Dendritic rods with a poly(triacetylene) backbone: insulated molecular wires

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Multinanometer long phenylacetylene-end-capped poly(triacetylene) (PTA) oligomers with dendritic side chains of generation one to three have been prepared; UV–VIS measurements indicate that there is no loss of π-electron conjugation along the PTA backbone in the higher generation compounds despite distortion from planarity due to the bulky dendritic wedges.

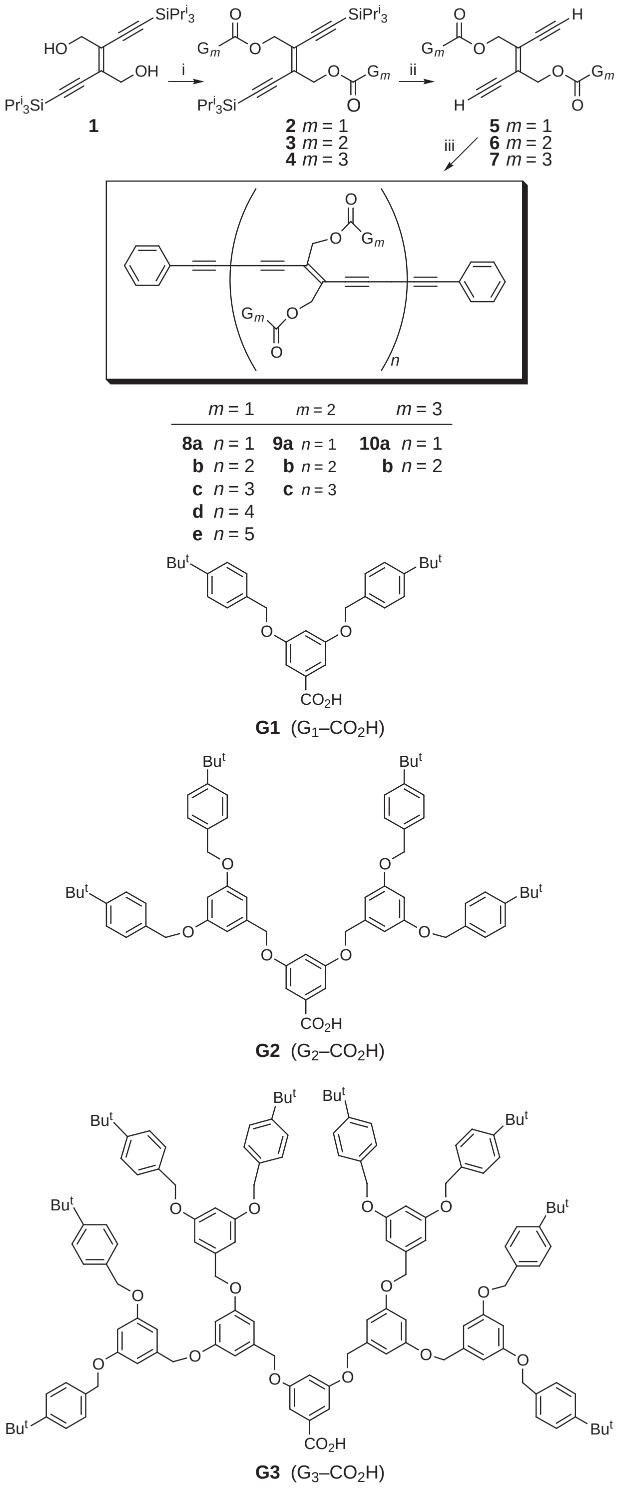
Rigid, linearly-conjugated rod-like oligomers and polymers with the poly(triacetylene) (PTA) backbone feature interesting electronic, nonlinear optical and mesomorphic properties.[1,2] We now describe the merger of dendrimer chemistry[3] with our ongoing development of functionalized PTAs to generate insulated molecular wires. Encapsulation of the linear π-conjugated backbone by laterally attached, sterically shielding dendritic wedges should enhance the processability and stability of PTA oligomers and polymers. At the same time, steric hindrance between adjacent dendritic wedges of higher generation could possibly cause nonplanarity and deconjugation of the backbone. Here, we report the synthesis of monodisperse multinanometer long dendritic PTA rods of first, second and third generation and show that π-electron conjugation in these tubular macromolecules is fully maintained at all generation levels. Previously, Schlüter and co-workers had described the preparation of cylindrical dendrimers with a poly(*p*-phenylene) backbone as the core.[4]

The convergent synthesis of the different dendritic rods is described in Scheme 1. Different generations (**G1**, **G2** and **G3**) of Fréchet-type dendrons[5] were attached to (*E*)-2,3-bis[(triisopropylsilyl)ethynyl]but-2-ene-1,4-diol **1**[1a] using the Mitsunobu reaction[6] to give the dendritic silyl-protected monomers **2**–**4**. The yield of the third generation compound **4** was very low (4%), possibly due to steric shielding of the carboxylic acid reaction centres by the bulky dendritic wedges in the molecule. After deprotection with TBAF in wet THF, the free *trans*-enediynes **5**–**7** were obtained. The dendritic wedges substantially stabilise the usually rather unstable free *trans*-enediynes, and compounds **5**–**7** can be stored in the air at ambient temperature for months without decomposition. Oxidative Hay coupling[7] of **5**–**7** in the presence of phenylacetylene as an end-capping reagent[1a] provided the oligomeric PTAs as solids. The first generation compound **5** afforded separable oligomers up to the pentamer (**8a**–**e**) which were isolated by size-exclusion chromatography (SEC), whereas, for steric reasons, the second generation derivative **6** only yielded isolable oligomers up to the trimer (**9a**–**c**).‡ Finally, due to severe steric overcrowding, conversion of the third generation enediyne **7** only gave end-capped monomer and dimer (**10a**,**b**) in pure form and sufficient yields.§

In the ^{1}H NMR spectra of the different generation oligomers, with averaged C_{2h}-symmetry, the number of *tert*-butyl resonances is equal to the number of monomeric sub-units. The ^{13}C NMR spectra did not display a significant difference in chemical shift between the clearly discernible acetylenic C-atom resonances in oligomers of same length but different dendritic generation. Force-field calculations of the third generation dimer **10b** showed clearly that the conformation of the PTA backbone, including the two end-capping phenyl groups, is not planar due to the steric hindrance of the bulky dendritic wedges. On the other hand, the first generation derivatives **8a**–**e**, similar to previous PTA oligomers,[1] should have a planar conjugated backbone. Such nonplanarity may be achieved by rotating around C(sp)–C(sp^2) and C(sp)–C(sp) single bonds in the backbone. This, in return, suggested that a decrease or even complete loss of the π-electron conjugation along the PTA backbone could occur in the higher generation compounds, which should be observable by means of spectroscopic measurements.[8]

In the electronic absorption spectra of all three oligomeric series ($CHCl_3$, Fig. 1), the longest-wavelength absorption maximum (λ_{max}) is bathochromically shifted with increasing rod length and evidently no saturation in either case was observed, confirming recent findings.[1b,2] A comparison of the spectra of dimers **8b**, **9b** and **10b** revealed that, 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 (around λ = 400 nm) with nearly identical fine structure and molar extinction coefficients [Fig. 1(*a*)]. Similarly, position, fine structure and molar extinction coefficients of the longer wavelength absorption bands in the spectra of trimers **8c** (first generation) and **9c** (second generation) are nearly identical [Fig. 1(*b*)]. A precise determination of λ_{max} required deconvolution of the UV–VIS spectra.¶ The obtained values for the dimers [Fig. 1(*a*)] showed a minimal bathochromic shift in changing from generation one to three: λ_{max} = 428.0 ± 0.2 (**8b**), 430.0 ± 0.3 (**9b**) and 431.1 ± 0.2 nm (**10b**). For all dendritic rods, the λ_{max} values were converted into energies (E_{max}/eV) which were then plotted against the reciprocal number of monomer units (1/*n*). These plots revealed for all three oligomeric series straight lines intersecting the ordinate at nearly identical E_{max} (2.57 ± 0.06 eV).[1b,2] All these data provide impressive support that π-electron delocalisation and effective conjugation length[1b] of the PTA backbone are not affected by distortions out of planarity due to steric compression of the bulky dendritic wedges at higher generations. Apparently, π-electron conjugation involving the acetylenic fragments in the PTA backbone is best described as being cylindrical rather than resulting from orbital overlap within a distinct plane and is therefore fully maintained upon rotation about C(sp)–C(sp^2) and C(sp)–C(sp) single bonds.[8–10]

The electrochemical properties of the dendritic rods **8a**–**e** and **9a**–**c** were studied by steady-state voltammetry and cyclic voltammetry in CH_2Cl_2 (+0.1 M Bu_4NPF_6).‖ All oligomers could not be oxidised in the accessible potential range but were reduced in several irreversible steps, with the electrons being transferred to the conjugated PTA backbone.[1a,b] The irreversibility increases with the dendritic generation due probably to steric hindrance.[11] As the oligomeric length increased, the first reduction step occurred at increasingly less negative potential. Plots of $E_{1/2}$ *vs.* 1/*n* (*n* = oligomeric length) gave a straight line in both series.



Scheme 1 *Reagents and conditions*: i, **G1**, **G2** or **G3**, *N,N,N′,N′*-tetramethylazodicarboxamide (TMAD), PBu$_3$, THF, 60 °C, 24 h, 81% (**2**), 61% (**3**), 4% (**4**); ii, TBAF, wet THF, 1 h, 99% (**5**), 99% (**6**), 99% (**7**); iii, **5**, **6** or **7**, CuCl, TMEDA, PhC≡CH, CH$_2$Cl$_2$, air, 25 °C, 2 h, 17% (**8a**, MW = 1193 D), 6% (**8b**, MW = 2185 D), 3% (**8c**, MW = 3176 D), 1% (**8d**, MW = 4167 D), 0.4% (**8e**, MW = 5159 D), or 9% (**9a**, MW = 2267 D), 6% (**9b**, MW = 4332 D), 2% (**9c**, MW = 6396 D), or 13% (**10a**, MW = 4414 D), 3% (**10b**, MW = 8626 D)

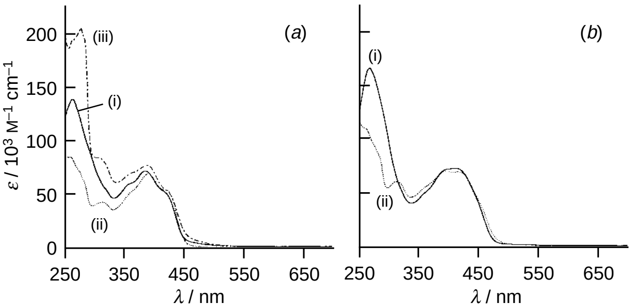


Fig. 1 Electronic absorption spectra of (*a*) (i) **8b**, (ii) **9b** and (iii) **10b** and (*b*) (i) **8c** and (ii) **9c** in CHCl$_3$ at 298 K

In the dendritic PTA rods described here, the insulating layer created by the dendritic wedges protects and stabilises the central conjugated backbone but does not alter its electronic characteristics. Efforts are now under way to prepare insulated molecular wires with the novel poly(pentaacetylene) backbone $[–(C{\equiv}C–C{\equiv}C–CR{=}CR–C{\equiv}C–C{\equiv}C)_n–]$ which, thus far, has proven quite unstable in the absence of dendritic encapsulation.[12]

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Notes and References

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‡ The dendritic rods extend in length from 19.4 (monomer) to 49.4 Å (pentamer).[1a]

§ The separation of the oligomers was achieved by preparative size-exclusion chromatography (SEC) on Bio-Beads S-X1 (Bio-Rad) with CH$_2$Cl$_2$ as eluent, and the purity of the fractions was checked by analytical SEC. All new compounds were fully characterised by ^{1}H and ^{13}C NMR, FT-IR, UV–VIS and elemental analyses (except **10b**) and MALDI-TOF-MS (matrix: 9-nitroanthracene), which depicted either the $[M + Na]^+$ or $[M + K]^+$ ions as base peaks.

¶ The UV–VIS spectra were deconvoluted using software programme PRO FIT, ver. 5.0.0 for Power Macintosh, Quantum Soft, Zürich, 1990–1996, with a self-written plug-in module.

‖ *Electrochemical data* in CH$_2$Cl$_2$ (+0.1 M Bu$_4$NPF$_6$, glassy carbon electrode). Half-wave potentials $E_{1/2}$ (V *vs.* Fc/Fc$^+$) and slopes (mV) in parenthesis: **8a**: −1.79 (98), −2.30 (120). **8b**: −1.60 (90), −1.76 (90). **8c**: −1.54 (140), −1.76 (110), −2.21 (100). **9a**: −1.84 (135), −2.35 (114). **9b**: −1.62 (105), −1.82 (110), −2.30 (75). **9c**: −1.56 (145), −1.78 (100), −2.22 (105).

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