



Multi-Nanometer-Long Poly(triacetylene) Wires

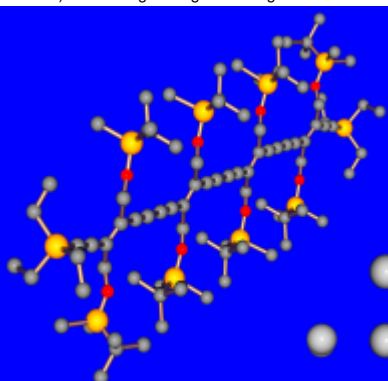
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Introduction

Poly(triacetylene)s (PTAs, $-\text{[C}=\text{C}-\text{CR}=\text{CR}-\text{C}=\text{C}]_n-$) are π -conjugated polymers with a non-aromatic all-carbon backbone, occupying an intermediate position between poly(acetylene) (PA, $-\text{[CR}=\text{CR}]_n-$) and carbyne ($-\text{[C}=\text{C}]_n-$) [1]. *Trans*-PA, when doped, exhibits electrical conductivity similar to that of copper, but the material is difficult to process and is air- and moisture sensitive. Poly(diacetylene)s (PDAs, $-\text{[CR}=\text{CR}-\text{C}=\text{C}]_n-$) are prepared by topochemical polymerization of suitable butadiynes, which limits their accessibility severely. They are not conductive but exhibit excellent second-order hyperpolarizabilities. PTAs are synthetically readily available, well soluble, and stable to normal laboratory conditions [2].

We prepared a series of stable, monodisperse PTA-oligomers from monomer **1a** up to a 17.8 nm long 24-mer **1h**. Recent synthetic efforts afforded probably a 23.6 nm long 32-mer **1i**. The 24-mer is currently the longest known molecular rod featuring a fully π -conjugated non-aromatic carbon backbone. These oligomers were synthesized by oxidative coupling of a *trans*-hex-3-ene-1,5-diyne as shown in the Synthesis part [3]. This series enabled for the first time the investigation of the evolution of the physicochemical properties of PTAs (e.g. NLO, UV/Vis, Raman) into the higher oligomeric regime where saturation of the properties becomes apparent.

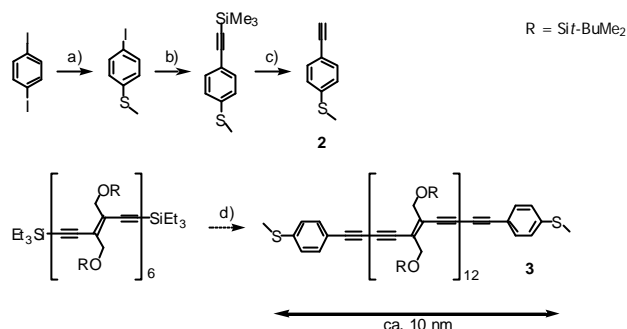


The X-ray crystal-structure of the tetramer **1c** clearly reveals a preference of the molecular rod for adopting a planar *s-trans* conformation. (orientation of two adjacent C=C bonds with respect to the bridging buta-1,3-diyndiyl linker).

The X-ray crystal-structure is shown on the left, the backbone C-atoms are shown below in three orthogonal representations.

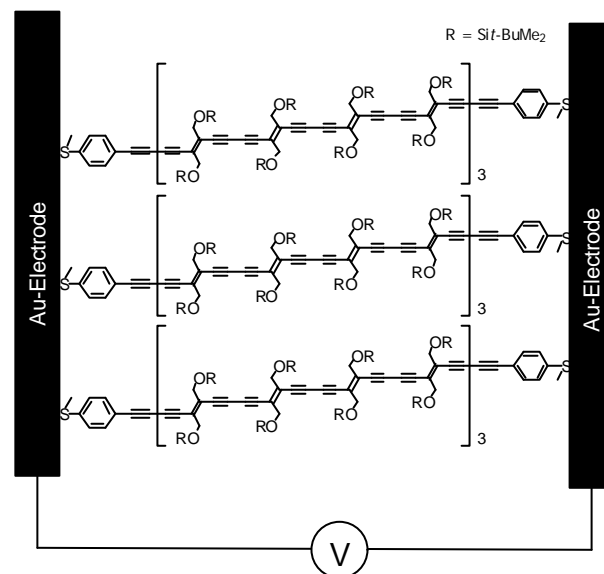
Work In Progress

As the X-ray crystal structure shows and according to results from previous experiments [4], the rod-like PTA oligomers are very rigid. In addition, there were yet no measurements of the electrical conductivity along a single PTA molecular wire. This leads to a further project, to construct a PTA molecular wire with alligator clips in order to attach the rod between gold electrodes. The minimal requirements are an end-to-end distance of ca. 10 nm, so we propose the 12-mer **3** with phenyl methyl thioether end-groups. The (possible) synthesis is described below:



a) i) *t*-BuLi, -78°C, THF; ii) S_8 ; iii) MeI, 73%; b) TMS-Acetylene, $\text{PdCl}_2(\text{PPh}_3)_2$, CuI, NEt_3 , 62%; c) 1M NaOH, THF/MeOH, quant.; d) **2**, CuCl, TMEDA, air, 1,2-DCB, 80°C

A possible setup for electrical measurements is shown below:

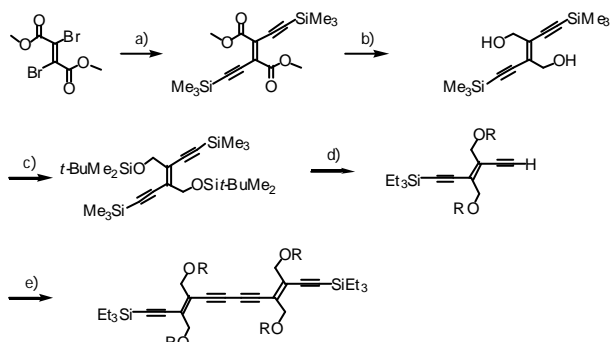


The electrical conductivity should be tunable upon doping, e.g. with metals or iodine. Introduction of different terminal or lateral groups should influence the electrical behavior as well.

Electrical conducting molecular rods with a length beyond 5 nm could be used in future assemblies of electronic circuits, e.g. in diodes, transistors, LEDs. Poly(thiophene)s polymers with a length around 5 nm were already investigated as new materials in electronic circuits [5] (see also [6] for further examples).

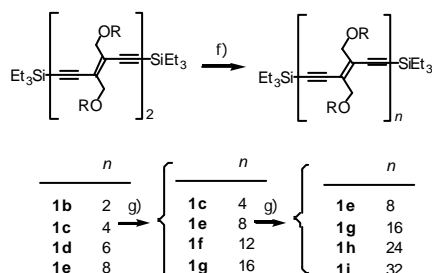
Synthesis

1. Synthesis of the 2-mer



a) TMS-Acetylene, $\text{PdCl}_2(\text{PPh}_3)_2$, CuI, THF/*i*-Pr₂NH, 45%; b) DIBALH, CH_2Cl_2 , 75%; c) *t*-BuMe₂SiCl, Imidazole, DMF, 90%; d) i) 1M NaOH, THF/MeOH; ii) BuLi, THF, -78°C; iii) Et₃SiCl, 87%; e) CuCl, TMEDA, air, CH_2Cl_2 , quant.

2. Synthesis of the higher PTA-oligomers



f) i) 1M NaOH, THF/MeOH, 15min; ii) CuCl, TMEDA, air, CH_2Cl_2 ; g) i) 1M NaOH, THF/MeOH, 10min; ii) CuCl, TMEDA, air, 1,2-DCB, 80°C.

Literature

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