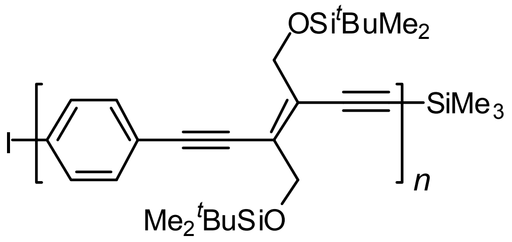
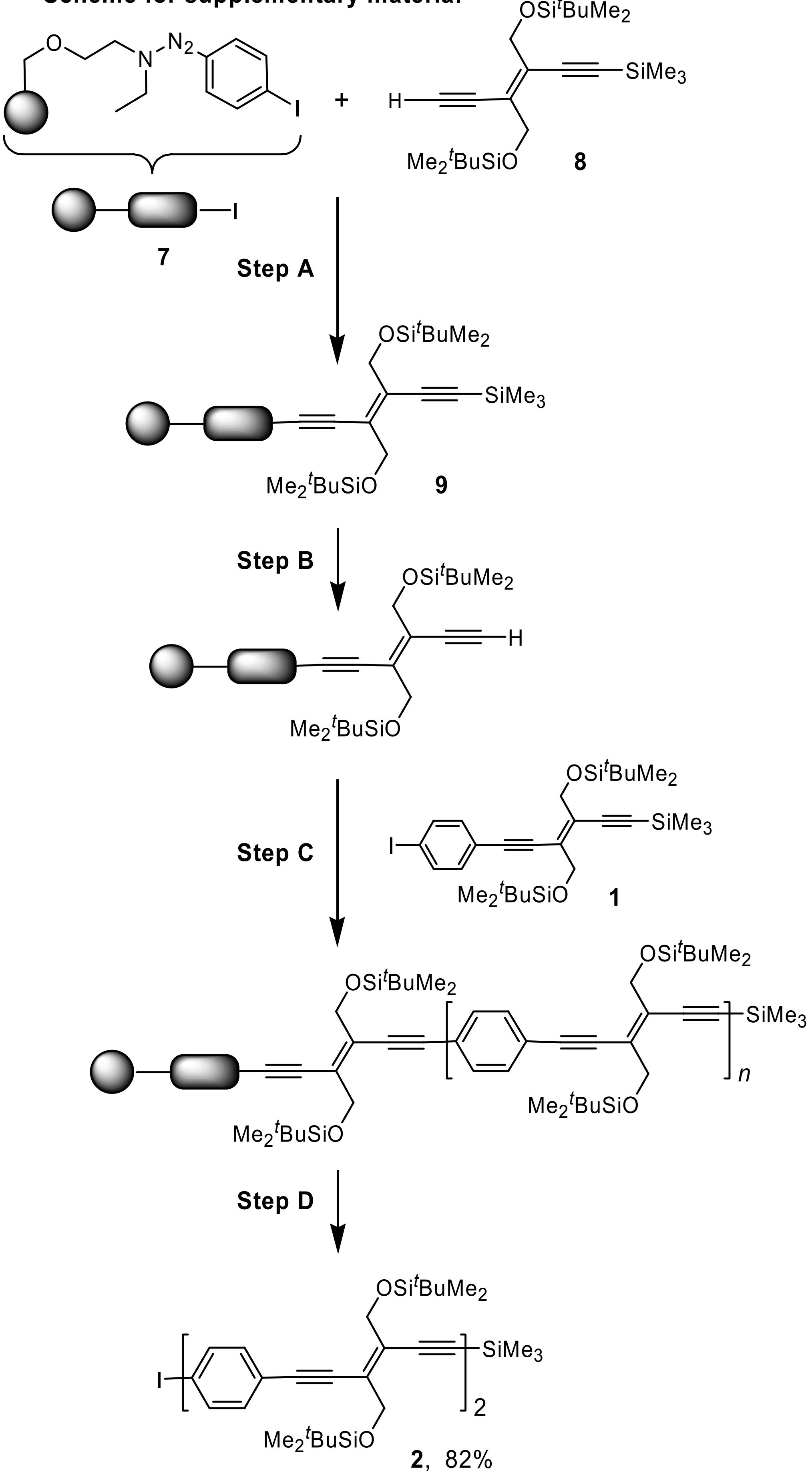
Supplementary material



1 $n = 1$
2 $n = 2$
3 $n = 3$
4 $n = 4$

Linearly π-conjugated Oligo(phenylene triacetylene)s with all-carbon backbones were prepared on solid support and shown to exhibit very high fluorescence intensities.

Scheme for supplementary material



Step A. Coupling of monodeprotected DEE 8 to the solid phase 7

To a dried, thick-walled flask with an argon inlet was added polymer-supported aryl iodide **7** (1.00 g, 0.17 mmol, 1.0 eq.), mono-deprotected DEE **8** (0.11 g, 0.24 mmol, 1.4 eq.) and THF/Et_2NH (4 : 1; 6 ml). This suspension was degassed by three freeze-pump-thaw- cycles and the flask was back-filled with argon. In a separate dry flask, a catalyst solution consisting of [$Pd_2(dba)_3$] (0.012 g, 0.013 mmol, 0.08 eq.), CuI (0.005 g, 0.025 mmol, 0.15 eq.), PPh_3 (0.022 g, 0.085 mmol, 0.50 eq.) and THF/Et_2NH (4 : 1; 12 ml) was degassed by three freeze-pump-thaw- cycles and stirred at 70 ºC for 2 h under argon. The supernatant of this solution was transferred *via* cannula to the flask containing the polymer-supported aryl iodide **7**. This flask was sealed and kept for 24 h at 70 ºC and agitated periodically. The resin was transferred to a fritted filter using CH_2Cl_2 and washed with the following solvents (50 ml each): CH_2Cl_2, DMF, a 0.05 M solution of sodium diethyl dithiocarbamate in DMF/$Et(^iPr)_2N$ (99 : 1), DMF, CH_2Cl_2, and MeOH. Finally it was dried *in vacuo* to constant mass.

Step B. Deprotection of the TMS group of polymer-bound alkyne 9

A suspension of polymer-bound TMS-protected alkyne **9** (0.60 g, 0.10 mmol), in MeOH/THF (1 : 1; 20 ml) and 2 N aq. NaOH (1 ml) was heated under gentle stirring to 70 ºC for 3 h. The resin was transferred to a fritted filter, washed sequentially with MeOH, H_2O, MeOH, CH_2Cl_2, DMF, CH_2Cl_2, and MeOH (50 ml each), and dried *in vacuo*.

Step C. Sonogashira coupling reaction of aryl iodide 1 with deprotected polymer-bound alkyne 9

To a dried, thick-walled flask with an argon inlet was added polymer-bound deprotected alkyne **9** (0.5 g, 0.06 mmol, 1.0 eq.), aryl iodide **1** (0.057 g, 0.09 mmol, 1.5 eq.) and THF/Et_2NH (4 : 1; 3 ml). This suspension was degassed by three freeze-pump-thaw- cycles and the flask was back-filled with argon. In a separate dry flask, a catalyst solution consisting of [$Pd_2(dba)_3$] (0.004 g, 0.005 mmol, 0.08 eq.), CuI (0.002 g, 0.009 mmol, 0.15 eq.), PPh_3 (0.009 g, 0.03 mmol, 0.50 eq.) and THF/Et_2NH (4 : 1; 6 ml) was degassed by three freeze-pump-thaw- cycles and stirred at 70 ºC for 2 h under argon. The supernatant of this solution was transferred *via* cannula to the flask containing the polymer-bound deprotected alkyne **9**. This flask was sealed and kept for 24 h at 70 ºC and agitated periodically. The resin was transferred to a fritted filter using CH_2Cl_2 and washed with the following solvents (30 ml each): CH_2Cl_2, DMF, a 0.05 M solution of sodium diethyl dithiocarbamate in DMF/Et(^{i}Pr)$_2$N (99 : 1), DMF, CH_2Cl_2, and MeOH. Finally it was dried *in vacuo* to constant mass.

Step D. Liberation of the dimer 2 from the solid support

1-((*E*)-3,4-Bis{[(*tert*-butyldimethylsilyl)oxy]methyl}-6-(4-iodophenyl)hex-3-en-1,5-diyn-1-yl)-4-((*E*)-3,4-bis{[(*tert*-butyldimethylsilyl)oxy]methyl}-6-(trimethylsilyl)hex-3-en-1,5-diyn-1-yl)benzene (2).

To a dried, thick-walled flask was added polymer-supported dimer (0.70 g, 0.084 mmol) and MeI (10 ml). The suspension was degassed by three freeze-pump-thaw-cycles, the flask was backfilled with argon and sealed. The suspension was stirred for 24 h at 120 ºC. After MeI had been removed *in vacuo* the resin was transferred to a fritted filter using CH_2Cl_2 and the product was extracted from the resin with hot CH_2Cl_2 (200 ml). The resulting solution was cooled down to r.t. and filtered through a plug of SiO_2. The solvent was removed *in vacuo* and purification of the crude product by column chromatography (hexane/CH_2Cl_2 2 : 1) gave 0.074 g (0.069 mmol, 82 %) of a yellow solid (**2**).

Mp.: 179 – 180°C. UV/Vis ($CHCl_3$) λ 273 (18900), 321 (37000), 360 (54200); FT-IR (CCl_4) ν 2952 *m*, 2928 *m*, 2925 *w*, 2857 *m*, 2129 *w*, 1504 *w*, 1481 *w*, 1471 *w*, 1465 *w*, 1387 *w*, 1359 *w*, 1251 *m*, 1101 *m*, 1006 *w*, 928 *w*, 838 *s*; ^{1}H-NMR (300 MHz, $CDCl_3$) δ 0.12 (s, 12 H, $Si((C(CH_3)_3)(CH_3)_2)$), 0.14 (s, 12 H, $Si((C(CH_3)_3)(CH_3)_2)$), 0.22 (s, 9 H, $Si(CH_3)_3$), 0.93 (s, 36 H, $Si((C(CH_3)_3)(CH_3)_2)$), 4.51 (s, 2 H, CH_2), 4.54 (s, 2 H, CH_2), 4.59 (s, 2 H, CH_2), 4.61 (s, 2 H, CH_2), 7.16 (d, *J* 8.4, 2 H, Ar-C*H*), 7.40 (s, 4 H, Ar-C*H*), 7.68 (d, *J* 8.4, 2 H, Ar-C*H*); ^{13}C-NMR (75 MHz, $CDCl_3$) δ – 4.9, 0.0, 18.5, 26.2, 63.9, 64.1(× 2), 64.2, 88.2, 88.7, 88.8, 94.5, 100.1, 100.7, 100.8, 101.8, 107.1, 122.6, 123.1, 123.2, 129.6 (× 2), 129.7, 130.3, 131.2 (× 2), 132.7, 137.5; FT-ICR-MALDI-MS (DHB tl) *m/z* 1099.4236 (100, $[M + Na]^+$; calcd. for $C_{55}H_{85}O_4Si_5INa^+$: 1099.4237), 1076.4361 (17, $[M]^+$; calcd. for $C_{55}H_{85}O_4Si_5I^+$: 1076.4339), 1019.3694 (32, $[M - (C(CH_3)_3)]^+$); Anal. calcd. for $C_{55}H_{85}O_4Si_5I$ (1077.61): C 61.30, H 7.95; found: C 61.51, H 7.93.