Angewandte Chemie
Eine Zeitschrift der Gesellschaft Deutscher Chemiker

Supporting Information

69451 Weinheim, Germany

Controlling Columnar Orientation of C_3-symmetric "Superbenzenes" by Alternating Polar/Apolar Substitutents

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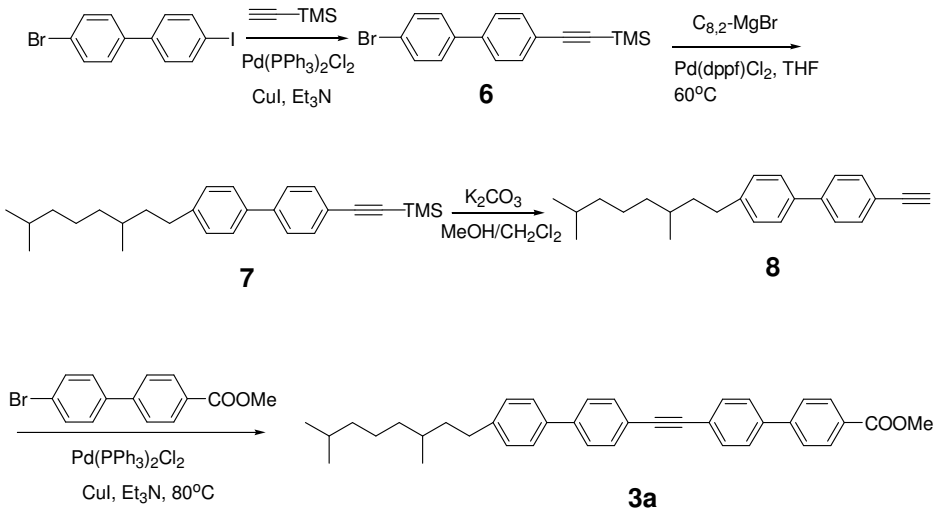
Experimental Section:

^{1}H NMR and ^{13} NMR spectra were recorded in deuterated solvents on a Bruker DPX 250, Bruker DPX 300 and Bruker DRX 500. UV-visible spectra were measured on a Perkin-Elmer Lambda 9 spectrophotometer at room temperature. Fluorescence spectra were determined on a Spex Fluorolog II (212). FD mass measurements were carried out on a VG instruments ZAB 2-SE-FPD. High-resolution MALDI-TOF mass spectra were recorded on a Bruker Reflex II-TOF Spectrometer using a 337 nm nitrogen laser with TCNQ as matrix. Melting point was measured by BüCHI Melting Point B-545 without correction. DSC was measured by Mettler DSC 30 with a heating rate of 10 K/min from –150 °C to 250°C. The optical textures of the compound were investigated using a Zeiss microscope with polarizing filters equipped with a Hitachi KP-D50 Colour digital CCD camera. The samples were sandwiched between two glass slides and then thermally treated on a Linkam hotstage regulated with a Linkam TMS 91 temperature controller. The 2D-WAXS experiments were performed by means of a rotating anode (Rigaku 18 kW) X-ray beam with a pinhole collimation and a 2D Siemens detector. A double graphite monochromator for the Cu-Kα radiation (λ=0.154 nm) was used.

Unless otherwise noted, all starting materials were purchased from Aldrich, Acros, ABCR and use as received without further purification.

Scheme S1. Synthesis of **3a**.



4-(4'-bromo)biphenylethynyl-trimethylsilane (6)

12.93g (36.0mmol) 4-bromophenyl-4'-iodobenzene, 759mg (3mol%) $Pd(PPh_3)_2Cl_2$ and 413 mg CuI (6mol%) were dissolved in 125 ml triethylamine, the mixture was degassed by bubbling through argon for 20 min and then 3.72g trimethylsilylacetylene was added. The mixture was stirred at r.t. overnight, poured into aqueous HCl and extracted with dichloromethane. The organic layer was washed by water and dried over $MgSO_4$. The solvent was removed under vacuum and the residue was purified by column chromatography (DCM:Hex=1:10) to provide 11.1 g white solid (94%).

Mp: 138~140°C.

FD-MS (8 KV): m/z 329.2, calcd.: 329.31 (M^+).

^{1}H NMR (CD_2Cl_2, 250 MHz): δ ppm.7.58~7.44(m, 8H), 0.24(s, 9H).

^{13}C NMR (62.5 MHz, CD_2Cl_2): δ ppm 140.20, 139.50, 132.72, 132.30, 128.95, 127.07, 122.83, 122.23, 104.90, 95.57, -0.035.

Elemental Analysis: Calculated: C 62.00, H 5.20, Br 24.26, Si 8.53; Found: C 62.10 , H 5.24.

4-(4'-(3''-7''-dimethyloctanyl))biphenylethynyl-trimethylsilane (7)

11.2g (34.0mmol) **6**, 1.38g (5mol%) $Pd(dppf)Cl_2$ and 10ml THF were added in the flask. Then the Gringard reagent $C_{8,2}MgBr$ (1.5eq) was added dropwise. The reaction was kept at 60°C overnight and quenched by adding the methanol. The solvent was removed under vacuum and purified by column chromatography (PE) to provide 12.2g light yellow oily-solid (92%).

FD-MS (8 KV): m/z 390.5, calcd.: 390.68 (M^+).

^{1}H NMR (CD_2Cl_2, 250 MHz): δ ppm 7.50(m, 6H), 7.25(d, 2H, J=7.88Hz), 2,51(m, 2H), 1.52~0.82(m, 19H), 0.25(s, 9H).

^{13}C NMR (62.5 MHz, CD_2Cl_2): δ ppm 143.52, 141.50, 137.70, 132.60, 129.29, 127.11, 127.02, 122.05, 105.25, 95.02, 39.71, 39.32, 37.51, 33.45, 32.93, 28.38, 25.08, 22.85, 22.76, 19.76, 0.02.

4-(4'-(3''-7''-dimethyloctanyl)biphenylacetylene (8)

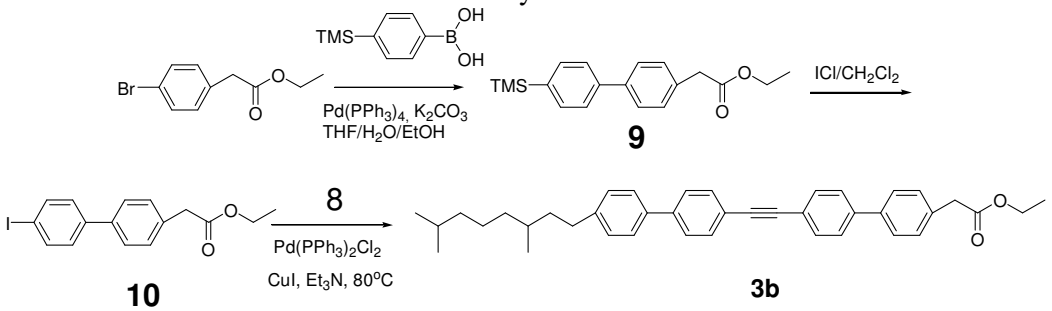
12.0g (30.71mmol) **7** and 3eq K_2CO_3 were dissolved in 40ml dichloromethane and 200 methanol, the mixture was stirred overnight and quenched by adding the water. The organic phase was extracted with dichloromethane and washed by brine, dried by $MgSO_4$, the organic solvent was removed under vacuum and purified by column chromatography (PE) to afford 9.59g light yellow oily-solid (98%).

FD-MS (8 KV): m/z 318.7, calcd.: 318.50 (M^+).

^{1}H NMR (CD_2Cl_2, 250 MHz): δ ppm 7.54(m, 6H), 7.25(d, 2H, J=7.88Hz), 3.17(s, 1H), 2.62(m, 2H), 1.52~0.82(m, 19H).
^{13}C NMR (62.5 MHz, CD_2Cl_2): δ ppm 143.60, 141.88, 137.63, 132.83, 129.30, 127.15, 127.10, 120.92, 83.79, 78.88, 39.68, 39.31, 37.49, 33.44, 32.92, 28.36, 25.06, 22.83, 22.74, 19.74.

4-(4'-methylcarbonylphenyl)-4''-(4'''-(3'''',7''''-dimethyloctanyl)phenyl)-diphenylacetylene (3a)
5.0 g (15.7 mmol) **8** and 4.35 g (14.9 mmol) 4'-bromo-biphenyl-4-carboxylic acid methyl ester were dissolved in 100 ml triethylamine, the mixture was degassed by bubbling through argon for 20 min and then 314 mg (3mol%) $Pd(PPh_3)_2Cl_2$ and 173 mg CuI (6mol%) were added. The mixture was stirred at 80^{o}C overnight, poured into aqueous HCl and extracted with dichloromethane. The organic layer was washed by water and dried over $MgSO_4$. The solvent was removed under vacuum and the residue was purified by column chromatography (DCM:Hex=1:1 then hot $CHCl_3$) to provide 5.85 g light yellow solid (74%).
FD-MS (8 KV): m/z 528.1, calcd.: 528.72 (M^+).
^{1}H NMR (CD_2Cl_2, 250 MHz): δ ppm 8.09(d, 2H, J=8.2Hz), 7.72~7.52(m, 12H), 7.26(d, 2H, J=8.2Hz), 3.90(s, 3H), 2.62(m, 2H), 1.53~1.12(m, 10H), 0.94~0.84(m, 9H).
^{13}C NMR (62.5 MHz, CD_2Cl_2): δ ppm 167.00, 144.87, 143.55, 141.45, 139.98, 137.69, 132.44, 132.34, 130.04, 129.30, 127.58, 127.26, 127.17, 127.11, 121.96, 90.86, 89.87, 39.68, 39.30, 37.48, 33.44, 32.92, 28.35, 25.05, 22.81, 22.72, 19.73.
Elemental Analysis: Calculated: C 86.32, H 7.63, O 6.05; Found: C 86.25, H 7.65.

Scheme S2. Synthesis of **3b**.



4-ethylacetate-4'-(4''-trimethylsilyl)phenylbenzene (9)
1.47 g (6.05 mmol) 4-ethylacetate-bromobenzene, 1.76g 4-trimethylsilylphenyl boronic acid, 347g (5mol%) $Pd(PPh_3)_4$, 4.9 g K_2CO_3, 20 ml THF, 5ml EtOH and 5ml H_2O were added into flask. The mixture was degassed by two "freeze-pump-thaw"cycles and then heated to reflux overnight. After standard work-up and purification by column chromatography (Silica gel, Hex:DCM=3:1) to afford 1.66g light yellow oil (88%).
FD-MS (8 KV): m/z 312.3, calcd.: 312.48 (M^+).
^{1}H NMR (250 MHz, CD_2Cl_2): δ ppm.7.56(m, 6H), 7.33(d, 2H, J=8.22Hz), 4.42(q, 2H), 3.63(s, 2H), 1.24(t, 3H, J=7.25Hz), 0.28(s, 9H).
^{13}C NMR (62.5 MHz, CD_2Cl_2): δ ppm 171.77, 141.34, 140.11, 139.74, 134.22, 134.04, 130.13, 127.45, 126.58, 61.21, 41.22, 14.37, -1.09

4-ethylacetate-4'-(4''-iodo)phenylbenzene (10)
1.60g (5.12mmol) **9** was dissolved in 150ml CH_2Cl_2, the solution was degassed by bubbling through argon for 20 min, then 9ml ICl (1M in dichloromethane) was added dropwise. After stirring for 1hr, the

reaction was quenched by adding aqueous $Na_2S_2O_3$. After standard work-up and purification by column chromatography (Silica gel, PE:DCM= 3:1), 1.78g white solid was obtained (95%).
FD-MS (8 KV): m/z 366.4, calcd.: 366.19 (M^+).
^{1}H NMR (250 MHz, CD_2Cl_2): δ ppm.7.77(d, 2H, J=8.52Hz), 7.52(d, 2H, J=8.52Hz), 7.33(d, 4H, J=7.52Hz), 4.14(q, 2H), 3.63(s, 2H), 1.24(t, 3H, J=7.25Hz).
^{13}C NMR (62.5 MHz, CD_2Cl_2): δ ppm 171.66, 140.61, 138.97, 138.23, 134.47, 130.26, 129.22, 127.23, 93.20, 61.24, 41.20, 14.37.
Elemental Analysis: Calculated: C 52.48, H 4.13, I 34.66, O 8.74; Found: C 52.43, H 4.11.

4-(4'-ethylacetate)phenyl)- 4''-(4'''-(3'''',7''''-dimethyloctanyl)phenyl)-diphenylacetylene (3b)
2.10g (5.73 mmol) **10** and 2.0g **8** were dissolved in 100 ml triethylamine, the mixture was degassed by bubbling through argon for 20 min and then 120 mg (3mol%) $Pd(PPh_3)_2Cl_2$ and 66 mg CuI (6mol%) were added. The mixture was stirred at 80^{o}C overnight, poured into aqueous HCl and extracted with dichloromethane. The organic layer was washed by water and dried over $MgSO_4$. The solvent was removed under vacuum and the residue was purified by column chromatography (DCM:Hex=1:1) to provide 2.78 g light yellow solid (87%).
FD-MS (8 KV): m/z 556.9, calcd.: 556.78 (M^+).
^{1}H NMR (CD_2Cl_2, 250 MHz): δ ppm 7.60~7.52(m, 12H), 7.35(d, 2H, J=8.22Hz), 7.27(d, 2H, J=8.22Hz), 4.12(q, 2H), 3.64(s, 2H), 2.63(m, 2H), 1.56~1.12(m, 13H), 0.95~0.85(m, 9H).
^{13}C NMR (62.5 MHz, CD_2Cl_2): δ ppm 171.71, 143.53, 141.33, 140.88, 139.27, 137.75, 134.43, 132.34, 132.33, 130.26, 129.31, 127.16, 127.12, 122.58, 122.14, 90.38, 90.12, 61.25, 41.24, 39.70, 39.32, 37.50, 33.46, 32.94, 28.37, 25.07, 22.83, 22.74, 19.75, 14.38.
Elemental Analysis: Calculated: C 86.29, H 7.97, O 5.75; Found: C 86.22, H 7.95.

Synthesis of **4a** and **5a**:
3.80 g (7.19 mmol) **3a** was dissolved in 140 ml dioxane, the mixture was degassed by bubbling through argon for 30min and 10 mmol% $Co_2(CO)_8$ 245 mg were added, the reaction mixture was mixed under reflux for 7hrs. Stopped the reaction, the solvent was removed under vacuum, the residue was purified by column chromatography (DCM:PE=2:1) to get the final product **4a** in 30% yield as white solid and **4b** in 63% yield as white solid.
1,3,5-trikis(4'-methylcarbonylphenyl)phenyl-2,4,6-trikis(4'-(3''-7''-dimethyloctanylphenyl))phenyl) -benzene (4a)
Mp: 228~231^{o}C.
FD-MS (8 KV): m/z 1586.0, calcd.: 1586.17 (M^+).
^{1}H NMR (CD_2Cl_2, 250 MHz): δ ppm 7.94(d, 6H, J=8.48Hz), 7.47(d, 6H, J=8.48Hz), 7.31~6.96(m, 36H), 3.84(s, 9H), 2.53(m, 6H), 1.50~1.08(m, 30H), 0.88~0.80(m, 27H).
^{13}C NMR (62.5 MHz, CD_2Cl_2): δ ppm: 167.07, 145.24, 142.75, 140.75, 140.53, 139.68, 138.12, 137.87, 136.90, 132.25, 130.10, 128.99, 126.93, 126.72, 125.80, 125.37, 52.23, 39.66, 37.44, 33.31, 32.82, 25.02, 22.86, 22.77, 19.69.
Elemental Analysis: Calculated: C 86.32, H 7.63, O 6.05; Found: C 86.32, H 7.60.

1,2,5-trikis(4'-methylcarbonylphenyl)phenyl-3,4,6-trikis(4'-(3''-7''-dimethyloctanylphenyl))phenyl) -benzene (5a)
Mp: 221~223^{o}C.
FD-MS (8 KV): m/z 1586.0, calcd.: 1586.17 (M^+).
^{1}H NMR (CD_2Cl_2, 250 MHz): δ ppm 7.92(d, 6H, J=8.48Hz), 7.47(d, 6H, J=8.48Hz), 7.32~6.97(m, 36H), 3.84(s, 9H), 2.53(m, 6H), 1.50~1.08(m, 30H), 0.88~0.80(m, 27H).
^{13}C NMR (62.5 MHz, CD_2Cl_2): δ ppm: 167.05, 145.19, 142.70, 141.22, 140.64, 140.41, 139.68, 138.12, 137.92, 136.93, 132.48, 132.25, 130.11, 129.07, 128.98, 126.89, 126.74, 125.82, 125.35, 52.24, 39.66, 39.27, 37.45, 33.32, 32.82, 28.33, 25.02, 22.80, 22.71, 19.69.
Elemental Analysis: Calculated: C 86.32, H 7.63, O 6.05; Found: C 86.28, H 7.55.

Synthesis of **4b** and **5b**:
2.80 g (5.03 mmol) **3b** was dissolved in 100 ml dioxane, the mixture was degassed by bubbling through argon for 30min and 10 mmol% $Co_2(CO)_8$ 172 mg was added, the reaction mixture was mixed under reflux for 7hrs. Stopped the reaction, the solvent was removed under vacuum, the residue was purified by column chromatography (DCM:PE=2:1) to get the final product **4b** in 31% yield as waxy sticky solid and **5b** in 63% yield as waxy sticky solid.

1,3,5-trikis(4'-ethylacetatephenyl)phenyl-2,4,6-trikis(4'-(3''-7''-dimethyloctanylphenyl))phenyl)-benzene (4b)

FD-MS (8 KV): m/z 1671.3, calcd.: 1670.33 (M^+).
^{1}H NMR (CD_2Cl_2, 250 MHz): δ ppm 7.33(m, 12H), 7.15(m, 24H), 6.99(m, 12H), 4.06(q, 6H), 3.55(s, 6H), 2.54(m, 6H), 1.53~1.09(m, 38H), 0.90~0.82(m, 27H).
^{13}C NMR (62.5 MHz, CD_2Cl_2): δ ppm:.171.71, 142.62, 140.72, 140.66, 140.31, 139.88, 139.59, 138.05, 137.65, 133.57, 132.35, 132.30, 129.86, 128.95, 127.06, 126.79, 125.42, 125.30, 61.11, 41.20, 39.67, 39.29, 37.46, 33.33, 32.84, 28.33, 25.02, 22.80, 19.69, 14.33.
Elemental Analysis: Calculated: C 86.29, H 7.97, O 5.75; Found: C 86.22, H 7.91.

1,2,5-trikis(4'-ethylacetatephenyl)phenyl-3,4,6-trikis(4'-(3''-7''-dimethyloctanylphenyl))phenyl)-benzene (5b)

FD-MS (8 KV): m/z 1671.2, calcd.: 1670.33 (M^+).
^{1}H NMR (CD_2Cl_2, 250 MHz): δ ppm 7.35(m, 12H), 7.16(m, 24H), 7.00(m, 12H), 4.07(q, 6H), 3.55(s, 6H), 2.54(m, 6H), 1.53~1.09(m, 38H), 0.90~0.82(m, 27H).
^{13}C NMR (62.5 MHz, CD_2Cl_2): δ ppm: 171.72, 142.62, 140.70, 140.30, 139.90, 139.60, 138.05, 137.66, 133.59, 132.31, 129.87, 128,96, 127.07, 126.80, 125.45, 125.31, 61.12, 41.21, 39.68, 39.29, 37.47, 33.34, 32.85, 28.34, 25.04, 22.82, 22.73, 19.71, 14.35.
Elemental Analysis: Calculated: C 86.29, H 7.97, O 5.75; Found: C 86.24, H 7.90.

1,7,13-trikis(4'-methylcarbonylphenyl)-4,10,16-trikis(4'-(3''-7''-dimethyloctanylphenyl)-hexa-peri-hexabenzocoronene (1a)

100 mg (0.0631 mmol) **4a** was dissolved in 50ml dichloromethane, the solution was then degassed by bubbling through argon for 20 min, and then 368 mg $FeCl_3$ (36eqv) in 1.5ml CH_3NO_2 was added dropwise. After being stirred for 1hr, the reaction was quenched by adding methanol, the yellow precipitate was collected, washed by water and methanol repeatedly and dried under vacuum to afford 80.4 mg yellow powder (81%).
MALDITOF-MS (TCNQ as matrix): m/z=1573.85, calcd. 1574.07 for $C_{114}H_{108}O_6$.
^{1}H NMR ($CDCl_2CDCl_2$, 500 MHz, 140^{o}C): δ ppm 7.56(brs, 12H), 6.77(br, 24H), 3.98(s, 9H), 2.60(brs, 6H), 1.67~0.99(m, 57H).
^{13}C NMR can not be clearly resolved due to poor solubility.
Elemental Analysis: Calculated: C 86.99, H 6.92, O 6.10; Found: C 86.16, H 7.03.

1,4,13-trikis(4'-methylcarbonylphenyl)-7,10,16-trikis(4'-(3''-7''-dimethyloctanylphenyl)-hexa-peri-hexabenzocoronene (2a)

100 mg (0.0631 mmol) **5a** was dissolved in 50ml dichloromethane, the solution was then degassed by bubbling through argon for 20 min, and then 368 mg $FeCl_3$ (36eqv) in 1.5ml CH_3NO_2 was added dropwise. After being stirred for 1hr, the reaction was quenched by adding methanol, the yellow precipitate was collected, washed by water and methanol repeatedly and dried under vacuum to afford 83.4 mg yellow powder (84%).
MALDITOF-MS (TCNQ as matrix): m/z=1573.95, calcd. 1574.07 for $C_{114}H_{108}O_6$.
^{1}H NMR ($CDCl_2CDCl_2$, 500 MHz, 140^{o}C): δ ppm 7.50(brs, 12H), 6.75(br, 24H), 3.96(s, 9H), 2.61(brs, 6H), 1.67~0.91(m, 57H).
^{13}C NMR can not be clearly resolved due to poor solubility.
Elemental Analysis: Calculated: C 86.99, H 6.92, O 6.10; Found: C 85.89, H 6.99.

1,7,13-trikis(4'-ethylacetatephenyl)-4,10,16-trikis(4'-(3''-7''-dimethyloctanylphenyl)-hexa-peri-hexabenzocoronene (1b)

184 mg (0.108 mmol) **4b** was dissolved in 100ml dichloromethane, the solution was then degassed by bubbling through argon for 20 min, and then 644 mg $FeCl_3$ (36eqv) in 3ml CH_3NO_2 was added dropwise. After being stirred for 45min, the reaction was quenched by adding methanol, the yellow precipitate was collected, washed by methanol repeatedly and purified by column chromatography (Silica, Ethylacetate:Tolune=1:1), dried under vacuum to afford 152 mg yellow powder (85%).

MALDITOF-MS (TCNQ as matrix): m/z=1657.82, calcd. 1658.23 for $C_{120}H_{120}O_6$.

^{1}H NMR ($CDCl_2CDCl_2$, 500 MHz, 140°C): δ ppm 8.21(brs, 12H), 7.53(brs, 12H), 7.42(brs, 6H), 7.34(brs, 6H), 4.44(q, 6H), 3.91(brs, 6H), 2.95(brs, 6H), 2.01(m, 3H), 2.00~1.23(m, 48H), 1.04(m, 15H).

^{13}C NMR (125MHz, CD_2Cl_2, 100°C): δ ppm 170.98, 141.85, 139.83, 138.43, 136.15, 135.63, 132.95, 129.62, 128.68, 128.38, 127.45, 127.34, 121.95, 118.96, 117.52, 60.46, 40.94, 39.45, 36.10, 37.35, 33.33, 33.12, 27.85, 24.73, 22.53, 22.46, 19.68, 14.30.

Elemental Analysis: Calculated: C 86.92, H 7.29, O 5.79; Found: C 86.34, H 6.81.

1,4,13-trikis(4'-ethylacetatephenyl)-7,10,16-trikis(4'-(3''-7''-dimethyloctanylphenyl)-hexa-peri-hexabenzocoronene (2b)

586 mg (0.344 mmol) **5b** was dissolved in 279ml dichloromethane, the solution was then degassed by bubbling through argon for 20 min, and then 2.05g $FeCl_3$ (36eqv) in 7ml CH_3NO_2 was added dropwise. After being stirred for 45min, the reaction was quenched by adding methanol, the yellow precipitate was collected, washed by methanol repeatedly and purified by column chromatography (Silica, Ethylacetate:Tolune=1:1), dried under vacuum to afford 496 mg yellow powder (87%).

MALDITOF-MS (TCNQ as matrix): m/z=1657.80, calcd. 1658.23 for $C_{120}H_{120}O_6$.

^{1}H NMR ($CDCl_2CDCl_2$, 500 MHz, 140°C): δ ppm 8.27(brs, 12H), 7.56(brs, 12H), 7.43(brs, 6H), 7.36(brs, 6H), 4.44(q, 6H), 3.91(brs, 6H), 2.96(brs, 6H), 2.02(m, 3H), 2.00~1.23(m, 48H), 1.04(m, 15H).

^{13}C NMR (125MHz, CD_2Cl_2, 100°C): δ ppm 170.99, 141.84, 139.84, 138.43, 136.17, 135.64, 132.97, 129.63, 128.68, 128.39, 127.44, 127.35, 121.97, 118.96, 117.53, 60.49, 40.95, 39.48, 39.10, 37.36, 33.32, 33.11, 27.88, 24.74, 22.54, 22.47, 19.69, 14.30.

Elemental Analysis: Calculated: C 86.92, H 7.29, O 5.79; Found: C 86.40, H 7.09.

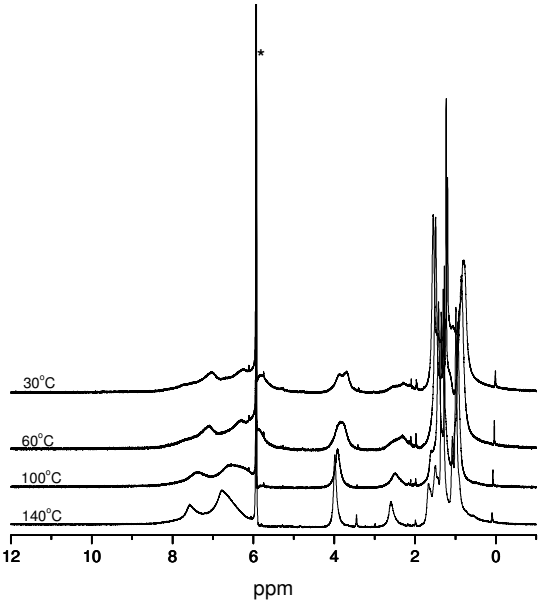


Figure S1. Temperature-dependant ^{1}H NMR (500 MHz) spectra of **1a** in [D_2]tetrachloroethane (*)

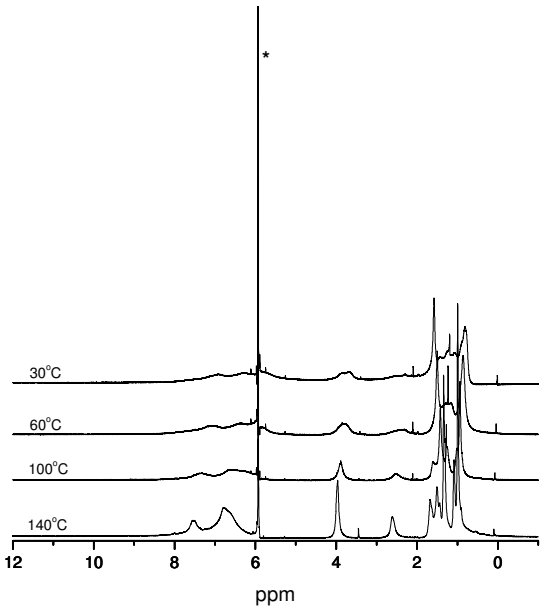


Figure S2. Temperature-dependant ^{1}H NMR (500 MHz) spectra of **2a** in [D_2]tetrachloroethane (*)

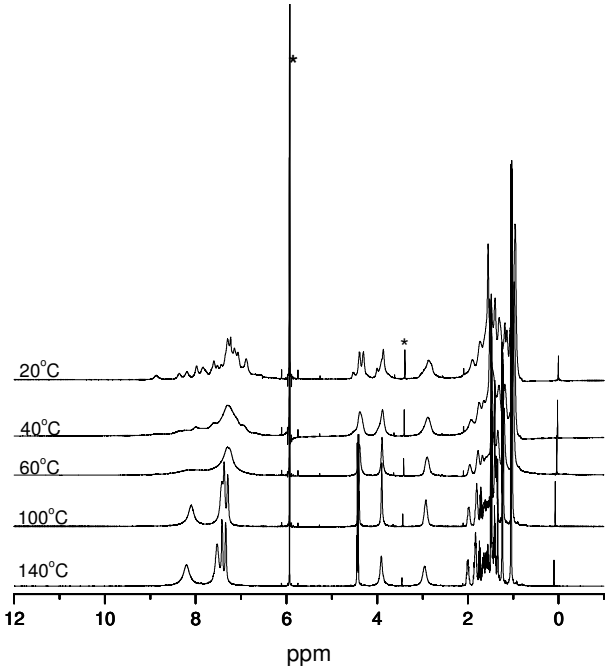


Figure S3. Temperature-dependant ^{1}H NMR (500 MHz) spectra of **1b** in [D_2]tetrachloroethane (*, solvent and with minor impurity)

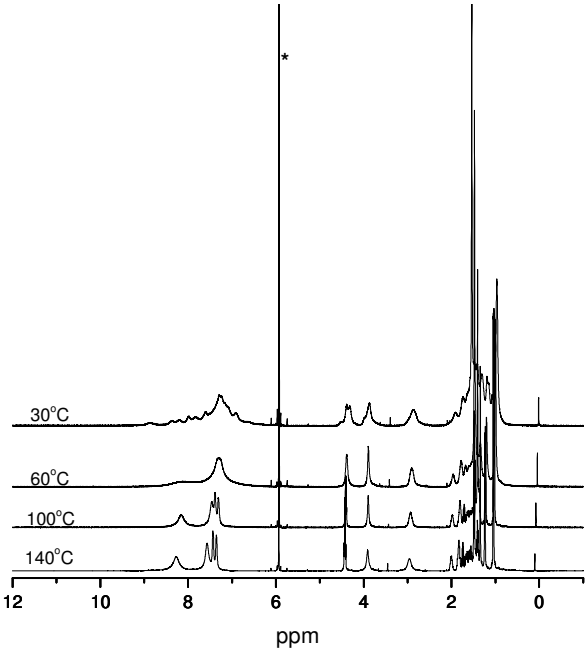


Figure S4. Temperature-dependant ^{1}H NMR (500 MHz) spectra of **2b** in [D_2]tetrachloroethane (*)

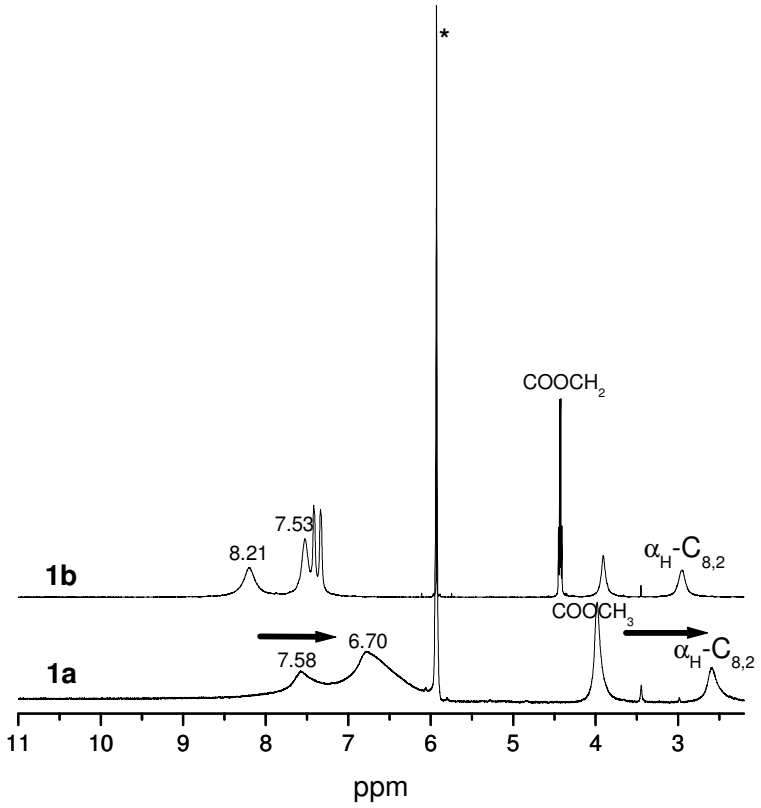


Figure S5. ^{1}H NMR spectra of **1a** and **1b** in *d*-tetrachloroethane at 140 °C.

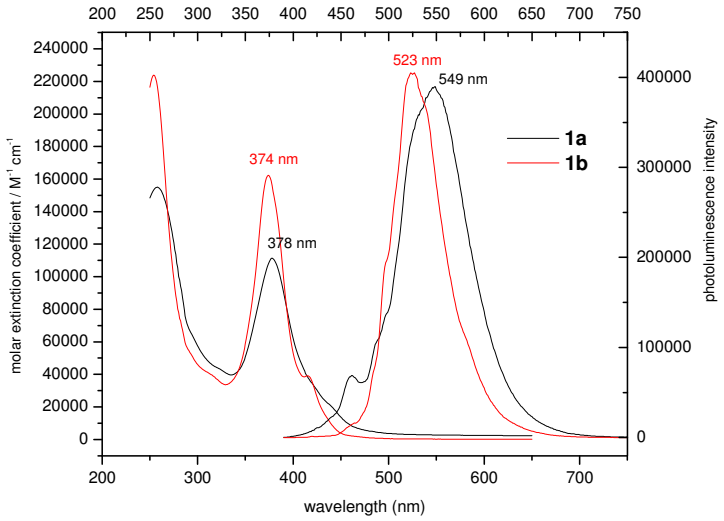


Figure S6. UV-vis and photoluminescence spectra for **1a** (black) and **1b** (red) in THF (5.0×10^{-6}M).

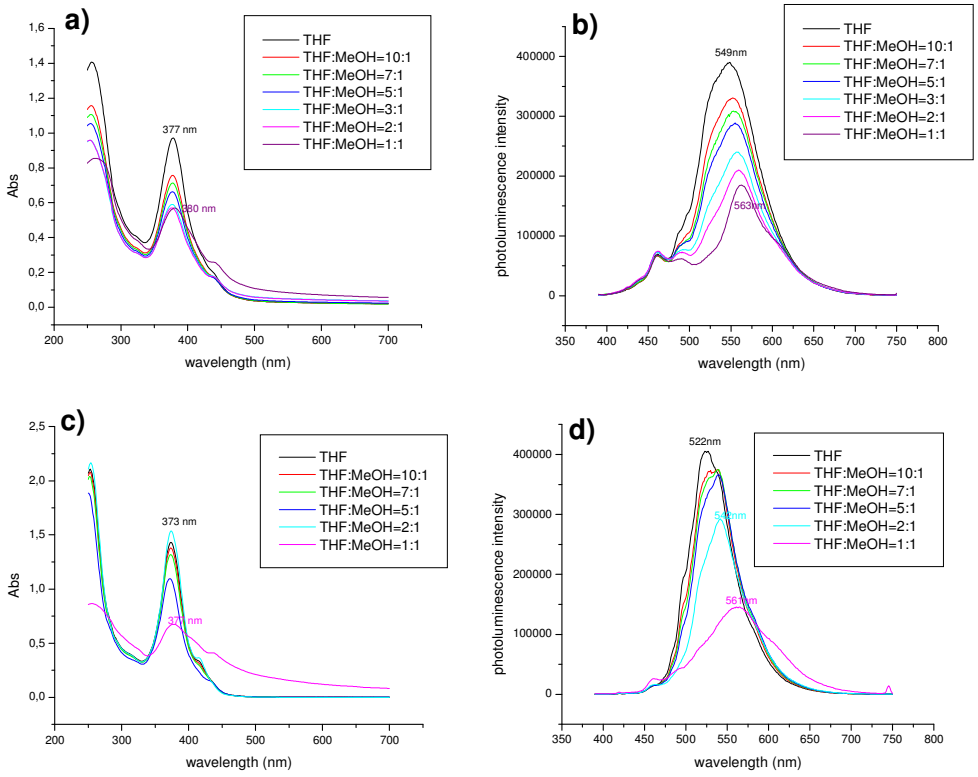


Figure S7. UV-vis and photoluminescence spectra for **1a** (a and b) and **1b** (c and d) in THF-MeOH mixed solvents (1.0×10^{-5}M).

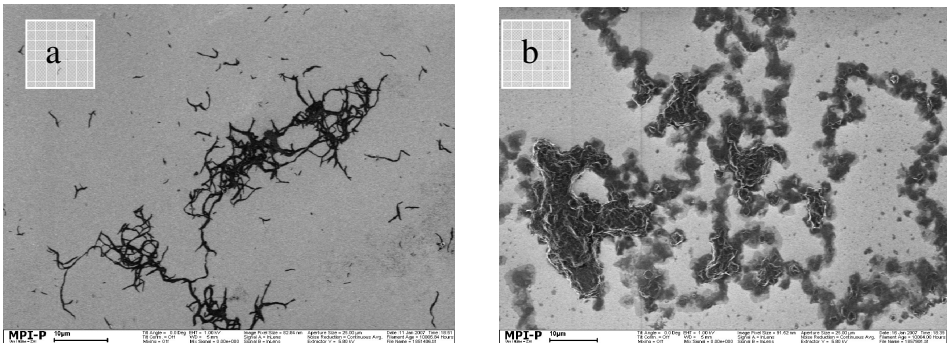


Figure S8. SEM pictures of **1a** (a) and **1b** (b) nanostructures grown from THF:MeOH=1:1 solution.

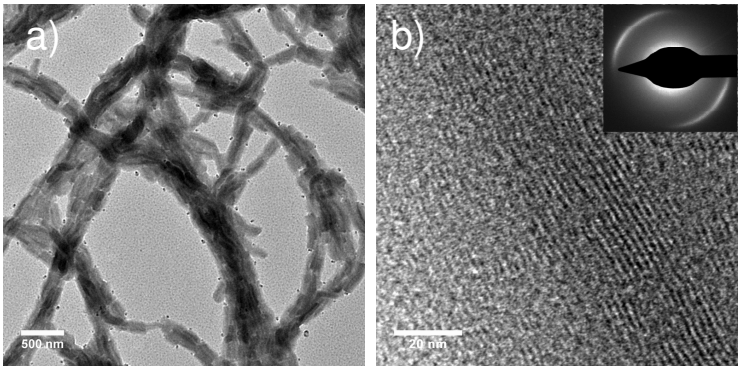


Figure S9.a) Electron microscopy of **1b** fibers grown from THF:MeOH=1:1 solution, b) HRTEM image of a fiber displaying columnar structures of **1b**, electron diffraction pattern with reflections (inset) assigned to the π-stacking distance of 0.35 nm.

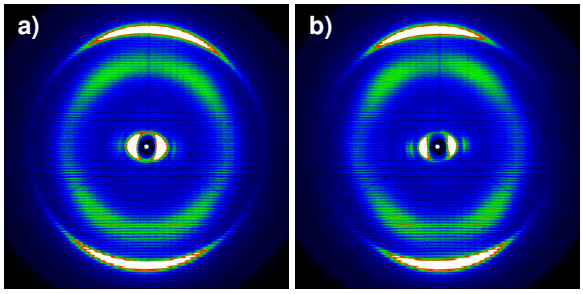


Figure S10. 2D-WAXS patterns of the corresponding alignment of the superstructures in the extruded filaments for a) **1b** and b) **2b**.