

SUPPORTING INFORMATION

“Self-organized nanofibers from a giant nanographene: effect of solvent and deposition method”

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Experimental procedures

Synthesis

Chemicals were obtained from Fluka, Aldrich and Merck and used as received. ^1H NMR and ^{13}C NMR spectra were recorded in CD_2Cl_2 or $\text{C}_2\text{D}_2\text{Cl}_4$ on a Bruker DPX 250, Bruker 300 AMX or Bruker 500 DRX with use of the solvent proton or carbon signal as internal standard. FD mass spectra were obtained on a VG Instruments ZAB 2-SEFPD. MALDI-TOF mass spectra were measured on a Bruker Reflex II-TOF spectrometer using a 337 nm nitrogen laser and 7,7,8,8-tetracyanoquinodimethane (TCNQ) as matrix. Elemental analysis was carried out on a Foss Heraeus Vario EL in the Institute for Organic Chemistry at the Johannes Gutenberg University, Mainz. The optical absorption measurements were performed on a UV/Vis Perkin-Elmer Lambda 900 spectrometer.

3,4-Bis[4-(3,7,11,15-tetramethylhexadecyl)phenyl]-2,5-diphenyl-2,4-cyclopentadien-1-one (2)

4,4'-Bis(3,7,11,15-tetramethylhexadecyl)benzyl (3.00 g, 3.8 mmol) and 1,3-diphenyl-propan-2-one (800 mg, 3.8 mmol) dissolved in *tert.*-butanol (5 ml) were heated to 80 °C. A solution of tetra-butyl ammonium hydroxide (2.6 ml of 55% solution in methanol, 2.1 mmol) and *tert.*-butanol (1.5 ml) was injected quickly. After 10 minutes, the reaction was quenched by adding ice water and subsequently dichloromethane. The organic phase was washed with water and dried with magnesium sulfate. The solvent was removed under reduced pressure and the crude product purified by column chromatography (silica gel, low boiling petroleum ether/dichloromethane 1:1) to afford **2** (2.7 g, 75 %) as a purple oil.

δ_{H} (CD_2Cl_2 , 300 MHz, 298 K) = 7.26-7.18 (10H, m), 7.00 (4H, d, $J = 8.0$), 7.83 (4H, d, $J = 8.0$), 2.69-2.47 (4H, m), 1.65-0.80 (78H, m); δ_{C} (CD_2Cl_2 , 75 MHz, 298 K) = 200.8, 155.3, 144.3, 131.7, 130.7, 130.5, 129.7, 128.3, 128.2, 127.6, 125.5, 39.7, 39.0, 38.9, 37.8, 37.8, 37.7, 33.6, 33.2, 32.8, 28.4, 25.2, 24.8, 22.9, 22.8, 19.9, 19.9, 19.9; m/z (FD-MS, 8 kV) (%) = 945.1 (100) [M^+] *Calc. mean mass*: 945.6.

Octa(3,7,11,15-tetramethylhexadecyl)-C132 precursor (3)

3,5,3',5'-Tetraethynyl-biphenyl (**1**) (137 mg, 0.55 mmol) and 3,4-bis[4-(3,7,11,15-tetramethylhexadecyl)phenyl]-2,5-diphenyl-2,4-cyclopentadien-1-one (**2**) (2.70 g, 2.85 mmol) were dissolved in *o*-xylene (10 ml) and heated under an argon atmosphere for 14 hours at 180 °C oil bath temperature. Evaporation of the solvent and purification of the crude product by column chromatography (silica gel, low boiling petroleum ether/ dichloromethane 5:1) afforded **3** (1.60 g, 76 %) as a pale yellow, highly viscous oil.

δ_{H} ($\text{C}_2\text{D}_2\text{Cl}_4$, 500 MHz, 343 K) = 7.15-7.05 (18H, m), 7.00 (4H, s), 6.87 (2H, s), 6.72-6.61 (38H, m), 6.59-6.51 (38H, m), 6.44-6.40 (4H, m), 2.45-2.20 (16H, m), 1.60-0.70 (312H, m); δ_{C} ($\text{C}_2\text{D}_2\text{Cl}_4$, 125 MHz, 298 K) = 142.5, 142.1, 141.5, 140.8, 140.7, 140.4, 140.2, 139.8, 139.7, 139.4, 138.1, 137.8, 132.0, 131.7, 131.7, 131.2, 130.7, 130.4, 127.4, 127.0, 126.8, 126.6, 126.1, 125.6, 39.7, 38.9, 38.8, 37.8, 37.7, 37.7, 37.6, 37.6, 37.5, 33.2, 33.2, 33.1, 32.5, 32.5, 28.3, 28.1, 24.9, 24.7, 24.6, 24.6, 22.8, 22.7, 20.0, 19.9, 19.9, 19.8, 19.8, 19.5, 14.4, 12.9; m/z (MALDI-TOF-MS) (%) = 3917 (15), 3918 (45), 3919 (100), 3920 (98), 3921 (80), 3922 (50), 3923 (20), 3924 (10); *Calc. mean mass*: 3920.5.

Octa(3,7,11,15-tetramethylhexadecyl)-C132 (4)

Argon was bubbled through a solution of octa(3,7,11,15-tetramethylhexadecyl)-C132 precursor (**3**) (100 mg, 2.55×10^{-2} mmol) in dry dichloromethane (150 ml). Dry iron (III) chloride (1.40 g, 8.57 mmol), dissolved in nitromethane (9 ml), was injected *via* a septum. The reaction was stirred for 4 h

and quenched by adding methanol (50 ml). The precipitate was collected by filtration, washed with methanol, dil. HCl, water and again methanol and dried *in vacuo* to afford **4** (80.0 mg, 82 %) as a soft, dark purple solid.

m/z (MALDI-TOF-MS) (%) = 3860.7 (33), 3861.7 (63), 3862.8 (99), 3863.8 (100), 3864.8 (79), 3865.8 (62), 3866.8 (38), 3867.9 (29), 3868.8 (22) [M^+]; *Calc. mean mass*: 3864.1; λ nm ($CHCl_3$; $\epsilon / 10^3 * 1 \text{ mol}^{-1} \text{ cm}^{-1}$) = 350 sh (67), 547 (58); Anal. found: C 88.30, H 8.75 ($C_{292}H_{354}$ requires C 90.77, H 9.23).¹

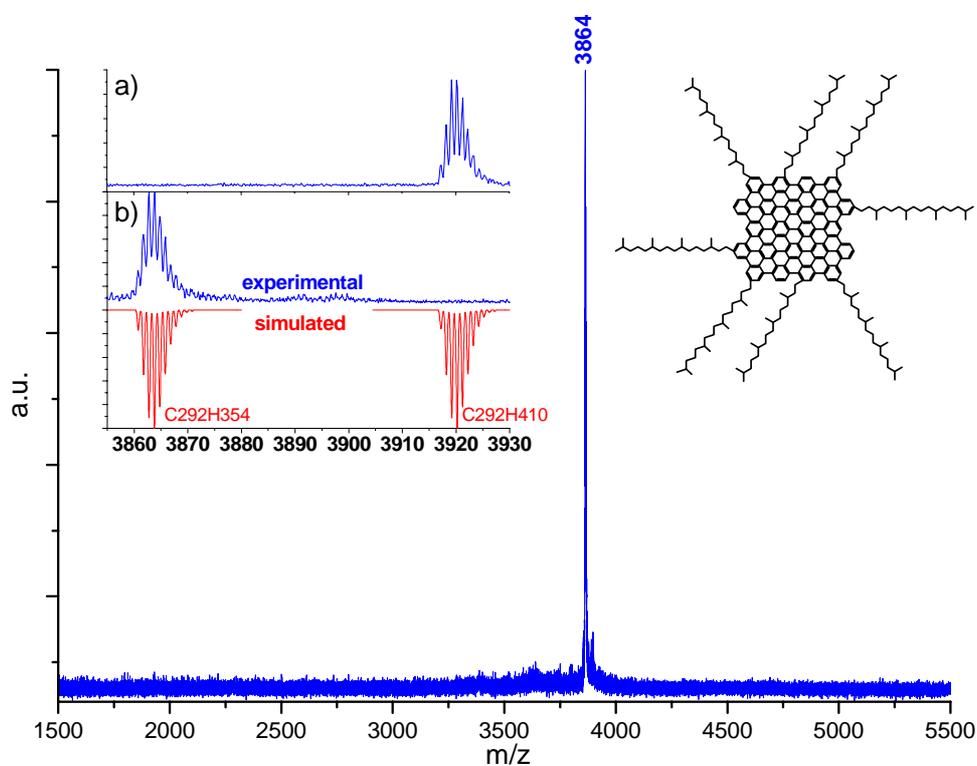


Figure S1: MALDI-TOF mass spectra of precursor molecule **3** (*inset a*) and octaalkyl **C132-C16** (**4**) (*main and inset b*). The respective calculated spectra are also shown.

¹ Because of the high carbon content in large PAHs, combustion may be incomplete (soot formation), resulting in values lower than expected