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Hexa-*peri*-hexabenzocoronene–*fluorene* hybrid: A platform for highly soluble, easily functionalizable HBCs with expanded graphitic core

Tushar S. Navale, Maxim V. Ivanov, Mohammad M. Hossain and Rajendra Rathore*[a]

This paper is dedicated to Sir Fraser D. Stoddart

Abstract: Materials based upon hexa-*peri*-hexabenzocoronenes (**HBC**s) 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 via incorporation of electro-active groups or groups that can prompt self-assembly. Herein, we report the successful synthesis of a new **HBC**-fluorene hybrid with expanded graphitic core that is highly soluble, resists aggregation, and can be readily functionalized at its vertices. We also show that this new **HBC** platform can be tailored to incorporate six electro-active groups at its vertices, as exemplified by a facile synthesis of a representative hexaaryl derivative of **_F_HBC**. Synthesis of new **_F_HBC** derivatives, containing electro-active functional groups which can allow controlled self-assembly, may serve as potential long range charge-transfer materials for photovoltaic applications.

Hexa-*peri*-hexabenzocoronenes (**HBC**s) 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 **HBC**s 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 via oxidative cyclodehydrogenation of hexaphenyl-benzene, it is insoluble in common organic solvents.[5,6] **HBC**s 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 **HBC**s restrict their further functionalization with desired electro-active groups.

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 1). Specifically, the hybrid structure provides (i) an expanded graphitic core, (ii) increased solubility, and (iii) contains unsubstituted vertices for subsequent functionalization (*vide infra*). Accordingly, we describe the successful synthesis of a highly-soluble **HBC**–*fluorene* hybrid, hereafter referred to as **_F_HBC**, and show that it can be readily functionalized at all six vertices (Figure 1). We will also show that expansion of the graphitic core of **HBC** affords multiple (reversible) $1\text{-}e^{-}$ oxidation, producing a stable, *non-aggregated* cation-radical 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.

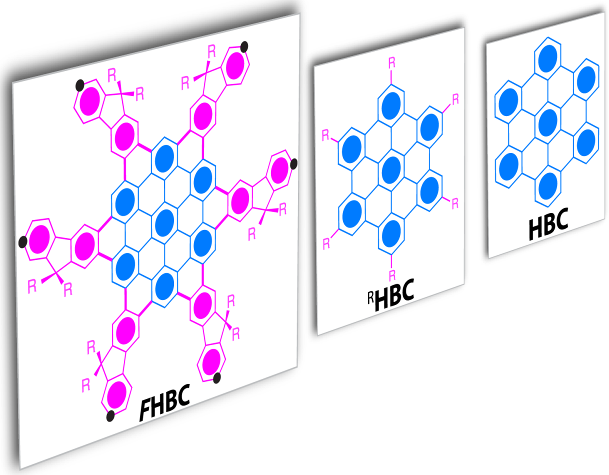

Figure 1. A comparison of the relative sizes of the parent **HBC**, **HBC** functionalized at its vertices with solubilizing groups (e.g. R = *n*-alkyl or *tert*-butyl), and newly designed **HBC**–fluorene hybrid (**_F_HBC**, R = *n*-alkyl) with provisions for both solubility and sites for on-demand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

The strategy for the preparation of **_F_HBC** involves an oxidative cyclodehydrogenation of a hexaphenylbenzene derivative **5,** in which alternate phenyl groups (i.e. 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)benzene[9] (**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, largely due to the poor solubility of **4** and its precursors. The solubility issues forced us to abandon this route for accessing **_F_HBC** (see Scheme 1 and Supporting Information for additional details).

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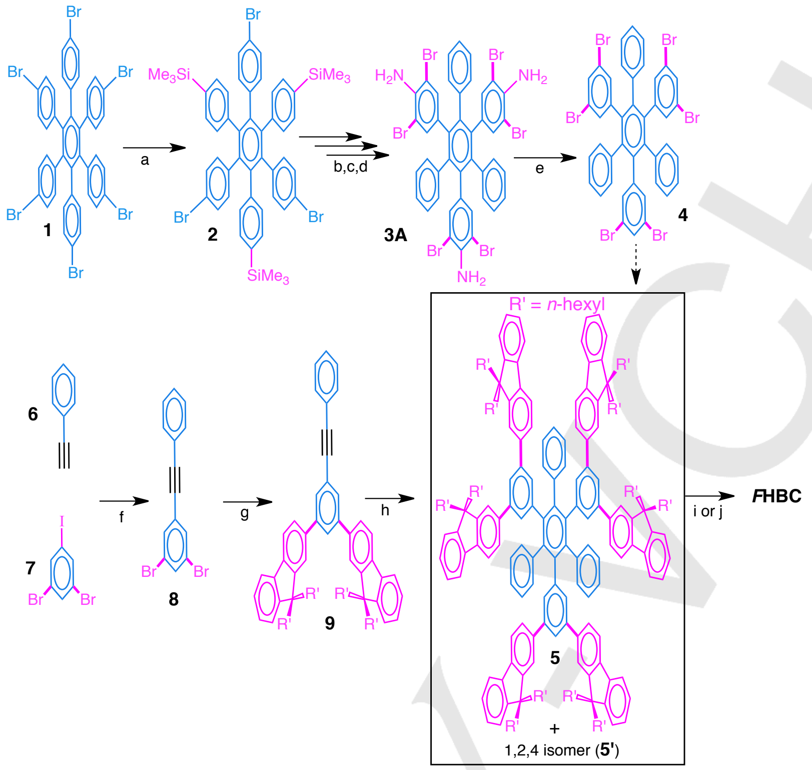

Scheme 1. Two different synthetic approaches for the preparation of ***F*HBC**. a. i) *t*BuLi (6 equiv)/-90°C; ii) Me_3SiCl/-90°C, yield: 76%. b. 70% HNO_3/Ac_2O/80 °C, yield: 40%. **c.** (i) Sn/HCl/DME/90 °C**, yield:** 74%; (ii) $Pd(OAc)_2/PPh_3$/aq K_2CO_3/***n*****-butanol**/100 °C, yield: 68%. d. aq. HBr (48%)/H_2O_2 **(30%)**/THF/ H_20, yield: ~76%. 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/4h, yield: 97%. g. 9,9-dihexylfluorene-2-boronic acid pinacol ester/$Pd(PPh_3)_4$/aq. K_2CO_3/ ethanol/toluene/ reflux/24h, yield: 89%. h. $Co_2(CO)_8$/p-dioxane/ reflux/14h, Yield: ~96%. i. DDQ (22 equiv)/CH_2Cl_2-CH_3SO_3H (9:1) mixture/0 °C/6h, yield: 28% (after chromatographic purification). j. $FeCl_3$ (100 equiv)/ CH_2Cl_2/CH_3NO_2/22 °C, yield: 18%.

In an alternative strategy, **5** could be prepared as an isomeric mixture in 3 simple steps (Scheme 1), via a practical if non-elegant route. First, a Sonogashira coupling of phenylacetylene (**6**) with readily-available 1,3-dibromo-5-iodobenzene[12] (**7**) returned alkyne **8** in excellent yield. A 2-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 mixture[13] in nearly quantitative yield (Scheme 1). 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 ***F*HBC** as an orange-red microcrystalline solid in 18% yield.[14] A much higher yield and purer ***F*HBC** (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 ***F*HBC**, and as the isomeric mixture of **5/5'** contains only ~33% of **5**, use of [DDQ/acid][15,16] as oxidant produces a nearly quantitative yield of ***F*HBC**.

The **HBC**-*fluorene* hybrid (***F*HBC**) was found to be highly soluble in common organic solvents, such as hexanes, CH_2Cl_2, $CHCl_3$, THF, DMF, etc., and its structure was established by $^1H/^{13}C$ NMR spectroscopy and MALDI-TOF mass spectrometry (see Supporting Information). A ^1H NMR spectrum of ***F*HBC** 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 **HBC**s, which generally show broad signals owing to extensive aggregation.[7,8]

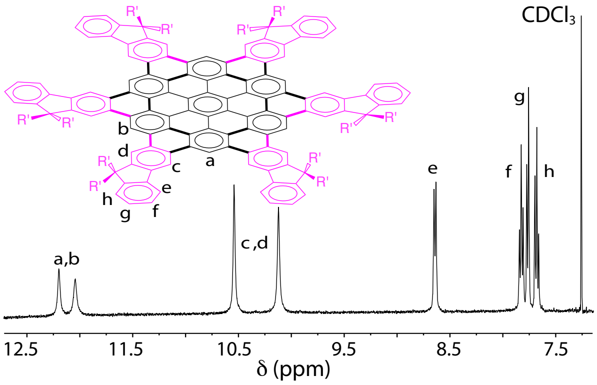

Figure 2. Partial ^1H NMR spectrum of 10 mM ***F*HBC** in $CDCl_3$ at 22 °C showing well-resolved resonances for equivalent aromatic protons (labeled).

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The UV-visible absorption spectrum of **_F_HBC** is compared with well-known $^{t\mathrm{Bu}}$**HBC**[6,17] in CH_2Cl_2 in Figure 3A. Each shows characteristic well-resolved vibronic structure; however, the significant expansion of the graphitic core in **_F_HBC**, leads to a large red shift (by ~90 nm) of its absorption bands (325, 451, and 486 nm; ε_{451} = 6.0 x 10^5 $M^{-1}cm^{-1}$) and increased molar absorptivity compared to $^{t\mathrm{Bu}}$**HBC** (230, 360, and 390 nm; ε_{360} = 1.9 x 10^5 $M^{-1}cm^{-1}$). Normalized emission spectra of **_F_HBC** and $^{t\mathrm{Bu}}$**HBC**, at the same concentrations, Figure 3B, show a red-shift of the emission bands of **_F_HBC** (582, 612 nm) compared to $^{t\mathrm{Bu}}$**HBC** (486, 520 nm). At higher concentrations, $^{t\mathrm{Bu}}$**HBC** shows a broad excimeric emission (at ~560 nm) indicating aggregate (i.e., dimer, and higher oligomers) formation.[17] In contrast, the emission spectrum of **_F_HBC** does not show the appearance of a new excimeric band (Figure S9 in the Supporting Information).

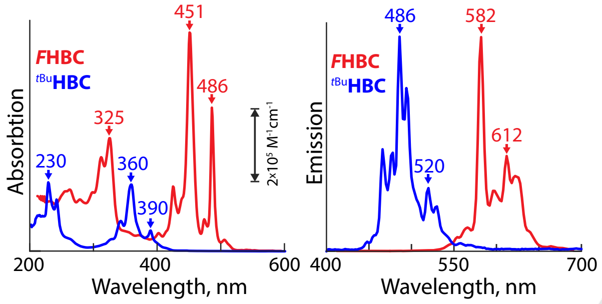


Figure 3. Comparison of the UV-vis absorption (10^{-6} M) and emission spectra of **_F_HBC** (red) and $^{t\mathrm{Bu}}$**HBC** (blue) in CH_2Cl_2 at 22 °C.

Electrochemical analysis showed that **_F_HBC** 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 4A). In contrast, $^{t\mathrm{Bu}}$**HBC** exhibits a single oxidation wave at 0.64 V vs Fc/Fc^+ in CH_2Cl_2 (see Figure S4 in the Supporting Information).[6,17] Moreover, the expansion of the size of the graphitic core in **_F_HBC** results in a significant lowering of the first oxidation potential (by ~240 mV) in comparison to $^{t\mathrm{Bu}}$**HBC**.

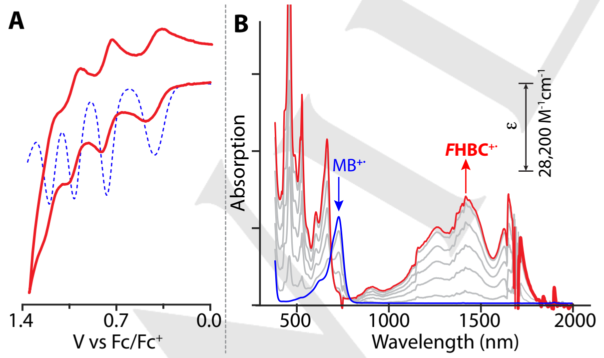


Figure 4. (A) Cyclic (solid red line) and square-wave (dashed blue line) voltammograms of **_F_HBC** (0.63 mM) in CH_2Cl_2 containing 0.2 M n-Bu_4NPF_6 at a scan rate of 200 mV s^{-1} and 22 °C. (B) The spectral changes observed upon the reduction of 5.5 x 10^{-6} M **MB**$^{+\bullet}SbCl_6^-$ by an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

The cation radical of **_F_HBC** was generated in solution via quantitative redox titrations using magic blue (i.e., **MB**$^{+\bullet}$ or tris-4-bromophenylamminium cation radical, E_{red} = 0.70 V vs Fc/Fc^+, λ_{max} = 728 nm, ε_{max} = 28,200 cm^{-1} M^{-1}) as an oxidant (Figure 4B).[18,19] The spectrum of **_F_HBC**$^{+\bullet}$ 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**$^{+\bullet}$ or **_F_HBC**$^{+\bullet}$/**_F_HBC** in solution. In contrast, $^{t\mathrm{Bu}}$**HBC**$^{+\bullet}$ readily forms a dimeric cation radical in solution, i.e. $^{t\mathrm{Bu}}$**HBC**$^{+\bullet}$ + $^{t\mathrm{Bu}}$**HBC** → [$^{t\mathrm{Bu}}$**HBC**]$_2^{+\bullet}$ with an equilibrium constant K = 1100 M^{-1} (see Figure S8 in Supporting Information). Expansion of the chromophoric size of **_F_HBC**$^{+\bullet}$ (λ_{max} = 460, 528, 664, 1261, and 1418 nm, ε_{1418} = 36,000 cm^{-1} M^{-1}) leads to an increased molar absorptivity (by a factor of ~6) when compared to $^{t\mathrm{Bu}}$**HBC**$^{+\bullet}$ (λ_{max} = 550, 836, 1570, 1740, 2100 nm, ε_{2100} = 5700 cm^{-1} M^{-1}), see Figure S7 in the Supporting Information.[6,17]

Summarizing, while $^{t\mathrm{Bu}}$**HBC** forms aggregates in neutral, excited, and cation radical states, as judged by, respectively, broad NMR spectra, observation of excimeric emission (at ~560 nm),[6,17] and observation of intervalence transition (at 1200 nm)[6,17] in its cation radical spectrum in the presence of neutral $^{t\mathrm{Bu}}$**HBC** (see Figures S8/S9 in the Supporting Information), such spectroscopic signatures of aggregation were completely absent in the case of **_F_HBC**. A cursory examination of the molecular structures of **_F_HBC** and $^{t\mathrm{Bu}}$**HBC** suggests that the narrow bay areas in **_F_HBC** do not afford arrangement of two hexyl chains in a staggered (sandwich-like) dimer. On the other hand, the relatively wider bay areas in $^{t\mathrm{Bu}}$**HBC** provide sufficient space for smaller methyl groups to be accommodated in a sandwich-like (staggered) dimeric structure (Figure 5A).

As a further probe of the lack of aggregation in **_F_HBC**, we performed (1-ns long) molecular dynamics (MD) simulations at ambient temperature, which showed that neutral $^{t\mathrm{Bu}}$**HBC** indeed forms a stable dimer (with the interplanar separations between the aromatic cores close to van der Waals contact (~3.5 Å), while in dimeric **_F_HBC** the pair of nanographenes lie at a separation of ~7.8 Å (Figure 5B-C). Indeed, the presence of the long hexyl chains in **_F_HBC** 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 5B/C). It is important to emphasize that access to **_F_HBC** 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.

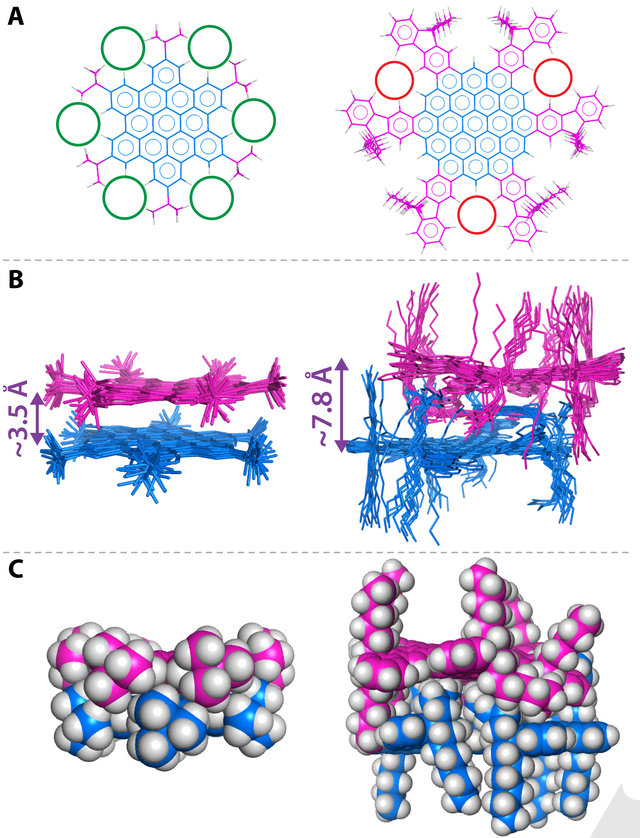
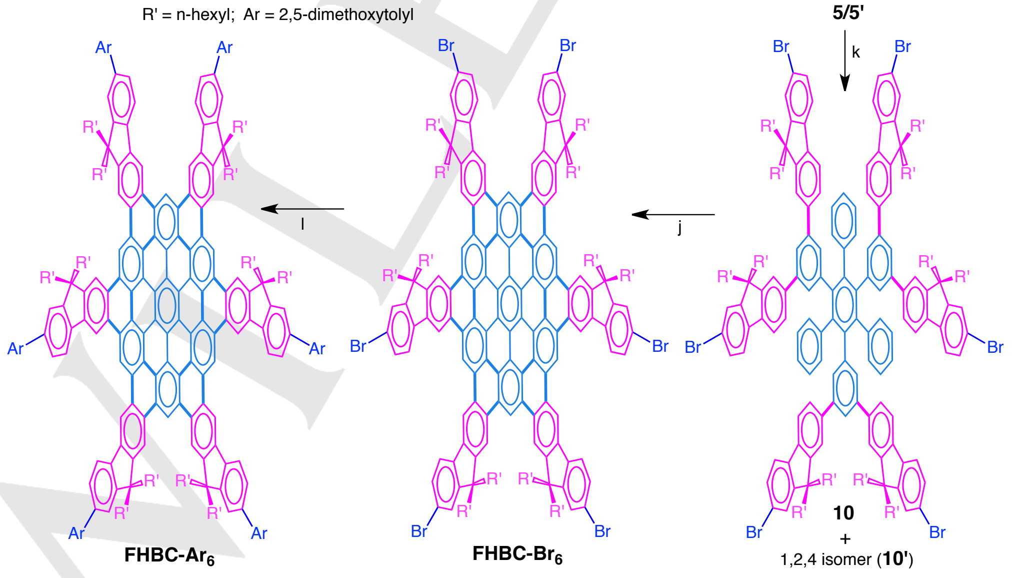


Figure 5. (A) Structures of ^{tBu}**HBC** and ***F*HBC** showing the different sizes of the bay areas with the aid of circles. (B) Superimposed structures of ^{tBu}**HBC** and ***F*HBC** dimers obtained from molecular dynamics simulations (see Supporting Information for details). (C) Space-filling representation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

Functionalizaton of ***F*HBC** at its vertices would require access to its hexabromo derivative **7** (Scheme 2). Initial attempts of a six-fold bromination of ***F*HBC** 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'** (i.e. the precursor to ***F*HBC**) in CH_2Cl_2 with bromine, in the presence of a catalytic amounts of iodine (in ~4h), 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 ***F*HBC**-Br_6 in 26% yield as a dark-red solid. The structure of ***F*HBC**-Br_6 was established by $^1H/^{13}C$ NMR spectroscopy and further confirmed by MALDI mass spectrometry (see Supporting Information section).

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

In conclusion, we have developed a highly soluble versatile **HBC** platform (i.e. ***F*HBC**) that contains an expanded graphitic core containing 19 Clar sextets and affords the ready introduction of multiple electro-active groups at its vertices. This ready tailoring of electro-active groups at vertices of ***F*HBC**, as demonstrated by a facile synthesis of a hexaarylbenzene derivative (i.e. ***F*HBC**-Ar_6), will allow the preparation of molecules with desirable electro-active 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]



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

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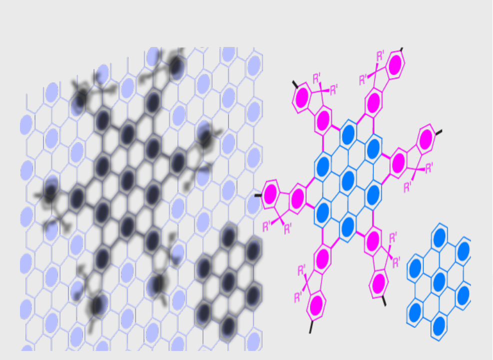
Keywords: HBC • graphitic nanocarbons • electron transfer

[1] M. Pfaff, P. Müller, P. Bockstaller, E. Müller, J. Subbiah, W. W. Wong, M. F. Klein, A. Kiersnowski, S. R. Puniredd, W. Pisula, A. Colsmann, D. Gerthsen, D. J. Jones, *ACS. Appl. Mater. Interfaces.* **2013**, *5*, 11554-11562.
[2] J. E. Anthony, *Chem. Rev.* **2006**, *106*, 5028-5048.
[3] Y. Segawa, H. Ito, K. Itami, *Nat. Rev. Mat.* **2016**, *1*, 15002.
[4] X. Li, W. Cai, J. An, S. Kim, J. Nah, D. Yang, R. Piner, A. Velamakanni, I. Jung, E. Tutuc, S. K. Banerjee, L. Colombo, R. S. Ruoff, *Science.* **2009**, *324*, 1312-1314.
[5] J. Wu, W. Pisula, K. Müllen, *Chem. Rev.* **2007**, *107*, 718-747.
[6] R. Rathore, C. L. Burns, *J. Org. Chem.* **2003**, *68*, 4071-4074.
[7] S. H. Wadumethrige, R. Rathore, *Org. Lett.* **2008**, *10*, 5139-5142.
[8] S. Ito, P. T. Herwig, T. Böhme, J. P. Rabe, W. Rettig, K. Müllen, *J. Am. Chem. Soc.* **2000**, *122*, 7698-7706.
[9] R. Rathore, C. L. Burns, *Org. Synth.* **2005**, 30-33.
[10] R. Rathore, C. L. Burns, I. A. Guzei, *J. Org. Chem.* **2004**, *69*, 1524-1530.
[11] T. Kojima, S. Hiraoka, *Org. Lett.* **2014**, *16*, 1024-1027.
[12] P. N. W. Baxter, *Chemistry.* **2003**, *9*, 5011-5022.
[13] R. Rathore, C. L. Burns, S. A. Abdelwahed, *Org. Lett.* **2004**, *6*, 1689-1692.
[14] The oxidative cyclodehydrogenation of the isomeric **5'** (i.e., 1,2,4 isomer) produces a complex mixture of products, which could not be separated by repeated chromatographic attempts and therefore their characterization was abandoned.
[15] K. L. Handoo, K. Gadru, *Current. Science.* **1986**, *55*, 920-922.
[16] R. Rathore, J. K. Kochi, *Acta. Chem. Scand.* **1998**, *52*, 114-130.
[17] V. J. Chebny, C. Gwengo, J. R. Gardinier, R. Rathore, *Tetrahedron. Letters.* **2008**, *49*, 4869-4872.
[18] M. R. Talipov, A. Boddeda, M. M. Hossain, R. Rathore, *J. Phys. Org. Chem.* **2015**, *29*, 227-233.
[19] M. R. Talipov, M. M. Hossain, A. Boddeda, K. Thakur, R. Rathore, *Org. Biomol. Chem.* **2016**, *14*, 2961-2968.
[20] The bromination of ***F*HBC** produced numerous brominated regioisomers whose structures could not be resolved.
[21] Z. Liu, S. P. Lau, F. Yan, *Chem. Soc. Rev.* **2015**, *44*, 5638-5679.
[22] A. Facchetti, *Chem. Mater.* **2010**, *23*, 733-758.

COMMUNICATION

Fluorene-HBC hybrid with large graphitic core is synthesized and found to be highly soluble and easily functionalized at its six vertices.



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