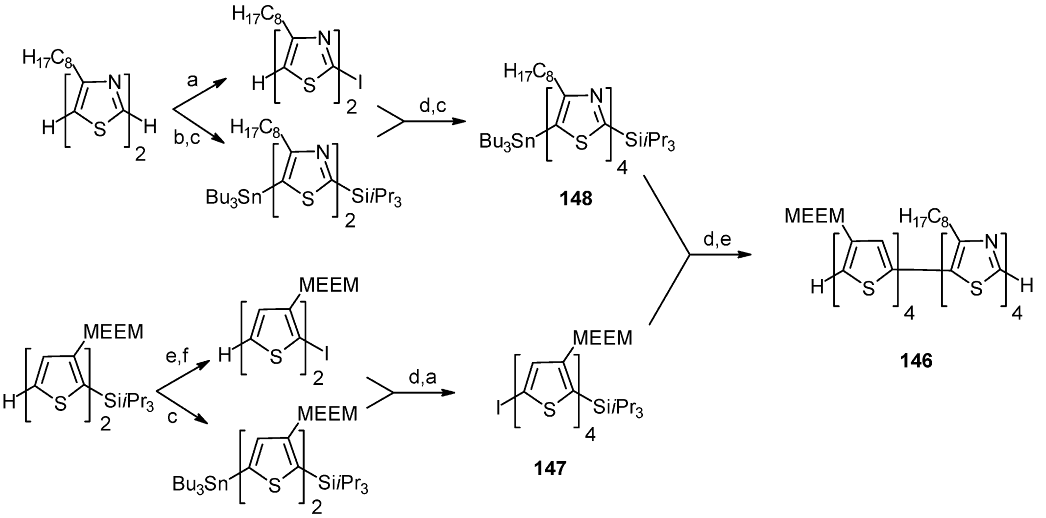
The metal to metal distance in compounds [***n***]**150** was approximated by molecular mechanics and ranged

Scheme 50[a]



[a] Conditions and reagents: (a) $PdCl_2(PPh_3)_2$, CuI, Et_2NH. (b) 2-Bromothiophene, $PdCl_2(PPh_3)_2$, CuI, Et_2NH. (c) $Ni(acac)_2$, PEt_3, DIBAH, THF, $HMe_2SiSiMe_2H$.

Scheme 51[a]



MEEM = methoxyethoxyethoxymethy

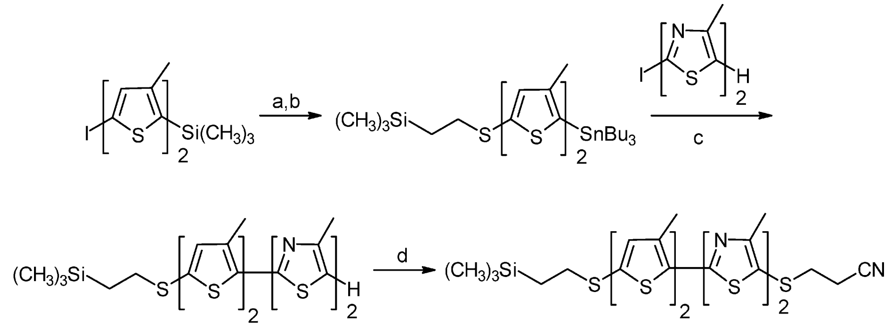
[a] Conditions and reagents: (a) LDA, THF, then I_2. (b) LDA, THF, then $i$$Pr_3SiOTf$. (c) BuLi, TMEDA, THF, then Bu_3SnCl. (d) $Pd_2(dba)_3$, PPh_3, Cu_2O, DMF. (e) Bu_4NF, THF. (f) NIS, CH_3Cl, HOAc.

from 6.2 (one double bond, cis) to 18.7 Å (six double bonds, trans).[179] In electrochemical studies, the shorter species (up to two double bonds) showed two oxidation peaks, while the higher ones showed only one. The long distance intervalence electron transfer and the decay law of the electronic interaction were measured on the mixed valence systems.

8.4. Ethene/Thiophene

Oligothienylvinylenes consist of alternating thiophene and ethene modules and represent an important, yet somewhat neglected, class of linear π-conjugated systems. The parent polymer, poly(thienylenevinylene), features a band gap that is 0.20−0.30 eV smaller than that of polythiophene.[180] The alter-

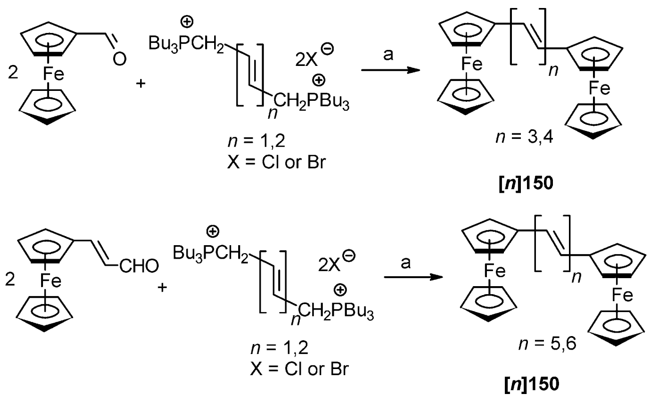
Scheme 52[a]



149

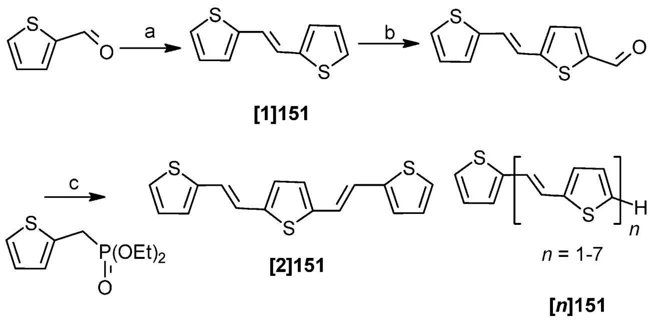
[a] Conditions and reagents: (a) (1) $(CH_3)_3SiCH_2CH_2SH$, CuI, NaO*t*-Bu, neocuproine, toluene; (2) TFA. (b) BuLi, then Bu_3SnCl. (c) $Pd_2(dba)_3$, PPh_3, Cu_2O, DMF. (d) (1) BuLi; (2) S_8; (3) $BrCH_2CH_2CN$.

Scheme 53[a]



[a] Conditions and reagents: (a) DMF, NaOEt, EtOH.

Scheme 54[a]



[a] Conditions and reagents: (a) (1) $TiCl_4$, THF; (2) Zn; (3) H_2O. (b) $POCl_3$, DMF. (c) DME.

nation of ethene and thiophene moieties reduces the overall aromatic character of the conjugated system and suppresses rotational disorder. As a result, these oligomers have the smallest HOMO−LUMO gap among all classes of π-conjugated oligomers of comparable length and display the best π-electron delocalization.

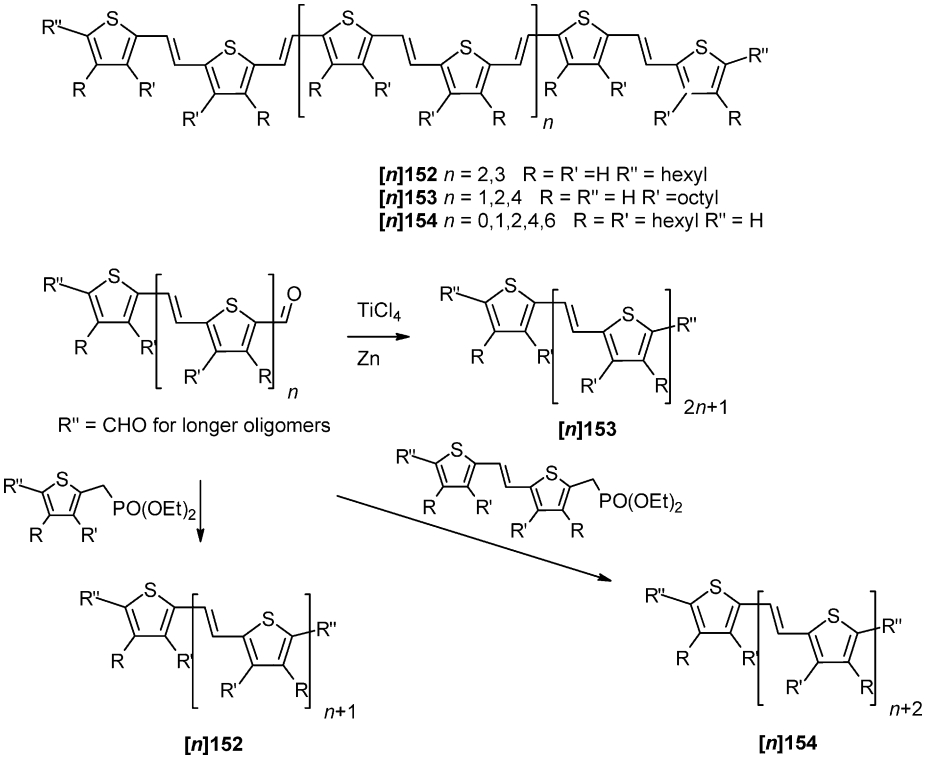
8.4.1. Ethene/Thiophene—Open Chain

Synthesis. Shorter oligomers containing alternating ethylene and thiophene units were first reported by Kossmehl et al. in low yields.[181] More recently, Nakayama and Fujimori[182] have developed a systematic synthesis of oligomeric *E*-(thiophene-2,5-diyl)-vinylenes [***n***]**151** in high yields (Scheme 54). A Wittig−Horner type reaction between thiophene-2-carbaldehydes and 2-thienylethylphosphonates was used for unsymmetrical coupling, allowing access to oligomers with an odd number of thiophene units. Symmetrical coupling of thiophene-2-carbaldehydes utilizing a low-valent titanium reagent provided chains containing an even number of thiophene rings. Both reactions yielded the desired *E* stereoisomer in at least a 95:5 ratio. Through a stepwise process of coupling and formylation or phosphonylation of the coupling product, oligomers containing from two to eight thiophene rings were isolated and characterized.

Another systematic study was performed by the group of Roncali.[183,184] Three different sets of oligomers, in the most recent case up to the hexadecamer, were reported, each distinguished by an increasing alkyl substitution pattern on the periphery (Scheme 55). For the first oligomeric series ([***n***]**152**), the rods were substituted with hexyl chains in both terminal α positions leading to a successful synthesis of a hexamer [**6**]**152**.[184] In the second series ([***n***]**153**), one β hydrogen on each thiophene module was replaced by an octyl chain. By a combination of a formylation reaction and a McMurry dimerization, oligomers up to the decamer [**10**]**153** were prepared.[185,186] However, an extension of the methodology to higher homologues was prevented by the failure to achieve sufficiently selective monoformylation beyond the trimeric intermediate. For the synthesis of the final series ([***n***]**154**), which is based on 3,4-dihexylthiophene modules, a new approach was developed.[187,188] All longer oligomers were synthesized by double formylation followed by 2-fold Wittig−Horner olefination of the dialdehydes with the appropriate phosphonate. At each iterative step, the method allows the increase of the chain length by four units, finally leading to the preparation of the hexadecamer [**16**]**154** with a chain length approaching 100 Å (Scheme 55).

Properties. The compounds are air stable solids with melting points above 200 °C. The solubility of unfunctionalized oligomers decreases dramatically with increasing rod length. The low solubility of the trimer [**3**]**151** (Scheme 54) in chloroform prevented the recording of its NMR spectrum. A synthesis of the octamer [**8**]**151** was attempted, but the product could not be purified and identified due to its low solubility.[184] The UV−visible spectra of [***n***]**152**−**154** were recorded and show a bathochromic shift of the

Scheme 55



absorption maxima and higher molar absorptivities with increasing rod length, thus confirming the full conjugation of the π system. By substitution with long alkyl chains, both in the α and in the β positions of the thiophene units, the solubility and therefore the processability of the compounds are dramatically improved. The solubility increases with the number and length of the alkyl chains incorporated per thiophene unit.[187] Analysis of single crystal X-ray structures unambiguously showed the planarity of the structure.[187] As in the unsubstituted counterparts, chain extension results in a red shift of the absorption maximum and a decrease of the band gap. All spectra show a well-developed vibronic fine structure. Further interpretation of the optical properties of the oligothienylvinylenes revealed a bathochromic shift of the absorption maximum with increasing number of substituents in β position due to the cumulative inductive effect of the alkyl chains. As expected, extension of the conjugated backbone leads to a negative shift of the first redox potential and an increase of the number of oxidation states. For example, the cyclic voltammogram (CV) of the octamer [**8**]**154** (Scheme 55) displays the coalescence of the first two redox steps into one two-electron wave, followed by two one-electron waves corresponding to the formation of the trication and tetracation. The hexadecamer [**16**]**154** can be similarly charged up to the hexacationic stage. A convergence limit around the 20–22-mer has been extrapolated.[187] The compounds appear very promising for use as organic field effect transistors due to their very small HOMO–LUMO gap.[189]

8.4.2. Ethene/Thiophene—Bridged

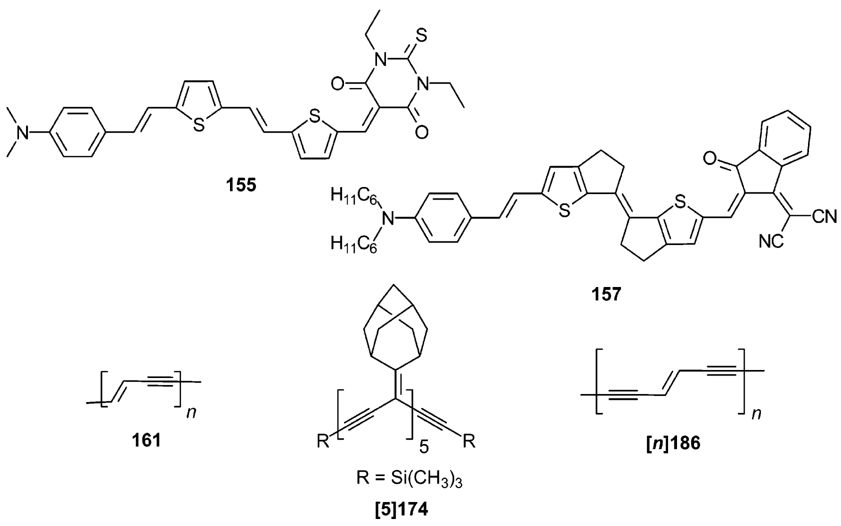
Synthesis. Raimundo and collaborators[190,191] reported the synthesis of a series of dithienylethylene-based rods **155** (Chart 3) linking *N*,*N*-dialkylaniline donors with various acceptors and their bridged analogues **156** (Scheme 56). The synthesis of the push–pull chromophores, such as **156**, was achieved by converting dithienylethylene and its bridged counterpart into monoaldehydes via Vielsmeier formylation, followed by Wittig olefination with phosphonium iodides to introduce the *N*,*N*-dialkylaniline group. After a second formylation, the molecules were extended in the opposite direction by Knoevenagel condensation with various acceptors carrying active methylene groups (Scheme 56).

Properties. The compounds show excellent thermal stability up to above 250 °C.[191] Introduction of long alkyl chains on the terminal amino group improved solubility in organic solvents significantly and allowed the measurement of optical absorption and second-order nonlinear hyperpolarizabilities.[191] The introduction of the bridges in the rods, as in **156**, improves conjugation and causes a considerable red shift of the absorption maxima by up to 100 nm. Furthermore, for any given acceptor, the bridging induces an up to 4-fold increase in the $\mu\beta$ value (the projection of the hyperpolarizability tensor β on the dipole moment μ), reaching 19400×10^{-48} esu for the dicyanovinylindan-3-one-based acceptor **157** (Chart 3).[190]

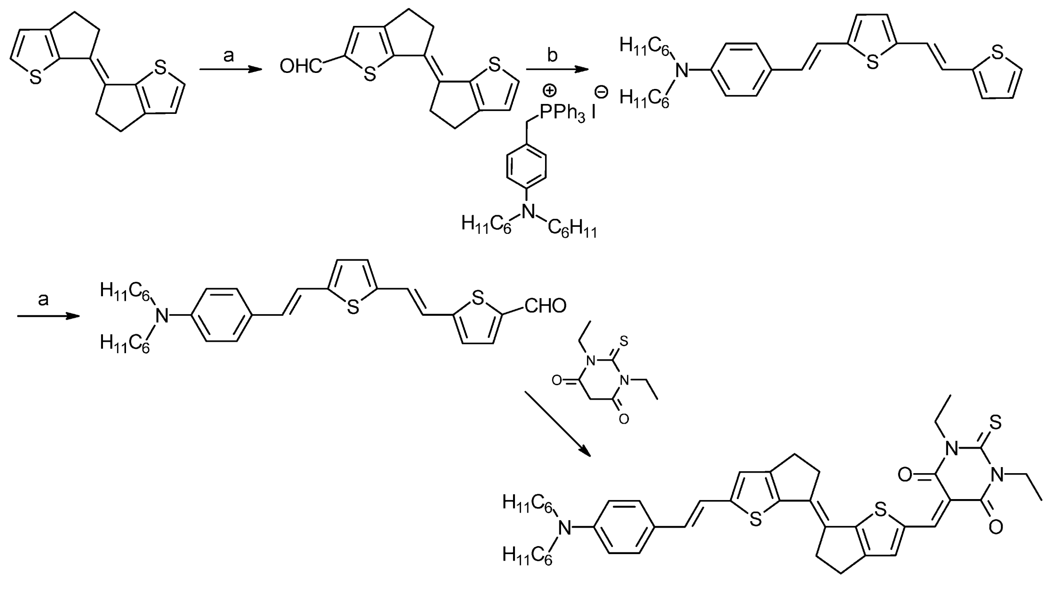
8.4.3. Quinodimethanethiophenes

Synthesis. Quinodimethane-terminated thiophene oligomers **158** up to the tetramer have been prepared starting from the parent oligothiophenes.[192,193,194] The quaterthiophene **159**[195] was iodinated using N-iodosuccinimide in good yield to make diiodoquarterthiophene **160**. This was followed by palladium-catalyzed cross-coupling with malononitrile, and the resulting thienyl malononitrile was deprotonated in

Chart 3



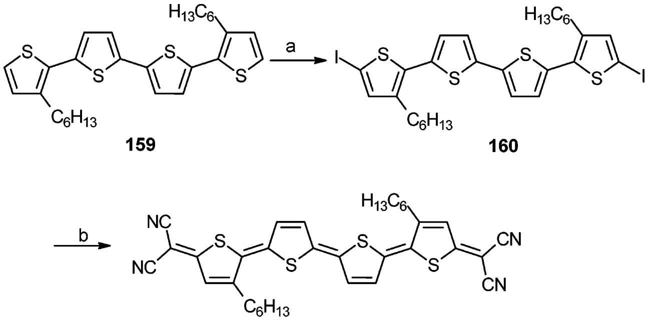
Scheme 56[a]



156

[a] Conditions and reagents: (a) $POCl_3$, DMF. (b) KO*t*-Bu, CH_3CN, THF.

Scheme 57[a]



[a] Conditions and reagents: (a) CH_2Cl_2, NIS, AcOH. (b) (1) NaH, malonitrile; (2) compound **160**, $Pd(PPh_3)_4$; (3) Br_2, H_2O.

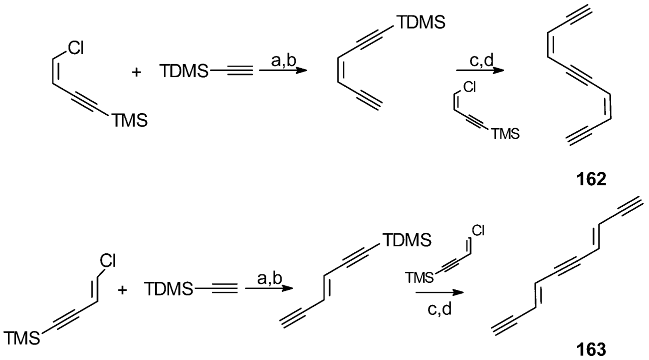
situ. The dianion was oxidized with excess bromine yielding the neutral quinoid bisdicyanomethylenedihydroquaterthiophene [4]**158** (Scheme 57).[194]

Properties. The quinoid quaterthiophene [4]**158** shows a reversible one-electron oxidation at 0.99 eV, a second quasi-reversible oxidation at 1.55 eV, and a reversible two-electron reduction at −0.09 eV.[194] The solution UV−vis spectrum displays a very intense low energy $\pi-\pi^*$ transition with a maximum at 779 nm, bathochromically shifted by about 110 nm with respect to the analogous trimer. A single crystal X-ray structure of [4]**158** is characterized by a very planar quinoidal backbone and short intermolecular π-stacking distances. As a result of the π-stacking, the compound has a one-dimensional electronic band structure. With these features, the compound appears suitable for both p and n biasing in FETs and therefore is a good candidate for ambipolar semiconductor materials.[194]

9. Co-oligomers of Axial and Zig-Zag Modules

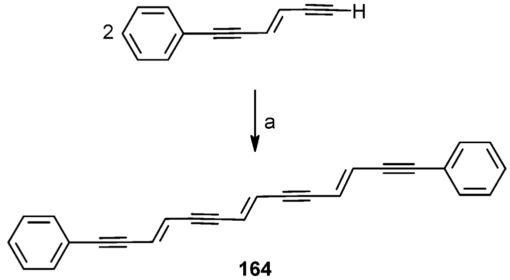
The number of ways in which the zig-zag modules discussed so far can be combined with the axial modules covered in Part 1[5] is vast, and many have

Scheme 58[a]



[a] Conditions and reagents: (a) THF, $Pd(PPh_3)_4$, CuI, NEt_3 (92%). (b) K_2CO_3, MeOH (94%). (c) THF, $Pd(PPh_3)_4$, CuI, Et_3N (80%). (d) TBAF, EtOH/THF (79%).

Scheme 59[a]



[a] Conditions and reagents: (a) (1) EtMgBr, THF; (2) *E*-1,2-dichloroethene, $NiCl_2(dppp)$.

been examined. In this section, we treat zig-zag modules other than five-membered rings.

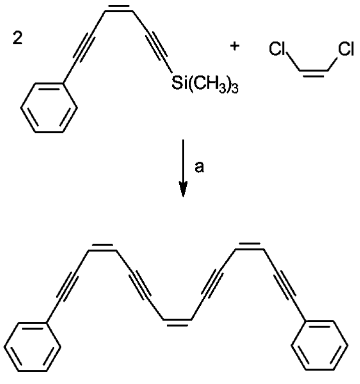
9.1. Oligodiacetylenes

In these oligomers (**161**, Chart 3), triple and double bonds alternate. Depending on the stereochemistry of the olefin module, *trans*- and *cis*-oligodiacetylenes can be distinguished. The compounds are also called oligoenynes.

9.1.1. Synthesis

The syntheses of the shortest oligomeric diacetylenes (*Z*,*Z*)-deca-3,7-diene-1,5,9-triyne (**162**) and (*E*,*E*)-deca-3,7-diene-1,5,9-triyne (**163**) were published by the group of Bergman (Scheme 58).[196] An extented phenyl end-capped all-trans oligomer (**164**) with four triple and three double bonds was prepared by Lindsell et al. (Scheme 59).[197] Wudl and Bitler[198] developed a methodology for producing an oligomeric series of *trans*-oligodiacetylenes **165** employing coupling reactions of alkynylmetal compounds with *trans*-1,2-dihaloethylene in the key step (Scheme 60). More recently, extended phenyl-capped *cis*-oligodiacetylenes, such as **166** with four triple and three double bonds, were prepared in low yields by Hirsch and co-workers applying Sonogashira coupling conditions (Scheme 61).[199] To prevent cis to trans isomerization that was observed for **166** in solution, cyclopentene moieties were incorporated into the backbone, effectively locking the conformation. The molecules are planar in the solid state but probably adapt helical conformations in solution, as suggested by NMR spectroscopy.[199]

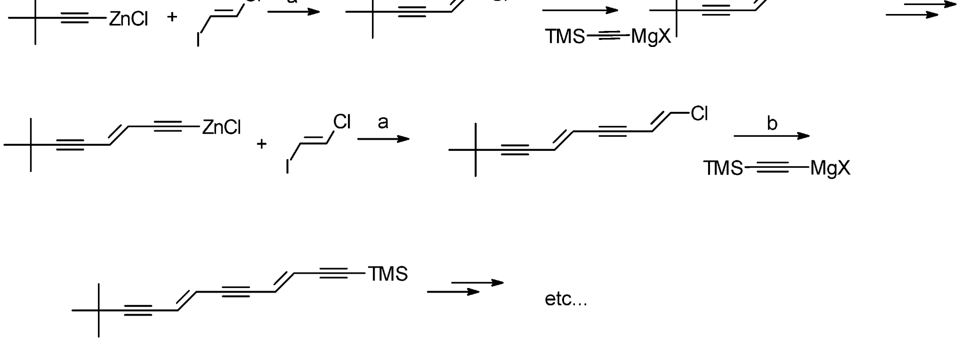
Scheme 61[a]



[a] Conditions and reagents: (a) K_2CO_3, CH_3OH, H_2O, $PdCl_2(PPh_3)_2$, CuI, $BuNH_2$, benzene.

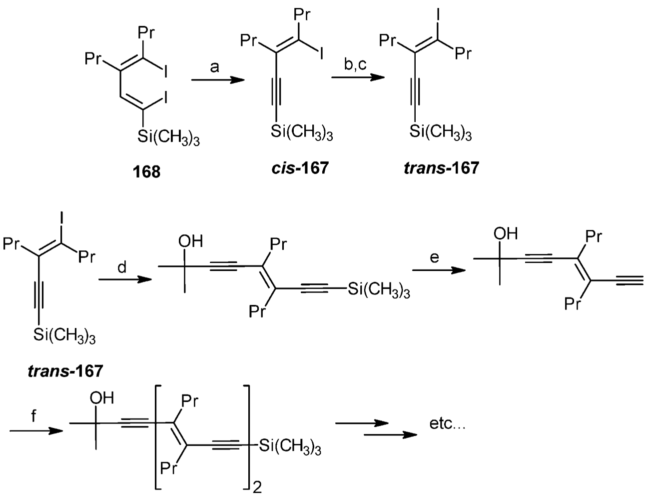
A novel approach to monodisperse oligodiacetylenes was recently presented by Sato's group, based on the use of 1-iodo-4-(trimethylsilyl)but-1-en-3-yne derivatives **167** with *trans*- and *cis*-olefin configurations (Scheme 62).[200] These key building blocks are obtained from a reaction of pyrrolidine and the 1-trimethylsilyl-1,4-diiodo-1,3-alkadiene **168**, accessible in an efficient one-pot reaction via regioselective coupling of internal acetylenes and ethynyltrimethylsilane in the presence of a divalent titanium reagent followed by iodination of the resulting titanacyclopentadienes. After one terminus was capped with 3-methyl-1-butyn-3-ol, the building blocks are then

Scheme 60[a]



[a] Conditions and reagents: (a) $PdCl_2(PPh_3)_2$. (b) $NiCl_2(dppp)$.

Scheme 62[a]



[a] Conditions and reagents: (a) Pyrrolidine. (b) *t*-BuLi, *n*-PrI. (c) NIS. (d) 1-Methyl-but-3-yn-2-ol, $PdCl_2(PPh_3)_2$, CuI, Et_2NH, THF. (e) K_2CO_3, THF, CH_3OH, H_2O. (f) *trans*-**167**, $Pd(PPh_3)_4$, CuI, Et_2NH, THF.

elongated by sequential reactions under Sonogashira coupling conditions.[200] Both all-*cis*-[***n***]**169** and all-*trans*-[***n***]**170** oligodiacetylenes with a backbone of 10-, 14-, 18-, and 22-carbon atoms were prepared (Scheme 63). They can be easily further modified at the termini. For example, a homocoupling reaction of the deprotected 22-carbon *trans*-oligoacetylene under Hay conditions led to the rod **171** consisting of 12 triple and 10 double bonds.[200]

9.1.2. Properties

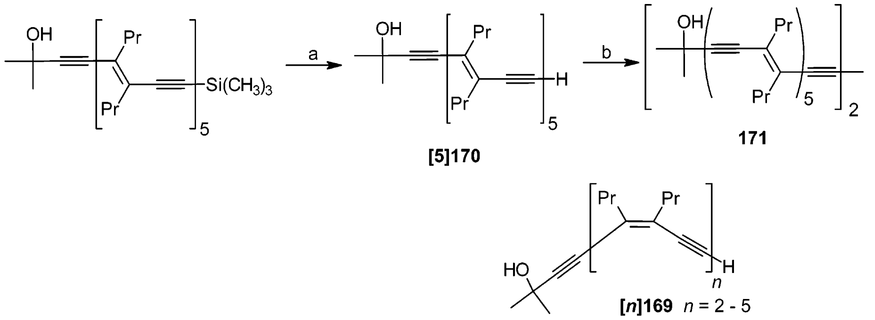
The absorption spectra of the oligomers revealed a significant difference between the cis and the trans isomers. While the trans isomers [***n***]**170** show a gradual red shift of the longest wavelength absorption band from the 10-carbon oligomer (λ_{max} = 346 nm) to the 22-carbon oligomer (λ_{max} = 400 nm), the cis oligomers [***n***]**169** have already converged at 345 nm starting from the 10-carbon oligomer.[200]

9.1.3. Iso-oligodiacetylenes

Iso-oligodiacetylenes are cross-conjugated constitutional isomers of oligodiacetylenes.

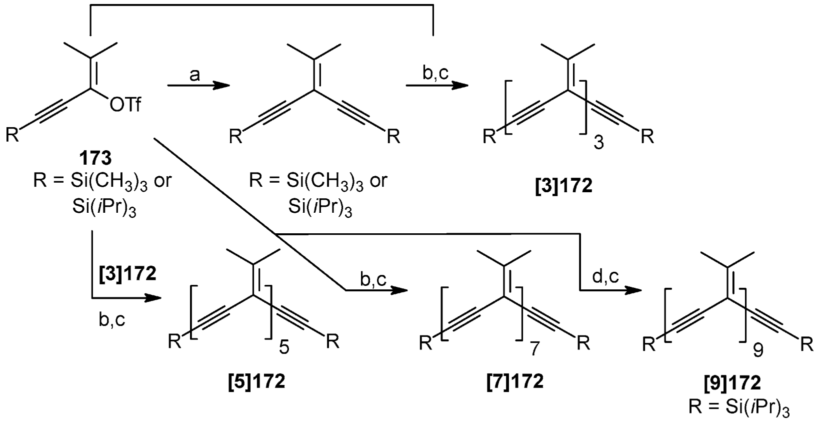
Synthesis. Tykwinski and co-workers[201,202] reported a novel iterative methodology for the synthesis of iso-oligodiacetylenes [***n***]**172** based on cross-coupling reactions between vinyl triflates and terminal alkynes under Pd catalysis (Scheme 64). For enhanced stability, instead of working with the parent compound, an isopropylidene or an adamantanylidene moiety was incorporated. Trimethylsilylacetylene or triisopropylsilylacetylene were treated sequentially with the trimethylsilyl or *trans*-bis-(tris-*iso*-propylsilyl) (TIPS)-protected vinyltriflates **173** followed by desilylation. This step provided oligomers with an odd number of repeating units up to the nonamer [**9**]**172** in the isopropylidene-substituted series, which spans 3.4 nm from Si to Si atom (Scheme 64) and up to the pentamer [**5**]**174** for the adamantyl-derived series (Chart 3). Homocoupling interfered only in the synthesis of the longer rods, yielding large cycles as byproducts. Iso-oligodiacetylenes with an even num-

Scheme 63[a]



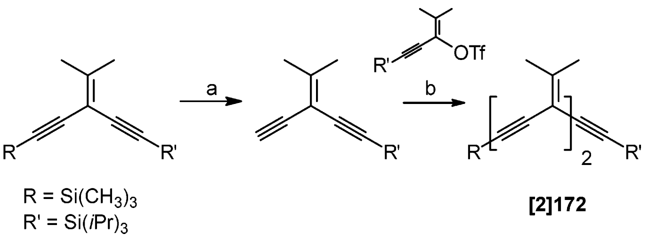
[a] Conditions and reagents: (a) K_2CO_3, THF, CH_3OH, H_2O. (b) CuCl, TMEDA.

Scheme 64[a]



[a] Conditions and reagents: (a) Silylacetylene, $PdCl_2(PPh_3)_2$, CuI, iPr_2NH, THF. (b) K_2CO_3, wet CH_3OH, THF. (c) $Pd(PPh_3)_4$, CuI, Et_2NH. (d) TBAF, wet THF.

Scheme 65[a]



[2]172

[a] Conditions and reagents: (a) K_2CO_3, wet CH_3OH/THF. (b) $Pd(PPh_3)_4$, CuI, Et_2NH, DMF.

ber of repeating units were synthesized making use of a differential protection scheme (Scheme 65).[202]

Additionally, Ciulei and Tykwinski[203] published the preparation of iso-polydiacetylene-based push−pull oligomers carrying *p*-*N*,*N*-dimethylaminophenyl and/or *p*-nitrophenyl groups as donor and acceptor moieties, respectively, at the termini (Scheme 66). The synthesis was accomplished starting from the differentially protected enediyene **175**, which was selectively protodesilylated with K_2CO_3. The singly deprotected building block was then extended by Pd-catalyzed cross-coupling reaction with the vinyl triflate **173**[204] to yield the differentially protected iso-oligodiacetylene dimer **176** and, after repetition of the sequence, the respective trimer **177**. Compounds **175**, **176**, and **177** were further modified after sequential monodesilylation by Pd-catalyzed cross-coupling, first with the donor, *p*-iodo-*N*,*N*-dimethylaniline, and then with the acceptor, *p*-iodonitrobenzene, to produce the desired homologous series of push−pull chromophores **178**, **179**, and **180** (Scheme 66).

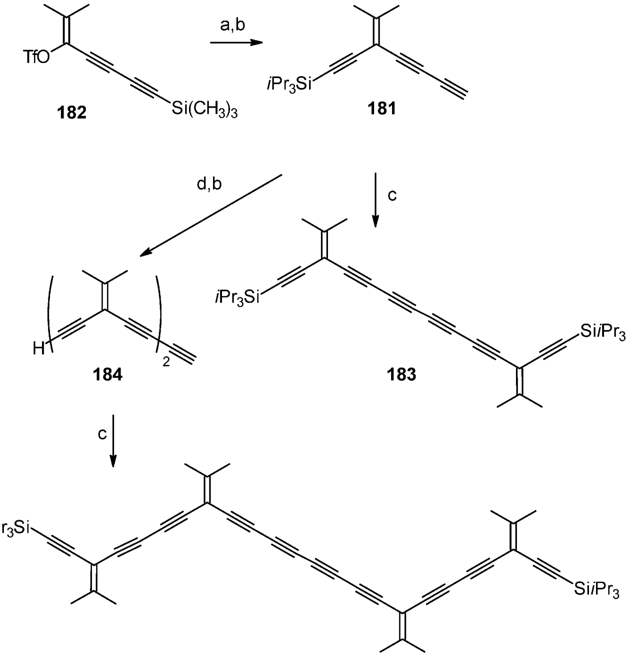
Properties. The oligomeric iso-oligodiacetylenes [***n***]**172** (Scheme 64) are reasonably stable solids with high melting points. The adamantanylidene-substituted compounds [***n***]**174** (Chart 3) can be stored at ambient temperature for weeks without decomposition.[202] Their solubility in common organic solvents is unexpectedly low. The analysis of the UV−visible spectra in solution and thin films indicates the presence of a slight π-electron communication along the backbone, which reaches a saturation point at the level of the nonamer.[202]

The donor−acceptor-substituted oligomers **178**, **179**, and **180** were isolated as air stable orange solids that show good thermal stability, with melting points around 150 °C and decomposition temperatures above 200 °C (Scheme 66).[203] UV−visible spectroscopy shows that only the shortest member of the series **178** allows efficient electronic communication between the donor and the acceptor through the backbone. For the two longer homologues **179** and **180**, no low-energy charge transfer absorption is detectable in the UV−visible spectrum.[203]

9.1.4. Isopolytetraacetylene

Synthesis. Tykwinski and co-workers[205] reported the synthesis of extended isopolydiacetylenes (Scheme 67). The key triacetylene building block **181** was prepared in excellent yield from the vinyl triflate **182** by coupling with triisopropylsilylacetylene followed by protodesilylation. The triyne **181** was then oxidatively homocoupled to the hexayne **183** in very high yield. Alternatively, compound **181** was extended to

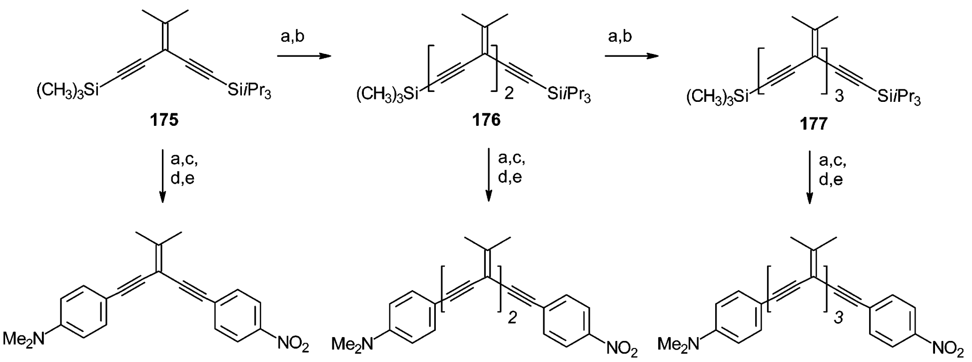
Scheme 67[a,b]



185

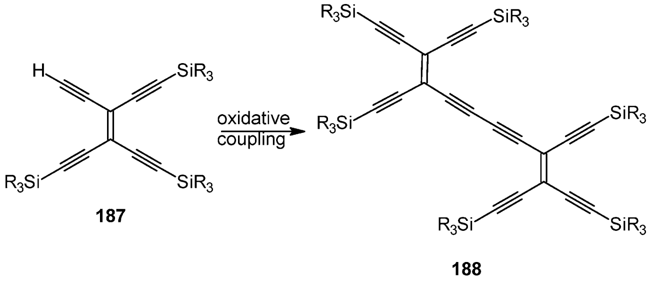
[a] Reprinted with permission from ref 205. Copyright 2000 Royal Society of Chemistry. [b]Conditions and reagents: (a) Triisopropylsilylacetylene, $PdCl_2(PPh_3)_2$, CuI, *i*Pr_2NH, THF. (b) K_2CO_3, wet MeOH−THF (1:1). (c) CuI, TMEDA, O_2, CH_2Cl_2. (d) Compound **182**, $PdCl_2(PPh_3)_2$, CuI, *i*Pr_2NH, THF.

Scheme 66[a]



[a] Conditions and reagents: (a) K_2CO_3, wet CH_3OH/THF. (b) Compound **173**, $Pd(PPh_3)_4$, CuI, Et_2NH, DMF. (c) *p*-iodo-*N*,*N*-dimethylaniline, $PdCl_2(PPh_3)_2$, CuI, Et_3N. (d) TBAF, wet THF. (e) *p*-iodonitrobenzene, $PdCl_2(PPh_3)_2$, CuI, Et_3N.

Scheme 68



the pentayne **184** by treatment with the vinyl triflate starting material and, after desilylation, homocoupled to produce the decayne **185**.

Properties. The cross-conjugated oligoenynes are stable, light yellow solids with fair solubility in halogenated solvents.[205] Crystals of **183** melt at 103 °C and are thermally stable up to 145 °C. Prolonged heating at 90 °C induces polymerization, but the material is not affected by extended UV irradiation. X-ray analysis of a single crystal of **183** showed a virtually linear acetylenic backbone and a planar π framework. Interestingly, all six triple bonds have the same bond length. Furthermore, the ^{13}C NMR spectrum of **185** reveals distinct resonances for all 10 acetylenic carbon atoms. The lack of bond length alternation confirms a lower degree of π conjugation as compared to the respective polydiacetylenes.[206] Above 300 nm, the absorption spectra of **183** and **185** are very similar to that of 1,8-bis(4-*tert*-butylphenyl)-octa-1,3,5,7-tetrayne and show three absorptions at ~405, 374, and 348 nm in chloroform. The observed absence of any contribution from cross-conjugation to effective π-conjugation contrasts notably with the oligomeric isopolydiacetylenes.[205]

9.2. Oligotriacetylenes

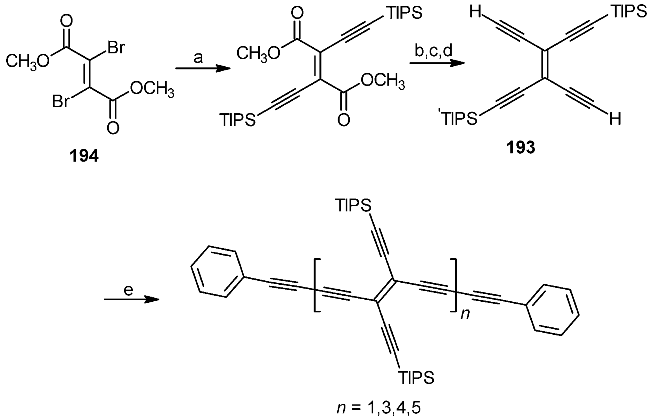
These rods [***n***]**186** (Chart 3) consist of repeating *E*-diethynylethene units. Thus, they can be considered intermediates between polyacetylene, polydiacetylenes, and carbyne. Reviews of these compounds have been published recently.[207,208]

9.2.1. Synthesis

The synthesis of tetraethynylethene, the parent of polytriacetylenes, was first reported by Diederich's group.[209] Through the use of various (trialkylsilyl)-alkyne protecting groups, virtually every substitution pattern on the parent is accessible.[210,211] The tris-(trialkylsilyl)-protected derivative **187** was oxidatively coupled to form the dimeric species **188** (Scheme 68). Selective deprotection of **188** was possible if both triethylsilyl and triisopropylsilyl groups were present. The tetra(triisopropylsilyl)-protected derivative was isolated and coupled with **187** again to obtain the oligomers with three, four, and five tetraethynylethene units, albeit in very low yields (Scheme 69).[212] Other substituted tetraethynylethenes were dimerized.[213] Donor−acceptor end-capped tetraethynylethene rods were obtained[214,215] from mixed cross-coupling of trisubstituted **189**, **190**, **191** and **192** (Chart 4).

For a one-step approach to the synthesis of polytriacetylene oligomers, TIPS-protected tetraethynylethene **193** was prepared as the monomer in five steps from dimethyl dibromofumarate (**194**, Scheme 70)[216] and subsequently was subjected to an oxidative polymerization reaction, which was quenched by the addition of phenylacetylene as an end-capping reagent. The dimeric through pentameric species were isolated by chromatography from the resulting mixture of oligomers, along with the end-capped monomer. The product distribution was adjustable by controlling the amount and timing of the addition of the end-capping reagent.[214]

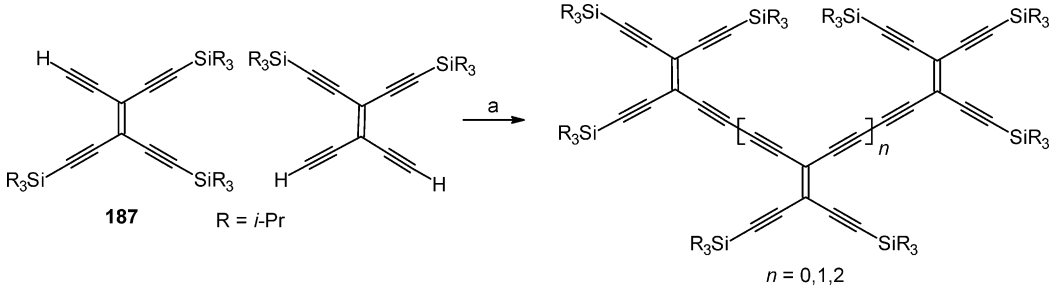
Scheme 70[a]



[a] Conditions and reagents: (a) 2-Tris(isopropyl)[(tributylstannyl)ethynyl]silane, PdCl$_2$(PPh$_3$)$_2$, THF. (b) (1) DiBAL-H, CH$_2$Cl$_2$; (2) PCC, CH$_2$Cl$_2$. (c) CBr$_4$, PPh$_3$, Zn, CH$_2$Cl$_2$. (d) LDA, THF. (e) (1) CuCl, TMEDA, CHCl$_3$; (2) phenylacetylene.

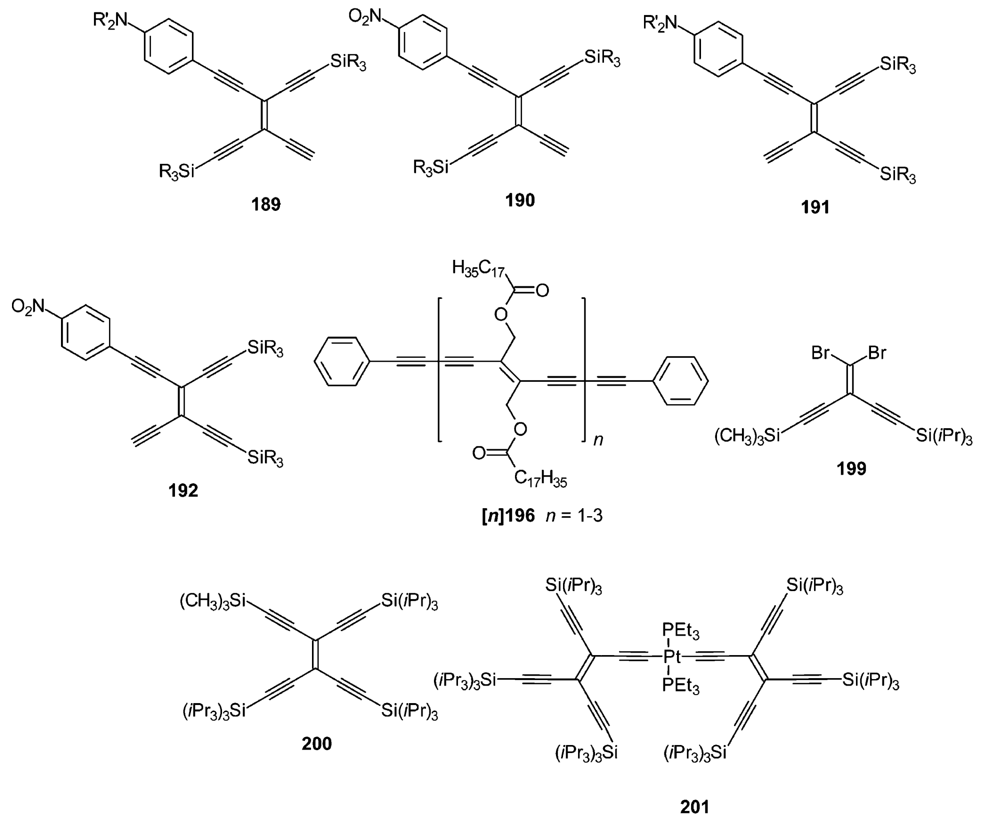
Significantly longer monodisperse oligotriacetylene rods [***n***]**195** up to the hexadecamer were prepared by Martin et al.[217,218] starting from the (*tert*-butyl)-dimethylsilyloxy-substituted dimer [**2**]**195**. Statistical deprotection of [**2**]**195** followed by Hay coupling of the mixture afforded predominantly tetrameric

Scheme 69[a]

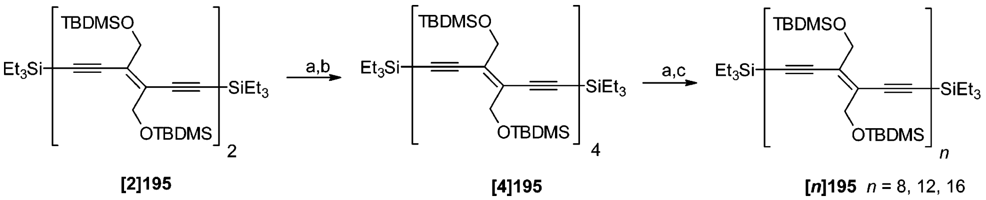


[a] Conditions and reagents: (a) Cu(OAc)$_2$, pyridine, benzene.

Chart 4

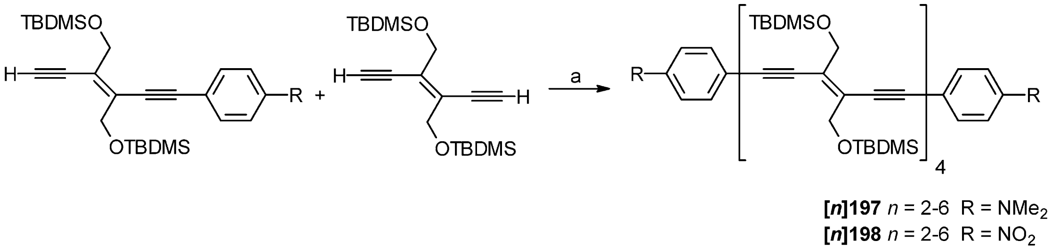


Scheme 71[a]



[a] Conditions and reagents: (a) NaOH, THF/MeOH. (b) CuCl, TMEDA, CH_2Cl_2, molecular sieves, air. (c) CuCl, TMEDA, toluene, molecular sieves, dry O_2, reflux.

Scheme 72[a]



[a] Conditions and reagents: (a) CuCl, TMEDA, CH_2Cl_2, molecular sieves, air.

[4]**195** (Scheme 71). The tetrameric species was then subjected to the same sequence yielding the octamer [8]**195**, dodecamer [**12**]**195**, and hexadecamer [**16**]**195** as the main products, which were separated by preparative SEC. The hexadecamer [**16**]**195** was more efficiently prepared by application of the deprotection–oligomerization steps to the octamer [**8**]**195**.

The introduction of long alkyl chains into the backbone was accomplished by Nierengarten et al.[219] in order to obtain compounds of the oligotriacetylene series [***n***]**196**, with liquid crystalline properties (Chart 4). More recently, two series of donor–donor [***n***]**197** and acceptor–acceptor [***n***]**198** end-functionalized oligotriacetylenes up to the hexamer were reported from Diederich's laboratory applying an oxidative Hay oligomerization under end-capping conditions and subsequent separation of the oligomers by SEC (Scheme 72).[220]

9.2.2. Properties

The monomer **193** is unusually stable in crystalline form, probably due to the insulating effect of the large TIPS groups. The reported oligomers are very air and light stable, high melting solids. All oligomers dissolve in chloroform; the shorter ones also dissolve in hexanes. Investigation of the redox properties revealed that none of the oligomers were oxidizable below +1.0 V (vs ferrocene) and that they were readily reducible. The number of reversible one-electron reduction steps corresponds to the number of tetraethynylethene units in the rod. The first reduction potential increases with increasing rod length. In the longer oligomers, the first and second reduction potentials are similar, as well as the third and fourth. Dianions and tetraanions apparently display a special stability, which is attributed to the separation of the dianionic centers by [**5**]cumulene units.[221]

The longer (*tert*-butyl)dimethylsilyloxy-substituted oligomers [***n***]**195** are highly stable, yellow solids with gradually increasing melting points from the tetramer [**4**]**195** (69 °C) to the hexadecamer [**16**]**195** (>220 °C).[217] They display good solubility in aprotic solvents but very limited solubility in protic solvents. The extended backbone length of the hexadecamer [**16**]**195** was estimated at 11.9 nm. Using the results obtained from UV−vis spectroscopy, an effective conjugation length of $n = 10$ was determined and confirmed in Raman scattering studies.[217,222] The effective conjugation length of the acceptor−acceptor-substituted rods [***n***]**198** was found to be similar, while the introduction of the two donor groups in [***n***]**197** reduced it dramatically to $n = 4$, which was attributed to the formation of strong CT bands.[220]

9.2.3. Linear Coupling

The tetraethynylethene building blocks were coupled to transition metals through their terminal acetylenes. Faust et al.[223] reported the synthesis of mono- and dinuclear platinum complexes containing tetraethynylethene ligands as building blocks for a two-dimensional transition metal-linked carbon network. For the synthesis, the dibromo olefin precursor **199** was coupled with monoprotected alkynes under Pd catalysis to obtain the differentially tetrasilylated tetraethynylethenes **200** (Chart 4). After specific protodesilylation and stannylation of the monodeprotected alkynes with Me_3SnCl, reaction with *trans*-$[PtCl_2(PEt_3)_2]$ under Cu mediation yielded the desired dimeric species **201** (Chart 4). The attachment of more than one metal fragment was demonstrated similarly, as a further step toward the construction of a proposed grid.

9.3. Oligopentacetylene

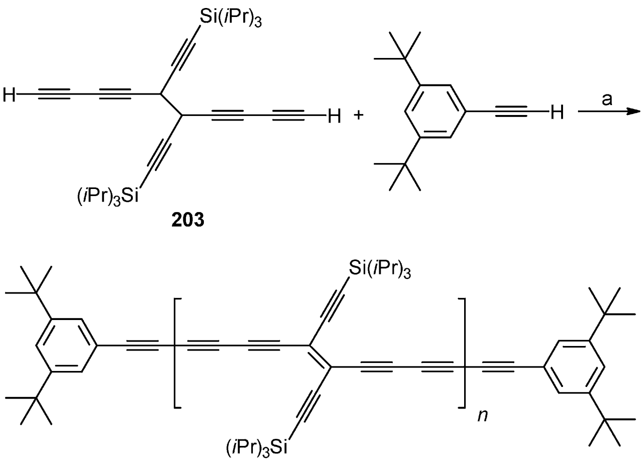
9.3.1. Synthesis

The synthesis of the first series of monodisperse poly(pentacetylene) (PPA) ([***n***]**202**) was described up to the trimer by Diederich.[207] Starting from the bisdiyne **203**, the rods [***n***]**202** were assembled under oxidative coupling conditions in the presence of 1,3-di-*tert*-butyl-5-ethynylbenzene as an end-capping reagent and separated in low yields (Scheme 73).

9.3.2. Properties

Compared to the respective oligotriacetylenes, the oligo(pentacetylene)s ([***n***]**202**) are considerably less stable and more difficult to process.[207]

Scheme 73[a]



203

[*n*]202 $n = 1\text{-}3$

[a] Conditions and reagents: (a) CuI, TMEDA, air, CH_2Cl_2.

9.4. Ethene/Benzene

Oligomers based on the stilbene unit are among the most important zig-zag rods.

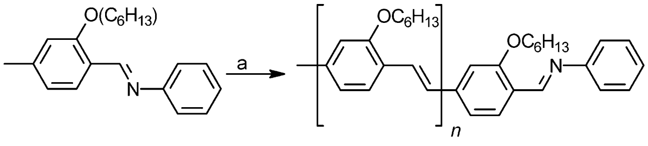
9.4.1. Oligo(phenylenevinylene)s (OPVs)

Replacement of every other double bond in a oligoene with a *p*-phenylene yields oligo(*p*-phenylenevinylene)s [***n***]**204** (Chart 5). In this section, we first cover some general aspects of this group of zig-zag rods before we turn to specific examples.

Oligo(*p*-phenylenevinylene)s−General. As in oligoenes, the rigidity of the zig-zag backbone is limited and is provided by π-electron delocalization between the phenylene and the vinylene units. The building blocks for the oligomers with alternating 1,4-phenylene and vinylene units are readily available and cheap.

Synthesis. Like other oligomers, oligo(*p*-phenylenevinylene)s are obtainable in a stepwise approach of sequential, repetitive condensation reactions or by a one-step synthesis of oligodisperse mixtures under polycondensation type polymerization conditions followed by chromatographic separation of the oligomers. The former methodology has been predominantly applied in practice, and several methods for the controlled synthesis of alkoxy derivatives [***n***]**205** of the oligomers [***n***]**204** (Chart 5) are in use (Scheme 74).[224] They can be divided into reactions that form double bonds between benzylic carbons and those that form single bonds between styrene and benzene units. The Wittig−Horner reaction is very versatile,[224] but the yields are usually in the range of 70−80%. Nevertheless, this reaction was used a long time ago in the preparation of the first series of unsub-

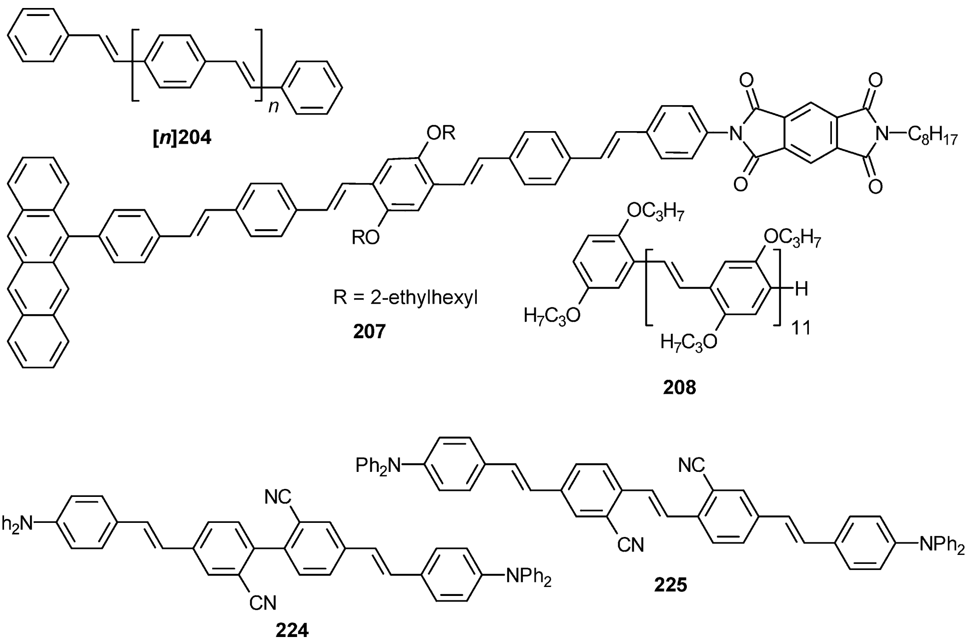
Scheme 74[a]



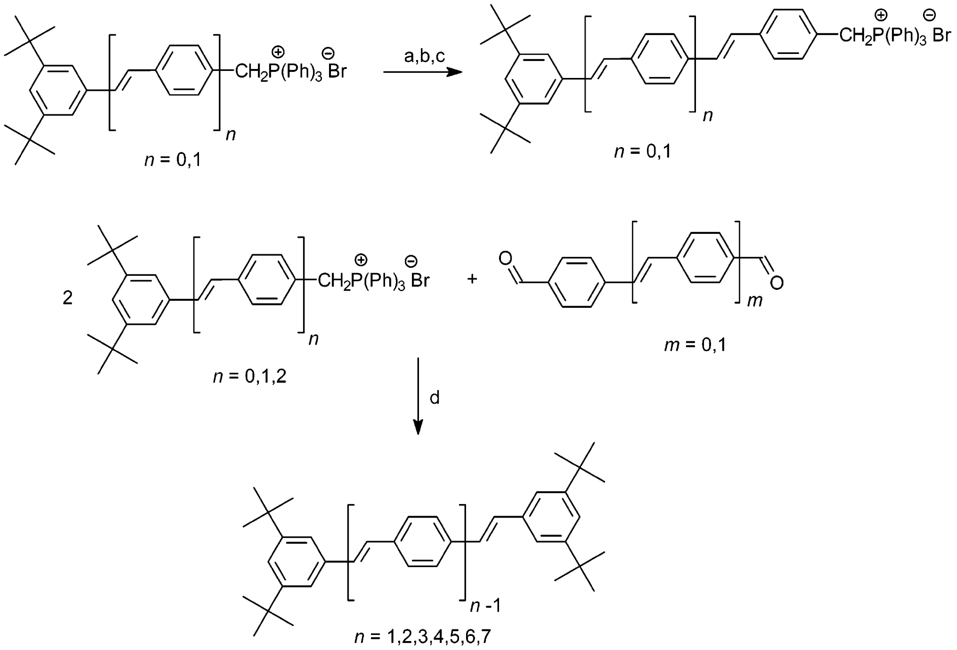
[*n*]205 n = up to 9

[a] Conditions and reagents: (a) KO*t*-Bu, DMF.

Chart 5



Scheme 75[a]

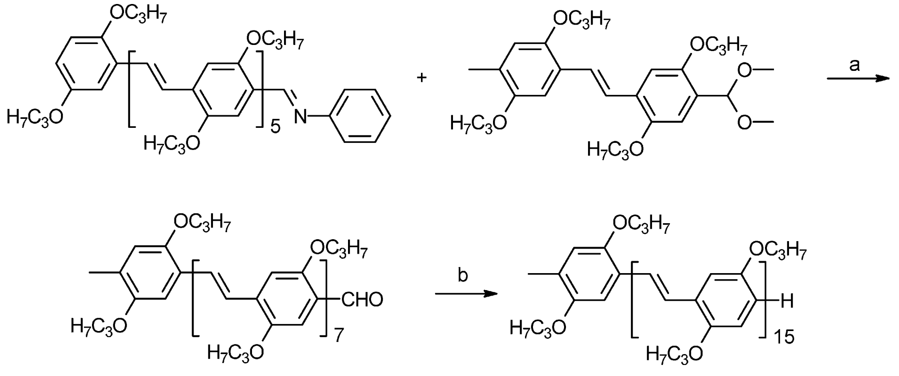


[n]206

[a] Conditions and reagents: (a) 4-Methylbenzaldehyde, LiOEt/EtOH, DMF. (b) NBS, CCl_4, 80 °C. (c) PPh_3, toluene, 110 °C. (d) LiOEt/EtOH, DMF.

stituted oligomers [***n***]**204** with up to eight repeating units.[225,226] Starting with 4-bromomethylbenzaldehyde and benzyltriphenylphosphonium chloride, Hörhold assembled the rods by repetitively generating the reactive triphenylphosphonium salt intermediate in situ.[227] More recently, a similar approach allowed Müllen and co-workers to prepare the more soluble oligomers [***n***]**206** with *tert*-butyl substituents on the terminal phenyl rings (Scheme 75).[228,229] Here, a three-step sequence was established, consisting of a Wittig type coupling reaction with 4-methylbenzaldehyde, NBS bromination of the resulting terminal methyl group, and conversion to the triphenylphosphonium salt. The target structures up to the heptamer [**7**]**206** were finally obtained by symmetrical condensation with terephthalic dialdehyde or 4,4′-stilbene dicarbaldehyde. The Knoevenagel condensation[230] is less versatile. It requires the presence of an electron-withdrawing group in the α-position on the methylene groups of a tolyl or xylyl precursor. McMurry coupling[231] can be used for obtaining mainly symmetric oligomers, and yields vary from good to moderate.[232] The three methods discussed above yield a mixture of cis and trans isomers, and additional workup is required to obtain individual isomers. The Siegrist method[233] is rather unique for tolyl-terminated oligomers [***n***]**204** (Chart 5) but gives only the all-trans isomers. The acyclic diene metathesis (AD-

Scheme 76[a]



210 **209**

[a] Conditions and reagents: (a) KO*t*-Bu, DMF. (b) $TiCl_4$, Zn.

MET) route is an alternative to the McMurry symmetric coupling, but it requires bisvinylbenzenes as precursors and yields α,ω-bisvinylene-terminated all-trans oligomers.[234] Schrock and co-workers used olefin methathesis to prepare the unsubstituted vinyl-terminated oligomers [***n***]**204** (Chart 5).[235]

A very powerful method of synthesis of [***n***]**204** is the Heck reaction.[236] It usually gives excellent yields and only all-trans isomers. The reaction proceeds even with sterically demanding substrates, such as bis-*ortho*-substituted aryl bromides and iodides. The major limitation is that electron-withdrawing groups on the aryl bromides or aryl iodides prevent palladium insertion into the aryl−halogen bond. Some side reaction, such as reductive dehalogenation and coupling into the α position of the vinylene group, may become crucial if the Heck reaction is used to obtain higher oligomers and polymers.[237−239] The styrene precursor for the Heck reaction may be activated by conversion into a tin or a boron derivative. In these cases, the coupling reactions will be more Stille- and Suzuki-like, respectively.

Properties. OPVs [***n***]**204** are very stable thermally.[224] Photochemical stability depends on substitution and environment and is fair to excellent. However, the oligomers are sensitive to oxygen. In the ground state, they are moderately stable to air, but upon intense irradiation, they can be oxidized in a matter of minutes. Ketones and aldehydes are the major products of oxidation.

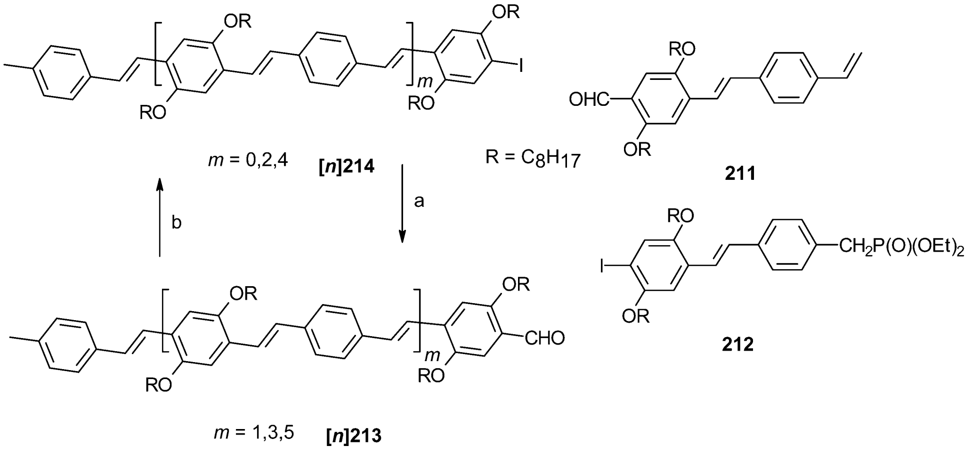
OPVs [***n***]**204** are rather flexible. Only the all-trans oligomers with no substituents on the vinylene groups can be useful as molecular rods. In the solid state, the double bonds are moderately twisted out of the plane of the aromatic rings.[240] OPV-based rods show a higher molecular conductance than their respective oligo(phenyleneethynylene) (OPE) counterparts. This phenomenon is rationalized with the higher coplanarity and correspondingly better π-conjugation of OPV systems in comparison to OPE systems in which the phenylene rings are rotating at room temperature. Theoretical support is given by calculations that show reduced conduction when the phenylene rings are twisted out of plane. In addition, recent theoretical and experimental studies on a crossed wire tunnel junction by Kushmerick et al.[241] have shown that the molecular wire conductance depends significantly on the extent of bond length alternation along the π-conjugated molecular backbone. In OPEs, the short ethynylene linkage (1.218 Å) disrupts the π-conjugated molecular backbone more than the longer vinylene linkage (1.352 Å) in OPVs. Because the extent of bond length alternation is directly correlated to the size of the HOMO−LUMO gap, the greater bond length alternation in OPE is connected with a larger HOMO−LUMO gap as compared to OPVs. Because charge transport at low applied biases is predominantly due to tunneling of electrons inside the HOMO−LUMO gap, the higher conductivity in OPVs can be rationalized.[241] From the viewpoint of solid state physics, OPVs are closer to a one-dimensional metal.[241]

Davis et al.[242] investigated an oligomeric series consisting of a tetracene donor and a pyromellitimide acceptor connected through an OPV bridge with up to five aryl units **207** (Chart 5). They measured the photoinduced electron transfer rates within these five compounds using femtosecond optical pump−probe spectroscopy. Their study reveals that there is only a very weak distance dependence for donor−acceptor separations up to 40 Å. The fact that the unsaturated bridge can apparently act as an incoherent molecular conductor is attributed to the very good match of the donor HOMO and the bridge LUMO in this system, allowing efficient charge injection into the wire.[242]

Charge conductivity can be increased by doping OPVs. The mobility of a photoinjected electron on a phenylenevinylene oligomer chain may be virtually independent of the length of the chain as long as the energy gap for donor-to-rod injection is small.

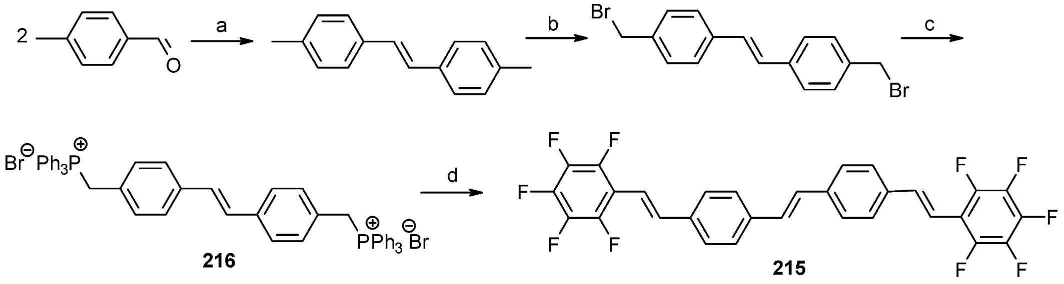
Oligo(*p*-phenylenevinylene)s−Specific Examples. *Example 1. Synthesis.* Combinations of various synthetic methods led to divergent−convergent methodologies for the synthesis of alkoxy-substituted oligomers **208** (Chart 5) and **209** (Scheme 76). The Wittig−Horner, the Siegrist, and the McMurry reactions have been used by Meier and co-workers to obtain oligomers up to $n = 11$.[243] The pentadecamer **209** was recently reported following a similar convergent strategy. Starting from hydroquinone and 2-methylhydroquinone, the heptamer **210** based on 2,5-dipropoxy-1,4-phenylenevinylene was synthesized in 17 steps and finally converted to the pentadecamer **209** by the formation of a C−C

Scheme 77[a]



[a] Conditions and reagents: (a) $Pd(OAc)_2$, P(*o*-tolyl)$_3$, Bu_3N, DMF, **211**. (b) (for $n = 2,4$) NaH, DME, **212**.

Scheme 78[a]



[a] Conditions and reagents: (a) $TiCl_4$, Zn. (b) NBS, AIBN. (c) PPh_3. (d) Pentafluorobenzaldehyhde, KO*t*-Bu.

double bond in a McMurry reaction.[244] The propoxy groups were chosen because they optimize photoconductivity through the rod. As determined by NMR spectroscopy, all C=C double bonds have an *E*-configuration after purification. A separation of diastereomers with one or two *Z*-configurations was achieved by crystallization.

Properties. Taking into account the inherent conformational freedom, the calculated length of Meier's pentadecamer **209** is 99−102 Å.[244] The maximum of the absorption peak in the UV−visible spectrum is at $\lambda_{max} = 482$ nm, and the absorption edge lies at 543 nm, matching the extrapolated limiting values for the maximum and the long-wavelength edge, respectively. The solubility of the red material in standard organic solvents is very limited. Its thermal stability is very high, and it decomposes only above 290 °C.[244]

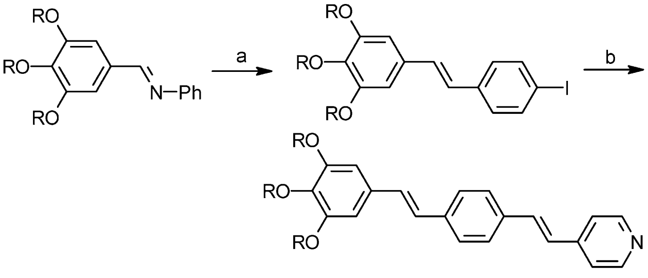
Example 2. Synthesis. By applying a repetitive stepwise sequence of Horner−Wadsworth−Emmons and Heck reactions to building blocks with mutually complementary functional groups (**211** and **212**) at their termini, Yu and co-workers[245] synthesized the oligomers [***n***]**213** and [***n***]**214**, with up to 12 aromatic rings in moderate yields, which decrease with the chain length (Scheme 77). Rods [***n***]**214** with 4*n* aryl groups carry an aldehyde at the end, and those ([***n***]**213**) with 4*n* + 2 aryl groups possess an iodine terminus.[245] The strategic placement of a vinyl and an aldehyde on one monomer and an iodine and phosphonate ester on the other allows for the sequential elongation of the chain, with the solubility the only limiting factor of the growth. It also permits a possible coupling to other oligomeric or polymeric units. Nonetheless, the synthesis of longer wires remains laborious, especially considering that the reactions produce small amounts of cis regioisomers, which have to be separated by repeated column chromatography.

Properties. The oligomers [***n***]**213** and [***n***]**214** show a brilliant green solution fluorescence with a high quantum yield.[245] The fluorescence spectra display the characteristic features expected from theory. Rods with more than four phenylenevinylene units exhibit a reversible thermochromic liquid crystalline phase.[245]

Example 3. Synthesis and Properties. In their search for self-organizing J aggregates of large aromatic chromophores, Feast et al.[246] reported the synthesis of 4,4′-bis(2,3,4,5,6-pentafluorostyryl)stilbene (**215**) by combining a McMurry coupling of *p*-toluylaldehyde and a subsequent Wittig reaction of the bis(phosphonium) salt **216** with pentafluorobenzaldehyde (Scheme 78). The crystal structure of the product reveals all double bonds to be trans. The molecules aggregate in a simple brickwall motif in which each one overlaps with two halves of its neighbors in the rows below and above.[246]

Example 4. Synthesis. Nierengarten and co-workers[247] used a Siegrist type coupling of a benzalimine with 4-iodotoluene followed by a Heck coupling of the resulting iodo compound with 4-vinylpyridine to synthesize the styrylstilbazole ligand **217** (Scheme 79), which was incorporated into discrete supramolecular structures with liquid crystalline properties. The same group reported the preparation of a novel calix[4]arene **218** with four oligophenylenevinylenes

Scheme 79[a]



217

[a] Conditions and reagents: (a) 4-Iodotoluene, KO*t*-Bu, DMF, 80 °C, 1 h (50%). (b) 4-Vinylpyridine, Pd(OAc)$_2$, P(*o*-tolyl)$_3$, Et$_3$N, toluene, 90 °C, 12 h (80%); R = $C_{12}H_{25}$.

attached to the upper rim of the core via a convergent route (Scheme 80). The construction of the phenylenevinylene units with a terminal double bond was achieved using a sequence of Siegrist and Wittig reactions. For the coupling of the rods to the tetraiodo-substituted calix[4]arene **219**, Heck cross-coupling reactions were applied in good yield.[248]

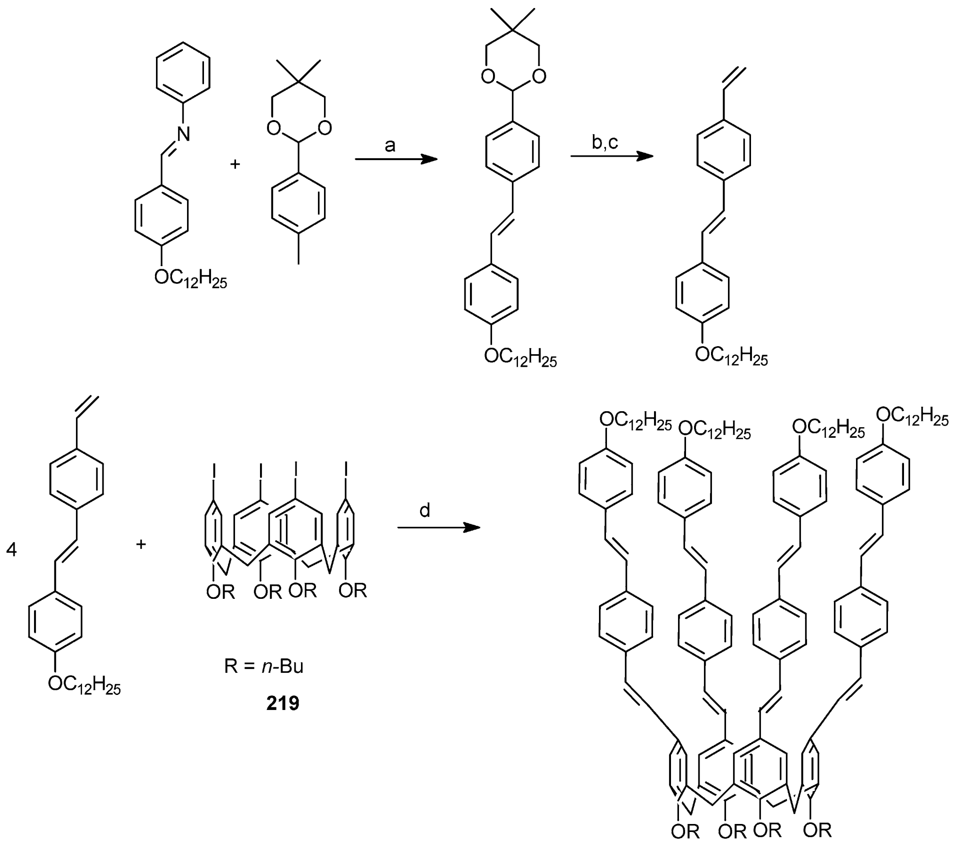
Properties. The absorption and fluorescence spectra of the strongly luminescent compounds, such as **218**, vary significantly from the sum of the disconnected building blocks, suggesting strong electronic coupling between the four attached OPV rods.[248]

Example 5. Synthesis and Properties. Utilizing aqueous Suzuki conditions, Anderson's group coupled aryl iodides with diboronic acids in the presence of cyclodextrins in high yield in order to prepare highly fluorescent [2]rotaxanes **220** in which stilbene rods are encapsulated in cyclodextrin cavities (Scheme 81).[249] A crystal structure shows a tight fit of the cyclodextrin around the double bond of the stilbene chromophore.[249]

Example 6. Synthesis. Blanchard-Desce's group[250] developed a strategy to obtain symmetrical conjugated phenylene–vinylene-based oligomers bearing two electron-donating dialkylamino groups at the termini with conjugation lengths that vary from 23 to 44 Å (Scheme 82). Starting from dihydrophenanthrene, three rods with push–push functionalization (**221**, **222**, and **223**) were prepared by a double Wittig reaction from the bisaldehyde or double Wittig–Horner condensation from the bisphosphonate, respectively.

Properties. The molecules **221**, **222**, and **223** prepared by Blanchard-Desce[250] are characterized by very large two-photon absorption (TPA) cross-sections in the visible NIR region and by high fluorescence quantum yields. An increase in the number of phenylene–vinylene modules results in a significantly higher TPA cross-section while maintaining a nearly constant fluorescence quantum yield. The TPA cross-section and fluorescence quantum yield depend both on the length and on the nature of the conjugated backbone, as well as the molecular environment. A more polar solvent can stabilize the intramolecular charge transfer and therefore increase the TPA cross-

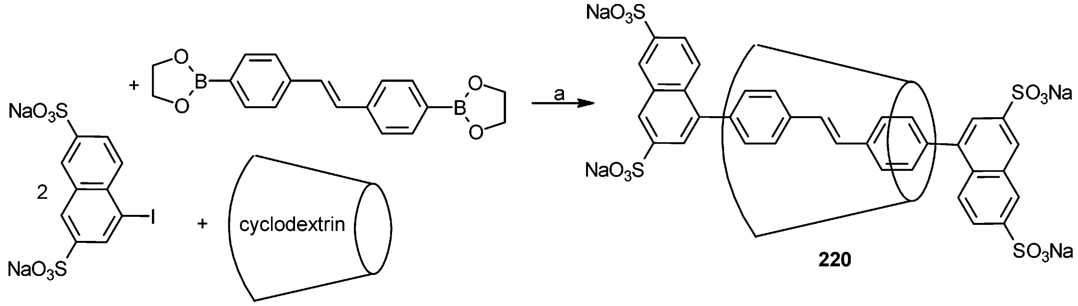
Scheme 80[a]



218

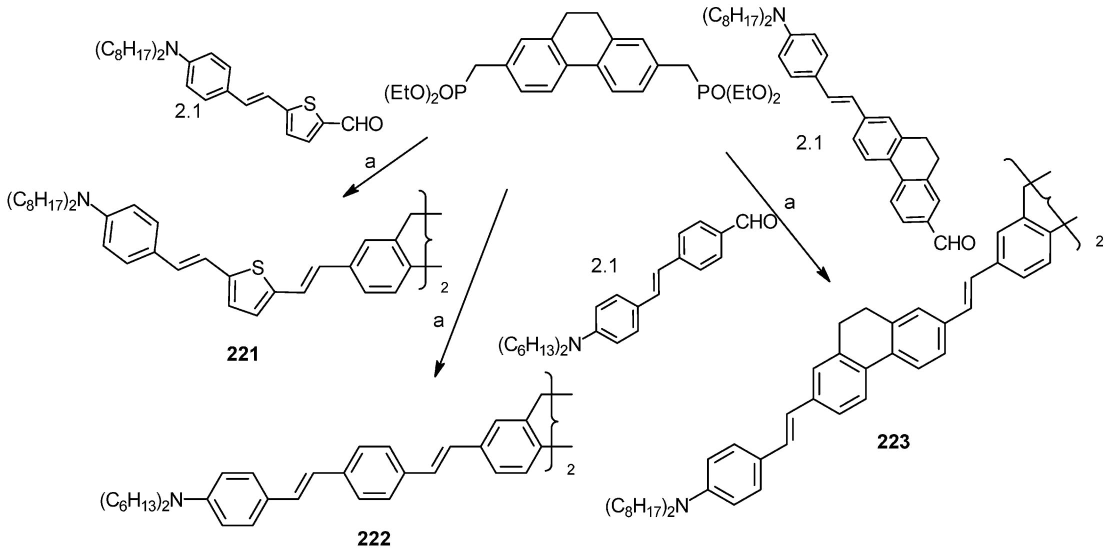
[a] Conditions and reagents: (a) KO*t*-Bu, DMF, 80 °C, 2 h (50%). (b) CF$_3$CO$_2$H, H$_2$O, CH$_2$Cl$_2$, 5 h (99%). (c) Methyl triphenylphosphonium bromide KO*t*-Bu, THF, room temperature (80%). (d) Pd(OAc)$_2$, P(*o*-tolyl)$_3$, Et$_3$N, xylene, reflux, 48 h (68%).

Scheme 81[a]



[a] Conditions and reagents: (a) H_2O, $Pd(OAc)_2$, Na_2CO_3.

Scheme 82[a]



[a] Conditions and reagents: (a) NaH (3 equiv), [18]crown-6, THF, 16 h.

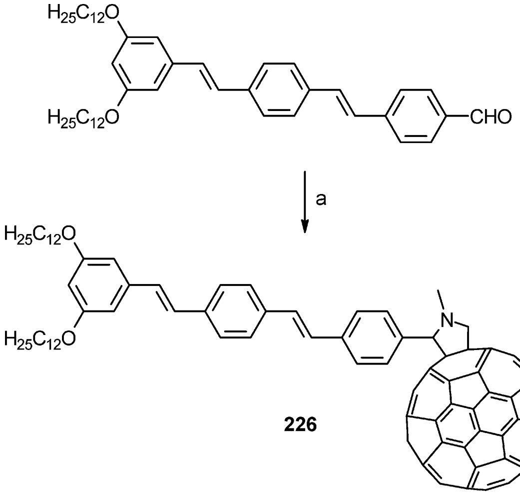
section. In addition, a higher conjugated length induces a significant broadening of the two-photon excited fluorescence spectra in the NIR region.[250]

Example 7. Synthesis. Using modified double Heck reactions, Li et al.[251] synthesized a series of OPV derivatives, such as **224** and **225** (Chart 5), that carry diphenyl amino substituents at the termini and two cyano groups in various positions on the central part of the backbone.

Properties. The cyano groups in the OPV dyes, such as **224** and **225**, enhance the efficiency of the electron delocalization along the backbone. By systematically changing their positions on the central aryl units, the fluorescence wavelength of the systems was tuned between blue (472 nm) and red (614 nm). Compound **224** shows electroluminescence in the blue region with good efficiency and might be suitable for OLED devices.

Example 8. Synthesis. Nierengarten and co-workers reported a number of OPVs connected to fullerene units. A fulleropyrrolidine **226** bearing an OPV trimer was prepared by 1,3-dipolar cycloaddition of the respective azomethine ylide to C_{60} (Scheme 83).[252] Very recently, an OPV pentamer **227** with two alcohol functions was attached as a core to a series of highly soluble dendritic branches with fullerene subunits, yielding dendrimers with two (**227**, Chart 6), four, and eight peripheral C_{60} groups.[253] The groups of Schenning and Meijer[254] published several monofunctional OPV rods that carry binding sites capable of hydrogen bonding as guest molecules to a variety of hosts. For example, compounds such as **228**[255] feature a glycinyl–urea functionality while rod **229**[256] (Chart 6) is capped by an urea-substituted triazine.

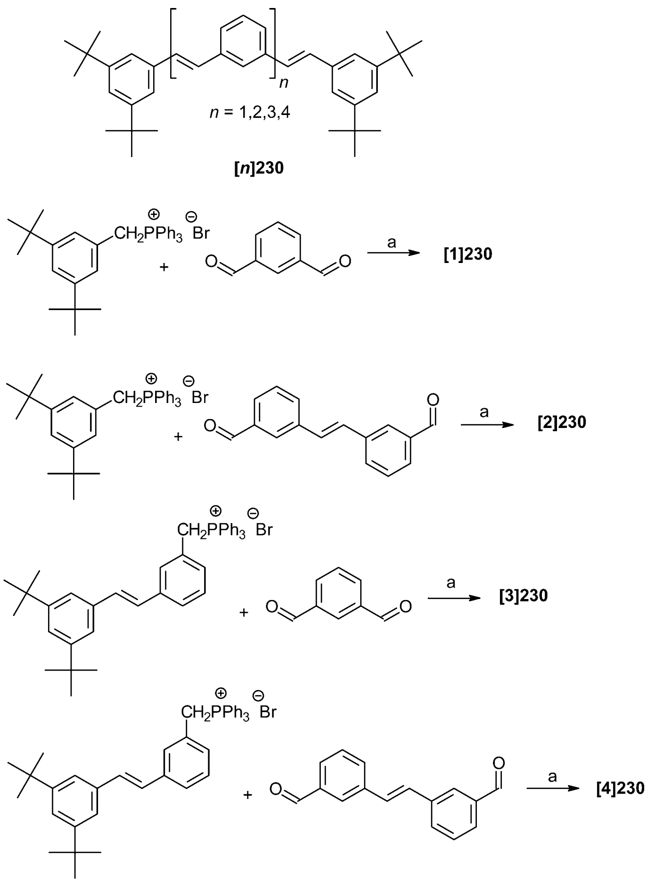
Scheme 83[a]



[a] Conditions and reagents: (a) C_{60}, sarcosine, toluene.

Properties. The fullerene–OPV rod **226** was incorporated into a photovoltaic cell and provided an open circuit voltage of 0.2 V and an efficiency of 1%.[252] Investigation of the photophysical properties of the

Scheme 84[a]



[a] Conditions and reagents: (a) Base.

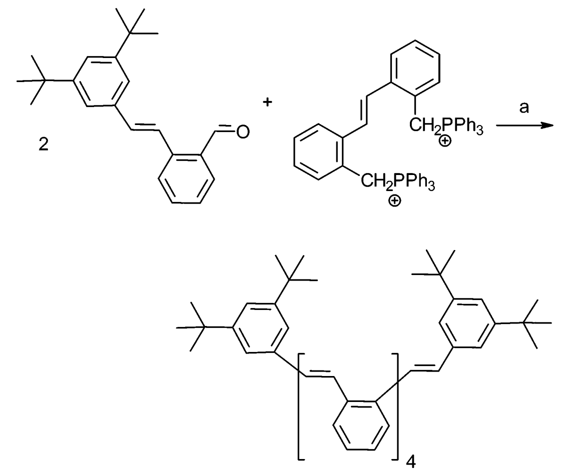
fullerene dendrimers containing core **227** (Chart 6) revealed a strong solvent dependence on the electron transfer energetics. For a given solvent, the efficiency of the electron transfer is diminished with larger dendrimer size because the OPV core is increasingly isolated by the dentritic architecture, suppressing solvent-induced stabilization of the transient ionic species.[254]

Oligo(*m*-phenylenevinylene)s. *Synthesis.* Using similar Wittig type chemistry as described for the corresponding oligo(*p*-phenylenevinylene)s, Müllen and co-workers synthesized a series of oligo(*m*-phenylenevinylene)s [***n***]**230** from the respective meta-substituted aldehyde and dialdehyde building blocks (Scheme 84).[257]

Properties. Just like their para-substituted analogues, the compounds [***n***]**230** are thermally and air stable solids. However, they show a markedly higher solubility in organic solvents. Their UV–visible absorption spectra are virtually independent of the chain length with an absorption maximum similar to that of stilbene. The meta substitution pattern on the benzene modules interrupts effective conjugation, similarly as in *m*-polyphenyls.[258]

Oligo(*o*-phenylenevinylene)s. *Synthesis.* Applying Wittig type coupling methods, the group of Müllen[259] has prepared a series of oligo(*o*-phenylenevinylene)s [***n***]**231** up to the hexamer (Scheme 85).

Scheme 85[a]



[5]231

[a] Conditions and reagents: (a) Base.

Properties. All compounds [***n***]**231** that were prepared are air stable solids with high melting points. Their electronic properties are intermediate between those of the para and meta counterparts. While the ortho substitution pattern does not inhibit efficient π-conjugation along the backbone in itself, the steric interactions of adjacent vinylene units do so by forcing the molecules out of a planar conformation.[258]

9.4.2. Oligo(phenylenevinylidene)s

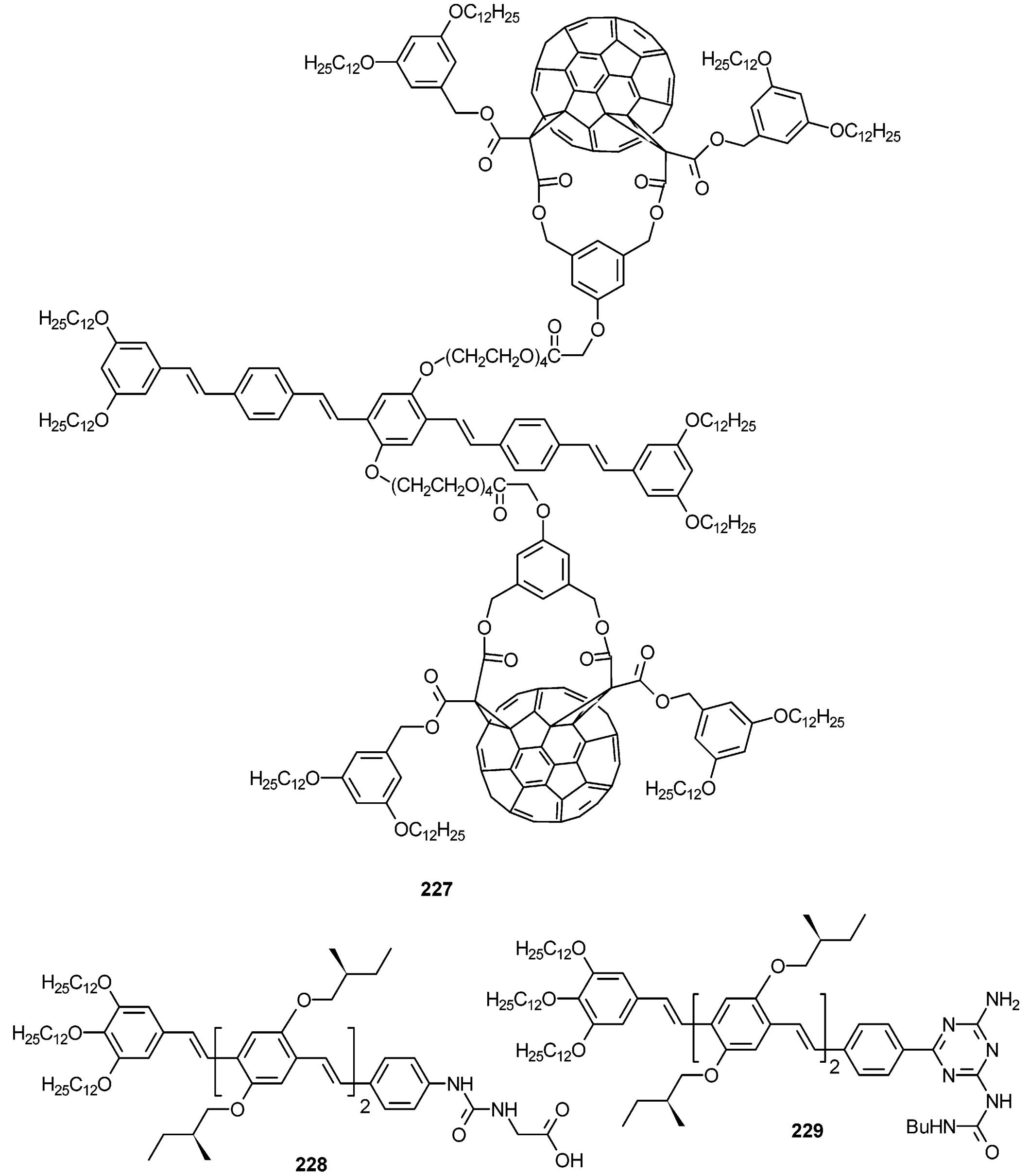
The cross-conjugated oligo(phenylenevinylidene)s [***n***]**232** (Scheme 86) are topological isomers of the much more extensively studied OPVs, in which the phenylene units are connected through a single sp^2 hybridized carbon atom. The shortest member of the class is the long known 1,1-diphenylethene, a commercial chemical that has recently gained importance in the area of controlled radical polymerizations.[260] The chemistry leading to the higher homologues shall be reviewed here.

Synthesis. Quite surprisingly, the chemical community had to wait until the 21st century before van Walree and co-workers[261] reported the first systematic synthesis of *p*-phenylenevinylidene oligomers [***n***]**232** (Scheme 86). A series of conversions involving the nucleophilic addition of phenyllithium compounds to acetophenone derivatives as well as coupling of the bromo alcohols **233**, followed by dehydration of the resulting alcohols **234**, was employed to make molecules [**4**]**232** with 2–4 double bonds. The overall yields are low due to the formation of aldol condensation side products during the synthesis of the alcohols involving dilithio compounds. A single crystal X-ray structure of the oligomer [**2**]**232** with two double bonds was obtained and analyzed.[261]

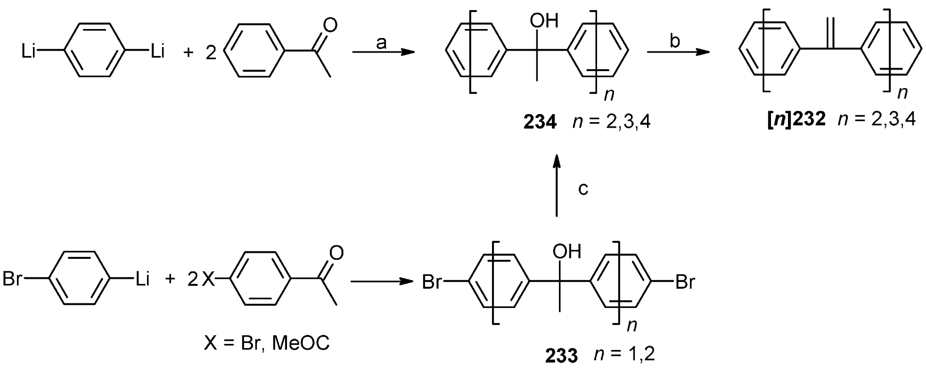
Properties. All isolated pure oligomers [***n***]**232** are white solids with good to high thermal stability. The melting point of the highest reported homologue lies above 200 °C. The X-ray analysis of [**2**]**232** reveals a nonplanar structure in which the phenylenevinylidene segments are twisted by 39 and 30°, respectively, out of the plane of the terminal benzene ring.[261]

Several spectroscopic techniques were used to characterize the homologous series [***n***]**232**. A pro-

Chart 6



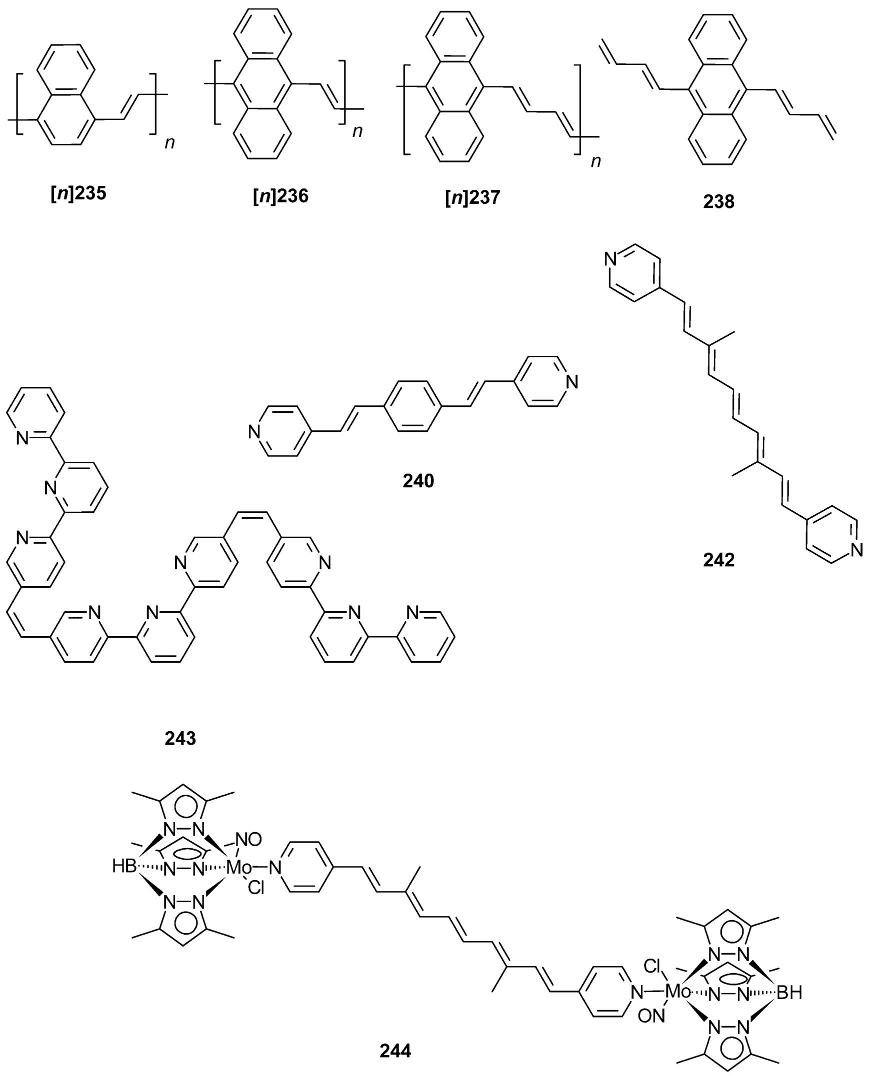
Scheme 86[a]



[a] Conditions and reagents: (a) $CeCl_3$. (b) p-Toluenesulfonic acid. (c) BuLi, acetophenone.

nounced red shift of both the UV and the fluorescence maxima is observed only upon going from the first ([**1**]**232**) to the second ([**2**]**232**) member of the series, in which a divinylbenzene unit forms the center of the dimer. At that point, the effective conjugation length is reached as far as UV−visible absorption maxima are concerned. The X-ray crystal structure of [**2**]**232** confirmed that electron delocalization by linear π conjugation is preferred to delocalization by cross-conjugation because quinoid character was found only in the central benzene unit, not in the outer phenyl groups. However, other information

Chart 7



indicated a further extension of conjugation. The oxidation potentials continue to change systematically with elongation, and AM1 results suggest that a small degree of quinoid character is present in all phenylene moieties of the longer members of the series. Even for these properties, the effective conjugation length appears to be approached already with the tetramer [**4**]**232**, containing four double bonds.[261]

9.5. Ethene/Arene

9.5.1. Synthesis

Oligo(1,4-naphthylenevinylene)s ([***n***]**235**), oligo(9,10-anthrylenevinylene)s ([***n***]**236**), and oligo(9,10-anthrylene-1,3-butadienylene)s ([***n***]**237**) have been prepared by the Müllen group (Chart 7). Similar synthetic methods should be applicable to the synthesis of all oligo(arylenevinylene)s. Oligomers up to the tetramer [**4**]**235** have been prepared by the Wittig and the McMurry reactions,[262] while the Horner−Emmons olefination of the appropriate precursors yielded the oligomers [***n***]**236**.[263] The Heck reaction does not give access to the oligomers **236** starting from 9,10-divinylanthracene, presumably because of the high steric hindrance around the reaction centers. The less sterically demanding 9,10-bis(1,3-butadienyl)anthracene (**238**), on the other hand, gives the oligomers [***n***]**237** without difficulties.[263]

9.5.2. Properties

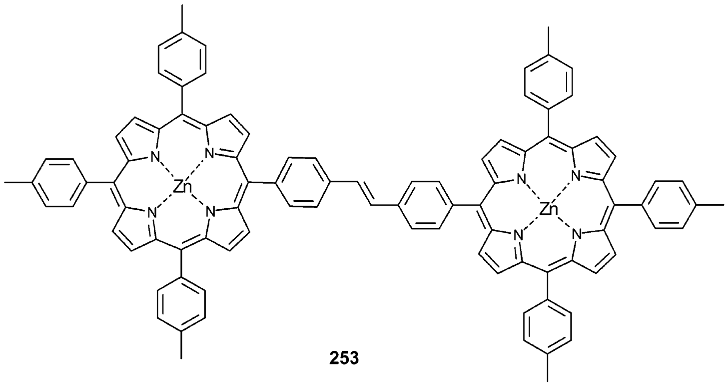
Extrapolation of the absorption energies obtained for the oligomer series [***n***]**236** (Chart 7) leads to an estimated value of approximately 2.0 eV for poly(9,10-anthrylenevinylene) as compared to 2.4 eV measured for the parent poly(*p*-phenylenevinylene).[263]

9.6. Ethene/Azabenzene

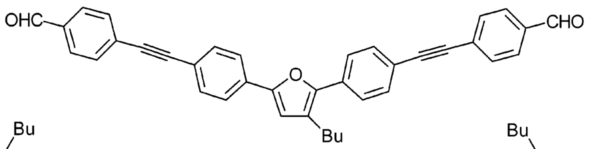
9.6.1. Synthesis

Pyridyl-terminated oligoene rods have been studied extensively after work with dipyridylethylene was reported.[264,265] 1,4-Di(4-pyridyl)butadiene [**2**]**239** (Scheme 87) was first synthesized in the group of Hünig.[266] Das et al.[267] reported the preparation of 1,4-bis[2-(4-pyridyl)ethenyl]benzene (**240**, Chart 7). Launay's group[268,269] synthesized a set of α,ω-dipyridyloligoenes [***n***]**239** (*n* = 3,4) by Wittig condensation of pyridine-4-carboxaldehyde with bisphosphonates [***n*-2**]**241** (Scheme 87). The pyridyl-terminated rod **242** (Chart 7) was prepared similarly by the group of Jones.[270]

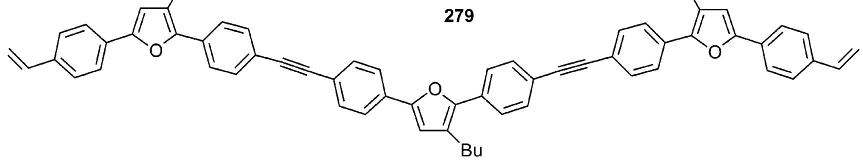
Chart 8



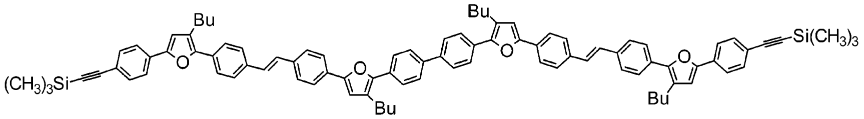
253



279

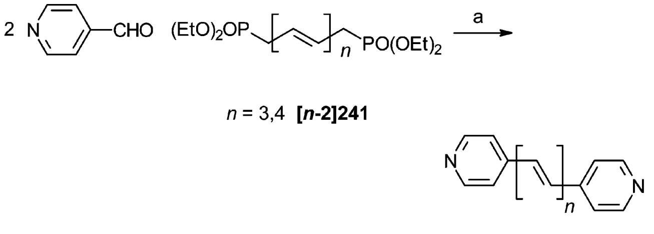


281



282

Scheme 87[a]



n = 3,4 **[n-2]241**

n = 3,4 **[n]239**

[a] Conditions and reagents: (a) KO*t*-Bu.

All-trans stereochemistry of the bidentate ligands [***n***]**239** leads to a distance of the complexing sites that ranges from 15.8 to 20.6 Å. A similar zig-zag rod **243** (Chart 7) was reported by Hasenknopf et al.[162,271,272] In this oligomer, three terpyridine-like moieties are linked by two ethylene units in cis fashion.

9.6.2. Properties

The rods are thermally very stable with melting points of over 150 °C. CVs of the free ligands generally show two reduction waves between −1.4 and −1.8 V with the separation of the waves decreasing with increasing rod length.

Launay and co-workers[269,273,274] linked pentaammineruthenium(II) moieties to the bidentate ligands **239** and investigated the electrochemical and spectroscopic properties of the resulting binuclear complexes. Successive oxidation led to mixed valence compounds. McCleverty, Jones, and their collaborators[275] used the partially methylated series of dipyridylpolyenes **242** (Chart 7) to measure the intermetallic interactions of molybdenum centers in **244** (Chart 7). The authors concluded that the limit for substantial interaction through the oligoene rod is around 20 Å.

9.7. Porphyrin Co-oligomers

9.7.1. Ethyne/Porphyrin

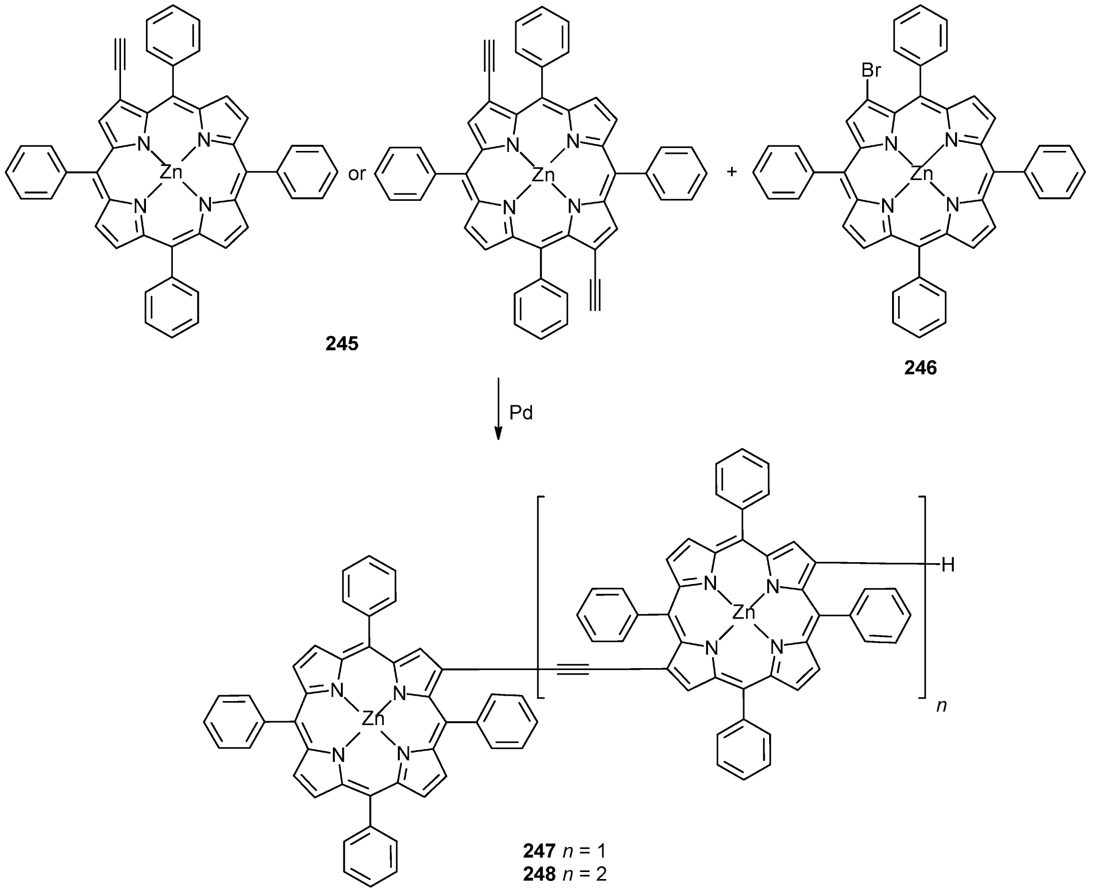
Synthesis. Lin and Therien[276] used Pd-catalyzed cross-coupling of the mono- and bis-ethynylated porphyrins **245** with the respective (bromoporphyrinato)-zinc derivatives **246** to synthesize the dimers **247** and trimers **248** in which ethyne groups link the porphyrin macrocycles directly (Scheme 88).

Properties. The arrays **247** and **248** exhibit excitonic coupling that is large but less pronounced than in their meso-to-meso linked counterparts. The electronic coupling decreases with increasing bridge length. Compound **248**, for example, has a split, very broad Soret region. The two sharpest transitions are split by 3800 cm^{-1}. The acetylene stretching frequency is unusually low suggesting that a substantial electronic delocalization is possible and that a cumulenic resonance form may be significant in the excited state.[276]

9.7.2. Ethene/Porphyrin

Synthesis. Higuchi et al.[277] and Yashunsky et al.[278] synthesized and investigated *trans*-ethylene-

Scheme 88



bridged dimers as possible rigid model structures resembling photosynthetic reaction centers (Scheme 89). 1,2-Bis(porphyrinyl)ethanes were transformed to the corresponding *trans*-ethylenes **249** in high yield by treatment with acetic acid in air.[279] Higuchi et al.[277] also prepared the respective trimer (**250**) by coupling of 2 equivalents of mono-*meso*-hydroxymethyl-substituted octaethylporphyrin with 1 equivalent of the para-disubstituted analogue and subsequent dehydrogenation of the ethano linkages. Bonfantini and Officer[280] used a Wittig reaction to synthesize a dimeric porphyrin containing a butadiene bridge attached in β positions (Scheme 90). The predominantly formed (E,Z)-isomer was converted into the (E,E)-isomer **251** by iodine-catalyzed isomerization.

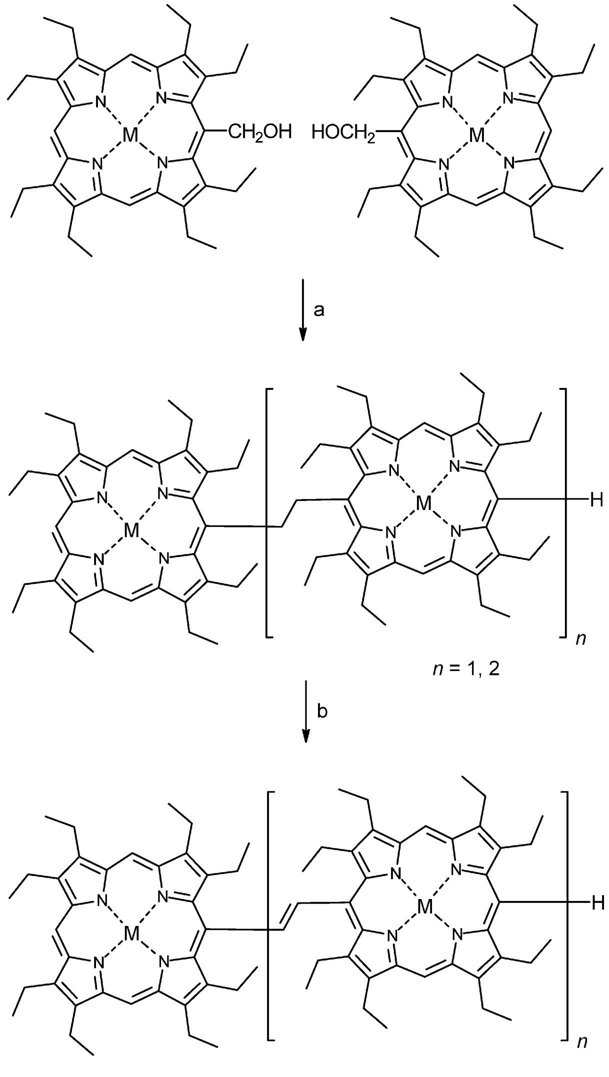
Properties. Data from picosecond time-resolved fluorescence spectroscopy on **249** showed that the photoinduced intramolecular electron and energy transfer events for mixed metal arrays are faster for the polyene-bridged systems than for the polyyne-bridged systems. The distance dependence of the transfer rates was found to be small. The linear π-conjugated polyyne and polyene spacers clearly enhance through-bond electronic coupling between the donor and the acceptor. Higuchi's array **250** shows a strong interaction between the porphyrin units, both through bond and through space.[278] According to NMR data, the porphyrin rings are not located in the same plane but lie in two parallel planes displaced relative to each other. The UV−visible spectrum of compound **251** provided no evidence for interaction between the porphyrin chromophores, suggesting an out-of-plane twisted geometry.[280]

9.7.3. Ethene/Benzene/Porphyrin

Synthesis. Osuka et al.[281] reported a series of oligoene rods attached at both ends to porphyrin meso-positions through benzene rings ([***n***]**252**) and studied the distance dependence of electron transfer and energy transfer rates in the free base/metal and mixed metal systems. The shorter members of the series [***n***]**252** ($n = 1, 2$) were synthesized from the corresponding dialdehydes by a double porphyrin cyclization reaction. Rods [***n***]**252** with three and four double bonds were obtained via a double Horner−Emmons−Wadsworth reaction (Scheme 91). Because of the existence of rotamers, the center to center distances are known only approximately and lie between 19.4 and 26.6 Å.

A stilbene-linked *meso*-tetraarylporphyrin pair **253** (Chart 8) was prepared by Müllen and co-workers[282] via a McMurry coupling reaction to investigate the capability of porphyrin-based arrays to store charge by successive addition of electrons. The dimer showed a doubled storing capacity of electrons as compared to the monomer unit. Ono et al.[283] used the Ramberg−Backlund reaction to synthesize dimeric porphyrins [***n***]**254**, which are separated by extended π-systems consisting of repeating stilbene units (Scheme 92). The number of the phenylenevinylene units can be controlled during the procedure, and systems with up to five double bonds were characterized.

Scheme 89[a]



249 *n* = 1
250 *n* = 2

[a] Conditions and reagents: (a) H_2SO_4. (b) AcOH, air.

Officer and co-workers[284] used the Wittig reaction of a tetraphenylporphyrin **255** containing an aldehyde moiety on a substituent located in a β-position with various porphyrin phosphonium chlorides to produce the corresponding β-bridged dimers **256** (Scheme 93). Following this scheme, mixed porphyrin systems with ethylene, butadiene, and bisvinylphenylene spacers were synthesized and both monometalated and heterobismetalated (Ni, Zn) dimers were obtained.

The aldehyde group on the β-substituted tetraphenylporphyrin **255** can also undergo a condensation reaction with dipyrrylmethane to yield a trimeric array **257** with *p*-styrene units linking the central porphyrin through its meso carbons to β carbons of the terminal porphyrins (Scheme 94). Without any significant change to the procedure, the substitution pattern on both styrene linkers was varied in order to obtain ortho **258** and meta **259** trimeric porphyrin arrays as well.[285]

9.7.4. Ethene/Pyridine/Porphyrin

Synthesis. Odobel et al.[286] reported the synthesis of a symmetrical bis-porphyrin dyad **260** connected through a polyene-based bipyridine spacer (Scheme 95). Starting from the *meso*-iodoporphyrin **261**, a mixed sequence involving a Stille coupling with the stannylated (*E*,*E*)-dienyl acetal[287] **262** and a Wittig–Horner reaction with the bipyridine bis-phosphonate **263** was used to assemble the fully delocalized π-conjugated system in which the bridge is directly linked to the meso positions of the porphyrin core (Scheme 95). Throughout the series of reactions, the all-trans double bond pattern was preserved. Both the free base and the zinc-metalated derivatives are accessible, but the Horner–Wittig reaction proceeds with significantly lower yield in the case of the zinc porphyrin.[286]

Properties. The dyad **260** exhibits a large red shift in both the absorption and the emission bands indicating the extension of the π-conjugation from the porphyrin ring into the polyene spacer. An efficient electronic communication between the two porphyrin moieties both in the ground and in the excited state is feasible.[286]

9.8. Ethene/Ethyne/Benzene/Fluorene

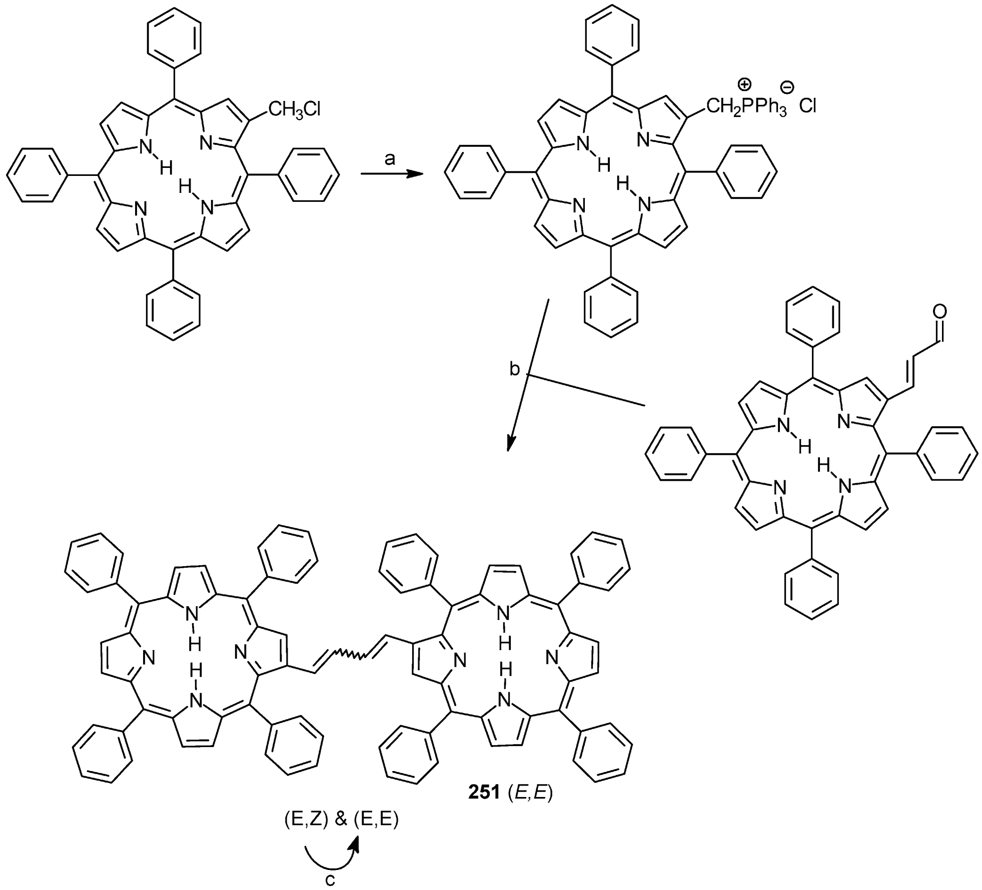
9.8.1. Synthesis

Blanchard-Desce's group[288] has published the synthesis of mixed co-oligomers consisting of end groups, linkers, and a core (Scheme 96). Using Sonogashira, Wittig, and Wittig–Horner–Emmons reactions, two different amino-functionalized end group building blocks **264** and **265** were attached to a 9,9-dinonylfluorene or biphenyl core to obtain four elongated push–pull fluorophores **266**, **267**, **268**, and **269** in good yields. While assembled through relatively straightforward and well-known methodology, the series is of interest since it allows a systematic comparison of the effects of the different modules.

9.8.2. Properties

The fluorene-based arrays **268** and **269** display a greatly enhanced solubility. All fluorophores **266**–**269** are characterized by intense absorption bands between 350 and 450 nm, while remaining transparent in the visible region above 450 nm, and also by high fluorescence quantum yields.[288] The influence of the central core on both the absorption and the emission characteristics was shown to be limited (only a small red shift in the absorption maximum was observed in the fluorene-based system), while the modulation of the linkers and the order of connectivity could be used to tune the extended electronic conjugation and consequently the spectral properties. Especially, the role of the topology is noteworthy, since the positioning of an ethene module close to the end groups lowers the quantum yield by 25–40%. In addition, a strong bathochromic shift of the luminescence with increasing solvent polarity was found.[288] Last but not least, compounds **266** and **267** feature TPA cross-sections among the highest reported for conjugated systems of quadrupolar, octupolar, or

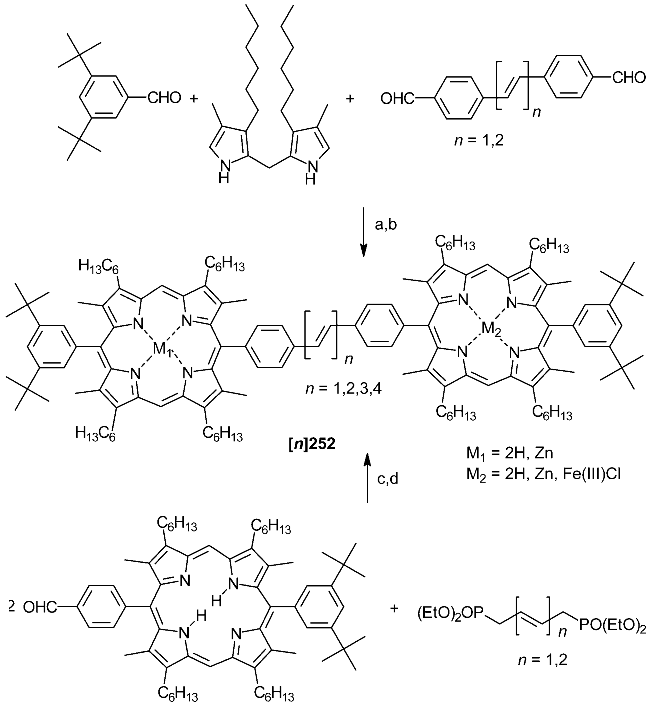
Scheme 90[a]



251 (*E*,*E*)

[a] Conditions and reagents: (a) 10 PPh_3, CH_2Cl_2, reflux. (b) NaOH(aq), CH_2Cl_2. (c) I_2 (catalytic).

Scheme 91[a]



[*n*]252

[a] Conditions and reagents: (a) Trichloroacetic acid, CH_3CN/CH_2Cl_2. (b) *p*-Chloranil, THF. (c) NaH, 15-crown-5, THF. (d) 2 M HCl, CH_2Cl_2.

branched symmetries and comparable molecular weights.[289,290]

9.9. Ethene/Ethyne/Benzene/Perylene Bisimide

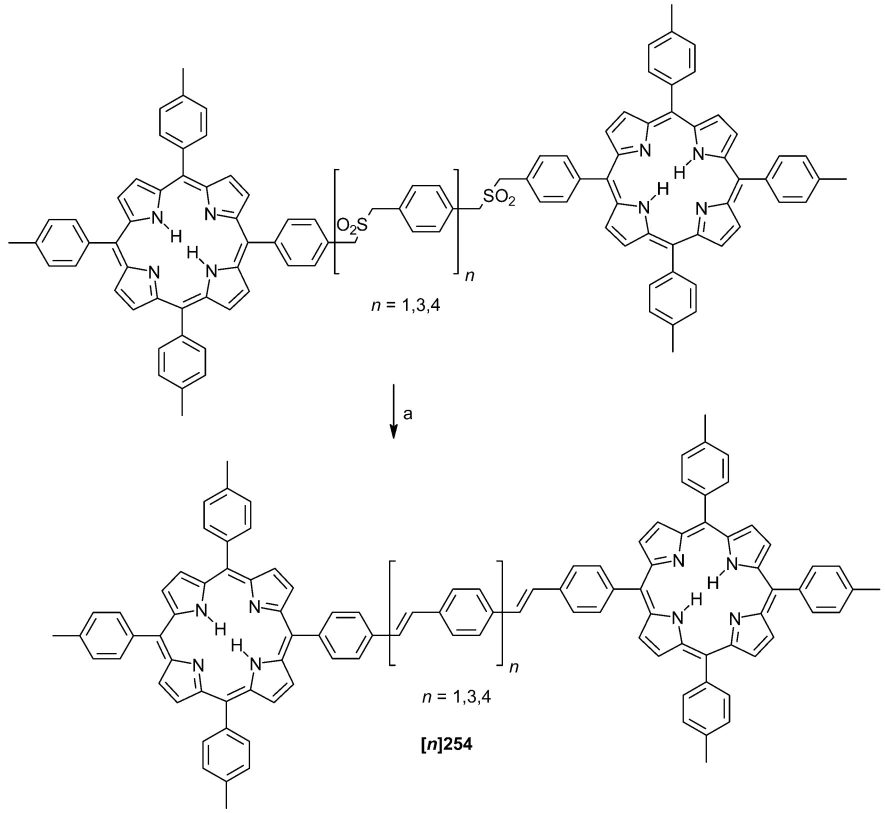
9.9.1. Synthesis

Very recently, Marcos Ramos et al.[291] published an interesting work on the convergent synthesis of a long rod **270**, consisting of a trimeric *p*-phenylene vinylene oligomer, a dodecameric *m*-phenylene ethynylene oligomer, and a perylene bisimide. Perylene monoanhydridemonoimide **271**[292] was treated with 4-iodoaniline to yield the iodine-functionalized building block **272**. Meanwhile, the trimeric *p*-phenylene vinylene bromide **273** was coupled with trimethylsilylacetylene to obtain compound **274** after desilylation. Applying the methodology developed by Moore, the dodecameric foldamer **275** carrying (*S*)-3,7-dimethyl-1-octanoxy side chains was synthesized and subsequently treated first with **274** to obtain zig-zag rod **276** before a final Sonogashira reaction with **272** produced the dyad **270** in low yield (Scheme 97).

9.9.2. Properties

The UV–vis absorption spectrum of **270** consists of a near superposition of the individual spectra of the building blocks because the meta linkages suppress conjugation along the backbone. A complete photophysical investigation of the system was reported.[291] The results indicate that the central foldamer unit adopts a random coil conformation in

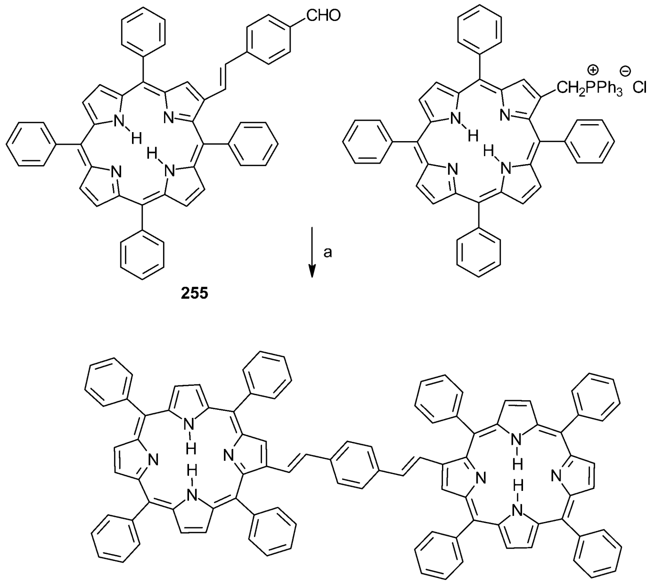
Scheme 92[a]



[n]254

[a] Conditions and reagents: (a) CCl_4, THF, NaOH or KOH, CH_3OH.

Scheme 93[a]



255

256

[a] Conditions and reagents: (a) NaOH(aq), CH_2Cl_2.

polar solvents, such as chloroform. By decreasing solvent polarity, the oligomeric phenylene ethynylene bridges fold into helical stacks, which self-assemble into columnar architectures. In this conformation, the proximity of the donor and acceptor units enhances the formation of a charge-separated state upon photoexcitation, an unusual occurrence in an apolar medium.[291]

9.10. Ethene/Ethyne/Benzene/Furan

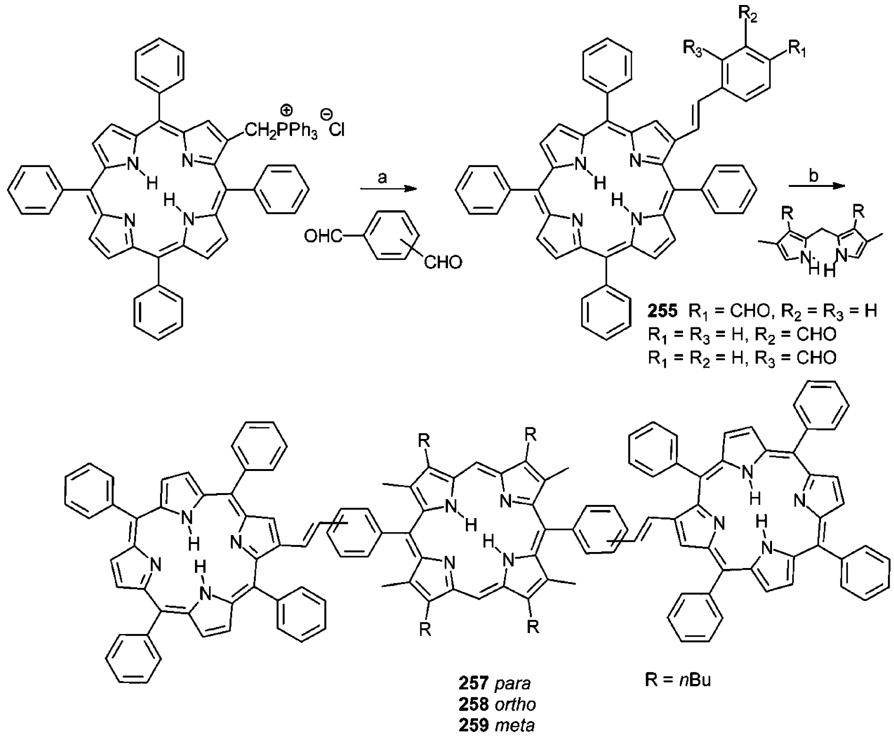
9.10.1. Synthesis

Recently, Luh and co-workers[293,294] developed a convenient one-pot synthesis of alternating oligoaryls **277** comprised of benzene and furan moieties (Scheme 98). The key furan annulation was accomplished by the in situ generation a thiolato-substituted allenyl anion from **278** and BuLi, followed by the addition of a dialdehyde and an acid-catalyzed ring closure (Scheme 98). Very importantly, the reaction conditions tolerate both vinyl and alkynyl functionalities, allowing for the extension of the rod using Heck and/or Sonogashira type coupling steps. On the basis of the combination of furan annulation, Heck reaction, and Sonogashira coupling, a bidirectional iterative synthesis of furan containing oligoaryls was elaborated.[295] Applying the methodology, rods with one diphenylfuran unit **279** (Chart 8), two diphenylfuran units **280** (Scheme 98), three diphenylfuran units **281** (Chart 8), and four diphenylfuran units **282** (Chart 8) were synthesized in moderate yield. The approach is promising for molecular wire synthesis, because chain extension to higher homologues is in principle limited only by solubility.

9.10.2. Properties

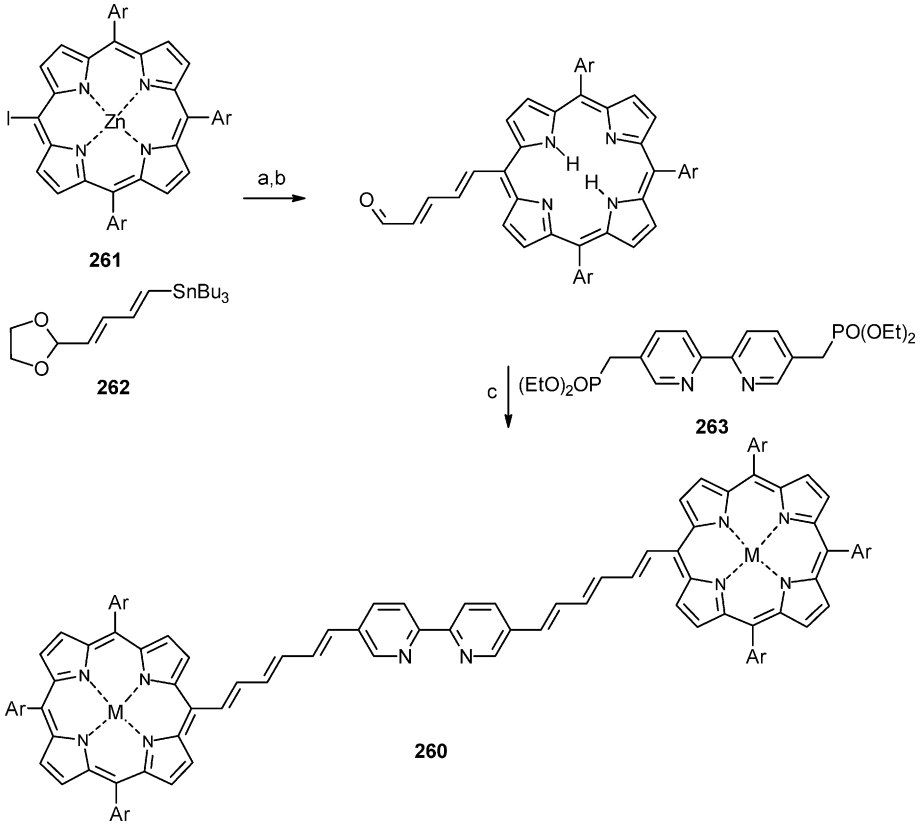
The oligoaryl rods, such as **277**, are thermally very stable and exhibit bright fluorescence in the blue light region.[294] Compound **277** performed as a hole-

Scheme 94[a]



[a] Conditions and reagents: (a) (1) DBU, CH_2Cl_2, room temperature; (2) I_2, CH_2Cl_2. (b) (1) CH_3CO_2H, CH_2Cl_2; (2) *o*-chlororaniline, reflux.

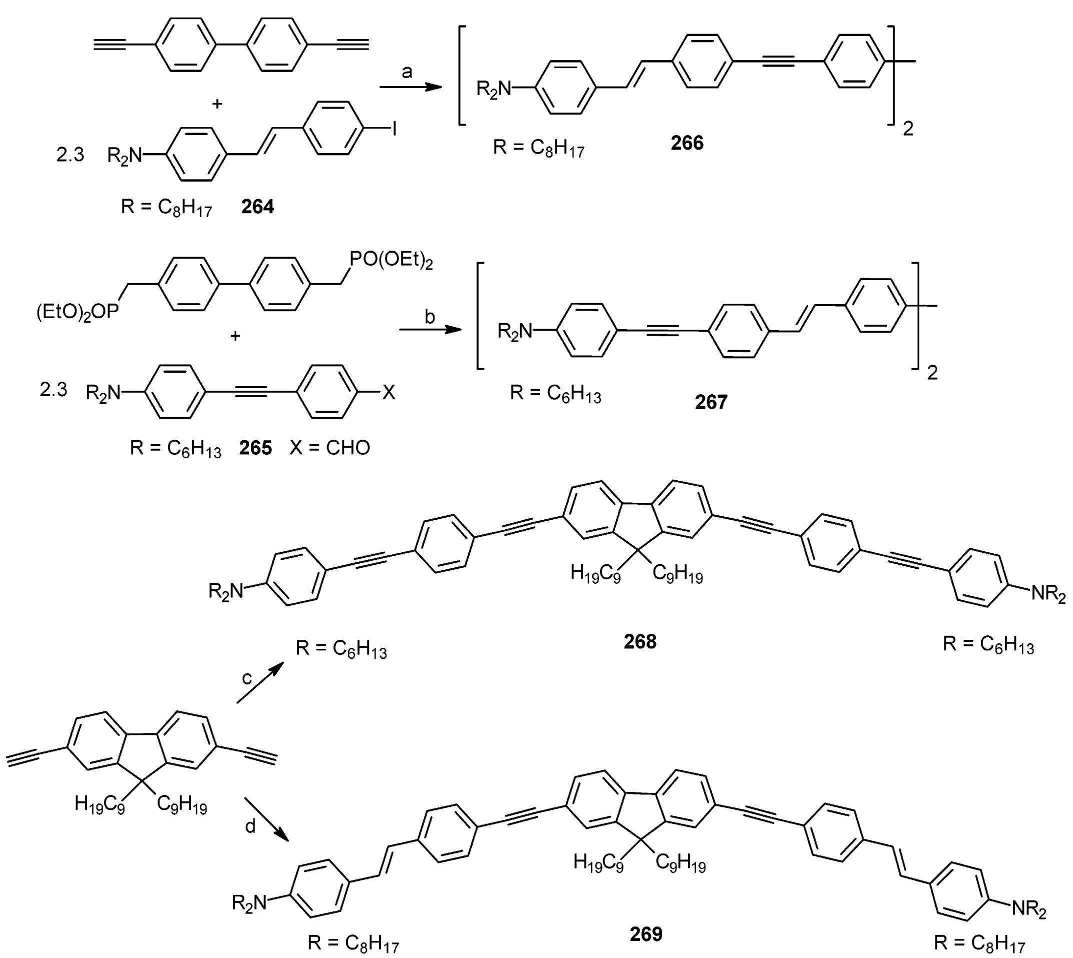
Scheme 95[a]



[a] Conditions and reagents: (a) $Pd(PPh_3)_4$, DMF. (b) AcOH, HCl, H_2O, CH_2Cl_2. (c) KO*t*-Bu, THF.

transporting material in electroluminescent devices with high efficiency. The mixed rods **279**–**282** display bluish green emission in chloroform with quantum efficiency as high as 0.91. Among them, only **282** decomposed slowly in solution when exposed to ambient light.[295]

Scheme 96[a]



[a] Conditions and reagents: (a) $PdCl_2(PPh_3)_2$, CuI, toluene/Et_3N, 20 °C, 3.5 h (81%). (b) NaH, THF, 18-crown-6, 40 °C, 3 h (84%). (c) Compond **265** (X = I) conditions as in a, 20 h (82%). (d) Compound **264**, conditions as in a, 15 h (83%).

9.11. Ethene/Ethyne/Heterocycle

9.11.1. Synthesis

By using a Sonogoshira coupling protocol, the group of Diederich[296] prepared a series of rods in which two (*E*)-1,2-diethynylethene (DEE) units are bridged through a heterocycle, such as a pyridine in compound **283**, a pyrazine in compound **284**, and a thiophene in compound **285** (Scheme 99).

Similarly, Sonogashira coupling of meso-iodinated porphyrins and DEE moieties led to porphyrin–DEE hybrids [***n***]**286** up to the trimer [**3**]**286** with a 5.3 nm long backbone (Chart 9).[297]

9.11.2. Properties

The compounds **283**, **284**, and **285** show interesting photophysical properties that are not detected in the individual components, such as a strong fluorescence emission with quantum yields up to 0.65 in the case of compound **284**. Protonation of the pyridine spacer in **283** significantly changed both the electronic absorption and the emission characteristics of the system, creating a pH sensitive reversible switch.[296]

Electrochemical and optical measurements of the mixed porphyrin–DEE rods [***n***]**286** (Chart 9) reveal strong electronic communication between the porphyrin rings. Stationary voltammetry indicates that the terminal DEE units act as strong electron acceptors, shifting the first reduction potential of the porphyrin ring considerably.[297]

9.12. Ethene/Benzene/Cyclopentadienyl Complex

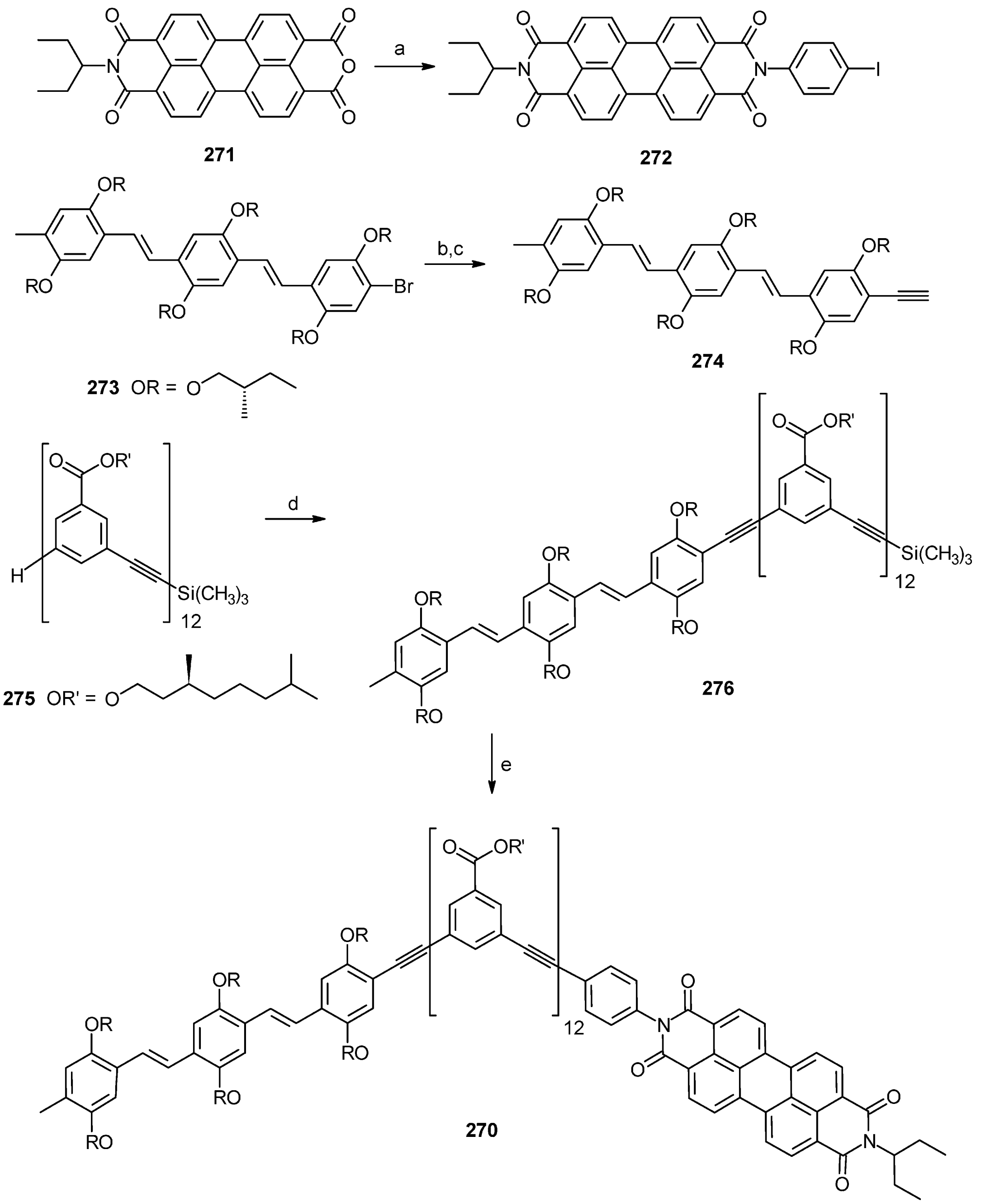
9.12.1. Synthesis

Seeking improved solubility, a lowered oxidation potential, and an amplified donor capacity as compared to their nonmethylated oligoene-bridged counterparts, Hradsky et al.[298] built phenylenevinylene-bridged methyl-substituted ferrocenes **287** carrying 5–9 methyl groups (Scheme 100). The phenylenevinylene spacers contained up to five subunits. Phenylenevinylene spacers were chosen because of their combined chemical stability and charge conductivity. The synthesis followed standard Wittig and Horner–Wittig procedures and was conducted in a stepwise manner using methylated ferrocene aldehydes **288**, terephthalaldehyde (**289**), and the corresponding hydroxymethyl derivatives **290** as the phosphonium precursors. Complexes with a metal to metal distance of up to 40 Å were obtained.

9.12.2. Properties

The methyl substitution provides the oxidized mixed valence complexes with higher solubility and

Scheme 97[a]



[a] Conditions and reagents: (a) 4-Iodoaniline, imidazole, $Zn(OAC)_2$. (b) Trimethylsilylacetylene, $PdCl_2$, PPh_3, $Cu(OAc)_2$, Et_3N. (c) Bu_4NF, THF. (d) Compound **274**, $Pd(dba)_3$, PPh_3, CuI, Et_3N. (e) Compound **272**, $Pd(PPh_3)_4$, KOAc, DMF, toluene.

increased stability. The pentamethyl derivative is the most soluble.

9.13. Ethene/Benzene/Squaraine

9.13.1. Synthesis

Meier and co-workers[299] succeeded in the synthesis of a series of symmetrical squaraines **291** that carry phenylenevinylene substituents in positions 1 and 3 (Scheme 101). Amino-terminated phenylenevinylene oligomers with up to three stilbenoid units were prepared by the Wittig−Horner reaction and condensed with squaric acid to obtain the donor−acceptor-substituted conjugated oligomers **291**.

9.13.2. Properties

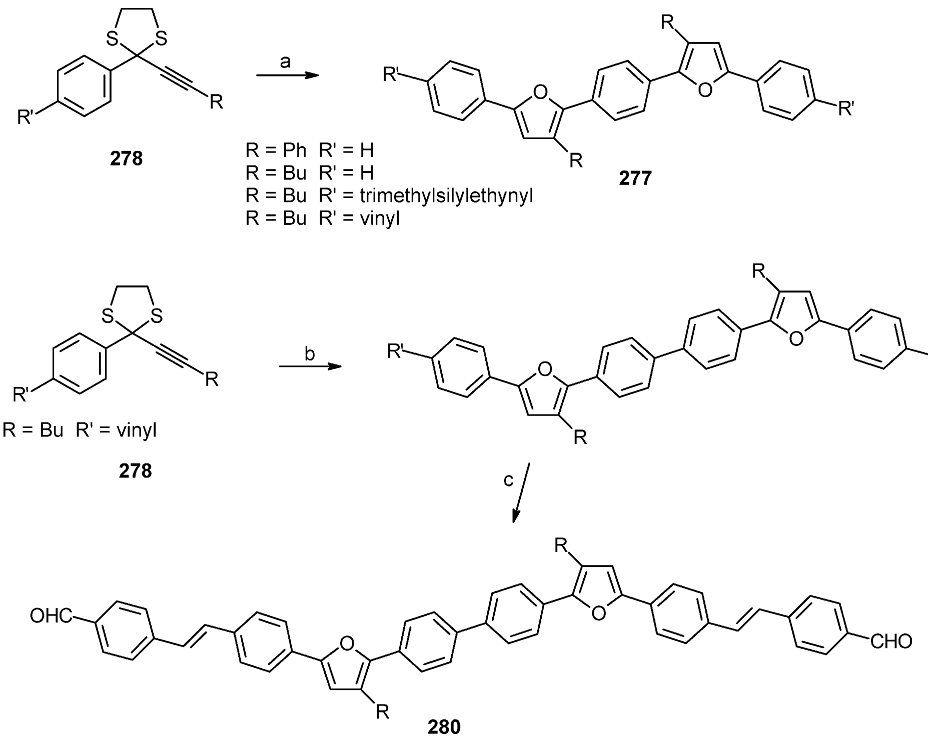
The UV−visible spectra of the stilbenoid squaraines **291** show a very interesting behavior. While the extension from diarylsquaraine to the next shortest homologue of the series produces a significant red shift into the NIR region due to the extension of conjugation, a hypsochromic effect is observed when the chain length is increased further, and this is attributed to the effect of the increased distance between the donor and the acceptor on the charge transfer transition.[299]

9.14. Ethene/Benzene/Perylene Bisimide

9.14.1. Synthesis

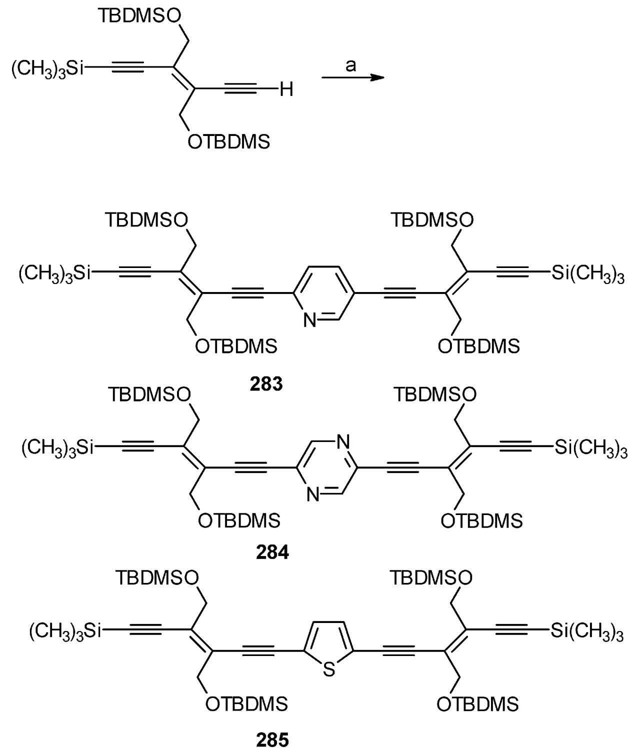
By connecting two oligo(*p*-phenylene vinylene) moieties to a central perylene bisimide core, Peeters et al.[300] constructed the novel donor−acceptor−donor system **292**. Starting from the trimeric aldehyde **293**[301] carrying flexible dodecyloxy side chains, a Wittig−Horner reaction with diethyl(4-nitrobenzyl) phosphonate was used for chain extension. The nitro

Scheme 98[a]



[a] Conditions and reagents: (a) (1) BuLi; (2) *p*-terephthaldehyde; (3) TFA. (b) (1) BuLi; (2) Biphenyl-4,4′-dicarbaldehyde; (3) TFA. (c) e eq 4-bromobenzaldehyde, Pd(OAc)$_2$, PPh$_3$, K$_2$CO$_3$.

Scheme 99[a]



[a] Conditions and reagents: (a) Compound **283**: 2,5-dibromopyridine, Et$_3$N, PdCl$_2$(PPh$_3$)$_2$, CuI; **284**: 2,5-dibromopyrazine, Et$_3$N, toluene PdCl$_2$(PPh$_3$)$_2$, CuI; **285**: 2,5-dibromopyrazine, Et$_3$N, toluene, PdCl$_2$(PPh$_3$)$_2$, CuI.

group was reduced to afford the amino-terminated rod **294**, whose condensation with 3,4,9,10-perylenetetracarboxydianhydride ultimately produced the extended dyad **292** (Scheme 102). An analogous molecule **295** with *p*-*tert*-butylphenoxy substituents on the perylene was published very recently by Beckers et al. (Chart 9).[302]

9.14.2. Properties

The electron-rich phenylene vinylene oligomer **292** with electron deficient perylene bisimide core displays a liquid crystalline mesophase between 215 and 310 °C.[300] Cyclic voltammetry and UV−visible absorption spectra indicate that the chromophores are not significantly coupled in the ground state in solution at low concentrations, because the spectra are a simple superposition of those of the individual units. At higher concentrations, a red shift of the absorption maximum is observed, which could be explained by the formation of *J* type aggregates.[300] Upon photoexcitation, the molecule **292** forms positive and negative charge carriers. The lifetime of the charge separation is significantly extended in thin films.[300]

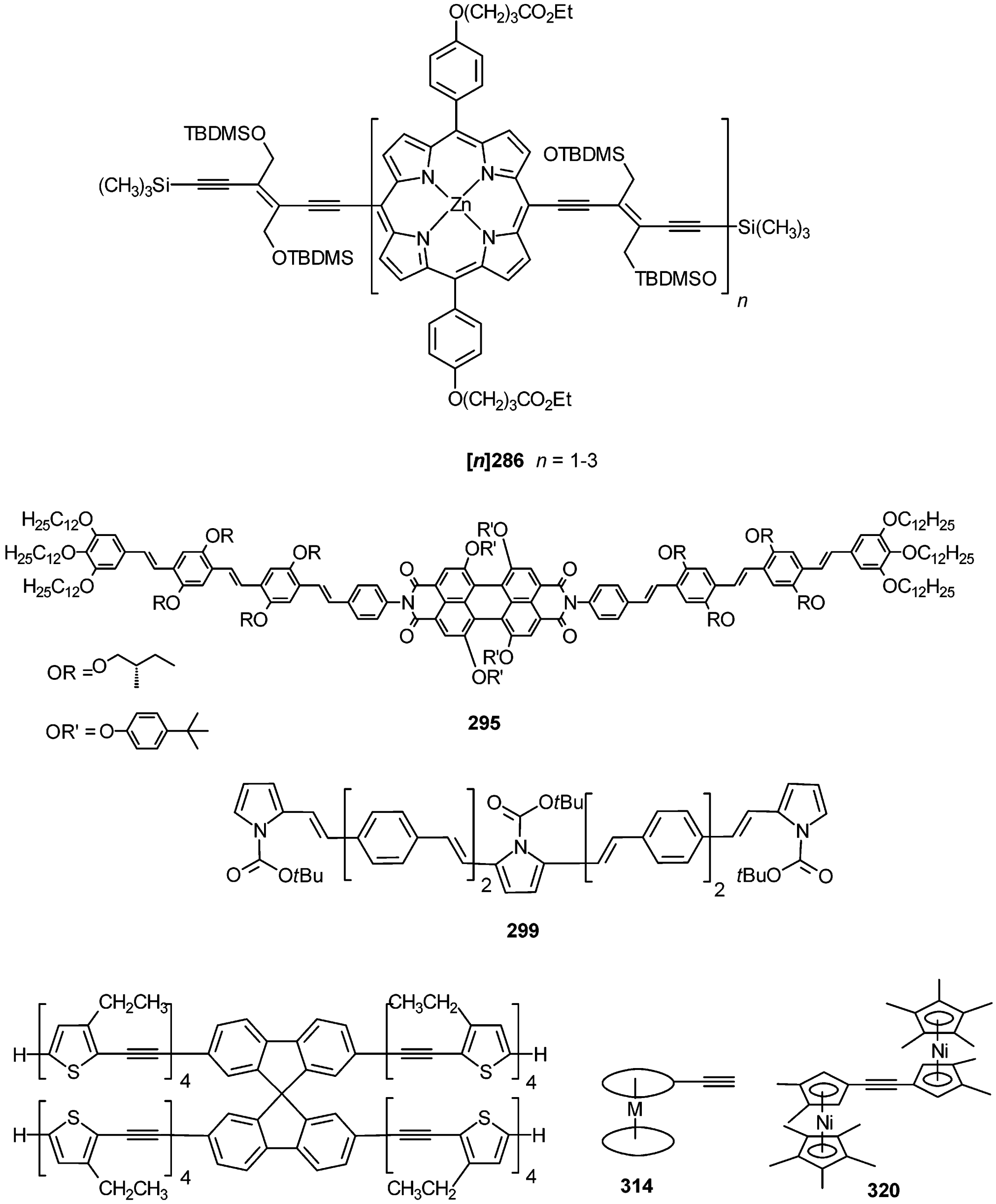
Because of efficient quenching in **295**, no fluorescence is detected in polar solvents, which indicates an efficient photoinduced electron transfer between the donor and the acceptor. In less polar solvents, fluorescence is observable but with a very low quantum yield (0.06). The value is independent of the excitation wavelength. A nearly quantitative energy transfer to the perylene core followed by fluorescence from the S$_1$ state of the perylene was suggested.[303]

9.15. Ethene/Benzene/Pyridine

9.15.1. Synthesis

Alain et al.[304] reported the homologous series of polyenic push−pull chromophores [***n***]**296** that carry an aminophenyl and a pyridinium substituent at the termini of an oligoene chain with up to five modules

Chart 9



[*n*]286 *n* = 1-3

295

299

313

314

320

(Scheme 103). Starting from *p*-dibutylaminobenzaldehyde, a series of polyenals [***n***]**297** was constructed by sequential vinylic homologation.[305] The polyenals were then condensed with an appropriate pyridine moiety[306] using a solid−liquid phase transfer modification of the Wittig−Horner reaction and alkylated to afford the desired amphiphilic rods [***n***]**296** as pure all-*E* isomers as shown by NMR spectra.

9.15.2. Properties

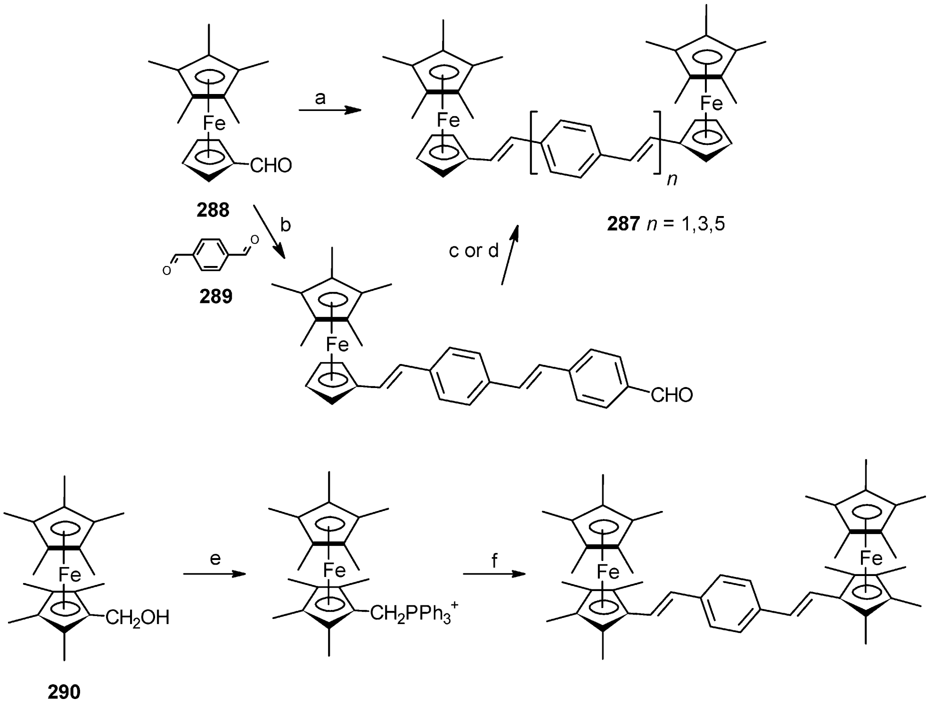
The pyridinium compounds [***n***]**296** are air stable solids that dissolve sufficiently in chloroform to use the EFISH (electric field induced second harmonic) technique[307] for measurement of their optical nonlinearities (hyperpolarizability and quadratic nonlinearity). Members of the homologous series exhibit large $\mu\beta$ values (the projection of the hyperpolarizability tensor β on the dipole moment μ) that increase significantly with chain length.[304] As expected, a bathochromic shift was observed as the conjugated bridge was extended. The loss of transparency with increasing chain length is less pronounced than with substitutents that are stronger acceptors.[304]

9.16. Ethene/Benzene/Pyrrole

9.16.1. Synthesis

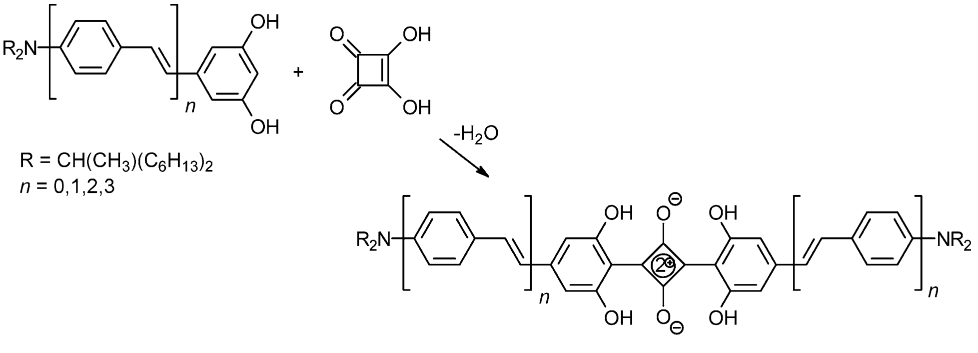
Starting from substituted *N*-Boc-vinylpyrroles, 2,5-diiodopyrrole, 1,4-divinylbenzene, *p*-vinylbenzaldehyde, and 1,3-diiodobenzene as building blocks, Tietze and co-workers[308] have synthesized several pyrrole-containing linear π-conjugated oligomers **298** in moderate yields using a sequence of Heck reaction followed by a Wittig and a second Heck reaction (Scheme 104). This straightforward modular approach allows for the synthesis of a large number of well-defined oligomers whose modular sequence can be varied deliberately and systematically. The longest reported pyrrole-containing oligomer **299** (Chart 9)

Scheme 100[a]



[a] Conditions and reagents: (a) $n = 1$ $Ph_3P{=}CHC_6H_4CH{=}P(C_6H_5)_3$. (b) $Ph_3PhCHC_6H_4CHO$, KO*t*-Bu. (c) $n = 3$, **288**, $(EtO)_2P(O){=}CHC_6H_4CH_2P(O)(OEt)_2$/KO*t*-Bu. (d) $n = 5$ $(EtO)_2OP{=}CHC_6H_4CH{=}PO(OEt)_2$. (e) PPh_3/HBr. (f) Compound **289**, KO*t*-Bu.

Scheme 101



291

consists of three pyrrole and four divinylbenzene moieties.[309]

9.16.2. Properties

All reported products are crystalline solids with a high thermal stability. The longer oligomers are red. The UV−visible spectrum of **299** (Chart 9) shows an absorption maximum at 436 nm ($\log \epsilon = 4.8$).[308] The *tert*-butoxycarbonyl protecting group prevents efficient π-stacking and therefore improves the solubility of the compounds. Nevertheless, the longer rods are poorly soluble. Compound **299** is best dissolved in warm chloroform.[309]

9.17. Ethene/Benzene/Tetrathiafulvalene

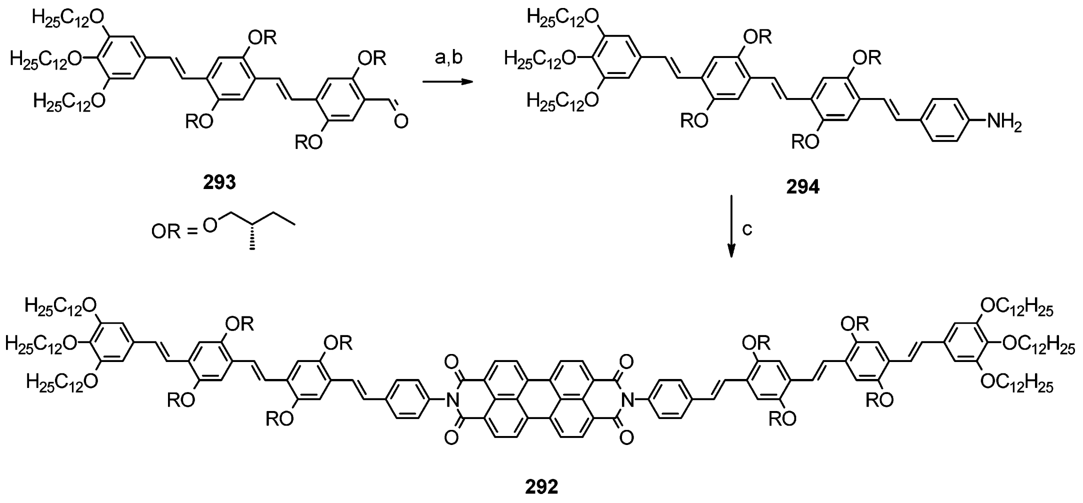
9.17.1. Synthesis

Two optically active tetrathiafulvalene dimers bridged by vinylbinaphthyl units were prepared by Gómez et al.[310] employing Wittig−Horner methodology (Scheme 105). The (*R*)-bisphosphonate-substituted binaphthyl derivative **300** was obtained from pure (*R*)-2,2′-didodecyloxy-6,6′-diformyl-1,1′-binaphthyl in three steps and coupled with formyltetrathiafulvalene **301** and its vinylogue **302**, respectively, to yield the dimers **303** and **304**, the latter as the all-trans isomer, albeit in low yield.

9.17.2. Properties

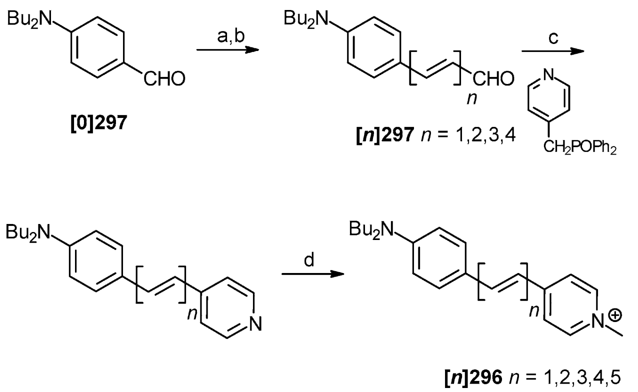
The chiral TTF dimers **303** and **304** are air stable solids, which show very good solubility in standard organic solvents due to the presence of long alkyl chains on the binaphthyl unit. The UV−visible absorption spectra revealed a new band for **303** at 432 nm and for **304** at 436 nm that can be assigned to the conjugated system formed from the TTF units, vinyl groups, and naphthalene rings.[310] Cyclic voltamogramms show two reversible two-electron waves for both compounds that are shifted to higher potentials compared to TTF, indicating that the two TTFs are oxidized independently to form the bis(radical cation) and tetracation. Because of their good donor

Scheme 102[a]



[a] Conditions and reagents: (a) Diethyl(4-nitrobenzyl) phosphonate, KO*t*-Bu, DMF. (b) $SnCl_2$, EtOH, EtOAc. (c) 3,4,9,10-Perylenetetracarboxy dianhydride, $ZnCl_2$, quinoline.

Scheme 103[a]



[a] Conditions and reagents: (a) (1,3-Dioxolan-2-ylmethyl)tributylphosphonium bromide (1.1 equiv), NaH (1.5 equiv), cat. 18-C-6, THF. (b) HCl (10%), THF. (c) THF, NaH (1.5 equiv), cat. 18-C-6. (d) MeI.

ability, compounds **303** and **304** form stable charge transfer complexes with DDQ.[310]

9.18. Ethene/Bicyclo[2.2.2]octane/Pyridine

A Wadsworth–Emmons reaction was used by Vögtle and collaborators[311] to synthesize 1,4-bis[2,2′-bipyridin-5-yl)ethenyl]bicyclo[2.2.2]octane (**305**, Scheme 106). Because of rotation around the single bonds connecting the ligands and the central bicyclooctane with the two ethylene units, there is some uncertainty in the separation of the chelating sites (16–18 Å).

9.19. Fluorene/Benzene

9.19.1. Synthesis

Tsolakis and Kallitsis[312] published the synthesis of the symmetrical biphenyl-substituted terfluorene derivatives **306** and **307** as building blocks in the construction of rod–coil AB or ABA block copolymers (Scheme 107). Starting from the substituted terfluorene[313,314] **308**, bromination with Br_2 led to a separable mixture of mono- and dibrominated products **309** and **310** in moderate yield. Their relative ratio was controlled to some extent by the stoichiometry of the reactants. Subsequent Suzuki type coupling with boronic acid functionalized biphenyl derivatives produced the desired rods **306** and **307**.

9.19.2. Properties

Compound **307** was isolated by column chromatography as a yellowish solid whose thermal behavior was investigated by differential scanning calorimetry, revealing a T_g at 43 °C. The UV–visible absorption maximum of **307** shows a small bathochromic shift of 14 nm with respect to the parent terfluorene. While the shift confirms an increased π-conjugation, the effect is subdued due to the lack of coplanarity between the biphenyl rings and the terfluorene block. Comparison of the fluorescence spectra in solution and in the solid state revealed a 10 nm shift of the emission peak.[312]

10. Co-oligomers of Axial and Five-Membered Ring Modules

We next take up the combinations of five-membered ring modules of Table 1 with axial modules of Part 1.[5]

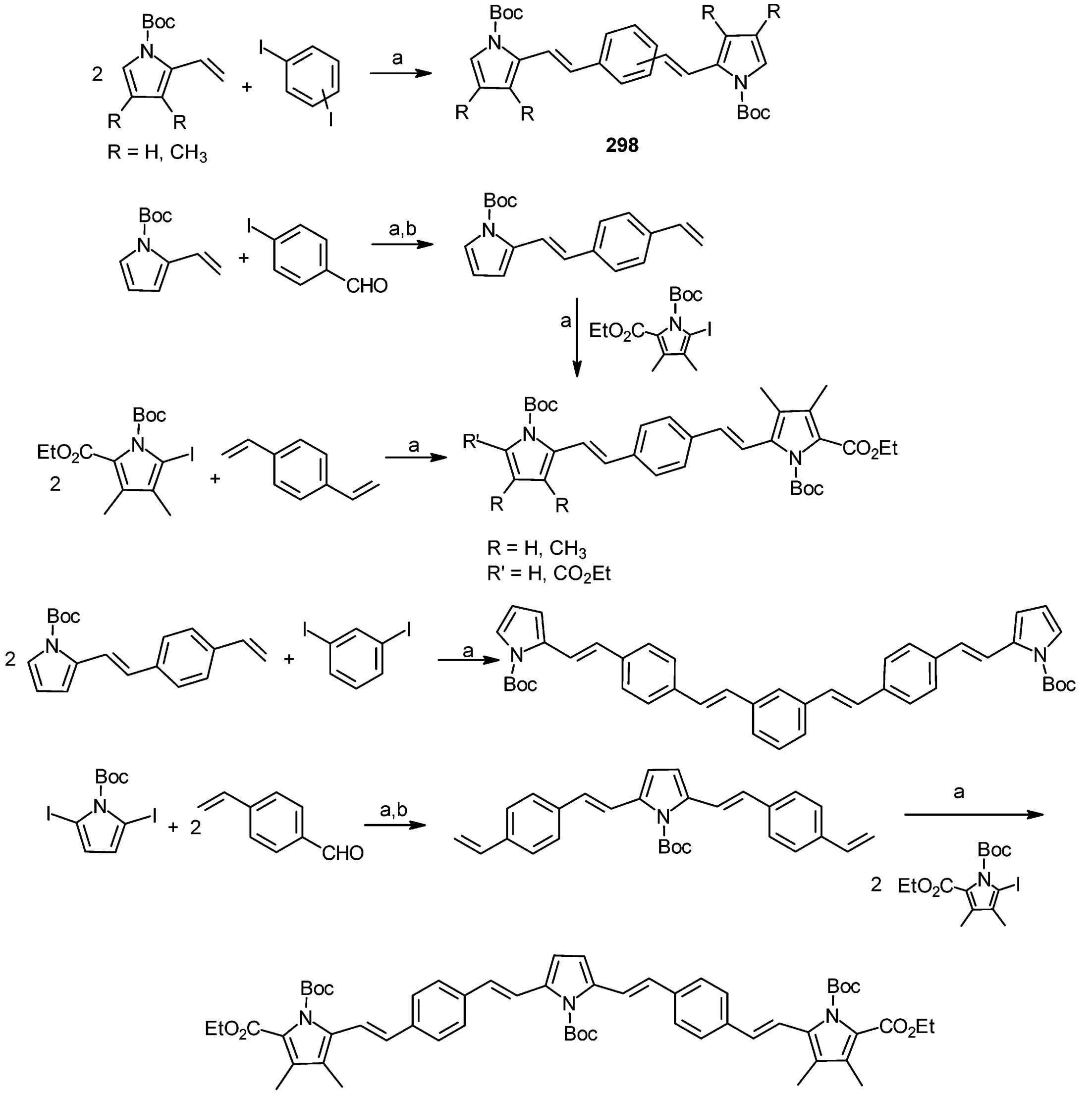
10.1. Ethyne/Thiophene

Oligo(2,5-thiopheneethynylene)s [***n***]**311** were reported by Pearson and Tour[315] as potential molecular wires and useful models for understanding bulk polymers built from this monomer (Scheme 108).

10.1.1. Synthesis

The monomer 3-ethyl-2-(trimethylsilylethynyl)thiophene (**312**) was prepared by palladium-catalyzed cross-coupling of 2-bromothiophene with trimethylsilylacetylene.[315] An ethyl group was introduced in position 3 to ensure solubility and separability of the oligomers. From the monomer, the dimer [**2**]**311** through the 16-mer [**16**]**311** were obtained following an iterative divergent/convergent approach in which the rod length doubles in each iteration step (Scheme

Scheme 104[a]



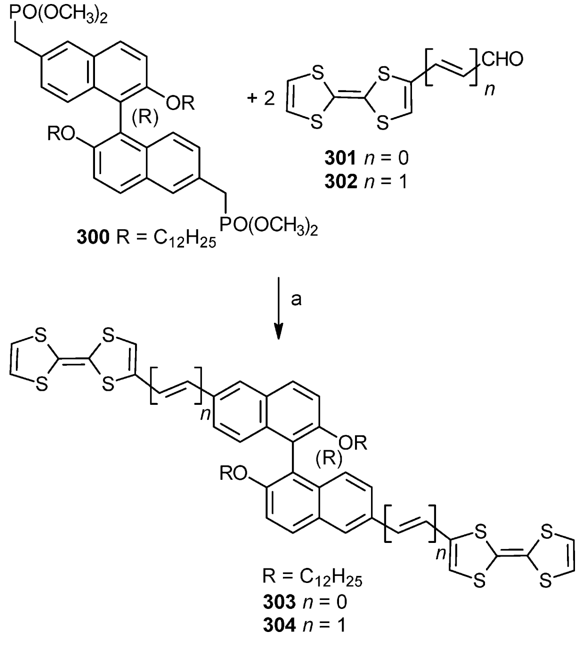
[a] Conditions and reagents: (a) Pd(0). (b) $Ph_3P{=}CH_2$.

108). The isolated oligomers have a thiophene unit at one end and a terminal acetylene on the other. They were treated with 1-acetylthio-4-iodobenzene to provide them with thiolester termini; these masked thiols are to be used for attachment to electrode surfaces. In addition, four oligomeric arms were connected to a tetraphenylbicyclopentane spiro core to obtain the interesting orthogonally fused system **313** (Chart 9).[316]

10.1.2. Properties

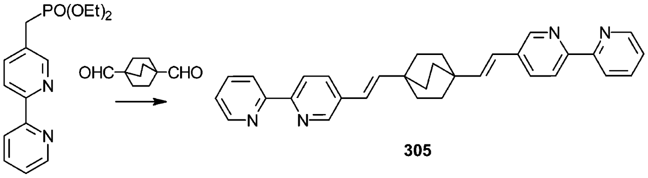
The compounds [***n***]**311** are stable to air and light and their degree of rigidity minimizes conformational flexibility but maintains solubility and processability. The end functionalization of the assembled rods is facile and versatile. The length of the 16-mer [**16**]**311** in its extended zig-zag conformation is about 100 Å. The optical spectra show that a saturation limit is reached at the octamer stage and that doubling of the rods thereafter has little effect on the absorbance maximum[315] and the third-order nonlinear optical intensities.[317]

Scheme 105[a]



[a] Conditions and reagents: (a) KO*t*-Bu, EtOH.

Scheme 106[a]



[a] Conditions and reagents: (a) NaH.

10.2. Ethyne/Cyclopentadienyl Complex

Interest in ferroceneacetylene oligomers mainly arises from the fact that the related phenyleneethynylenes exhibit interesting properties, such as photoluminescence and nonlinear optical activity. Furthermore, the presence of metal centers that are well coupled with each other could give rise to interesting new properties as compared to fully organic polymers or polymers with isolated metal atoms. To develop an understanding of the principles governing the intermetallic interactions, well-defined oligomeric ferroceneacetylenes have been the target of synthetic efforts.

On several occasions, acetylene and diacetylene rod termini were connected to transition metal complexed cyclopentadienyl rings to obtain organometallic rigid rod structures. The simplest building blocks are metallocenylacetylenes **314** (Chart 9) and ethynylcymantrenes **315** (Scheme 109). While the latter can only be used in zig-zag type rods, the metallocenylacetylenes offer at least in principle the possibility for linear albeit nonrigid geometries by substituting alternatively the top and bottom units of the sandwiches.

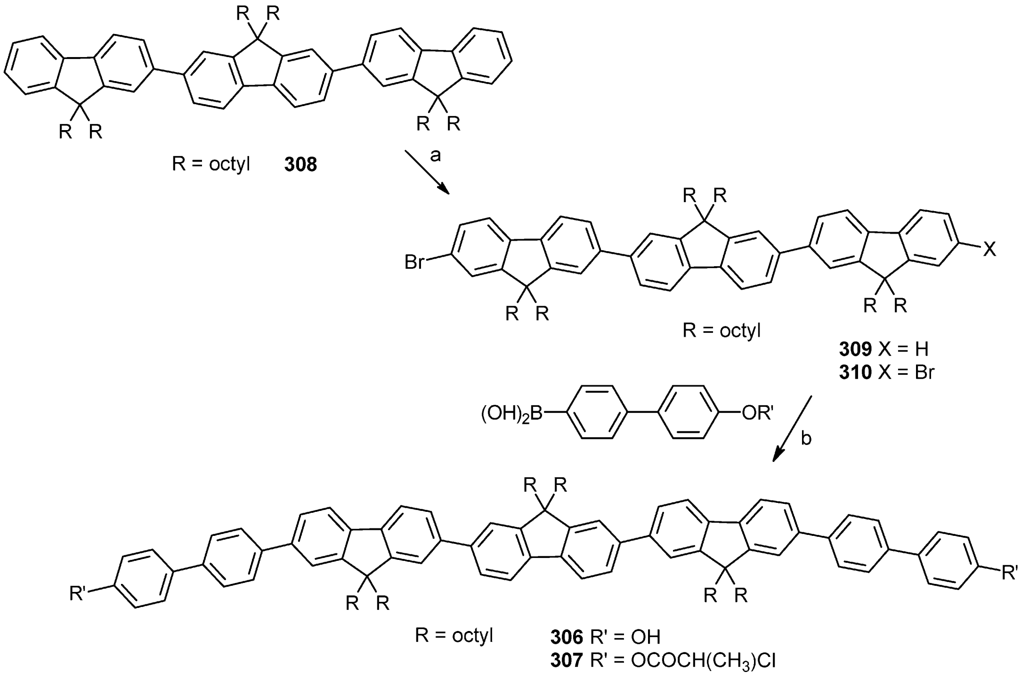
10.2.1. Synthesis

Ferrocenylacetylene **316** was first synthesized by Rosenblum et al.[318] from acetylferrocene in two steps via the chloroaldehyde **317** (Scheme 110). A one-step procedure from acetylferrocene was reported by Doisneau et al.[319] based on Negishi's method for converting ketones into acetylenes.[320] Pudelski and Callstrom[321] prepared the stable bis(trimethylsilyl) derivative of 1,1′-diethynylferrocene **318** by Pd-catalyzed cross-coupling of 1,1′-diiodoferrocene with trimethylsilylacetylene (Scheme 111). It is also accessible from 1,1′-diacetylferrocene.[319] Buchmeiser and Schottenberger[322] reported the corresponding ethynylruthenocenes. The acetylene-bridged methylated nickelocene (**320**, Chart 9) and ferrocene (**321**, Chart 10) dimers were prepared by Bunel et al.[323] when dilithiated bis(3,4-dimethylcyclopentadienyl)-acetylene was treated with a solution of (η-C_5Me_5)M(acac) (M = Fe, Ni; acac = acetylacetonate).

Monoethynylcymantrenes **315** were synthesized by Lo Sterzo and Stille[324] and converted to homo- and heterobismetallic dimers (Scheme 109). Bunz and his group[325] prepared both 1,2- and 1,3-[bis-(trimethylsilyl)ethynyl]cymantrenes **322** and **323** in the presence of Beletskaya's catalyst[326] and converted them to a mixture of oligomers from which dimeric up to heptameric butadiynylenecymantrenes [***n***]**324** were isolated by HPLC and characterized (Scheme 112).

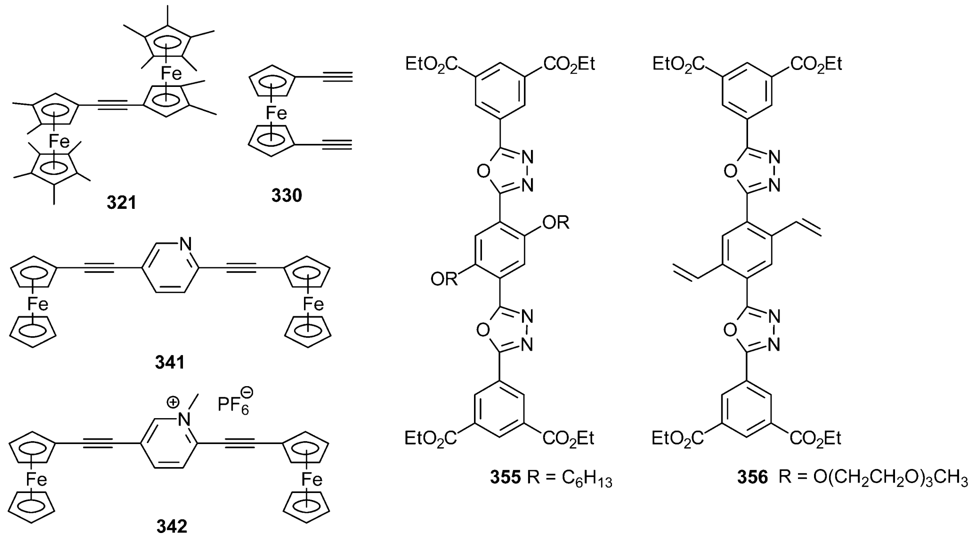
A series of optically active oligomeric 1,2,3-substituted ferrocenes [***n***]**325** up to the tetramer were reported by Plenio et al. (Scheme 113).[327] Starting from (*S*)-1-iodoferrocene-2-carbaldehyde (**326**), which was converted conventionally to the stable methyl ether **327**, the oligomers [***n***]**325** were built in a stepwise fashion using Sonogashira type coupling conditions with silyl-protected acetylenes. Originally, the development of a divergent−convergent approach was planned in order to have fast access to long rods, but the necessary regioselective lithiation of the

Scheme 107[a]

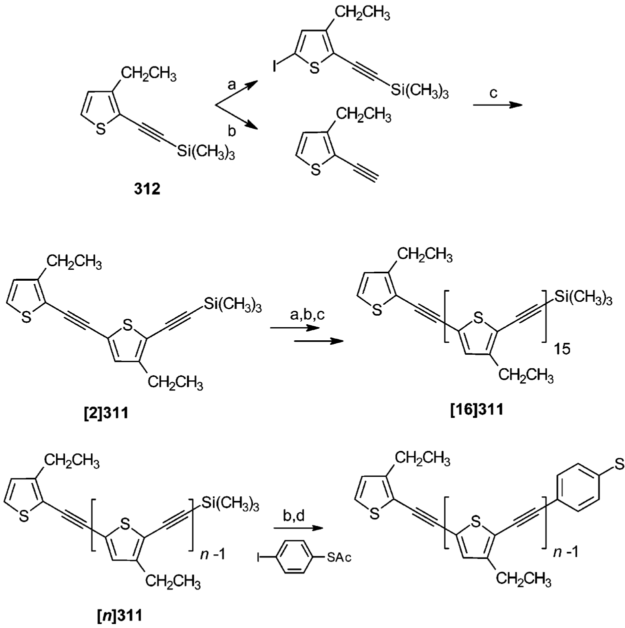


[a] Conditions and reagents: (a) Br_2, $FeCl_3$. (b) From **310**, $Pd(PPh_3)_4$, Na_2CO_3.

Chart 10

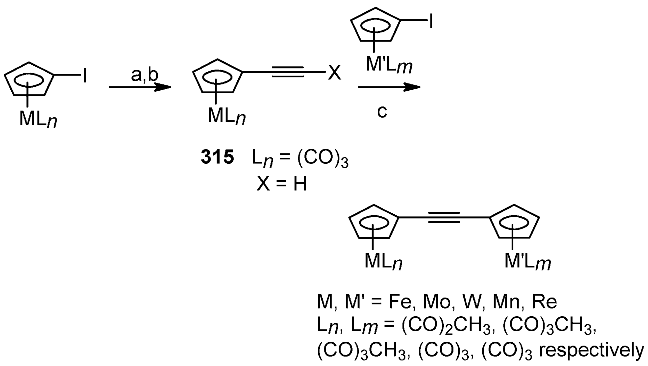


Scheme 108[a]



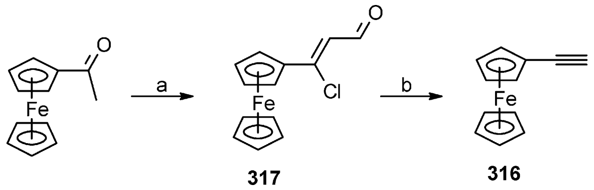
[a] Conditions and reagents: (a) LDA, ether, I_2. (b) K_2CO_3, MeOH. (c) $PdCl_2(PPh_3)_2$, CuI, THF, *i*Pr_2NH. (d) $PdCl_2(PPh_3)_2$, CuI.

Scheme 109[a]



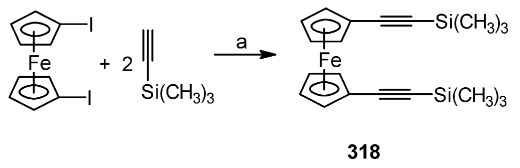
[a] Conditions and reagents: (a) Bu_3SnCCH, $PdCl_2(CH_3CN)_2$, DMF, X = H. (b) Et_2NSnR_3, X = SnR_3. (c) $PdCl_2$ $(CH_3CN)_2$, DMF.

Scheme 110[a]



[a] Conditions and reagents: (a) DMF, $POCl_3$. (b) NaOH.

Scheme 111[a]



[a] Conditions and reagents: (a) $PdCl_2(PPh_3)_2$, $Cu(OAc)_2$; H_2O, *i*Pr_2NH.

dimeric species failed. As a result, the longest rod with alternating modules was the tetrameric species [4]**325**. In principle, longer species are accessible, but the stepwise procedure is time-consuming. A bisacetylene-bridged tetranuclear ferrocene **328** was synthesized by applying Eglington−Glaser conditions to the deprotected dimer **329** (Scheme 114). To investigate the dependence of the electronic communication on the sequential connectivity of the modules, several other multinuclear species with varying substitution patterns were prepared.[327]

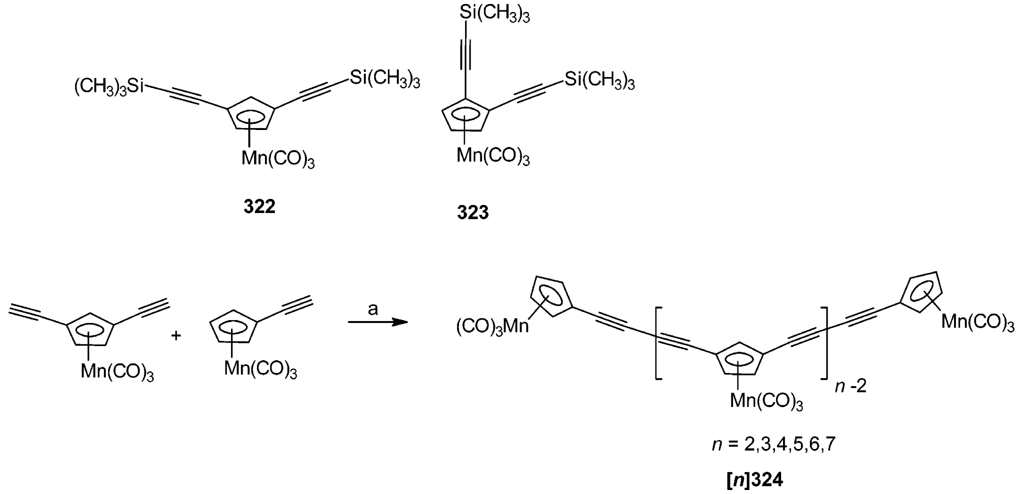
10.2.2. Properties

Ferrocenylacetylene **316** (Scheme 110) is a stable low melting solid, but 1,1′-diethynylferrocene (**330**, Chart 10) is very sensitive under atmospheric conditions.[318] The trimethylsilyl derivatives are easier to handle.[319]

The mono- and diethynylcymantrenes are low melting solids, which can be sublimed for purification. The oligomers derived from these building blocks are air stable, crystalline substances with melting points above 150 °C. The use of such compounds as nonlinear optical materials has been investigated.[328]

In the study published by Plenio et al.,[327] oligomers [***n***]**325** (Scheme 113) with up to three ferrocene modules are reported as red oils, while the tetrameric

Scheme 112[a]



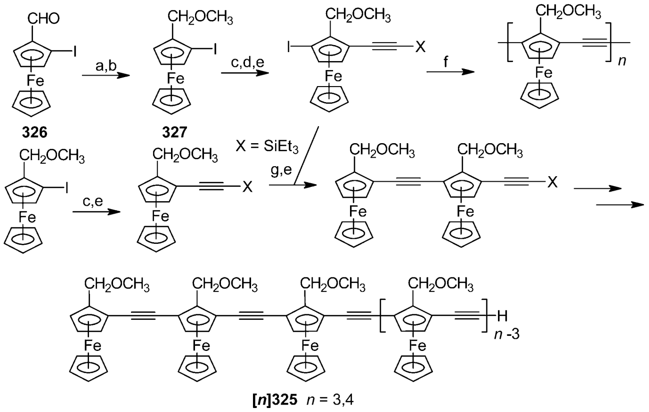
322

323

[*n*]324

[a] Conditions and reagents: (a) CuCl, TMEDA, O_2, acetone.

Scheme 113[a]

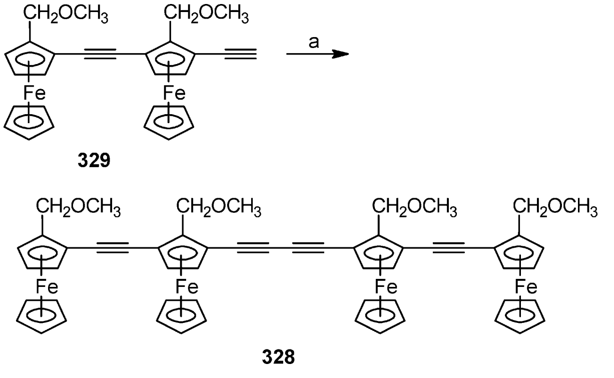


326 **327**

[*n*]325

[a] Conditions and reagents: (a) $NaBH_4$. (b) KOH, CH_3I, DMSO. (c) Triethylsilylacetylene, $PdCl_2(PPh_3)_2$, CuI, X = $SiEt_3$. (d) *t*-BuLi, ICH_2CH_2I, ether. (e) TBAF, THF, X = H. (f) *i*Pr_2NH-DMF (1:1:), $Pd(Ph_3P)_4$, CuI. (g) $Pd(Ph_3P)_4$, CuI.

Scheme 114[a]



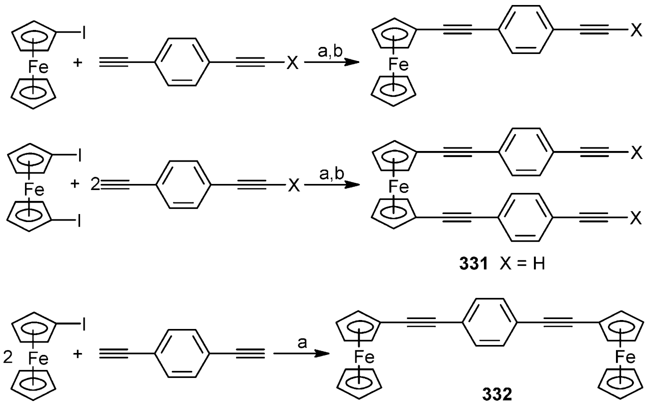
329

328

[a] Conditions and reagents: (a) TMEDA, CuCl, O_2.

species is a red solid with good thermal stability. The CV of all compounds exhibit reversible redox processes, attributed to the stabilizing effect of the methoxy substituent. The CV of the tetranuclear oligomer [4]**325** shows four well-separated, reversible waves between 0.4 and 1.2 V when measured at −30 °C, indicating that even the tetracationic species possesses a reasonable stability. UV−visible measurements on the oligomeric series [***n***]**325** showed that the ferrocene d−d transition is electronically coupled to the conjugated chain since the λ_{max} value of the d−d transition is inversely proportional to the number of ferrocene units in the chain. However, because of the low extinction coefficient of the metal-to-metal charge transfer bands, the electronic coupling of the metal centers as expressed in the exchange integrals is significantly less pronounced than in the corresponding C=C analogue.[327]

Scheme 115[a]



331

332

[a] Conditions and reagents: (a) $PdCl_2(PPh_3)_2$, $Cu(OAc)_2$, *i*Pr_2NH, X = Si(*i*Pr)$_3$. (b) TBAF, THF, X = H.

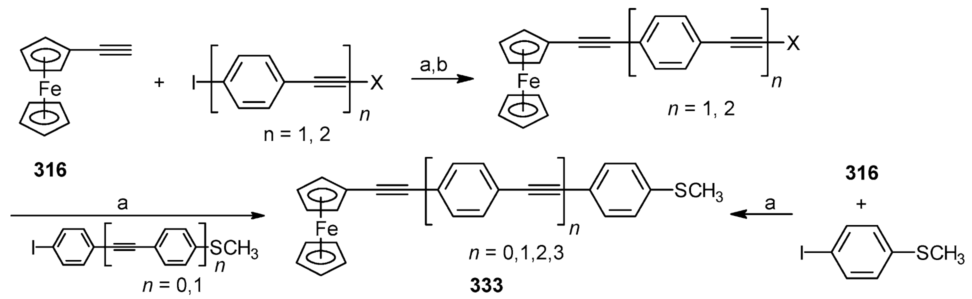
10.3. Ethyne/Benzene/Cyclopentadienyl Complex

Because of their rich and reversible redox chemistry, chemical stability, and synthetic versatility, ferrocenyl units are increasingly selected as redox active components in multiresponsive, photo- and electrochemically active molecular architectures.

10.3.1. Synthesis

The 1,4-diethynylphenyl-substituted ferrocenes, 1-(1,4-diethynylphenyl)ferrocene and bis-1,1′-(1,4-diethynylphenyl)ferrocene (**331**), and the 1,4-diethynylphenyl-bridged ferrocene dimer **332** were synthesized in the group of Dixneuf[329,330] by Pd-catalyzed cross-coupling between 1-iodoferrocene or 1,1′-iodoferrocene and 1,4-diethynylbenzene utilizing silyl protection (Scheme 115). The bifunctional tetrayne was used as a monomer in the preparation of mixed

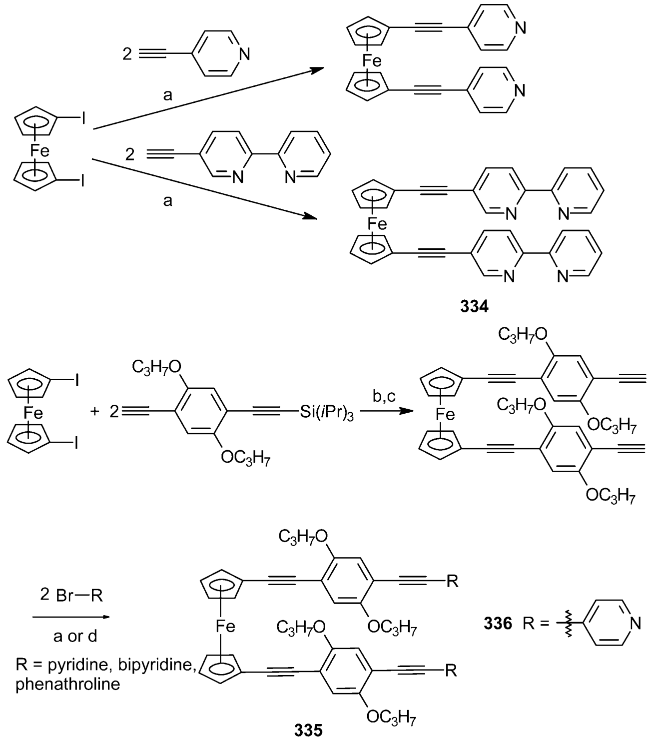
Scheme 116[a]



[a] Conditions and reagents: (a) $PdCl_2(PPh_3)_2$, CuI, Et_2NH, X = $Si(CH_3)_3$. (b) TBAF, CH_2Cl_2, X = H.

d^6/d^8 metal-containing oligomers by reaction with Pd(II) or Ni(II) salts. Similarly, Sita and co-workers[331] synthesized a series of unsymmetical ferrocene-terminated phenylethynyl oligomers **333** with up to four phenylethynyl units from ferrocenylacetylene **316** utilizing stepwise Pd-catalyzed coupling techniques (Scheme 116). At the other terminus, thiols or masked thiol groups provide binding sites for self-assembled monolayers on a gold metal interface in order to study electron transfer rates across the interfacial barrier as a function of structure.

Scheme 117[a]



[a] Conditions and reagents: (a) $PdCl_2(PPh_3)_2$, CuI, DIPA. (b) $PdCl_2(PPh_3)_2$, CuI, DIPA, TEA. (c) Bu_4NF, THF. (d) $Pd(PPh_3)_4$, $PdCl_2(PPh_3)_2$, CuI, DIPA, nPrNH$_2$, THF.

10.3.2. Properties

The compounds with organic substituents are all crystalline materials with melting points above 100 °C.[331]

10.4. Ethyne/Benzene/Cyclopentadienyl Complex/Pyridine

10.4.1. Synthesis

The group of Lindner[332] has published a series of rigid ligands **334** in which 1,1′-ferrocenediyl units are connected to nitrogen-based complexation sites through conjugated linkers (Scheme 117). Using palladium-catalyzed Sonogashira C−C coupling reactions, the rods **335** were constructed from ferrocene-, pyridine-, bipyridine-, and phenanthroline-based building blocks in moderate yields. Propoxy-substituted 1,4-diethynylbenzene was incorporated into extended systems in order to improve the solubility. Starting from 1,1′-diiodoferrocene, the linear spacers were built in a divergent stepwise fashion and ultimately capped by reaction with the bromo-substituted pyridine derivatives. A crystal structure of the shortest homologue **336** was obtained and shows π-stacking of the pyridine units in the solid state.[332]

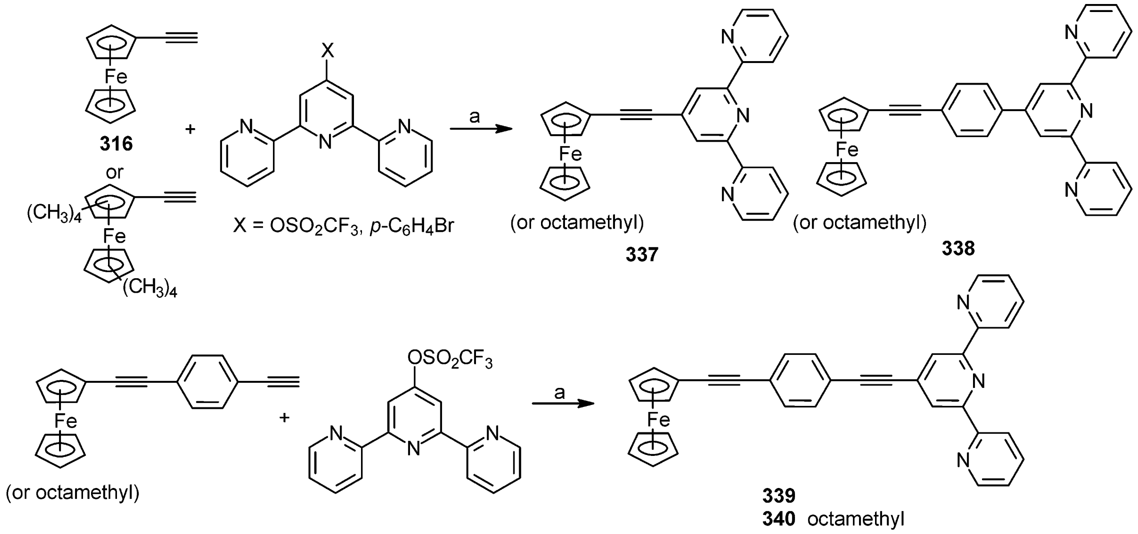
Siemeling et al.[333] have reported rods **337**, **338**, **339**, and **340** that contain a terpyridyl group at one end and a ferrocenyl or octamethylferrocenyl unit at the other, bridged by a rigid spacer comprised of acetylene and phenylene modules (Scheme 118). These redox functionalized ligands **337**−**340** were synthesized by standard Sonogashira type cross-coupling reactions in good yields. Ethynylferrocene (**316**) or ethynyloctamethylferrocene was either coupled directly with 4′-(4-bromophenyl)-2,2′:6′,2″-terpyridine or (trifluoromethanesulfonyloxy)-2,2′:6′,2″-terpyridine in order to obtain the short rods **337** and **338** or first extended by reaction with 4-bromo(trimethylsilylethynyl)benzene and then coupled with (trifluoromethanesulfonyloxy)-2,2′:6′,2″-terpyridine to yield **339** and **340**.

Entrakul and Sita[334] have coupled two ferrocene units through an unsymmetrical 2,5-diethynylpyridine spacer applying a standard palladium-catalyzed Sonogashira reaction. The resulting linear diferrocene complex **341** was methylated at the pyridine nitrogen with methyl iodide producing **342** as a potentially viable switching element for a molecular diode (Chart 10).

10.4.2. Properties

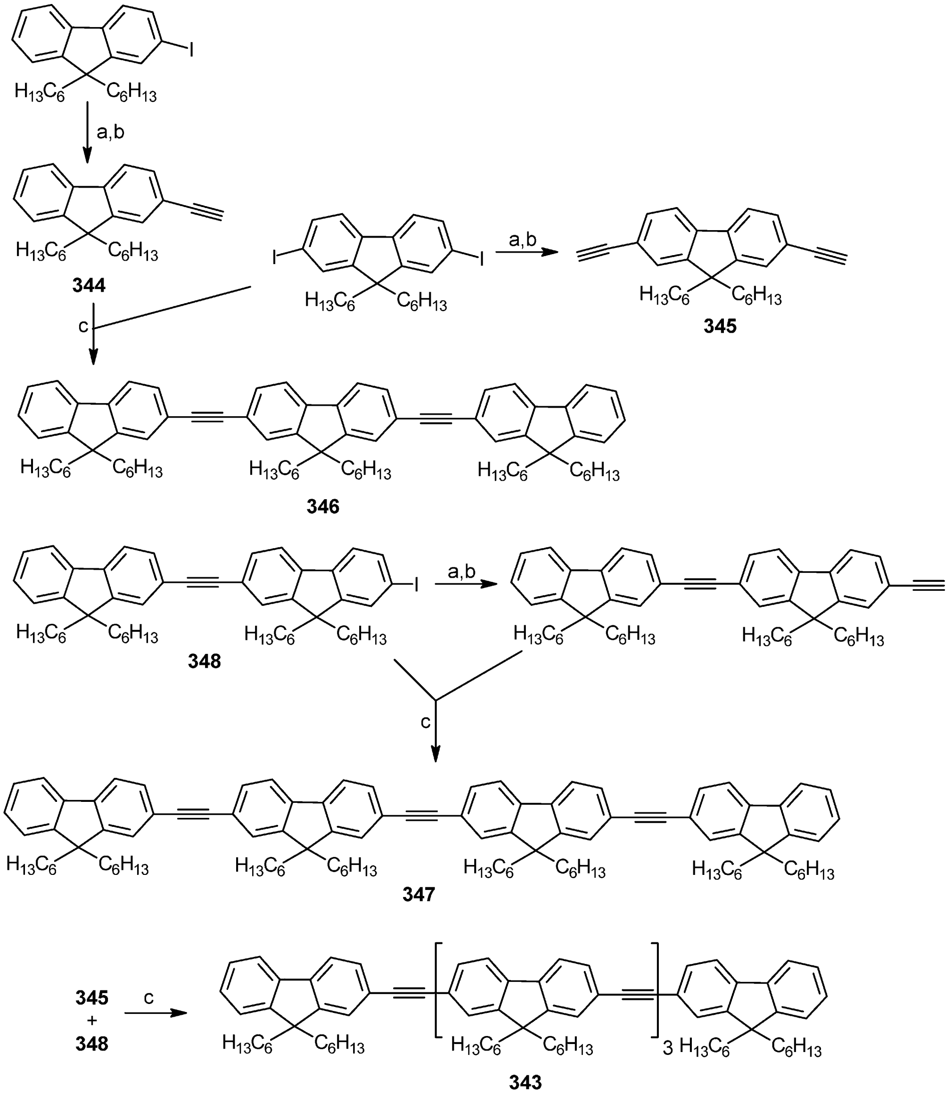
In Lindner's study,[332] the short bipyridine derivative **336** (Scheme 117) is a red air stable solid with good thermal stability but low solubility in common organic solvents. The bisethynylbenzene-bridged compounds are soluble in chlorinated solvents and THF and are isolated as air stable orange powders with melting points above 150 °C. The extent of electronic communication through these systems in currently under investigation.[332]

Scheme 118[a]



[a] Conditions and reagents: (a) $Pd(PPh_3)_4$, Et_3N.

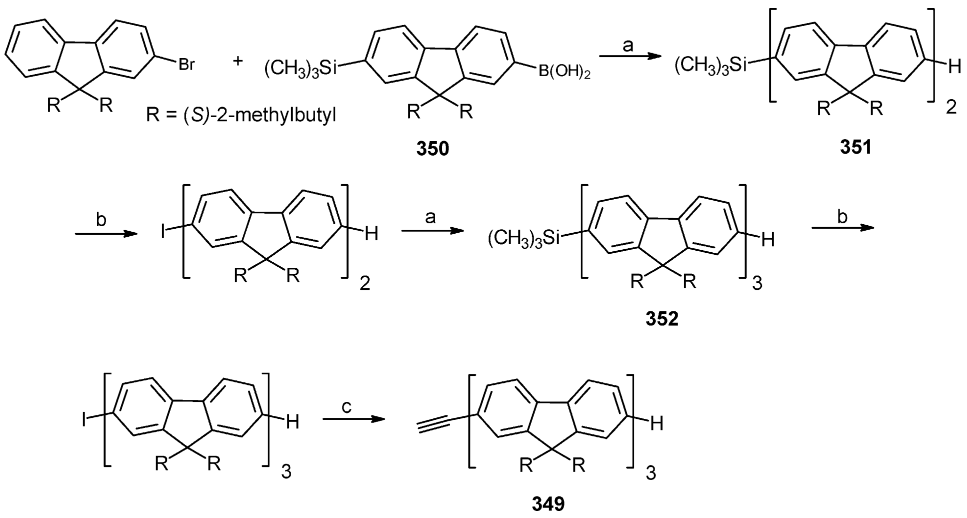
Scheme 119[a]



[a] Conditions and reagents: (a) 3-Methyl-1-butyn-3-ol, $PdCl_2(PPh_3)_2$, PPh_3, CuI, Et_3N. (b) KOH, 2-propanol. (c) $PdCl_2(PPh_3)_2$, PPh_3, CuI, Et_3N.

Siemeling's compounds[333] **337−340** are all air-stable orange solids. The octamethyl-substituted derivatives are prone to oxidation in solution. The electrochemical measurements revealed that the rods

Scheme 120[a]



[a] Conditions and reagents: (a) $Pd(PPh_3)_4$, Na_2CO_3, toluene. (b) ICl, CH_2Cl_2. (c) (1) Trimethylsilylacetylene, $PdCl_2(PPh_3)_2$, PPh_3, Et_2NH; (2) KF, CH_2Cl_2, CH_3OH.

337−**340** are oxidized at a more positive potential than ferrocene and octamethylferrocene, respectively, in accordance with the anticipated electron-withdrawing effect of the acetylene spacer augmented by the attached terpyridyl unit. The influence of the terpyridyl is strongest for the cases in which efficient π delocalization is possible through the spacer, namely, for C≡C and C≡C-*p*-C_6H_4-C≡C units, and less pronounced if the *p*-phenylene group is directly attached to the terpyridyl unit. The electron-withdrawing effect of the acetylene group is also observed in the UV−visible spectra, which show a red shift of 10 nm compared to ferrocene and of 60 nm compared to octamethylferrocene.[333]

Compounds **341** and **342** (Chart 10) are crystalline solids for which single crystal X-ray structures were obtained. The central pyridine unit in **341** was shown to be almost coplanar with the cyclopentadienyl rings, while in **342**, the methylated pyridinium unit is tilted by 10° in respect to those moieties. The C−C bond lengths are virtually identical. Compound **342** displays a strong metal-to-ligand charge transfer transition at 540 nm from the ferrocene units to the pyridinium cation as the acceptor. Electrochemical measurements revealed only a single reversible two-electron redox couple for **341** but the presence of two one-electron couples for compound **342** whose separation could be maximized by using a nonpolar, noncoordinating solvent and a noncoordinating anion.[334]

10.5. Ethyne/Fluorene

10.5.1. Ethyne/Fluorene—Alternating

Synthesis. Starting from fluorene, Tsutsui and coworkers[335] prepared oligofluoreneethynylene (OFE) arrays consisting of alternating ethynyl and fluorene units up to the pentamer **343** (Scheme 119). The key building blocks, 2-ethynyl-9,9-dihexylfluorene (**344**) and 2,7-diethynyl-9,9-dihexylfluorene (**345**), were obtained by electrophilic iodination and subsequent replacement reaction with hexyl bromide, followed by Pd/Cu-catalyzed cross-coupling with 3-methyl-1-butyn-3-ol and base-promoted deprotection. The trimer **346** was constructed via Sonogashira coupling. However, for the synthesis of the tetramer **347** and pentamer **343**, the synthetic strategy had to rely on the use of a side product of the trimer synthesis, the iodo dimer **348**, leading to low overall yields.[335] A more efficient and general approach would require an unsymmetrical derivatization of fluorene in positions 2 and 7.

Properties. Because of the long alkyl chains present in the molecules, even the longer oligomers including **343** are well soluble in common organic solvents such as chloroform, dichloromethane, and THF. The OFEs show a significant red shift in their absorption spectra with increasing length, and the position of the absorption maxima approaches that of polyfluoreneethynylene[335] (2.88 eV).[335] From the data, an effective conjugation length of about 10 fluorene units can be calculated. The quantum yield of fluorescence shows a positive dependence on the conjugation length of the π-conjugated system. The pentamer **343** is characterized by a strong blue fluorescence near 402 nm and a weaker peak at 445 nm, red shifted about 50 nm as compared to the respective dimer, and a photoluminescence quantum efficiency of 0.64. The compound can be spin-coated to obtain an OLED. The electroluminescence spectrum displays a blue light emission with a maximum at 424 nm, a shift that indicates strong intermolecular interaction in the solid state.[335]

10.5.2. Fluorene/Ethyne—Terminal

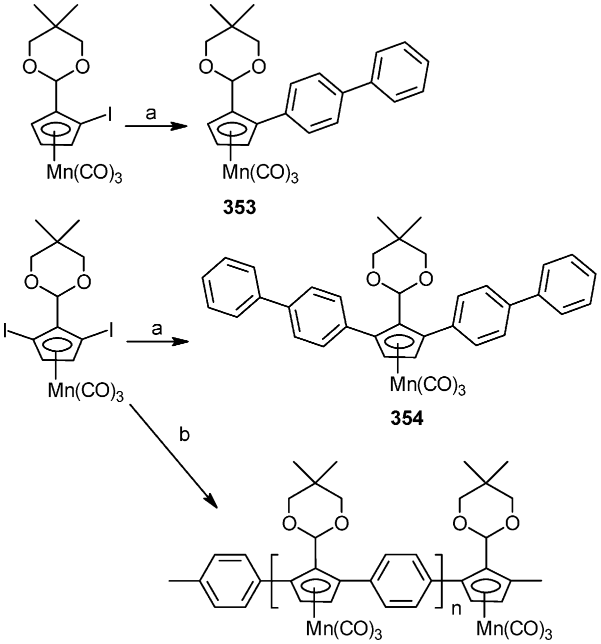
Synthesis. Very recently, Mastrorilli et al.[337] reported the monoethynylated terfluorene **349** as a monomer for the preparation of polyacetylenes bearing fluorene-based pendant groups (Scheme 120). For the synthesis of the nonsymmetrical rod, 2-trimethylsilyl-9,9-[(*S*)-2-methylbutyl]fluoren-7-ylboronic acid (**350**) was utilized as the key intermediate since it carries both the reactive boronic acid substitutent and the trimethylsilyl group, which can be activated by iododesilylation. Thus, compound **350** was cross-coupled with 2-bromo-9,9-[(*S*)-2-methylbutyl]fluorene employing Suzuki conditions and the resulting fluorene dimer **351** was selectively monoiodinated. Repetition of the sequence yielded the iodoterfluorene **352**, which was finally converted to the desired rod **349** via Pd-catalyzed Sonogashira coupling with trimethylsilylacetylene and subsequent deprotection.

Properties. Compound **349** was isolated as an air stable white solid with a UV−visible absorption maximum at 353 nm due to the $\pi-\pi^*$ transition of the terfluorene unit. In the fluorescence spectrum, **349** displays the typical vibronic pattern of oligofluorenes with maxima at 400, 422, and 447 nm.[337]

10.6. Benzene/Cyclopentadienyl Complex

Setayesh and Bunz[338] synthesized the mono- and bis(biphenylylated) cymantrenes **353** and **354** as model compounds and monomers for the corresponding polymers (Scheme 121).

Scheme 121[a]



[a] Conditions and reagents: (a) Biphenylboronic acid, $PdCl_2(dppf)$, THF, H_2O, Na_2CO_3. (b) *p*-Phenylenediboronic acid, $Pd(PPh_3)_4$, $NaHCO_3$.

10.7. Benzene/Oxadiazole

10.7.1. Synthesis

A rod **355** (Chart 10) consisting of alternating phenylene and oxadiazole modules was prepared by Peng et al.[339] from triethyl benzene-1,3,5-tricarboxylate in three steps and a moderate yield. After conversion of the two lateral alkoxy groups on the central benzene ring to vinyl groups,[340] the resulting building block **356** (Chart 10) was polymerized to a poly(*p*-phenylenevinylene).

10.8. Benzene/Thiophene

In an effort to fine tune the electronic band gap of polythiophene and to create materials with improved electron transport properties in polymer-based devices, several oligomeric model systems based on alternating benzene and thiophene modules were reported in recent years.

10.8.1. Synthesis

Tilley and co-workers[341] developed a versatile strategy for the synthesis of alternating phenylene−thiophene oligomers and their derivatives, based on the zirconocene coupling of diynes (Scheme 122). Unsymmetrical diynes were coupled with aryl halides in repetitive sequences to obtain extended propylene-bridged diethynylbenzene chains. Conversion to the corresponding zirconacyclopentadiene derivatives **357** was achieved by zirconocene coupling according to the Negishi method. Further transformation in situ yielded alternating phenylene−thiophene ([***n***]**358**) and phenylene-thiophene-1-oxide ([***n***]**359**) oligomers up to the pentamer in one step by treatment with S_2Cl_2 and SO_2, respectively. Both steps are very efficient. Oxidation of [***n***]**359** gives rise to structures comprised of phenylene-thiophene-1,1-dioxide units.[342]

10.8.2. Properties

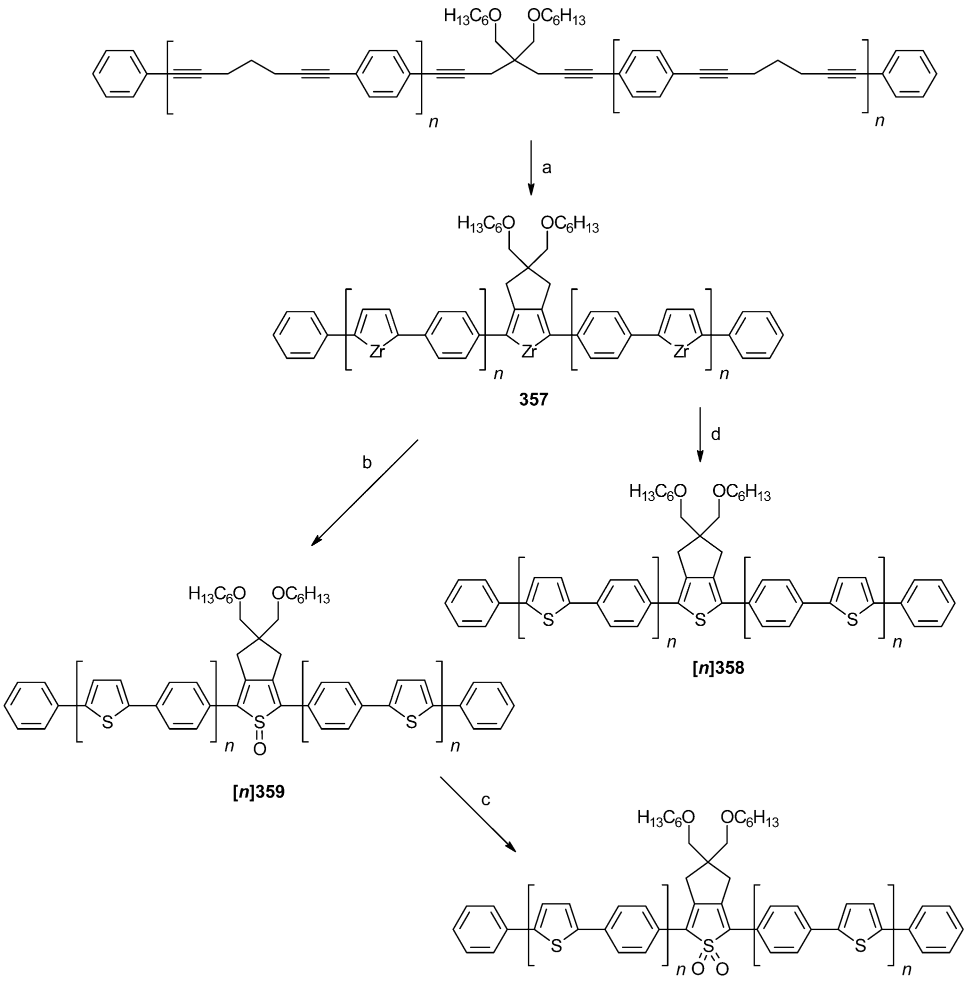
All isolated compounds [***n***]**358** and [***n***]**359** are air and thermally stable solids.[342] A single crystal X-ray structure of the phenylene−thiophene trimer [**3**]**358** revealed coplanarity between the inner phenylene and thiophene rings while the terminal phenyl rings were twisted by 31 and 28°, respectively, with respect to the central benzene unit.[341] The absorption maxima of the oligomers [***n***]**358** and [***n***]**359** show a significant red shift as the oligomer chain is extended. The optical band gaps deduced from the absorption edges converge smoothly. Values of about 15−20 rings were estimated for the conjugation length in the polymer, in agreement with the results published for polythiophene. The analysis of the band gaps both from the absorption measurements and from cyclic voltammetry allows a comparison of the effective delocalization along the oligomeric backbone.[341] The phenylene-thiophene-1-oxide [***n***]**359** has the lowest band gap, followed by the dioxide derivative and the phenylene−thiophene [***n***]**358**, reflecting the higher conjugation for diene structures as compared to aromatic structures and the higher planarity of the thiophene-1-oxide relative to the corresponding sulfone.[342] The narrow band gaps and high electron affinities are of vital importance for the creation of efficient electron-transporting materials.

10.9. Benzene/Ethyne/Thiophene

10.9.1. Synthesis

Huang and Tour[343] published the synthesis of alternating block co-oligomers **360** consisting of oligo(*p*-phenyleneethynylene)s and oligo(2,5-thiopheneethynylene)s using a newly developed divergent/convergent solid support methodology in nine steps, with an overall yield of 21% (Scheme 123). 1,4-Diiodo-2,5-di(5′-hydroxypentyl)benzene was attached to a dihydropyran-modified Merrifield resin through the hydroxy group and extended in both directions by stepwise treatment with 1-ethynyl-4-(trimethylsilyl-

Scheme 122[a]



[a] Conditions and reagents: (a) "Cp_2Zr". (b) SO_2. (c) *m*-CPBA. (d) S_2Cl_2.

ethynyl)benzene and, after desilylation, with 2,5-didodecyl-1,4-diiodobenzene in order to produce a polymer-supported pentamer **361**. After treatment with trimethylsilylacetylene and desilylation, compound **361** was cross-coupled with the oligo(thiophene-ethynylene) tetramer **362** yielding the triblock 21-mer **363**. Repetition of this methodology with the free oligo(phenylene ethynylene) pentamer **364** led to the desired ABABA block 23-mer **360**, which was easily cleaved from the resin and measures 160 Å along its extended backbone (Scheme 123).[343] Because two terminal iodine moieties remain in the molecule, further elongation appears possible.

10.9.2. Properties

The block copolymers such as **360** were isolated as air stable yellow solids after cleavage from the resin.[343] The longest rod **360** displayed sufficient solubility in halogenated organic solvents and THF to be spectroscopically characterized. Both the optical absorption and the emission showed a superposition of the spectra of the individual block units.[343]

10.10. Benzene/Ethyne/Silole

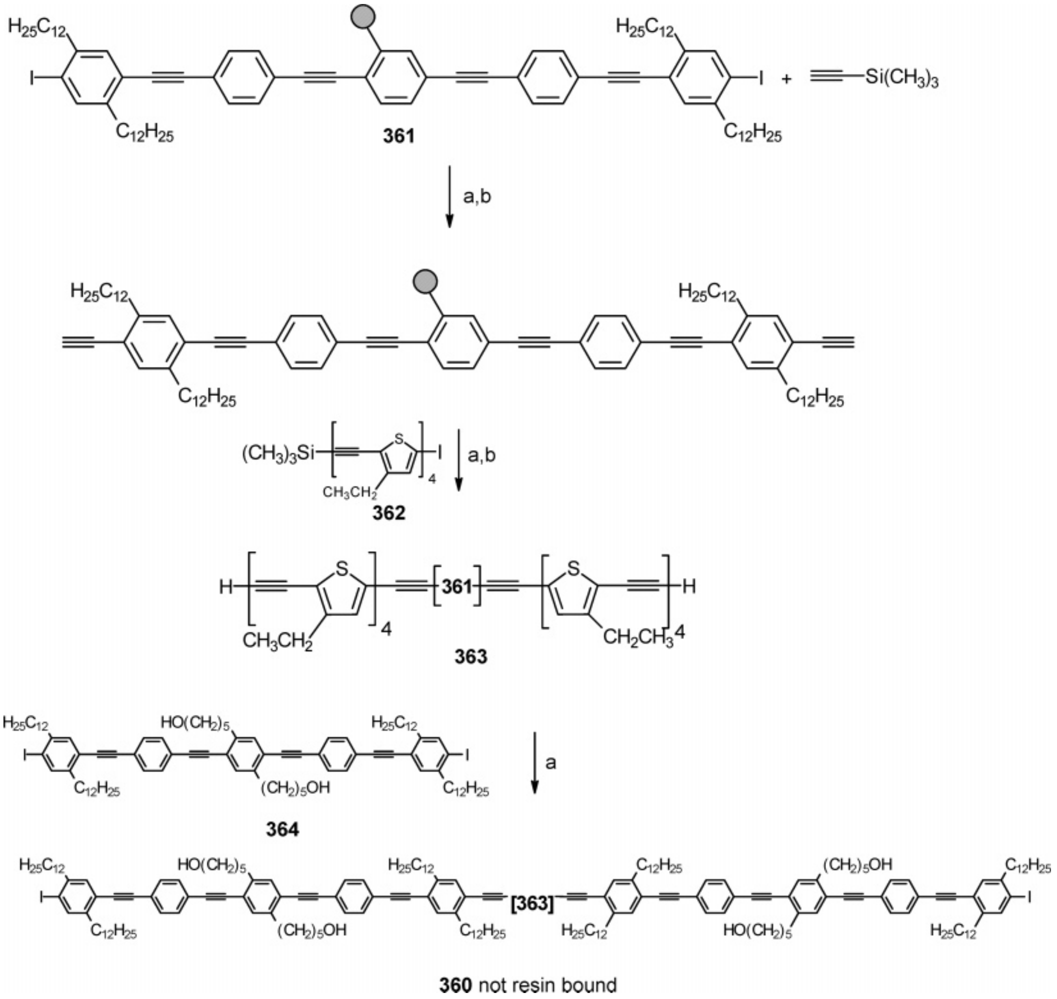
10.10.1. Synthesis

Relying on their recently developed efficient methodology[344] for the preparation of mixed halo siloles and their optimized in situ regiospecific cross-coupling with terminal alkynes, Boydston et al.[345] assembled a novel series of conjugated siloleneethynylene co-oligomers [***n***]**365** up to the pentamer. Chloroiodosilole **366** was selectively cross-coupled with phenylacetylene in order to obtain the key building block **367**. The longer end-capping unit **368** was prepared from **367** in three steps. Subsequently, the even-numbered rods [**2**]**365** and [**4**]**365** were prepared by treatment of **367** and **368** with *p*-diethynylbenzene under Pd catalysis, respectively (Schemes 124 and 125). For the assembly of the odd-numbered species, a central bridging unit **369** was synthesized. The longest rod [**5**]**365** was obtained in good yield by the coupling of **369** with **368** again under Negishi conditions (Scheme 126).

10.10.2. Properties

The co-oligomers [***n***]**365** are stable orange-red to red powders that can be purified by crystallization. Up to the trimer [**3**]**365**, they display good solubility in common organic solvents. The higher oligomers are considerably less soluble.[345] UV−visible absorption spectra suggest that the effective conjugation length of the compound class is reached at the tetrameric stage. The compounds have very high extinction coefficients, and the molar absorptivity increases linearly with the number of silole rings. The value

Scheme 123[a]



[a] Conditions and reagents: (a) $Pd(dba)_2$, PPh_3, CuI, Et_2NH, THF. (b) TBAF, THF.

for the pentamer [**5**]**365** reaches 190000 M^{-1} cm^{-1}.[345] As compared to nonsilole containing OPEs, the absorption maxima of the chromophores [***n***]**365** are shifted by more than 100 nm to the red if the total number of rings is the basis for the comparison.[345]

10.11. Pyridine/Thiophene

10.11.1. Synthesis

The pyridine/thiophene oligomers [***n***]**370**, termed thionoviologens, were reported by Nakajima et al.[346] and Albers et al.[347] (Scheme 127). The former group used a Busch type reaction, involving catalytic palladium amalgam in the presence of hydrazine. The latter group prepared molecules **370** with up to five thiophene units using the cross-coupling reactions of organozinc reagents with haloarenes under Pd catalysis. Modifications on the terminal pyridyl group included complexation to various transition metals and alkylation with methyl iodide to the viologen-like bispyridinium salt **371**. The oligomers were coated onto octadecanethiol-coated gold electrodes in order to investigate their potential as molecular wires in biological systems. In this context, insertion of the pyridine moiety into a redox protein is desirable.[348]

10.11.2. Properties

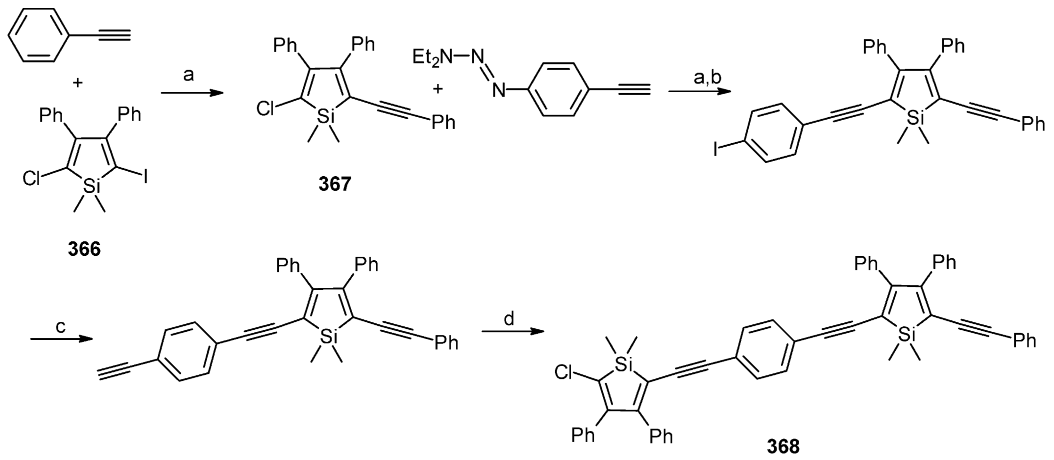
The compounds [***n***]**370** are chemically and physically very stable. The shortest members with one thiophene unit form stable radical monocations with strong NIR absorptions. The oligomers are highly fluorescent. Because of their electrochromic properties, they might be of interest as optoelectronic materials.[349]

10.12. Ethyne/Pyridine/Thiophene

10.12.1. Synthesis

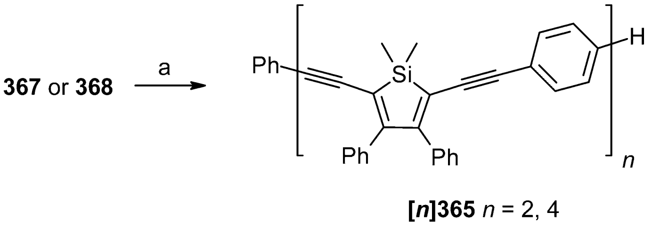
De Nicola et al.[350] have developed a new one-pot method for the synthesis of 2,5-diethynyl-3,4-dibutylthiophene bridged bipyridine derivatives (Scheme 128). The dimer **372** was prepared in respectable yield from 5-bromo-2,2′-bipyridine and 2,5-diethynyl-3,4-dibutylthiophene activated by in situ double deprotection. Under similar conditions, 1-iodo-5-ethynyl-3,4-dibutylthiophene (**373**), 5-ethynyl-2,2′-bipyridine (**374**), and 5,5′-dibromo-2,2′-bipyridine (**375**) were coupled in one step to form the trimer **376** in moderate yield. The respective Ru(II) complexes, such as **377**, were obtained by treatment with the appropriate equivalents of $[Ru(bipy)_2Cl_2]$.[350]

Scheme 124[a]



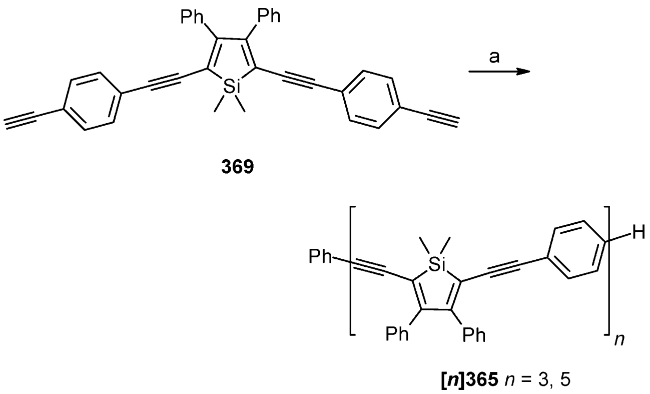
[a] Conditions and reagents: (a) $Pd(PPh_3)_4$, $ZnCl_2$, Et_3N, THF. (b) CH_3I, 105 °C, sealed tube. (c) Ethynylmagnesium bromide, $Pd(PPh_3)_4$, THF. (d) Compound **366**, $Pd(PPh_3)_4$, $ZnCl_2$, Et_3N, THF.

Scheme 125[a]



[a] Conditions and reagents: (a) 1,4-Diethynylbenzene, $Pd(PPh_3)_4$, $ZnCl_2$, Et_3N, THF.

Scheme 126[a]



[a] Conditions and reagents: (a) Compound **367** or **368**, $Pd(PPh_3)_4$, $ZnCl_2$, Et_3N, THF.

10.12.2. Properties

CVs of the Ru complexes **377** display the expected typical single one-electron oxidation wave from Ru(II) to Ru(III). The bipy units become easier to reduce with increasing substitution.[350] All complexes exhibit a strong $\pi-\pi^*$ transition in the 360–425 nm range, whose intensity increases with the chain length, and a weaker metal-to-ligand charge transfer band between 460 and 500 nm. The emission bands of the compounds **377** that are photoluminescent at room temperature are red-shifted with respect to $[Ru(bipy)_3]^{2+}$.[350]

10.13. Pyridine/Other

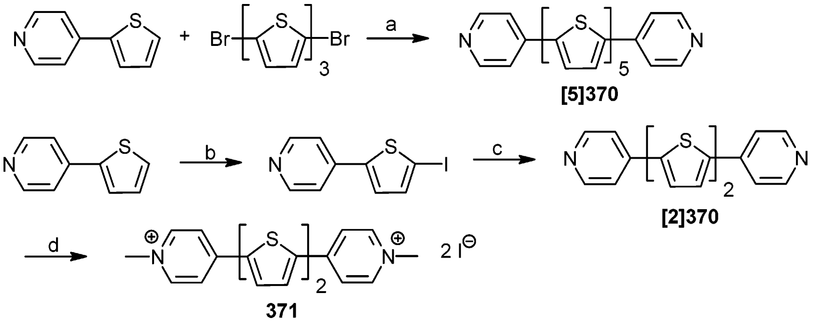
10.13.1. Synthesis

5,5′-Bis(2-pyridyl)-3,3′-bi(1,2,4-triazole) (**378**) was prepared from 2-cyanopyridine in three steps (Scheme 129).[351] Launay and co-workers[269] reported furan- and thiophene-containing rods capped with two 4-pyridyl substituents.

10.13.2. Properties

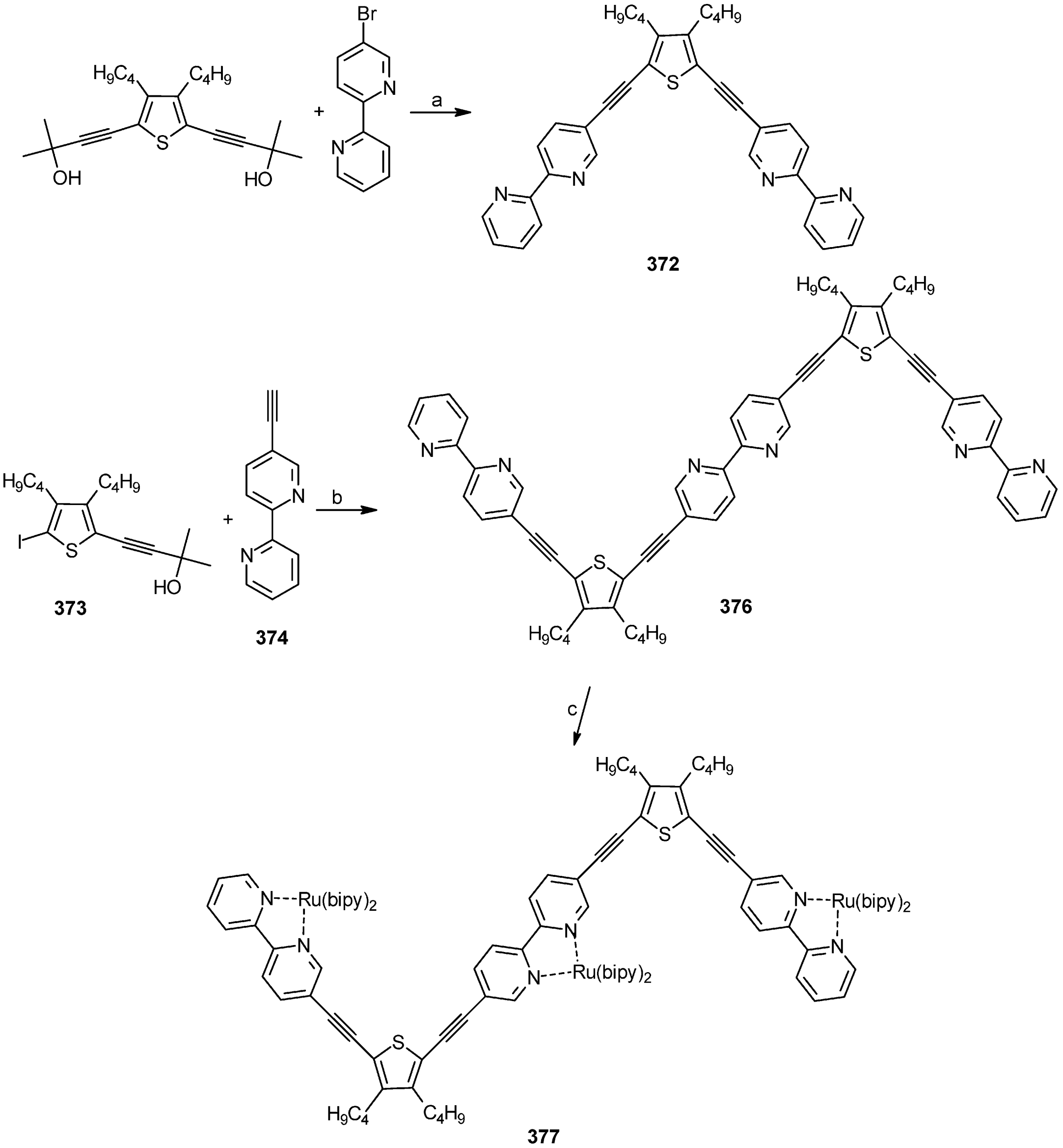
Compound **378** is thermally very stable and does not melt below 300 °C. It is capable of chelating up to four metal centers.[351] The mono-, bi-, and trinuclear complexes **379** with Ru(II) have been characterized and investigated. These arrays were also partially oxidized.

Scheme 127[a]



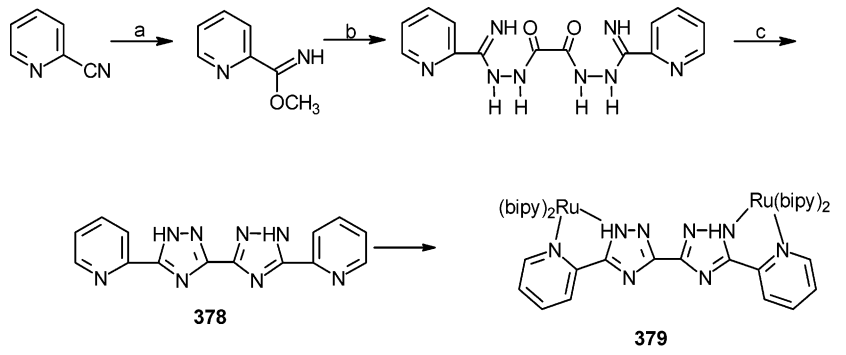
[a] Conditions and reagents: (a) (1) BuLi; (2) $ZnCl_2$, Pd(dppf). (b) $HIO_3/2H_2O$, I_2, 80% AcOH. (c) N_2H_4/H_2O, PdHg, NaOH, 50% CH_3OH. (d) CH_3I, CH_2Cl_2.

Scheme 128[a]



[a] Conditions and reagents: (a) Et_3BzNCl, $Pd(PPh_3)_4$, CuI, benzene, NaOH(aq). (b) Same as a and 5,5′-dibromo-2,2′-bipyridine (**375**). (c) $[Ru(bipy)_2Cl_2]$.

Scheme 129[a]

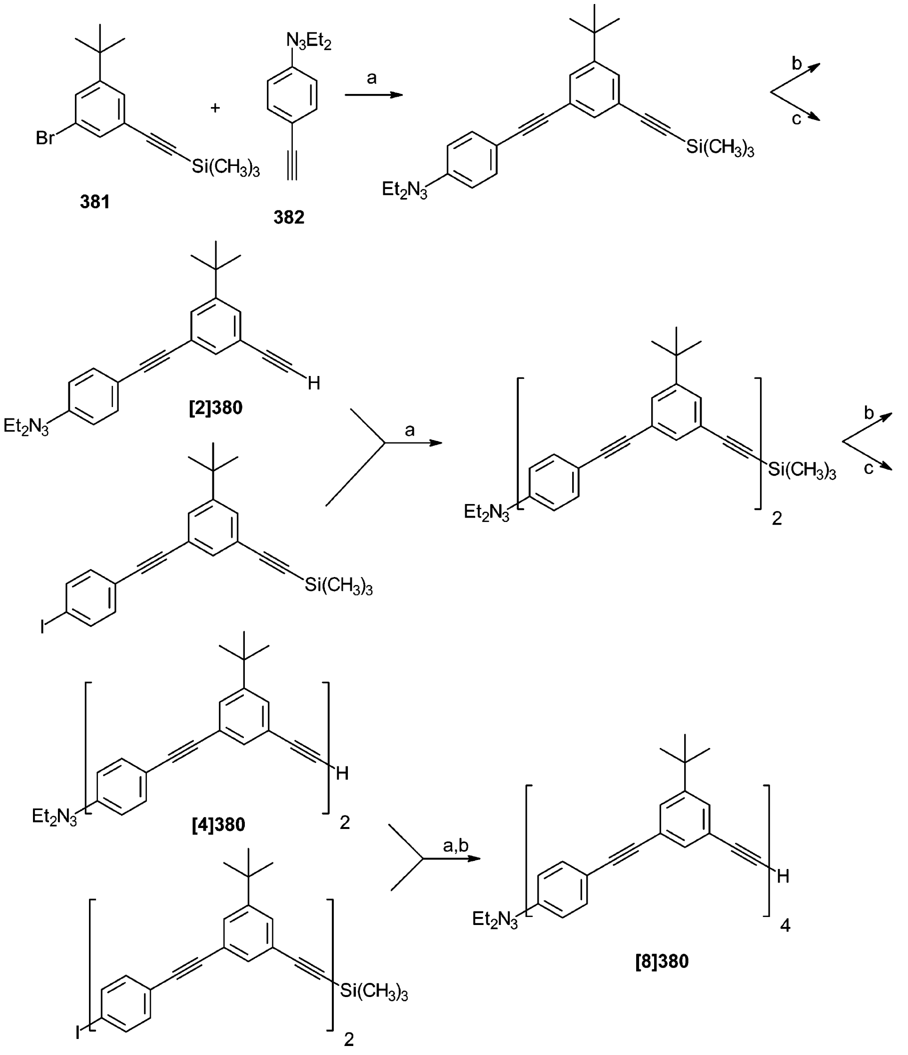


[a] Conditions and reagents: (a) CH_3OH, CH_3ONa (cat.). (b) $NH_2NHCOCONHNH_2$, AcOH (cat.). (c) 250 °C.

11. Axial Rods with Zig-Zag Connectivity

Six-membered aromatic rings can be used as axial modules when they are linked in para-positions. However, they can also be linked in meta- or ortho-positions, in which case they act as zig-zag modules, and the present section treats the resulting oligomers.

Scheme 130[a]



[a] Conditions and reagents: (a) Pd(dba), CuI, PPh_3, Et_3N. (b) CH_3OH, CH_2Cl_2, K_2CO_3. (c) CH_3I.

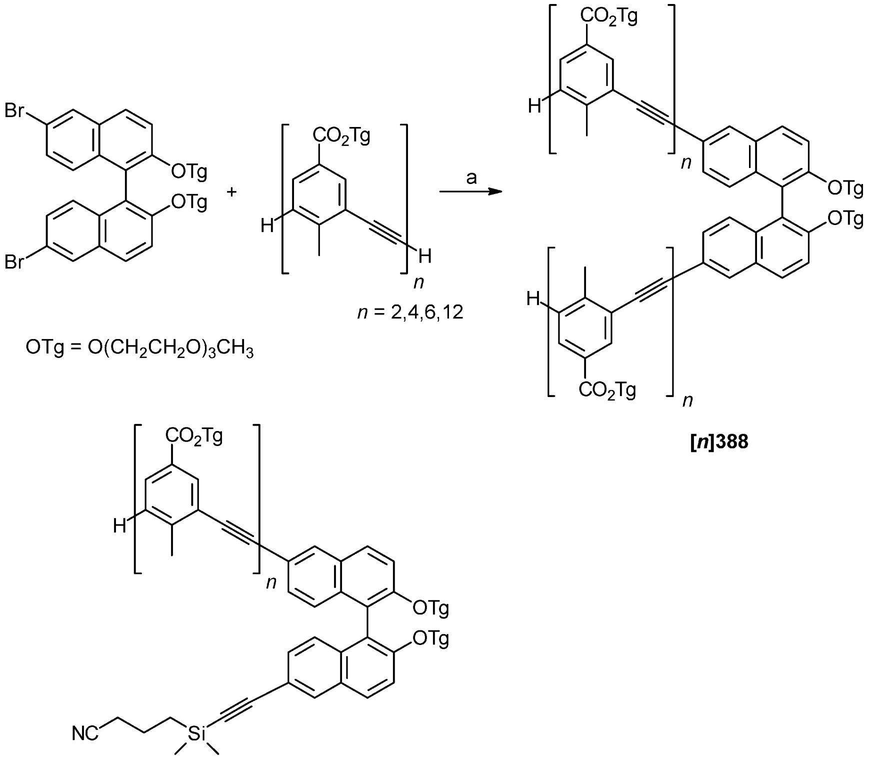
11.1. Benzene/Ethyne

Co-oligomers of benzene and ethyne modules with para connectivity were described thoroughly in Part 1.[5] Similar phenylacetylene sequences can be constructed by connecting the modules through the meta- or ortho-positions of the benzene units, and at least on paper, zig-zag rods are created. However, because the barrier for the internal rotation of diphenylacetylene is only ~0.6 kcal/mol,[352] simple ortho and meta oligomers presumably adopt random conformations in solution. Clearly, the loss of axiality is accompanied by an increase of flexibility and additional degrees of rotational freedom that severely puts into question their classification as rodlike molecules. Nonetheless, because of the fact that they are frequently shown and referred to as linear arrays and that there might be ways to rigidify them in a unidirectional way, as will be shown below, this substance class was considered worthy of inclusion in this review.

11.1.1. Meta

Synthesis. Moore's group[353,354] developed a stepwise, convergent methodology for the preparation of linear phenylacetylene sequences [***n***]**380** based on 1,3-substituted benzene modules (Scheme 130). The crucial basis for this effective approach was the employment of two independent yet complementary protecting groups for the terminal acetylene and aryl iodide, respectively, which can be selectively removed in each other's presence and which are both stable under the cross-coupling conditions. Pd-catalyzed cross-coupling of the trimethylsilyl-protected aryl bromide **381** with the 3,3-diethyltriazine-substituted ethynylbenzene **382** yielded a monomer that was further elaborated into the dimer [**2**]**380**, whose protecting groups were selectively removed. To complete the sequence, the two resulting compounds were cross-coupled, effectively doubling the rod length to the tetramer [**4**]**380**. After the procedure is repeated n times, the resulting array has a length of 2^n units. The longest rod characterizable with only *tert*-butyl substituents as solubilizing groups proved to be the 16-mer [**16**]**380**. Parallel repetitive cycles could be merged to obtain chain lengths other than 2^n units or to vary the substitution pattern along the backbone. The compatibility of the methodology with a wide variety of functional groups is noteworthy as well. Following the same basic recipe, Moore's group[355−358] synthesized several homologous series of

Scheme 131[a]



[*n*]387

[a] Conditions and reagents: (a) $Pd(dba)_2$, CuI, PPh_3, Et_3N, CH_3CN.

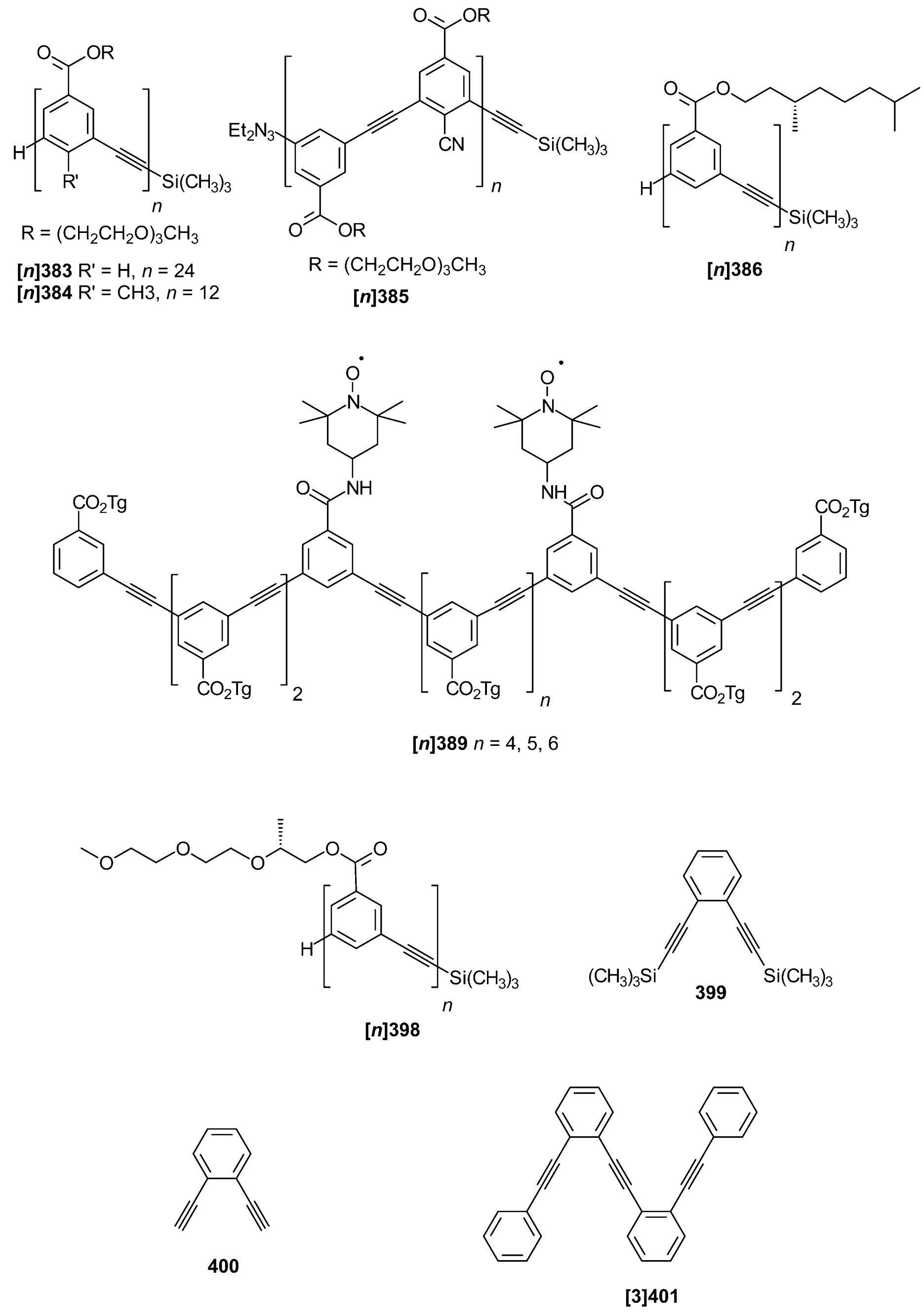
oligo(*m*-phenyleneethynylene)s with tri(ethylene glycol) monomethyl ether side chains [***n***]**383** (Chart 11) up to the 24-mer,[359,360] and with additional methyl substituents [***n***]**384**[360] or cyano groups [***n***]**385** up to the octadecamers,[362] as well as with the nonpolar, chiral (*S*)-3,7-dimethyl-1-octanoxy side chains [***n***]**386** (Chart 11).[363] Furthermore, two sets of tri(ethylene glycol) monomethyl ether and methyl-substituted OPEs with perturbations were prepared by Pd-catalyzed coupling reactions with bromobinaphthol derivatives, one ([***n***]**387**) up to the dodecamer with the binaphthol moiety at the end, and another ([***n***]**388)** up to the 24-mer with the binaphthol unit in the center (Scheme 131).[361] Recently, three arrays [***n***]**389** up to the dodecamer were reported with two nitroxide spin labels attached to the backbone at various distances from each other (Chart 11).[361]

A very interesting evolution of the concept was presented by Gong's group[364] who rigidified the oligo(*m*-phenylene ethynylene) backbone using intramolecular hydrogen bonds (Scheme 132). From methyl 3-nitrobenzoate, two ester-amide-substituted monomers **390** and **391** were synthesized in several steps and used to build up the desired rods [***n***]**392** up to the heptamer following the known divergent−convergent methodology.

Very recently, Sugiura et al.[365] reported the synthesis of a series of acyclic ethynylhelicene oligomers [***n***]**393** up to the nonamer using a two-directional method. For the odd-numbered members, the silylated trimer **394**[366] was deprotected and coupled with 2 equiv of the helicene building block **395**, yielding the pentamer [**5**]**393** in excellent yield. Repetition of the sequence produced the heptamer [**7**]**393** and nonamer [**9**]**393**, respectively. For the even-numbered series, the monosilylated helicene **396** was coupled with the ditriflate **397** to obtain the dimer [**2**]**393**. Repetitive application of the desilylation/coupling routine afforded the tetramer, hexamer, and octamer (Scheme 133).

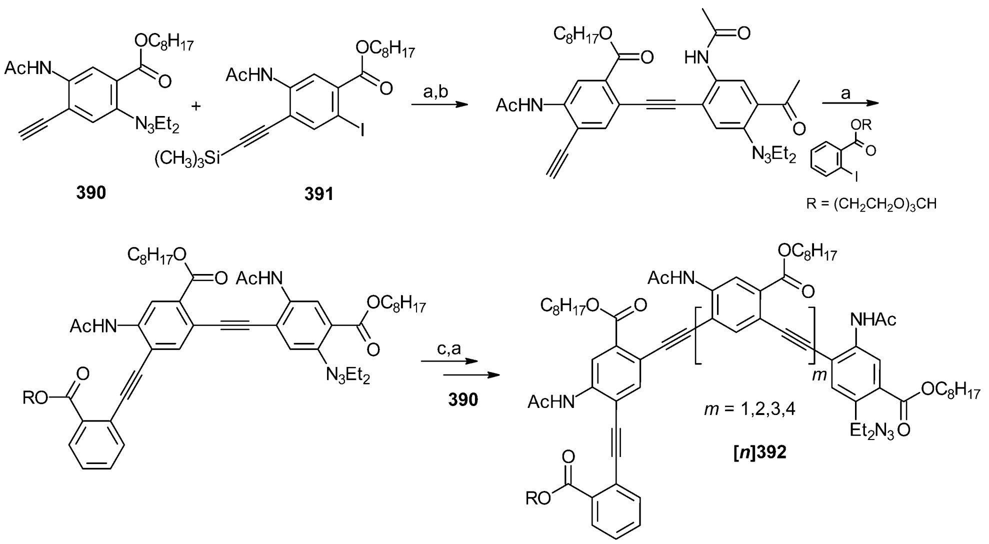
Properties. All oligo(*m*-phenyleneethynylene)s [***n***]-**380** are air stable solids or waxes at room temperature. Their solubility strongly depends on the nature of the peripheral substituents. Rods with ethylene glycol-based side chains [***n***]**383** (Chart 11) were soluble in both nonpolar and polar solvents and even in water. Their conformational behavior was investigated and showed a strong dependence on solvent polarity and chain length. In nonpolar solvents, the intensity of the fluorescence emission increased gradually as expected with each additional phenyleneethynylene unit, suggesting random orientations as a mixture of transoid and cisoid states. In polar solvents, however, efficient fluorescence quenching was observed for rods with more than eight repeating units, indicating π stacking. Along with circular dichroism spectra, these results were used to propose a self-assembly of the oligomers into helical columns. The stability of this ordered state increased with the chain length. Nonpolar side chain-carrying oligomers [***n***]**386** (Chart 11) longer than the decamer could be forced into the helical structure in apolar solvents, such as heptane. Here, the aromatic backbone becomes sufficiently polar relative to the periphery, even though the structural amphiphilicity is less distinct. In addition, the possible control of the bias of the helical twist was thoroughly investigated. Incorporation of chiral modules, such as binaphthol

Chart 11



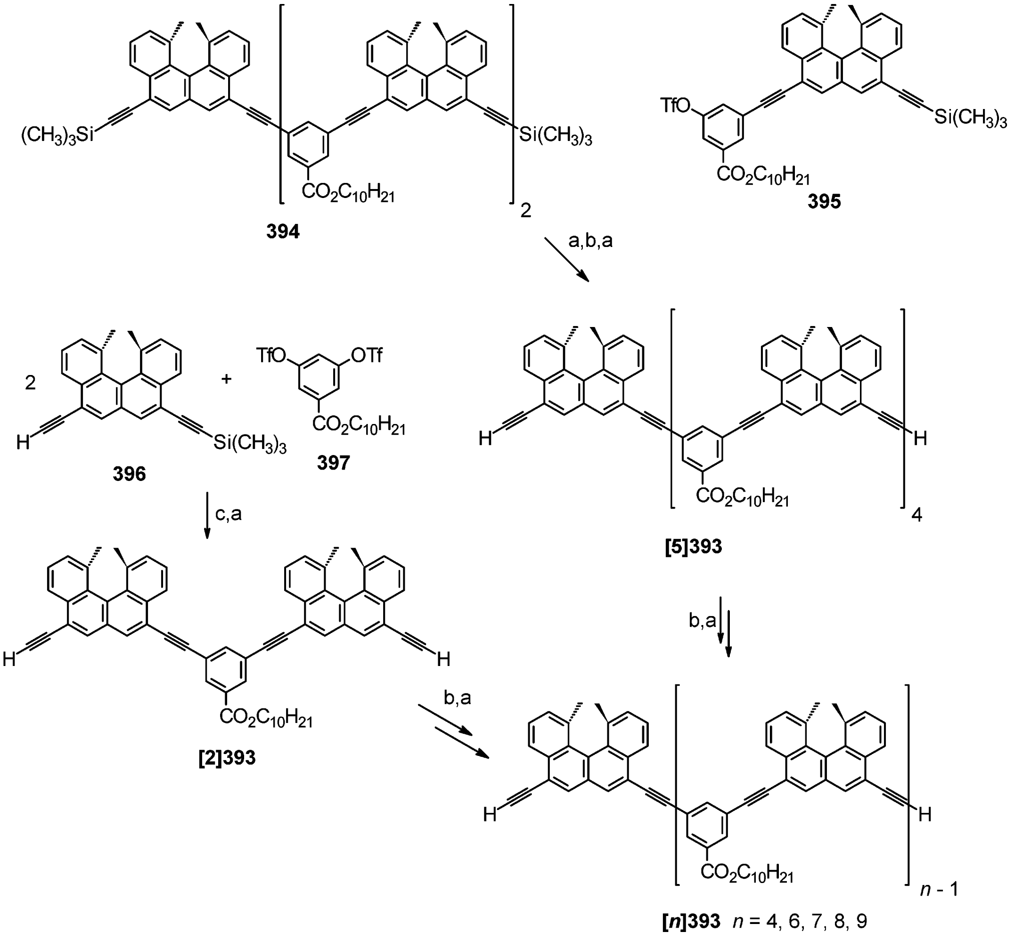
units in [***n***]**387** and [***n***]**388** (Scheme 131) into the backbone induced chirality in the molecule as desired.[361] However, the system was destabilized by this large distortion. The introduction of a small chiral perturbation into the polyether side chains, as in [***n***]**398** (Chart 11), was sufficient to flip the sense of the helical twist without disrupting the equilibrium of the structure.[367] The direction of the helix could be changed upon complexation with chiral guest molecules, such as α-pinene.[368] Because of poor crystallinity, characterization of the solid state proved challenging. The oligomers [***n***]**383** (Chart 11) with triethylene glycol ester-linked side chains are viscoelastic waxy solids at room temperature with birefringent textures that reversibly melt into isotropic fluids at higher temperatures.[359] Increasing chain length was accompanied by an asymptotic rise in the melting point indicating a homologous mode of packing. X-ray studies indicated a lamellar solid state order.[359] The introduction of a methyl group into the backbone as in [***n***]**384** (Chart 11) results in a hexagonal arrangement of helical nanotubules in the solid state.[369] The spin-labeled derivatives [***n***]**389**[370] (Chart 11) showed the same solvent-dependent conformational behavior. Therefore, in polar solvents, the spatial proximity of the radicals as judged from the line broadening in the EPR spectrum could be utilized to determine that six repeating units likely constitute one helical turn as would be expected for a hexagonal helical structure.[364] The rigidified oligomers [***n***]**392** created by Gong and co-workers (Scheme 132) overcame the solvent dependence of helix formation. Even in nonpolar solvents, the pentamer, hexamer, and heptamer folded into the helical confor-

Scheme 132^a



^{a} Conditions and reagents: (a) Pd(dba)$_2$, PPh$_3$, CuI, Et$_3$N. (b) K$_2$CO$_3$, CH$_3$OH. (c) CH$_3$I.

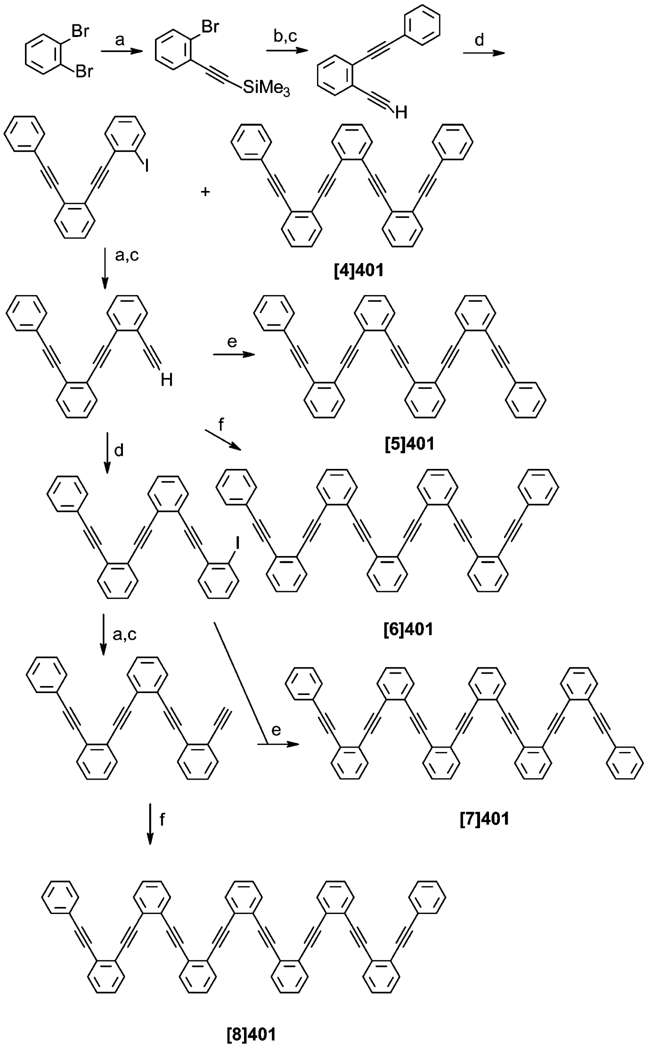
Scheme 133^a



^{a} Conditions and reagents: (a) Bu$_4$NF, THF. (b) Two equiv **395**, Pd$_2$(dba)$_3$, CHCl$_3$, CuI, Mes$_3$P, Ph$_3$P, Bu$_4$NI, Et$_3$N, DMF, toluene (or THF). (c) Pd$_2$(dba)$_3$, CHCl$_3$, CuI, Mes$_3$P, Ph$_3$P, Bu$_4$NI, Et$_3$N, DMF.

mation. The ability to purposefully design stable unnatural oligomeric structures with predefined cavity sizes is an important advance toward complex artificial molecular architectures. Among the ethynylhelicene oligomers [***n***]**393**, the species with more than six helicene units adopt highly ordered helical and dimeric structures in solution, while the shorter ones form a random coil structure in solution. The heptamer [**7**]**393** gradually unfolds to a random coil structure with the rate constant of this conformational change showing a strong dependence on the hardness and softness of the aromatic solvents.[365] In addition, a theoretical study has very recently examined computational methods for the precise pre-

Scheme 134[a]



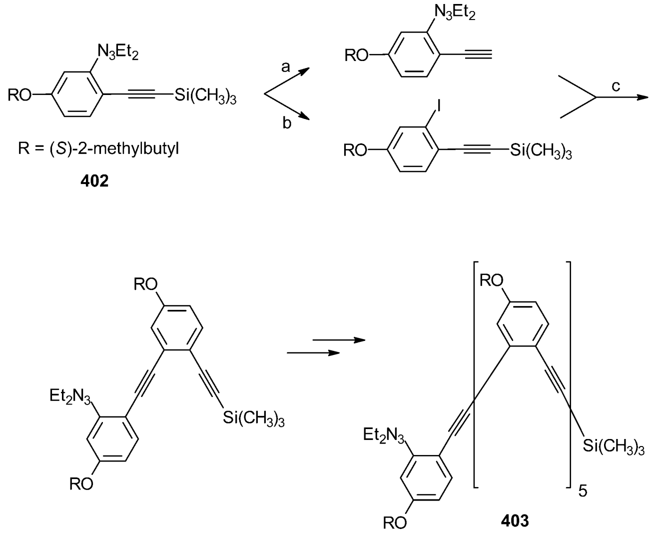
[a] Conditions and reagents: (a) TMS−acetylene, $Pd(PPh_3)_4/CuI$, Et_3N. (b) Phenylacetylene, $Pd(PPh_3)_4/CuI$, Et_3N. (c) $KF/DMF/H_2O$. (d) 1,2-Diiodobenzene (2 equiv), $Pd(PPh_3)_4/CuI$, Et_3N. (e) $Pd(PPh_3)_4/CuI$, Et_3N. (f) 1,2-Diiodobenzene $Pd(PPh_3)_4/CuI$, Et_3N.

diction of the helical structure in substituted phenylene ethynylene oligomers.[371] For further details on this topic, we recommend an excellent review on foldamers.[372]

11.1.2. Ortho

Synthesis. The ortho isomers of OPEs have received much less attention than their para and meta counterparts.[373,374] While the two shortest homologues **399**[375] and **400**[376] (Chart 11) have been known for quite some time, Grubbs and Kratz[377] undertook the first systematic investigation of the unsubstituted oligomers only a decade ago. Starting from 1,2-dibromobenzene, a step-by-step methodology was used to assemble a series up to the octamer [**8**]**401** employing standard Pd-catalyzed coupling conditions between terminal acetylenes and aryl halides (Scheme 134). A strategy involving protecting group chemistry was avoided by adjusting the ratios of the diiodobenzene to the terminal acetylenes and separating the mono- and disubstituted products from the reaction mixture by column chromatography. While such an approach limits the number of reaction steps, it appears laborious in the workup and does not provide opportunities for a targeted upscaling of individual components.

Scheme 135[a]

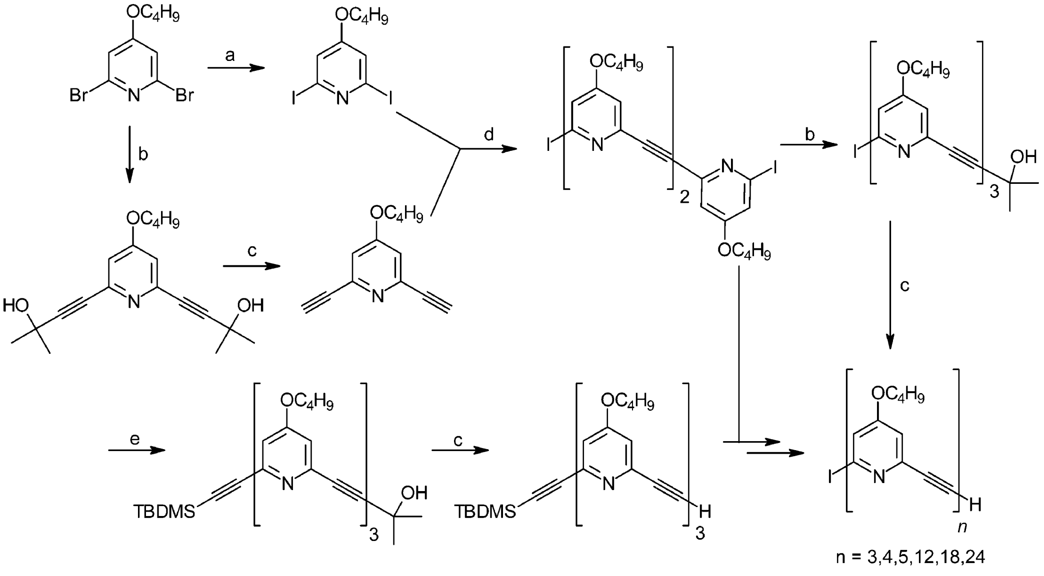


[a] Conditions and reagents: (a) K_2CO_3, CH_3OH. (b) CH_3I, 110 °C. (c) $Pd(dba)_2$, PPh_3, CuI, NEt_3.

Very recently, Tew and co-workers[378] have reported the first synthesis of alkoxy-substituted *o*-phenyleneethynylene derivatives up to the hexamer applying the same convergent/divergent methodology that was described above for the meta isomers. From the key monomer **402** accessible in five steps and carrying both the diethyltriazine and the trimethylsilyl protecting groups, a cycle of acetylene deprotection and triazine activation was initiated in order to produce the desired oligomers [***n***]**403** (Scheme 135). It is noteworthy that the reactions proceed in very good yields despite the close proximity of the triazine and acetylene functionalities. In addition, the convergent synthesis and coupling of two appropriate trimer molecules yielded the hexamer [**6**]**403**.

Properties. All of the oligomers [***n***]**401** are crystalline white solids with good solubilities in benzene and chlorinated hydrocarbons.[377] In addition, the ether-substituted derivatives [***n***]**403** dissolve well in THF, ethyl acetate, and hexanes.[378] The thermal analysis of the parent series [***n***]**401** (Scheme 134) showed a distinct melting point above 100 °C for chains up to the tetramer and a broader exothermic process, likely a conformational rearrangement, for the higher homologues. More interestingly, all oligomers revealed a sharp exothermic behavior around 300 °C indicative of a cyclization process, possibly forming derivatives of higher condensed benzenoid hydrocarbons.[377] Single X-ray crystal structures of the trimer [**3**]**401** (Chart 11) and tetramer [**4**]**401** (Scheme 134) illustrated some interesting features. Compound [**3**]**401** is oriented almost exactly the way it is drawn in the formula, with the triple bonds defining a nearly perfect plane and only the two terminal phenyl groups rotated in opposite directions. Compound [**4**]**401** shows a similar planar arrangement except for the final phenylethynyl unit, which instead of continuing the zig-zag mode folds back onto the second benzene ring into a helical topology that maximizes $\pi-\pi$ interactions.[377] The UV−visible ab-

Scheme 136[a]



n = 3,4,5,12,18,24

[*n*]404

[a] Conditions and reagents: (a) CuI, KI, DMF. (b) 2-Methyl-3-butyne-2-ol, $PdCl_2(PPh_3)_2$, CuI, Et_2NH. (c) NaH, toluene. (d) $Pd(dba)_3-CHCl_3$, PPh_3, CuI, $i$$Pr_2NH$. (e) ($t$-Butyldimethylsilyl)acetylene, $PdCl_2(PPh_3)_2$, CuI, $i$$Pr_2NH$.

sorption spectra in solution displayed the expected chain length dependence, with the absorption maximum of the octamer in the parent series [***n***]**401** (Scheme 134) reaching 388 nm. The extinction coefficient of the long-wavelength absorption, however, decreased in value for the longer oligomers. The absorption maxima of the ether-substituted analogues [***n***]**403** (Scheme 135) show very little length dependence[378] but display the three peak pattern of the diphenylacetylene chromophore.[379] In both series, fluorescence emissions exhibit a gradual subdued shift of the lowest energy transition around 400 nm toward longer wavelengths. While the trend is clear, the small differences between the higher oligomers point toward a limited number of effectively conjugated phenyleneethynylene units. Clearly, possible rotations around the sp–sp^2 bonds reduce long-range delocalization.[377]

11.2. Ethyne/Pyridine

11.2.1. Synthesis

To model the behavior of certain biopolymers that change from disordered to ordered conformational states upon noncovalent interaction with small molecules, a series of oligo(m-ethynylpyridine)s [***n***]**404** consisting of the 2-, 3-, 4-, 5-, 6-, 12-, 18-, and 24-mer was synthesized by Inouye et al.[380] utilizing Sonogashira coupling conditions (Scheme 136). 2,6-Dibromo-4-butoxypyridine was first converted to the corresponding diiodopyridine and then treated with various acetylene derivatives to obtain unsymmetrically substituted ethynylpyridine and iodoethynylpyridine modules. Systematic cross-coupling of these building blocks produced the desired zig-zag rods.

11.2.2. Properties

In halogenated organic solvents, oligo(m-pyridine-ethynylene)s [***n***]**404** exist in a disordered conformation.[380] However, UV–visible absorption measurements at low concentrations and fluorescence emission spectra reveal the presence of intramolecular π interactions for oligomers longer than 12 units as judged by the deviation from the linear increase of the molar extinction coefficient with the oligomer length and the appearance of a new, broad, featureless emission above 500 nm. In the presence of saccharides, especially β-glucosides, the oligomers starting from the octadecamer are induced into helical structures through uncharged hydrogen-bonding interactions.[380] The chirality of the saccharides that are enclosed in the inner sphere of the helix is thereby transferred to the supramolecular structure.

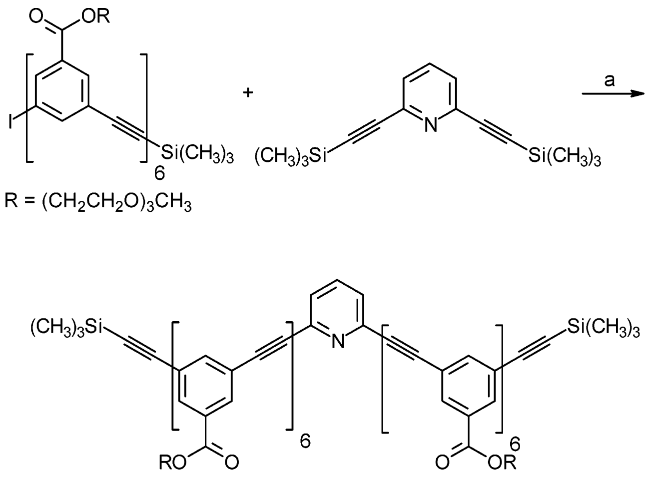
11.3. Benzene/Ethyne/Pyridine

11.3.1. Synthesis

Building on its rich experience with oligo(m-phenyleneethynylene)s, Moore's group[381] recently published an extension of their chemistry by incorporating pyridine modules into the backbone and therefore introducing a basic binding site into the system. For the synthesis, 2,6-diethynylpyridines with a variety of electron-donating and -withdrawing groups in position 4 were connected by a Pd-catalyzed Sonogashira cross-coupling to 2 equiv of the previously reported iodo-substituted m-phenyleneethynylene hexamer, thus generating the rods **405** (Scheme 137).

In a very recently published work, Orita et al.[382] reported the preparation of two enantiomeric rods (R)-**406** and (S)-**406** consisting of pyridine-containing phenylethynylene units connected to the 2- and 2′-positions of (R)- and (S)-1,1′-binaphthyl templates. The synthesis was accomplished using a convergent approach. The enantiomerically pure binaphthyl derivative (R)-**407** or (S)-**407** was coupled with the reactive iodobenzene **408** followed by a second Sonogashira coupling with the bromopyridine derivative **409** prepared in four steps from 2,5-dibromopyridine (Scheme 138). Similarly, extended rods (R)-**410** und

Scheme 137[a]



405

[a] Conditions and reagents: (a) (1) TBAF; (2) $Pd_2(dba)_3$, CuI, PPh_3, Et_3N, CH_3CN.

(*S*)-**410** containing an anthracene spacer were obtained (Scheme 139).

11.3.2. Properties

The inclusion of pyridine units in the backbone apparently did not disrupt the known folded conformation of the oligomer **405**.[381] Furthermore, the functionalization in pyridine position 4 allows for the modulation of the basicity of the binding site. A well-defined cavity inside the helix is created that might direct substrate binding and might act as an "artificial enzyme".[381] Strands **406** and **410** self-assembled with Ag(I) and Cu(I) ions to form enantiopure double helicates.[382]

11.4. Benzene/Naphthalene Bisimide

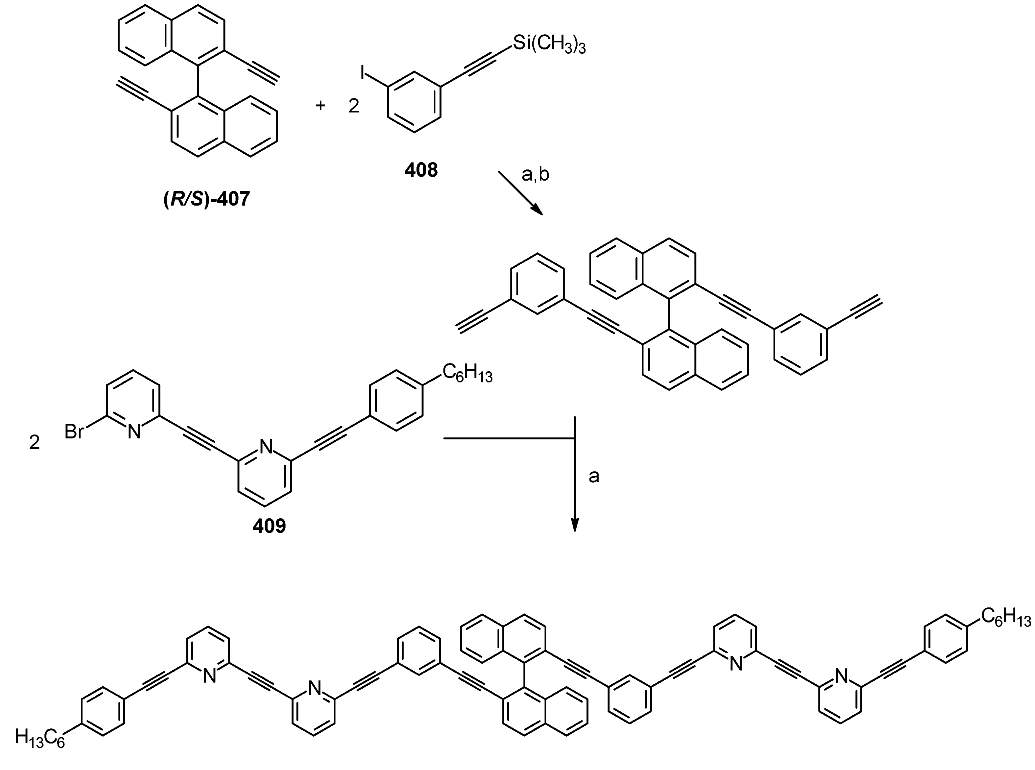
11.4.1. Synthesis

Shimizu's group[383] presented an interesting concept for the creation of materials with shape memory. On the basis of alternating benzene and naphthalene bisimide modules, zig-zag rods [***n***]**411** were assembled that are connected through $C_{aryl}-N_{imide}$ bonds with restricted rotation and therefore have two stable conformations. The rescricted rotation was accomplished by incorporation of octadecyl *ortho*-ethers on the benzene rings. The trimeric system [**3**]**411** was prepared in a stepwise fashion. The diamine **412** was obtained by condensation of *meta*-diaminobenzene **413** with 1,4,5,8-naphthalenetetracarboxylic dianhydride and was subsequently condensed with the monoanhydride **414** to produce [**3**]**411** (Scheme 140).[383]

11.4.2. Properties

In case of [**3**]**411**, the hindered rotation is restricted to the four bonds connecting the central bisimide unit with the rest of the molecule. As a result, two conformational isomers (*syn*[**3**]**411** and *anti*[**3**]**411**) exist, which were isolated by preparative TLC.[383] From the equilibration rates of the pure syn and anti isomers, a rotational barrier of about 27 kcal/mol was calculated. At higher temperatures, the formation of the anti isomer is preferred in nonpolar solvents in

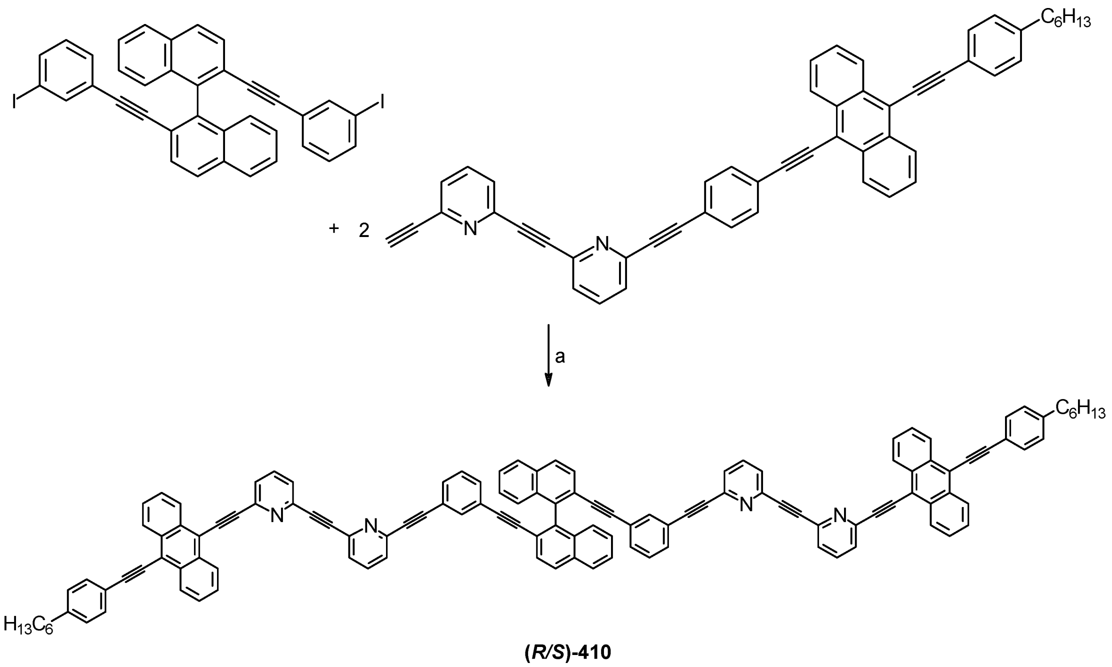
Scheme 138[a]



(*R*/*S*)-406

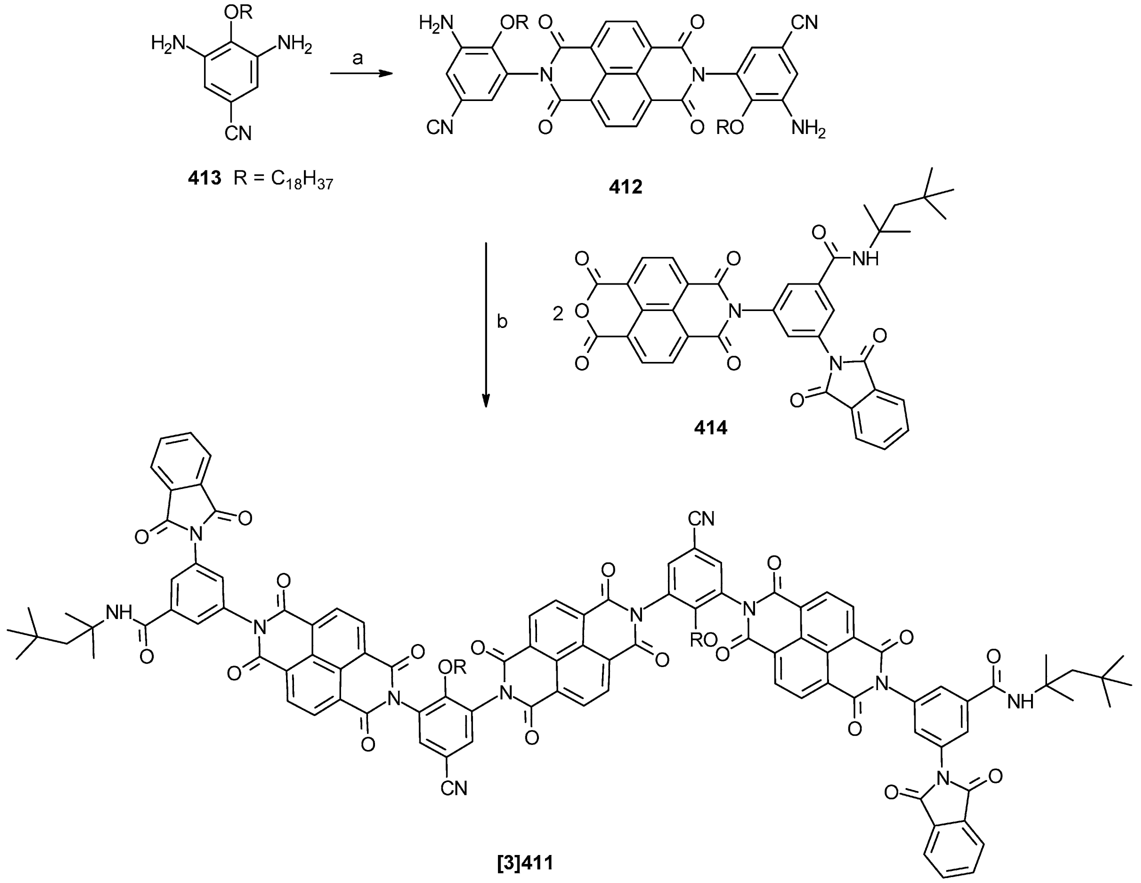
[a] Conditions and reagents: (a) $Pd(PPh_3)_4$, CuI, $i$$Pr_2NH$, toluene. (b) K_2CO_3, CH_3OH.

Scheme 139[a]



[a] Conditions and reagents: (a) $Pd(PPh_3)_4$, CuI, $i$$Pr_2NH$, toluene, THF.

Scheme 140[a]



[a] Conditions and reagents: (a) 0.5 equiv 1,4,5,8-naphthalenecarboxylic dianhydride, CH_2Cl_2. (b) CH_2Cl_2, then neat, 170 °C.

a 64:36 ratio, while the syn isomer is predominantly present in the solid state (35:65) after heating at 80 °C. On cooling, the conformational preferences are preserved, allowing for at least a partially controlled shaping of the molecule with a memory effect.[383]

12. Concluding Remarks

The research area reviewed here has seen a tremendous amount of activity over the past decade. Numerous rodlike oligomers have been synthesized and examined, and chemically pure rods of well-defined lengths of many nanometers that have been prepared would have been mind-boggling just a few years ago. It is difficult to review and summarize such a varied area in a balanced manner.

Two main points of focus stand out very clearly. On one hand, oligomers have been of interest as short chain models for specialty polymers. Here, the long-range goal is to enhance the understanding of the underlying structure−property relationships and to ultimately control and improve polymer properties. On the other hand, numerous oligomers have been prepared as functional building blocks for nanoscale architectures with specific and tunable properties.

For the first objective, the challenge is relatively simple and well defined. The oligomers need to be synthesized only for a study of specific properties, usually on a small scale. The synthesis usually does not exceed the laboratory scale. Synthetic efficiency and reproducibility are therefore of secondary importance, and a multistep reaction sequence or a tedious separation and purification of a complex oligodisperse mixture may be perfectly acceptable. Accordingly, progress is well visible and steady. Nonetheless, in many cases, basic information on fundamental properties such as the effective conjugation length is still missing or disputed. It has been shown that even small changes at the periphery of the oligomers, perhaps only introduced to improve solubility and processability of the longer rods, can have a profound impact on electronic properties, rendering comparisons difficult. These findings should be taken into consideration when data are extrapolated from oligomers to polymers.

Conjugation length seems to be a particularly difficult quantity to establish. If the rods were perfectly planar and homogeneous, one could simply look at the change in the electronic spectrum as a function of rod length and state that the conjugation length has been reached when the spectra have stopped changing. This is often exactly what is done, even though it need not be justified. If the rods are mixtures of conformers, because they are only approximately or not at all planar and the slight twists can be in-phase or out-of-phase at various locations or because they contain *s*-cis and *s*-trans links, the spectra may keep changing long after the effective conjugation length has been exceeded, simply because the chain end effects on the conformational composition have not yet converged.

For the second objective, the design and construction of nanoscale architectures, the use of rigid oligomeric rods goes beyond that of a modeling. Here, such arrays are an integral part of the final product and are ultimately needed in large, reliably available quantities. This demand requires that their syntheses be measured in terms of efficiency, practicability, upscalability, and cost. Now, an efficient synthetic strategy becomes a critical issue, at least when some application has been discovered and needs to be tested. While many of the reported examples display very clever synthetic pathways, most of them come up short in these categories. Standing out as the most promising and realistic approach for the synthesis of longer oligodisperse rods at this point clearly is the divergent/convergent methodology. However, because it requires very specific and compatible conditions for each step, such a procedure has only been developed for a few oligomeric families. More progress in this area is badly needed.

Another very interesting topic for discussion is the degree of intrinsic rigidity required of the building blocks needed for molecular architectures. The answer clearly depends on the application. Nobody would use cooked spaghetti to build a skyscraper nor favor a completely rigid extension cord for a home appliance. However, if the task is to bridge point A and point B with a molecule on the nanometer scale, the answer is less obvious. A rigid spacer clearly has fewer degrees of freedom and its effective length is better defined. However, a very floppy molecule could conceivably bridge two points more reliably, and perhaps a combination of the two types of structure would work best. In any event, a solution of this particular problem that does not involve self-assembly in some way or another is difficult to imagine.

If “truly rigid” molecules turn out to be required, at least for construction work on a nanometer scale, more effort is needed for their development. We have already mentioned that most molecules that one draws as a rigid straight line are far away from this state under realistic conditions, particularly as they get longer. Single strand molecules will hardly ever fulfill the requirement. Clever ways to bundle and thus rigidify molecules in a three-dimensional fashion will have to be devised, always keeping in mind the standard issues of solubility, processability, and end functionalization. Carbon nanotubes are only one example where progress is already apparent. They have other disadvantages, and it will be interesting to see whether molecules can keep pace.

Where do we go from here? The effort to find the best possible molecular rods for a particular function, such as an electron or hole-conducting molecular wire, will surely become more systematic after many of the basic questions have been answered and more reliable and easier methods for testing such particular functions have been developed. It may even involve some kind of high throughput approach. Ultimately, on the synthetic front, the challenges will be overcome.

With advances in synthesis and with a better availability of materials, the notion of whether well-defined oligomers can and should replace polydisperse polymers in specific cases could become very interesting. At least from the very limited knowledge of today, it appears that in certain applications such as thin film technology, monodispersity could provide decisive advantages.

However, the true challenges for the molecular approach to nanotechnology are more fundamental. What should we be building from the building blocks once we know how to produce them? Does it really make sense to rebuild the standard elements of today’s electronics, such as transistors, with molecules and to assemble them into a circuit? If so, how can the assembly take place fast, reliably, and cheaply? Also, how should the systems be connected to the outside world? Should they communicate directly with lithographically produced silicon nanostructures? Many open questions remain, and there are many opportunities for gifted scientists. Attempts to improve and use molecular rods will be with us for a long time to come.

13. Acknowledgment

The work was supported by the National Science Foundation (CHE 0140478).

14. References

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