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Synthesis and electronic properties of *iso*-alkyl substituted hexa-*peri*-hexabenzocoronenes (HBC's) from a versatile new HBC synthon, *hexakis*(4-acetylphenyl)benzene

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ABSTRACT

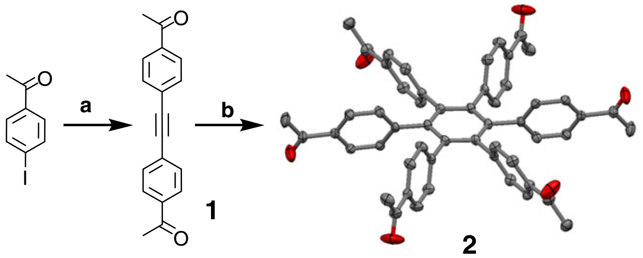
Simple syntheses of a variety of soluble hexa-*peri*-hexabenzocoronenes are accomplished using an easily prepared *hexakis*(4-acetylphenyl)benzene as a common precursor. The concentration-dependent emissions of various HBC's in solution indicate that they undergo extensive aggregation despite the presence of bulky (peripheral) isoalkyl and *tert*-butyl groups. The various planar HBC's undergo reversible electrochemical oxidations and form stable monomeric cation-radical salts in solution.

Polycyclic aromatic hydrocarbons (PAH) hold potential as building blocks for the preparation of electro-active materials for the practical applications in the emerging areas of molecular electronics and nanotechnology.[1] Although Clar[2] in his classical papers in the early 1960s suggested that 'fully benzenoid' hexa-*peri*-hexabenzocoronene (HBC) should possess exceptional thermal and photochemical stability, the study of this novel PAH was not vigorously pursued owing to its insolubility in most organic solvents. Recently, Mullen and co-workers have shown in a series of publications[3] that the solubility problem is overcome by attaching the long alkyl chains and/or bulky *tert*-butyl groups in the *para* positions of hexa-*peri*-hexabenzocoronene and its derivatives. Despite numerous ingenious designs of novel hexa-*peri*-hexabenzocoronenes using multi-step syntheses,[3,4] need still remains for the development of simple, rational synthetic approaches which will allow easy access to a wide variety of functionalized hexa-*peri*-hexabenzocoronenes (HBC) in order to realize their full potential in materials' applications.

Our continued interest in HBC framework[5,6] recently led us to a practical one-pot synthesis of a soluble HBC, which is substituted in the *para* positions with bulky *tert*-butyl groups, from readily available hexaphenylbenzene in high yield.[5] We observed concentration dependent emission for this derivative, a likely result of self association. In order to further probe the self-association characteristics of HBC's framework, we required a series of derivatives with different solubilizing groups other than *tert*-butyls. Accordingly, we now describe a synthesis of the *hitherto* unknown *hexakis*(4-acetylphenyl)benzene (**2**), which can serve as a versatile precursor for the preparation of a variety of HBC's by exploiting the myriad of various transformations of the acetyl group. The synthetic utility of **2** is first demonstrated herein by the preparation of various *iso*-alkyl substituted HBC's (isopropyl, isobutyl, and isooctyl were chosen as solubilizing groups). The HBC derivatives obtained herein were characterized by $^1H/^{13}C$ NMR spectroscopy and mass spectrometry, and their redox and optical properties were measured by electrochemistry, UV–vis, and emission spectroscopy.

The common precursor, that is, *hexakis*(4-acetylphenyl)-benzene (**2**), was easily synthesized by a $Co_2(CO)_8$-catalyzed trimerization of diarylacetylene **1** in refluxing dioxane, which in turn was prepared from a modified Sonogashira coupling[7] of the commercially available 4-iodoacetophenone (see Supplementary data for the experimental details). The identity of **2** was established by $^1H/^{13}C$ NMR spectroscopy, mass spectrometry, and was further confirmed by X-ray crystallography (see Scheme 1).

The X-ray structure of **2** comprises of two symmetrically independent molecules, which are positioned at their respective crystallographic inversion centers. Both molecules showed a similar



Scheme 1. Reagents and conditions: (a) benzene/DBU/H_2O/$(PPh_3)_2PdCl_2$/CuI/Me_3SiCCH, reflux; (b) $Co_2(CO)_8$/dioxane/reflux. X-ray structure of **2** showing 'three-up, three-down' configuration of carbonyl oxygens.

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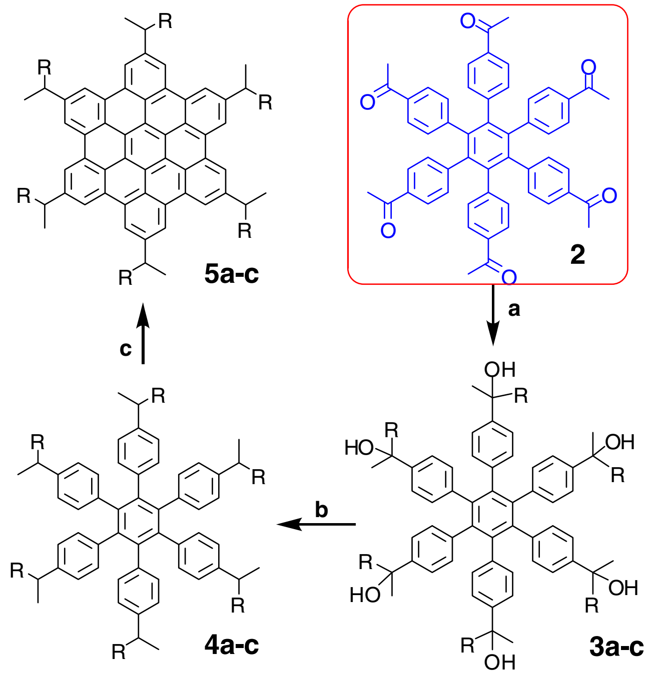
propeller-shaped arrangement of the peripheral aryl groups with the dihedral angles between the plane of the central and peripheral aryl rings varying in the range of 66–87°.[8] Interestingly, both independent molecules adopt a 'three-up, three-down' configuration with carbonyl oxygens of three neighbouring acetyl groups oriented toward the one face of the central phenyl group. The unusual 'three-up, three-down' configurational preference of **2** in the crystal lattice most likely arises due to the intermolecular C–H···O contacts among the molecules in the perpendicular layers (i.e., O2···H_{66A}–C_{66} with O···H distance 2.44 Å and O–H–C angle 145°; and O_6···H_{26A}–C_{26} with O···H 2.35 Å and O···H–C angle of 148°, see Supplementary data for the numbering schemes of the atoms in the two independent molecules of **2**).

Having the multi-gram quantities of hexaacetyl derivative **2** at hand, we next examined its conversion to the precursors for the preparation of soluble HBC's as follows. Thus, a treatment of **2** with excess methylmagnesium chloride (10 equiv) in tetrahydrofuran for 12 h followed by a standard aqueous workup afforded the hexa-alcohol **3a** in 96% yield. The crude **3a** was reduced by hydrogenation in the presence of catalytic amounts of methanesulfonic acid and Pd/C (10%) in ethyl acetate to a hydrogen pressure of 50 psi for 6 h to afford the *hexakis*(4-isopropylphenyl)benzene **4a** in nearly quantitative yield. Similarly, **4b** (from ethylmagnesium bromide) and **4c** (from hexylmagnesium bromide) were obtained via a similar 2-step route as outlined in Scheme 2.

The *hexakis*(4-alkylphenyl)benzenes **4a–c** were easily converted to the corresponding HBC's (i.e., **5a–c**) via oxidative cyclodehydrogenation using excess $FeCl_3$ (18 equiv) in a 2:1 mixture of dichloromethane/nitromethane at 0 °C under a constant flow of argon (see Scheme 1). Various HBC's were purified by a simple filtration through a short pad of silica gel and were characterized by $^1H/^{13}C$ NMR spectroscopy and mass spectrometry. For a detailed procedure and $^1H/^{13}C$ NMR spectra of **5a–c**, see the Supplementary data.

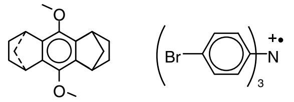
The electron-donor strengths of various HBC's were evaluated by electrochemical oxidation at a platinum electrode as 2×10^{-3} M solutions in dichloromethane containing 0.1 M tetra-*n*-butylammonium hexafluoro-phosphate as the supporting electrolyte. The reversible cyclic voltammograms (CV) obtained at scan rates between 25 and 400 mV s^{-1} (see Fig. 1) showed anodic/cathodic peak current ratios of $i_a/i_c = 1$ (theoretical) at ambient temperatures. The calibration of the CV peaks of **5a–c** with ferrocene as an internal standard provided the reversible oxidation potentials $E_{ox1} = 0.97$, 0.98 and 0.98 V versus SCE, respectively (see Fig. S1 and S2 for the cyclic voltammograms of **5b** and **5c** in the Supplementary data). Expectedly, the oxidation potentials (E_{ox}) of **5a–d** were rather invariant upon changing the peripheral alkyl groups from isopropyl to isobutyl to isooctyl to *tert*-butyl[5] (**5d**, $E_{ox} = 0.98$ V vs SCE).



(**a**) R = methyl, (**b**) R = ethyl, (**c**) R = hexyl

Scheme 2. Reagents and conditions: (a) THF/RMgBr or RMgCl; (b) H^+/H_2 50 psi/10% Pd–C; (c) $FeCl_3/CH_2Cl_2/CH_3NO_2$.

The reversibility of 1-electron oxidation by cyclic voltammetry of various HBC's prompted us to evaluate the stability of their cation-radical salts using stable triarylamine (**MB**)[9] and/or a hydroquinone ether (**MA**)[10] cation-radical salt as robust 1-electron oxidants.



$MA^{+\bullet}$ $MB^{+\bullet}$

E^{o}_{red} 1.11 1.15 (V *vs.* SCE)

Figure 2 shows the spectral changes attendant upon oxidation of **5a** to its cation radical $\mathbf{5a}^{\cdot+}$ by incremental addition of $\mathbf{MB}^{\cdot+}$ $SbCl_6^-$ [λ_{max} (log ε) = 728 nm (4.45)] in dichloromethane at 22 °C. The well-defined isosbestic points at $\lambda = 585$ and 768 nm and the stoichiometry of the spectral changes (disappearance of bands for $\mathbf{MB}^{\cdot+}$ or the appearance of those for $\mathbf{5a}^{\cdot+}$, inset of Fig. 2) established an uncluttered one-electron transfer.

Furthermore, a plot of the depletion of $MB^{\cdot+}$ and formation of $\mathbf{5a}^{\cdot+}$ against the increments of added neutral **5a** (inset Fig. 2) established that $\mathbf{MB}^{\cdot+}$ was completely consumed after the addition of 1 equiv of **5a**; the resulting highly structured absorption spectrum of $\mathbf{5a}^{\cdot+}$ [λ_{max} (log ε) = 551, 753 (sh), 810 (sh), 840 (3.93)] remained unchanged upon further addition of neutral **5a** (i.e., Eq. 1).

$$\mathbf{5a} + \mathbf{MB}^{\cdot+} \rightarrow \mathbf{MB} + \mathbf{5a}^{\cdot+} \qquad (1)$$

Furthermore, the cation-radical absorption spectra of $\mathbf{5a}^{\cdot+}$, $\mathbf{5b}^{\cdot+}$ [λ_{max} (log ε) = 551, 753 (sh), 810 (sh), 840 (3.92)], $\mathbf{5c}^{\cdot+}$ [λ_{max} (log ε) = 551, 753 (sh), 810 (sh), 840 (3.99)], as well as of the corresponding *tert*-butyl derivative **5d**[5] were similar irrespective the oxidant used, that is, $\mathbf{MB}^{\cdot+}$ or $\mathbf{MA}^{\cdot+}$.

The observed spectra of the cation radicals of **5a–d** were readily assigned to the corresponding monomeric cation radicals by comparison to the calculated spectrum of hexamethyl-HBC cation radical.[6] The HBC cation radicals did not show any sign of aggregation in solution, such as the formation of dimeric cation radicals

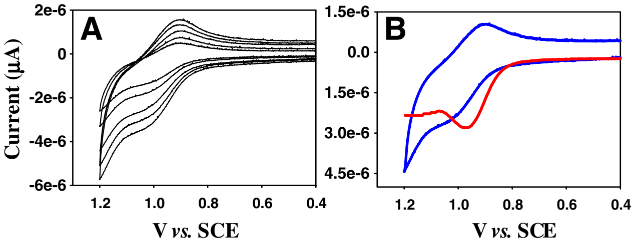


Figure 1. (A) Representative cyclic voltammograms of 2×10^{-3} M **5a** in CH_2Cl_2 containing 0.1 M $(n\text{-Bu})_4NPF_6$ at 22 °C at scan rates between 25 and 400 mV s^{-1}. (B) A cyclic voltammogram (blue) and the corresponding square-wave voltammogram (red) of **5a** at a scan rate of $v = 200$ mV s^{-1}.

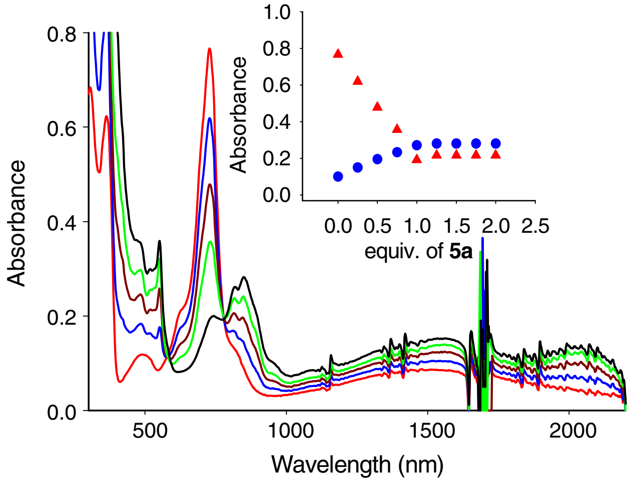


Figure 2. Spectral changes upon the reduction of 2.6×10^{-5} M $\mathbf{MB}^{\cdot+}$ (red line) by incremental addition of 1.0×10^{-3} M **5a** to its radical cation (black line) in CH_2Cl_2 at 22 °C. Inset: A plot of depletion of absorbance of $\mathbf{MB}^{\cdot+}$ (red triangles, at 728 nm) and an increase of the absorbance of $\mathbf{5a}^{\cdot+}$ (blue circles, at 840 nm) against the equivalent of added neutral **5a**.

resulting from the cofacial stacking of $\mathbf{5}^{+}$ with neutral **5**, as judged by the singular absence of a new charge-resonance transition[11] even in the presence of a large excess of the corresponding neutral HBC. It is also noted that various HBC cation radicals did not show any change in their absorption spectra even when the concentration was increased by 10-fold.

The excited state emission spectra of the hexa-substituted HBC's are concentration dependent, exemplified by the hexaisopropyl derivative **5a** (Fig. 3). In dilute solution (10^{-6} M), **5a** showed a structured cyan [1931 CIE (*XYZ*) coordinates: 0.127, 0.366, 0.507][12] emission with the characteristic emission band at $\lambda_{max} = 488$ nm. At higher concentrations (10^{-5} to $\sim 10^{-3}$ M), lower energy emission bands centered near 520 nm and 558 nm, tentatively assigned as excimer-based, grow in intensity at the expense of the higher energy (488 nm) band, with an apparent isosbestic point at 500 nm. Concomitant with the change in band intensities in this concentration range, the emission changes from cyan (10^{-6} M) to yellow-green [10^{-3} M, 1931 CIE (*XYZ*) coordinates: 0.299, 0.580, 0.121]. In the solid state, HBC's **5a–d** give yellow-orange emission [1931 CIE (*XYZ*) coordinates: 0.405, 0.563, 0.032]. For **5a**, this emission occurs as a broad band ($\lambda_{max} = 544$ nm) centered near 558 nm with detectable fine structure. The solubility limit for these hexa-substituted **HBC's** regardless of the substitution pattern described in this work is between 10^{-4} M and 10^{-3} M. Thus, the apparent discrepancy between the yellow-green color from calculated CIE coordinates of the '10^{-3} M' sample and the yellow-orange color of the sample in the right inset of Figure 3 is due, in part, to the heterogeneous nature of the mixture, that is, extensive aggregation of HBC's in solution at higher concentrations.

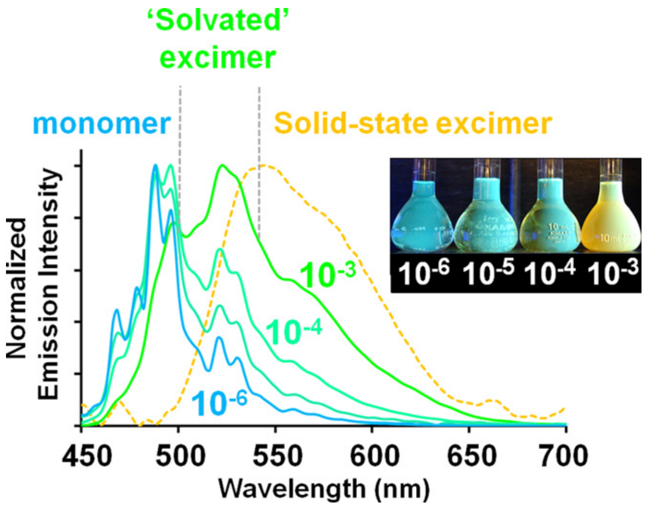


Figure 3. Concentration-dependent emission spectra of **5a** in CH_2Cl_2 at 22 °C. The emission spectrum of **5a** in solid state is shown as yellow line.

The observation of concentration dependent emission of various HBC's is most likely due to aggregation resulting in excimer-based emissions, similar to those of other polyaromatic hydrocarbons such as pyrene (Supplementary data).[13] The tentative assignment of *two* lower energy excimer-based emission bands (∼520 and 588 nm) likely reflects the different 'solvation' environments around dimers when in solution versus the solid state. The bulkier substituents give rise to powder excimer emissions that are more closely energy-matched to their solution-based excimer band. We cannot exclude the possibility that in concentrated solution simple dimeric species (higher energy excimer emission) predominate over higher-order aggregates (lower energy excimer emission) as might likely be found in the solid-state powder. However, the crystal structure of *tert*-butyl derivative **5d**, which showed similar emission characteristics to those described for **5a**, has been reported[14] which shows a herringbone arrangement of slipped (cofacial) dimers (two molecules related by inversion symmetry). The perpendicular distance between mean planes of the aromatic ring systems in the dimers is ∼3.69 Å, the centroid–centroid distance is 4.98 Å, and the slip angle, β, is 44.5°; all these values are outside the accepted ranges for an effective π–π interaction in the ground state.[15] There are two mutual CH $\cdots$ π interactions involving the hydrogen donor from a *tert*-butyl substituent on one molecule and the HBC core of a neighbouring molecule with a distance and angle of 2.69 Å, 175.7°.[16] Owing to the paucity of structural information on **HBC** derivatives, it is unclear whether more extensive slipped stacking arrangements (such as trimers or higher-order aggregates) can exist in the solid state. Similar low-energy dimeric arrangements were also found from PM3 geometry optimization for the dimers, each of the hexa-substituted HBC's, exemplified for **5a** in Figure 4.

In each case, the offset or slipped arrangement with C_i symmetry was energetically more favorable than the aligned, cofacially-arranged ($\beta = 0°$) D_{6d} symmetric dimer, as expected from the repulsion of π-electron clouds. In the slipped arrangement, the methyl groups of peripheral substituents penetrate into the

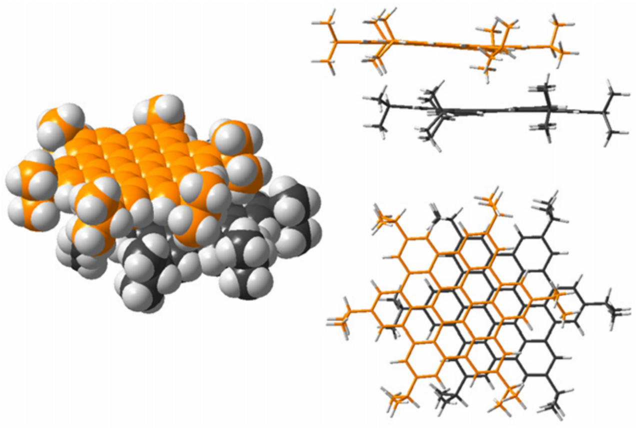


Figure 4. PM3 geometry optimized structure of **5a** dimer.

aromatic ring to allow favorable CH–π interactions. It is unclear whether CH–π interactions might also be able to mediate this electronic interaction, clearly a hypothesis warranting further investigation.

In summary, we have developed a versatile synthesis of soluble hexa-*peri*-hexabenzocoronenes from an easily synthesized *hexakis*(4-acetylphenyl)benzene as a common precursor. Various HBC's undergo reversible electro-chemical oxidations and form stable monomeric cation radicals in solution. The emission spectra of the hexa-substituted HBC's are concentration-dependent and show an excimer-based emission both in solution at higher concentrations and in solid state. We are continuing attempts to obtain suitable single crystals of various HBC cation radicals and their co-crystals with various neutral aromatic donors such as substituted benzenes, naphthalenes, triphenylenes, and pyrenes for X-ray crystallographic studies and evaluation of their solid-state properties.

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Supplementary data

Synthetic details, spectral data, and NMR spectra of various compounds in Schemes 1 and 2. Crystallographic data (excluding structure factors) for **2** have been deposited with the Cambridge Crystallographic Data Centre CCDC-686846. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK, (fax: +44-(0)1223-336033 or e-mail: deposit@ccdc.cam.ac.uk). Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2008.06.005.

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