Electronic Supplementary Material (ESI) for Polymer Chemistry.

Supporting Information for:

Chemical Doping Enhances Electronic Transport in Networks of Hexabenzocoronenes Assembled in Non-Aqueous Electrolyte

Laura C. H. Gerber,[a,b] Peter D. Frischmann,[a,b] Teresa E. Williams,[b] Martijn Tichelaar,[b] Erica Y. Tsai,[b] Yi-Sheng Liu,[c] Jinghua Guo,[c] C. D. Pemmaraju,[b] David Prendergast[a,b] and Brett A. Helms *[a,b]

[a] The Joint Center for Energy Storage Research, Lawrence Berkeley National Laboratory, 1 Cyclotron Road, Berkeley, CA 94720 USA.
[b] The Molecular Foundry, Lawrence Berkeley National Laboratory, 1 Cyclotron Road, Berkeley, CA 94720 USA.
[c] The Advanced Light Source, Lawrence Berkeley National Laboratory, 1 Cyclotron Road, Berkeley, CA 94720 USA.

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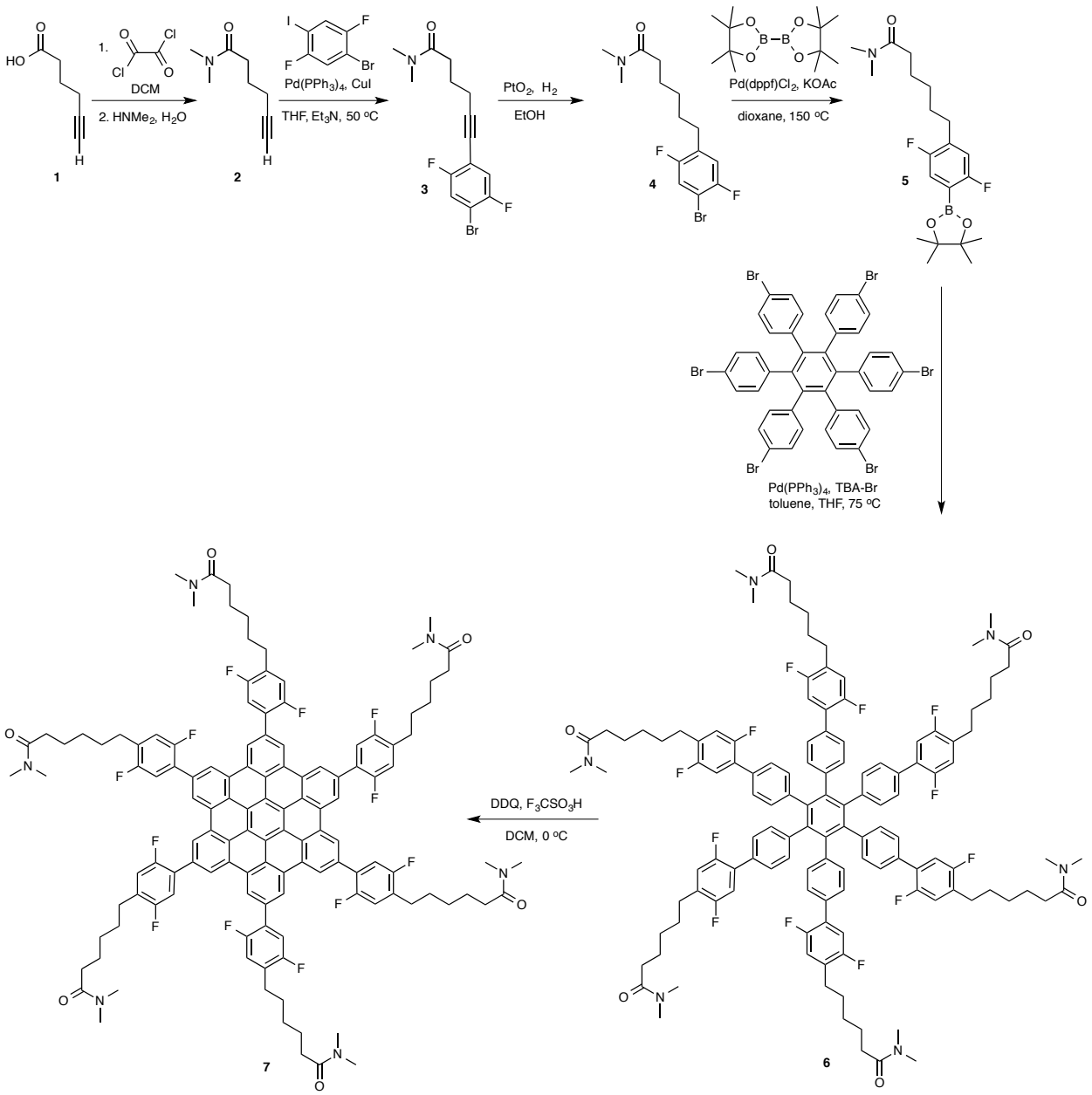
General Information

Materials. Hexakis(4-bromophenyl)benzene[1] was prepared according to a literature procedure. DCM, toluene, and THF were sparged with N_2 and passed through activated alumina. Benzonitrile was sparged with Ar, brought into an Ar-filled glove box, and dried over 3 Å molecular sieves. $TBAPF_6$ was dried for 16 h at 70 °C under vacuum. All other reagents were purchased from commercial suppliers and used as received. The water content of 0.1 M $TBAPF_6$ in benzonitrile was below 20 ppm.

Methods. Water content was tested with a Mettler Toledo C20 Coulometric KF Titrator Karl-Fischer apparatus. Column chromatography was performed using a Biotage HPFC SP4 Flash Purification System with Biotage SNAP cartridges containing KP-Sil. ^{1}H and ^{13}C NMR spectra were obtained with a Bruker Avance II 500 MHz NMR Spectrometer. ^{1}H and ^{13}C NMR spectra are reported in δ (parts per million) relative to tetramethylsilane (TMS) and referenced to residual ^{1}H/^{13}C signals of the deuterated solvent (^{1}H (δ) chloroform 7.27; ^{13}C (δ) chloroform 77.23). ^{19}F NMR spectra are referenced to an internal standard of α,α,α-trifluorotoluene (δ − 63.72). UV-visible-NIR spectra were measured with a Cary 5000 UV-Vis-NIR spectrophotometer; variable temperature measurements were conducted with a Quantum Northwest t2x2 dual temperature-controlled cuvette holder. FT-IR spectra were measured with a Perkin Elmer Spectrum One FT-IR spectrometer. MALDI-TOF mass spectrometry was carried out with an AB SCIEX TF4800 MALDI TOF-TOF Mass Spectrometer. ESI-MS was measured with a Bruker microTOF-Q. Elemental analyses were performed by the University of California, Berkeley's College of Chemistry Microanalytical Facility. SEM micrographs were acquired using a Zeiss Gemini Ultra-55 Analytical Field Emission Scanning Electron Microscope. Electrochemical experiments were conducted with a BioLogic VMP3 potentiostat. All electrochemical measurements were performed in an Ar-filled glove box with <2 ppm O_2 and H_2O. Gold interdigitated array (IDA) electrodes with 65 pairs of electrodes with width, length, and spacing of 10 μm, 2 mm, and 5 μm, respectively, were purchased from CH Instruments (Austin, TX, USA). All IDA measurements were made with one set of electrodes connected to the working electrode lead and the other set connected to the reference and auxiliary leads of the potentiostat. Unless otherwise noted, solutions of HBC **7** nanowires in electrolyte were formed by mixing solid HBC **7** and electrolyte (benzonitrile, 0.1 M $TBAPF_6$) at room temperature until all HBC is dissolved and the resulting solution was allowed to equilibrate for >15 min before measurements were performed.



Synthesis of *N,N*-dimethylhex-5-ynamide (2)

A flame-dried 500 mL round bottom flask purged with nitrogen was charged with 5-hexynoic acid (15.1 g, 135 mmol) and anhydrous DCM (300 mL). A solution of oxalyl chloride (17.4 g, 137 mmol) in anhydrous DCM (45 mL) was added drop-wise over a period of 1.5 h. The resulting solution was stirred for 21 h under a nitrogen atmosphere and subsequently concentrated *in vacuo*. The crude product was slowly added (30 min) to a 150 mL Parr bottle containing an ice-cold stirred solution of dimethylamine in water (40% *w*/*w*, 95 mL). After addition of the first 2 mL, an ice bath was used to maintain a strict sub-ambient temperature. The bottle was sealed and stirring continued for 15 min, after which the ice bath was removed. After stirring for an additional 2 h at room temperature, the flask was cooled to 0 °C in the refrigerator before removing the seal. Excess dimethylamine was evaporated by bubbling nitrogen through

the reaction mixture in a fume hood with adequate ventilation; aqueous 5 M NaOH solution (20 ml) was then added slowly. The product was extracted from the reaction mixture with DCM (3 x 200 mL). The combined organic layers were dried on $NaSO_4$ and concentrated *in vacuo* to give the product as a yellow oil (16.5 g, 118 mmol, 88%). ^{1}H NMR ($CDCl_3$): δ 3.03 (s, 3H), 2.95 (s, 3H), 2.46 (t, J = 7.4 Hz, 2H), 2.29 (td, J = 6.8 Hz, J = 2.7 Hz, 2H), 1.97 (t, J = 2.7 Hz, 1H), 1.87 (m, 2H); ^{13}C NMR ($CDCl_3$): δ 172.4, 84.1, 69.0, 37.3, 35.5, 31.8, 23.9, 18.1; FT-IR (neat): $\tilde{\nu}$ 3291 (w), 3233 (w), 2940 (w), 2115 (w), 1636 (s), 1498 (m), 1456 (m), 1410 (m),1399 (s), 1353 (w), 1335 (w), 1264 (m), 1217 (w), 1179 (w), 1141 (m), 1058 (w), 1045 (w), 1013 (w), 970 (w), 909 (w), 857 (w), 809 (w) cm^{-1}. ESI-MS (MeOH) m/z = 162.09 $[M+Na]^+$. Anal Calc'd for $C_8H_{13}NO$: C, 69.03; H, 9.41; N, 10.06. Found: C, 68.79; H, 9.44; N, 10.23.

Synthesis of 3

Et_3N (250 mL) was added to a 1 L Schlenk flask and it was capped with a septum. The head-space was evacuated and refilled with N_2. *N*,*N*-dimethylhex-5-ynamide (7.23 g, 52 mmol) was added, followed by dry THF (250 mL). The solution was deoxygenated by bubbling N_2 through for 1 h. 1-bromo-2,5-difluoro-4-iodobenzene (15.0 g, 47 mmol), $Pd(PPh_3)_4$ (0.543 g, 0.47 mmol), and CuI (0.185 g, 0.97 mmol) were added as solids while the reaction mixture purged with nitrogen. The solution was heated to 50 °C for 18 h, over which time a white precipitate formed. The mixture was filtered and the solids were washed with toluene. The filtrate was washed with 3 x 50 mL water. The filtrate was concentrated and purified by column chromatography (SiO_2, 3:7 hexanes:EtOAc) to yield 13.4 g (89 %) of a pale yellow solid. ^{1}H NMR ($CDCl_3$) δ 7.268 (dd, $^3J_{HF}$ = 8 Hz, $^4J_{HF}$ = 6 Hz, 1H, Ar*H*), 7.124 (dd, $^3J_{HF}$ = 8 Hz, $^4J_{HF}$ = 6 Hz, 1H, Ar*H*), 3.034 (s, 3H, CH_3), 2.960 (s, 3H, CH_3), 2.544 (t, $^3J_{HH}$ = 7 Hz, 2H, CH_2), 2.508 (t, $^3J_{HH}$ = 7 Hz, 2H, CH_2), 1.959 (quintet, $^3J_{HH}$ = 7 Hz, 2H, CH_2); ^{13}C{^{1}H} NMR ($CDCl_3$) δ 172.3 (s, *C*=O), 158.7 (dd, $^1J_{CF}$ = 249 Hz, $^4J_{CF}$ = 3 Hz, *C*F), 155.2 (dd, $^1J_{CF}$ = 243 Hz, $^4J_{CF}$ = 3 Hz, *C*F), 120.3 (dd, $^2J_{CF}$ = 25 Hz, $^3J_{CF}$ = 0.6 Hz, Ar*C*H), 120.0 (dd, $^2J_{CF}$ = 25 Hz, $^3J_{CF}$ = 2 Hz, Ar*C*H), 113.1 (dd, $^2J_{CF}$ = 18 Hz, $^3J_{CF}$ = 9 Hz, C_{ipso}), 108.8 (dd, $^2J_{CF}$ = 24 Hz, $^3J_{CF}$ = 9 Hz, C_{ipso}), 97.7 (d, $^3J_{CF}$ = 3.5 Hz, Ar*C*ΞC), 73.6 (d, $^4J_{CF}$ = 2.3 Hz, Ar*C*Ξ*C*), 37.3, 35.6, 31.8, 23.8, 19.3 (aliphatic *C*); ^{19}F NMR ($CDCl_3$) δ –114.39 (m), –115.9 (m). ESI-MS (MeOH) m/z = 356.03 $[M + Na]^+$, 689.08 $[2M + Na]^+$. Anal Calc'd for $C_{14}H_{14}BrF_2NO$: C, 50.93; H, 4.27; N, 4.24. Found: C, 51.09; H, 4.35; N, 4.33.

Synthesis of 4

Compound **3** (1.38 g, 4.18 mmol), EtOH (50 mL), and PtO_2 (50 mg, 0.22 mmol) were added to a 100 mL flask. The solution was sparged with N_2 for 30 min. A 3-way valve connected to a balloon filled with hydrogen was attached. The head-space of the flask was evacuated and refilled three times with H_2. The reaction was stirred for 16 h under H_2 atmosphere after which time a ^{1}H NMR spectrum of an aliquot showed complete conversion of **3**. The reaction mixture was filtered over Celite, which was then washed with EtOH. The volatiles were removed *in vacuo* from the filtrate to yield 1.36 g (98 %) as an orange oil. ^{1}H NMR ($CDCl_3$) δ 7.204 (dd, $^3J_{HF}$ = 9 Hz, $^4J_{HF}$ = 6 Hz, 1H, Ar*H*), 6.950 (dd, $^3J_{HF}$ = 9 Hz, $^4J_{HF}$ = 6 Hz, 1H, Ar*H*), 2.995 (s, 3H, CH_3), 2.943 (s, 3H, CH_3), 2.592 (t, $^3J_{HH}$ = 7.5 Hz, 2H, CH_2), 2.303 (t, $^3J_{HH}$ = 7.5 Hz, 2H, CH_2), 1.669 (quintet, $^3J_{HH}$ = 7.5 Hz, 2H, CH_2), 1.615 (quintet, $^3J_{HH}$ = 7.5 Hz, 2H, CH_2), 1.381 (quintet, $^3J_{HH}$ = 7.5 Hz, 2H, CH_2); ^{13}C{^{1}H} NMR ($CDCl_3$) δ 173.0 (s, *C*=O), 156.7 (dd, $^1J_{CF}$ = 244 Hz, $^4J_{CF}$ = 3 Hz, *C*F), 155.4 (dd, $^1J_{CF}$ = 242 Hz, $^4J_{CF}$ = 3 Hz, *C*F), 130.7 (dd, $^2J_{CF}$ = 18.5 Hz, $^3J_{CF}$ = 6.5 Hz,

C_{ipso}), 119.9 (d, $^2J_{CF}$ = 28 Hz, Ar*C*H), 117.5 (dd, $^2J_{CF}$ = 24 Hz, $^3J_{CF}$ = 6 Hz, Ar*C*H), 105.7 (dd, $^2J_{CF}$ = 23 Hz, $^3J_{CF}$ = 10 Hz, C_{ipso}), 37.4, 35.5, 33.2, 29.7, 29.0, 28.7, 24.9 (aliphatic *C*); ^{19}F NMR ($CDCl_3$) δ –115.35 (m), –123.26 (m). ESI-MS (MeOH) *m/z* = 352.00 $[M + Na]^+$, 681.01 $[2M + Na]^+$. Anal Calc'd for $C_{14}H_{18}BrF_2NO$: C, 50.31; H, 5.43; N, 4.19. Found: C, 50.33; H, 5.54; N, 4.33.

Synthesis of 5

Compound **4** (1.04 g, 3.12 mmol), bis(pinacolato)diboron (1.97 g, 7.76 mmol), Pd(dppf)Cl_2•DCM (0.130 g, 0.160 mmol), potassium acetate (2.62 g, 26.7 mmol), and dioxane (18 mL) were added to a septum-capped microwave flask. The reaction mixture was at 150 °C with microwave irradiation for 1 h. The reaction mixture was filtered, and the solids were washed with DCM. The volatiles were removed *in vacuo* from the combined filtrate. The mixture was purified by column chromatography (SiO_2, 0–50 % of 100:5:1 DCM:MeOH:Et_3N in DCM) to yield 1.01 g (85 %) of **5** as a yellow oil. ^{1}H NMR ($CDCl_3$) δ 7.322 (dd, $^3J_{HF}$ = 9.5 Hz, $^4J_{HF}$ = 4.5 Hz, 1H, Ar*H*), 6.848 (dd, $^3J_{HF}$ = 9 Hz, $^4J_{HF}$ = 6 Hz, 1H, Ar*H*), 2.993 (s, 3H, N(CH_3)$_2$), 2.940 (s, 3H, N(CH_3)$_2$), 2.642 (t, $^3J_{HH}$ = 7.5 Hz, 2H, CH_2), 2.296 (t, $^3J_{HH}$ = 7.5 Hz, 2H, CH_2), 1.663, 1.624 (overlapping quintets, $^3J_{HH}$ = 7.5 Hz, 4H, CH_2), 1.374 (quintet overlapping with next signal, $^3J_{HH}$ = 7.5 Hz, 2H, CH_2), 1.348 (s, 12H, BOC*Me*$_2$); ^{13}C{^{1}H} NMR ($CDCl_3$) δ 173.2 (*C*=O), 163.0 (dd, $^1J_{CF}$ = 245 Hz, $^4J_{CF}$ = 1.5 Hz, *C*F), 157.0 (dd, $^1J_{CF}$ = 240 Hz, $^4J_{CF}$ = 2 Hz, *C*F), 135.2 (dd, $^2J_{CF}$ = 19 Hz, $^3J_{CF}$ = 8.5 Hz, C_{ipso}), 122.1 (dd, $^2J_{CF}$ = 24 Hz, $^3J_{CF}$ = 9 Hz, Ar*C*H), 117.1 (dd, $^2J_{CF}$ = 26.5 Hz, $^3J_{CF}$ = 5 Hz, Ar*C*H), 84.12 (BO*C*$_2$Me$_4$), 37.5, 35.6, 33.4, 29.7, 29.2, 29.1, 25.04, 24.99 (N*Me*$_2$, *C*H$_2$, BO_2C_2*Me*$_4$). The C bonded to B could not be detected due to line broadening caused by the quadrupole moment of ^{11}B (I = 3/2)[2]; ^{19}F NMR ($CDCl_3$) δ –110.54 (m), –127.28 (m). ESI-MS (MeOH) *m/z* = 404.20 $[M + Na]^+$, 785.43 $[2M + Na]^+$.

Synthesis of 6

Compound **5** (2.29 g, 6.00 mmol), hexakis(4-bromophenyl)benzene (0.667 g, 0.662 mmol), $Pd(PPh_3)_4$ (0.232 g, 0.201 mmol), and TBABr (0.153 g, 0.474 mmol) were added to 250 mL Schlenk flask. The flask was evacuated and refilled three times with N_2. Deoxygenated toluene (28 mL), THF (28 mL), and 1.0 M Na_2CO_3(aq) (24 mL) were added by syringe. The mixture was sparged with N_2 for 30 min, and then heated to 75 °C for 48 h. The organic and aqueous layers were separated and the organic washed with 3 x 50 mL water, dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The mixture was purified by column chromatography (Biotage SNAP 100g KP-Sil, pure DCM to 95:5:1 DCM:MeOH:Et_3N over 12 column volumes. Fractions containing pure product and impure product were collected separately. To remove residual Pd, the mixtures were stirred with propylmercapto modified silica until the supernatant was colorless, then filtered, and extracted with 95:5 DCM:MeOH until the filtrate did not absorb UV light when spotted on a SiO_2 TLC plate. The impure product was subjected to column chromatography again with the same conditions (Biotage SNAP 50 g KP-Sil). The products from both columns were combined to yield 0.710 g (52% yield) as a white foam. ^{1}H NMR ($CDCl_3$) δ 7.094 (d, 2H, J_{HH} = 8 Hz, Ar*H*), 6.944 (d, 3H integrated with next signal, J_{HH} = 8 Hz, Ar*H*), 6.926 (dd, integrated with previous signal, J_{HF} = 10 Hz, J_{HH} = 7 Hz, Ar*H*), 6.851 (dd, 1H, J_{HF} = 11 Hz, J_{HH} = 7 Hz, Ar*H*), 2.982 (s, 3H, CO(CH_3)$_2$), 2.930 (s, 3H, CO(CH_3)$_2$), 2.584 (t, 2H, J_{HH} = 8 Hz, CH_2), 2.291 (t, 2H, J_{HH} = 8 Hz, CH_2), 1.654 (apparent quintet, 2H, J_{HH} = 8 Hz, CH_2), 1.603 (apparent quintet, 2H, J_{HH} = 8 Hz, CH_2), 1.373 (apparent quintet, 2H, J_{HH} = 8 Hz, CH_2); ^{13}C{^{1}H} NMR ($CDCl_3$) δ 173.2 (*C*=O), 157.1 (dd, $^1J_{CF}$ = 240 Hz, $^4J_{CF}$ = 2 Hz, *C*F), 155.6 (dd, $^1J_{CF}$ = 240

Hz, $^4J_{CF}$ = 2 Hz, *C*F), 140.4, 140.2, 3 (d, J_{CF} = 31 Hz), 132.1, 131.8, 129.8 (dd, J_{CF} = 19 Hz, J_{CF} = 8 Hz), 127.43, 127.40 (m), 117.5 (dd, J_{CF} = 25 Hz, J_{CF} = 6 Hz), 116.4 (dd, J_{CF} = 26 Hz, J_{CF} = 4 Hz), 37.5, 35.5, 33.4, 29.9, 29.2, 28.7, 25.0; MS (MALDI-TOF, DCTB) *m/z* = 2053.90 $[M]^+$, 2075.85 $[M+Na]^+$; Anal Calc'd for $C_{126}H_{132}F_{12}N_6O_6$: C, 73.66; H, 6.48; N, 4.09. Found: C, 73.50; H, 6.67; N, 3.97.

Synthesis of 7

Compound **6** (0.499 g, 0.243 mmol) and DDQ (0.345 g, 1.52 mmol) were added to a 25 mL Schlenk flask, which was then evacuated and refilled three times with N_2. DCM (10 mL, dry, deoxygenated) was added, and the flask was cooled to 0 °C. TfOH (0.25 mL, 2.8 mmol) was added dropwise and a brown precipitate formed on the sides of the flask. MALDI-TOF MS of an aliquot taken after 30 min showed residual unreacted **6**. Additional portions of DDQ (0.172 g, 0.755 mmol) and TfOH (0.20 mL, 2.3 mmol) were added. MALDI-TOF MS of an aliquot taken after 30 m min of the second addition showed complete conversion of **6**. To quench the reaction, saturated $NaHCO_3$(aq) (15 mL) was added slowly. The reaction mixture was then filtered, and the solids washed successively with H_2O, MeOH, and $CHCl_3$. The organic and aqueous phases were separated. The aqueous was extracted with 3 x 15 mL of $CHCl_3$. The combined organic phase was washed with 4 x 15 mL H_2O, dried with $MgSO_4$, filtered, and dried under reduced pressure. The compound was purified by Bio-bead (S-X1, $CHCl_3$) size exclusion chromatography. Fractions were analyzed by TLC (SiO_2, 95:5:1 DCM:MeOH:Et_3N) and only those containing pure **7** were combined to yield 126 mg (25 %) as a yellow powder. The ^{1}H NMR spectrum is broad and ^{13}C NMR spectrum was unobtainable due to aggregation of **7**. All peaks in the ^{1}H NMR spectrum are broad singlets and integration is unreliable. ^{1}H NMR (3.8 x 10^{-4} M, $CDCl_3$): δ 9.019, 8.598, 7.056, 3.195, 3.098, 3.026, 2.782, 2.586, 2.456, 1.831. UV/vis (1.85 x 10^{-5} M, $CHCl_3$): λ_{max}/nm (ε/L mol^{-1} cm^{-1}): 370 (169000), 416 (shoulder, 25900); MS (MALDI-TOF, DCTB) *m/z* = 2040.55 $[M]^+$, 2063.59 $[M+Na]^+$; Anal Calc'd for $C_{126}H_{122}F_{12}N_6O_7$ (HBC•H_2O): C, 73.45; H, 5.97; N, 4.08. Found: C, 73.12; H, 5.70; N, 4.15.

DFT calculations.

Density functional theory (DFT) calculations were performed using the Q-Chem software package[3] with the B3LYP functional[4] and the cc-pVDZ basis set[5]. A polarizable continuum solvent model (dielectric constant 9) was applied.

UV-Visible Spectroscopy of HBC 7 in the Solid State

A solution of HBC **7** (1 mM) in benzonitrile was dropcast onto a glass slide and dried under vacuum.

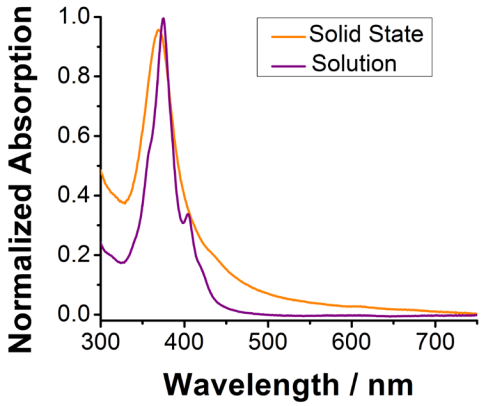


Figure S1. UV-Vis spectra (normalized absorption) of HBC **7** in solution (1.1 μM in benzonitrile, 0.1 M $TBAPF_6$) and in the solid state.

Titration of HBC 7 with Magic Blue

A solution of HBC **7** (3 mL, 1.5 x 10^{-4} M) in electrolyte (benzonitrile, 0.10 M $TBAPF_6$) was prepared inside a dry box and added to a 1 cm screw-capped cuvette. A Magic Blue solution (15 mM in benzonitrile, 0.10 M $TBAPF_6$) was added in portions (6 μL each, 0.2 eq each) and UV-Vis-NIR spectra were obtained after each addition (450–1500 nm). After 1.0 equivalents, excess Magic Blue is observed, indicated by the emergence of a peak at λ_{max} = 720 nm from the baseline. This indicates a quantitative one-electron oxidation to the HBC radical cation **8**.

Zn powder (< 5 mg) was added to the cuvette and the solution was shaken for 30 min. A spectrum was obtained from 450–1500 nm that shows no signal at higher wavelengths indicating complete, reversible reduction of **8** (Figure S1). The mixture was then diluted 15-fold to 1.0 x 10^{-5} M and a spectrum was obtained from 300–800 nm, which closely overlays with a spectrum of unreacted HBC **7** at the same concentration. The small difference in absorption is likely due to the presence of $Zn(SbPF_6)_2$ and tris(4-bromophenyl)amine. Addition of Zn(II) ions may enhance aggregation of HBC **7** by linking stacks of **7** through coordination of Zn(II) at the peripheral dimethylamido substituents. An increase in aggregation strength would manifest in the UV-Vis spectrum as a reduction in optical density around 350–450 nm as is observed in Figure S1.

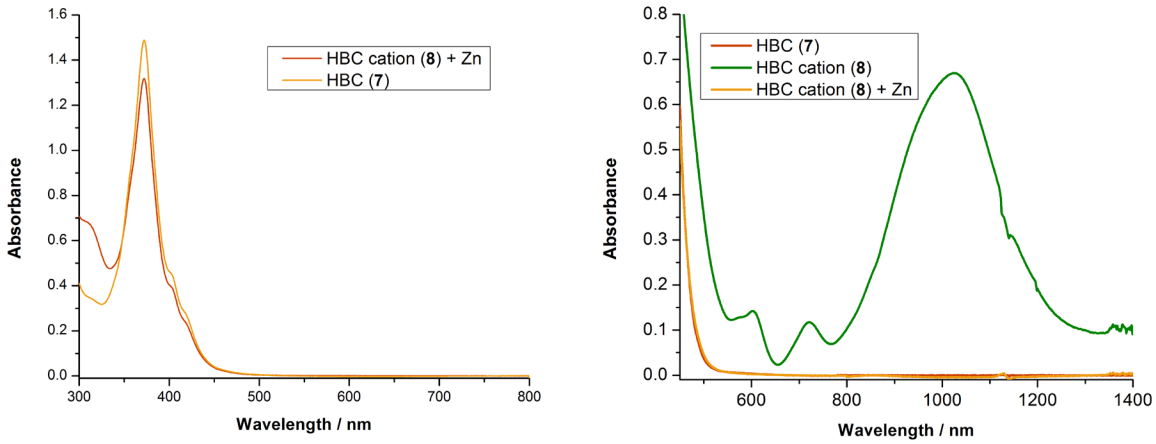


Figure S2. Reversible reduction of HBC radical cation **8**. Left: 10 µM. Right: 150 µM.

Variable Temperature UV-Vis Spectroscopy

All measurements were made in dual beam mode with an electrolyte reference (0.10 M $TBAPF_6$ in benzonitrile) held at the same temperature as the analyte. The temperature of both analyte and reference cuvettes was monitored internally and allowed to stabilize for five minutes prior to data collection. The concentration of **7** in electrolyte was 10 µM for the study of HBC assembly in a neutral state. A partially oxidized solution of HBC was prepared with a concentration of **7** in electrolyte of 10 µM followed by addition of 0.25 equivalents of Magic Blue from a concentrated stock solution (1.5 mM).

X-Ray Spectroscopy

Samples of **7** were dropcast from EtOH (180 µM) onto Si wafers. XAS and XES spectra were collected at the Advanced Light Source Beamline 8.0.1. XAS spectra were recorded in total-electron-yield (TEY) mode by monitoring the sample drain current. The energy scale was calibrated to the π* peak at 285.5 eV in the XAS spectrum of highly oriented pyrolitic graphite (HOPG). XES spectra were collected using a Nordgren-type spectrometer.

EPR Spectroscopy

Solutions of HBC **7** (2.0 mM) and Magic Blue (20 mM) were prepared in 0.10 M $TBAPF_6$ in benzonitrile. 200 µL of HBC **7** solution and 10 µL of MB solution were mixed to give 50 % oxidation of HBC **7** to $HBC^{\bullet+}$ **8** (1 mM concentration of $HBC^{\bullet+}$ **8**). The solution was added to a capillary with a 1 mm inner diameter and an X-band EPR spectrum was obtained.

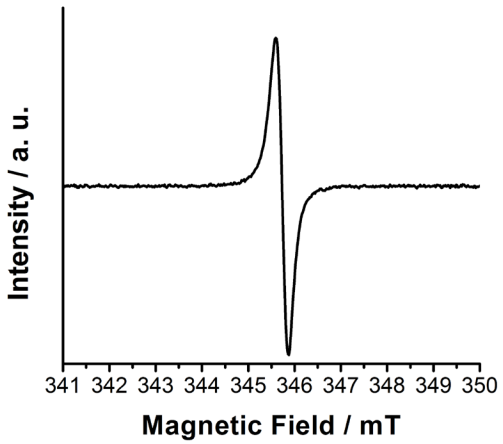


Figure S3. EPR spectrum of $HBC^{\bullet+}$ **8** (1 mM in benzonitrile with 0.1 $TBAPF_6$) at ambient temperature formed from oxidation of HBC **7** with Magic Blue. g = 2.0054.

IV Measurements

Stock solutions of HBC (1.5 mM) and Magic Blue (375 µM, 750 µM, 1.875 mM, 3.75 mM, 7.5 mM) were prepared in 0.10 M $TBAPF_6$ in benzonitrile. 50 µL of HBC stock and 10 µL of MB stock were mixed and 4 µL of the final solution was added onto an interdigitated array (IDA). The IDA features 65 pairs of Au electrodes with width, length, and spacing of 10 µm, 2 mm, and 5 µm, respectively (CH Instruments, Austin, TX, USA). The measurements were made with one set of electrodes connected to the working electrode lead and the other set connected to the reference and auxiliary leads of the potentiostat. The voltage was swept from V_{oc} ± 0.2 V at 20 mV/s. The full set of IV curves is depicted in Figure S2.

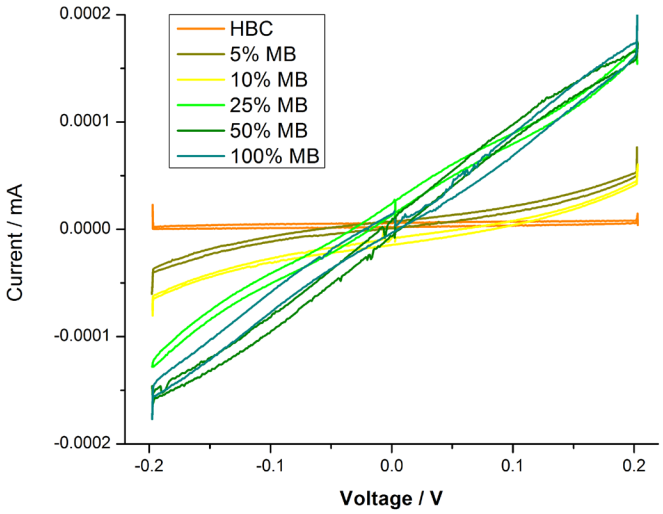


Figure S4. IV curves of HBC with increasing amounts of Magic Blue.

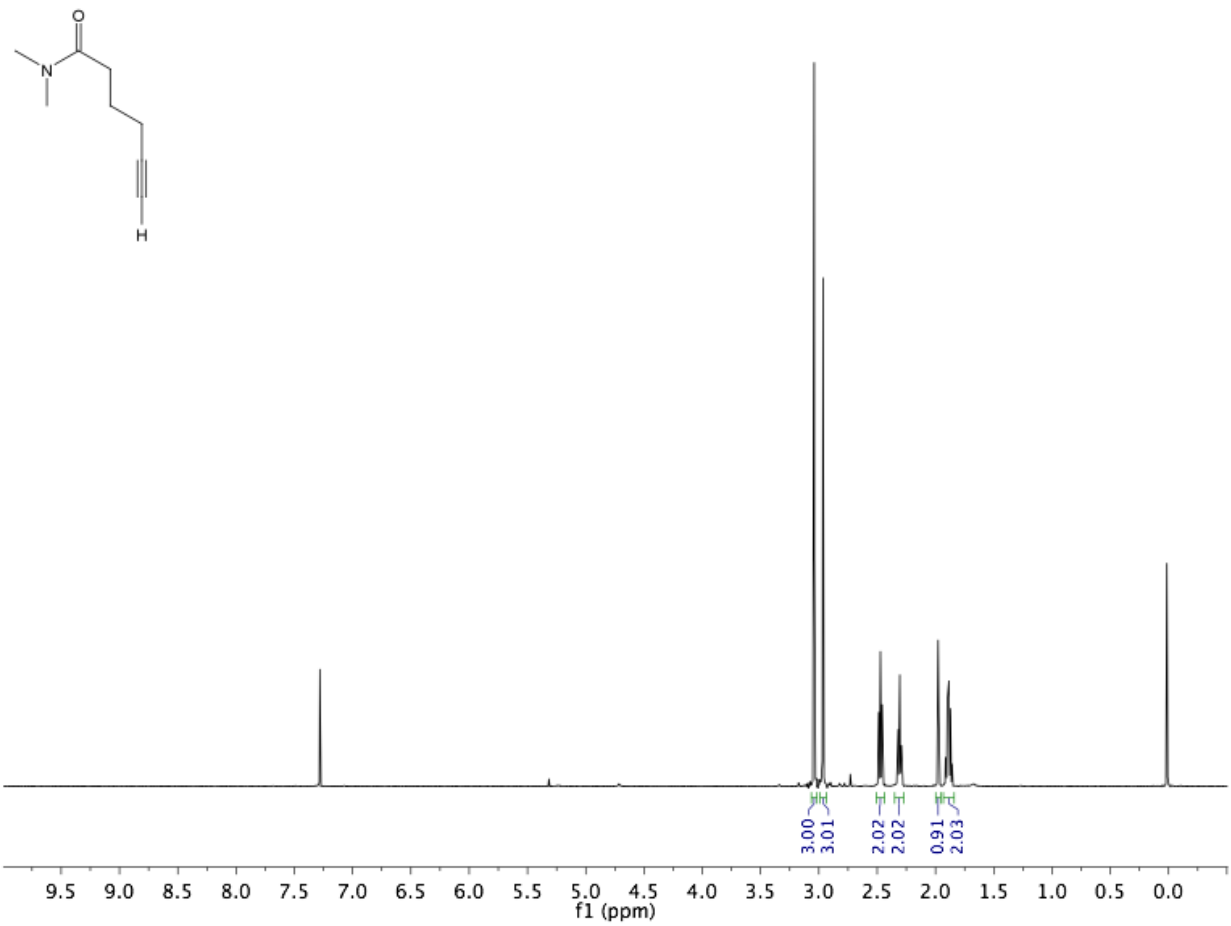


Figure S5. ^{1}H NMR spectrum of **2**.

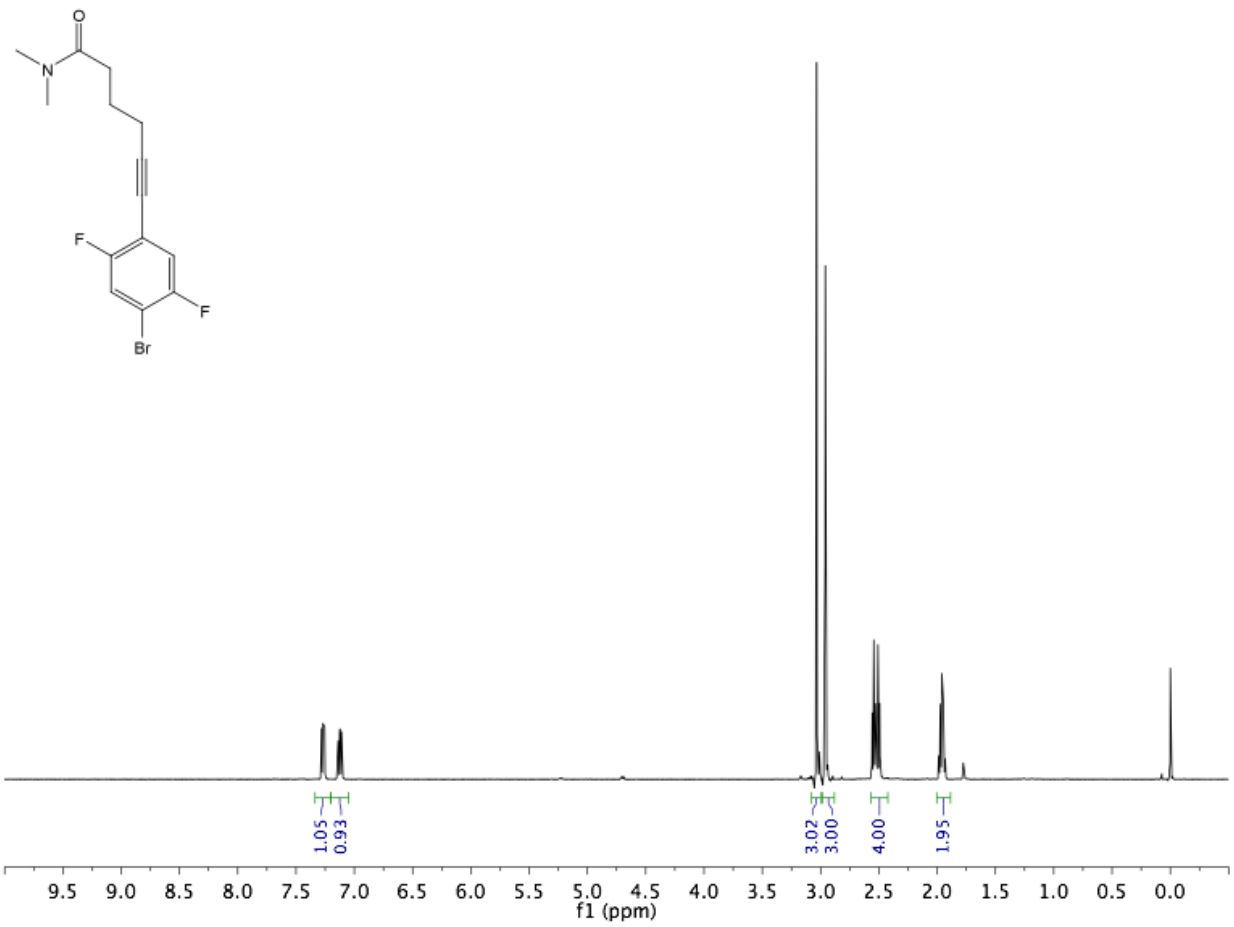


Figure S6. ^{1}H NMR spectrum of **3**.

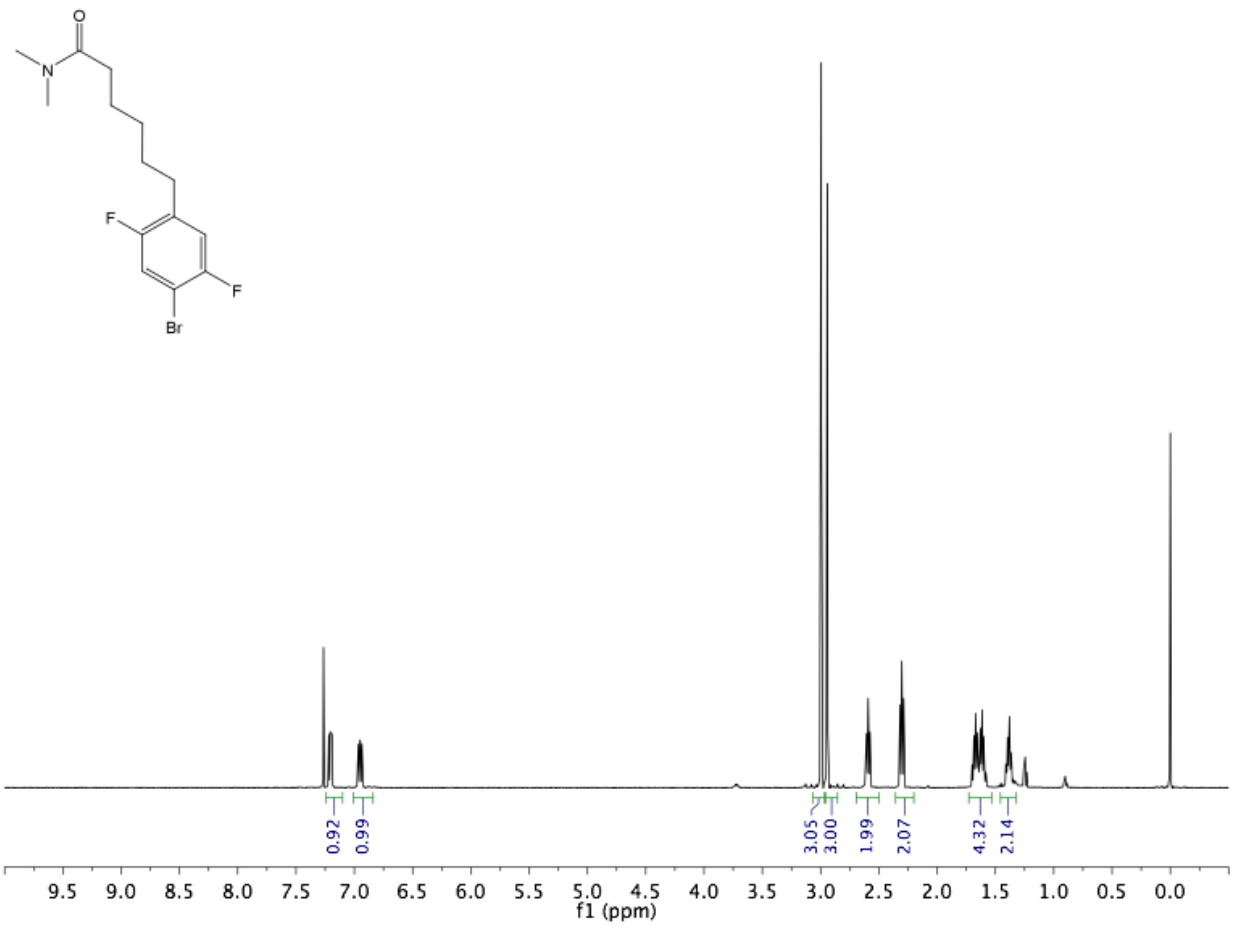


Figure S7. ^{1}H NMR spectrum of **4**.

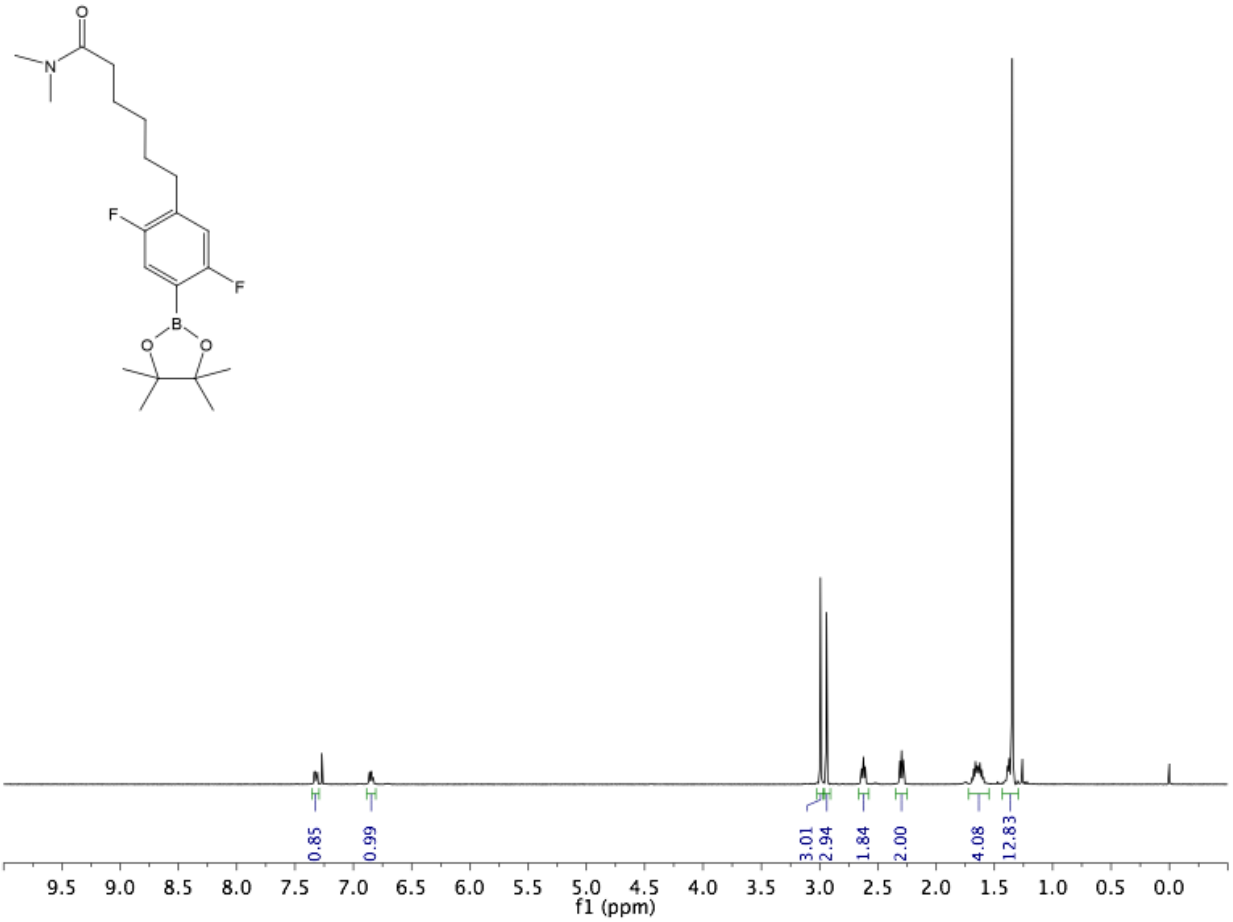


Figure S8. ^{1}H NMR spectrum of **5**.

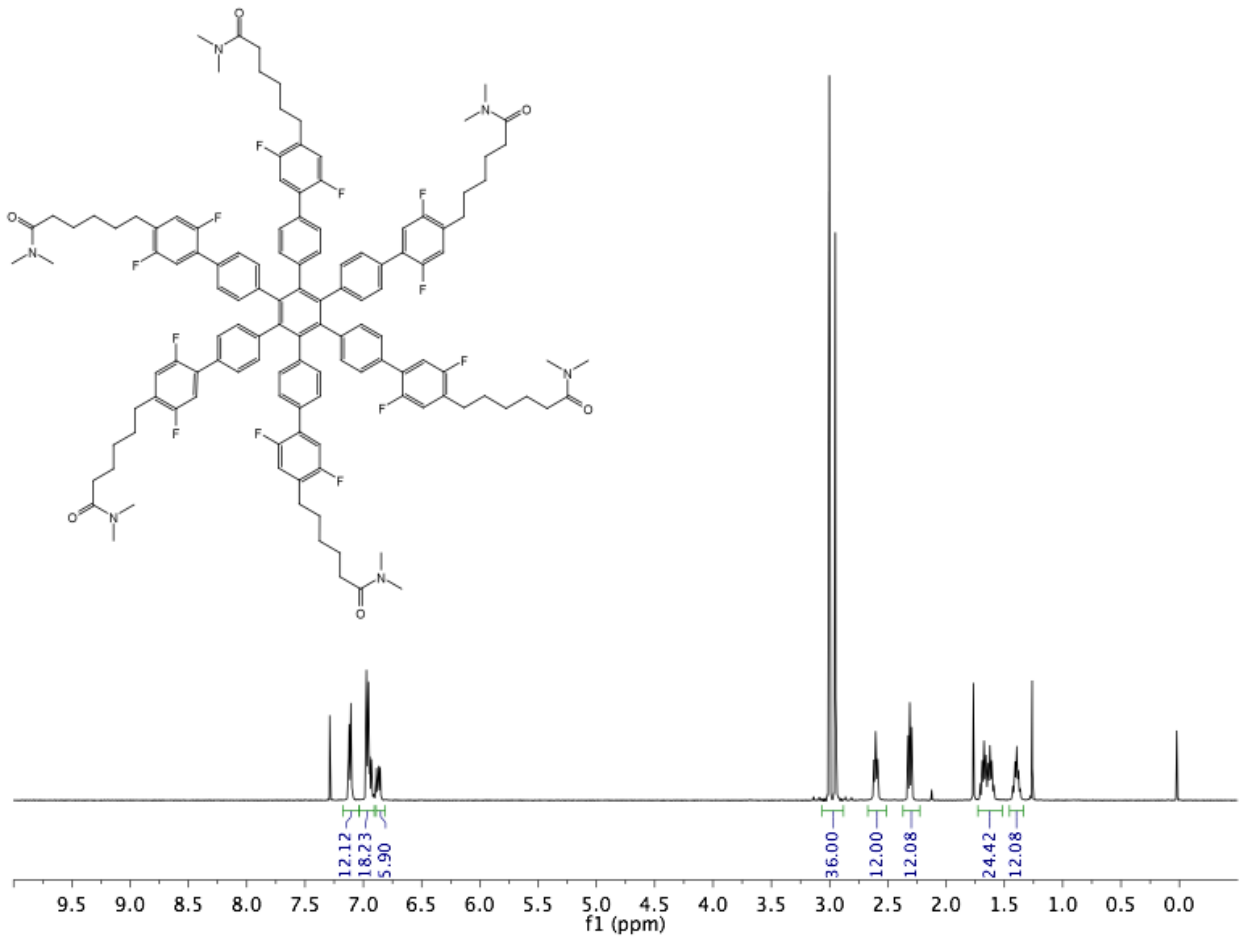


Figure S9. ^{1}H NMR spectrum of **6**.

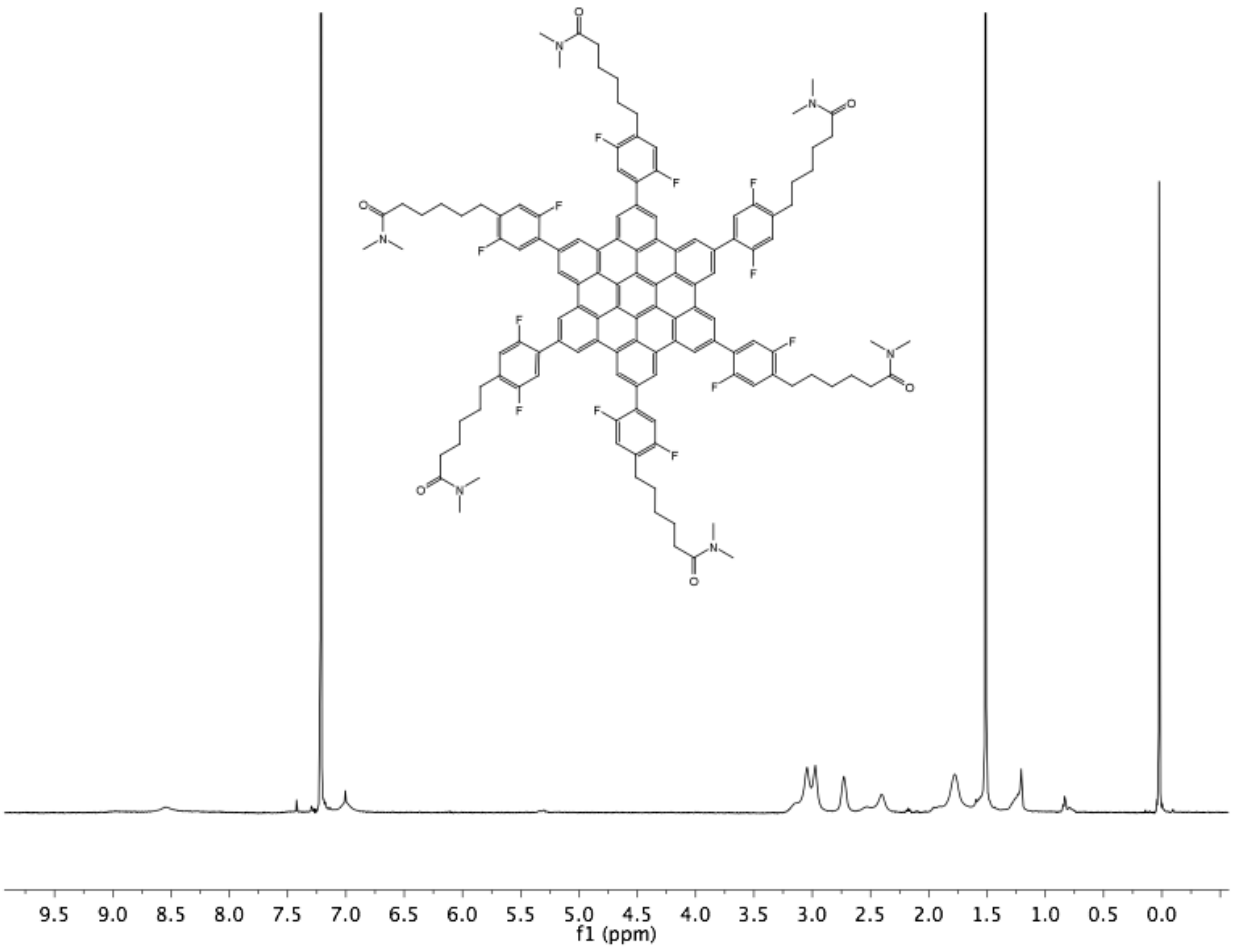


Figure S10. ^{1}H NMR spectrum of **7**.

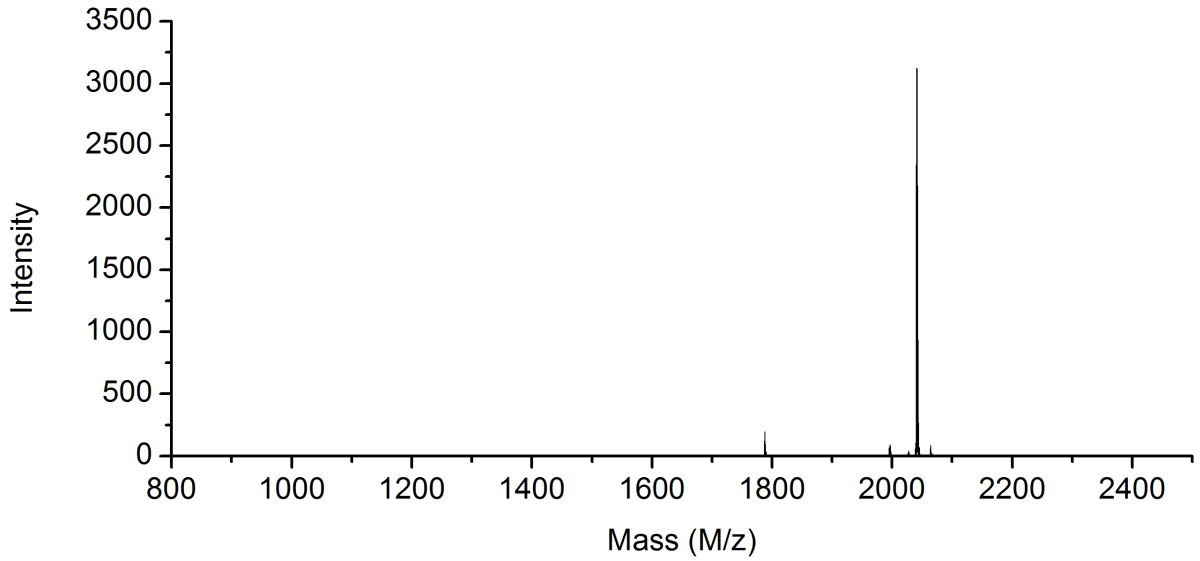


Figure S11. MALDI-TOF mass spectrum of HBC **7**.

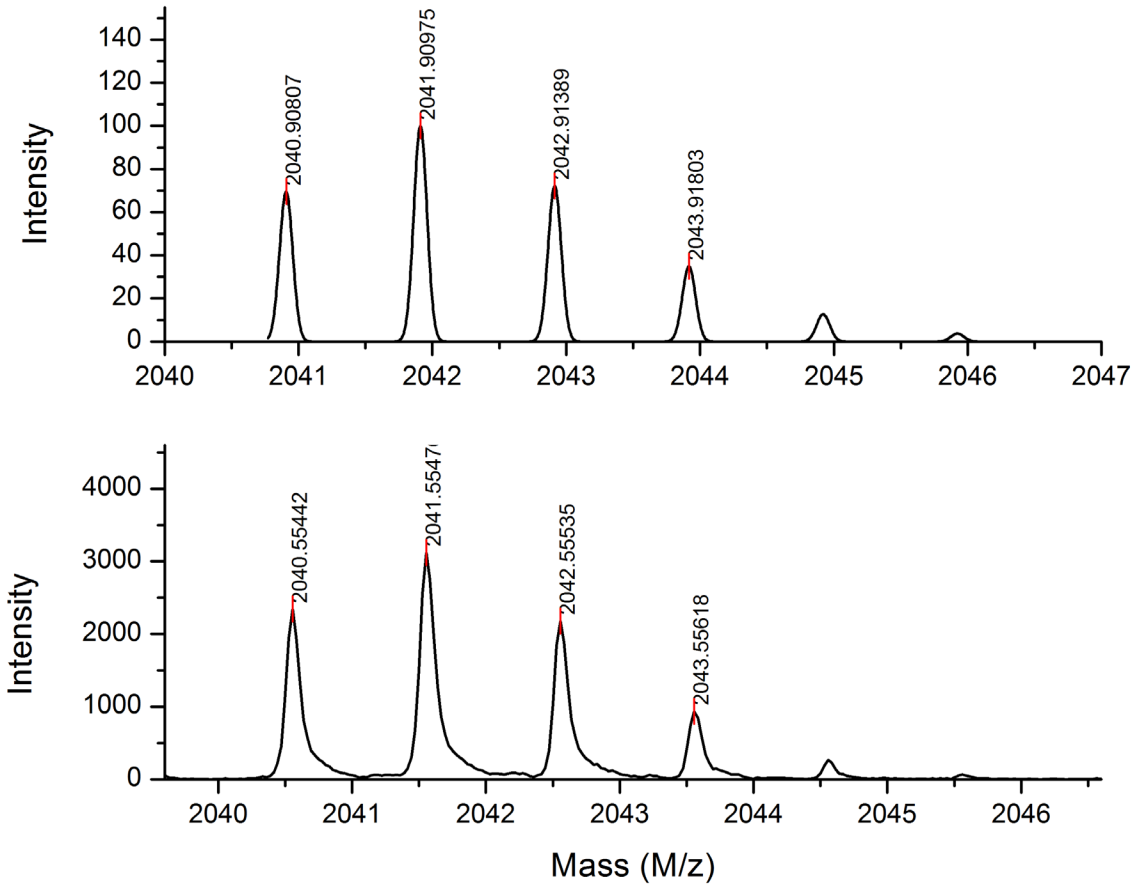


Figure S12. Isotope distribution of the calculated (top) and experimental (bottom) base peak from the MALDI-TOF mass spectrum of HBC **7**. The spectrum is not high resolution, resulting in the offset of 0.35 mass units, but the isotope distribution of the product is as expected.

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