Supplementary material

Linearly $\pi$-conjugated Oligo(phenylene triacetylene)s with all-carbon backbones were prepared on solid support and shown to exhibit very high fluorescence intensities.
**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/Et₂NH (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 [Pd₂(dba)₃] (0.012 g, 0.013 mmol, 0.08 eq.), CuI (0.005 g, 0.025 mmol, 0.15 eq.), PPh₃ (0.022 g, 0.085 mmol, 0.50 eq.) and THF/Et₂NH (4 : 1; 12 ml) was degassed by three freeze-pump-thaw-cycles and stirred at 70 °C 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 °C and agitated periodically. The resin was transferred to a fritted filter using CH₂Cl₂ and washed with the following solvents (50 ml each): CH₂Cl₂, DMF, a 0.05 M solution of sodium diethyl dithiocarbamate in DMF/Et(²Pr)₂N (99 : 1), DMF, CH₂Cl₂, 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 °C for 3 h. The resin was transferred to a fritted filter, washed sequentially with MeOH, H₂O, MeOH, CH₂Cl₂, DMF, CH₂Cl₂, 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/Et₂NH (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 [Pd₂(dba)₃] (0.004 g, 0.005 mmol, 0.08 eq.), CuI (0.002 g, 0.009 mmol, 0.15 eq.), PPh₃ (0.009 g, 0.03 mmol, 0.50 eq.) and THF/Et₂NH (4 : 1; 6 ml) was degassed by three freeze-pump-thaw cycles and stirred at 70 °C 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 °C and agitated periodically. The resin was transferred to a fritted filter using CH₂Cl₂ and washed with the following solvents (30 ml each): CH₂Cl₂, DMF, a 0.05 M solution of sodium diethyl dithiocarbamate in DMF/Et(ɪPr)₂N (99 : 1), DMF, CH₂Cl₂, 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 °C. After MeI had been removed in vacuo the resin was transferred to a fritted filter using CH₂Cl₂ and the product was extracted from the resin with hot CH₂Cl₂ (200 ml). The resulting solution was cooled down to r.t. and filtered through a plug of SiO₂. The solvent was removed in vacuo and purification of the crude product by column chromatography (hexane/CH₂Cl₂ 2 : 1) gave 0.074 g (0.069 mmol, 82 %) of a yellow solid (2).

Mp.: 179 – 180°C. UV/Vis (CHCl₃) λ 273 (18900), 321 (37000), 360 (54200); FT-IR (CCl₄) 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; ¹H-NMR (300 MHz, CDCl₃) δ 0.12 (s, 12 H, Si((C(CH₃)₃)(C₃H₃))), 0.14 (s, 12 H, Si((C(CH₃)₃)(C₃H₃))), 0.22 (s, 9 H, Si(CH₃)₃), 0.93 (s, 36 H, Si((C(CH₃)₃)(C₃H₃))), 4.51 (s, 2 H, CH₂), 4.54 (s, 2 H, CH₂), 4.59 (s, 2 H, CH₂), 4.61 (s, 2 H, CH₂), 7.16 (d, J 8.4, 2 H, Ar-CH), 7.40 (s, 4 H, Ar-CH), 7.68 (d, J 8.4, 2 H, Ar-CH); ¹³C-NMR (75 MHz, CDCl₃) 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_{4}Si_{5}INa^+: 1099.4237), 1076.4361 (17, [M]^+; calcd. for C_{55}H_{85}O_{4}Si_{5}I^+: 1076.4339), 1019.3694 (32, [M − (C(CH_3)_3)]^+); Anal. calcd. for C_{55}H_{85}O_{4}Si_{5}I (1077.61): C 61.30, H 7.95; found: C 61.51, H 7.93.