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SPECIAL ISSUE

Synthesis of Cyclopenta-HBCs and their Regioselective Chlorination During Oxidative Cyclodehydrogenation

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Abstract: Hexa-*peri*-hexabenzocoronenes with a bay-fused five-membered ring are synthesized from fluorenyl precursors. The key oxidative cyclodehydrogenation step is accompanied by regioselective chlorination that is enhanced by methylation at the cyclopenta-ring or increased reaction concentration. The CpHBC products undergo mild electrophilic aromatic bromination, without catalyst, to afford adducts suitable for π-extension by cross-coupling.

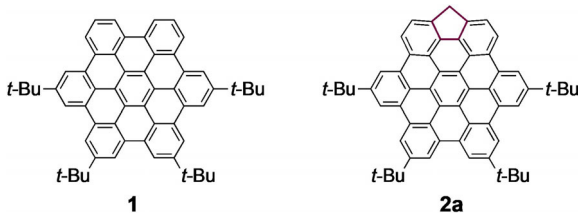
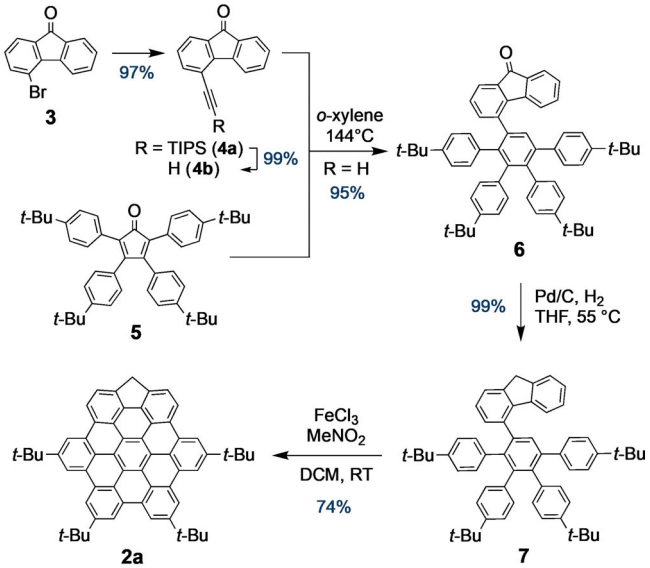


Figure 1. Tetra(*tert*-butyl)-hexa-*peri*-hexabenzoncoronene (HBC, **1**) and its cyclopenta-annulated derivative, CpHBC (**2a**).

Annulation of five-membered rings onto polycyclic aromatic hydrocarbons (PAHs) has proven to be an effective method to distort the electronic properties and structure of the aromatic system,[1] either by enforcing rigidity, as in the case of truxene,[2] or inducing curvature, as with the buckybowl sumanene.[3] Additionally, the benzylic methylene carbon offers a new reactive site, allowing for further modification, such as the formation of cyclopentadienyl-type ligands able to form metallocenes, of importance as Ziegler–Natta catalysts,[4] or for tuning of the electronic/supramolecular properties, such as the modification of polyfluorenes to yield more photochemically stable polymers.[5] Our group has reported the synthesis of cyclopentatriphenylene,[6] and as an expansion of this, our sights were set on annulation to the larger PAH, hexa-*peri*-hexabenzocoronene (HBC), an extensively studied, well-defined 'nanographene" which participates in robust π-stacking interactions[7] leading to long-range order as applied in organic electronics.[8] Although a cyclopentadiene bis-*ortho*-annulated by two HBCs with the trivial name "superfluorene" has been reported,[9] we endeavoured to "bridge" a bay region with a methylene group to give a cyclopenta-HBC (CpHBC, **2a**, Figure 1) as a step toward systematically modulating the structure and reactivity of the HBC core.

Although the five-membered ring could be incorporated following cyclodehydrogenation to the HBC core, we chose to have the five-membered ring present from the beginning by incorporating a fluorene moiety. To this end, 4-bromofluorenone (**3**) was the starting material chosen and was synthesized via an adapted method of Thiery et al.[10] After Sonogashira cross-coupling with TIPS-acetylene to give **4a**, then deprotection with TBAF, the alkyne **4b** was obtained (Scheme 1). Alkyne **4b** was subjected to a Diels–Alder cycloaddition with cyclopentadienone **5** to yield the central arene ring. The ^{1}H NMR spectrum of **6** contains several regions of broad signals attributed to the restricted rotation of the fluorenonyl moiety. A distinct singlet at 7.52 ppm assigned to the single proton of the central ring was indicative a successful reaction. Fluorenone **6** was hydrogenated efficiently to afford fluorenylbenzene **7** which exhibited a highly convoluted ^{1}H NMR spectrum with a number of broad signals, similar to those of **6**; the appearance of two inequivalent, geminally-coupled benzylic methylene protons at *ca* 3.8 ppm is consistent with restricted rotation of the fluorenyl group at room temperature.

A key step in the synthesis of HBCs is cyclodehydrogenation of an oligophenylene precursor such as a hexaphenylbenzene,



Scheme 1. Synthesis of fluorenyl precursors and CpHBC (**2a**).

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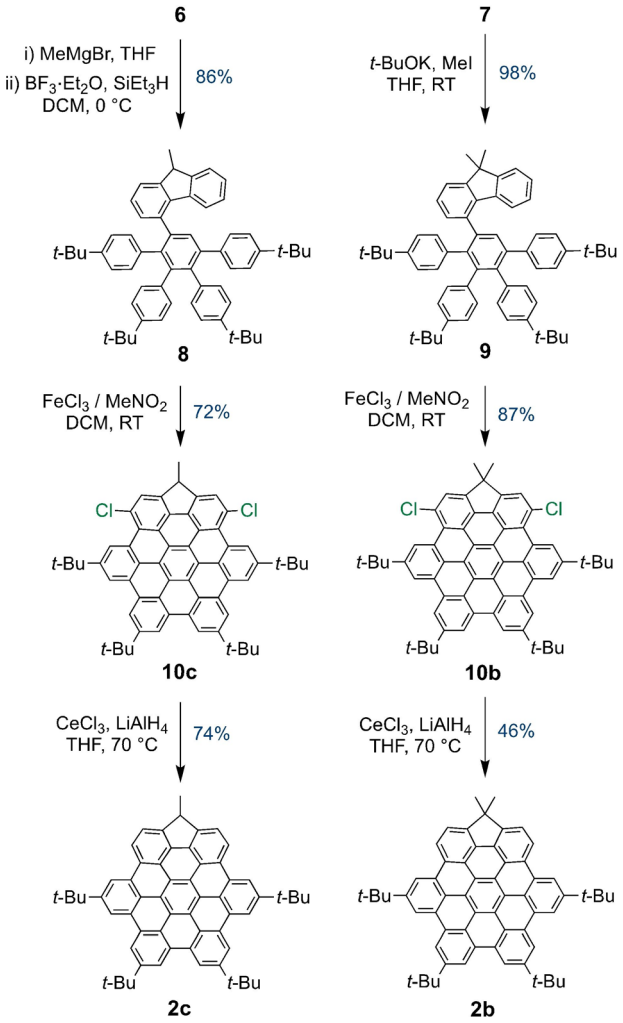
and is sometimes complicated by rearrangements,[11] functional group transformations[11,12] or incomplete C–C bond formation.[13] A preferred reagent for such transformations is anhydrous $FeCl_3$ due to its demonstrated effectiveness and ease of handling. Accordingly, treatment of **7** with 24 equiv of anhydrous $FeCl_3$ in Scholl-like cyclodehydrogenation conditions[14] initially yielded a mixture of partially-fused compounds as identified by MALDI-TOF MS. An increase to 36 equiv of $FeCl_3$ and doubling of the reaction time to 1 h was found to afford CpHBC **2a** in good yields as an orange powder that was poorly soluble in most organic solvents. Purity was supported by MALDI-TOF MS (albeit with trace amounts of an inseparable dimeric side-product) and with a vast simplification of the ^{1}H NMR spectrum, displaying six distinct aromatic environments downfield from the broad, convoluted spectrum of the precursor. Of particular note are two doublets assigned to vicinally-coupled protons on the rings bridged by the methylene group. In order to obtain a more soluble CpHBC, the methylene bridge was alkylated to impose steric hindrance in an effort to reduce the aggregation common in HBCs. The benzylic site was mono- and di-methylated in high yield using variations on literature methods, starting from **6** or **7**, respectively (Scheme 2).[15]

Dimethylated **9** was subjected to cyclodehydrogenation with 36 equiv of $FeCl_3$ as used successfully for the non-alkylated precursor **7**. A yellow-orange powder with significantly increased solubility in chloroform was isolated. ^{1}H NMR revealed a single product with a spectrum consisting of 5 aromatic singlets, as opposed to the expected 4 singlets and 2 doublets. Corroboration with a MALDI-TOF spectrum revealed that along with the formation of 6 new C–C bonds to generate the CpHBC core, site selective, quantitative dichlorination was also occurring. Although chlorinated by-products are known to occur during cyclodehydrogenation,[16] to our knowledge this is the first instance of regioselective, quantitative chlorination on an HBC with $FeCl_3$. Chlorination was thought to be occurring at what were the 2- and 7-positions of fluorene; this was unequivocally confirmed by X-ray crystallographic analysis of a single crystal of **10b** (Figure 2).

Repetition of the cyclodehydrogenation did not always result in solely dichlorinated product, with a monochlorinated species sometimes present as observed by NMR and MS. Furthermore, under similar conditions the mono-methylated analogue **8** cyclodehydrogenated to an inseparable mixture of fully fused, non- and mono-chlorinated products. The capricious nature of the cyclodehydrogenation led us to carefully investigate the effect of stoichiometry and concentration on product distribution. Upon increasing the $FeCl_3$ to 60 equiv, dichlorinated **10b** and **10c** were able to be obtained cleanly. In an attempt to minimise chlorination, concentration effects were investigated by diluting the $FeCl_3$ with a fixed stoichiometry (Table 1). Significant amounts of chlorinated products were obtained at all concentrations up to the point where no reaction occurred at high dilution (entry 1). Accordingly, it became apparent that in the case of the mono- and dimethyl-substituted CpHBC compounds, the only way to access non-chlorinated products was to remove the chloro groups following cyclodehydrogenation. This was successfully achieved using $CeCl_3$/$LiAlH_4$, based on the general method of Imamoto et al.,[17] thereby allowing the isolation of halogen-free CpHBCs **2b** and **2c** in 40–53% yield for the two steps (cyclodehydroge-



Scheme 2. Cyclopenta-ring methylation, cyclodehydrogenation to CpHBCs and their dechlorination.

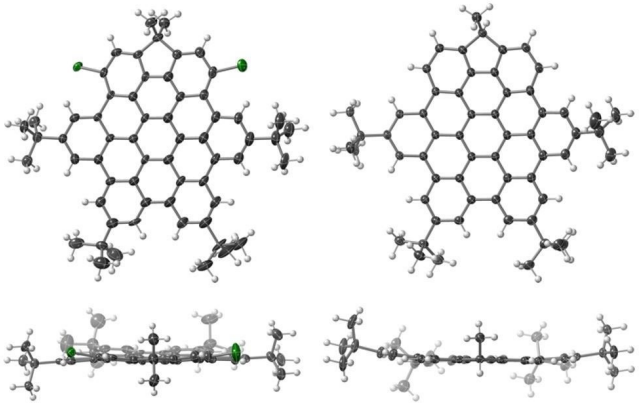


Figure 2. X-ray crystal structure diagrams (50% displacement ellipsoids) of dichloro-CpHBC **10b** (left) and CpHBC **2c** (right).

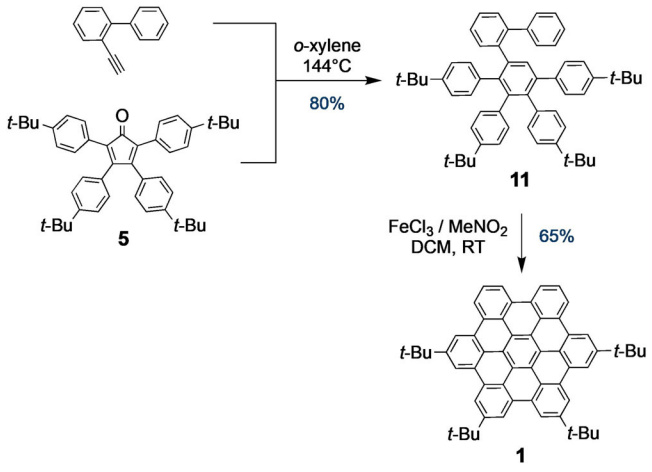
Table 1. Concentration of $FeCl_3$ used in the cyclodehydrogenation of **9** and the relative amounts of the products formed.[a]

Entry	$[FeCl_3]$ 10^{-3} mol L^{-1}	Relative Yield [%] **2b**	**2b"**[b]	**10b**
1	5.6	0	0	0
2	28.6	80	20	0
3	54.6	70	30	0
4	152.0	0	0	100

[a] Calculated by relative intensity in the ^{1}H NMR spectrum of the crude mixture. 24 equiv. of $FeCl_3$ used in all reactions, *ca* 0.0125 mmol **9**, 30 min, RT. [b] **2b"** is the monochlorinated HBC product from the reaction of **9**.

nation, then dechlorination) (Scheme 2; crystal structure of **2c**, Figure 2). These compounds were found to slowly re-chlorinate when left in chloroform over days, indicative of their high reactivity.

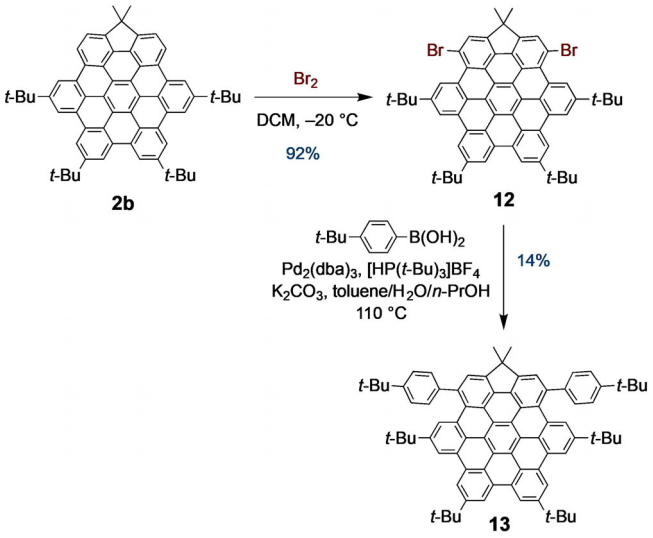
Clearly the methylene bridge alkylation is having an substantial impact on the degree of chlorination during cyclodehydrogenation, with the more electron-rich dimethylated **9** more susceptible than the non-methylated **7**. Furthermore, the site of chlorination is consistent with electrophilic aromatic chlorination of the parent fluorene. To further explore the effect of the methylene bridge, the related non-bridged tetra(tert-butyl)HBC **1** was synthesised from the precursor (2-biphenyl)tetra(4-*tert*-butylphenyl)benzene **11** (Scheme 3). Despite the use



Scheme 3. Synthesis of tetra(*tert*-butyl)HBC **1**.

$FeCl_3$ with the same stoichiometry and reaction concentrations that resulted in cyclodehydrogenation with chlorination for the fluorenyl precursors, the HBC formed in good yield without chlorination of the core (^{1}H NMR, MS) but displaying poor solubility like **2a**.

To examine the reactivity of CpHBC **2b**, electrophilic aromatic substitution with elemental bromine was investigated. At room temperature with 2 equiv of bromine, a mixture of brominated products were obtained, including a tri-brominated adduct, within 10 minutes and without the addition of catalyst. By reducing the temperature to −20 °C, selective di-bromination was achieved, even with an excess of bromine (Scheme 4). ^{1}H NMR and supporting 2D experiments support dibromination at the 1 and 5 sites that were chlorinated during cyclodehydrogenation. Utilisation of this introduced functionality was



Scheme 4. Bromination of the CpHBC and subsequent Suzuki cross-coupling at the bromo sites.

demonstrated through a Suzuki cross-coupling with 4-*tert*-butylphenylboronic acid in modest isolated yields of **13**. In an attempt to annulate the pendant phenylene groups to HBC core to give an extended PAH, $FeCl_3$ cylodehydrogenation of **13** was undertaken; however, mostly starting material was recovered from the reaction mixture. Future work will look at alternative reagents and/or substituents to effect cyclodehydrogenation.

The incorporation of a cyclopenta-ring at the periphery of HBC is expected to distort the geometry of the aromatic core. The X-ray crystal structures of **10b** and **2c** (Figure 2 and SI) reveal that, although the core shows a deviation from planarity, the curvature is no greater than that seen for other all-benzenoid HBCs, such as HBC(*t*Bu)$_6$.[18] However, the in-plane geometrical parameters in the region adjacent to the cyclopenta-ring are distorted: analysis of **2c** shows that the peripheral bonds are mostly elongated and the internal bonds shortened. Similarly, bond angles involving the benzenoid rings of **2c** are also distorted in this region when compared to HBC(*t*Bu)$_6$, becoming less so toward the centre of the core. Both **10b** and **2c** crystallise as offset dimer pairs.

HBC's strong optical absorption and emission, as well as its multiple redox states[7b,8b,18,19] were probed for a range of CpHBCs synthesised and compared to the HBC analogue **1**. Analysis of the cyclic voltammetric data (Table 2) shows two pseudo-reversible oxidations in the range of 0.9–1.3 V (vs. SCE), with **1** and **2a** exhibiting broadened voltammograms due to low solubility and electrode precipitation processes. The oxidation potential was found to increase moving from the methylated HBCs **2a**–**c** to their chlorinated derivatives, consistent

Table 2. Cyclic voltammetry data for CpHBCs and related compounds.[a]

Compound	$E_{1/2}^1$ [V]	Δ^1 [V]	$E_{1/2}^2$ [V]	Δ^2 [V]
2a	0.91	0.06	1.26	0.10
2b	0.99	0.06	1.13	0.06
2c	0.86	0.10	1.11	0.06
10b	1.05	0.08	1.21	0.13
10c	0.95	0.06	1.25	0.08
1	1.12	0.08		

[a] Measured in 0.1 M Bu_4NPF_6 in DCM at 100 mV s^{-1}, referenced against decamethylferrocene/decamethylferrocenium (V relative to SCE).

with the electron-withdrawing nature of the Cl substituents. Greater bridge alkylation is expected to decrease the potential as more methyl groups were added. While this is the general trend, the di-methylated **2b** exhibits anomalous behaviour which may relate to its lower tendency to aggregate in solution and is under further investigation. No reduction processes were observed out to −1.8 V for any of the compounds measured.

Fluorene and fluorene derivatives are known for their efficient emissive behaviour leading to application as fluorophores in OLED devices;[5,20] thus, incorporation into a HBC makes the fluorene-based CpHBCs of interest for their optical properties. Accordingly, the absorption and emission spectra of **2a–c**, **10b** and **10c** were surveyed, displaying strong absorption and emission bands consistent with those reported for HBCs.[9] CpHBCs **2a–c** exhibit absorption maxima at 356 nm with molar absorptivity increasing as additional methyl groups were added, presumably through increasing steric repulsion between molecules, resulting in a decreasing degree of aggregation occurring in solution (Table 3, Figure 3). Upon incorporation of chloro groups, there was a slight red-shift of 6 nm in the absorption and emission when compared to the non-halogenated **2b** and **2c**. The emission spectra for all CpHBCs are similar to that of **1**, albeit with an enhancement of the 0-0 transition which becomes more allowed with a reduction in symmetry.

In summary, a synthetic methodology to hexa-*peri*-hexabenzocoronenes with a bay-annulated five-membered ring has been developed. Methylation of the five-membered ring was found to facilitate selective chlorination during the key oxidative cyclodehydrogenation step; chlorination can be further augmented by utilising high reaction concentrations (but not longer times). The optical profile of the system was found to be similar to that of an alkyl HBC, albeit with a pronounced transition in the emission spectrum. Further studies on the utilisation of the reactive sites for electrophilic substitution providing scope to access new PAH architectures and tune the physical properties are currently underway.

Table 3. UV-visible absorption and emission data for CpHBCs and **1**.[a]

Compound	Absorption λ_{max} [nm]	ε [10^3 L mol^{-1} cm^{-1}]	Emission λ_{max} [nm]
1	356	177	464
2a	356	89	463
2b	356	222	463
2c	356	179	463
10b	362	174	469
10c	362	167	469

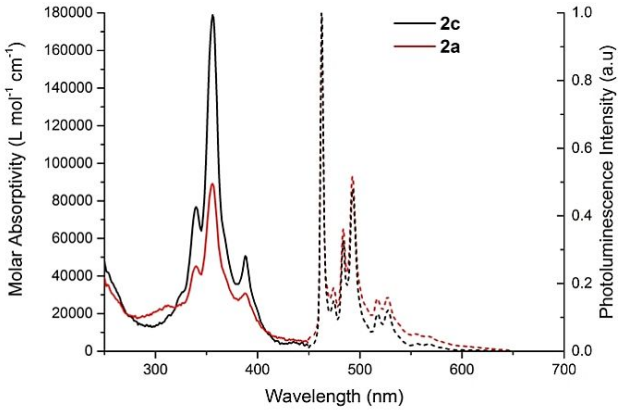


Figure 3. Representative absorption (solid line) and emission (dashed line) spectra of **2a** and **2c** (solvent: dichloromethane).

Experimental Section

Synthetic procedures and compound data, ^1H and ^{13}C NMR spectra, MALDI-TOF spectra, details of single-crystal X-ray diffraction data collection/refinement along with additional crystallographic plots and selected structural parameters, UV-visible absorption/emission spectra, and cyclic voltammetry traces are provided in the Supporting Information. CCDC 1883892–1883893 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.

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Conflict of interest

The authors declare no conflict of interest.

Keywords: annulation · aromatic substitution · fused-ring systems · hexabenzocoronene · oxidative cyclodehydrogenation

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COMMUNICATION

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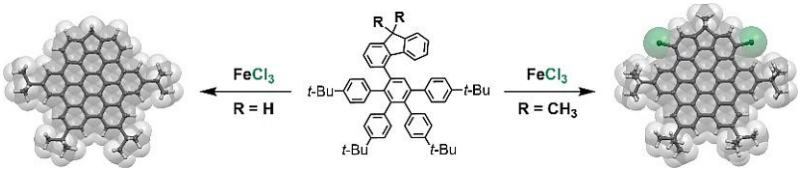
Synthesis of Cyclopenta-HBCs and their Regioselective Chlorination During Oxidative Cyclodehydrogenation



At bay: Hexa-*peri*-hexabenzocoronenes (HBCs) with a bay-fused five-membered ring are synthesized from fluorenyl precursors. Oxidative cyclodehydrogenation with $FeCl_3$ is accompanied by regioselective chlorination, dependent on cyclopenta-ring methylation and reagent concentration. The CpHBC products undergo mild aromatic bromination to afford adducts suitable for extension of the carbon framework via cross-coupling.