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Supporting Information

for

Polymerization of Acetylene: Polyynes, but not Carbyne

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1. General Information

Solid-state IR spectra were recorded with a Varian 660-IR in ATR mode. **UV-vis spectra** were recorded with a Varian Cary 5000 UV-vis-NIR spectrophotometer. **HPLC analyses** were conducted with a Thermo Quest instrument package (pump / autosampler / detector P4000 / AS 3000 / UV6000LP; NP-Column: Macherey-Nagel ET 200/4 Nucleosil 100/5; RP-column: Varian Microsorb-MV 100-5 C18 and EC 250/4 Nucleodur 100-5 C18 HTec). **HPLC separation** was conducted with an AlphaCrom instrument package (pump / autosampler / detector / fraction collector Varian PrepStar 218 / Model 410 / ProStar325 / Model 701; RP-column: Macherey-Nagel VP 250/10 Nucleodur C18 HTec, 5 µm. Reagents were purchased reagent grade from commercial suppliers and used without further purification. THF was distilled from sodium / benzophenone. $MgSO_4 \bullet H_2O$ was used as the drying agent after aqueous work up. Unless otherwise noted in the individual procedures, all reactions were performed in standard, dry round bottom flask glassware under N_2 atmosphere. Solvent ratios are given as volume : volume. The Tr*-endcapping groups **Tr*[1–3]** were synthesized according to known procedures.[1]

2. Acetylene Gas Purification

Acetylene gas was used as the acetylene source. It can explode if the pressure of the gas exceeds about 200 kPa as a gas or when in liquid or solid form. The crude welding gas is therefore shipped and stored dissolved in acetone or dimethylformamide (DMF), contained in a metal cylinder with a porous filling (Agamassan), which renders it safe to transport and use, given proper handling. These impurities may influence the reaction, thus purification was performed in an apparatus outlined in Fig. S1.

1 R. R. Tykwinski, W. Chalifoux, S. Eisler, A. Lucotti, M. Tommasini, D. Fazzi, M. Del Zoppo and G. Zerbi, *Pure Appl. Chem.*, 2010, **82**, 891.

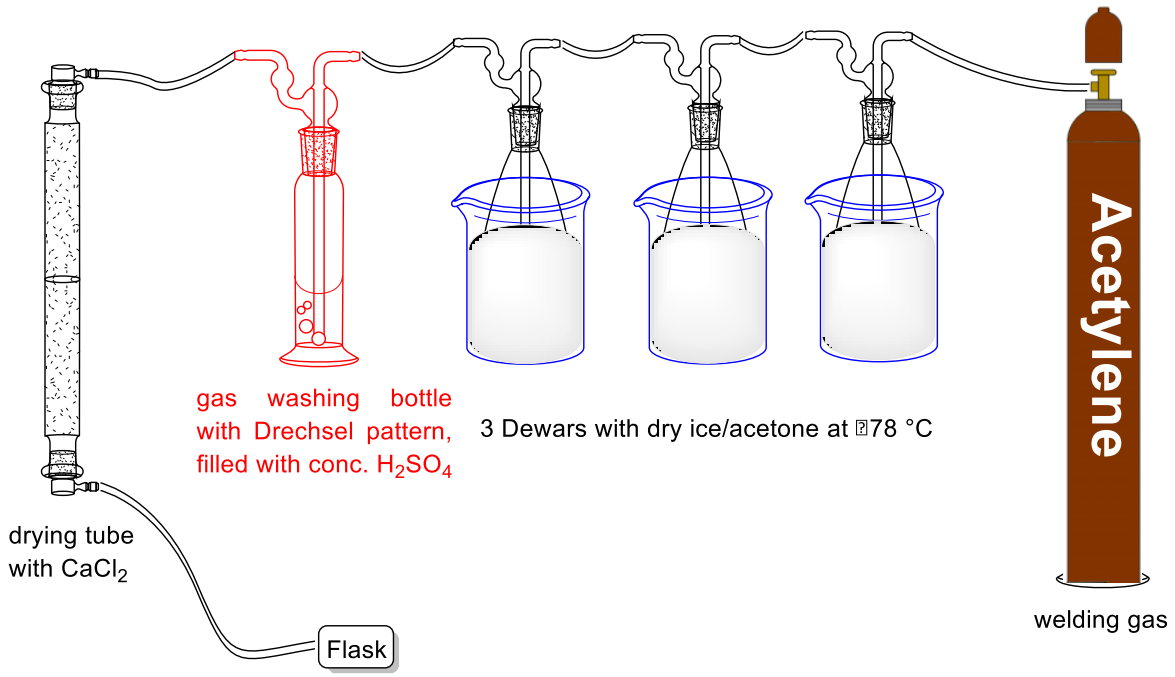

Fig. S1 Set-up for purification of acetylene gas: the crude welding gas was purified, by first passing through three cooling traps cooled by a dry ice / acetone bath, followed by a gas washing bottle with a Drechsel pattern, filled with conc. H_2SO_4, followed by a drying tube with $CaCl_2$.

3. Experimental

"Initial" polymerization procedure:

$PdCl_2(PPh_3)_2$ (1 equiv) and CuI (2 – 4 equiv) in a 100-mL three-necked flask were dissolved in dry THF (40 mL / equiv) under N_2 atmosphere. After the addition of Et_3N (800 equiv) and ethyl bromoacetate (11 equiv), acetylene gas was bubbled for 10 min *via* a gas dispersing tube into the stirring solution at rt. The endcapping group **Tr*[1–3]** (5 – 10 equiv) in dry THF (10 mL) was added and the bubbling of acetylene gas into the solution was continued for 1 h. The reaction was then stirred at rt for 16 – 22 h and quenched via the addition of H_2O (20 mL). The insoluble products were collected by filtration and washed several times with THF and dried under vacuum (for IR analysis, see Fig. S2). The filtrate was extracted with CH_2Cl_2 (40 mL), washed with saturated aqueous NaCl (2 x 40 mL), and then dried ($MgSO_4$). The solvent was removed *in vacuo* and dissolved in hexanes for UV-vis spectroscopic analysis.

Experiment 1: Using **Tr*[1]** (10 equiv) as an endcapping group

As per the "initial" polymerization procedure: $PdCl_2(PPh_3)_2$ (21 mg, 0.030 mmol), CuI (11 mg, 0.058 mmol) in dry THF (40 mL). Et_3N (2.43 g, 3.35 mL, 24.0 mmol), ethyl bromoacetate (550 mg, 0.36 mL, 3.3 mmol) in dry THF (20 mL). Compound **Tr*H[1]** (0.18 g, 0.30 mmol) in dry THF (10 mL), was used as an endcapping agent. The residue from the reaction was collected as a black solid and subjected to IR spectroscopy (Fig. S2). A soluble product (for UV-vis spectrum see Fig. S3) was isolated as a light brown solid that contained no assignable polyyne decomposition product along with ~5% of **Tr*H[1]** (~9 mg isolated after column chromatography). Summary of observations/conclusions:

- Little, or no, formation of **Tr*[*n*]** polyynes, based on IR and UV-vis spectroscopy (Figures S2 and S3).
- Only decomposition products, which could not be identified, are recovered from this reaction.
- The Tr*-group of terminal monoyne **Tr*H[1]** is too bulky to allow a coupling reaction for endcapping.

Experiment 2: Using **Tr*[2]** (5 equiv) as an endcapping group

As per the "initial" polymerization procedure: $PdCl_2(PPh_3)_2$ (21 mg, 0.030 mmol), CuI (11 mg, 0.058 mmol) in dry THF (40 mL). Et_3N (2.43 g, 3.35 mL, 24.0 mmol), ethyl bromoacetate (550 mg, 0.36 mL, 3.3 mmol). Compound **Tr*H[2]** (90 mg, 0.14 mmol) in dry THF (10 mL). After aqueous work up, the reaction mixture was passed through a pad of celite with hexanes. The filtered, insoluble solids were not further examined. Removal of the solvent resulted in a black solid (for UV-vis spectrum see Fig. S4). Summary of observations:

- Only a few absorptions were observed in lower energy region of the UV-vis spectrum
- Very small concentration of longer polyynes
- **Tr*[2]** still likely too bulky or unreactive for coupling reaction[2]

2 The homocoupling of **Tr*[2]** does not occur under standard Hay coupling conditions.

"Final" procedure: Using **Tr*[3]** (5 equiv) as an endcapping group and EBA

As per the "initial" polymerization procedure: $PdCl_2(PPh_3)_2$ (21 mg, 0.030 mmol), CuI (15 mg, 0.079 mmol) was used in dry THF (40 mL), adding Et_3N (2.43 g, 3.35 mL, 24.0 mmol), ethyl bromoacetate (0.55 g, 0.36 mL, 3.3 mmol). Compound **Tr*[3]** (91 mg, 0.14 mmol) in dry THF (10 mL) was added dropwise over 1 h, and the bubbling of acetylene gas into the solution was continued for ca. 1 h until small amounts of a black, grainy precipitate started to form. At this point, the reaction was judged complete, and N_2 was bubbled for 10 min through the solution, to remove unreacted acetylene (if this step was skipped, significant amounts of an insoluble, black precipitate were formed, which hampered the following workup). The reaction was stirred at rt for ca. 16 h and an additional portion of ethyl bromoacetate (0.55 g, 0.36 mL, 3.3 mmol) was added. After 6 h the reaction was quenched *via* the addition of H_2O (25 mL). The mixture was extracted with hexanes (3 x 90 mL), washed with saturated aqueous NaCl (75 mL) and dried ($MgSO_4$). The solvent was concentrated under reduced pressure to about 30 mL and passed through a small pad of silica gel with hexanes to give **Sample A** (ca. 180 mg of light brown solid after evaporation), before using ~5% for HPLC analysis. **Sample C** was prepared by mixing **Sample A** (20 mL) with of CH_3CN (50 mL) and of Et_2O (20 mL) to enhance solvent mixing. Solvents other than CH_3CN were then removed under reduced pressure. A brown precipitate formed after the solution was left standing for 1 d in CH_3CN. The heterogeneous mixture was then passed through a plug of SiO_2 with CH_3CN (50 mL) and concentrated to about 10 mL to give **Sample C**, which was subjected to analysis via reversed phase HPLC.

"Final" procedure: Using **Tr*[3]** (5 equiv) as an endcapping group and I_2

As per the "initial" polymerization procedure: $PdCl_2(PPh_3)_2$ (21 mg, 0.030 mmol), CuI (15 mg, 0.079 mmol) was used in dry THF (40 mL), adding Et_3N (2.43 g, 3.35 mL, 24.0 mmol), I_2 (419 mg, 3.3 mmol). Compound **Tr*[3]** (91 mg, 0.14 mmol) in dry THF (10 mL) was added dropwise over 1 h, and the bubbling of acetylene gas into the solution was continued for ca. 1 h until small amounts of a black, grainy precipitate started to form. At this point, the reaction was judged complete, and N_2 was bubbled for 10 min through the solution, to remove unreacted acetylene (if this step was skipped, significant amounts of an insoluble, black precipitate were formed, which hampered the following workup). The reaction was stirred at rt for ca. 16 h and an additional portion of I_2 (420 mg, 3.3 mmol) was

added. After 6 h the reaction was quenched *via* the addition of H_2O (25 mL). The mixture was extracted with hexanes (3 x 90 mL), washed with saturated aq $Na_2S_2O_3$ (75 mL), saturated aqueous NaCl (75 mL), and dried ($MgSO_4$). The solvent was concentrated under reduced pressure to about 30 mL and passed through a small pad of silica gel with hexanes to give **Sample B** (50 mL, yield was not estimated).

4. IR and UV-vis Spectra

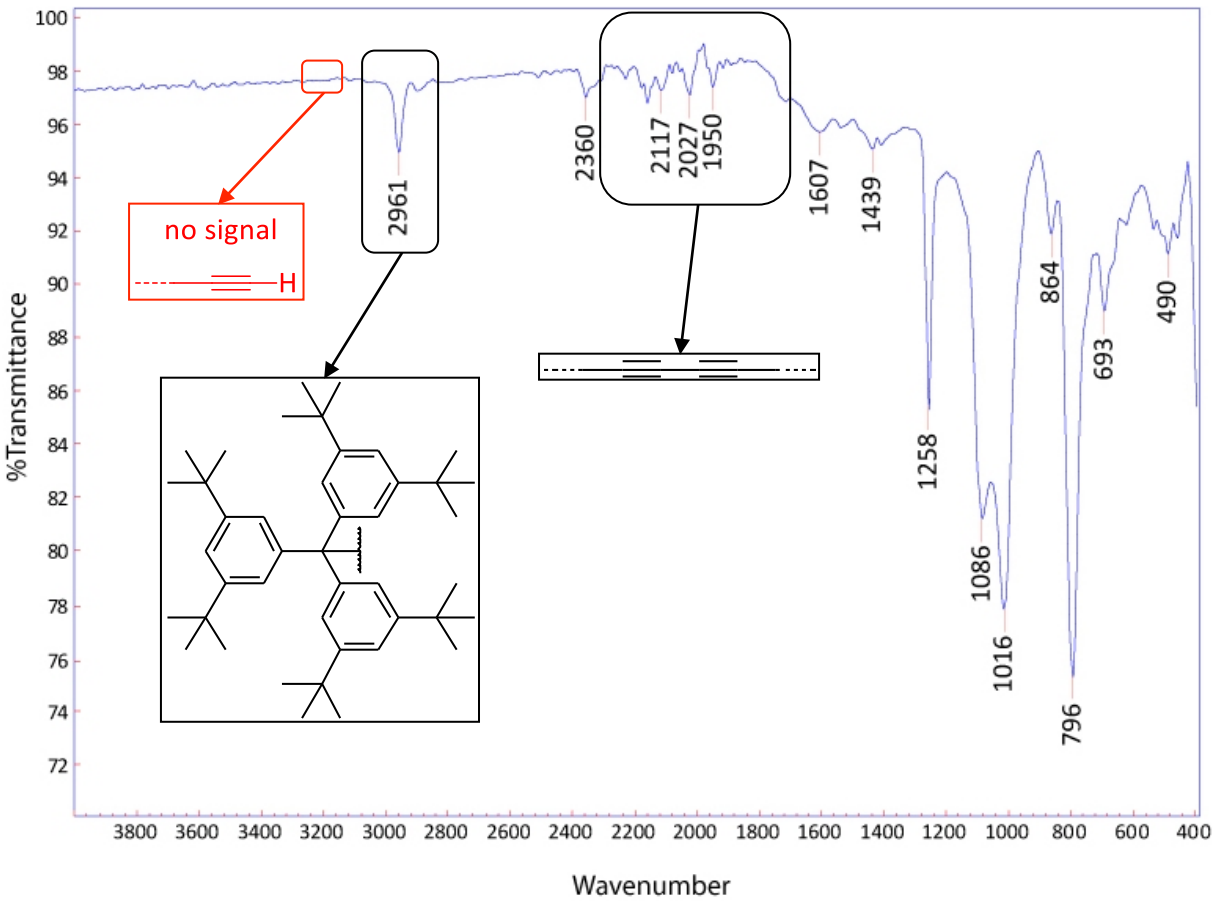

Fig. S2 IR spectrum of the solid product from **Experiment 1**. Tr*-characteristic signal at approximately 2960 cm^{-1}, but no signal for a terminal acetylene (expected at ca. 3300 cm^{-1}). Only weak signals are observed in the alkyne region.

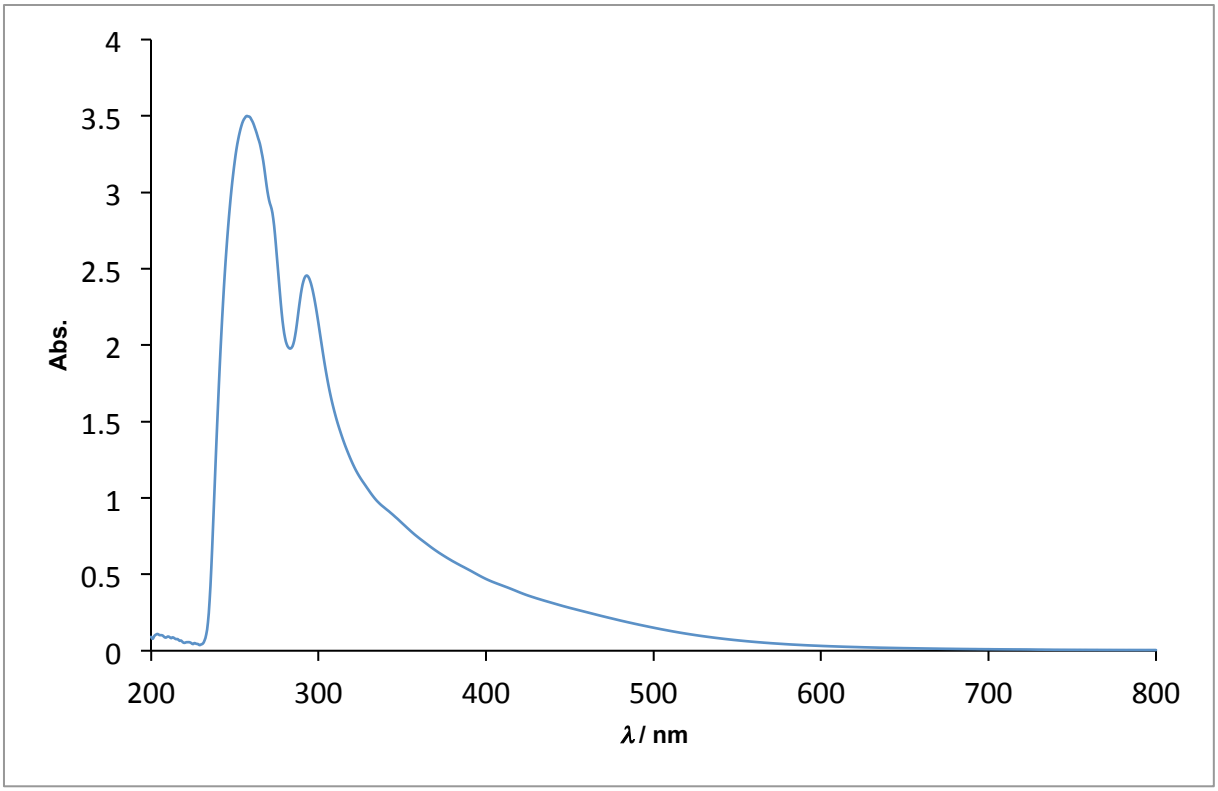

Fig. S3 UV-vis spectrum of product from **Experiment 1**, measured in hexanes.

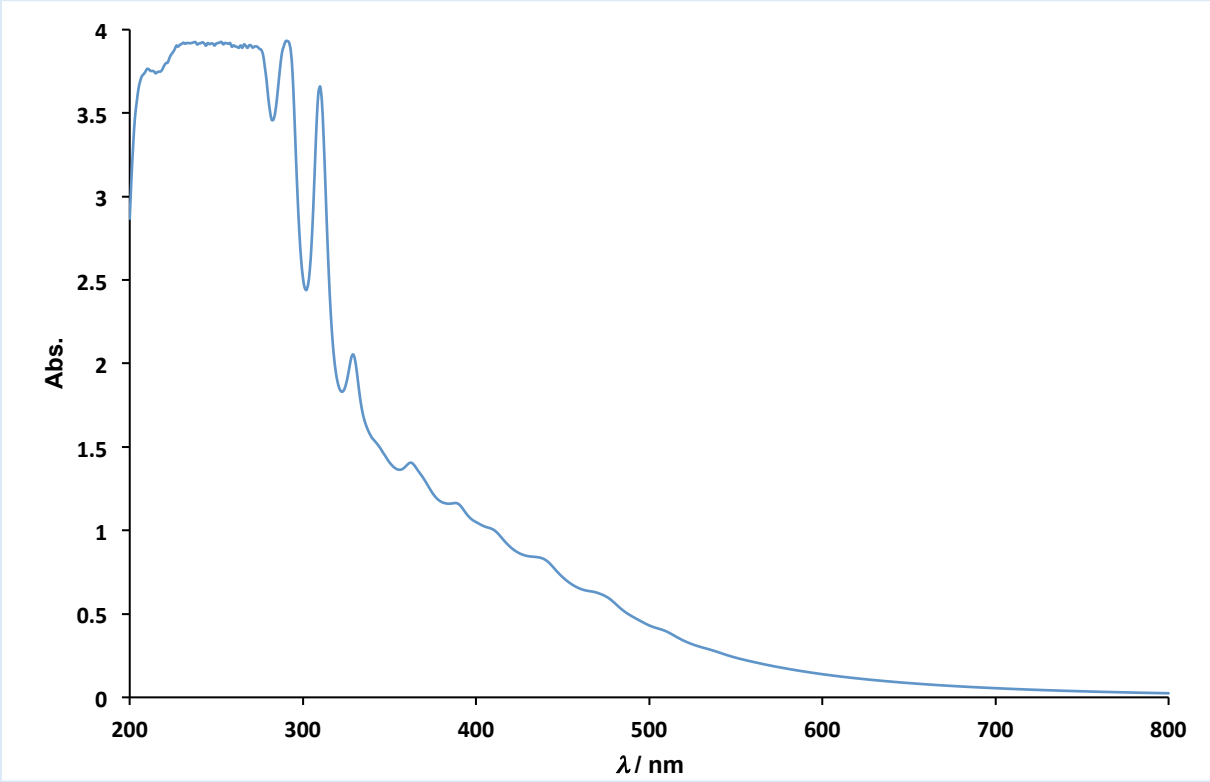

Fig. S4 UV-vis spectrum of highly concentrated reaction mixture of **Experiment 2** in hexanes.

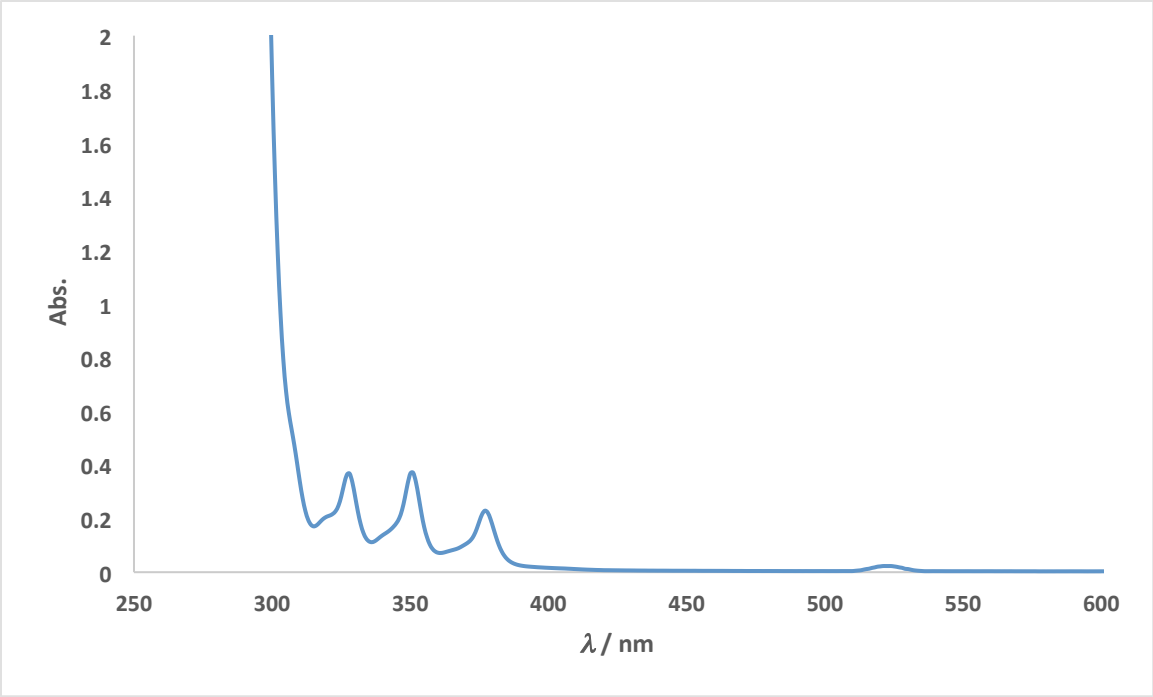

Fig. S5 UV-vis spectrum of concentrated reaction mixture of **Sample B,** in hexanes, before plugging through silica gel (y-axis is increased to enhance visibility of polyyne signals). Absorption at ca. 520 nm is assigned to residual I_2 from the reaction mixture (see ref 3).

3 R. I. Gray, K. M. Luckett and J. Tellinghuisen, *J. Phys. Chem. A*, 2001, **105**, 11183.

5. (MA)LDI Spectra

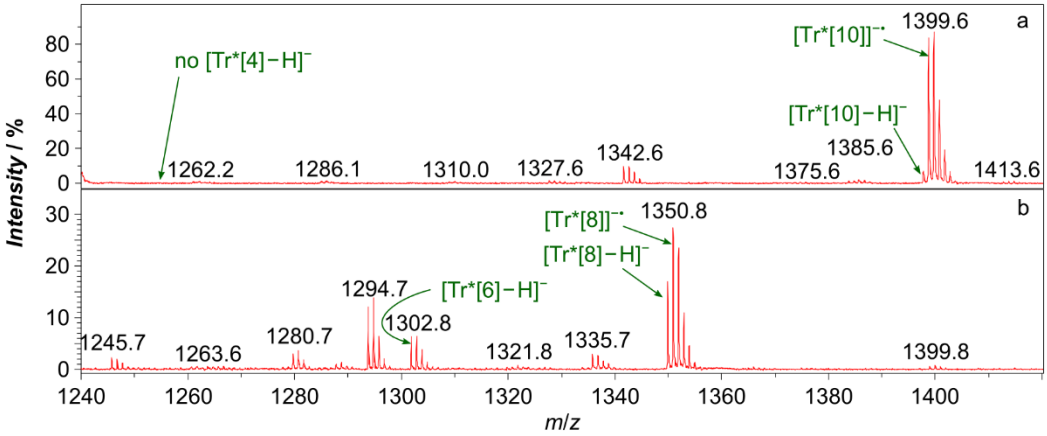

Fig. S6 MS calibration experiments, a) LDI-TOF mass spectrum (negative-ion mode) of an equimolar mixture of pure **Tr*[4]** and **Tr*[10]**. b) LDI-TOF mass spectrum (negative-ion mode) of an equimolar mixture of pure **Tr*[6]** and **Tr*[8]**. The ionization / desorption efficiency depends strongly on the chain length of the polyyne. In Figure S5a there is no anion of the **Tr*[4]** species observed although its amount in sample is equal to the amount of **Tr*[10]**, which forms efficiently [**Tr*[10]**]$^{-\bullet}$. This experiment comprises a mixture of only two polyynes. Therefore it is hard to elucidate the composition of bulk solution with a multitude of polyynes differing in their chain lengths.

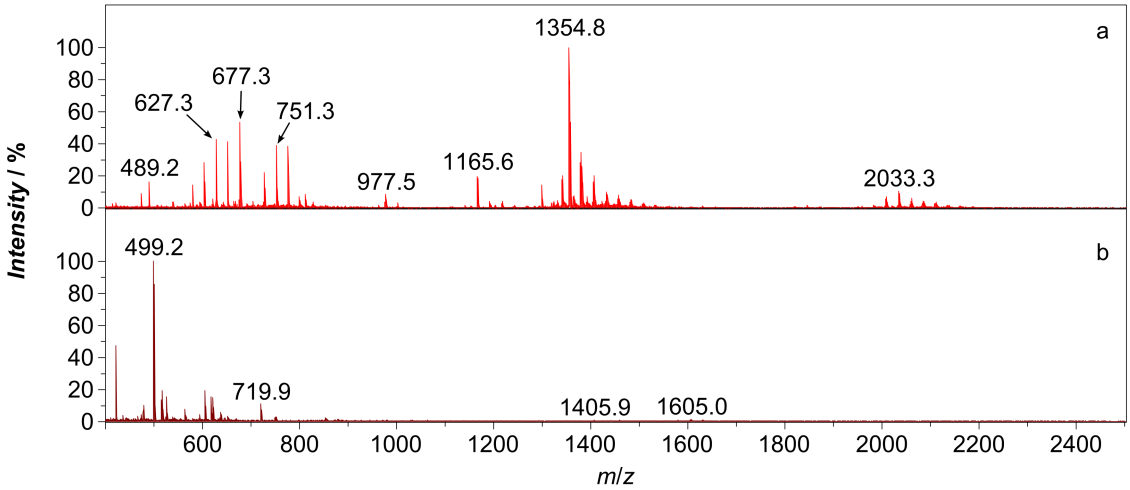

Fig. S7 a) LDI-TOF mass spectrum (negative-ion mode) of **Sample A**, and b) MALDI-TOF mass spectrum (negative-ion mode) of **Sample A** (DCTB matrix). At first glance, signals centered around *m/z* 1354.8 appear reasonable to support polyyne formation, but neither the pattern nor values of these signals are consistent with those expected for the series of **Tr*[*n*]** products.

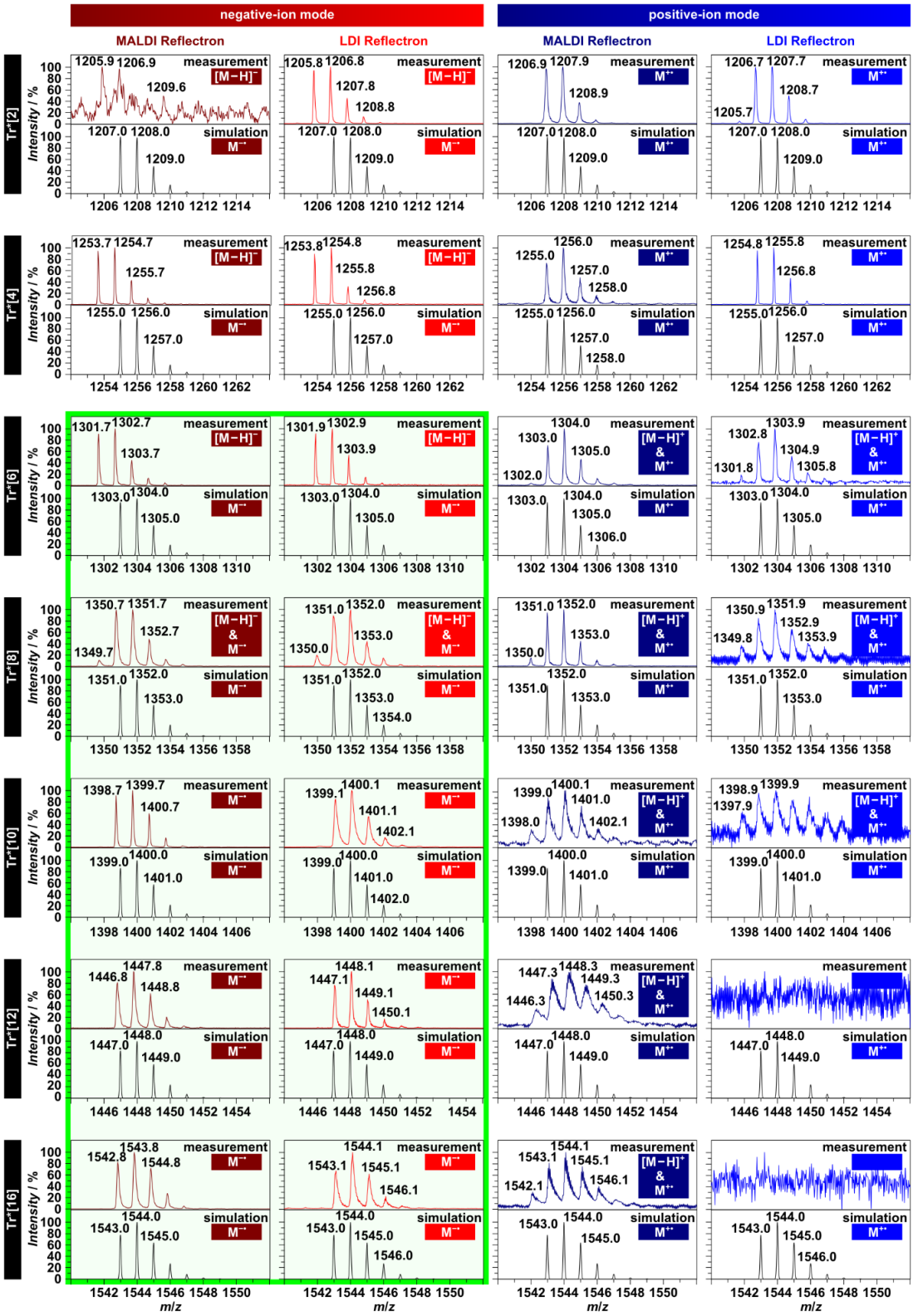

Fig. S8 (MA)LDI-ReTOF spectra (using **Sample B**): Negative-ion mode (red) and positive-ion mode (blue) of **Tr*[*n*]** polyynes of different chain lengths (n = 2, 4, 6, 8, 10, 12 and 16). The presented m/z-ranges show the $M^{+/-\bullet}$ and/or $[M-H]^{+/-}$ signal of each polyyne. Additionally each isotope pattern is compared to the corresponding simulated isotope pattern. The degree of the formal deprotonation in the negative-ion mode decreases with an increasing chain length. However, in the positive-ion mode, the lack of one hydrogen atom becomes more abundant when the chain length of the polyyne increases.

6. X-ray crystallographic data

Single crystals of **Tr*H[1]** suitable for X-ray crystallographic analysis were grown by slow evaporation of a CH_2Cl_2 solution at rt. $C_{45}H_{64}$•CH_2Cl_2, M_r = 689.88 g mol^{-1}; monoclinic crystal system; space group $P2_1/n$, a = 10.4263(9), b = 10.2668(9), c = 40.789(4) Å; β = 90.6212(14) °; V = 4366.0(7) Å^3; Z = 4; ρ_{calcd} = 1.050 g cm^{-3}; μ = 0.176 mm^{-1}; λ = 0.71073 Å; T = −80 °C; 2θ max = 51.36 °; total data collected = 31531; R_1 = 0.0607 for 6236 observed reflections with [$F_o^2 \geq 2\sigma(F_o^2)$]; wR_2 = 0.1593 for 455 variables, 6 restraints, and 8298 unique reflections with [$F_o^2 \geq -3\sigma(F_o^2)$]; residual electron density = 0.431 and −0.245 e Å^{-3}. The following distances in two of the disordered *t*-butyl groups were constrained to be equal (within 0.03 Å) during refinement: d(C21−C22A) = d(C21−C23A) = d(C21−C24A) = d(C41−C42A) = d(C41−C43A) = d(C41−C44A). Attempts to refine peaks of residual electron density as disordered or partial-occupancy solvent CH_2Cl_2 chlorine or carbon atoms were unsuccessful. The data were corrected for disordered electron density through use of the SQUEEZE procedure as implemented in *PLATON.*[4] A total solvent-accessible void volume of 494 Å^3 with a total electron count of 165 (consistent with four molecules of solvent CH_2Cl_2, or one molecule per formula unit of **Tr*H[1]**) was found in the unit cell. CCDC 1507657.

Single crystals of **Tr*H[2]** suitable for X-ray crystallographic analysis were grown by slow evaporation of a $CDCl_3$ solution at rt. $C_{47}H_{64}$, M_r = 628.98 g mol^{-1}; triclinic crystal system; space group P-1, a = 10.3367(13), b = 10.4631(13), c = 19.275(2) Å; α = 88.5549 (18), β = 78.0127(18), γ = 88.5903(19) °; V = 2038.2(4) Å^3; Z = 2; ρ_{calcd} = 1.025 g cm^{-3}; μ = 0.057 mm^{-1}; λ = 0.71073 Å; T = −80 °C; 2θ max = 54.96 °; total data collected = 17675; R_1 = 0.0523 for 7037 observed reflections with [$F_o^2 \geq 2\sigma(F_o^2)$]; wR_2 = 0.1467 for 451 variables, 0 restraints, and 9200 unique reflections with [$F_o^2 \geq -3\sigma(F_o^2)$]; residual electron density = 0.330 and −0.140 e Å^{-3}. CCDC 1507658.

Single crystals of **Tr*H[3]** suitable for X-ray crystallographic analysis were grown by slow evaporation of a xylenes solution at rt. $C_{49}H_{64}$, M_r = 653.00; trigonal crystal system; space group $P31c$, a = 14.154(3), c = 12.123(2) Å; V = 2103.4(7) Å^3; Z = 2; ρ_{calcd} = 1.031 g cm^{-3}; μ = 0.057 mm^{-1}; λ = 0.71073 Å; T = −100 °C; 2θ max = 51.43 °; total data collected = 15255; R_1 = 0.0411 for 1988 observed reflections with [$F_o^2 \geq 2\sigma(F_o^2)$]; wR_2 = 0.0882 for 148 variables, 0 restraints, and 2685 unique reflections with [$F_o^2 \geq -3\sigma(F_o^2)$]; residual electron density = 0.130 and –0.164 e Å^{-3}. CCDC 1507659.

[4] A. L. Spek, *Acta Crystallogr.* 2015, **C71**, 9–18 (*PLATON* - a multipurpose crystallographic tool. Utrecht University, Utrecht, The Netherlands).

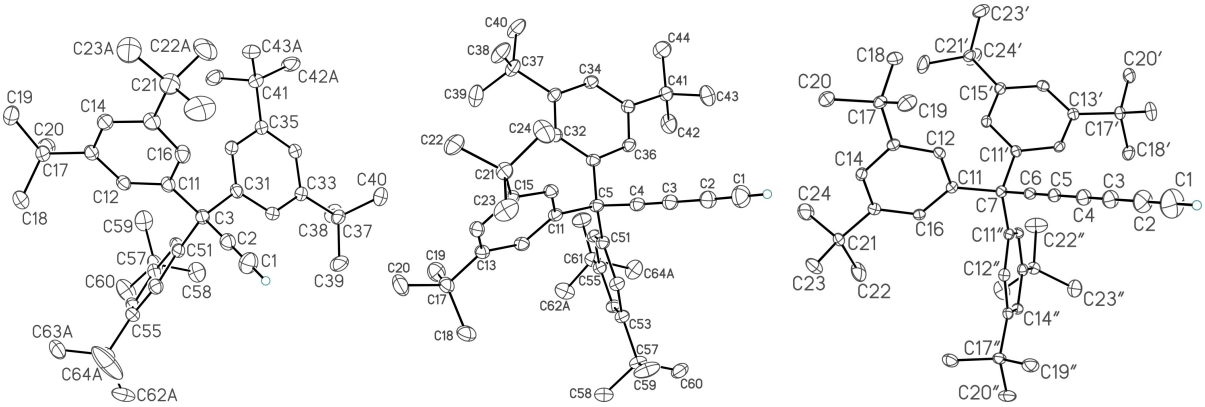

Table S1. Selected bond lengths for **Tr*H[1]–Tr*H[3]** (all values in Å).

cpmd	C1–C2	C2–C3	C3–C4	C4–C5	C5–C6	C6–C7
Tr*H[1]	1.185(3)	1.487(3)				
Tr*H[2]	1.180(2)	1.377(2)	1.200(2)	1.480(2)		
Tr*H[3]	1.177(9)	1.368(9)	1.192(8)	1.377(8)	1.199(7)	1.478(7)

Discussion of BLA. A couple of weak trends are identified for bond lengths in **Tr*H[1]–Tr*H[3]** based on molecular length.

1. The terminal alkyne bond (C1–C2) is the shortest in each molecule (in red).

2. The most internal alkyne bond is the longest in each molecule (in blue).

3. For there is a tenuous trend of bond elongation in **Tr*H[3]** from C1–C2 (1.177(9) Å) to C3–C4 (1.192(8) Å) to C5–C6 (1.199(7) Å).

4. The C–C single bond connecting the polyyne chain to the Tr* group appears to shorten ever so slightly as a function of length (green), as might be expected as the chain becomes more electron deficient.