Carbon-rich acetylenic scaffolding: rods, rings and switches†

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Derivatives of tetraethynylethene (TEE, 3,4-diethynylhex-3-ene-1,5-diyne) and (*E*)-1,2-diethynylethene ((*E*)-DEE, (*E*)-hex-3-ene-1,5-diyne) provide a unique class of π-conjugated building blocks for modular construction of one- and two-dimensional carbon-rich scaffolds such as monodisperse, linearly π-conjugated oligomers extending in length beyond 10 nm or large macrocyclic all-carbon cores. Lateral functionalisation of these novel chromophores with donor–acceptor substituents strongly enhances their advanced materials properties and leads to exceptional third-order optical nonlinearities. New photochromic molecules were prepared which undergo photochemical *cis → trans* and *trans → cis* isomerisation without competing thermal isomerisation pathways, thereby paving the way for applications as light-driven molecular switches in optoelectronic devices.

Introduction

Acetylenic scaffolding started in 1869 with the discovery of the oxidative alkyne coupling by Glaser.[1,2] Soon after, Baeyer recognized the potential of this reaction for forming infinite all-carbon chains, [–C≡C–]$_n$, known today as carbyne.[3] The advent of the Eglinton–Galbraith variant of the Glaser coupling reaction in 1956,[4] which uses cupric salts in donor solvents such as pyridine, paved the way for the pioneering work by Sondheimer and co-workers, who described the first synthesis of [18]annulene in 1959.[5,6] This milestone in physical organic chemistry, which provided experimental support for the Hückel rule defining aromaticity, was followed by the synthesis and investigation of a large number of macrocyclic π-electron perimeters, including many dehydroannulenes containing acet-

† Dedicated to Professor Jean François Normant on the occasion of his 65th birthday.

François Diederich, born in 1952 in the Grand Duchy of Luxembourg, received his PhD degree in 1979 from the University of Heidelberg. Following postdoctoral studies at the University of California at Los Angeles (UCLA) from 1979–1981, he was a research associate at the Max-Planck-Institut für medizinische Forschung in Heidelberg. After his Habilitation in 1985, he joined the faculty of the Department of Chemistry and Biochemistry at UCLA where he became full professor in 1989. Since April 1992, he has been a professor of organic chemistry at ETH Zürich. His research interests encompass the development of covalent fullerene chemistry, the preparation of novel carbon allotropes and acetylenic carbon-rich advanced materials, the exploration of functional dendrimers as models for globular proteins and molecular recognition studies with synthetic and biological receptors.

ylenic bonds.[7–9] Methodological advances such as the Hay variant for oxidative homo-coupling[10] and the Cadiot–Chodkiewicz protocol for oxidative hetero-coupling[11] expanded the application of acetylenic scaffolding into the fields of polymer and natural product synthesis.[2] Today, progress in acetylene-based molecular construction is greatly fueled by the advent of powerful novel metal-catalyzed acetylenic homo- and cross-coupling protocols.[2,12,13]

In the mid 80s, the observation of fullerene formation by mass spectrometry[14] stimulated our research group to search for other, synthetic carbon allotropes.[15,16] We developed 'precursor' routes to the cyclocarbons (*cyclo*-C$_n$), *n*-membered monocyclic rings of sp-hybridised C atoms with unique electronic structures resulting from two perpendicular systems of conjugated π-orbitals, one in-plane and one out-of plane.[15–17] In collaborative efforts, we showed that these all-carbon molecules undergo ion-molecule coalescence reactions in the gas phase under clean formation of fullerenes.[18,19] At the same time, we identified two-dimensional all-carbon networks,[20] containing as repeat unit the cross-conjugated framework of tetraethynylethene (**1**, TEE, 3,4-diethynylhex-3-ene-1,5-diyne) (Scheme 1), as potential advanced materials and attractive
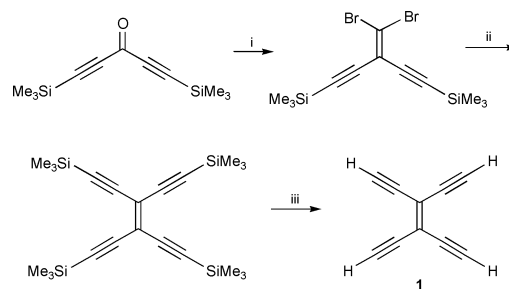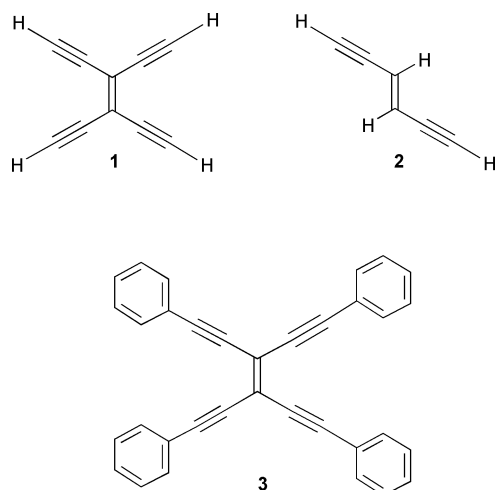

Scheme 1 Synthesis of tetraethynylethene (**1**).[38] i, CBr$_4$, PPh$_3$, 50%; ii, Me$_3$Si–C≡C–H, [Pd(PPh$_3$)$_4$], CuI, BuNH$_2$, PhH, 88%; iii, K$_2$CO$_3$, wet MeOH, 87%.

synthetic targets.[15,16] While our hope of producing such networks with high crystallinity was not substantiated, it initiated the research featured in this article.

Tremendous synthetic efforts are currently ongoing in the area of acetylenic scaffolding, targeting exceptional molecular architecture and functional advanced materials, and the reader is referred to review articles and monographs for a better appreciation of these developments.[21–32] Here, we describe how derivatives of tetraethynylethene (**1**) and (*E*)-1,2-diethynyl-ethene (**2**, (*E*)-DEE, (*E*)-hex-3-ene-1,5-diyne) have been used to prepare a great diversity of functional carbon-rich compounds such as chromophores with high second- and third-order optical nonlinearities, molecular photochemical switches, large two-dimensional carbon cores, and linearly π-conjugated molecular rods extending in length beyond 10 nm.

Scheme 4 TEEs by acid-catalysed orthoester thermolysis. i, $(EtO)_3CH$, cat. CSA, CH_2Cl_2, 94%; ii, CSA, 150 °C, 0.1 Torr, 5 min, 25–33%.[41] CSA = camphorsulfonic acid.

Synthesis and properties of tetraethynylethenes and (E)-1,2-diethynylethenes

Tetrakis(phenylethynyl)ethene (**3**) was the first TEE derivative synthesised by Hori *et al.* in 1969,[33,34] and the first peralkylated and persilylated derivatives were reported later in the 70s by Hauptmann.[35] Taking advantage of modern Pd(0)-catalyzed cross-coupling methods,[12] our research group introduced in the early 90s more general synthetic protocols, providing access not only to the parent compound **1**[36] but also to virtually any desired substitution pattern about the central ten-carbon TEE core. These methods have been comprehensively reviewed;[37] they are illustrated in Schemes 1 and 2 for the synthesis of TEE **1**[38] and (E)-DEE **4**.[39]
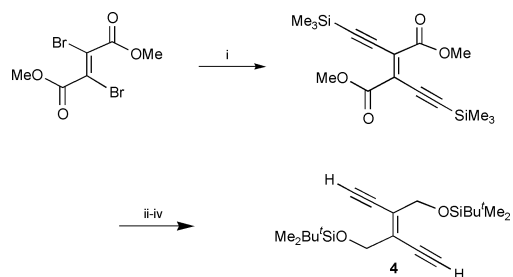
Scheme 2 Synthesis of (E)-1,2-diethynylethene **4**.[39] i, $Me_3Si–C≡C–H$, $[PdCl_2(PPh_3)_2]$, CuI, NEt_3, 20 °C, ≈50%; ii, DIBAL-H, CH_2Cl_2, 0 °C, 85%; iii, Me_2Bu^tSiCl, Et_3N, DMAP, 25 °C, 98%; iv, K_2CO_3, MeOH, 25 °C, 90%. DIBAL-H = diisobutylaluminum hydride, DMAP = 4-(*N,N*-dimethylamino)pyridine.
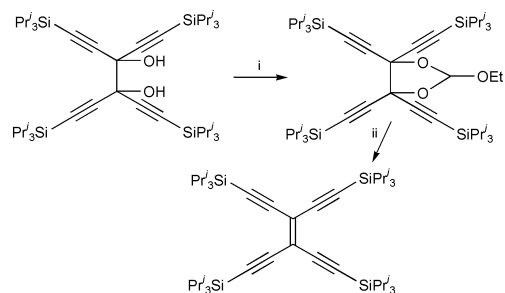
Recently, another general procedure for the synthesis of hex-3-ene-1,5-diynes was described by Jones and co-workers which does not rely on Pd(0)-catalyzed cross-coupling.[40] A large variety of (E)- or (Z)-DEE and TEE derivatives could be prepared using the carbenoid coupling–elimination strategy shown in Scheme 3.
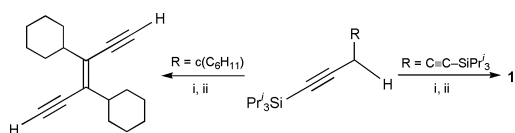
Scheme 3 DEEs and TEEs by a carbenoid coupling–elimination strategy. i, LHMDS, HMPA, THF, −80 °C; ii, Bu_4NF, THF, 70% (DEE), 90% (**1**); yields over 2 steps.[40] LHMDS = lithium hexamethyldisilazane, HMPA = hexamethylphosphorous triamide.

Another synthesis of TEE derivatives results from the acid-catalyzed thermal elimination of an orthoester moiety from 1,1,2,2-tetraethynylethane (3,4-diethynylhexa-1,5-diyne) derivatives (Scheme 4).[41]

The stability of TEE and DEE derivatives largely depends on the number of free ethynyl residues in the molecule. If all acetylene residues are silylated, alkylated or arylated, the compounds are kinetically very stable and display high melting points or decomposition points which in the case of arylated derivatives reach 200 °C and higher. With increasing number of free terminal alkyne groups, the stability rapidly decreases: derivatives with two ethynyl residues already are quite labile in the neat state and the parent TEE **1** rapidly decomposes at 25 °C. Remarkably, we never observed any Bergman cycloaromatisation of TEEs and DEEs;[42,43] at higher temperatures, other decomposition channels presumably become dominant.

Over 30 X-ray crystal structures of TEE and DEE derivatives have been solved.[44] They all revealed fully or nearly planar π-conjugated carbon cores, which in most cases, also include terminal aryl rings. In some solid-state structures, terminal aryl rings are not in plane with the central core, presumably due to crystal packing effects. In these cases, they adopt an orthogonal orientation, thereby maintaining conjugation with the second set of π-orbitals in the adjacent C≡C bond. The length of the central C=C double bond in TEE and DEE cores usually varies between 1.34 and 1.37 Å, whereas the C≡C triple bond lengths vary between 1.17 and 1.22 Å.[45]

One of the striking characteristics of TEE derivatives is the complete chemical inertness of the central olefinic bond. All attempts to add electrophiles, carbenes, 1,3-dienes or 1,3-di-poles to this electron-deficient[46] bond failed.[47] Thus, 1,3-dipo-lar cycloaddition with diazomethane occurred at one of the C≡C bonds rather than at the central C=C bond. Similarly, oxidations or epoxidations of this bond were unsuccessful and epoxide **5** could only be prepared in an indirect way as shown in Scheme 5.[48]
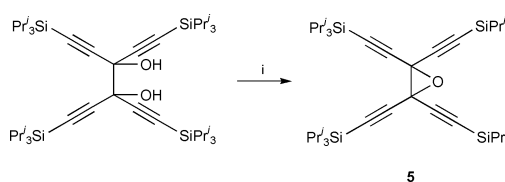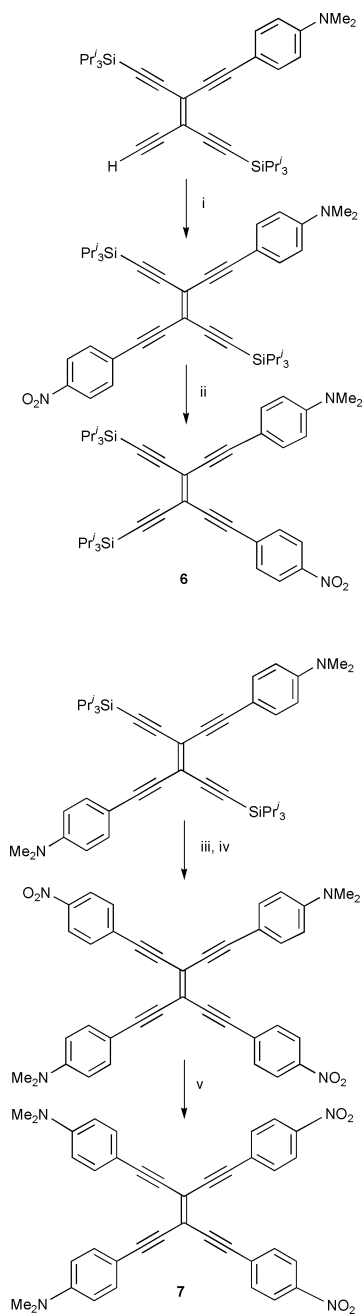

Scheme 5 Synthesis of epoxide **5**. i, $MeSO_2Cl$, NEt_3, CH_2Cl_2, −20 °C → 20 °C, 80%.[48]

Functional advanced materials based on arylated TEEs and DEEs

The physical properties of the TEE and DEE chromophores are further enhanced by arylation, generating a variety of desirable functional derivatives for advanced materials applications. Thus, the fully planar tetraphenyl derivative **3** and the π-acceptors 2,4,7-trinitrofluoren-9-one or (2,4,7-trinitrofluoren-9-ylidene)malononitrile form highly ordered donor–acceptor π-complexes of 1:2 donor–acceptor stoichiometry in the solid state.[49,50] The donor/acceptor orientation in the extended layer structures seen in the crystals is electrostatically controlled and shows a good correlation with the calculated atom-centered point charges on both components.

One of the most interesting properties of arylated TEEs and DEEs is their ability to undergo reversible, photochemical *trans* → *cis* and *cis* → *trans* isomerisation.[51] These isomerisations are not observed in the corresponding derivatives lacking aryl substituents. Since both *cis* and *trans* forms benefit from strain-free planarity—in contrast to azobenzenes[52] and stilbenes[53] which are nonplanar in the *cis* forms—the photochemical processes are not accompanied by undesirable thermal isomerisation, a quality reached only in a very small number of photochromic materials known today.[54] The photoisomerisation is of substantial preparative use and was applied to the synthesis of donor–acceptor substituted TEEs, such as **6** and **7**, for nonlinear optical studies (Scheme 6).[44c] A detailed in-

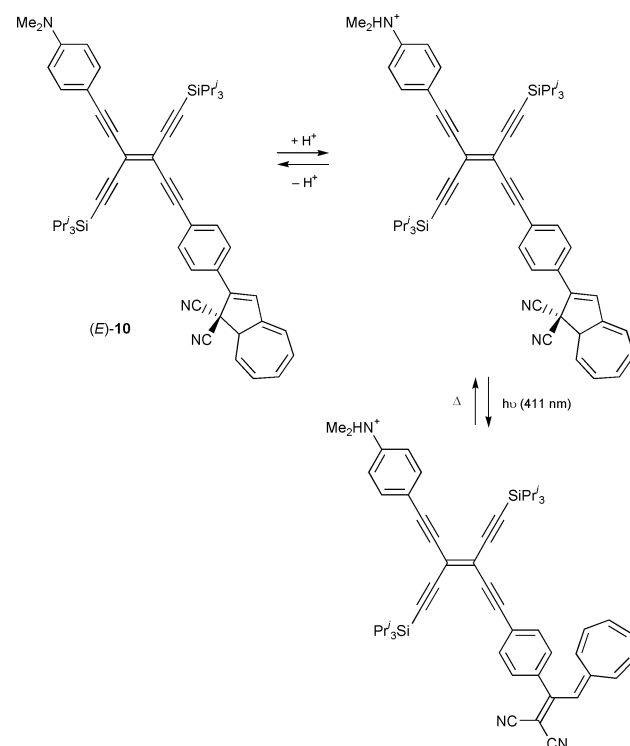merisation was also shown to occur electrochemically at the stage of the dianion.[45c]

We have taken advantage of the photochemical *trans–cis* isomerisation process to construct light-driven molecular switches.[55] Compounds (*R,R*)-**8** and (*R,R*)-**9** are hybrid systems consisting of a TEE core with two attached (*R*)-configured 1,1′-binaphthalene moieties (Scheme 7).[56] They can be reversibly
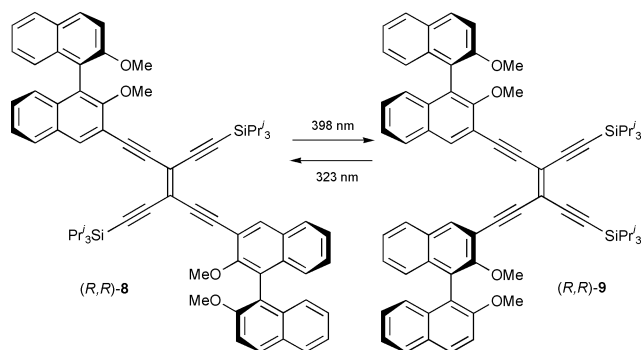
Scheme 7 The couple (*R,R*)-**8**/(*R,R*)-**9** represents a novel, fully light-driven molecular switch.[56]

interconverted in CH₂Cl₂ solutions with light of λ = 398 or 323 nm. No thermal isomerisation was observed at room temperature, and the system displayed high resistance to photofatigue.

A further enhancement in complexity of molecular functions that can be expressed with TEE derivatives was achieved with the synthesis of the three-way chromophoric molecular switch (*E*)-**10** (Scheme 8).[57] This compound contains three addressable

Scheme 6 Synthesis of donor–acceptor substituted TEEs **6** and **7** by photochemical *trans–cis* isomerisation.[44c] i, *p*-O₂N-C₆H₄I, [PdCl₂(PPh₃)₂], CuI, NEt₃, 20 °C, 66%; ii, *hv* (366 nm), Et₂O, 37%; iii, Bu₄NF, wet THF; iv, *p*-O₂N-C₆H₄I, [PdCl₂(PPh₃)₂], CuI, NEt₃, 20 °C, 56% (2 steps); v, *hv* (366 nm), CHCl₃, 20%.

Scheme 8 Two of the three switching functions expressed by the three-way chromophoric molecular switch (*E*)-**10**.[57] The third one (not shown) is the *trans–cis* isomerisation of the TEE core.

vestigation revealed a strong dependence of the quantum yields for photoisomerisation from the pattern and degree of aryl functionalisation, solvent polarity and excitation wavelength.[51] For a bis(4-nitrophenyl)-substituted DEE, the *trans–cis* iso-

subunits which undergo individual reversible switching cycles: (i) a central TEE core which can be reversibly photoisomerised between its *cis* and *trans* forms, (ii) a dihydroazulene unit that can be transformed upon irradiation into a vinylheptafulvene (vinyl-7-methylenecyclohepta-1,3,5-triene) moiety[58] and (iii) a proton-sensitive *N,N*-dimethylanilino group. Of the eight resulting possible interconverting states, a total of six could be detected. Individual interconversion processes such as three

'write–erase' processes and one process mimicking the function of an AND logic gate could be separatively addressed. The latter process relies on the interesting observation that the photochemical opening of the dihydroazulene to the vinylheptafulvene moiety occurs only after protonation of the dimethylamino group, as shown in Scheme 8. We are now investigating in interdisciplinary collaboration, whether TEE- and DEE-based molecular switches could find application in photoaddressable memory storage and readout devices or as waveguides.[59]

Donor–acceptor substituted TEEs display some of the highest known third-order optical nonlinearities[60] and in case of acentricity, also very large second-order nonlinear optical effects.[61] Comprehensive investigations by Günter, Bosshard and co-workers under non-resonant conditions helped to establish structure–property relationships which provide useful guidance for the future design of nonlinear optical materials.[60] In particular, these studies clearly demonstrated the important role of two-dimensional conjugation in enhancing third-order nonlinear optical effects.[62] The highest values of the second hyperpolarisability, γ, that describes molecular third-order nonlinear optical effects,[63] were measured for perarylated TEEs such as 7 (Scheme 6), 11,[44c] 12[44b] or 13[44b] in which as many as six conjugation paths are effective (Scheme 9). In addition to
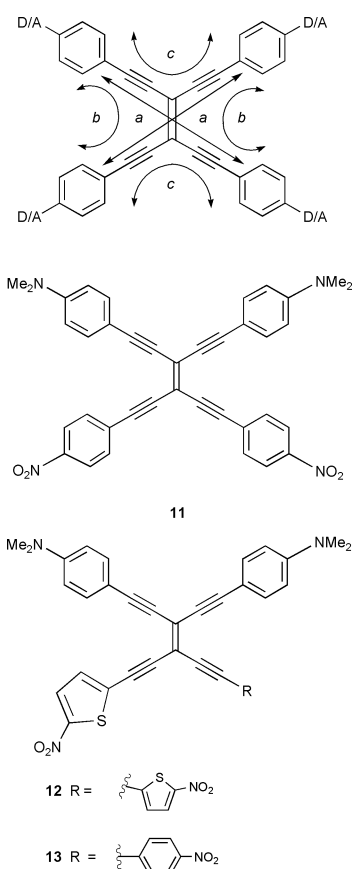
Scheme 9 Top: schematic representation of the possible conjugation pathways in perarylated TEEs. Paths *a* and *b* depict *trans*- and *cis*-linear conjugation, and path *c* depicts geminal cross conjugation. (D donor, A acceptor). Bottom: fully two-dimensionally conjugated chromophores with high second hyperpolarisabilities, γ.[60,64]

full two-dimensional conjugation, low molecular symmetry was also found to be of particular importance for enhancing third-order nonlinear optical effects. Thus, the lower-symmetrical nitrothienyl derivative 13 gave a higher value for γ than obtained for 7, 11 or 12 possessing higher molecular symmetries. A theoretical model was derived to explain these experimental findings;[64] the reader is referred to the original literature for more details.

## Two-dimensional scaffolding: expanded carbon cores

Two families of molecules featuring large all-carbon cores were constructed from suitably functionalised TEE derivatives, perethynylated dehydroannulenes and expanded radialenes. Oxidative Glaser–Hay macrocyclisation of *cis*-bis(trialkyl-silyl)-protected TEEs yielded the per(silylethynylated) octadehydro[12]annulenes 14a,b and dodecadehydro[18]annulenes 15a,b with fully planar π-conjugated carbon cores as evidenced by X-ray crystallography (Scheme 10).[65,66] The yellow-colored
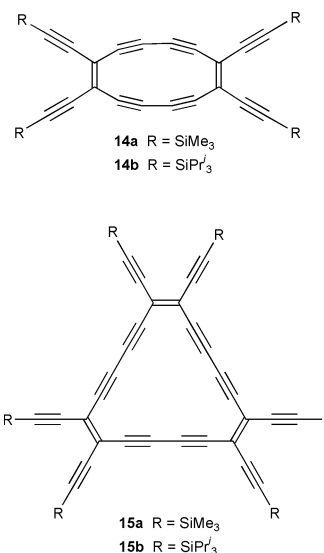
Scheme 10 Planar, perethynylated aromatic (15a,b) and antiaromatic (14a,b) dehydroannulenes.[65,66]

[18]annulenes 15a,b, with a large HOMO–LUMO gap (2.57 eV in pentane) are aromatic, whereas the purple-colored [12]annulenes 14a,b, with a smaller HOMO–LUMO gap (1.87 eV), are antiaromatic. Electrochemical studies[46,66] showed that [12]annulene 14b undergoes stepwise one-electron reductions (E^o = −0.99 and −1.46 eV *vs.* Fc/Fc+ (ferrocene/ferricinium couple) in THF) more readily than [18]annulene 15a (E^o = −1.12 and −1.52 V). This redox behavior is best explained by the formation of an aromatic [4n + 2] π-electron dianion from antiaromatic 14b, whereas 15a loses its aromaticity upon reduction. Removal of the six silyl-protecting groups in 15a yielded the perethynylated derivative with the molecular formula $C_{30}H_6$ which was stable in dilute solutions for a few days at −20 °C in the dark. All attempts, however, to prepare crystalline networks[15,16] by oxidative acetylenic coupling failed.

Formal insertion of ethynediyl[67] or buta-1,3-diynediyl moieties between each pair of vicinal *exo*-methylene units in the cyclic framework of radialenes leads to the carbon-rich expanded radialenes of which the perethynylated derivatives 16a–c are the first representatives (Scheme 11).[66,68] They possess nanometer-sized carbon sheets with diameters, not including the SiPr$^i_3$ groups, of *ca.* 17 (16a), 19 (16b) and 22 (16c) Å. They are amazingly stable and readily soluble compounds with melting points above 220 °C and can be viewed as persilylated C_{40}, C_{50} and C_{60} isomers, respectively. Mass spectrometric analysis revealed that even larger carbon sheets extending to C_{120} cores are formed and, with the recent advances in gel permeation chromatographic (GPC) techniques, we are currently attempting their separation and characterisation. Electrochemical investigations showed that 16a–c are powerful electron acceptors, capable of undergoing multiple reversible one-electron reductions, but are not readily oxidized. Both UV/Vis and electrochemical analyses suggested that cross-conjugation is not very effective in the macrocyclic perimeters and that the extent of π-electron delocalisation in all

16a $n = 2$
16b $n = 3$
16c $n = 4$

(C$_{12}$H$_{25}$)$_2$N ...

17a $n = 1$
17b $n = 2$
17c $n = 3$
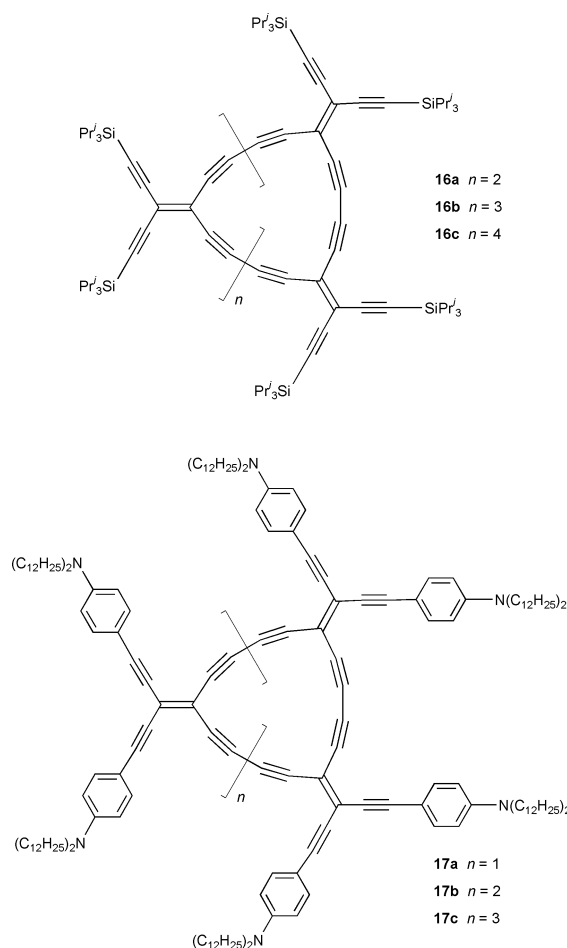
Scheme 11 Expanded radialenes **16a–c** and **17a–c**.[66,68,69]

three compounds is limited to the longest linearly-conjugated π-electron fragment corresponding to a dodeca-3,9-diene-1,5,7,11-tetrayne-1,12-diyl moiety (–C≡C–CR=CR–C≡C–C≡C–CR=CR–C≡C–).

The materials properties of the expanded radialenes were greatly enhanced upon donor functionalisation, leading to the stable derivatives **17a–c** with fully planar π-chromophores.[69] These compounds exhibit large third-order nonlinear optical coefficients, can be reversibly reduced or oxidised, and form Langmuir monolayers at the air–water interface. Particularly intriguing is the UV/Vis spectrum of trimeric **17a**, which features a strong low-energy absorption band in the visible region with an exceptionally large molar extinction coefficient ($\varepsilon = 171\,000$ dm^3 cm^{-1} mol^{-1} at $\lambda_{max} = 646$ nm). The studies with expanded radialenes executed so far suggest that π-electron delocalisation in these cross-conjugated macrocycles is not well understood, and high-level theoretical calculations of the structural and electronic properties of these large perimeters would be very desirable.

## Novel linearly π-conjugated oligomers and polymers with all-carbon backbones

After the introduction of the Pd(0)-catalysed cross-coupling-based syntheses of TEEs and DEEs in 1991,[36] we rapidly became interested in applying these building blocks to the construction of novel oligomers[70] and polymers with linearly π-conjugated all-carbon backbones. In particular, we targeted the first synthesis of poly(triacetylene)s (PTAs),[71] thereby extending the progression of all-carbon polymer backbones which leads from polyacetylene[72] to poly(diacetylene)[73] and, ultimately, to carbyne[74] (Scheme 12).[39]

Starting from suitable TEE or DEE monomers, we prepared by oxidative acetylenic coupling under end-capping conditions


trans-Polyacetylene (PA)

trans-Poly(diacetylene) (PDA)

trans-Poly(triacetylene) (PTA)

trans-Poly(pentaacetylene) (PPA)
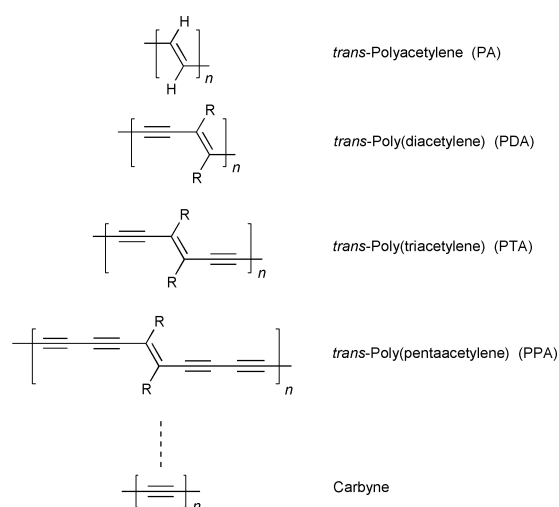
Carbyne

Scheme 12 Progression of linearly π-conjugated all-carbon backbones from *trans*-polyacetylene to carbyne.[39]

several larger-chain PTA polymers such as air-stable **18–20** (Scheme 13).[39,69] Deep red–brown **18** was soluble in hot CHCl$_3$
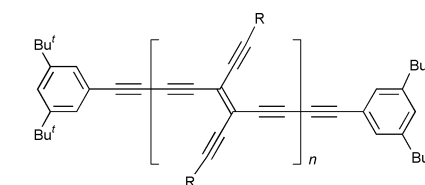
18 R = SiPr$^i_3$ $M_n = 9600$, $X_n = 22$
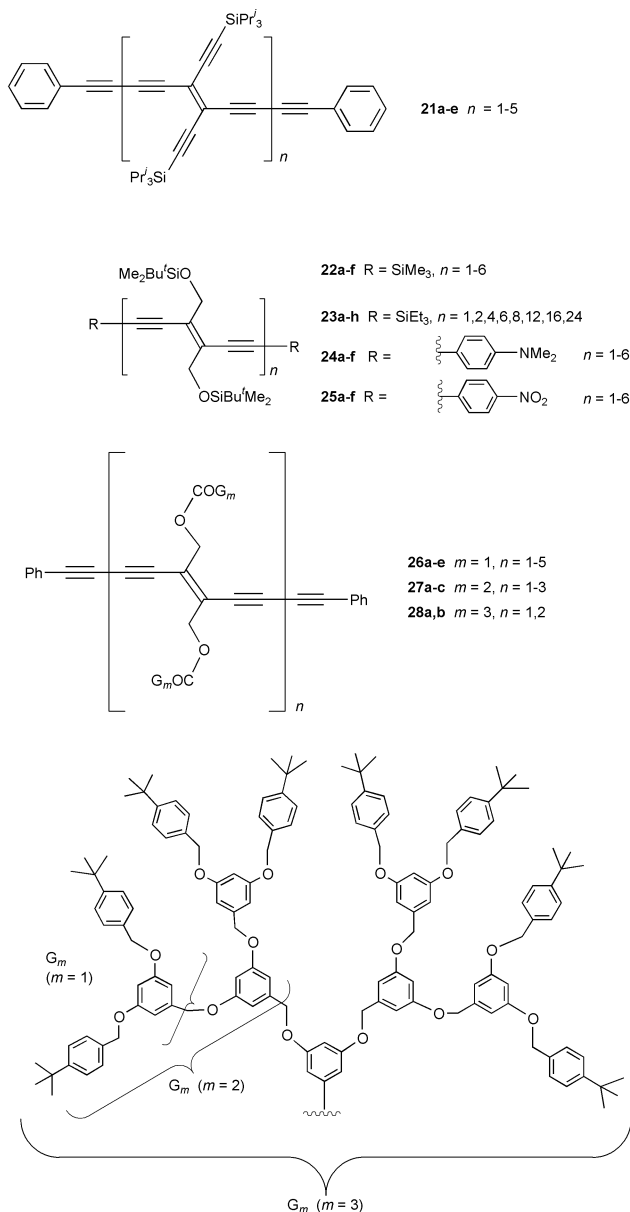**19** R = —⟨ ⟩—N(C$_{12}$H$_{25}$)$_2$ $M_n = 16800$, $X_n = 17$
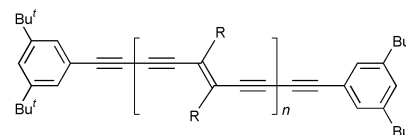
20 R = CH$_2$OSiBu^{t}Me$_2$ $M_n = 11300$, $X_n = 31$

Scheme 13 Poly(triacetylene) polymers prepared by oxidative acetylenic coupling under end-capping conditions.[39,69] M_n = number-averaged molecular weight, X_n = degree of oligomerisation.

and in 1,2-dichlorobenzene above 65 °C and showed an optical gap of $E_g = 2.0$ eV which is in the range of the values measured for poly(diacetylene)s.[75] It can be reversibly reduced at the remarkably low potential of $E = -0.65$ V (*vs.* Fc/Fc$^+$).[39] In polymer **19**, with laterally appended donor groups, the optical gap is substantially reduced as compared to **18** and appears at $E_g = 1.6$ eV.[69] Lacking the laterally appended alkynyl groups, the optical gap in **20** is raised to $E_g = 2.4$ eV.

A particularly interesting accomplishment in the chemistry of poly(triacetylene)s is their first synthesis by topochemically controlled polymerisation of hexa-1,3,5-triynes in the crystal, which was recently described by Fowler and co-workers.[76] A highly original supramolecular control of spatial alignment and orientation of the hexa-1,3,5-triynes in the crystal lattice was required for this 1,6-polymerisation to occur.

In the largest body of our work on PTA rods, we focused on the preparation and study of monodisperse oligomeric series as models for the corresponding infinite polymers.[77] We first prepared by oxidative coupling under end-capping conditions the two oligomeric series **21a–e**[78,79] and **22a–f**,[80] extending in length up to 5 nm (Scheme 14). Compounds in series **21a–e** undergo facile one-electron reduction, with the number of reversible reduction steps being equal to the number of TEE moieties in each molecular rod. Thus, the first reduction of **21a**

21a-e *n* = 1-5

22a-f R = SiMe₃, *n* = 1-6

23a-h R = SiEt₃, *n* = 1,2,4,6,8,12,16,24

24a-f R = ―⟨benzene⟩―NMe₂   *n* = 1-6

25a-f R = ―⟨benzene⟩―NO₂   *n* = 1-6

26a-e *m* = 1, *n* = 1-5
27a-c *m* = 2, *n* = 1-3
28a,b *m* = 3, *n* = 1,2

Scheme 14 Poly(triacetylene) oligomers prepared by oxidative acetylenic coupling.[78–80,82,83,85,86]

occurs at $E = -1.57$ V (*vs.* Fc/Fc⁺ in THF) whereas the first reduction of 49.2 Å long **21e** is much more facile, occurring at -1.07 V. The highly colored oligomers are amazingly stable to air and can be stored on the laboratory bench for months without decomposition. Correspondingly, no oxidation of these rods was observed in THF below 1.0 V (*vs.* Fc/Fc⁺).

Of particular interest was the determination of the effective conjugation length (ECL)[81] in PTA oligomers and polymers. The effective conjugation length indicates the number of repeat units in a conjugated polymer that is required to furnish size-independent properties. From the chain-length dependence of the linear and third-order nonlinear optical properties of oligomers **22a–f** (Scheme 14), the effective conjugation length was extrapolated in the range of 7–10 monomer units, corresponding to 42–60 carbon–carbon bonds. It is noticeable that most linearly π-conjugated polymers show an ECL in this length range.[77a,81]

In more recent work, we prepared the series of stable monodisperse PTA oligomers **23a–h** (Scheme 14) which extend up to a 17.8 nm long 24-mer.[82,83] This is the longest known molecular rod featuring a fully conjugated non-aromatic carbon backbone. This series enabled for the first time the investigation of the evolution of the physicochemical properties of PTAs into the higher oligomeric regime where saturation of the properties

becomes apparent. In good agreement with the extrapolative studies conducted with the previous oligomeric series **22a–f**, evaluation of linear (UV/Vis) and nonlinear (third-harmonic generation (THG) and degenerate four-wave mixing (DFWM)) optical properties, Raman scattering and electrochemical data supported an onset of saturation at about *n* = 10 monomeric units, corresponding to 60 carbon–carbon bonds. Based on the spectroscopic data, we had proposed a preference of the molecular rods for adopting a planar s-*trans* conformation (orientation of two adjacent double bonds with respect to the bridging buta-1,3-diynediyl linker) of the π-conjugated backbone.[82] Such a conformational preference was recently confirmed by an X-ray crystal structure analysis of 4-mer **23c**.[83] The nonlinear optical investigations showed a power law dependence ($\gamma \propto n^a$ with $a \approx 2.5$) of the second hyperpolarisability γ on the number of monomeric repeat units *n* until a smooth saturation is reached. The experimentally observed power law dependence as well as the measured upper boundary for electron delocalisation in a one-dimensional molecular wire (about 60 carbon–carbon bonds) were nicely reproduced in quantum-mechanical calculations using the Valence Effective Hamiltonian (VEH) method combined to a Sum-Over-States (SOS) formalism.[84]

These investigations were further extended to two families of monodisperse terminally donor–donor and acceptor–acceptor functionalised PTA oligomers **24a–f** and **25a–f** (Scheme 14).[85] A dramatic influence of the end-groups on the electronic properties of these materials was observed. As an example, saturation of the linear optical properties in the donor–donor series **24a–f** occurred already at the stage of 4-mer **24d**, whereas the properties of the acceptor–acceptor series **24a–f** resembled much more those of the Me₃Si-end-capped PTA oligomers **22a–f**.

In another approach,[86] the PTA oligomers were dendritically encapsulated[87] into shells of Fréchet-type[88] (**26–28**, Scheme 14) or carbosilane dendrons.[89] As an important result, UV/Vis studies demonstrated that the insulating dendritic layers do not alter the electronic characteristics of the PTA backbone, even at higher generation level. Electronic conjugation involving the acetylenic fragments in the PTA backbone is presumably best described as being cylindrical rather than resulting from orbital overlap within a distinct plane and is therefore maintained upon rotation about C(sp)–C(sp) and C(sp)–C(sp²) single bonds. This conclusion, which requires further validation coming from other studies, is of substantial importance for the rich area of acetylenic scaffolding.[90]

Moving further along the progression from polyacetylene to carbyne (Scheme 12), we recently prepared the first series of monodisperse poly(pentaacetylene) (PPA) oligomers **29a–c** (Scheme 15).[86b] Compared to the corresponding PTA oligo-


29a-c *n* = 1-3
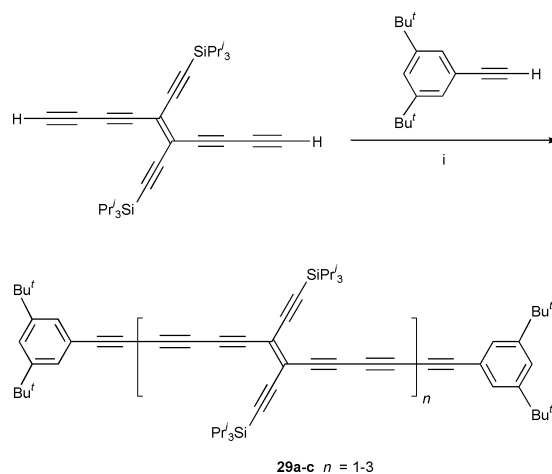
Scheme 15 Synthesis of the first poly(pentaacetylene) oligomers **29a–c**.[86b] i, CuCl, TMEDA, air, CH₂Cl₂, 20 °C, 10% (**29a**), 6% (**29b**), 3% (**29c**).

mers **21a–e**, we find the PPA derivatives much more delicate in terms of stability and processability. Therefore, it will be interesting to see how much further we will be able to move synthetically along the backbone progression leading to carbyne.

Hybrid systems

TEEs and DEEs are readily combined with other building modules for further enhancement of advanced materials properties. We prepared by Sonogashira cross-coupling a large series of mixed oligomers with a spacer inserted between two DEE moieties (Scheme 16) and found that the resulting hybrid
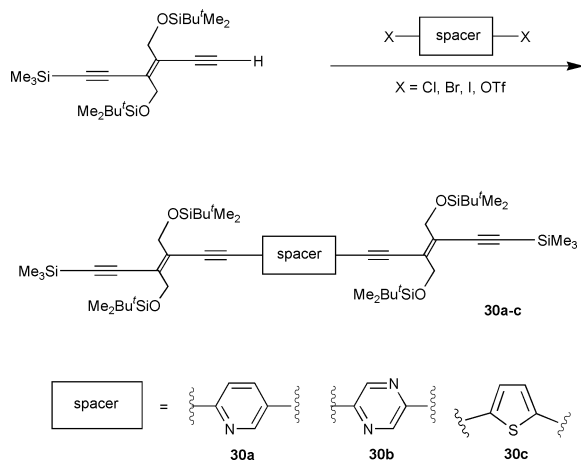
Scheme 16 Incorporation of spacer moieties into DEE oligomers.[91]

systems featured properties not displayed by the individual components.[91] Thus, the heterocyclic derivatives **30a–c** containing pyridine, pyrazine or thiophene spacers, respectively, showed a strong fluorescence emission (fluorescence quantum yields in CHCl$_3$ at 20 °C: Φ_F: 0.40 (**30a**), 0.65 (**30b**), 0.21 (**30c**)) which was present to a significant extent neither in DEE oligomers nor in the individual heteroaromatic spacer components. Pyridine derivative **30a** provided an interesting example of a molecular system, in which both the electronic absorption and emission characteristics can be reversibly switched as a function of pH. Upon protonation, the most intense electronic absorption band shifts from 337 to 380 nm and the fluorescence quantum yield decreases strongly from Φ_F = 0.40 to Φ_F = 0.07.

In another study, the porphyrin–DEE hybrid rods **31a–c**, extending in length from 2.3 (**31a**) to 3.8 (**31b**) and 5.3 nm (**31c**), were prepared by synthetic routes featuring Sonogashira cross-couplings between *meso*-iodinated porphyrin components and DEE moieties as key steps (Scheme 17).[92] Both UV/Vis and
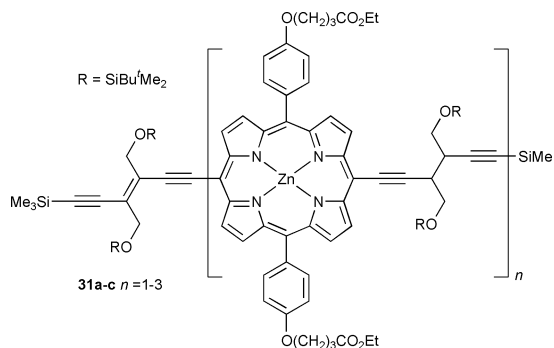

Scheme 17 Porphyrin–DEE hybrid molecular rods.[92]

electrochemical studies confirmed the existence of substantial electronic communication between the two porphyrins rings in **31b** across the *trans*-enediynediyl bridge. On the other hand, the spectra of **31b** and **31c** closely resemble each other, indicating

that saturation of the optical properties in the oligomeric series already occurs at the stage of 'dimeric' **31b**. Stationary voltammetric investigations in CH$_2$Cl$_2$ showed that the terminal DEE substituents act as strong electron acceptors which induce large anodic shifts (up to ΔE = 190 mV) in the first, porphyrin-based reduction potential.

Finally, novel classes of organometallic macrocycles (such as **32**, Scheme 18)[93] and long molecular rods have become
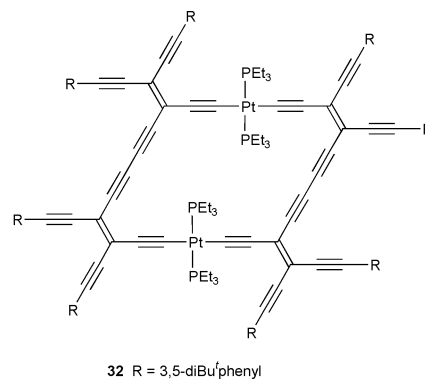
32 R = 3,5-diBu^{t}phenyl
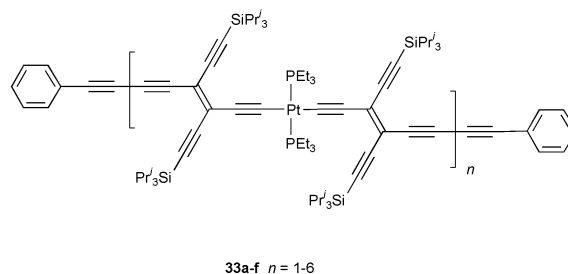
33a-f n = 1-6

Scheme 18 Novel organometallic macrocycles and molecular rods by Pt–TEE molecular scaffolding.[93,95]

available by Pt–TEE molecular scaffolding.[94,95] The series of stable oligomers **33a–f** was prepared by oxidative Glaser–Hay oligomerisation under end-capping conditions. They extend in length from 3.3 (monomeric **33a**) to 12.1 nm (hexameric **33f**). Both linear and nonlinear optical properties of these compounds revealed an almost complete lack of π-electron conjugation along the linear backbones due to the insulating character of the Pt centers and the absence of π-character in the Pt–C(sp) bonds. Purification, separation and characterisation of these remarkable organic–inorganic hybrid materials reached the performance limits of currently available analytical and preparative gel permeation chromatography.

Conclusions

Ten years after we started this research, tetraethynylethene (TEE) and (*E*)-diethynylethene ((*E*)-DEE) building blocks clearly represent one of the most versatile known molecular construction kits for the development of functional molecular architecture. Acetylenic scaffolding, starting from these modules, provided donor–acceptor substituted chromophores with exceptional optical nonlinearities, monodisperse poly(triacetylene) (PTA) oligomers with linearly π-conjugated all-carbon backbones expanding to unprecedented lengths, large carbon sheets with unusual chromophoric properties and a new class of light-driven molecular switches. This research has clearly contributed to expanding the limits in size and complexity of stable, monodisperse functional scaffolds that are accessible by organic synthesis. At the same time, it has advanced the fundamental knowledge of π-electron delocalisation in acetylenic molecular architecture. Only the tip of an immense 'iceberg' of structural diversity accessible through TEE and

DEE scaffolding has been explored today, and this chemistry will undoubtfully provide in the future many new classes of chromophores with multinanometer dimensions which could find use in optoelectronic devices and in the development of molecular-scale electronic circuitry.

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