Supporting Information for

Discotic Hexa-*peri*-hexabenzocoronenes with Strong Dipole: Synthesis, Self-Assembly and Dynamic Studies

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Experimental Section

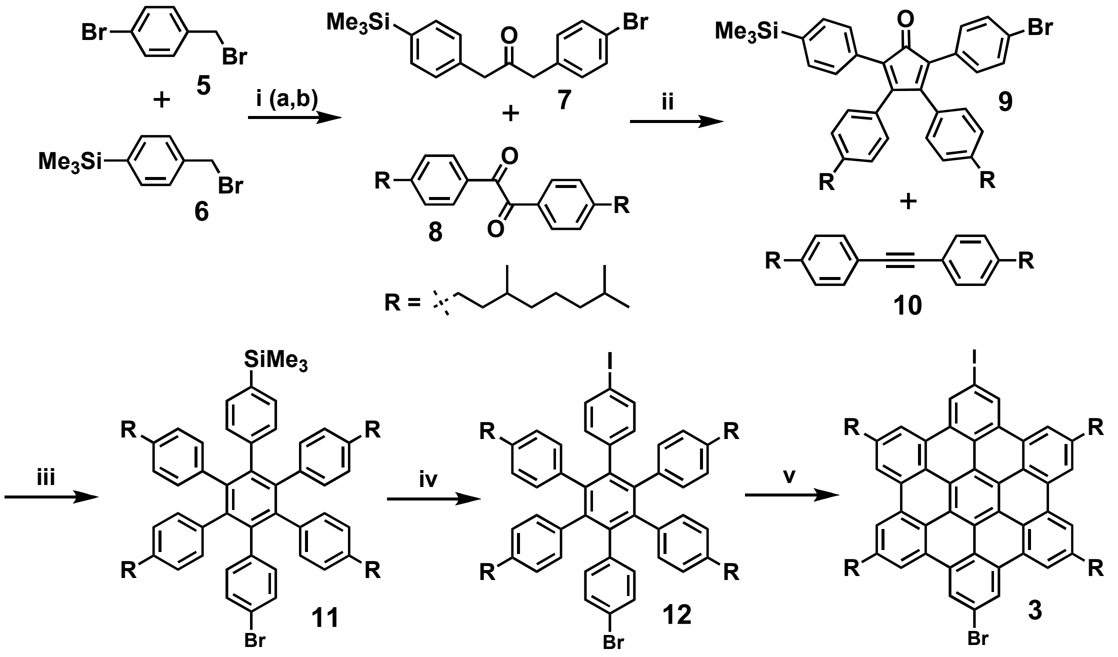
Chemicals were obtained from Fluka, Aldrich, and ABCR and used as received. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker DPX 250, Bruker DRX 500 or Bruker DRX 700 spectrometer with use of the solvent proton or carbon signal as an internal standard. Field Desorption (FD) mass spectra were obtained on a VG Instruments ZAB 2-SEFPD. MALDI-TOF mass spectra were measured using 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 at ambient temperature using a UV/vis/NIR Perkin-Elmer Lambda 900 spectrometer. Differential scanning calorimetry (DSC) was conducted with a mettler DSC 30 with a heating and cooling rate of 10°C/min. 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. Dielectric measurements were made under "isobaric" conditions as a function of temperature for temperatures in the range 123.15-423.15 K, at atmospheric pressure, and for frequencies in the range from 10^{-2} to 10^6 Hz. In every case the complex dielectric permittivity $\varepsilon^* = \varepsilon' - i\varepsilon''$, where ε' is the real and ε'' is the imaginary part, was obtained as a function of frequency ω, temperature T, and pressure P, i.e., ε*(T,P,ω). The analysis of both T- and P-dependent experiments was made using the empirical **equation of Havriliak-Negami (HN)**[19]:

$$\varepsilon^*(\mathrm{T},P,\omega) = \varepsilon_\infty(T,P) + \frac{\Delta\varepsilon(T,P)}{\left[1+\left(i\omega\tau_{HN}(T,P)\right)^m\right]^n} + \frac{\sigma_0(T,P)}{i\varepsilon_f\omega}$$

where ε_∞(T,P) is the high frequency permittivity, τ_{HN}(T,P) is the characteristic relaxation time in this equation, $\Delta\varepsilon(T,P)=\varepsilon_o(T,P)-\varepsilon_\infty(T,P)$ is the relaxation strength, m, n (with limits $0<m$, $mn\leq 1$) describe, respectively, the symmetrical and asymmetrical broadening of the distribution of relaxation times, σ_o is the dc-conductivity and ε_f is the permittivity of free space. From τ_{HN}, the relaxation time at maximum loss, τ_{max}, is obtained analytically following:

$$\tau_{max} = \tau_{HN}\left[\frac{\sin\left(\frac{\pi m}{2+2n}\right)}{\sin\left(\frac{\pi mn}{2+2n}\right)}\right]^{-1/m}$$

Synthesis



Scheme S1. Synthesis of the dipole functionalized HBCs (**1** and **2**): i-a) Collman's reagent, NMP, 0 °C, 90 min. i-b) 45 °C, 16 h, 66%; (ii) Bu_4NOH, t-BuOH, 85 °C, 10 min, 51%; (iii) diphenyl ether, 185°C, 12 h, 49%, (iv) ICl, 0 °C → r.t., 40 min, 95%; (v) $FeCl_3/CH_3NO_2$, DCM, r.t., 93%.

1-(4'-Trimethylsilylphenyl)-3-(4'-bromophenyl)-propan-2-one (7):

Freshly prepared Collman's reagent (450 mg, 1.2 mmol) was charged in a flame-dried 50 mL Schlenk tube. 4-Trimethylsilybenzyl bromide **6** (243 mg, 1 mmol) in 7 mL dry NMP was carefully degassed with three "freeze-pump-thaw" cycles method three times in another 25 mL Schlenk tube. The solution of **6** was then transferred to the Schlenck tube containing Collman's reagent dropwise at 0 °C. The mixture was stirred at 0 °C for 30 min followed by warming to r.t. 1 h later, the mixture was cooled to 0 °C again and 4-bromobenzyl bromide **5** (500 mg, 2 mmol), which was dissolved in 10 mL dry NMP and carefully degassed with "freeze-pump-thaw" method, was added dropwise. The reaction mixture was allowed to be heated to 45 °C and stirred for 14 h. large amount of saturated NH_4Cl aqueous solution (10 mL) was used to quench the excess Collman's reagent after cooling down. The crude product was extracted with CH_2Cl_2 (150 mL × 3) and washed with brine. After being dried over $MgSO_4$, the organic phase was filtered out and the solvent was removed under reduced pressure. The residue was purified by column chromatography (eluent, hexane/ethyl acetate 20/1). Compound **7** was collected as white solid (238 mg) in a yield of 66%.

FD-MS (8 kV): *m/z* = 362.5 (100%, M^+), (calcd. for $C_{18}H_{21}BrOSi$ = 361.4 g mol^{-1}).

^{1}H-NMR (250 MHz, CD_2Cl_2): δ = 7.50 (d, ^3J = 7.9Hz, 2H, aryl-*H*), 7.46 (d, ^3J = 8.4Hz, 2H, aryl-*H*), 7.16 (d, ^3J = 7.8Hz, 2H, aryl-*H*), 7.04 (d, ^3J = 8.3Hz, 2H aryl-*H*), 3.74 (s, 2H, -CH_2-CO-), 3.71 (s, 2H, -CH_2-CO-), 0.26 (s, 9H, -CH_3) ppm.

^{13}C-NMR (62.5 MHz, CD_2Cl_2): δ = 205.03, 139.47, 134.89, 134.04, 133.72, 131.93, 131.74, 129.27, 121.17, 49.65, 48.65, -1.11 ppm.

2-(4'-Trimethylsilylphenyl)-5-(4'-bromophenyl)-3,4-bis[4'-(3'',7''-dimethyloctyl)phenyl]cyclopentadien-1-one (9):

Compound **7** (210 mg, 0.6 mmol) and compound **8** (299 mg, 0.6 mmol) were dissolved in 3 mL *t*-butanol in a 25 mL Schlenk tube under argon. The mixture was heated to 85 °C. Subsequently, Bu_4NOH (0.75 mL, 1 M solution in methanol) was added dropwise. 10 min later, the mixture was cooled in an ice bath and diluted with CH_2Cl_2 (10 mL). After being washed with brine (30 mL) and extracted with CH_2Cl_2 (30 mL × 3), the organic layer was dried over $MgSO_4$. The solvent was removed in vacuo and the residue was purified by column chromatography with an eluent of petroleum ether (PE) /CH_2Cl_2 (6/1). Compound **9** was collected as dark reddish solid (297 mg) in a yield of 51%.

FD-MS (8 kV): *m/z* = 816.7 (100%, M^+), (calcd. for $C_{52}H_{67}BrOSi$ = 816.1 g mol^{-1}).

^{1}H-NMR (250 MHz, CD_2Cl_2): δ = 7.43 (d, ^3J = 8.2Hz, 2H, aryl-*H*), 7.39 (d, ^3J = 8.6Hz, 2H, aryl-*H*), 7.21 (d, ^3J = 8.1Hz, 2H, aryl-*H*), 7.13 (d, ^3J = 8.6Hz, 2H, aryl-*H*), 7.03 (d, ^3J = 8.1Hz, 2H aryl-*H*), 6.86 (d, ^3J = 7.1Hz, 2H, aryl-*H*), 6.83 (d, ^3J = 6.9Hz, 2H, aryl-*H*), 2.62-2.53 (m, 4H, α-CH_2), 1.40-1.14 (m, 20H, alkyl-*H*), 0.89-0.86 (m, 36H, -CH_3), 0.25 (s, 9H, -CH_3) ppm.

^{13}C-NMR (62.5 MHz, CD_2Cl_2): δ = 200.36, 156.11, 155.27, 144.66, 144.43, 140.12, 133.27, 132.09, 131.81, 131.46, 130.69, 130.64, 130.44, 129.59, 129.54, 128.36, 128.27, 125.59, 124.25, 121.77, 39.68, 38.91, 38.88, 37.49, 33.64, 32.83, 28.34, 25.09, 22.82, 22.75, 19.73, -1.15 ppm.

Elemental Analysis: C 76.90%, H 8.65% (calcd. for $C_{52}H_{67}BrOSi$, C 76.53%, H 8.28%, Br 9.79%, O 1.96%, Si 3.44%).

1-(4’-Trimethylsilylphenyl)-4-(4’-bromophenyl)-2,3,5,6-tetrakis[4’-(3’’,7’’-dimethyloctyl)phenyl] benzene (11):

Compound **9** (4.2 g, 5.15 mmol) and compound **10** (2.36 g, 5.15 mmol) were dissolved in 9 mL diphenyl ether. The mixture was heated to 185 °C under argon atmosphere. The reaction lasted for 12 h and diluted with CH_2Cl_2 after being cooled to r.t.. The organic phase was washed with brine (30 mL), extracted with CH_2Cl_2 and dried with $MgSO_4$. After evaporation of solvent under reduced pressure, the product was purified by column chromatography with gradient eluent (petroleum ether → petroleum ehter/CH_2Cl_2 8/1 → petroleum ehter/CH_2Cl_2 5/1). Compound **11** was collected as white solid (3.14 g) in a yield of 49%.

FD-MS (8 kV): *m/z* = 1245.8 (100%, M^+), (calcd. for $C_{85}H_{117}BrSi$ = 1246.87 g mol^{-1})

^{1}H-NMR (250 MHz, CD_2Cl_2): δ = 7.01 (d, ^3J = 7.8Hz, 2H, aryl-*H*), 6.98 (d, ^3J = 8.2Hz, 2H, aryl-*H*), 6.72-6.63 (m, 18H, aryl-*H*), 2.40-2.33 (m, 8H, α-CH_2), 1.27-1.14 (m, 41H, alkyl-*H*), 0.88-0.80 (m, 35H, -CH_3), 0.10 (s, 9H, -CH_3) ppm.

^{13}C-NMR (125 MHz, CD_2Cl_2): δ = 141.81, 141.22, 140.80, 140.73, 140.59, 140.51, 140.41, 139.51, 138.27, 138.19, 136.94, 133.61, 131.71, 131.61, 131.13, 129.87, 127.05, 126.83, 119.38, 39.77, 39.74, 39.25, 38.96, 37.48, 33.32, 33.18, 32.73, 32.42, 28.37, 25.06, 25.04, 22.84, 22.77, 19.78, 19.75, 1.15, -1.13 ppm.

Elemental Analysis: C 81.83%, H 9.45% (calcd. for $C_{85}H_{117}BrSi$, C 81.88%, H 9.46%, Br 6.41%, Si 2.25%).

1-(4’-iodophenyl)-4-(4’-bromophenyl)-2,3,5,6-tetrakis[4’-(3’’,7’’-dimethyloctyl)phenyl] benzene (12):

Compound **11** (860 mg, 0.69 mmol) was dissolved in 30 mL chloroform. The solution was bubbled with argon for 20 min at 0 °C. ICl in CH_2Cl_2 solution (0.72 mL, 1 M) was then added dropwise. After being stirred for 10 min at 0 °C, the mixture was allowed to warm to ambient temperature. 40 min. later, large amount of 10 % Na_2SO_3 aqueous solution (50 mL) was added to quench the excess ICl. The crude compound was further washed with brine (50 mL) and extracted with CH_2Cl_2 (100 mL × 3). The combined organic layer was dried over $MgSO_4$ and filtered. The solvent was evaporated under reduced pressure and the residue was further purified by column chromatography with petroleum ether (PE) /CH_2Cl_2 15/1 as eluent affording **12** as white solid (854 mg) in a yield of 95%.

FD-MS (8 kV): *m/z* = 1301.6 (100%, M^+), m/z = 650.5 (8%, M^{2+}), (calcd. for $C_{82}H_{108}BrI$ = 1300.6 g mol^{-1}).

^{1}H-NMR (250 MHz, CD_2Cl_2): δ = 7.17 (d, ^3J = 7.9Hz, 2H, aryl-*H*), 6.97 (d, ^3J = 8.1Hz, 2H, aryl-*H*), 6.69 (s, 18H, aryl-*H*), 6.58 (d, ^3J = 8.0Hz, 2H, aryl-*H*), 2.43-2.35 (m, 8H, α-CH_2), 1.26-1.14 (m, 38H, alkyl-*H*), 0.88-0.81 (m, 36H, -CH_3) ppm.

^{13}C-NMR (175 MHz, CD_2Cl_2): δ = 141.20, 140.78, 140.73, 140.66, 139.96, 139.89, 138.02, 135.96, 133.85, 133.58, 131.59, 129.94, 127.12, 119.50, 90.98, 39.80, 39.01, 37.52, 33.23, 32.49, 30.11, 28.41, 25.11, 22.88, 22.82, 19.82, 19.78 ppm.

Elemental Analysis: C 74.98%, H 8.31% (calcd. for $C_{82}H_{108}BrI$, C 75.73%, H 8.37%, Br 6.14%, I 9.76%).

2-Iodo-11-bromo-5,8,14,17-tetra(3',7'-dimethyloctyl)-hexa-*peri*-hexabenzocoronene (3):

Compound **12** (89 mg, 0.07 mmol) was dissolved in CH_2Cl_2 (83 mL). The solution was bubbled with argon for 15 min at r.t. $FeCl_3$ (255.6 mg, 1.57 mmol) in nitromethane (0.84 mL) solution was then added dropwise. The mixture was stirred for 40 min at r.t. and the reaction was quenched with methanol (300 mL). The solvent was removed in vacuo and the residue was filtered through a silica gel pad with hot toluene. After removing toluene, the residue was dissolved in THF (2mL) and precipitated in methanol (100 mL). Compound **3** was collected as yellow powder (84 mg) in a yield of 93%.

MALDI-TOF MS (TCNQ): *m/z* = 1288 (100%, M^+), (calcd. for $C_{82}H_{96}BrI$ = 1288.49 g mol^{-1}).

^{1}H-NMR (250 MHz, CD_2Cl_2): δ = 6.95-6.41 (m, 12H, aryl-*H*), 2.11-2.03 (m, 8H, α-CH_2), 1.43-0.84 (m, 76H, alkyl-*H*) ppm.

^{13}C-NMR (125 MHz, CD_2Cl_2): δ = 138.18, 138.01, 133.66, 131.13, 129.84, 128.88, 127.93, 127.69, 127.31, 126.62, 126.08, 125.79, 125.62, 125.51, 121.82, 121.73, 119.95, 119.48, 118.99, 116.20, 115.74, 115.48, 115.34, 91.49, 40.24, 39.92, 37.74, 34.49, 33.91, 30.07, 28.51, 25.46, 23.09, 22.95, 20.01 ppm.

Elemental Analysis: C 76.05%, H 7.47% (calcd. for $C_{82}H_{96}BrI$, C 76.44%, H 7.51%, Br 6.20%, I 9.85%).

2-Cyano-11-bromo-5,8,14,17-tetra(3',7'-dimethyloctyl)-hexa-*peri*-hexabenzocoronene (4):

para-Iodo bromo HBC **3** (130 mg, 0.10 mmol), CuCN (10.8 mg, 0.12 mmol) and $Pd(PPh_3)_4$ (5.8 mg, 0.01 mmol) were mixed with THF (6 mL) in a 25 mL Schlenk tube with a cooling condenser. The system was degassed with two "freeze-pump-thaw" cycles. After warming to r.t., the mixture was heated to 65 °C and stirred for 15 h under argon atmosphere. Methanol (15 mL) was then added to quench the reaction when the mixture was cooled down. The organic phase was washed with brine (3 × 100 mL) and extracted with DCM. After being dried over $MgSO_4$, the solvents were removed *in vacuo*. The residue was absorbed on minimum silica gel and purified by column chromatography (eluent: petroleum ether (PE) / CH_2Cl_2 (7/4)). The product was further precipitated in methanol (100 mL) affording compound **4** as yellow powder (97 mg) in a yield of 81%.

MALDI-TOF MS (TCNQ): *m/z* = 1188 (100%, M^+) (calc. for $C_{83}H_{96}BrN$ = 1187.56 g mol^{-1}).

^{1}H-NMR (500 MHz, $CDCl_2$-$CDCl_2$, 140 °C): δ = 8.17 (s, 2H, aryl-*H*), 8.13 (s, 2H, aryl-*H*), 7.94 (s, 4H, aryl-*H*), 7.84 (s, 2H, aryl-*H*), 7.78 (s, 2H, aryl-*H*), 3.01 – 2.99 (m, 8H, α-CH_2), 2.05 – 1.29 (m, 40H, alkyl-*H*), 1.04 – 0.87 ppm (m, 36H, -CH_3).

^{13}C-NMR (125 Hz, $CDCl_2$-$CDCl_2$, 140 °C): δ =157.50, 141.36, 140.41, 128.52, 127.91, 126.69, 123.16, 122.81, 122.46, 121.36, 120.66, 108.75, 39.81, 39.30, 38.03, 37.64, 34.43, 33.64, 29.73, 28.24, 25.15, 25.12, 22.85, 22.79, 20.49, 19.98 ppm.

Elemental Analysis: C 82.54%, H 7.98%, N 1.01%, (calcd. for $C_{83}H_{96}BrN$, C 83.94%, H 8.15%, N 1.18%).

2-Cyano-11-(ditolyamino)-5,8,14,17-tetra(3',7'-dimethyloctyl)-hexa-*peri*-hexabenzocoronene (1):

Compound **4** (120 mg, 0.11 mmol), ditolyl amine (99.7 mg, 0.51 mmol), $Pd_2(dba)_3$ (4.6 mg, 0.01 mmol), *t*-Bu_3P (2.0 mg, 0.01 mmol) and sodium *tert*-butoxide (48.5 mg, 0.51 mmol) were mixed in a pre-dried 25 mL Schlenck tube with dry toluene (12 mL). The system was degassed with three "freeze-pump-thaw" cycles. After warming to r.t., the mixture was heated to 80 °C and stirred for 16 h under argon atmosphere. Methanol (10 mL) was then added to quench the reaction after the mixture was cooled down. The organic phase was then washed with brine (3 × 100 mL) and extracted with DCM. After being dried over $MgSO_4$, the solvents were removed *in vacuo*. The residue was absorbed on minimum silica gel and purified by column chromatography (eluent: petroleum ether (PE) / CH_2Cl_2 (3/1)). The product was further precipitated in methanol (100 mL) affording compound **1** as yellow powder (104 mg) in a yield of 79%.

MALDI-TOF MS (TCNQ): *m/z* = 1303 (100%, M^+) (calc. for $C_{97}H_{110}N_2$ = 1302.87 g mol^{-1}).

^{1}H-NMR (500 MHz, $CDCl_2$-$CDCl_2$, 90 °C): δ = 8.56 (s, 2H, aryl-*H*), 8.28 (s, 2H, aryl-*H*), 8.20 (s, 2H, aryl-*H*), 8. 09 (s, 2H, aryl-*H*), 7.89 (s, 2H, aryl-*H*), 7.66 (s, 2H, aryl-*H*), 7.49 (d, ^{3}J = 8.05 Hz, 4H, aryl-*H*), 7.36 (d, ^{3}J = 8.00 Hz, 4H, aryl-*H*), 3.13 – 3.07 (m, 4H, α-CH_2), 2.88 – 2.80 (m, 4H, α-CH_2), 2.50 (s, 6H, aryl-CH_3), 2.00 – 1.17 (m, 40H, alkyl-*H*),0.96 - 0.92 ppm (m, 36H, -CH_3).

^{13}C-NMR (125 Hz, $CDCl_2$-$CDCl_2$, 110 °C): δ = 147.38, 147.35, 145.89, 141.03, 140.95, 133.60, 131.70, 130.57, 129.73, 129.60, 129.47, 127.81, 125.61, 123.09, 123.02, 122.61, 122.22, 121.93, 121.84, 121.13, 120.18, 120.01, 119.93, 119.89, 118.91, 115.73, 108.92, 39.80, 39.59, 39.47, 37.77, 37.74, 34.80, 34.74, 33.50, 33.40, 29.82, 28.21, 25.13, 25.07, 22.88, 22.80, 21.12, 20.04, 20.02 ppm.

Elemental Analysis: C 86.88%, H 8.40%, N 2.05%, (calcd. for $C_{97}H_{110}N_2$, C 88.35%, H 8.50%, N 2.15%).

2-Cyano-11-[bis-(4’-methoxylphenyl)-amino]-5,8,14,17-tetra(3’,7’-dimethyloctyl)-hexa-*peri*-hexabenzocoronene (2):

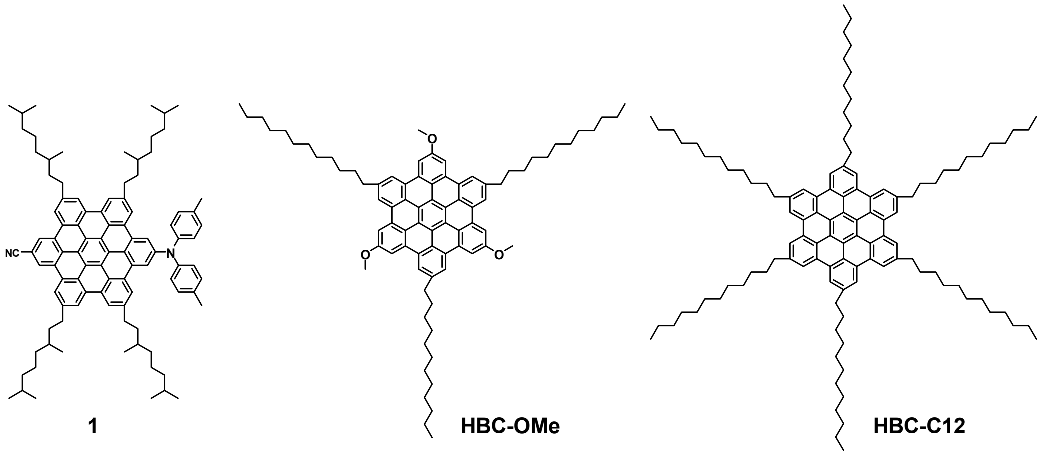
Compound **4** (120 mg, 0.11 mmol), di-(4-methoxylphenyl) amine (125 mg, 0.55 mmol), $Pd_2(dba)_3$ (5.0 mg, 0.01 mmol), *t*-Bu_3P (2.2 mg, 0.01 mmol) and sodium *tert*-butoxide (52.5 mg, 0.55 mmol) were mixed in a pre-dried 25 mL Schlenck tube with dry toluene (12 mL). The system was degassed with two “freeze-pump-thaw” cycles. After warming to r.t., the mixture was heated to 80 °C and stirred for 16 h under argon atmosphere. Methanol (10 mL) was then added to quench the reaction after the mixture was cooled down. The organic phase was then washed with brine (3 × 100 mL) and extracted with DCM. After being dried over $MgSO_4$, the solvents were removed *in vacuo*. The residue was absorbed on minimum silica gel and purified by column chromatography (eluent: petroleum ether (PE) / CH_2Cl_2 (2/3)). The product was further precipitated in methanol (100 mL) affording compound **2** as yellow powder (108 mg) in a yield of 74%.

MALDI-TOF MS (TCNQ): *m/z* = 1336 (100%, M^+) (calc. for $C_{97}H_{110}N_2O_2$ = 1335.92 g mol^{-1}).

^{1}H-NMR (700 MHz, $CDCl_2$-$CDCl_2$, 90 °C): δ = 8.57 (s, 2H, aryl-*H*), 8.43 (s, 2H, aryl-*H*), 8.31 (s, 2H, aryl-*H*), 8. 27 (s, 2H, aryl-*H*), 8.16 (s, 2H, aryl-*H*), 7.90 (s, 2H, aryl-*H*), 7.54 (d, ^{3}J = 7.56 Hz, 4H, aryl-*H*), 7.14 (d, ^{3}J = 7.57 Hz, 4H, aryl-*H*), 3.96 (s, 6H, -OCH_3), 3.16 – 3.12 (m, 4H, α-CH_2), 2.96 – 2.89 (m, 4H, α-CH_2), 2.02 – 1.16 (m, 40H, alkyl-*H*),0.96 - 0.92 ppm (m, 36H, -CH_3).

^{13}C-NMR (75 Hz, $CDCl_2$-$CDCl_2$, 120 °C): δ = 195.00, 191.14, 190.59, 157.23, 141.56, 141.34, 131.80, 130.03, 129.90, 129.87, 128.24, 127.41, 123.37, 123.10, 122.54, 122.13, 121.45, 120.38, 119.19, 115.89, 109.22, 91.86, 56.08, 39.76, 39.48, 37.72, 34.77, 34.73, 33.41, 33.28, 29.78, 28.17, 25.05, 25.01, 22.81, 22.74, 20.03, 19.98 ppm.

Elemental Analysis: C 87.24%, H 8.33%, N 2.02%, (calcd. for $C_{97}H_{110}N_2O_2$, C 87.21%, H 8.30%, N 2.40%).



1 **HBC-OMe** **HBC-C12**

Scheme S2. Molecular structure of control HBCs **1**, **HBC-OMe** and **HBC-C12**.

Table S1. Concentration dependent ^{1}H-NMR experimental data of **1** and **HBC-OMe**.

Experimental data of compound **1**										
concentration / M	2.05×10^{-2}	2.05×10^{-3}	1.02×10^{-3}	5.12×10^{-4}	6.00×10^{-5}	3.00×10^{-5}	1.00×10^{-5}	5.00×10^{-6}	1.00×10^{-6}	5.00×10^{-7}

chemical shift[a] **/ ppm**	8.51	8.63	8.67	8.71	8.76	8.82	8.89	8.98	9.04	9.06

Experimental data of **HBC-OMe**

concentration / M	1.19×10^{-2}	7.16×10^{-3}	2.38×10^{-3}	1.19×10^{-3}	7.16×10^{-4}	2.38×10^{-4}	1.19×10^{-4}	7.16×10^{-5}	2.38×10^{-5}
chemical shift[b] **/ ppm**	8.36	8.44	8.62	8.65	8.79	8.88	8.90	8.93	8.95

a the chemical shift values correspond to *Ha*
b the chemical shift values correspond to the proton directly next to the methoxy group.

Table S2. Thermodynamic parameters of **1**, **HBC-OMe** and **HBC-C12**[27] calculated according to the AK model; K_A: association constant; φ: a factor by which dimer formation differs from other aggregate formation in AK model ($K_2 = \varphi K_A/2$); P_α: chemical shift of monomer; P_ξ: chemical shift of the interior molecule within molecular stacks.

AK model calculation				
1	K_A **=1405.93 L/mol**	$\varphi = 25.915$	$P_\alpha = 8.985$ **ppm**	$P_\xi = 6.520$ **ppm**
HBC-OMe	K_A **=658.05 L/mol**	$\varphi = 3.653$	$P_\alpha = 8.88$ **ppm**	$P_\xi = 7.459$ **ppm**
HBC-C12	$K_A = 457.32$ **L/mol**	$\varphi = 3.834$	$P_\alpha = 8.978$ **ppm**	$P_\xi = 7.239$ **ppm**

Table S3. Parameters of the Vogel-Fulcher-Tammann (VFT) equation and the corresponding glass temperature (T_g) (at τ~10 s).

compound	***process***	τ_0 ***(s)***	***B (K)***	T_0 ***(K)***	T_g ***(K)***
4	*α*	$6.7x10^{-10}$	*1900*	*186*	*267*
	α’	$7.1x10^{-11}$	*3150*	*163*	*286*
2	*α*	$1.4x10^{-11}$	*3470*	*144*	*271*
	α’	$5.5x10^{-9}$	*2090*	*194*	*292*
1	*α*	$2.3x10^{-10}$	*2240*	*202*	*293*
	α’	$3.5x10^{-9}$	*1800*	*244*	*326*

Vogel-Fulcher-Tammann (VFT) equation:

$$\tau_{\max} = \tau_0 \exp\left(\frac{B}{T - T_0}\right)$$

where τ_0 is the limited time at very high temperatures, B is the activation parameter and T_0 is the "ideal" glass temperature. The usual glass temperature, T_g, can be obtained from the VFT equation at τ~10 s and is depicted in Table S3 together with the VFT parameters.

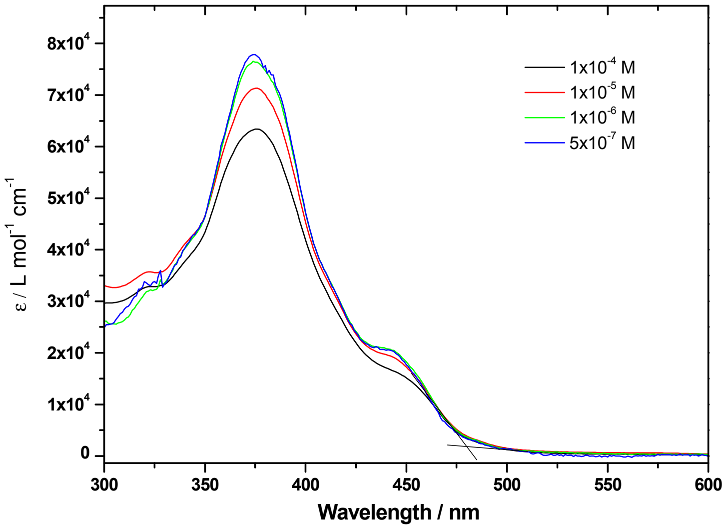


Figure S1. UV/Vis absorption spectra of compound **1** recorded at different concentrations in chloroform measured at 25 °C.

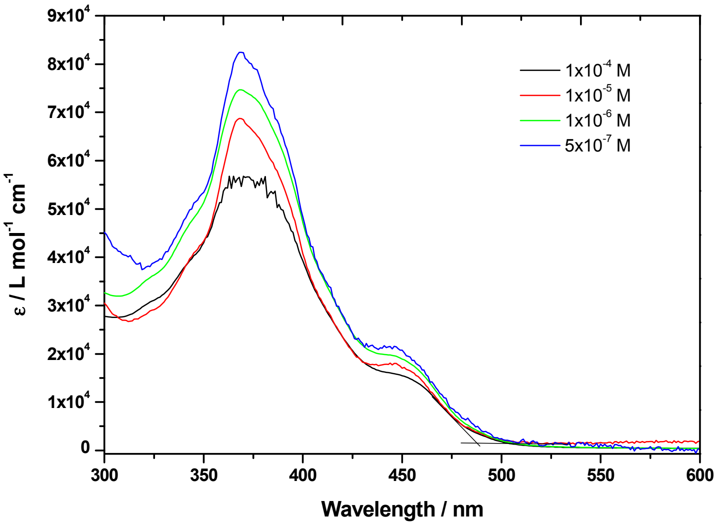


Figure S2. UV/Vis absorption spectra of compound **2** recorded at different concentrations in chloroform measured at 25 °C.

Like other alkyl substituted HBCs, [10] the non-Lambert-Beer behavior and broader bands at higher concentrations, indicates the existence of molecular aggregates.[10,14] Bathochromic shifts of absorption maximum of 8 nm and 10 nm were found for **1** (λ_{max}= 368 nm) and **2** (λ_{max}= 370 nm) compared with that of the **HBC- C12** (λ_{max}= 360 nm), respectively. This could be ascribed to the extended conjugation of the donor-acceptor system of **1** and **2**.

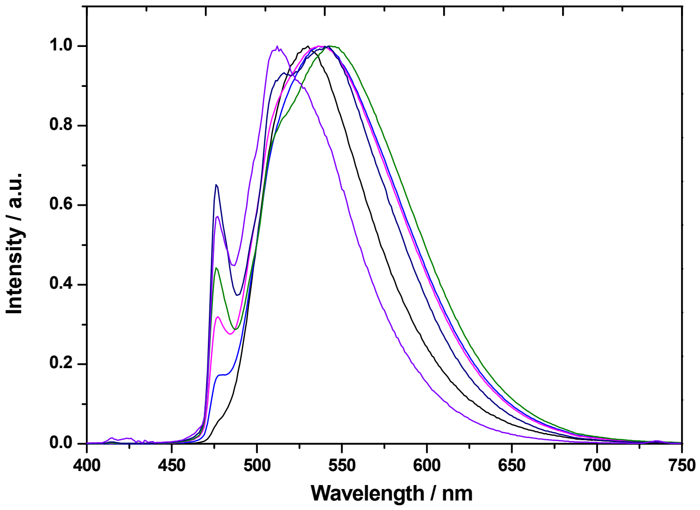


Figure S3. Normalized PL emission spectra of compound **1** recorded at different concentration in chloroform measured at 25 °C (excited at 368 nm). The PL emission spectra of compound **2** are similar to that of **1** which were not shown.

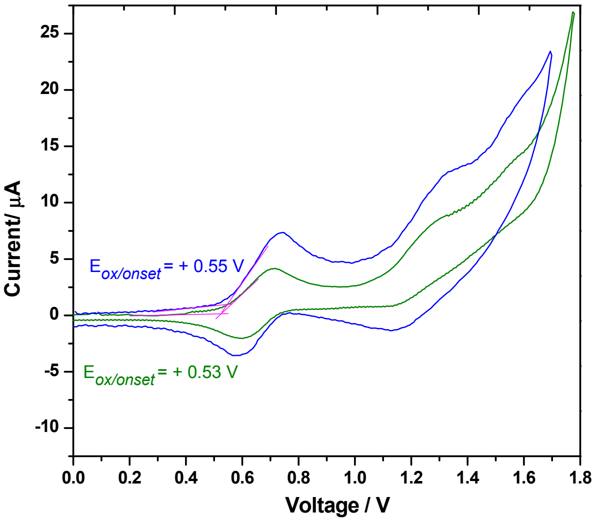


Figure S4. Cyclic voltammetric profile of compound **1** (blue line) and **2**(green line) in dichloromethane solution (0.5 mM) containing 0.1 M Bu_4NPF_6. Potentials are reported versus the Fc/Fc^+ redox couple as an internal standard, scan rate = 100 mV/s. Both compounds show a typical triphenylamine reversible redox curves and the oxidation curve of HBC core. The summary of the electrochemical data is shown in Table S4.

Table S4. Optical and redox data of HBC **1** and **2**.

Compounds	λ_{abs} [nm][a]	E_{gap} [eV][b]	$E_{ox/onset}$[V] [c]	HOMO[eV][d]	LUMO[eV][e]
1	368	2.58	0.55	-5.35	-2.77
2	370	2.55	0.53	-5.33	-2.78

[a] In $CHCl_3$, $1*10^{-5}$ M, 295K. [b] Determined from the onset of absorption($1*10^{-5}$ M). [c] In CH_2Cl_2, 0.5 mM, Bu_4NPF_6 (0.1 M), 295 K, scan rate = 100 mV/s, versus Fc/Fc^+. [d] Determined from $E_{HOMO} = -(E_{ox/onset} + 4.80)$ (eV). [e] Calculated from $E_{LUMO} = E_{HOMO} + E_{gap}$

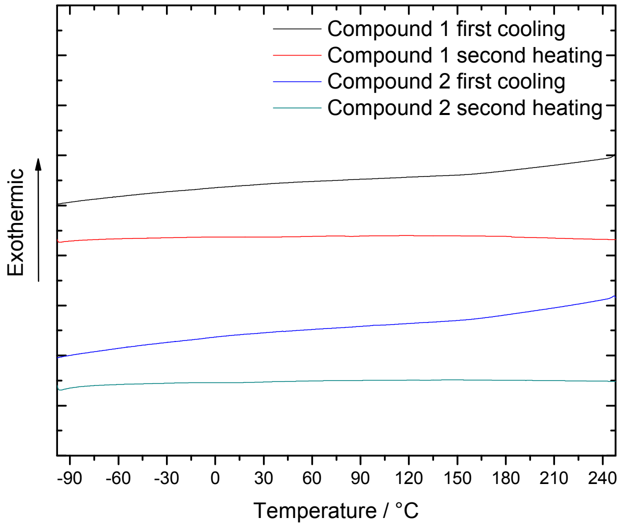


Figure S5. DSC traces of **1** and **2** recorded at 10 K/min.

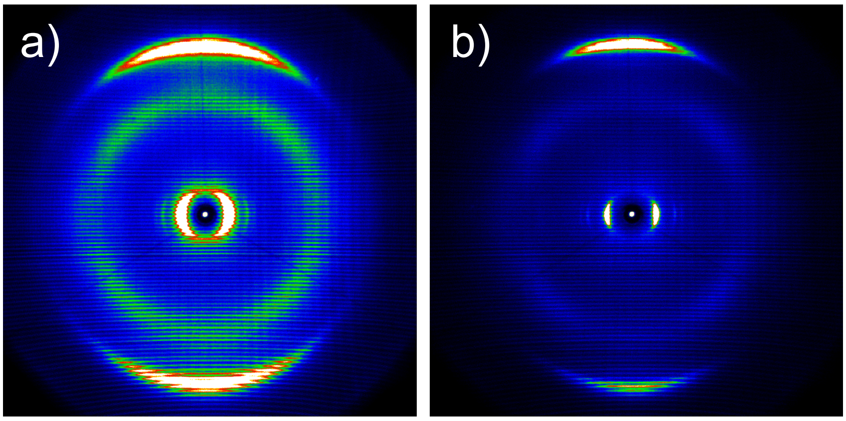


Figure S6. 2D WAXS patterns of 2 recorded at a) 30 °C, b) -80 °C.

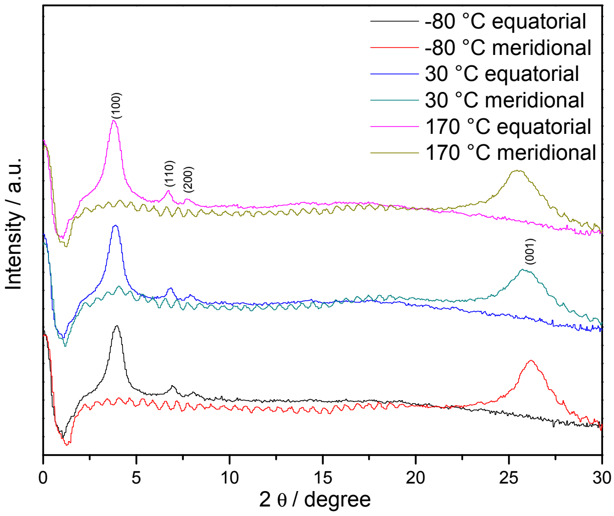


Figure S7. Equatorial and meridional intensity distributions of 2D WAXS patterns of 2 (same as compound 1); unit cell parameters: a_{hex} = 2.52 nm, d = 0.34 nm at -80 °C, a_{hex} = 2.59 nm, d = 0.34 nm at 30 °C, a_{hex} = 2.65 nm, d = 0.36 nm at 170 °C.