

Experimental Section

A. Synthesis

18d,18f,18h-Triaza-18e,18g,18i-tribora-hexabenzob[bc,ef,hi,kl,no,qr]coronene (BN-HBC)

Under a gentle argon flow of 2.5 sccm/min, 3.53 g (6.1 mmol) N-tribiphenylborazol-acetonitrile adduct synthesized according to literature^[1] were heated up to 550 °C. At around 350 °C a colorless melt was obtained that quickly became brownish at higher temperatures. After 2 h at 550 °C the melt solidified and after 6 h (at 550 °C) the reaction product was allowed to slowly cool down to around 400 °C. Then it was taken out of the oven and quickly cooled to RT. The resulting black solid showed some colorless crystals on its surface that proved to be the known **4** according to X-ray analysis.^[2] The black remaining was suspended three times in 25 ml of dichloromethane and filtered through a Soxhlet sleeve. After that a twofold Soxhlet extraction (600 ml of dichloromethane each) followed. While the first extraction was conducted for 23 h, the second lasted 100 h in addition. The remaining solid (1.8795 g) in the sleeve was subjected to sublimation in a specially prepared Schlenk tube with a KW25 joint that allows for direct attachment to a vacuum system (oil diffusion pump with a rotary vane backing pump). The Schlenk tube (length 330 mm, inner diameter 25 mm tapering to a diameter of 20 mm at 35 mm from the end of the tube) was filled with 14 glass rings (inner diameter 20 mm, height 20 mm). A glass shuttle containing 499.8 mg of the black solid was placed at the bottom of the tube and the tube was placed into the oven so that 5 glass rings could still be seen. Then the tube was evacuated for 20.5 h at pressures of $2.3 \cdot 10^{-5}$ to $1.9 \cdot 10^{-6}$ mbar and 300 °C to get rid of lightweight side products. After cooling down to rt 6 glass rings were taken out, substituted by fresh ones and placed in the oven again. Within 21 h at pressures of $7.7 \cdot 10^{-6}$ to $1.7 \cdot 10^{-6}$ mbar and 400 °C a yellow sublimate is received. Back at rt 7 glass rings were taken out of the tube and sonicated in 150 ml of acetone. The suspension was evaporated and a yellow solid was obtained. As it was difficult to scratch the flask completely the remaining solid was resuspended in 2 ml of acetone and subjected to centrifugation (5 min at 13.4 krpm). After drying and combining with the first batch 14.7 mg of a yellow solid could be isolated. Deriving a yield proves to be difficult but is estimated to around 3-5 %.

δ_C (ssNMR, 50 MHz) 120.3, 125.0, 132.3, 139.5; LDI-MS (TOF) m/z: 525 (100 %); IR (KBr) cm^{-1} 668w, 753m, 768m, 1330m, 1361m, 1384 s, 1420m, 1446m, 1467m, 1504m, 1581w, 1603m, 3064w; mp > 410 °C (starts to become dark at 390 °C).

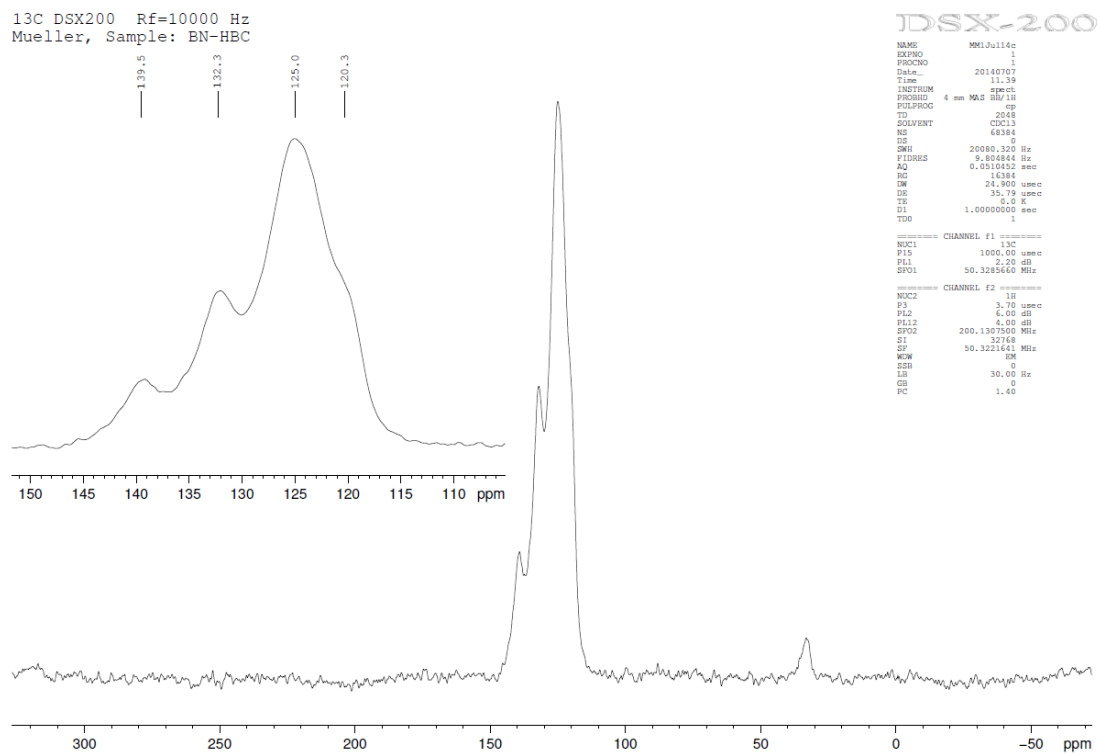


Fig. S1. ^{13}C ssNMR (50 MHz) of BN-HBC.

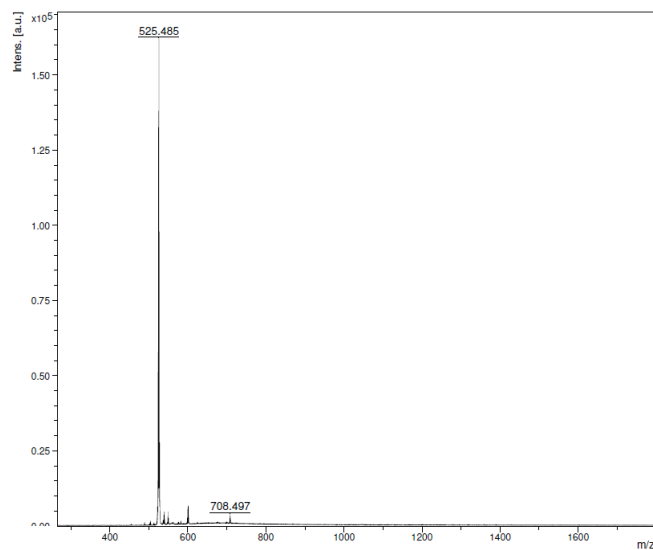
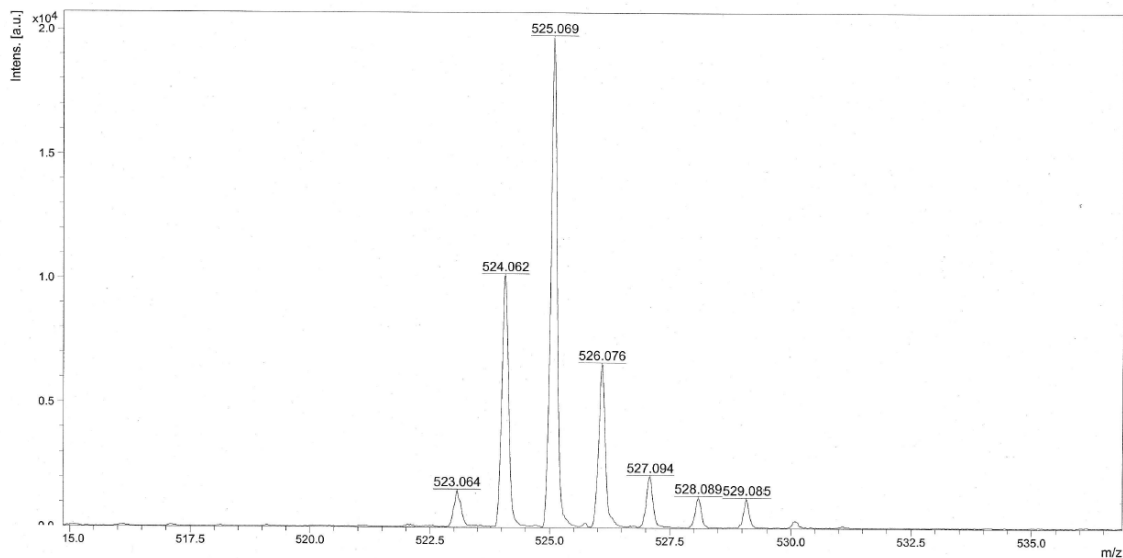


Fig. S2. Mass spectrum (LDI-TOF) of BN-HBC.

D:\Data\oi\Bettinger\Mueller\MMI838_1 (LDI)\0_K18\1

Comment 1 MMI838_1 (LDI) Susp.
Comment 2 RP Mode, ACN, 31%



Bruker Daltonics flexAnalysis

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Fig. S3. Mass spectrum (LDI-TOF) of BN-HBC, enlarged

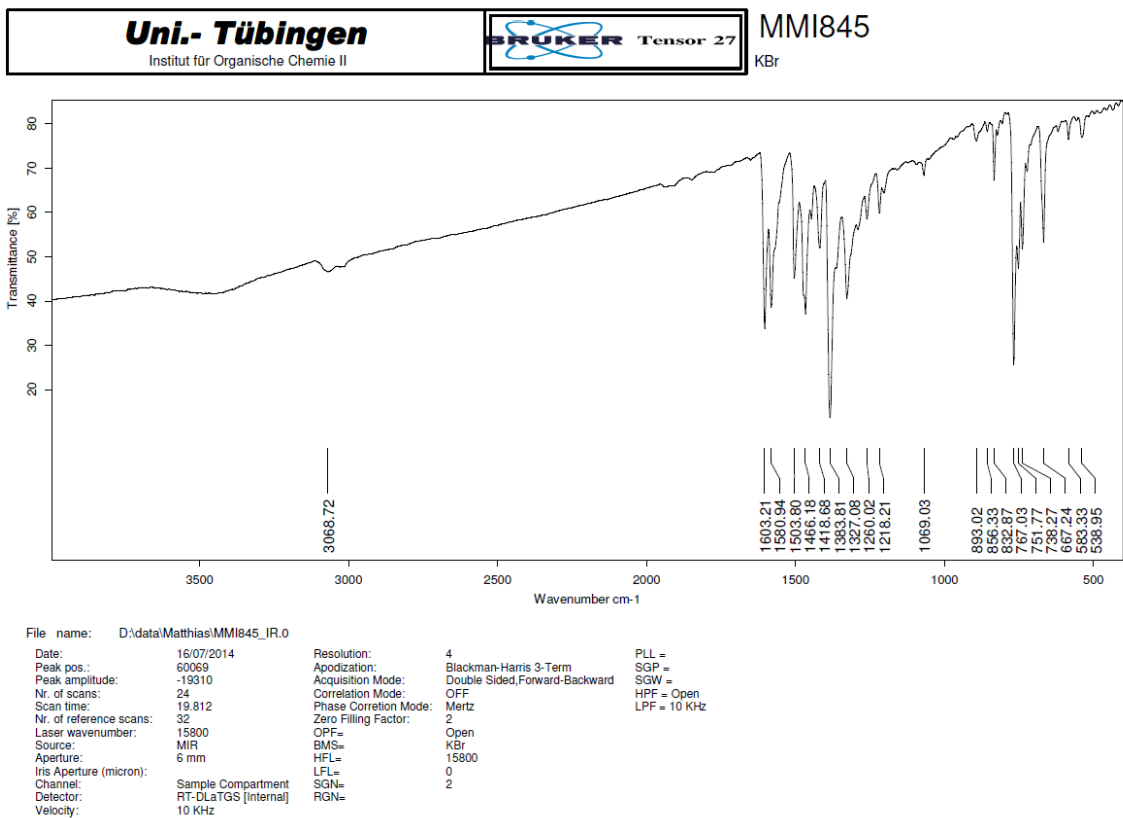


Fig. S4. IR spectrum (KBr) of BN-HBC

B. Powder Diffraction

The substance was inspected by powder X-ray diffraction (StadiP, Stoe, Darmstadt, Ge-monochromated Cu-K $_{\alpha 1}$ radiation) in the range $2.5 < \Theta < 30^\circ$. Due to the low intensities above $15^\circ/\Theta$ and the presence of the side phase **4** in the substance a Le Bail-Fit^[3] with the space group and lattice constants of HBC as starting values was performed. Resulting χ^2 value 2.066.

HBC^[4]: space group P 2 $_1/a$ (No. 14), $a = 18.431(3)$ Å, $b = 5.119(1)$ Å, $c = 12.929(2)$ Å, $\beta = 112.57(1)^\circ$, $V = 1126.4(4)$ Å³

Le Bail fit: space group P 2 $_1/a$ (No. 14), $a = 18.430(2)$ Å, $b = 5.1001(5)$ Å, $c = 13.010(1)$ Å, $\beta = 112.464(5)^\circ$, $V = 1130.0(2)$ Å³ at 20 °C

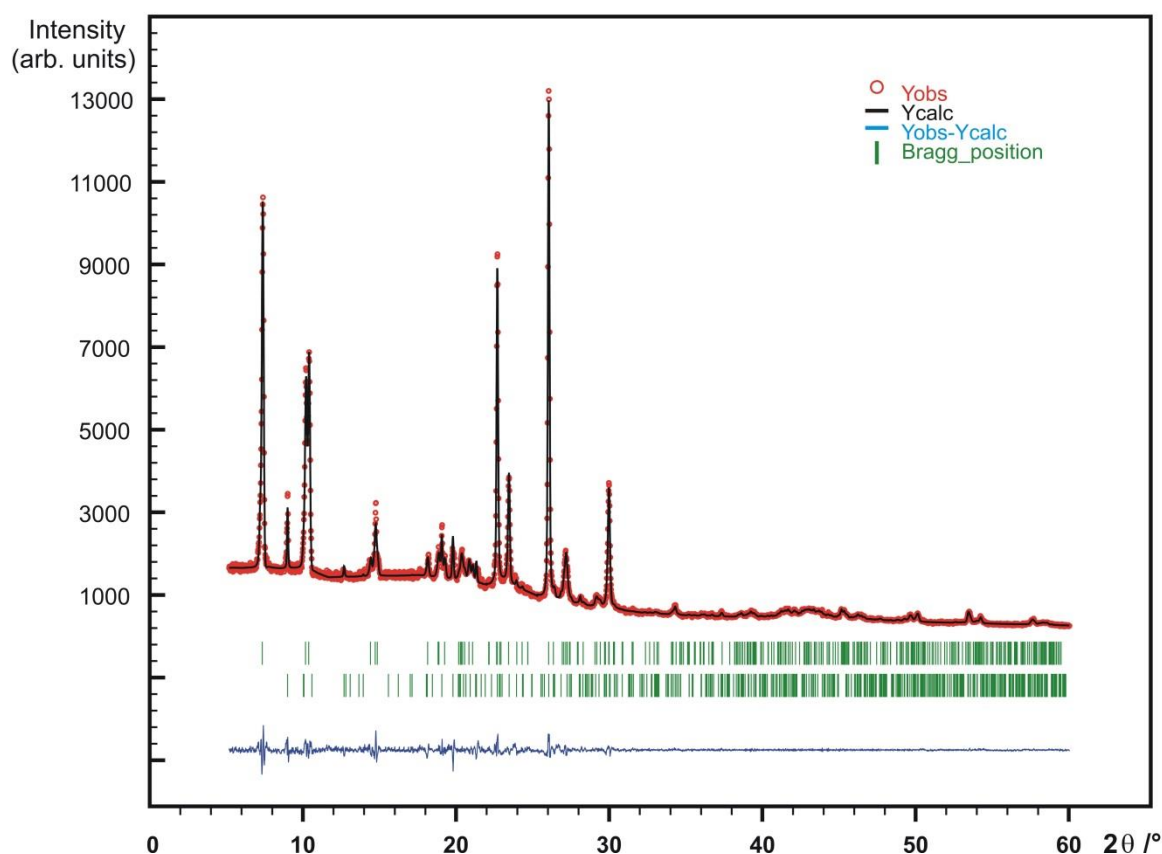


Fig. S5. Le Bail refinement of BN-HBC based on powder X-ray data. Circles represent measured data; the calculated pattern is superimposed with the observed pattern. Ticks mark the Bragg reflections (top: BN-HBC, bottom: **4**). The difference curve between the observed and calculated pattern is shown in the lower part of the graph.

C. STM Investigations

Experiments were performed in an ultrahigh vacuum (UHV) surface analysis system, with a base pressure below 1×10^{-10} mbar, consisting of a preparation chamber allowing for standard sample preparation and molecular deposition, and a microscope chamber housing a CreaTec low-temperature STM. The Au(111) crystal was cleaned by repeated cycles of Ar⁺ sputtering at 300 K, and annealing in vacuum at 770 K. STM acquisition was performed at liquid helium temperature (LHe, 4 K) using the constant-current mode and homemade W tips. The BN-HBC molecules were deposited using a molecular evaporator that was degassed at

approximately 570 K for several hours. The molecules were dosed for 1 minute at approximately 670 K at a partial pressure of 8×10^{-9} mbar. During deposition, the Au(111) sample was kept at a temperature of 300 K. After deposition, the sample was quenched down to LHe temperature for STM data acquisition. The sublimation temperature used here is compatible with what is reported for the sublimation of unsubstituted HBC molecules.^[5]

D. Solid state ^{11}B NMR

Boron-11 Solid-State NMR Spectroscopy: A powdered sample was packed in 4 mm o.d. zirconia rotor and transferred into a double-bearing MAS probe head. ^{11}B MAS experiments were carried out at 4.7 T using a Bruker DSX-200 NMR spectrometer operating at 200.13 (1H) and 64.207 MHz (11B). Boron-11 free induction decays were acquired under MAS at a spinning rate of 7 kHz using a one-pulse sequence of 1 ms pulse width, which corresponds to a solution 258 flip angle, a recycle delay of 1 s, and high-power proton decoupling during acquisition. Chemical shifts are referenced to the primary standard $\text{BF}_3 \cdot \text{OEt}_2$ using solid NaBH_4 as secondary reference at $\delta = 42.06$ ppm.^[7] Spectral simulations of the second-order broadened ^{11}B central transition^[8] were carried out using WSolids1,^[9] a software package that incorporates the POWDER algorithm of Alderman et al.^[10] Experimental ^{11}B MAS-NMR spectra contain a strong background signal arising from boron nitride ceramics in the probe head, identified by obtaining ^{11}B MAS spectra for an empty rotor. The background signal was included in the simulation phenomenologically by using a chemical shift anisotropy static powder pattern.

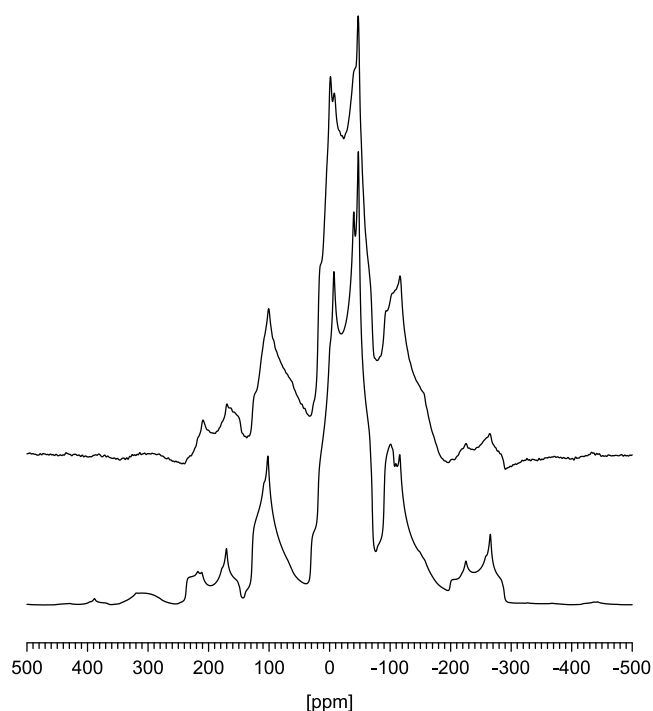


Fig. S6. Experimental (top) and calculated (bottom) ^{11}B MAS NMR spectrum of BN-HBC and side product **4** obtained at 4.7 T and a spinning rate of 7 kHz. The probe head background signal, acquired for an empty spinner, has been subtracted from the experimental spectrum. The theoretical spectrum has been calculated using DMFit 20111221^[11].

E. Theory

The chemical shielding of the carbon atoms of the HBC molecule and a trimeric aggregate were computed using the structure of a trimeric stack or of the monomer taken from the X-ray structure without any further geometry optimization.^[12] The chemical shielding was computed

using the GIAO^[13] method at the B3LYP/6-31G*^[14] level as used in our earlier computations.^[15] The computations were performed with Gaussian 09.^[16]

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