Supporting Information

From Helical to Staggered Stacking of Zigzag Nanographenes

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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.

1,4-di (trimethylsilyl)-2,5-diphenylbenzene (3a)

3.00g (6.32mmol) **2,** 2.31g (18.9mmol) phenylboronic acid, 584mg (0.505mmol) $Pd(PPh_3)_4$, 5.24g (37.9mmol) K_2CO_3, 50ml THF, 12ml EtOH and 12ml H_2O were added into 100ml Schlenk 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, PE(petroleum ether) :DCM(dichloromethane) = 6:1) , 1.99g (5.31mmol) white solid was obtained (84%).

FD-MS (8 KV): m/z 373.1, calcd.: 374.67 (M^+).

^{1}H NMR (250 MHz, CD_2Cl_2): δ ppm 7.41~7.31(m, 12H), 0.02(s, 18H).

^{13}C NMR (62.5 MHz, CD_2Cl_2): δ ppm 147.33, 144.96, 139.17, 135.90, 129.86, 128.11, 127.37, 0.542.
Elemental Analysis: Calculated: C 76.94, H 8.07, Si 14.99; Found: C 76.91, H 8.08.

1,4-di(trimethylsilyl)-2,5-di(4'-*t*-butyl)phenylbenzene (3b)
3.00g (6.32mmol) **2,** 3.38g (18.9mmol) *t*-butylphenylboronic acid, 584mg (0.505mmol) $Pd(PPh_3)_4$, 5.24g (37.9mmol) K_2CO_3, 50ml THF, 12ml EtOH and 12ml H_2O were added into 100ml Schlenk 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, PE:DCM = 10:1) , 2.85g (5.85mmol) white solid was obtained (92%).
Mp: 284-287^{o}C.
FD-MS (8 KV): m/z 486.5, calcd.: 486.88 (M^+).
^{1}H NMR (250 MHz, CD_2Cl_2): δ ppm 7.43(m, 6H), 7.25(m, 4H), 1.36(s, 18H), -0.03(s, 18H).
^{13}C NMR (62.5 MHz, CD_2Cl_2): δ ppm 150.52, 147.16, 141.99, 139.28, 135.95, 129.43, 124.97, 34.80, 31.55, 0.56.
Elemental Analysis: Calculated: C 78.94, H 9.52, Si 11.54; Found: C 78.92, H 9.50.

1,4-di(trimethylsilyl)-2,5-di(4'-*n*-dodecyl)phenylbenzene (3c)
1.06 (2.23mmol) **2,** 1.42g (4.89mmol) *n*-dodecylphenylboronic acid, 129mg (0.111mmol) $Pd(PPh_3)_4$, 1.85g (13.4mmol) K_2CO_3, 20ml THF, 5ml EtOH and 5ml H_2O were added into 50ml Schlenk 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, PE), 1.25g (1.76mmol) white solid was obtained (79%).
Mp: 93-95^{o}C.
FD-MS (8 KV): m/z 711.0, calcd.: 711.30 (M^+).
^{1}H NMR (250 MHz, CD_2Cl_2): δ ppm 7.41(s, 2H), 7.21(s, 8H), 2.65(t, 4H, J=8.20Hz), 1.61(m, 4H), 1.31~1.26(m, 36H), 0.86(m, 6H), -0.02(s, 18H).
^{13}C NMR (62.5 MHz, CD_2Cl_2): δ ppm 147.25, 142.28, 139.26, 129.68, 128.15, 35.96, 32.31, 32.01, 30.07, 30.03, 29.89, 29.74, 29.60, 23.07, 14.26, 0.60.
Elemental Analysis: Calculated: C 81.05, H 11.05, Si 7.90; Found: C 81.02, H 10.99.

1,4-diiodo-2,5-diphenylbenzene (4a)
500mg (1.33mmol) **3a** was dissolved in 60ml $CHCl_3$, the solution was degassed by bubbling through argon for 20 min, then 4eq 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= 5:1), 611mg (1.27mmol) white solid was obtained (95%).
Mp: 269-272^{o}C.
FD-MS (8 KV): m/z 482.3, calcd.: 482.10 (M^+).
^{1}H NMR (250 MHz, CD_2Cl_2): δ ppm 7.87(s, 2H), 7.45~7.34(m, 10H).
^{13}C NMR (75 MHz, CD_2Cl_2): δ ppm 147.43, 142.75, 140.55, 129.54, 128.47, 98.37.
Elemental Analysis: Calculated: C 44.84, H 2.51, I 52.65; Found: C 44.83, H 2.56.

1,4-diiodo-2,5-di(4'-*t*-butyl)phenylbenzene (4b)

2.44g (5.01mmol) **3b** was dissolved in 300ml $CHCl_3$, the solution was degassed by bubbling through argon for 20 min, then 4eq 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 purified by precipitation from methanol, 2.74g (4.61mmol) white solid was obtained (92%).

Mp: >300^oC.

FD-MS (8 KV): m/z 594.1, calcd.: 594.31 (M^+).

^1H NMR (250 MHz, CD_2Cl_2): δ ppm 7.86(s, 2H), 7.46(d, 4H, J=8.22Hz), 7.30(d, 4H, J-8.22Hz), 1.36(s, 18H).

^{13}C NMR (62.5 MHz, CD_2Cl_2): δ ppm 151.54, 147.06, 140.77, 139.69, 129.19, 125.38, 98.35, 34.94, 31.45.

Elemental Analysis: Calculated: C 52.54, H 4.75, I 42.71; Found: C 52.50, H 4.71.

1,4-diiodo-2,5-di(4'-*n*-dodecyl)phenylbenzene (4c)

811.g (1.14mmol) **3c** was dissolved in 20ml $CHCl_3$, the solution was degassed by bubbling through argon for 20 min, then 4eq 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 purified by column chromatography (Silica gel, PE), 849mg (1.04mmol) white solid was obtained (91%).

Mp: 98~99^oC.

FD-MS (8 KV): m/z 818.3, calcd.: 818.73 (M^+).

^1H NMR (250 MHz, CD_2Cl_2): δ ppm 7.85(s, 2H), 8.00(s, 8H), 2.65(t, 4H, J=7.56Hz), 1.65(m, 4H), 1.25(m, 36H), 0.84(m, 6H).

^{13}C NMR (62.5 MHz, CD_2Cl_2): δ ppm 147.23, 143.52, 140.64, 140.01, 129.39, 128.44, 98.54, 36.06, 32.32, 31.82, 30.04, 29.99, 29.88, 29.74, 23.08, 14.27.

Elemental Analysis: Calculated: C 69.95, H 5.56, Br 24.49; Found: C 69.92, H 5.55.

1,4-di(2'-bromo)phenyl-2,5-diphenylbenzene (5a)

670mg (1.39mmol) **4a**, 586mg (2.92mmol) 2-bromophenylboronic acid, 80.0mg (0.0690mmol) $Pd(PPh_3)_4$, 1.15g (8.32mmol) K_2CO_3, 25ml Toluene, 6ml EtOH and 6ml H_2O were added into 50ml Schlenk 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, PE:DCM = 4:1) , 600mg (1.11mmol) white solid was obtained (80%).

Mp: 230~231^oC.

FD-MS (8 KV): m/z 540.3, calcd.: 540.29 (M^+).

^1H NMR (250 MHz, CD_2Cl_2): δ ppm 7.57 (t, 2H, J=7.6Hz), 7.42 (d, 2H, J=6.95Hz), 7.32~7.10 (m, 16H).

^{13}C NMR (62.5 MHz, CD_2Cl_2): δ ppm 142.30, 142.18, 140.71, 139.93, 139.81, 139.63, 139.56, 133.09, 132.96, 132.88, 132.72, 132.52, 129.85, 129.06, 128.17, 128.12, 127.29, 127.10, 124.09.

Elemental Analysis: Calculated: C 66.69, H 3.73, Br 29.58; Found: C 66.68, H 3.74.

1,4-di(2'-bromo)phenyl-2,5-di(4'-*t*-butyl)phenylbenzene (5b)

.3.24g (5.45mmol) **4b**, 2.30g (11.4mmol) 2-bromophenylboronic acid, 315mg (0.272mmol) $Pd(PPh_3)_4$, 4.52g (32.7mmol) K_2CO_3, 55ml THF, 12ml EtOH and 12ml H_2O were added into 100ml Schlenk 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, PE:DCM = 6:1) , 2.88g (4.44mmol) white solid was obtained (81%).
Mp: 318~320^{o}C.
FD-MS (8 KV): m/z 652.5, calcd.: 652.50 (M^+).
^{1}H NMR (250 MHz, CD_2Cl_2): δ ppm: 7.58(t, 2H, J=7.25Hz), 7.38(d, 2H, J=6.32Hz), 7.16(m, 14H), 1.24(s, 18H).
^{13}C NMR (62.5 MHz, CD_2Cl_2): δ ppm 150.10, 142.47, 139.43, 139.37, 137.76, 133.35, 133.13, 132.91, 129.79, 129.34, 127.64, 125.50, 124.15, 34.66, 31.77.
Elemental Analysis: Calculated: C 69.95, H 5.56, Br 24.49; Found: C 69.92, H 5.55.

1,4-di(2'-bromo)phenyl-2,5-di(4'-*n*-dodecyl)phenylbenzene (5c)
935mg (1.14mmol) **4c**, 482mg (2.40mmol) 2-bromophenylboronic acid, 66mg (0.057mmol) $Pd(PPh_3)_4$, 950mg (6.87mmol) K_2CO_3, 22ml THF, 5ml EtOH and 5ml H_2O were added into 50ml Schlenk 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, PE:DCM = 6:1) , 900mg (1.03mmol) white solid was obtained (90%).
Mp: 84~86^{o}C.
FD-MS (8 KV): m/z 875.9, calcd.: 876.93 (M^+).
^{1}H NMR (250 MHz, CD_2Cl_2): δ ppm: 7.57(t, 4H, J=7.58Hz), 7.39(d, 4H, J=8.2Hz), 7.21~7.09(m, 10H), 7.00(d, 4H, J=8.2Hz), 2.52(t, 4H, J=7.25Hz), 1.51(m, 4H), 1.32~1.24(m, 36H), 0.86(t, 6H, J=6.0Hz).
^{13}C NMR (62.5 MHz, CD_2Cl_2): δ ppm 142.60, 142.47, 141.99, 139.56, 137.99, 133.11, 132.95, 132.77, 132.56, 129.66, 128.94, 128.24, 127.27, 124.15, 35.85, 32.30, 31.68, 30.05, 29.97, 29.85, 29.65, 23.07, 14.26.
Elemental Analysis: Calculated: C 73.96, H 7.82, Br 18.22; Found: C 73.74, H 7.78.

1,4-di(2'-(2''-(4'''-*n*-dodecyl)phenylethynyl)biphenyl)-2,5-diphenylbenzene (6a)
1.00g (1.85mmol) **5a**, 2.00g (5.12mmol) *o*-(4-dodecyl)phenylethynylbenzeneboronic acid, 107mg (0.0925mmol) $Pd(PPh_3)_4$, 1.53g (11.1mmol) K_2CO_3, 45ml Toluene, 11ml EtOH and 11ml H_2O were added into 100ml Schlenk 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, PE:DCM = 4:1) , 1.65g (1.54mmol) of light yellow oil was obtained (83%).
FD-MS (8 KV): m/z 1072.5, calcd.: 1071.56 (M^+).
^{1}H NMR (250 MHz, CD_2Cl_2): δ ppm 7.35~6.99(m, 34H), 2.54(t, 4H, J=7.58Hz), 1.55(m, 4H), 1.25(m, 38H), 0.86(m, 6H).
^{13}C NMR (62.5 MHz, CD_2Cl_2): δ ppm 143.57, 141.00, 138.95, 134.40, 131.76, 130.98, 130.46, 130.21, 129.91, 128.67, 128.00, 127.77, 127.31, 126.71, 126.55, 123.26, 121.09, 92.39, 89.47, 36.19, 32.30, 31.69, 30.04, 29.96, 29.87, 29.73, 29.65, 23.07, 14.26.
Elemental Analysis: Calculated: C 91.91, H 8.09; Found: C 91.83, H 8.10.

1,4-di(2'-(2''-(4'''-*n*-dodecyl)phenylethynyl)biphenyl)-2,5-di(4'-*t*-butyl)phenylbenzene (6b)

500mg (0.766mmol) **5b**, 897mg (2.30mmol) *o*-(4-dodecyl)phenylethynylbenzeneboronic acid, 44mg (0.038mmol) $Pd(PPh_3)_4$, 638mg (4.62mmol) K_2CO_3, 25ml Toluene, 6ml EtOH and 6ml H_2O were added into 50ml Schlenk 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, PE:DCM = 4:1) , 771mg (0.651mmol) of light yellow oil was obtained (85%).
FD-MS (8 KV): m/z 1185.0, calcd.: 1183.77 (M^+).
^{1}H NMR (250 MHz, CD_2Cl_2): δ ppm 7.43~6.96(m, 32H), 2.55(t, 4H, J=7.58Hz), 1.56(m, 4H), 1.25(m, 56H), 0.86(m, 6H).
^{13}C NMR (62.5 MHz, CD_2Cl_2): δ ppm 143.54, 138.90, 134.50, 132.06, 131.65, 130.28, 129.65, 128.63, 127.78, 126.56, 124.74, 89.84, 82.28, 36.21, 34.47, 32.29, 31.79, 31.36, 30.01, 29.95, 29.72, 23.07, 14.25.
Elemental Analysis: Calculated: C 91.32, H 8.68; Found: C 91.42, H 8.54.

1,4-di(2'-(2''-(4'''-*n*-dodecyl)phenylethynyl)biphenyl)-2,5-di(4'-*n*-dodecyl)phenylbenzene (6c)
885mg (1.01mmol) **5c**, 1.02g (2.61mmol) *o*-(4-dodecyl)phenylethynylbenzeneboronic acid, 35mg (0.030mmol) $Pd(PPh_3)_4$, 830mg (6.01mmol) K_2CO_3, 22ml Toluene, 5ml EtOH and 5ml H_2O were added into 50ml Schlenk 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, PE:DCM = 6:1) , 1.08g (0.767mmol) of light yellow oil was obtained (76%).
FD-MS (8 KV): m/z 1406.5, calcd.: 1408.20 (M^+).
^{1}H NMR (250 MHz, CD_2Cl_2): δ ppm 7.35~6.97(m, 32H), 2.52(m, 8H), 1.52(m, 8H), 1.25(m, 74H), 0.84(m, 12H).
^{13}C NMR (62.5 MHz, CD_2Cl_2): δ ppm 143.50, 142.97, 141.45, 138.92, 134.33, 131.59, 130.50, 129.76, 128.61, 127.81, 126.60, 123.06, 89.61, 36.25, 35.79, 32.31, 31.82, 30.11, 30.08, 30.04, 29.44, 29.89, 29.77, 29.75, 23.08, 14.27.
Elemental Analysis: Calculated: C 90.41, H 9.59; Found: C 90.50, H 9.52.

1,4-di(9'-(4''-iodo-5''-(4'''-*n*-dodecyl)phenyl)phenanthrenyl)-2,5-diphenylbenzene (7a)
1.38g (1.29mmol) **6a** in 65ml dry dichloromethane was cooled down to –78^{o}C in dry ice-acetone bath, then 4eq ICl (5.1mmol, 1M in dichloromethanee) was added dropwise over 5min. The mixture was kept at –78^{o}C for 3h and then quenched by adding aqueous $Na_2S_2O_3$ solution. The organic layer was washed with water two times, dried over $MgSO_4$. The solvent was removed and the residue was purified by column chromatography (Silica gel, PE:DCM= 10:1), 1.46g (1.10mmol) light yellow solid was obtained (86%).
FD-MS (8 KV): m/z 1323.4, calcd.: 1323.35 (M^+).
^{1}H NMR (250 MHz, CD_2Cl_2): atropisomer, δ ppm 8.66(d, 1.09H, J=8.22Hz), 8.40~24(m, 2.49H), 7.66~7.28(m, 20.83H), 7.17~6.77(m, 9.61H), 2.74(t, 4H, J=7.85Hz), 1.73(m, 4H), 1.50~1.23(m, 38H), 0.87(m, 6H).
^{13}C NMR (62.5 MHz, CD_2Cl_2): δ ppm 145.84, 145.72, 143.39, 143.25, 143.15, 140.71, 140.57, 138.94, 134.59, 134.10, 133.69, 133.01, 132.66, 132.58, 131.05, 130.26, 130.17, 130.07, 129.99, 129.31, 128.79, 128.53, 128.32, 128.20, 127.85,

127.59, 126.69, 126.26, 125.95, 107.25, 36.22, 32.32, 31.91, 30.06, 30.02, 29.93, 29.79, 29.76, 23.09, 14.27.
Elemental Analysis: Calculated: C 74.42, H 6.40, Br 19.18; Found: C 74.41, H 6.38.

1,4-di(9'-(4''-iodo-5''-(4'''-*n*-dodecyl)phenyl)phenanthrenyl)-2,5-di(4'-*t*-butyl)phenylbenzene (7b)

200mg (0.169mmol) **6b** in 20ml dry dichloromethane was cooled down to –78°C in dry ice-acetone bath, then 4eq ICl (0.68mmol, 1M in dichloromethanee) was added dropwise over 5min. The mixture was kept at –78°C for 3h and then quenched by adding aqueous $Na_2S_2O_3$ solution. The organic layer was washed with water two times, dried over $MgSO_4$. The solvent was removed and the residue was purified by column chromatography (Silica gel, PE:DCM= 4:1), 221mg (0.159mmol) light yellow solid was obtained(91%).
FD-MS (8 KV): m/z 1435.4, calcd.: 1435.57 (M^+).
^{1}H NMR (250 MHz, CD_2Cl_2): atropisomer, δ ppm 8.55(d, 1.14H, J=8.48Hz), 8.27(d, 1.7H, J=8.20Hz), 7.73(s, 1.15H), 7.61~6.69(m, 23.34H), 6.51(d, 2.59H, J=8.20Hz), 2.75(t, 4H, J=7.85Hz), 1.73(m, 4H), 1.50~1.23(m, 38H), 1.13(s, 18H), 0.87(m, 6H)
^{13}C NMR (62.5 MHz, CD_2Cl_2): δ ppm 149.60, 145.49, 143.37, 143.32, 143.07, 140.83, 139.14, 137.46, 134.29, 133.89, 133.48, 132.52, 132.27, 131.07, 130.35, 130.26, 130.13, 130.02, 129.87, 128.78, 128.67, 128.38, 128.07, 127.74, 126.38, 125.67, 124.38, 124.15, 107.09, 36.21, 34.44, 32.32, 31.91, 31.43, 31.38, 30.09, 30.06, 30.01, 29.93, 29.79, 29.75, 23.08, 14.27.
Elemental Analysis: Calculated: C 75.30, H 7.02, Br 17.68; Found: C 75.43, H 6.98.

1,4-di(9'-(4''-iodo-5''-(4'''-*n*-dodecyl)phenyl)phenanthrenyl)-2,5-di(4'-*n*-dodecyl)phenylbenzene (7c)

813mg (0.577mmol) **6c** in 55ml dry dichloromethane was cooled down to –78°C in dry ice-acetone bath, then 4eq ICl (2.31mmol, 1M in dichloromethanee) was added dropwise over 5min. The mixture was kept at –78°C for 3h and then quenched by adding aqueous $Na_2S_2O_3$ solution. The organic layer was washed with water two times, dried over $MgSO_4$. The solvent was removed and the residue was purified by column chromatography (Silica gel, PE:DCM= 10:1), 824mg (0.496mmol) light yellow sticky solid was obtained(86%).
FD-MS (8 KV): m/z 1657.4, calcd.: 1659.99 (M^+).
^{1}H NMR (250 MHz, CD_2Cl_2): antropisomer, δ ppm 8.64(d, 1.30H, J=8.48Hz), 8.34(d, 2.06H, J=8.20Hz), 7.66~6.62(m, 28.64H), 2.75(t, 4H, J=7.52Hz), 2.37(m, 4H), 1.73~1.23(m, 80H), 0.85(m, 12H).
^{13}C NMR (62.5 MHz, CD_2Cl_2): δ ppm 145.64, 143.43, 143.32, 143.09, 141.74, 140.65, 139.20, 137.75, 134.47, 134.19, 134.02, 133.63, 132.72, 132.45, 131.13, 130.34, 130.21, 130.09, 129.94, 129.09, 128.96, 128.76, 128.39, 128.31, 128.18, 127.70, 126.26, 125.84, 107.20, 36.23, 35.80, 32.32, 31.99, 31.92, 30.06, 30.04, 29.95, 29.82, 29.77, 23.09, 14.27.
Elemental Analysis: Calculated: C 76.70, H 8.01, I 15.29; Found: C 76.83, H 8.13.

1,4-di(9'-(4'',5''-di(4'''-*n*-dodecyl)phenyl)phenanthrenyl)-2,5-diphenylbenzene (8a)

470mg (0.355mmol) **7a**, 310mg (1.07mmol) *n*-dodecylphenylboronic acid, 12mg (0.010mmol) $Pd(PPh_3)_4$, 300mg (2.17mmol) K_2CO_3, 16ml THF, 4ml EtOH and 4ml H_2O were added into 50ml Schlenk 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, PE:DCM = 4:1) , 493mg (0.316mmol) of light yellow solid was obtained (89%).

FD-MS (8 KV): m/z 1558.9, calcd.: 1560.39 (M^+).

^{1}H NMR (250 MHz, CD_2Cl_2): atroipsomer, δ ppm 8.75(d, 1.17H, J=8.22Hz), 8.34(d, 0.58H, J=8.20Hz), 7.74~6.89(m, 40,22H), 2.56(m, 8H), 1.58(m, 8H), 1.27~1.20(m, 72H), 0.87(m, 12H).

^{13}C NMR (62.5 MHz, CD_2Cl_2): δ ppm 143.66, 143.56, 141.40, 141.35, 141.10, 140.99, 140.70, 139.11, 138.95, 137.64, 137.60, 137.46, 137.33, 133.93, 133.67, 133.31, 133.04, 131.69, 131.32, 131.19, 131.05, 130.48, 129.78, 129.42, 129.32, 128.10, 127.89, 127.59, 126.60, 126.27, 125.76, 124.73, 35.96, 32.34, 31.81, 30.12, 30.08, 29.94, 29.78, 29.62, 23.09, 14.28.

Elemental Analysis: Calculated: C 90.83, H 9.17; Found: C 91.03, H 9.17.

1,4-di(9'-(4'',5''-di(4'''-*n*-dodecyl)phenyl)phenanthrenyl)-2,5-di(4'-*t*-butyl) phenylbenzene (8b)

400mg (0.278mmol) **7b**, 243mg (0.837mmol) *n*-dodecylphenylboronic acid, 10mg (0.0086mmol) $Pd(PPh_3)_4$, 400mg (2.89mmol) K_2CO_3, 14ml THF, 3ml EtOH and 4ml H_2O were added into 50ml Schlenk 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, PE:DCM = 4:1) , 423mg (0.253mmol) of light yellow solid was obtained (91%).

FD-MS (8 KV): m/z 1672.4, calcd.: 1672.60 (M^+).

^{1}H NMR (250 MHz, CD_2Cl_2): atroipsomer, δ ppm 8.81(d, 1.07H, J=8.22Hz), 8.33(d, 0.59H, J=8.20Hz), 7.63~7.34(m, 14.99H), 7.04~6.94(m, 23.44H), 2.56(m, 8H), 1.57(m, 8H), 1.27~1.1(m, 90H), 0.86(m, 12H).

^{13}C NMR (62.5 MHz, CD_2Cl_2): δ ppm 149.76, 143.56, 141.36, 139.99, 139.39, 138.01, 137.77, 137.67, 134.03, 133.75, 133.47, 131.28, 130.58, 129.63, 129.04, 128.16, 127.87, 127.74, 127.47, 126.24, 124.75, 35.93, 34.54, 32.32, 31.79, 31.34, 30.11, 30.06, 29.92, 29.76, 29.61, 23.08, 14.27.

Elemental Analysis: Calculated: C 90.48, H 9.52; Found: C 90.57, H 9.53.

1,4-di(9'-(4'',5''-di(4'''-*n*-dodecyl)phenyl)phenanthrenyl)-2,5-di(4'-*n*-dodecyl)phenylbenzene (8c)

350mg (0.211mmol) **7c**, 184mg (0.634mmol) *n*-dodecylphenylboronic acid, 7.3mg (0.0063mmol) $Pd(PPh_3)_4$, 290mg (2.10mmol) K_2CO_3, 12ml THF, 3ml EtOH and 3ml H_2O were added into 50ml Schlenk 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, PE:DCM = 10:1) , 303mg (0.160mmol) of light yellow sticky solid was obtained (76%).

FD-MS (8 KV): m/z 1896.2, calcd.: 1897.03 (M^+).

^{1}H NMR (250 MHz, CD_2Cl_2): atroipsomer, δ ppm 8.78(d, 1.11H, J=8.48Hz), 8.32(d, 0.43H, J=8.32Hz), 7.66~6.61(m, 38.45H), 2.58~2.39(m, 12H), 1.57~1.27(m, 120H), 0.85(m, 18H)
^{13}C NMR (62.5 MHz, CD_2Cl_2): δ ppm 143.56, 141.55, 141.39, 141.34, 140.36, 139.29, 138.26, 137.69, 137.52, 137.41, 137.35, 133.96, 133.68, 133.14, 131.74, 131.25, 130.57, 129.72, 129.19, 128.16, 127.86, 127.43, 126.23, 125.70, 124.74, 35.96, 32.33, 31.81, 30.12, 30.07, 29.94, 29.88, 29.78, 29.74, 29.63, 23.09, 14.27.
Elemental Analysis: Calculated: C 89.90, H 10.10; Found: C 90.03, H 9.98.

3,4,12,13-tetrakis-(4'-*n*-dodecylphenyl)-dibenzo[*hi,uv*]phenanthro-[3,4,5,6-*bcdef*]-ovalene (1a)
60.0mg (0.0384mmol) **8a** was dissolved in 40ml dichloromethane, the solution was then degassed by bubbling through argon for 20 min, and then 18eq $FeCl_3$ in 0.5ml CH_3NO_2 was added dropwise. After being stirred for 30 min, the reaction was quenched by adding 50ml methanol, the yellow precipitate was collected, washed by methanol repeatedly, redissolved in THF and passed through a short silica column, the solution was collected and dried under vacuum and then reprecipitated to afford 39.0mg (0.0252 mmol) yellow powder (66%).
MALDITOF-MS (TCNQ as matrix): m/z=1548.15, calcd. 1548.29 for $C_{118}H_{130}$.
^{1}H NMR (500 MHz, $CDCl_2CDCl_2$, 140^{o}C): 9.25(brs, 4H), 9.17(brs, 4H), 8.49(brs, 4H), 8.21(s, 2H), 7.47(d, 8H, J=7.14Hz), 7.29(d, 8H, J=7.63Hz), 2.80(t, 8H, J=7.49Hz), 1.81~1.28(m, 90H), 0.93(m, 12H).
^{13}C NMR can not be well resolved because of the large disc.
Elemental Analysis: Calculated: C 91.54, H 8.46; Found: C 90.94, H 8.48.

3,4,12,13-tetrakis-(4'-*n*-dodecylphenyl)-8,17-bis-*t*-butyl-dibenzo[*hi,uv*]phenanthro-[3,4,5,6-*bcdef*]-ovalene (1b)
150mg (0.0896mmol) **8b** was dissolved in 70ml dichloromethane, the solution was then degassed by bubbling through argon for 20 min, and then 30eq $FeCl_3$ in 1.5ml CH_3NO_2 was added dropwise. After being stirred for 45 min, the reaction was quenched by adding methanol, the yellow precipitate was collected, washed by methanol repeatedly, redissolved in THF and passed through a short silica column, the solution was collected and dried under vacuum and then reprecipitated to afford 129mg (0.0777mmol) yellow powder (87%).
MALDITOF-MS (TCNQ as matrix): m/z=1661.04, calcd. 1660.51 for $C_{126}H_{146}$.
^{1}H NMR (500 MHz, $CDCl_2CDCl_2$, 140^{o}C): 9.56(s, 4H), 9.47(d, 4H, J=8.80Hz), 8.58(d, 4H, J=8.80Hz), 7.45(d, 8H, J=7.14Hz), 7.25(d, 8H, J=7.49Hz), 2.76(t, 8H, J=7.84Hz), 1.94~1.33(m, 98H), 0.91(m, 12H).
^{13}C NMR can not be well resolved because of the large disc.
Elemental Analysis: Calculated: C 91.14, H 8.86; Found: C 90.98, H 8.75.

3,4,12,13-tetrakis-(4'-*n*-dodecylphenyl)-8,17-bis-*n*-dodecyl-dibenzo[*hi,uv*]phenanthro-[3,4,5,6-*bcdef*]-ovalene (1c)
30.0mg (0.0158mmol) **8c** was dissolved in 20ml dichloromethane, the solution was then degassed by bubbling through argon for 20 min, and then 24eq $FeCl_3$ in 0.4ml CH_3NO_2 was added dropwise. After being stirred for 45 min, the reaction was quenched by adding methanol, the yellow precipitate was collected, washed by

methanol repeatedly, redissolved in THF and passed through a short silica column, the solution was collected and dried under vacuum and then reprecipitated to afford 11mg (0.0058mmol) yellow powder (37%).
MALDITOF-MS (TCNQ as matrix): m/z=1884.42, calcd. 1884.93 for $C_{142}H_{178}$.
^{1}H NMR (500 MHz, $CDCl_2CDCl_2$): 9.48(s, 4H), 9.27(brs, 4H), 8.59(brs, 4H), 7.44(d, 8H, J=7.14Hz), 7.25(d, 8H, J=7.48Hz), 3.39(m, 2H), 2.75(t, 8H, J=7.84Hz), 2.15(m, 2H), 1.77~0.83(m, 138H).
^{13}C NMR can not be well resolved because of the large disc.
Elemental Analysis: Calculated: C 90.48, H 9.52; Found: C 90.73, H 9.45.

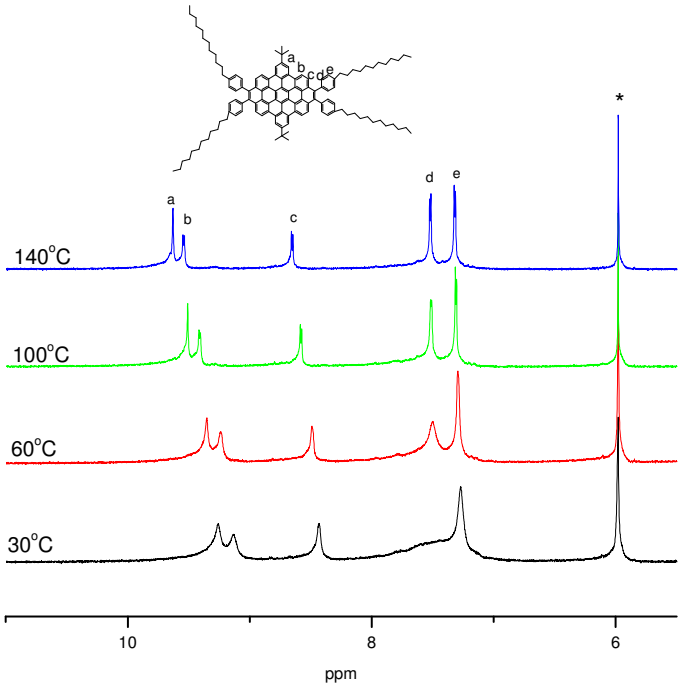

Figure S1. Temperature-dependant ^{1}H NMR (500MHz) spectra of **1b** in *d*-$CD_2Cl_2CD_2Cl_2$.

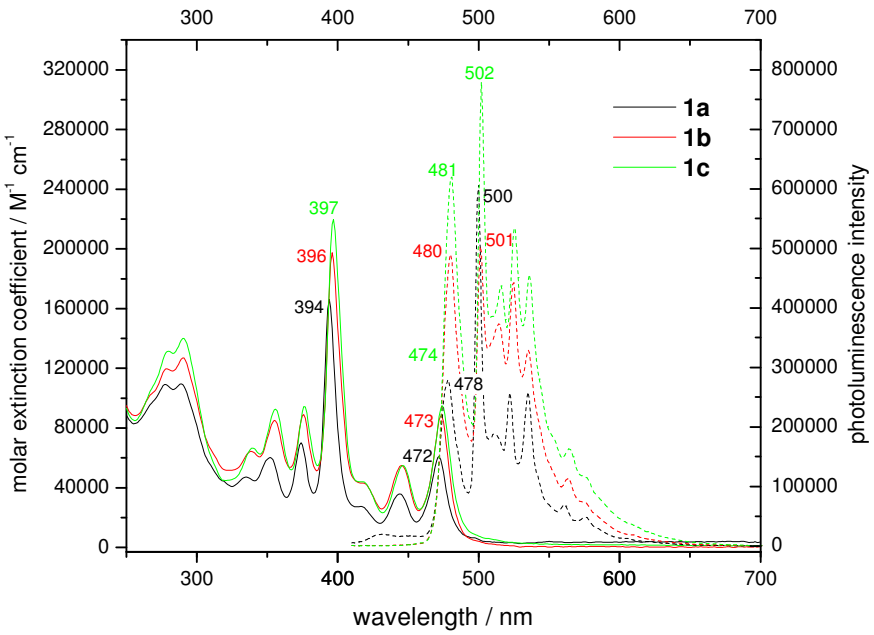

Figure S2. UV-vis and photoluminescence spectra of **1a** (black), **1b** (red) and **1c** (green) (1.0×10^{-6}M in $CHCl_3$).

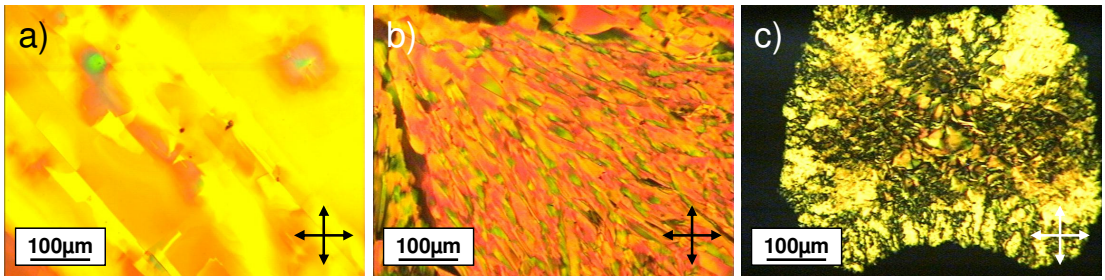

Figure S3. Polarized optical microscopy images of **1b** cooled from the isotropic phase by a) 0.1 °C/min, b) 1 °C/min and c) 10 °C/min.

Table S1. Phase transitions of **1a**, **1b** and **1c** determined by DSC and unit cells for **1a** and **1c**.

compound	2nd heating	cooling	hexagonal unit cell parameter
1a	16 °C (8.4 J/g)	10 °C (8.6 J/g)	3.91 nm
	111 °C (5.4 J/g)	99 °C (6.4 J/g)	4.59 nm
1b	8 °C (2.0 J/g)	-8 °C (1.9 J/g)	-
1c	14 °C (10 J/g)	4 °C (11.2 J/g)	3.27 nm
	108 °C (1.6 J/g)	96 °C (2.0 J/g)	3.36 nm

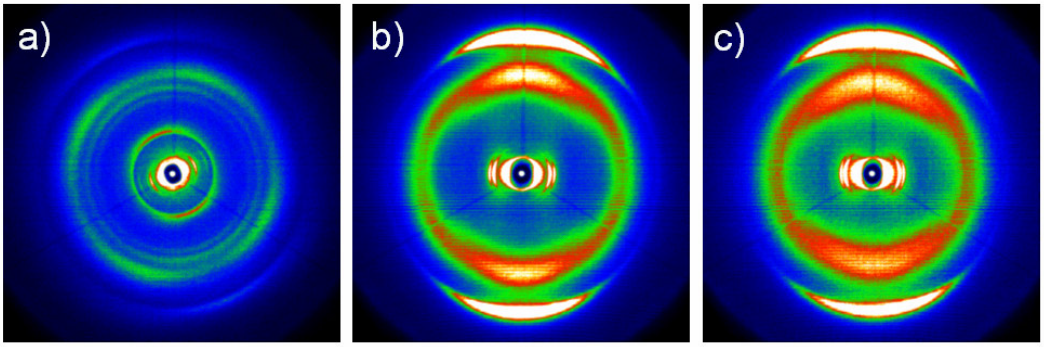

Figure S4. 2D-WAXS patterns of a) **1a** at 180 °C, and **1c** at b) 30 °C and c) at 160 °C.

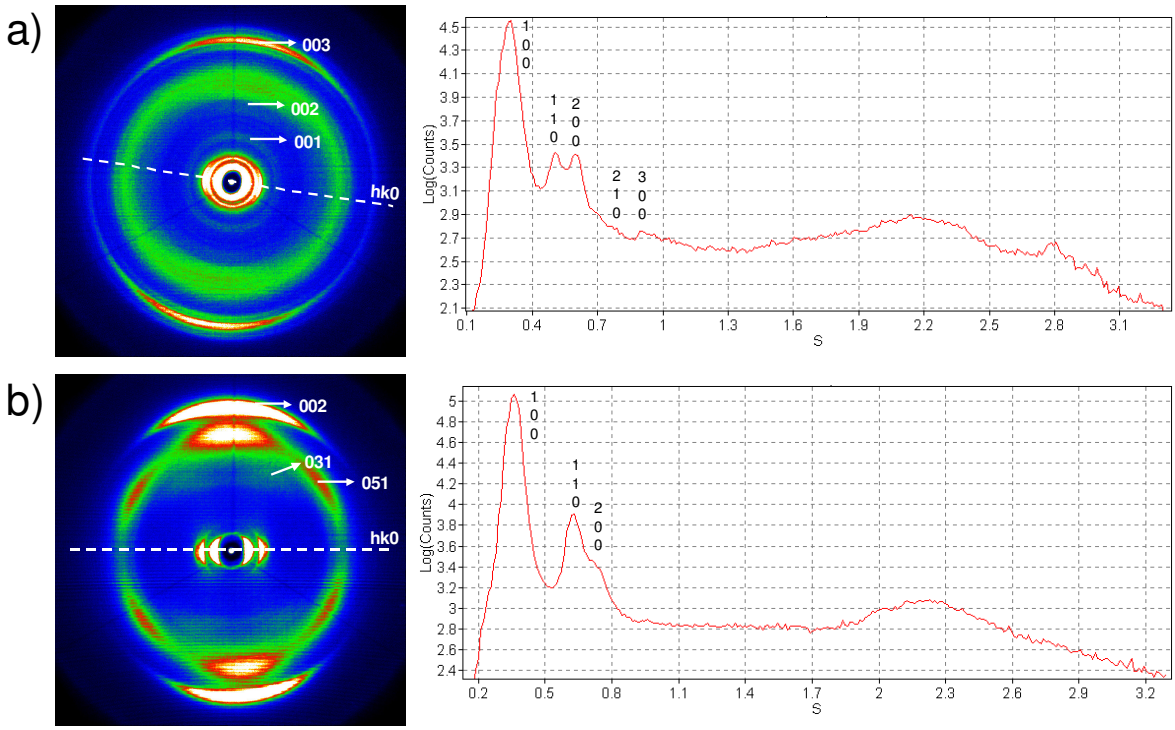

Figure S5. Indexed 2D-WAXS patterns of a) **1a** and b) **1c** shown in the main text.