

Functional acetylenic molecular architecture*

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Abstract: A diversity of perethynylated building blocks, in particular derivatives of tetraethynylethene (TEE, 3,4-diethynylhex-3-ene-1,5-diyne), were prepared for the construction of multinanometer-sized functional molecular objects. Macrocyclic acetylenic scaffolding yielded perethynylated antiaromatic octadecahydro[12]annulenes and aromatic dodecacyclo[18]annulenes as well as highly stable expanded radialenes with extended all-carbon cores. An attempted new synthesis of perethynylated octadecahydro[12]annulenes was unsuccessful and led to the isolation of a highly strained permethylenated cycloocta-1,5-diyne instead. Acyclic acetylenic scaffolding using both TEEs and 1,2-diethynylethenes (DEEs (*E*-hex-3-ene-1,5-diynes)) afforded the first oligomers and polymers with the poly(triacetylene) backbone [PTA, $-(C\equiv C-CR=CR-C\equiv C)_n-$]. The effective conjugation length for this third class of linearly conjugated polymers with a nonaromatic all-carbon backbone, besides polyacetylene and poly(diacetylene), was determined to be in the range of 7–10 monomeric units. By lateral attachment of dendrons along the conjugated backbone of PTA oligomers, cylindrically shaped dendrimers were obtained which can be viewed as insulated molecular wires. Donor-acceptor substituted arylated TEEs and DEEs were prepared, and their unusual electrochemical properties and tendency to undergo photochemical *trans* → *cis* isomerization were investigated. Measurements of third-order nonlinear optical effects by third harmonic generation revealed useful structure-function relationships. The highest second hyperpolarizabilities γ were obtained for two-dimensionally fully conjugated systems with reduced molecular symmetry.

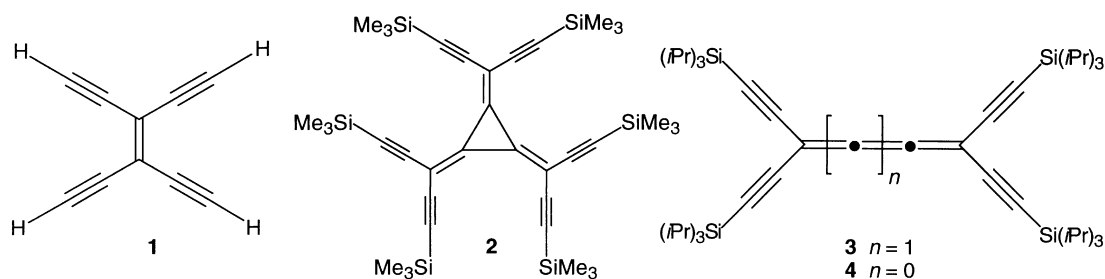
PERETHYNYLATED BUILDING BLOCKS FOR MODULAR CHEMISTRY

Acetylenic molecular scaffolding in one, two, and three dimensions aims at producing new nanoscale molecular and polymeric materials that exhibit unusual electronic and optical function and properties. These efforts have greatly benefited from the recent renaissance in preparative acetylene chemistry [1] and, in particular, from the discovery of novel metal-catalyzed cross-coupling reactions for C–C bond formation [2]. A rich variety of peralkynylated building blocks have been prepared as starting materials in this modular synthetic approach to new advanced materials [3–6] and, among these, derivatives of tetraethynylethene (**1**, TEE, 3,4-diethynylhex-3-ene-1,5-diyne) [7–9] are particularly useful. Today, TEEs of nearly any desired functionalization and silyl-protection are available. Additional perethynylated chromophores such as the [3]radialene **2** [10] and [3]cumulene **3** [11] have been prepared in our laboratory. On the other hand, all efforts to synthesize the perethynylated allene **4**, a precursor to three-dimensional networks and for formation of helical polymers, have failed in the past [12] (Scheme 1).

MACROCYCLIC ACETYLENIC SCAFFOLDING

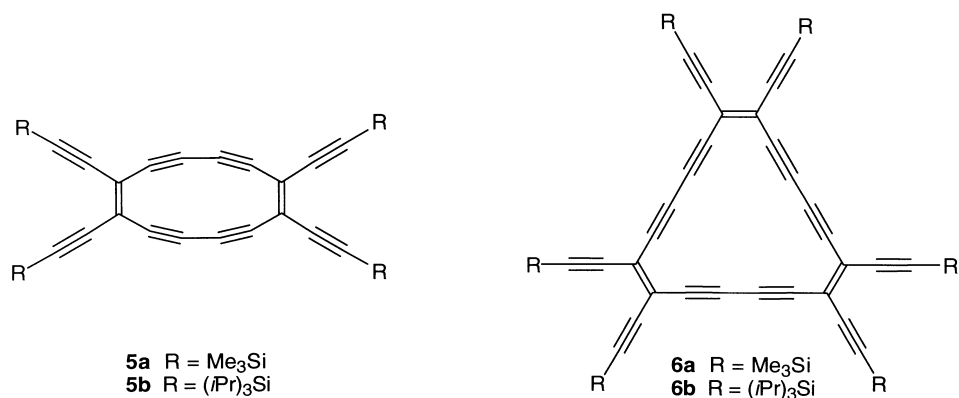
Oxidative Glaser–Hay macrocyclization of *cis*-bis(trialkylsilyl)-protected TEEs yielded the per(silyl-ethynyl)ated octadecahydro[12]annulenes **5a/b** and dodecacyclo[18]annulenes **6a/b** [13]. Both annulene perimeters are perfectly planar according to X-ray crystal structure analysis [14]. The buta-1,3-diyne diyl moieties in **5a/b** are considerably bent with C≡C–C angles as low as 164.5°, whereas those

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Scheme 1

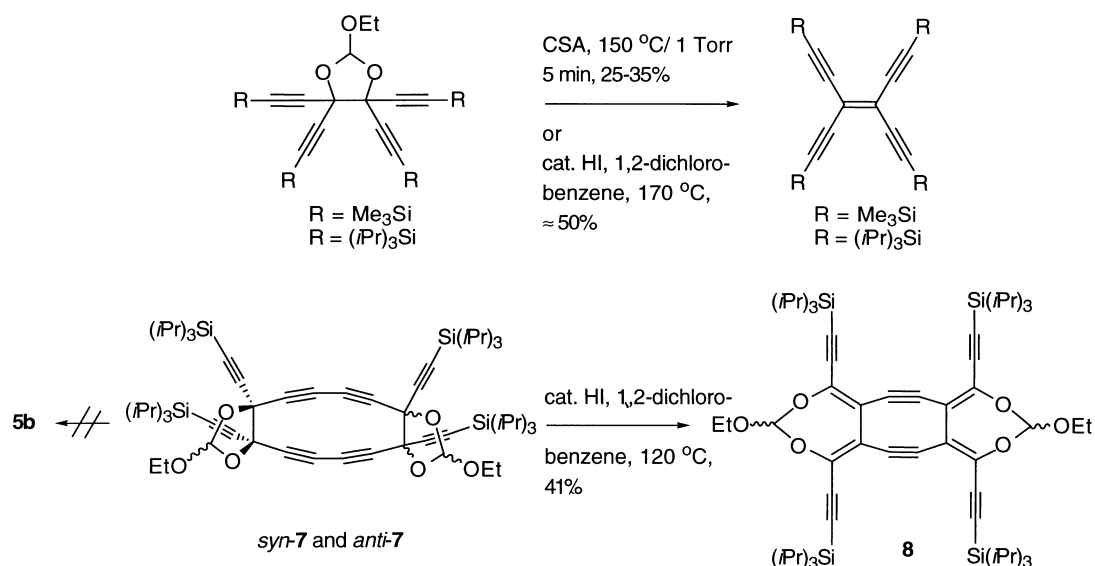
in **6a/b** are practically linear. A detailed analysis of the UV/Vis spectra revealed that the yellow-colored [18]annulenes **6a/b**, with a large HOMO-LUMO gap (2.57 eV in pentane), are aromatic, whereas the purple-colored [12]annulenes **5a/b**, with a smaller HOMO-LUMO gap (1.87 eV), are antiaromatic. This analysis was confirmed by ^1H NMR spectroscopic investigations on the diatropicity and paratropicity of related macrocycles. Electrochemical studies were also in agreement with these findings [15]: octadecahydro[12]annulene **5b** undergoes two stepwise one-electron reductions ($E^\circ = -0.99$ and -1.46 V vs. Fc/Fc^+ (ferrocene/ferricinium couple) in THF) more readily than the dodecadihydro[18]annulene **6a** ($E^\circ = -1.12$ and -1.52 V). This redox behavior is best explained with the formation of an aromatic $(4n+2)$ π -electron dianion from antiaromatic **5b**, whereas **6a** loses its aromaticity upon reduction (Scheme 2).



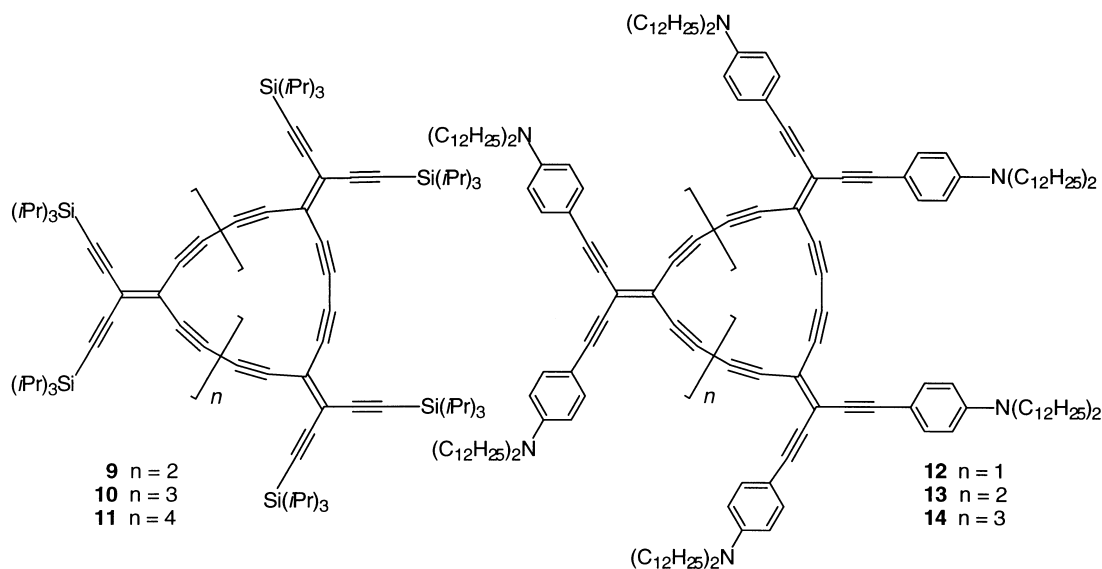
Scheme 2

We recently found that TEEs can be readily synthesized by heating cyclic orthoesters of 1,1,2,2-tetraethynylethanes either with camphorsulfonic acid (CSA) at 150°C or with HI (cat.) in 1,2-dichlorobenzene at 170°C for short periods of time (Scheme 3) [16,17]. When this methodology was applied to a new synthesis of **5b** starting from a diastereoisomeric mixture of *syn*-**7** and *anti*-**7**, we failed to isolate any of the desired [12]annulene. Instead, heating *syn*-**7**/*anti*-**7** in the presence of catalytic amounts of HI at 120°C produced, to our great surprise, exclusively the rearranged product **8** (Scheme 3). This product was isolated in 41% yield as an inseparable 2:1 mixture of diastereoisomers and featured unexpectedly high kinetic and thermal stability [17]. The structure of **8** as a highly strained permethylenated cycloocta-1,5-diyne was elucidated by X-ray analysis of a crystal which contained only one of the two possible diastereoisomers bearing an *anti* arrangement of the ethoxy groups. In the eight-membered ring of **8**, the transannular distance between the triple bonds is 2.59 Å and the internal bond angles at the sp C-atoms (157.4°) differ considerably from the regular geometry [18]. The unexpected formation of **8**, which requires acid catalysis, was tentatively rationalized by assuming a cascade mechanism [19] consisting of electrocyclic or radical reactions.

Formal insertion of ethynediyl or buta-1,3-diyne diyl moieties between each pair of vicinal *exo*-methylene units in the cyclic framework of radialenes [20] leads to the carbon-rich *expanded radialenes* of which the perethynylated compounds **9–11** are the first representatives (Scheme 4). They possess nanometer-sized carbon sheets with diameters, not including the $(i\text{Pr})_3\text{Si}$ groups of ≈ 17 (**9**), 19 (**10**), and 22 Å (**11**) [14,21].



Scheme 3 Top: formation of tetraethynylethenes by acid-catalyzed thermal elimination of cyclic orthoesters of 1,1,2,2-tetraethynylethanes. Bottom: unexpected formation of the highly strained cycloocta-1,5-diyne **8** in the acid-catalyzed thermal rearrangement of orthoesters *syn-7* and *anti-7*.



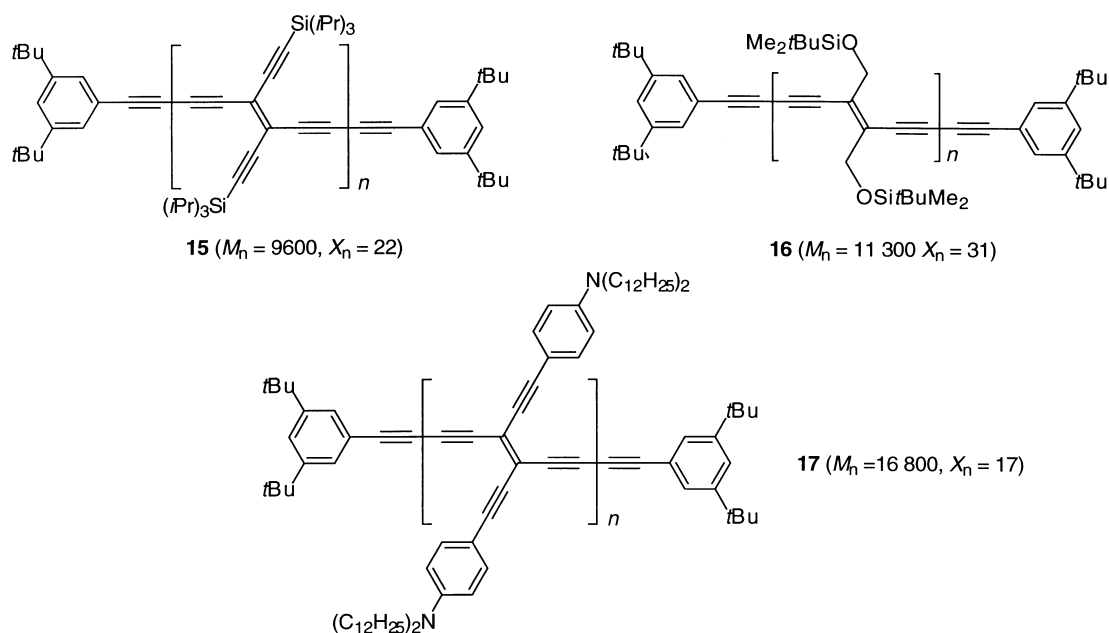
Scheme 4

They are amazingly stable and readily soluble compounds, with melting points above 220 °C, and can be viewed as persilylated C₄₀, C₅₀, and C₆₀ isomers, respectively. The materials properties of the expanded radialenes could be greatly enhanced upon donor functionalization, leading to the stable derivatives **12**–**14**, with fully planar, conjugated π-chromophores [22] (Scheme 4). These compounds exhibit large third-order nonlinear optical coefficients, can be reversibly reduced or oxidized, and form Langmuir monolayers at the air–water interface. Particularly intriguing is the electronic absorption spectrum of trimeric **12**, which displays a strong low-energy absorption band in the visible region with an exceptionally large molar extinction coefficient ($\epsilon = 171\,000\text{ dm}^3/\text{cm}/\text{mol}$ at $\lambda_{\text{max}} = 646\text{ nm}$). The origin of this remarkable absorption is not yet well understood.

MOLECULAR WIRES: OLIGOMERS AND POLYMERS WITH THE POLY(TRIACETYLENE) (PTA) BACKBONE

Poly(triacetylene)s [PTAs, $-(\text{C}\equiv\text{C}-\text{CR}=\text{CR}-\text{C}\equiv\text{C})_n-$] are the third class of linearly conjugated

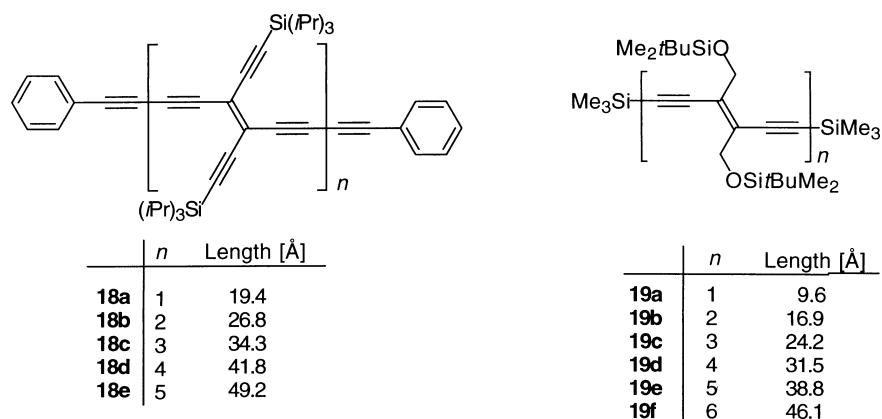
polymers with a nonaromatic all-carbon backbone in the progression that starts with polyacetylene [PA, $-(\text{CR}=\text{CR})_n-$] and poly(diacetylene) [PDA, $-(\text{C}\equiv\text{C}-\text{CR}=\text{CR})_n-$], and ultimately leads to carbyne [$-(\text{C}\equiv\text{C})_n-$]. Polymers such as **15** and **16** are readily prepared by oxidative Glaser–Hay polymerization of either *trans*-bis-deprotected TEEs or 1,2-diethynylethenes (DEEs (*E*)-hex-3-ene-1,5-diyne) [22,23] (Scheme 5). In order to stabilize the polymers, they are end-capped by 3,5-bis(*tert*-butyl)phenylethynyl residues. These groups also allow for a reliable determination of the molecular weights by ^1H NMR integration, comparing the intensities of the signals of the monomeric subunits with those of the end-capping groups. The physical properties of the polymers can be further enhanced by introducing lateral groups such as the *p*- $\text{C}_6\text{H}_4\text{N}(\text{C}_{12}\text{H}_{25})_2$ donor groups in **17** [22]. Thus, polymer **17**, with a number-averaged molecular weight of $M_n = 16\,800$ and a degree of polymerization of $X_n = 17$, electrochemically undergoes one reversible $1-e^-$ reduction and one reversible $1-e^-$ oxidation and the optical gap ($E_g = 1.6\text{ eV}$) is substantially reduced as compared to **15** ($E_g = 2.0\text{ eV}$). The length of the polymers shown is determined by their solubility in the solvents in which they are prepared; any larger polymers formed are insoluble and have not been isolated. Polymers prepared from DEE monomeric units, such as **16**, are substantially more soluble than those constructed from TEE monomers, such as **15** (Scheme 4).



Scheme 5

Monodisperse oligomers serve as excellent models to provide specific information concerning the structural, electronic, and optical properties of their corresponding polydisperse long-chain polymeric analogs [24]. A second interest in monodisperse π -conjugated oligomers of defined length and constitution arises from their potential to act as molecular wires in molecular scale electronics and nanotechnological devices [25]. Therefore, we prepared two series of oligomers **18a–e**, end-capped with phenylethynyl residues [26,27] and Me_3Si -end-capped **19a–f** [28] in order to estimate, by extrapolation, the properties of infinite-chain PTA polymers (Scheme 6). The series of monomer to hexamer **19a–f** has recently been extended to a monodisperse hexadecamer with a length of 11.9 nm [29]. Compounds in both series are highly stable and can be stored in the air for months without decomposition; as in the polymeric series, the oligomers **19a–f** derived from DEE monomers are more soluble than those constructed from TEE precursors (**18a–e**).

Compounds **18a–e** underwent facile one-electron reductions with the number of reversible reduction steps being equal to the number of TEE moieties in each molecular rod [15,26]. Thus, the first reduction of **18a** occurs at $E^\circ = -1.57\text{ V}$ (vs. Fc/Fc^+ , in THF +0.1 M Bu_4NPF_6) whereas the first reduction of **18e** is much more facile and is observed at -1.07 V . No oxidation of the rods was detected in THF below 1.0 V in the cyclic voltammetric studies.



Scheme 6

The enhanced solubility of oligomers **19a–f** allowed an estimation of the effective conjugation length [30] of PTA polymers [28]. The effective conjugation length indicates the number of repeat units in a conjugated polymer required to furnish size-independent redox, optical, and other properties. Evaluation of both the chain-length-dependent UV/Vis spectra as well as the third-order nonlinear optical properties of **19a–f** in comparison to those of longer-chain polymers such as **16** yielded convergence of the linear and nonlinear optical properties in the range of 7–10 monomer units, corresponding to 21–30 conjugated double and triple bonds.

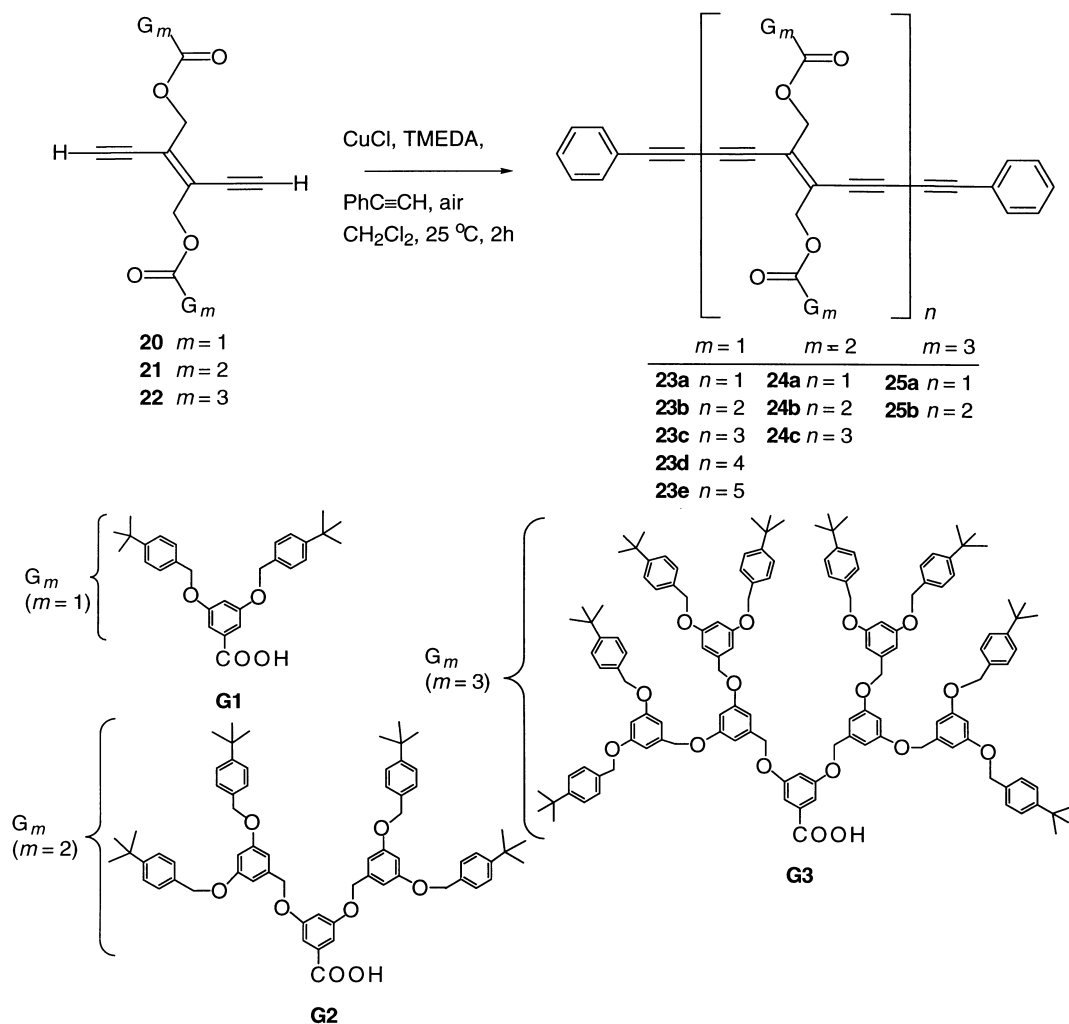
By lateral attachment of Fréchet-type dendrons [31], the PTA molecular wires can be insulated. Oxidative Glaser–Hay coupling of DEEs **20–22** in the presence of phenylacetylene as end-capping reagent provided the dendritic oligomers shown in Scheme 7 [32]. While the first generation compound **20** afforded separable oligomers up to the pentamer (**23a–e**), the second generation derivative **21** only yielded isolable oligomers up to the trimer (**24a–e**). Due to severe steric overcrowding, conversion of the third generation enediyne **22** only gave end-capped monomer and dimer (**25a,b**) in pure form.

In these tubular macromolecules, the insulating layers created by the dendritic wedges protect and stabilize the central conjugated backbone but do not alter its electronic characteristics. UV/Vis spectroscopic measurements indicated that there is no loss of π -electron conjugation along the PTA backbone in the higher generation compounds, despite their distortion from planarity due to the bulky dendritic wedges. Independent of the dendritic generation number, the longer-wavelength absorptions, which originate from electronic transitions within the conjugated PTA backbone, appear at almost the same positions with nearly identical fine structure and molar extinction coefficients. This was shown by comparing the UV/Vis spectra of trimeric **23c/24c** and dimeric **23b/24b/25b**, respectively.

An interesting observation was made during purification of the end-capped third generation monomer **25a** by preparative size exclusion chromatography. Instead of the expected single resonance, two *tert*-butyl resonances were observed in the ^1H NMR spectrum, and thin layer chromatography of the solution showed two spots. After column chromatography (SiO_2 , hexane/ CH_2Cl_2 1:1) in the dark, **25a** was obtained as a pure substance and only one *tert*-butyl resonance was observed. When a solution of isomerically pure **25a** was irradiated with sunlight, two *tert*-butyl resonances were observed again, indicating that **25a** underwent *trans* \rightarrow *cis* isomerization of the central double bond [33]. This phenomenon was not observed for the end-capped monomers of the first and second generation (**23a** and **24a**, respectively) and resembles observations made with dendrimers also containing Fréchet-type dendritic wedges around a photoisomerizable azobenzene core, in which infrared excitation of the aromatic wedges, followed by energy transfer, induced *cis* \rightarrow *trans* isomerization of the core [34].

PHYSICAL PROPERTIES OF DONOR-ACCEPTOR SUBSTITUTED TETRAETHYNYLETHENES

A library of more than 50 different arylated TEEs and DEEs, such as compounds **26–37** (Scheme 8), was prepared for systematic investigations of nonlinear optical properties in two-dimensionally



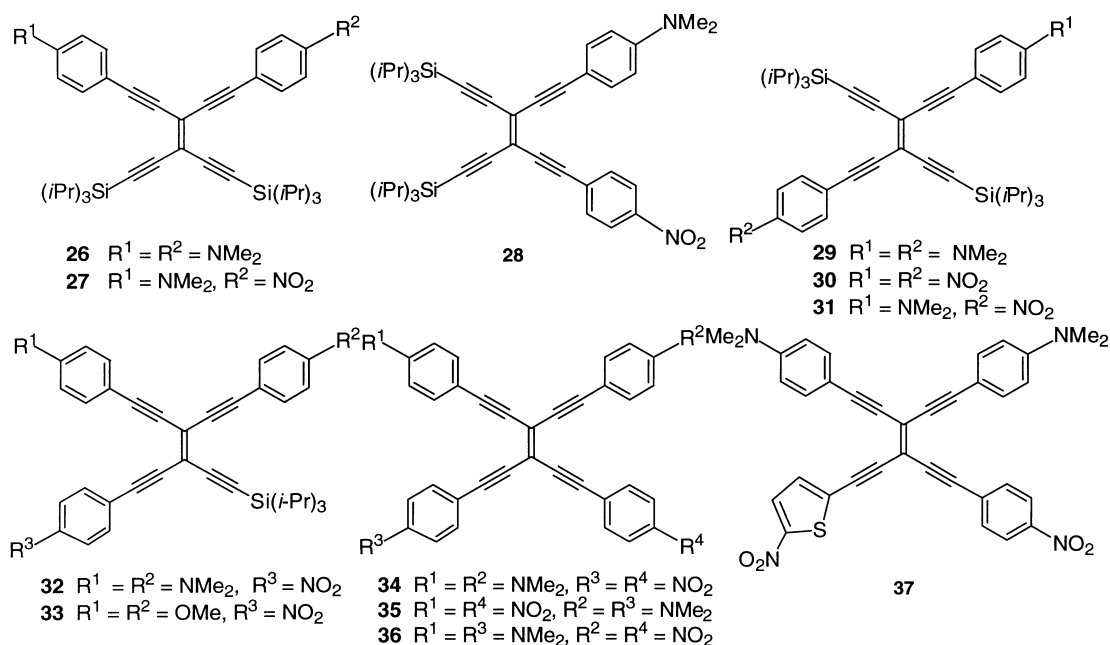
Scheme 7 Synthesis of cylindrical dendrimers as insulated molecular wires.

conjugated molecules [35,36]. In these chromophores, a total of six conjugation pathways in two dimensions are effective: two linear *cis*- and two linear *trans*-conjugation as well as two *geminal* cross-conjugation paths. The planarity of the π -conjugated carbon frames in these thermally and environmentally stable molecules was revealed by several X-ray crystal structure analyses. The optical spectra of donor-acceptor substituted derivatives displayed characteristic long-wavelength bands resulting from intramolecular charge transfer. Intramolecular donor-acceptor interactions are much more effective in TEEs **28** and **31**, with *cis*- and *trans*-linearly conjugated electronic pathways between donor and acceptor, than in **27**, with a *geminal* cross-conjugated electronic pathway. Many of the compounds fluoresce strongly.

Cyclovoltammetric studies revealed an unusual redox behavior of derivatives containing *p*-nitrophenyl substituents [37]. Multiple *p*-nitrophenyl redox centers present on the TEE core apparently behave independently from one another in electrochemical reduction steps. Thus, the first reversible one-electron reduction of one *p*-nitrophenyl ring in **27**, **28**, **31**, **32**, or **33** occurred in CH_2Cl_2 (+0.1 M Bu_4NPF_6) at the same potential (around -1.37 V vs. Fc/Fc^+) than the two first reduction steps in **30**, **34**, or **35** [38]. These findings suggested that the electrochemically generated charges localize on individual *p*-nitrophenyl rings; high level computing, however, clearly revealed that delocalization of the incurred charges is effectively conveyed by the alkyne moieties into the entire π -conjugated carbon framework. In the dianion, this delocalization imparts a sufficiently high single bond character to the central TEE double bond to allow rotation and *cis-trans* isomerization.

TEEs such as **29–31** and DEEs undergo photochemical *trans* → *cis* isomerizations which were investigated as a function of structure, solvent, excitation wavelength, and temperature [33]. In general, the partial quantum yields for isomerization were highest for bis-acceptor derivatives, followed by donor-donor and donor-acceptor substituted molecules. TEEs do not undergo thermal *cis* → *trans* isomerization, presumably due to the lack of steric hindrance in the planar chromophore in both *cis*- and *trans*-isomers. This sets them apart from stilbenes and azobenzenes: due to the nonplanarity, *cis*-stilbenes and *cis*-azobenzenes undergo thermal isomerization into the planar *trans*-derivatives. Therefore, TEE and DEE derivatives, in contrast to stilbenes and azobenzenes, allow investigation and quantification of electronic and solvent effects on *cis-trans* isomerizations separated from steric influences.

A comprehensive investigation of the second- [39] and third-order [40] nonlinear optical properties of donor/acceptor substituted TEEs and DEEs was undertaken, and a comparative discussion of the obtained structure-property relationships for third-order effects has just been published [41]. Third harmonic generation (THG) experiments in CHCl₃ were performed at the fundamental laser wavelength of either $\lambda = 1.9$ or $2.1 \mu\text{m}$, and the second hyperpolarizability γ that describes molecular third-order nonlinear optical effects was determined. Two important criteria were fulfilled in order to obtain meaningful structure-function relationships. All compounds are planar in solution, and differences in γ are therefore not due to nonplanarity-induced deconjugation. Furthermore, the absorption of the compounds at the third harmonic is either zero or negligible so that the measured γ -values do not originate from resonance effects (Scheme 7).



Scheme 8

A series of fundamental conclusions was obtained [41]:

- (i) Donor substitution of TEEs gives higher γ -values than acceptor substitution, and the magnitude of γ increases with donor strength.
- (ii) Acentricity greatly enhances the γ -values.
- (iii) Molecules with donor and acceptor in *trans*- and *cis*-configurations give much higher nonlinearities due to favorable linear donor-acceptor conjugation than those with substituents at the geminal position where only the weaker cross-conjugation is effective.
- (iv) A substantial increase in γ is observed upon extending the conjugation length.
- (v) Full two-dimensional conjugation, as in **34–37**, with as many as six conjugation paths, leads to very large γ -values.

These structure–function relationships provide extremely useful guidance for the future rational design of molecules and polymers for nonlinear optical device applications.

CONCLUSIONS

When graduate student Yves Rubin started the synthesis of tetraethynylethene (TEE, **1**) in my laboratory in 1989 [9], the broad applicability of this building block and its derivatives for modular construction of functional nanoscale molecular architecture was not foreseeable. It is clear today, that only the tip of a large iceberg of structural diversity and technological perspectives in TEE chemistry has been explored and many exciting discoveries await to be made in future years.

ACKNOWLEDGEMENT

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