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FHBC, a Hexa-*peri*-hexabenzocoronene–Fluorene Hybrid: A Platform for Highly Soluble, Easily Functionalizable HBCs with an Expanded Graphitic Core

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Abstract

Materials based upon hexa-*peri*-hexabenzocoronenes (HBCs) show significant promise in a variety of photovoltaic applications. There remains the need, however, for a soluble, versatile, HBC-based platform, which can be tailored by incorporation of electroactive groups or groups that can prompt self-assembly. The synthesis of a HBC–fluorene hybrid is presented that contains an expanded graphitic core that is highly soluble, resists aggregation, and can be readily functionalized at its vertices. This new HBC platform can be tailored to incorporate six electroactive groups at its vertices, as exemplified by a facile synthesis of a representative hexaaryl derivative of FHBC. Synthesis of new FHBC derivatives, containing electroactive functional groups that can allow controlled self-assembly, may serve as potential long-range charge-transfer materials for photovoltaic applications.

Keywords

electron transfer, fluorene, graphitic nanocarbons, hexa-peri-hexabenzocoronene

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Introduction

Hexa-*peri*-hexabenzocoronenes (HBCs) are promising materials for application in thin-film electronic devices, field-effect transistors, and photovoltaic applications.[1, 2] Indeed, the design and synthesis of improved HBCs continues to garner tremendous attention,[3] as expanding the size of the flat π-conjugated graphitic core is expected to result in high charge-carrier mobility.[4, 5] While the parent HBC (Figure 1) can be readily accessed by oxidative cyclodehydrogenation of hexaphenylbenzene, it is insoluble in common organic solvents.[5, 6] HBCs incorporating alkyl groups at the vertices (^{R}HBC, Figure 1) display improved solubility, yet often form aggregates in solution, as evidenced by broadened signals in their ^{1}H/^{13}C NMR spectra at ambient temperatures.[7, 8] Unfortunately, the incorporation of solubilizing groups at the vertices of HBCs restrict their further functionalization with desired electroactive groups.

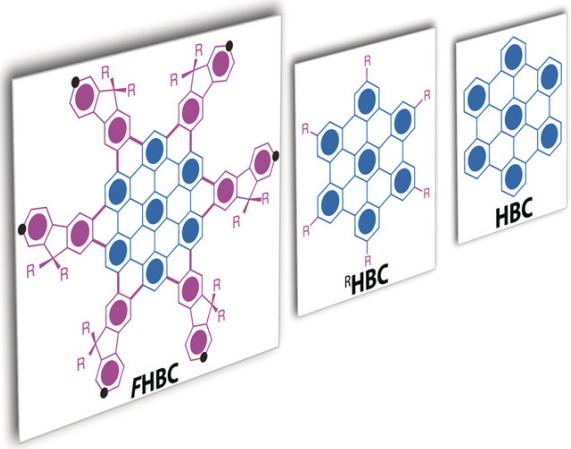
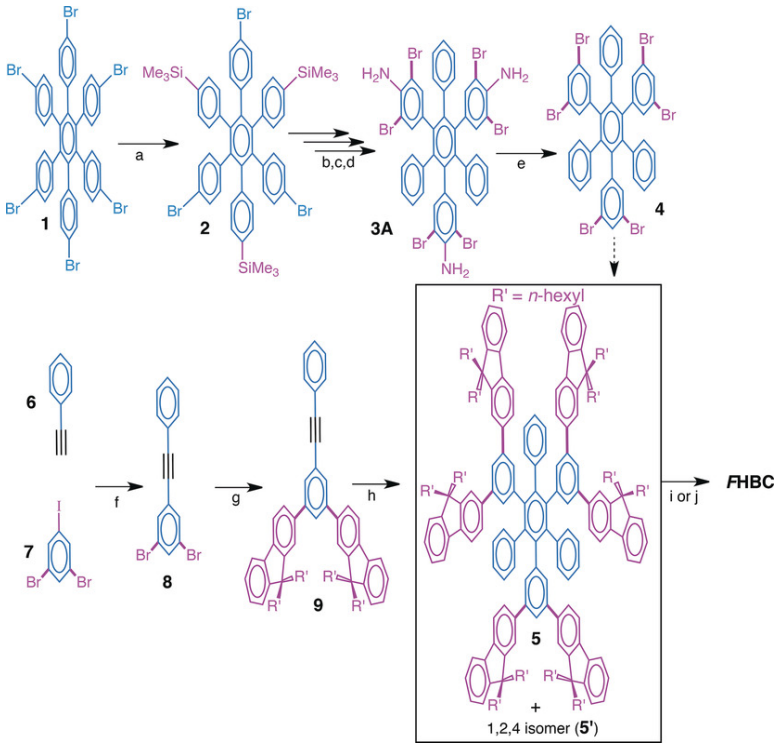


Figure 1. A comparison of the relative sizes of the parent HBC, HBC functionalized at its vertices with solubilizing groups (for example, R=n-alkyl or tert-butyl), and the newly designed HBC–fluorene hybrid (FHBC, R=n-alkyl) with provisions for both solubility and sites for on-demand functionalization (indicated by black dots).

To address this issue, we will show that incorporating six fluorene rings, substituted with solubilizing groups at their C9 methylenes, into the bay areas of parent HBC core produces a hybrid structure that eliminates the

issues plaguing parent HBC (see Figure 2). Specifically, the hybrid structure provides 1) an expanded graphitic core, 2) increased solubility, and 3) contains unsubstituted vertices for subsequent functionalization (see below). Accordingly, we describe the successful synthesis of a highly-soluble HBC–fluorene hybrid, hereafter referred to as FHBC, and show that it can be readily functionalized at all six vertices (Figure 2). We will also show that expansion of the graphitic core of HBC affords multiple (reversible) 1 e^- oxidation, producing a stable, non-aggregated radical cation salt in solution. The successful synthesis of this new, readily functionalizable graphitic platform detailed here, offers potential for the design and syntheses of next-generation materials for applications in modern photovoltaic devices.

The strategy for the preparation of FHBC involves an oxidative cyclodehydrogenation of a hexaphenylbenzene derivative **5,** in which alternate phenyl groups (that is, 1,3,5-phenyls) are functionalized with two fluorenyl rings (Scheme 1). Initially, we attempted to access **5** via the selective conversion of readily available hexakis(4-bromophenyl)benzene9 (**1**) to a symmetrical 1,3,5-TMS derivative **2** by lithiation with ^{t}BuLi at −90 °C followed by reaction with TMSCl.10, 11 Although **2** was easily prepared in high yield, a series of functional group transformations onto **2** (Scheme 1) returned the desired hexabromo derivative **4** in meager yield, which was largely due to the poor solubility of **4** and its precursors. The solubility issues forced us to abandon this route for accessing FHBC (see Scheme 1 and the Supporting Information for additional details).



Scheme 1. Two different synthetic approaches for the preparation of FHBC. a) i) *t*BuLi (6 equiv)/−90 °C; ii) Me_3SiCl/−90 °C, 76 % yield. b) 70 % HNO_3/Ac_2O/80 °C, 40 % yield. c) (i) Sn/HCl/DME/90 °C, 74 % yield; (ii) $Pd(OAc)_2/PPh_3$/aq K_2CO_3/*n*-butanol/100 °C, 68 % yield. d) aq. HBr (48 %)/H_2O_2 (30 %)/THF/ H_20, ca. 76 % yield. e) i) $NaNO_2/H_2SO_4$; ii) H_3PO_2, produced a highly insoluble mixture of products which could not be fully characterized. f) $PdCl_2(PPh_3)_2$/CuI/diisopropylamine/40 °C/4 h, 97 % yield. g) 9,9-dihexylfluorene-2-boronic acid pinacol ester/$Pd(PPh_3)_4$/aq. K_2CO_3/ ethanol/toluene/ reflux/24 h, 89 % yield. h) $Co_2(CO)_8$/*p*-dioxane/ reflux/14 h, ca. 96 % yield. i) DDQ (22 equiv)/CH_2Cl_2–CH_3SO_3H (9:1) mixture/0 °C/6 h, 28 % yield (after chromatographic purification). j) $FeCl_3$ (100 equiv)/ CH_2Cl_2/CH_3NO_2/22 °C, 18 % yield.

In an alternative strategy, **5** could be prepared as an isomeric mixture in three simple steps (Scheme 2), via a practical if non-elegant route. First, a Sonogashira coupling of phenylacetylene (**6**) with readily available 1,3-

dibromo-5-iodobenzene12 (**7**) returned alkyne **8** in excellent yield. A two-fold Pd-catalyzed Suzuki coupling of **8** with 9,9-dihexylfluorene-2-boronic acid afforded alkyne derivative **9** in 86 % yield in two steps. Finally, a $Co_2(CO)_8$-catalyzed cyclotrimerization of **9** afforded **5** (1,3,5-isomer) and **5'** (1,2,4-isomer) as a statistical mixture13 in nearly quantitative yield (Scheme 2). Repeated attempts to separate highly soluble isomeric mixture of **5**/**5'**, using flash chromatography and fractional crystallizations, were unsuccessful.

We subjected the isomeric mixture of **5**/**5'** to oxidative cyclodehydrogenation, using $FeCl_3$ as an oxidant, which afforded a deep-red solid. A chromatographic purification of the red-solid using hexanes as eluents easily separated FHBC as an orange-red microcrystalline solid in 18 % yield.14 A much higher yield and purer FHBC (28 %) was obtained by oxidative cyclodehydrogenation of **5**/**5'**, using our recently developed procedure with [DDQ/acid] as an oxidant system in CH_2Cl_2.15, 16 Note that oxidative cyclodehydrogenation of only **5** (1,3,5 isomer) can produce FHBC, and as the isomeric mixture of **5**/**5'** contains only about 33 % of **5**, use of [DDQ/acid]15, 16 as oxidant produces a nearly quantitative yield of FHBC.

The HBC–fluorene hybrid (FHBC) was found to be highly soluble in common organic solvents, such as hexanes, CH_2Cl_2, $CHCl_3$, THF, DMF, and its structure was established by $^1H/^{13}C$ NMR spectroscopy and MALDI-TOF mass spectrometry (see the Supporting Information). A ^1H NMR spectrum of FHBC in $CDCl_3$ showed well-resolved resonances for all unique protons, indicating minimal or no aggregation at ambient temperatures (Figure 2). This is distinct from the solution-phase NMR spectra of other HBCs, which generally show broad signals owing to extensive aggregation.7, 8

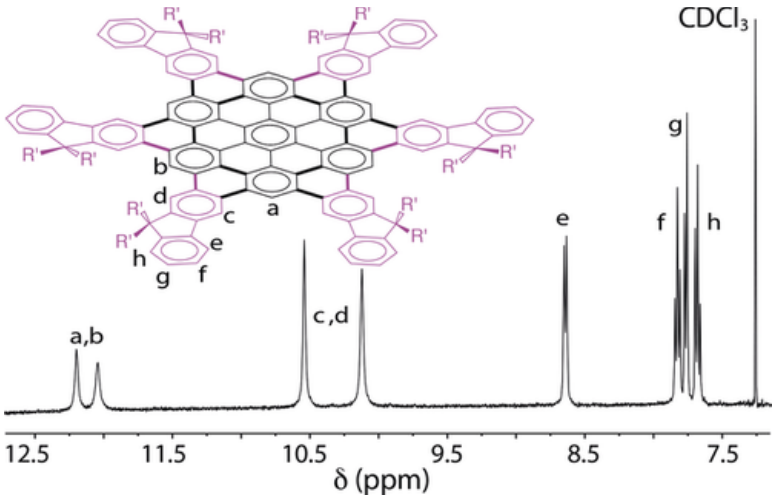


Figure 2. Partial ^1H NMR spectrum of 10 mM FHBC in $CDCl_3$ at 22 °C showing well-resolved resonances for equivalent aromatic protons (labeled).

The UV/Vis absorption spectrum of FHBC is compared with well-known $^{t\text{Bu}}$HBC6, 17 in CH_2Cl_2in Figure 3 A. Each shows characteristic well-resolved vibronic structure; however, the significant expansion of the graphitic core in FHBC, leads to a large red-shift (by about 90 nm) of its absorption bands (325, 451, and 486 nm; ϵ_{451}=6.0×10^5 L mol^{-1} cm^{-1}) and increased molar absorptivity compared to $^{t\text{Bu}}$HBC (230, 360, and 390 nm; ϵ_{360}=1.9×10^5 L mol^{-1} cm^{-1}). Normalized emission spectra of FHBC and $^{t\text{Bu}}$HBC, at the same concentrations, Figure 3 B, show a red-shift of the emission bands of FHBC (582, 612 nm) compared to $^{t\text{Bu}}$HBC (486, 520 nm). At higher concentrations, $^{t\text{Bu}}$HBC shows a broad excimeric emission (at about 560 nm) indicating aggregate (that is, dimer, and higher oligomers) formation.17 In contrast, the emission spectrum of FHBC does not show the appearance of a new excimeric band (Supporting Information, Figure S9).

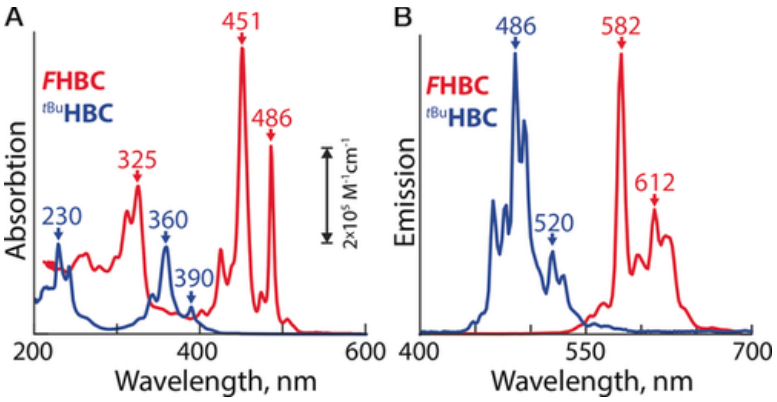


Figure 3. Comparison of the A) UV/Vis absorption (10^{-6} M) and B) emission spectra of FHBC (red) and ^{tBu}HBC (blue) in CH_2Cl_2 at 22 °C.

Electrochemical analysis showed that FHBC displays four reversible oxidation waves at 0.40, 0.76, 1.01, and 1.19 V (vs. Fc/Fc^+) corresponding to the formation of monocation, dication, trication, and tetracation, respectively (Figure 4 A). In contrast, ^{tBu}HBC exhibits a single oxidation wave at 0.64 V vs. Fc/Fc^+ in CH_2Cl_2 (Supporting Information, Figure S4).6, 17Moreover, the expansion of the size of the graphitic core in FHBC results in a significant lowering of the first oxidation potential (by about 240 mV) in comparison to ^{tBu}HBC.

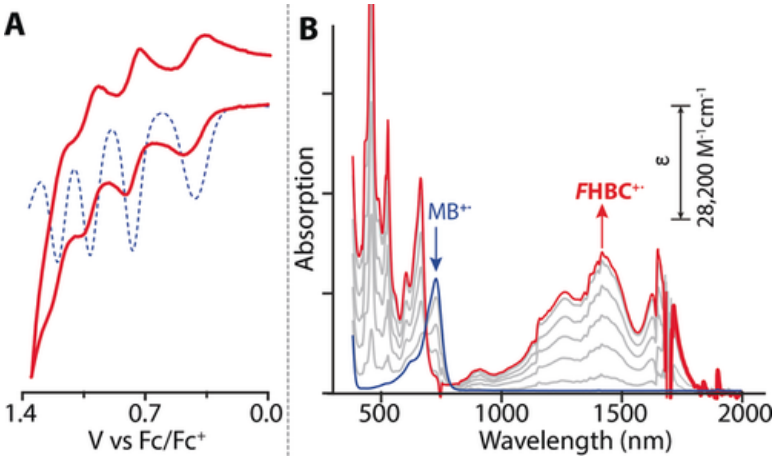


Figure 4. A) Cyclic (solid red line) and square-wave (dashed blue line) voltammograms of FHBC (0.63 mM) in CH_2Cl_2 containing 0.2 M n-Bu_4NPF_6 at a scan rate of 200 mV $s^{-1}$and 22 °C. B) The spectral changes observed upon the reduction of 5.5×10^{-6} M$MB^{+\cdot}SbCl_6^-$ by an incremental addition of sub-stoichiometric amounts of FHBC in CH_2Cl_2 at 22 °C.

The radical cation of FHBC was generated in solution via quantitative redox titrations using magic blue ($MB^{+\cdot}$; tris-4-bromophenylamminium radical cation, E_{red}=0.70 V vs. Fc/Fc^+, λ_{max}=728 nm, ϵ_{max}=28,200 L mol^{-1} cm^{-1}) as an oxidant (Figure 5 B).18, 19 The spectrum of $FHBC^{+\cdot}$ remained unchanged at ten-fold higher concentration, as well as in the presence of excess (up to 10 equiv) neutral FHBC, suggesting a lack of aggregation either between the molecules of $FHBC^{+\cdot}$ or $FHBC^{+\cdot}$/FHBC in solution. In contrast, $^{tBu}HBC^{+\cdot}$ readily forms a dimeric radical cation in solution, that is, $^{tBu}HBC^{+\cdot}+{}^{tBu}HBC\rightarrow[^{tBu}HBC]_2^{+\cdot}$ with an equilibrium constant K=1100 L mol^{-1} (Supporting Information, Figure S8). Expansion of the chromophoric size of $FHBC^{+\cdot}$ (λ_{max}=460, 528, 664, 1261, and 1418 nm, ϵ_{1418}=36 000 L mol cm^{-1}) leads to an increased molar absorptivity (by a factor of about 6) when compared to $^{tBu}HBC^{+\cdot}$ (λ_{max}=550, 836, 1570, 1740, 2100 nm, ϵ_{2100}=5700 L mol^{-1} cm^{-1}; Supporting Information, Figure S7).6, 17

Summarizing, while ^{tBu}HBC forms aggregates in neutral, excited, and radical cation states, as judged by, respectively, broad NMR spectra, observation of excimeric emission (at about 560 nm),6, 17 and observation of intervalence transition (at 1200 nm)6, 17 in its radical cation spectrum in the presence of neutral ^{tBu}HBC

(Supporting Information, Figures S8,S9), such spectroscopic signatures of aggregation were completely absent in the case of FHBC. A cursory examination of the molecular structures of FHBC and ^{tBu}HBC suggests that the narrow bay areas in FHBC do not afford arrangement of two hexyl chains in a staggered (sandwich-like) dimer. On the other hand, the relatively wider bay areas in ^{tBu}HBC provide sufficient space for smaller methyl groups to be accommodated in a sandwich-like (staggered) dimeric structure (Figure 5 A).

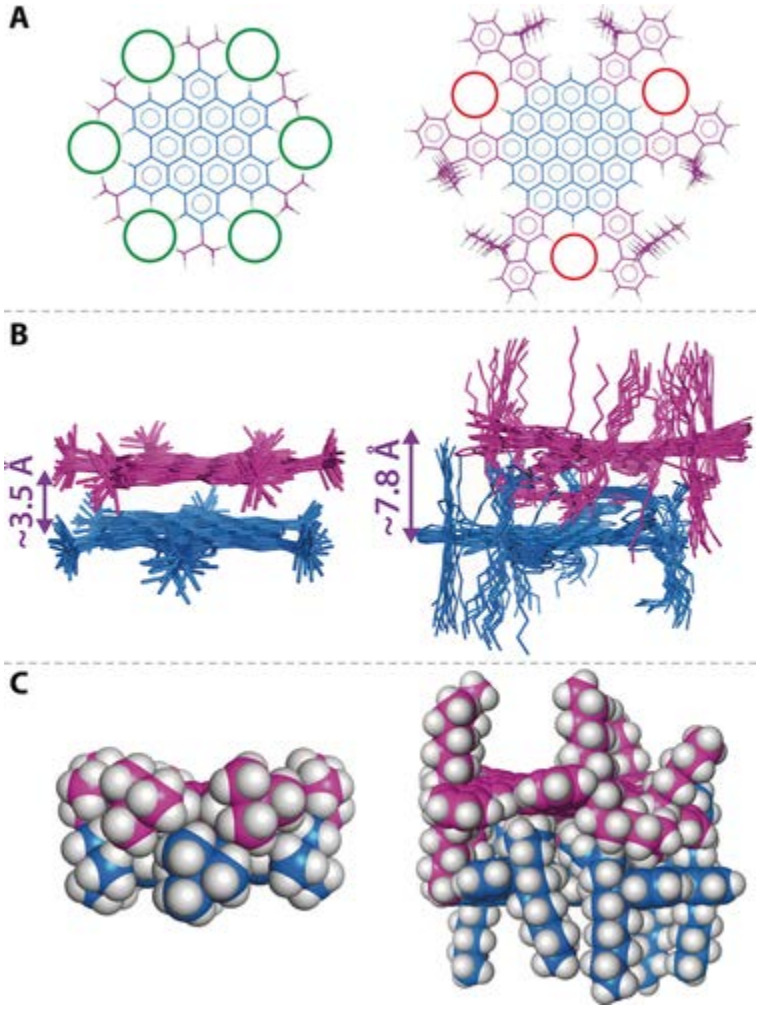
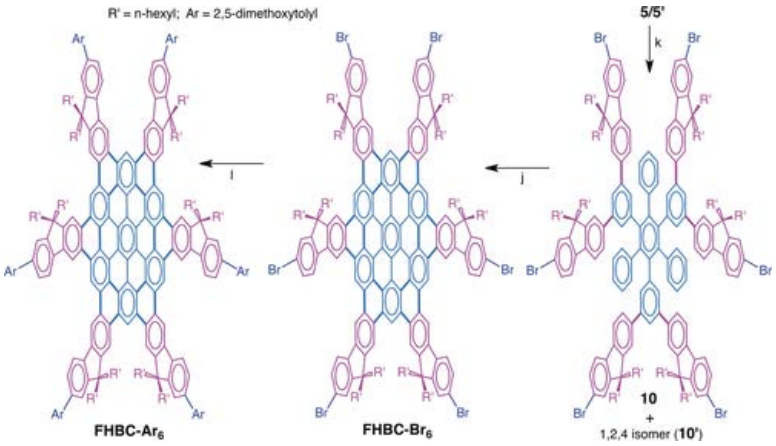


Figure 5. A) Structures of ^{tBu}HBC and FHBC showing the different sizes of the bay areas with the aid of circles. B) Superimposed structures of ^{tBu}HBC and FHBC dimers obtained from molecular dynamics simulations (see the Supporting Information for details). C) Space-filling representation of ^{tBu}HBC and FHBC dimers.

As a further probe of the lack of aggregation in FHBC, we performed (1 ns long) molecular dynamics (MD) simulations at ambient temperature, which showed that neutral ^{tBu}HBC indeed forms a stable dimer (with the interplanar separations between the aromatic cores close to van der Waals contact (ca. 3.5 Å), while in dimeric FHBC the pair of nanographenes lie at a separation of about 7.8 Å (Figure 6 B,C). Indeed, the presence of the long hexyl chains in FHBC hinders the approach of the graphitic cores in the dimer in favor of multiple CH–π interactions between the large π-system and alkyl chains (Figure 5 B/C). It is important to emphasize that access to FHBC platform, which resist self-aggregation, will open new avenues for the preparation of 2-dimensional extended aggregates via π–π contacts between the outer phenylenes of fluorene moieties that can be functionalized with appropriate groups at its vertices.

Functionalizaton of FHBC at its vertices would require access to its hexabromo derivative **7**(Scheme 2). Initial attempts of a six-fold bromination of FHBC in CH_2Cl_2 using bromine resulted in an inseparable mixture of

polybrominated products.[20] However, a bromination of the isomeric mixture of **5**/**5'** (that is, the precursor to FHBC) in CH_2Cl_2 with bromine, in the presence of a catalytic amounts of iodine (in about 4 h), afforded isomers **10**/**10'**, appropriately brominated at the desired positions of all fluorenes (Scheme 2). An oxidative cyclodehydrogenation of this isomeric mixture (**10**/**10'**) using DDQ/acid oxidant system followed by column chromatography returned FHBC-Br_6 in 26 % yield as a dark-red solid. The structure of FHBC-Br_6 was established by $^1H/^{13}C$ NMR spectroscopy and further confirmed by MALDI mass spectrometry (see the Supporting Information).



Scheme 2. Synthetic strategy for functionalization of FHBC at its vertices. k) Br_2/I_2 (catalytic amount)/CH_2Cl_2/22 °C/4 h, 100 % yield. j) DDQ (22 equiv)/CH_2Cl_2-CF_3SO_3H (9:1) mixture/0 °C/1 h, 26 % yield (after chromatographic purification). l) 2,5-dimethoxy-4-methylphenylboronic acid/$Pd(PPh_3)_4$/aq. K_2CO_3/ethanol/toluene/reflux/24 h, 85 % yield.

As a proof-of-concept experiment, a six-fold Suzuki coupling of FHBC-Br_6 with 2,5-dimethoxy-4-methylphenylboronic acid, under standard reaction conditions, afforded FHBC-Ar_6 as a deep-red solid in 91 % yield. The structure of FHBC-Ar_6 was established by $^1H/^{13}C$ NMR spectroscopy and MALDI mass spectrometry. A ^1H NMR spectrum of FHBC-Ar_6 in $CDCl_3$showed well-resolved resonances (see the Supporting Information) similar to FHBC (Figure 6).

In conclusion, we have developed a highly soluble versatile HBC platform (namely, FHBC) that contains an expanded graphitic core containing 19 Clar sextets and affords the ready introduction of multiple electroactive groups at its vertices. This ready tailoring of electroactive groups at vertices of FHBC, as demonstrated by a facile synthesis of a hexaarylbenzene derivative (FHBC-Ar_6), will allow the preparation of molecules with desirable electroactive functional groups suited for controlled assembly to form aggregates with tunable properties such as long-range charge transport for applications in the modern area of photovoltaics.[21, 22]

Dedicated to Sir Fraser D. Stoddart

Acknowledgements

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Conflict of interest

The authors declare no conflict of interest.

Supporting information

FHBC, a Hexa-peri-hexabenzocoronene–Fluorene Hybrid: A Platform for Highly Soluble, Easily Functionalizable HBCs with an Expanded Graphitic Core

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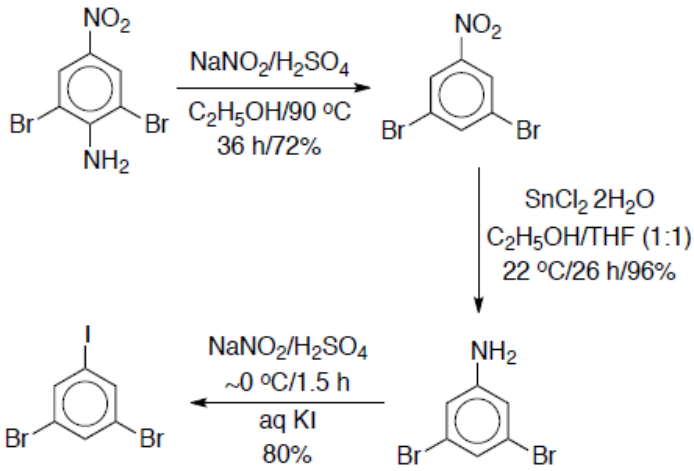
Synthesis

Synthetic scheme for the preparation of 1,3-dibromo-5-iodobenzene (7).[1] A large-scale synthesis of 1,3-dibromo-5-iodobenzene was accomplished in three high yielding step from commercially-available 2,6-dibromo-4-nitroaniline (see Scheme below) by adaptation of the standard literature procedures.[1]



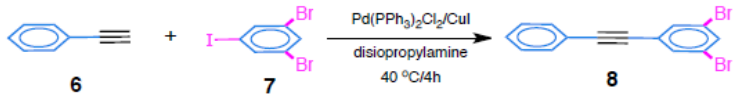
*Synthesis of 1,3-dibromo-5-nitrobenzene***.** To a refluxing solution of 2,6-dibromo-4-nitroaniline (40 g, 135 mmol) in a mixture of ethanol (450 mL) and conc. H_2SO_4 (45 mL) was added solid $NaNO_2$ (30 g, 435 mmol) in small portions to prevent excessive foaming. After all $NaNO_2$ was added, the resulting reaction mixture was stirred at ~90°C for an additional 24 h. The reaction mixture was cooled to room temperature and poured into ice-cold water (500 mL), which then resulted in the precipitation of the product. The solid was filtered using a Buchner funnel and repeatedly washed with water (3 x 100 mL). The crude solid was crystallized from boiling ethanol to afford 1,3-dibromo-5-nitrobenzene as orange needles. Yield: 27 g, 72%; mp 95°C; ^{1}H NMR ($CDCl^3$) δ: 7.99 (t, 1H, J = 1.7 Hz), 8.32 (d, 2H, J = 1.7 Hz); ^{13}C NMR ($CDCl^3$) δ: 123.68, 125.79, 140.27.

Synthesis of 3,5-dibromophenylamine. To a solution of 1,3-dibromo-5-nitrobenzene (27 g, 96 mmol) in a mixture of THF (200 mL) and ethanol (200 mL) was added slowly $SnCl^2.2H^2O$ (108 g, 480 mmol) in several portions and the resulting mixture was stirred for 20 h at ambient temperatures. The solvent was removed on a rotavap and

the resulting semisolid material was treated with aqueous NaOH (2 M, 250 mL), stirred for 2 h, and then extracted with diethyl ether (3 x 100 mL). The combined ether layers were dried over $MgSO^4$, filtered, and evaporated to afford 3,5-dibromophenylamine which was used in the next step without further purification. Yield: 24 g, 96 %; ^{1}H NMR ($CDCl^3$) δ: 3.76 (s, 2H), 6.76 (s, 2H), 7.01 (s, 1H).

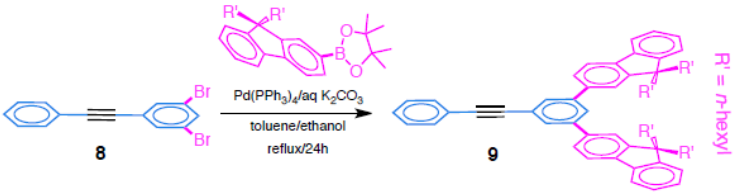
Synthesis of 1,3-dibromo-5-iodobenzene (7). The 3,5-dibromophenylamine (13 g, 52 mmol),obtained above, was dissolved in conc. H^2SO^4 (100 ml) by stirring in a heated (~50°C) water bath. The resulting solution was cooled to ~0°C and solid sodium nitrite (7.85 g, 113.9 mmol) was added in small portions with continuous stirring and maintaining the temperature below 5°C. The reaction mixture was allowed to stir for an additional 2 h at 0°C and then poured onto ice-cold solution of KI (25 g, 150 mmol) in water (120 mL). The resulting mixture was slowly warmed to room temperature (~1 h) and then heated to ~80°C for an additional 15 minutes. The resulting reaction mixture produced a lot of solid which was filtered and washed with cold water (3 x 50 mL). Drying and crystallization of the solid product from ethanol afforded the desired 1,3-dibromo-5-iodobenzene (7) in good yield (15 g, 80%). mp 123-124 °C ; ^{1}H NMR ($CDCl^3$) δ: 7.63 (s, 1H), 7.79 (s, 2H); ^{13}C NMR ($CDCl^3$) δ: 94.67, 123.58, 133.85, 138.70.

Synthesis of 1,3-dibromo-5-phenylethynylbenzene (8)[2]



To a solution of 1,3-dibromo-5-iodobenzene (6.0 g, 16.6 mmol) in diisopropylamine (30 mL) was added $PdCl_2(PPh_3)_2$ (0.29 g, 0.40 mmol), CuI (0.08 g, 0.40 mmol), and phenylacetylene (1.82 mL, 16.6 mmol) were added successively at room temperature and under an argon atmosphere. The resulting mixture was stirred at ~40°C (water bath) for 4 h. The mixture was then cooled to room temperature and diluted with hexanes (100 mL). The contents were filtered through a short pad of silica gel and silica pad was washed with hexanes (3 x 25 mL). Evaporation of the solvent in vacuo led to an oil which was purified by flash chromatography using a mixture of ethyl acetate and hexanes (1:9) as eluent to afford the pure 1,3-dibromo-5- phenylethynylbenzene (8) as a white solid (5.4 g, 97%). mp 106- 108 °C; $_1$H NMR ($CDCl_3$) δ: 7.34-7.40 (m, 3H), 7.49-7.54 (m, 2H), 7.60 (d, 2H, J = 1.78 Hz), 7.63 (t, 1H, J = 1.78 Hz); $_{13}$C NMR ($CDCl_3$) δ: 86.58, 92.14, 122.42, 122.82, 126.90, 128.67, 129.17, 131.94, 133.17, 134.07.

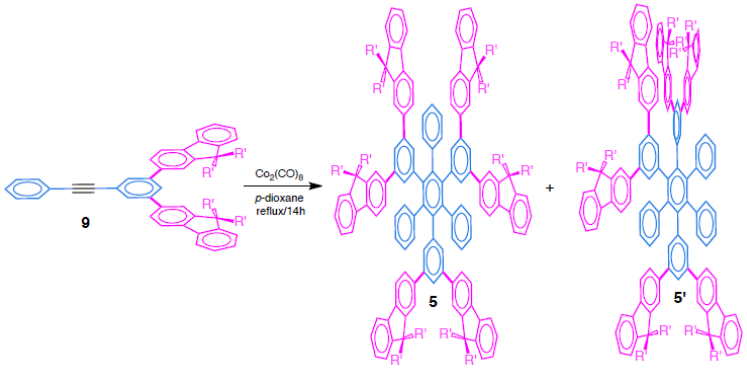
Synthesis of 1,3-difluoranyl-5-phenylethynylbenzene (9).



To a degassed solution of **8** (1.1 g, 3.3 mmol), 2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan)-9,9- dihexylfluorene (4.0 g, 8.7 mmol), and $Pd(PPh_3)_4$ (0.09 g, 0.08 mmol) in a mixture of predegassed toluene (50 mL) and ethanol (13 mL) in a Schlenk flask, was added a degassed solution of potassium carbonate (2 M, 20 mL) with the aid of a syringe. The resulting mixture was refluxed for 24 hours while protected from light by aluminum foil. The reaction mixture was then cooled to room temperature and poured onto 5% aqueous HCl (50 mL) and then extracted with dichloromethane (3 x 30 mL). The combined extracts were washed with water (50 mL) and brine (50 mL) and dried over anhydrous $MgSO_4$. Removal of the solvent in *vacuo* afforded crude product which was purified by flash chromatography on silica gel using a mixture of ethyl acetate and hexanes (1:99) as eluent to

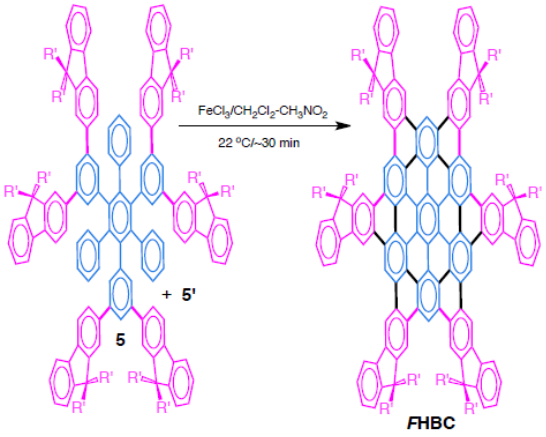
afford 1,3-difluoranyl-5-phenylethynylbenzene **9** as a viscous oil (2.5 g, 89%). $_1$H NMR ($CDCl_3$) δ: 0.60- 0.73 (m, 8H), 0.77 (t, 12H, *J* = 6.7 Hz), 1.02- 1.16 (m, 24H), 2.0- 2.08 (m, 4H), 7.32- 7.41 (m, 10H), 7.60- 7.65 (m, 4H), 7.68 (dd, 2H, *J* = 8.0 Hz, 1.6 Hz), 7.73- 7.77 (m, 2H), 7.80 (d, 2H, *J* = 8.0Hz), 7.82 (d, 2H, J= 1.7 Hz), 7.90 (t, 1H, *J* = 1.7 Hz); $_{13}$C NMR ($CDCl_3$) δ: 14.24, 22.80, 23.96, 29.92, 31.70, 40.64, 55.45, 89.73, 89.80, 120.03, 120.05, 120.22, 123.12, 124.27, 126.30, 127.02, 127.39, 128.64, 129.22, 131.91, 139.43, 140.84,141.10, 142.76, 151.20, 151.76.

Trimerization of 1,3-difluoranyl-5-phenylethynylbenzene 9 to an isomeric mixture of hexaarylbenzenes 5 and 5'.



To a degassed solution of **9** (3.52 g, 4.2 mmol) in *p*-dioxane (80 mL) was added octacarbonyldicobalt (0.48 g, 1.4 mmol) under a strict inert atmosphere. The resulting mixture was refluxed for 14 hours and then evaporated *in vacuo*. The resulting solid was dissolved in dichloromethane (100 mL) and filtered through a short pad of celite and the celite pad was washed with dichloromethane (25 mL). Evaporation of the dichloromethane and repeated precipitations from a mixture of dichloromethane and ethanol afforded a light brown solid which contained a mixture of isomeric **5** and **5'** (3.4 g, 96%) as confirmed by MALDI mass spectrometry and $_1$H/$_{13}$C NMR spectroscopy (see spectra below). Repeated attempts to separate the isomeric mixture of **5** and **5**' by chromatography and crystallizations were unsuccessful.

Synthesis of FHBC from a mixture of 5 and 5' using $FeCl_3$ or DDQ.

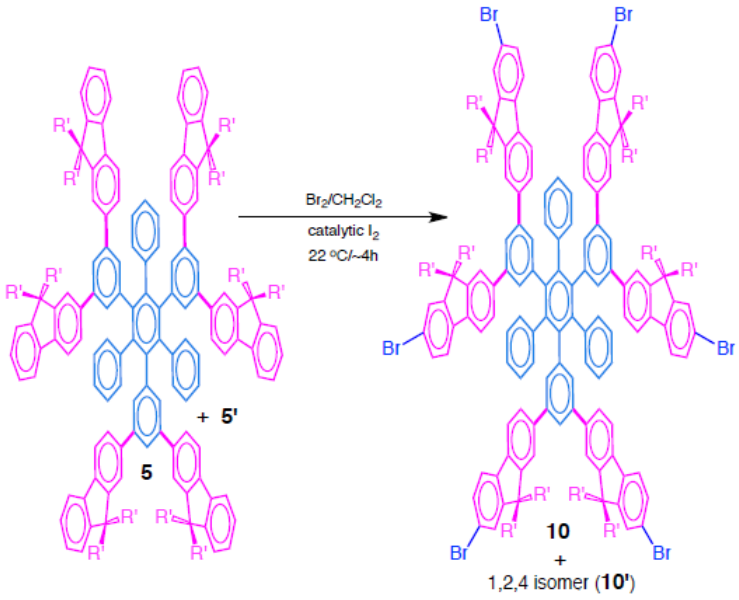


FeCl3 procedure*:* To a solution of **5** and **5'** (1.5 g, 0.6 mmol) in dry dichloromethane (50 mL) was added dropwise a solution of ferric chloride (3.3 g, 20 mmol) in nitromethane (30 mL) at ~0 $_o$C during the course of 20 min. The ice bath was removed and the resulting mixture was stirred for an additional 30 minutes at ~22 °C and was then quenched by an addition of methanol (25 mL) followed by water (100 mL). The organic layer was separated and the aqueous layer was further extracted with dichloromethane (3 x 50 mL). The combined organic layers were washed with water (3 x 50 mL) and dried over anhydrous magnesium sulfate and filtered. The resulting dark-red solution was then passed through a short pad of silica gel to remove iron containing

Impurities, and the solvent was evaporated to afford dark red solid. A careful flash column chromatography using a mixture of benzene and hexanes (1:19) as eluent afforded ***F*HBC** (0.27 g, 18%) as a dark-red solid. mp >450 ^{o}C; ^{1}H NMR ($CDCl_3$) δ: 0.79 (s, 6H), 1.1- 1.5 (m, 14H), 2.45- 2.85 (m, 4H), 7.17 (t, 1H, *J* = 7.2 Hz), 7.79 (d, 1H, *J* = 7.2 Hz), 7.86 (t, 1H, *J* = 7.2 Hz), 8.67 (d, 1H, *J* = 7.2 Hz), 10.12 (s, 1H), 10.56 (s, 1H), 12.04 (s, 1H), 12.22 (s, 1H); ^{13}C NMR ($CDCl_3$) δ: 14.25, 22.88, 24.58, 30.25, 31.88, 41.66, 55.93, 115.57, 116.07, 118.61, 121.06, 121.12, 121.61, 122.94, 122.97, 123.77, 127.70, 127.73, 127.87, 128.58, 130.85, 131.00, 141.23, 142.20, 151.39, 152.24. MS: MALDI-TOF (M^+) = 2505.

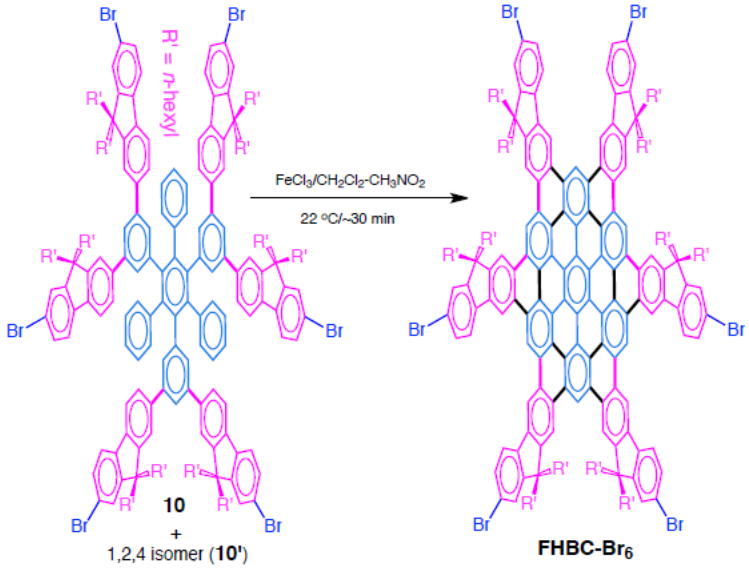
DDQ procedure*:* A solution of a mixture of **5** and **5'** (0.5 g, 0.2 mmol) in dichloromethane (18 mL) containing a protic acid (e.g. CH_3SO_3H, 10% v/v) or Lewis acid ($BF_3.OEt_2$, ~25 equiv.) at ~0 ^{o}C was treated with DDQ (4.4 mmol, 22 equiv), and the solution immediately took on a darkred coloration. The progress of the reaction was monitored by TLC. After completion of the reaction (~6 h), it was quenched with a saturated aqueous solution of $NaHCO_3$ (40 mL). The dichloromethane layer was separated and washed with water and brine solution and dried over anhydrous $MgSO_4$ and filtered. Removal of the solvent in vacuo followed by flash column chromatography using a mixture of benzene and hexanes (1:19) as eluent afforded ***F*HBC** (0.14 g, 28%) as a dark-red solid.

Synthesis of hexabrominated 10 and 10' by bromination of isomeric mixture 5 and 5'.



To a solution of mixture of **5** and **5'** (1.2 g, 0.48 mmol) in dichloromethane (100 mL) containing a crystal of iodine was added dropwise a solution of bromine (0.46 g, 2.9 mmol) in dichloromethane (50 mL) with the aid of a dropping funnel during a course of 15 minutes. The resulting mixture was stirred for an additional 3.5 h at room temperature. The reaction was quenched by addition of aqueous NaOH (1 M, 100 mL). The dichloromethane layer was separated and the aqueous layer was further extracted with dichloromethane (2 x 25 mL). The combined organic layers were washed with saturated aqueous sodium bisulfite (2 x 30 mL) solution, followed by water (50 mL) and brine (30 mL) and dried over anhydrous magnesium sulfate. The solvent was evaporated under vacuum to afford a mixture of **10** and **10'** as a light brown solid (1.42 g, 99%). This mixture was used in the next step without further purification.

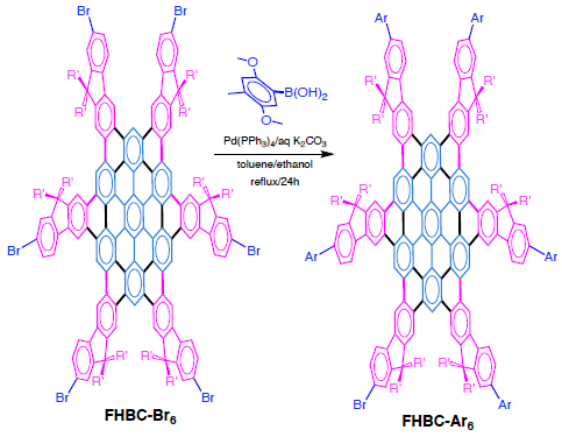
Synthesis of Synthesis of FHBC-Br_6 from mixture of 10 and 10' using $FeCl_3$ or DDQ.



FeCl3 procedure: To a solution of **10** and **10'** (0.81 g, 0.27 mmol), from above, in dry dichloromethane (100 mL) was added dropwise a solution of ferric chloride (2.7 g, 17 mmol) in nitromethane (25 mL) at ~0 ^{o}C during the course of 20 min. The ice bath was removed and the resulting mixture was stirred for an additional 3 h at ~22 °C and was then quenched by an addition of methanol (30 mL) followed by water (100 mL). The organic layer was separated and the aqueous layer was further extracted with dichloromethane (3 x 50 mL). The combined organic layers were washed with water (3 x 50 mL) and dried over anhydrous magnesium sulfate and filtered. The resulting dark-red solution was then passed through a short pad of silica gel to remove iron containing impurities, and the solvent was evaporated to afford dark red solid. A careful flash column chromatography using ethyl acetate, which eluted only the undesired **FHBC-Br6** products, followed by dichloromethane that eluted the desired **FHBC-Br$_6$** (0.16 g, 20%) as a dark-red solid. mp > 450 ^{o}C, ^{1}H NMR ($CDCl_3$) δ: 0.70–0.80 (m, 36H), 1.10-1.40 (m, 96H), 2.44-2.75 (m, 24H), 7.87 (s, 6H), 7.93 (d, 6H, *J* = 8.0 Hz, 1.5 Hz), 8.47 (d, 6H, J = 8.0 Hz), 10.07 (s, 6H), 10.47 (s, 6H), 12.00 (s, 3H), 12.12 (s, 3H). See MALDI and ^{1}H/^{13}C NMR spectra below.

DDQ procedure: A solution of a mixture of **10** and **10'** (0.6 g, 0.2 mmol) in dichloromethane (18 mL) containing CF_3SO_3H, 10% v/v) at ~0 ^{o}C was treated with DDQ (4.4 mmol, 22 equiv), and the resulting mixture was stirred for ~4 h. It was quenched with a saturated aqueous solution of $NaHCO_3$ (40 mL). The dichloromethane layer was separated and washed with water and brine solution and dried over anhydrous $MgSO_4$ and filtered. Removal of the solvent in vacuo followed by flash column chromatography as above (used for the material generated by $FeCl_3$ method) afforded desired ***F*HBC-Br6** (0.17 g, 26%) as a dark-red solid.

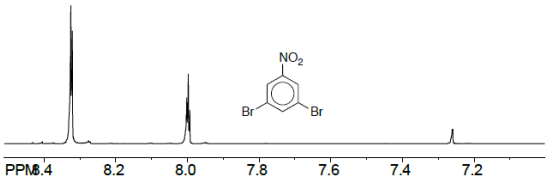
Synthesis of FHBC-Ar$_6$.



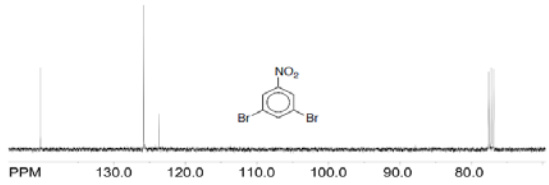
To a degassed solution of ***F*HBC-Br6** (50 mg, 0.017 mmol), 2,5-dimethoxy-4-methylphenylboronic acid (0.04 g, 0.20 mmol), Pd $(PPh_3)_4$ (0.06 g, 0.005 mmol) in a mixture of dry toluene (25 mL) and ethanol (7 mL), was added a degassed solution of potassium carbonate (2 M, 10 mL) using a syringe. The resulting mixture was refluxed for 24 h under a complete exclusion of light. The reaction mixture was then cooled to room temperature, poured into 5% aqueous HCl (50 mL), and extracted with dichloromethane (3 x 30 mL). The combined extracts were washed with water (50 mL) and brine (50 mL) and dried over anhydrous MgSO4. Removal of the solvent in vacuo afforded a solid that was purified using column chromatography on silica gel using a mixture of ethyl acetate and hexanes (1:19) as eluent to afford FHBC-Ar6 as a deep red solid (48 mg, 85%). m.p >400 oC. 1H NMR (CDCl3) δ: 0.76- 0.84 (m, 36H), 1.20- 1.48 (m, 96H), 2.56- 2.82 (m, 24H), 3.94 (s, 18H), 4.03 (s, 18H), 7.02 (s, 6H), 7.19 (s, 6H), 7.92-8.02 (m, 12H), 8.69 (d, 6H, J = 8.7 Hz), 10.17 (s, 6H), 10.59 (s, 6H), 12.09 (s, 3H), 12.25 (s, 3H). 13C NMR (CDCl3) δ: 14.24, 16.64, 22.90, 24.67, 30.31, 31.89, 41.62, 55.92, 56.47, 57.26, 113.55, 115.53, 116.26, 118.73, 120.66, 121.19, 121.26, 121.62, 121.72, 123.03, 125.25, 127.17, 127.81, 127.90, 128.90, 129.52, 130.78, 131.11, 138.91, 139.87, 142.11, 150.74, 151.88, 152.54. See MALDI and 1H/13C NMR spectra below.

$_1$H/$_{13}$C NMR spectroscopy

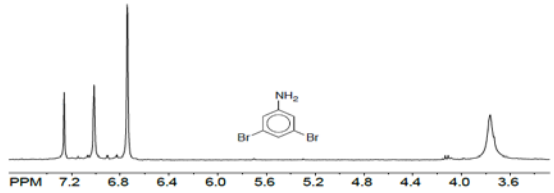
^{1}H NMR of 1,3-dibromo-5-nitrobenzene



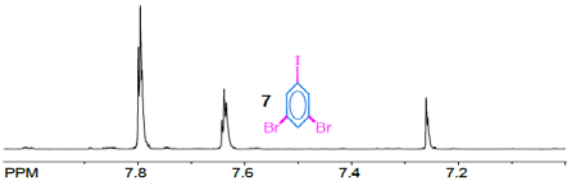
^{13}C NMR of 1,3-dibromo-5-nitrobenzene



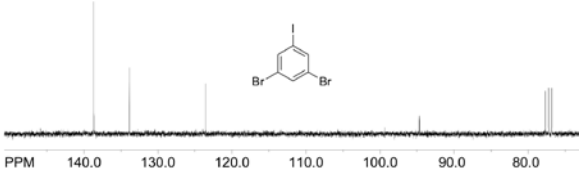
^{1}H NMR of 3,5-dibromo-phenylamine



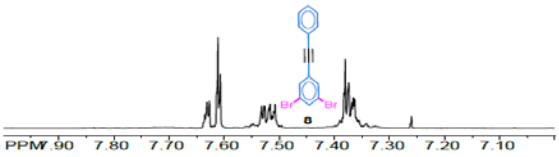
^{1}H NMR of 1,3-dibromo-5-iodobenzene (7)



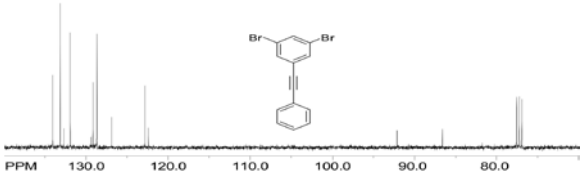
^{13}C NMR of 1,3-dibromo-5-iodobenzene (7)



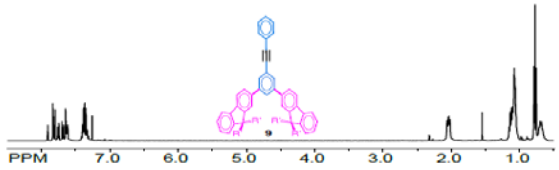
^{1}H NMR of 1, 3-dibromo-5-phenylethynylbenzene (8)



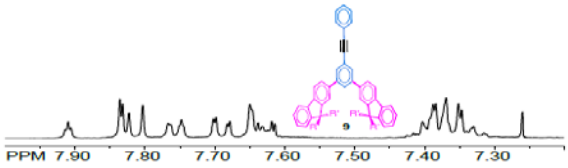
^{13}C NMR of 1, 3-dibromo-5-phenylethynylbenzene (8)



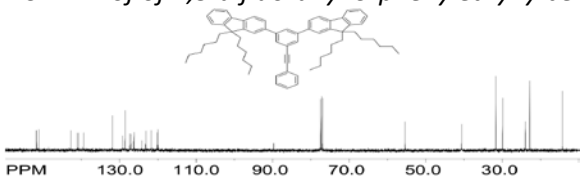
^{1}H NMR of 1,3-difluoranyl-5-phenylethynylbenzene (9)



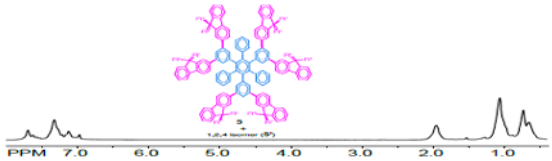
Zoomed ^{1}H NMR of 1,3-difluoranyl-5-phenylethynylbenzene (9)



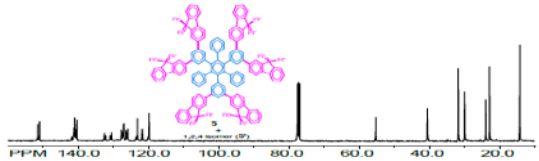
^{13}C NMR of of 1,3-difluoranyl-5-phenylethynylbenzene (9)



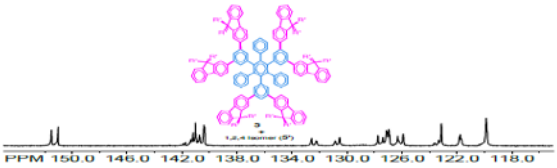
^{1}H NMR of the mixture of hexaarylbenzenes 5 and 5'



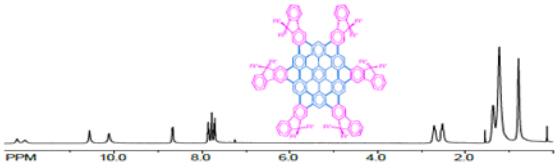
^{13}C NMR of the mixture of hexaarylbenzenes 5 and 5'



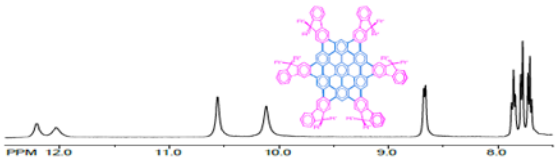
Zoomed ^{13}C NMR of the mixture of hexaarylbenzenes 5 and 5'



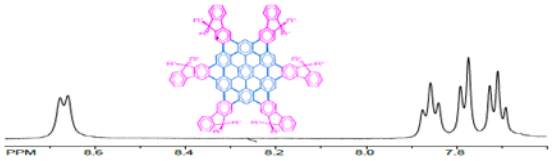
^{1}H NMR of FHBC



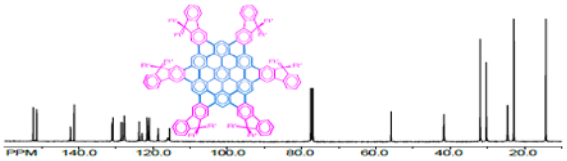
Zoomed ^{1}H NMR of FHBC



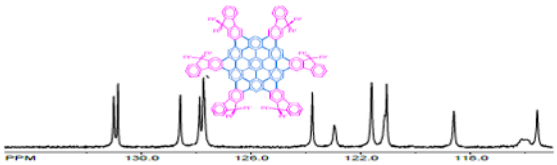
Zoomed ^{1}H NMR of FHBC



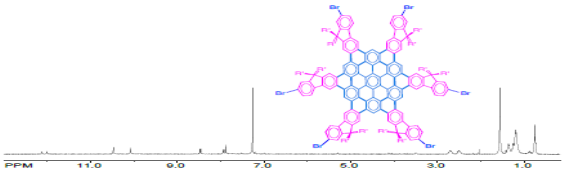
^{13}C NMR of FHBC



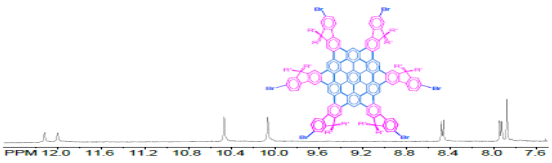
Zoomed ^{13}C NMR of FHBC



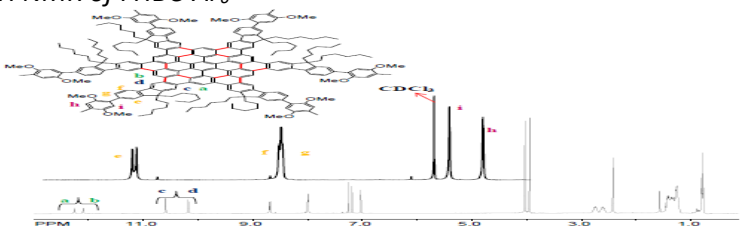
^{1}H NMR of FHBC-Br_6



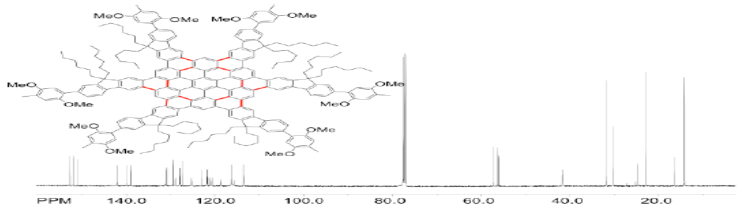
Zoomed ^{1}H NMR of FHBC-Br_6



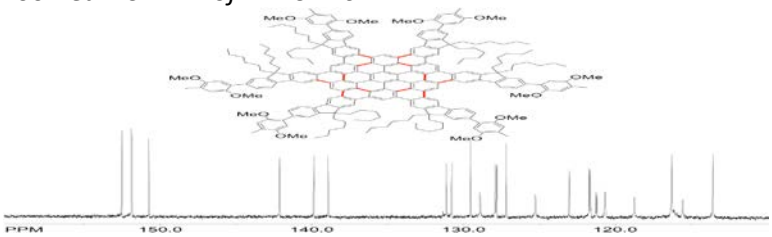
^{1}H NMR of FHBC-Ar$_6$



^{13}C NMR of FHBC-Ar$_6$:



Zoomed ^{13}C NMR of FHBC-Ar6:



MALDI-TOF mass spectrometry

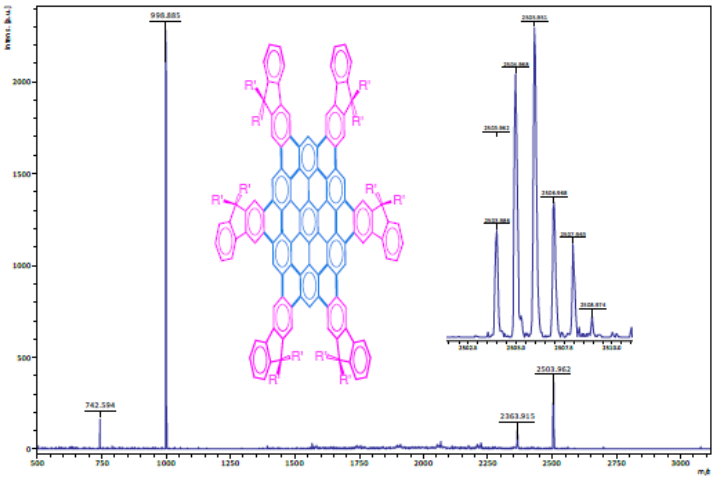


Figure S1. MALDI-TOF mass spectra of ***F*HBC** obtained using dithranol as a matrix. Inset showing the isotope distribution for the molecular ion of ***F*HBC**.

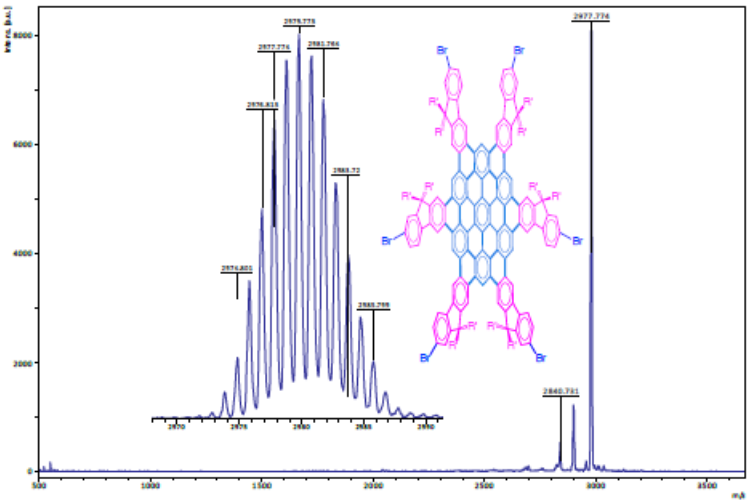


Figure S2. MALDI-TOF mass spectra of ***F*HBC**-Br_6 obtained using dithranol as a matrix. Inset showing the isotope distribution for the molecular ion of ***F*HBC** -Br_6.

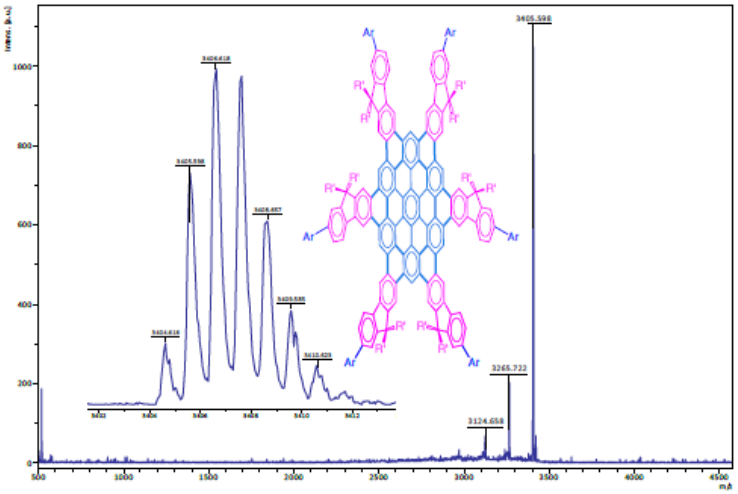
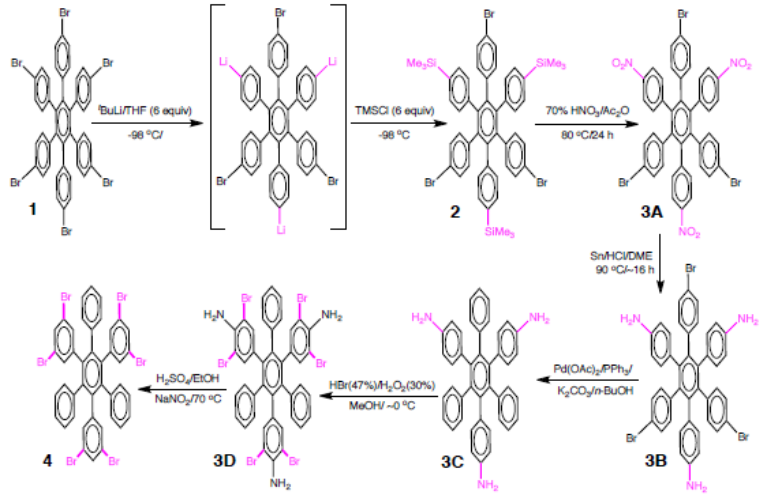
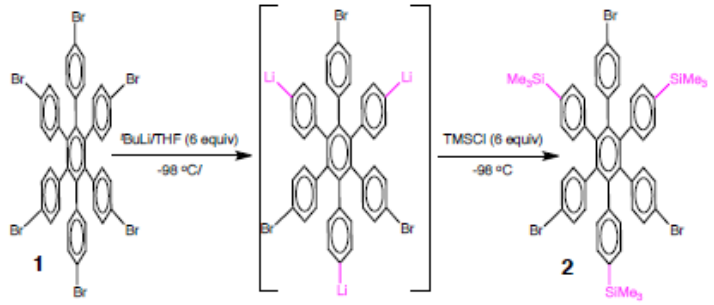


Figure S3. MALDI-TOF mass spectra of ***F*HBC**-Ar_6 obtained using dithranol as a matrix. Inset showing the isotope distribution for the molecular ion of ***F*HBC** -Ar_6.

Synthetic scheme for the preparation of 4

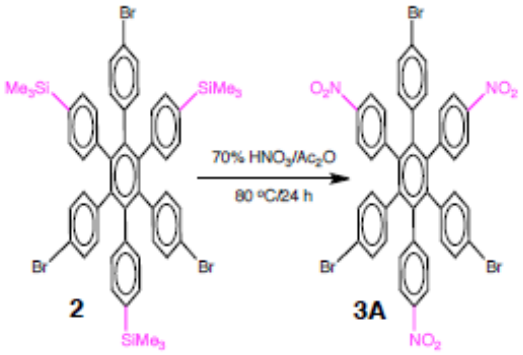


Synthesis of 2[3,4]



A dry Schlenk flask containing *hexakis*(4-bromophenyl)benzene[5] (10.0 g, 9.92 mmol) and THF (100 mL) was cooled to −98°C in a liquid nitrogen/methanol bath (~15 min). A hexane solution of *t*BuLi (6 equivalent, 35.3 mL, 60 mmol) was added slowly with the aid of syringe under an argon atmosphere. The resulting mixture was stirred for an additional 10 minutes at −98°C. The cooling bath was then removed and the reaction mixture was stirred for an additional 1 hour. During this time, the color of reaction mixture turned from greenish yellow to pink. The pink solution was cooled again to −98°C and maintained at this temperature for 10 minutes before slowly adding trimethylsilylchloride (TMSCl) (6 eq, 7.6 mL, 60 mmol) with the aid of a syringe. After completing the addition of TMSCl, the cooling bath was removed. The color of the reaction mixture changed from colorless to pink to white. This mixture was stirred for an additional hour before quenching by addition of aqueous ammonium chloride (40 mL). The resulting mixture was extracted with chloroform (3 x 50 mL) and the combined organic extracts were dried over $MgSO_4$ and solvent was evaporated under reduced pressure. The resulting solid was recrystallized from a mixture of $CHCl_3$/EtOH (70:30) to afford pure **2** (7.43 g, 76%). ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 6.62 (d, 2H, *J* = 8.46 Hz), 6.72 (d, 2H, *J* = 8.08 Hz), 6.95 (d, 2H, *J* = 8.45 Hz), 7.03 (d, 2H, *J* = 8.08 Hz). ^{13}C NMR ($CDCl_3$, 400 MHz) δ: -0.99, 119.66, 129.94, 130.69, 132.08, 133.09, 137.70, 139.43, 139.45. 140.33, 140.69.

Synthesis of 3A

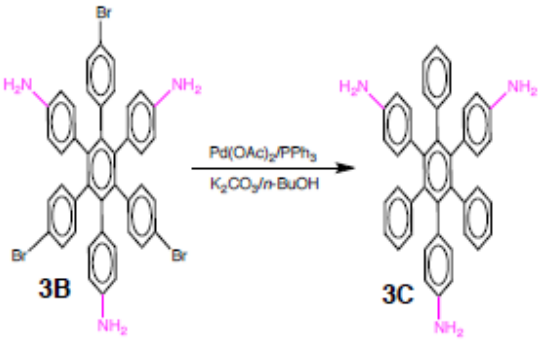


In a dry Schlenk flask containing **2** (2.5 g, 2.53 mmol) was added acetic anhydride (10 mL) followed by a dropwise addition of 70% HNO_3 (2.5 mL) with the aid of a syringe at ambient temperatures. The resulting mixture was heated at ~80°C for 24 h, cooled to room temperature, and poured onto a cold (~0°C) 10% aqueous NaOH solution (100 mL). The reaction mixture was extracted with dichloromethane (3 x 25 mL) and the combined organic extracts were dried over $MgSO_4$ and the solvent was removed under reduced pressure. The resulting crude solid was purified by column chromatography using silica gel and hexane : ethyl acetate (80 : 20) mixture as eluent to return pure **3A** (1.0 g, 44%). ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 6.63 (d, 2H, *J* = 8.66 Hz), 6.97 (d, 2H, *J* = 8.92 Hz), 7.07 (d, 2H, *J* = 8.57 Hz), 7.84 (d, 2H, *J* = 8.88 Hz). ^{13}C NMR ($CDCl_3$, 400 MHz) δ: 121.61, 122.94, 131.25, 131.86, 132.29, 137.26, 139.37, 140.03. 146.18, 146.30.

Synthesis of 3B

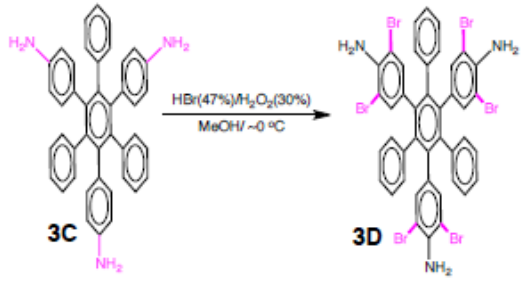
To a mixture of trinitro derivative **3A** (0.8 g, 0.9 mmol), concentrated HCl (20 mL), and 1,2-dimethoxyethane (20 mL) powdered tin (0.94 g, ~8 mmol) was added in small portions. The resulting mixture was stirred for ~13 h at 90℃. After which time, more HCl (15 mL) and powdered tin (200 mg) were added and the stirring was continued for additional 3 h at 90℃. The reaction mixture was cooled to room temperature and 10% aqueous NaOH solution was added until the solution turned basic (pH = 9, pH paper). This solution was extracted with diethyl ether (3 x 40 mL) and the combined ether extracts were dried over anhydrous $MgSO_4$. The solvent was removed under reduced pressure and the crude product was treated with concentrated HCl to form a solid precipitate, which was washed by a mixture of ethyl acetate/hexanes (10:90). The resulting solid was filtered and treated with pyridine until the solid dissolve and then the solution was extracted with diethyl ether and the solvent was removed under reduced pressure to afford brown color compound **3B** (0.53 g, 74%). ^{1}H NMR ($CDCl_3$, 400 MHz), δ in ppm = 6.23 (d, 2H, *J* = 8.56 Hz), 6.47 (d, 2H, *J* = 8.57 Hz), 6.64 (d, 2H, *J* = 8.56 Hz), 7.00 (d, 2H, *J* = 8.50 Hz), 3.369 (-NH_2, br hump). ^{13}C NMR ($CDCl_3$, 400 MHz), δ in ppm = 114.28, 119.36, 130.02, 130.62, 132.26, 133.27, 139.70, 140.25, 140.51, 143.83.

Synthesis of 3C



To a dry Schlenk flask **3B** (0.97 g, 1.2 mmol), $Pd(OAc)_2$ (27 mg, 0.12 mmol), PPh_3 (124 mg, 0.472 mmol), K_2CO_3 (372 mg, 2.36 mmol) and *n*-butanol (35 mL) were successively added under argon atmosphere and the resulting mixture was subjected to additional degassing and purguing with argon. The reaction mixture was then stirred at 100℃ for overnight. The reaction was quenched by addition of water (100 mL) and extracted with dichloromethane (4 x 30 mL). The combined organic extracts were dried over $MgSO_4$ and the solvent was removed under reduced pressure. The crude product was treated with concentrated HCl (5 mL) and the oily residue formed was washed with benzene and then added pyridine and dichloromethane (100 mL) and evaporated. The resulting solid was washed by a mixture of hexane and ethyl acetate (4:1) to afford pure compound **3C** (0.46 g, 68%). ^{1}H NMR ($CDCl_3$, 400 MHz), δ in ppm = 6.18 (d, 2H, *J* = 8.66 Hz), 6.54 (d, 2H, J = 8.50 Hz), 6.73- 6.99 (m, 5H). ^{13}C NMR ($CDCl_3$, 400 MHz), δ in ppm = 113.88, 124.90, 126.74, 131.62, 131.79, 132.49, 140.35, 140.70, 141.59, 143.35.

Synthesis of 3D

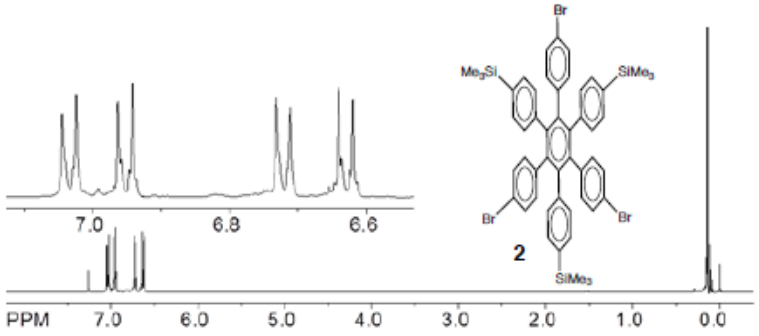


Compound **3C** (0.65 g, 1.12 mmol) in MeOH (110 mL) was taken in a Schlenk flask and 1.7 mL (10 mmol) concentrated aqueous HBr (47% wt/wt) was carefully added. To this resulting mixture, 30% aqueous H_2O_2 (0.76 mL, 6.7 mmol) was added slowly at $0° - 4℃$ during the course of 15 minutes and was allowed to stir overnight.. The reaction was quenched with aqueous NaOH solution (2 g, 100 mL water) and the resulting solid thus formed was filtered and washed with water. The solid was dissolved in $CHCl_3$ (100 mL) and dried over $MgSO_4$, filtered and the solvent was removed under reduced pressure to afford **3D** (0.9 g, 76%). ^{1}H NMR ($CDCl_3$, 400 MHz), δ in ppm = 4.25 (br hump –NH_2), 6.78 (s, 2H), 6.79-6.85 (m, 2H), 6.89-7.08 (m, 3H). ^{13}C NMR ($CDCl_3$, 400 MHz), δ in ppm = 107.40, 126.15, 127.46, 131.07, 131.96, 134.54, 138.00, 139.38, 139.75, 141.35.

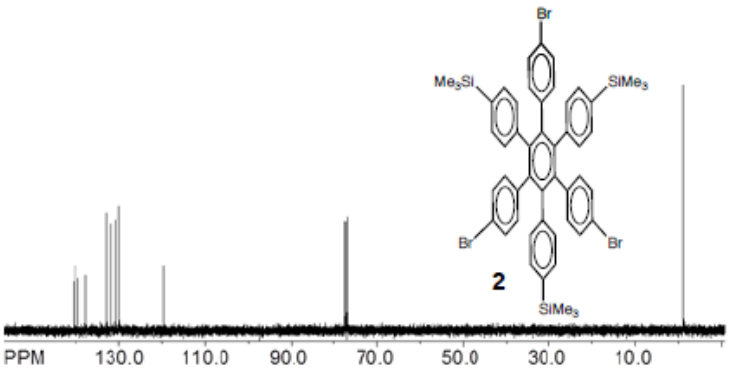
Synthesis of 4[6]

Compound **3D** (0.9 g, 0.86 mmol) from above was suspended in EtOH (100 mL) and heated to $50℃$. To this solution was added dropwise concentrated H_2SO_4 (5 mL) and the temperature was raised to $70℃$. To this mixture, solid $NaNO_2$ (0.7 g, 10 mmol) was added in portions over 45 minutes and it was heated at $80℃$ for overnight, cooled to room temperature, and poured into ice water. The resultant highly colored solid was filtered and could not be characterized due to rather poor solubility.

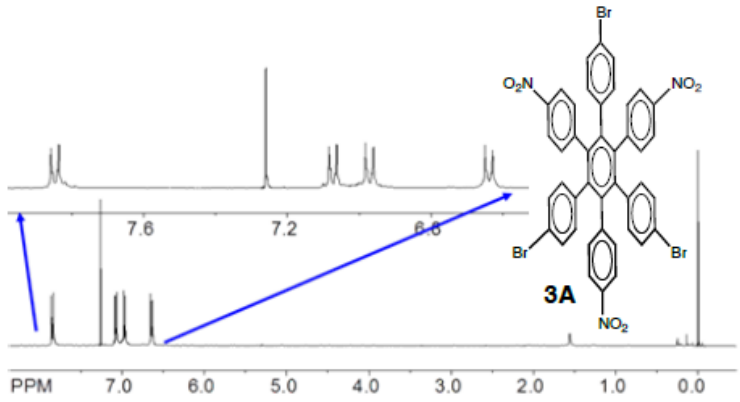
^{1}H NMR spectrum of 2



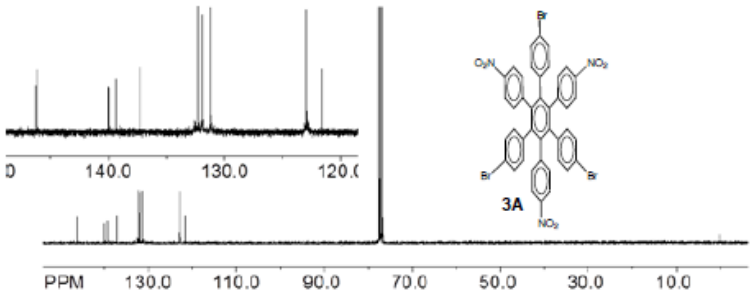
^{13}C NMR spectrum of 2



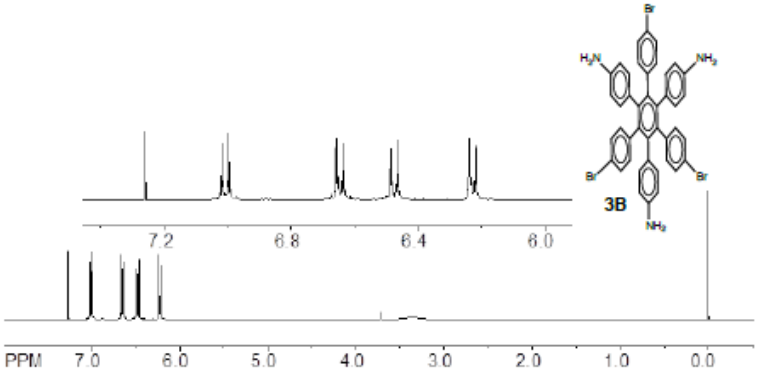
[1]H NMR spectrum of 3A



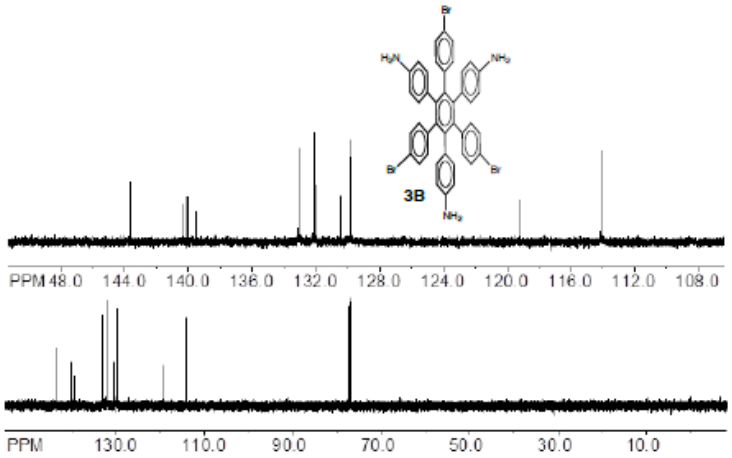
[13]C NMR spectrum of 3A



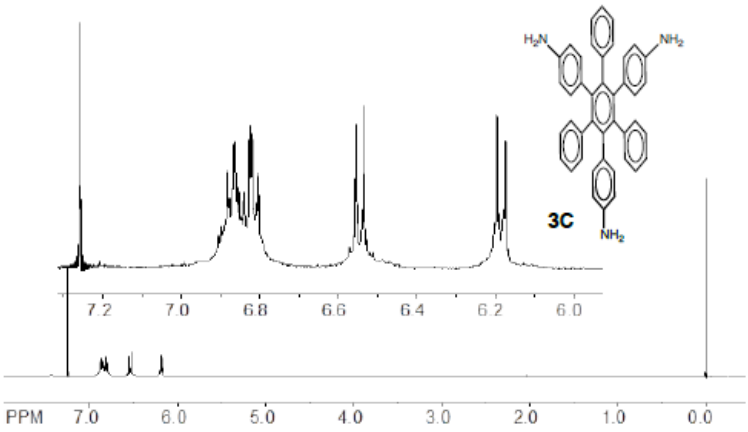
[1]H NMR spectrum of 3B



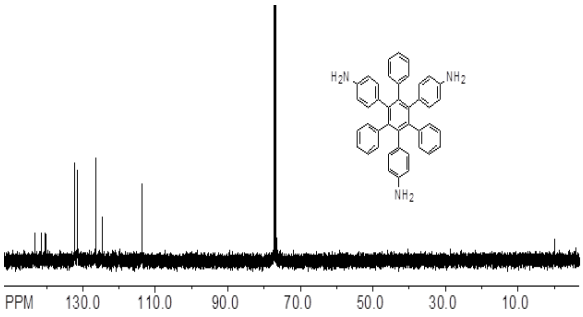
^{13}C NMR spectrum of 3B



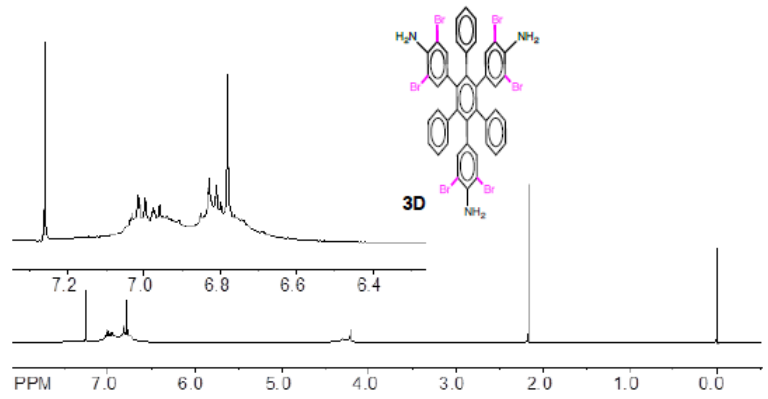
^{1}H NMR spectrum of 3C



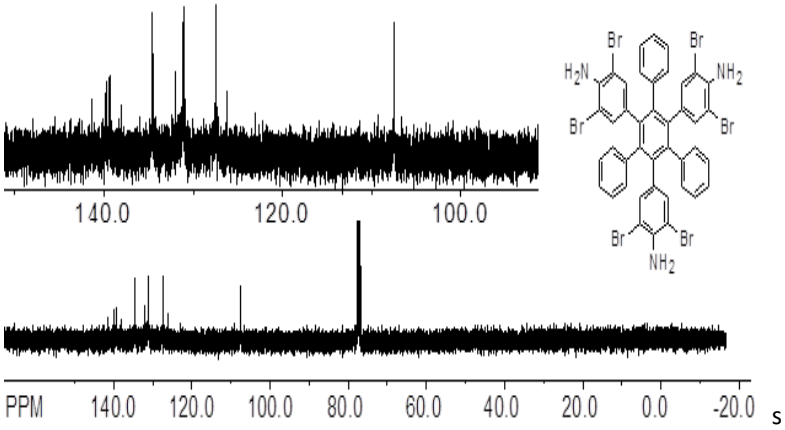
^{13}C NMR spectrum of 3C



^{1}H NMR spectrum of 3D



^{13}C NMR spectrum of 3D



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Electrochemistry

The electron donor strength of ***F*HBC** and *t*Bu**HBC** was evaluated by electrochemical oxidation at a platinum electrode in dichloromethane containing 0.2 M *n*-Bu_4NPF_6 as the supporting electrolyte. The cyclic voltammograms of ***F*HBC**, when terminated before the start of the fifth oxidation event, showed three reversible oxidation waves, which consistently met the reversibility criteria at various scan rates of 200-500 mV/s, as they all showed cathodic/anodic peak current ratios of i_a/i_c=1.0 (theoretical) as well as the differences between anodic and cathodic peak potentials of E_{pa}-E_{pc} ~ 70 mV at 22 ^{o}C. The reversible oxidation potentials of ***F*HBC** were calibrated with ferrocene as internal standard (E_{ox} = 0.45 V *vs* SCE) and were found to be 0.40, 0.76, 1.01 and 1.19 V vs Fc/Fc^{+} corresponding to the formation of mono, di, tri and tetracation respectively. It is noted that the fourth oxidation wave in the cyclic voltammogram of ***F*HBC** displays a quasi-reversible oxidation wave. In contrast, *t*Bu**HBC** exhibits a single oxidation wave at (E_{ox} =) 0.64 V vs Fc/Fc^{+} in CH_2Cl_2 (Figure S4).[7,8]

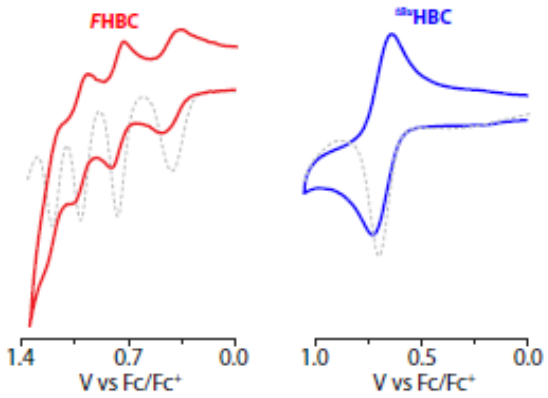

Figure S4. Cyclic (solid lines) and square-wave (dashed lines) voltammograms of ***F*HBC** (red) and $_{tBu}$**HBC** (blue) in CH_2Cl_2 containing 0.2 M *n*-Bu_4NPF_6 at a scan rate of 200 mV s^{-1} and 22°C.

Generation of *F*HBC cation radical

Reproducible spectra of ***F*HBC** cation radical were obtained in CH_2Cl_2 solution at 22°C by quantitative redox titrations using magic blue (tris-4-bromophenylamminium cation radical, **MB**$^{+}$•, E_{red} = 0.70 V vs Fc/Fc^{+}, λ_{max} = 728 nm, ε_{max} = 28200 cm^{-1} M^{-1}).[9,10]

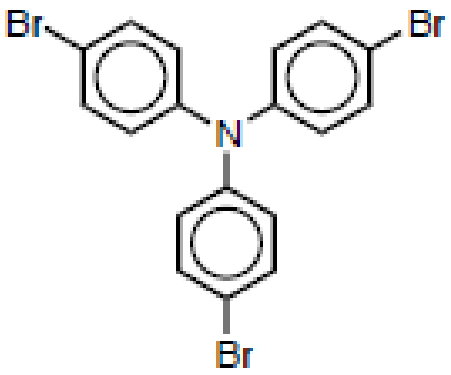

Figure S5. Chemical structure of magic blue

Redox titration experiment was carried out by an incremental addition of sub-stoichiometric amounts of electron donor (***F*HBC**) to the solution of **MB**+•. The 1-*e*- oxidation of ***F*HBC** to ***F*HBC**+• and reduction of **MB** +• to **MB** can be described by an equilibrium equation:

$$\boldsymbol{MB}^{+\bullet} + \boldsymbol{FHBC} \rightleftarrows \boldsymbol{MB} + \boldsymbol{FHBC}^{+\bullet} \quad \text{(eq. 1)}$$

Depletion of **MB**+• and formation of ***F*HBC**+•established that **MB**+• was completely consumed (Figure S6).

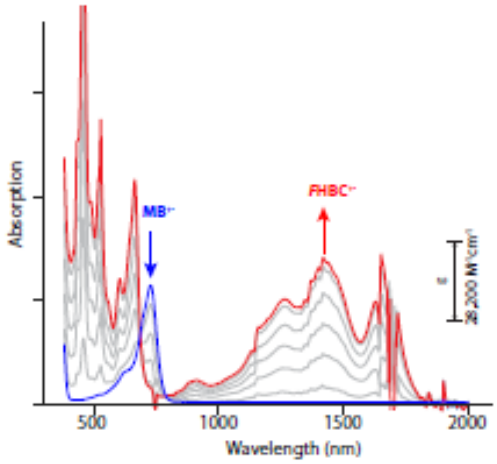

Figure S6. The spectral changes observed upon the reduction of 5.5 x 10^{-6} M **MB**$^{+\bullet}$ by an incremental addition of substoichiometric amounts of ***F*HBC** in CH_2Cl_2 at 22 ^{o}C.

Numerical deconvolution[9,10] of the UV-VIS absorption spectrum at each increment of the titration produced the individual spectra of ***F*HBC**$^{+\bullet}$ and **MB**$^{+\bullet}$. Obtained electronic spectrum of ***F*HBC+•** shows a significant increase of molar absorptivity (by a factor of ~6) as compared to $^{t\text{Bu}}$**HBC**$^{+\bullet}$ (Figure S7).

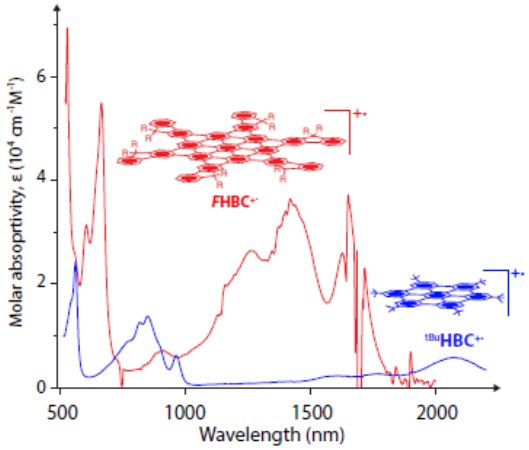

Figure S7. Comparison of the electronic absorption spectra of ***F*HBC+•** and $^{t\text{Bu}}$**HBC+•**.

The spectrum of ***F*HBC+•** remained unchanged at tenfold higher concentration, as well as in the presence of excess (up to 10 equivalents) neutral ***F*HBC**, suggesting a lack of aggregation either between the molecules of ***F*HBC+•** or ***F*HBC+•/*F*HBC** in solution. This is in contrast with $^{t\text{Bu}}$**HBC+•**, which forms a dimeric cation radical in solution, i.e. $^{t\text{Bu}}$**HBC+•** + $^{t\text{Bu}}$**HBC** ![$^{t\text{Bu}}$**HBC**]$_2$**+•** as judged by the observation of intervalence transition (at 1200 nm) in its cation radical spectrum (Figure S8).

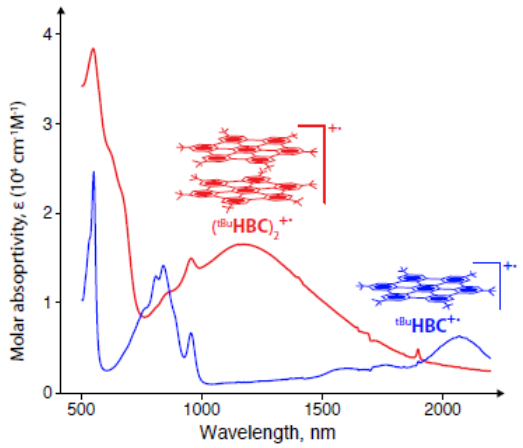

Figure S8. Electronic absorption spectrum of *t*Bu**HBC+•** (blue) and its spectrum in the presence of neutral *t*Bu**HBC**

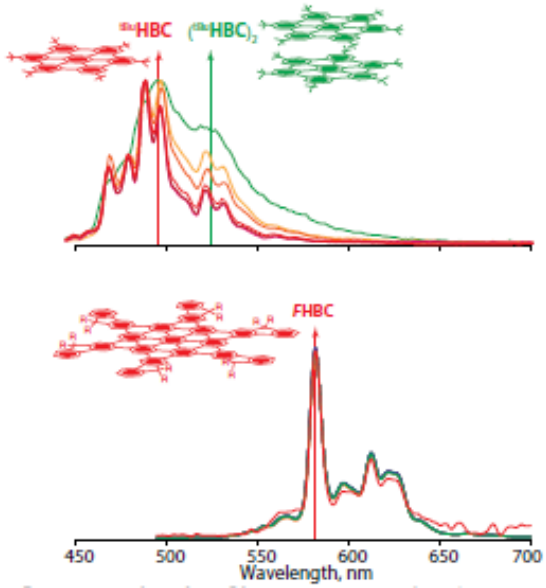

Figure S9. Emission spectra of *t*Bu**HBC** (10^{-8}-10^{-3} M)[7,8] and ***F*HBC** (10^{-6}-10^{-4} M) at varied concentrations. At higher concentrations *t*Bu**HBC** shows excimeric-like band, which is absent in ***F*HBC**.

Computational details

In order to investigate if ***F*HBC** allows formation of dimeric sandwich-like structures, we performed molecular dynamic simulations of a ***F*HBC** and *t*Bu**HBC** dimers. Molecular dynamics simulations were performed using Amber package.[11] Molecules of ***F*HBC** and *t*Bu**HBC** were modeled using Amber force field parameters generated using *antechamber*.[12-14] For temperature control we have used the Langevin thermostat with default friction coefficient to maintain temperature at 300 K. Long range interactions were treated exactly, i.e., without cutoff. Solvent was treated implicitly using generalized Born model of Hawkins, Cramer and Truhlar.[15]

Starting from the (pre-optimized) well-separated complex of two ***F*HBC** molecules, simulation showed that within 20 ps, two ***F*HBC** molecule approach each other at the separation distance of ~7.8 Å, as measured between geometrical centers of the HBC core, and remain at about the same distance for the rest of the 1-ns simulation. Two ***F*HBC**s are stabilized by multiple CH-π interactions between long alkyl chains and the aromatic core and prevent the van der Waals contact between the **HBC** cores that is required for a dimer stabilization.[16,17] In contrast, two well-separated *t*Bu**HBC** readily form a dimer contact with the separation distance of ~3.5 Å between the centers of the aromatic cores.

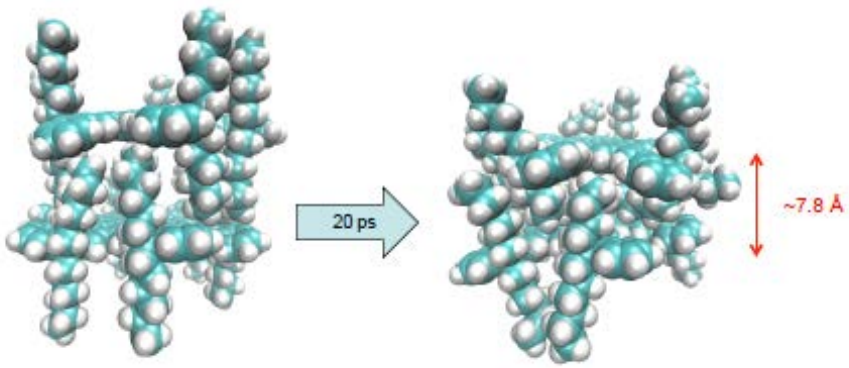

Figure S10. Illustration of the lack of ***F*HBC** aggregation. Starting from two well-separated ***F*HBC** molecules, simulation showed that within 20 ps, molecules approach each other at the separation distance of ~7.8 Å.
20 ps

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