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### COMMUNICATION

#### Synthesis of electron-poor hexa-peri-hexabenzocoronenes†‡

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The oxidative cyclodehydrogenation of electron-poor arenes was achieved using DDQ–CF<sub>3</sub>SO<sub>3</sub>H resulting in hexa-*peri*-hexabenzocoronenes with electron withdrawing Br, F and CF<sub>3</sub> groups. This method will lead to their expansion into a new class of electron transport materials.

Hexa-peri-hexabenzocoronene (HBC) is a six-fold symmetric polycyclic aromatic hydrocarbon that has been extensively studied in the literature.<sup>1</sup> As a result of strong  $\pi$ - $\pi$  stacking interactions, unsubstituted HBC has very poor solubility in common organic solvents. Functionalisation of the HBC core improves solution processability and has also been used to tune structural and photophysical properties. Appropriate functional groups, such as alkyl or aryl, on the periphery of the HBC core have led to liquid crystalline systems as well as assembly into macroscopic nanotube arrays.<sup>2</sup> Chromophores and various electroactive substituents have also been tethered to the HBC molecule leading to applications as sensor materials<sup>3</sup> and light harvesting semiconductors in organic solar cells.<sup>4</sup> While the inclusion of substituents results in changes to the properties of the material, the electronic property of the HBC core often remains largely the same. The HBC molecule is moderately electron rich and displays hole transporting (p-type) semiconducting property in organic electronic devices. Hole mobility of up to  $3 \times 10^{-2}$  cm<sup>2</sup> V s<sup>-1</sup> has been measured in organic field effect transistor (OFET) devices with vacuum deposited unsubstituted HBC films.<sup>5</sup>

In order to tune the electronic properties of the HBC core, electron donating and/or withdrawing functional groups must be directly attached. Several examples of electron donating groups, such as alkoxy<sup>6</sup> and amines,<sup>7</sup> have been reported in the literature. Perhaps more interesting is functionalization with electron withdrawing substituents. 2,5,8,11,14,17-Hexafluoro-hexa-*peri*-hexabenzocoronene **1** is one of two examples in the literature (Fig. 1).<sup>8</sup> In OFET devices, an electron transport mobility of  $1.6 \times 10^{-2}$  cm<sup>2</sup> V s<sup>-1</sup> has been reported. The second example is a dodecafluoro-HBC with alkoxy solubilising substituents **2** (Fig. 1).<sup>9</sup> An intrinsic charge (either hole or electron)

mobility of 0.5 cm<sup>2</sup> V s<sup>-1</sup> has been estimated for this material by pulse-radiolysis time-resolved microwave conductivity (PR-TRMC). The primary reason for the rarity of electron-poor HBC compounds is difficulty in synthesis. In this communication, a clean synthetic procedure for electron-poor HBC compounds is presented. The photophysical properties of fluoro- and trifluoromethyl-substituted HBCs are discussed.

The synthesis of HBC was first reported by Clar and Ironside in 1958.<sup>10</sup> Only small quantities of HBC compounds could be prepared until the development of the oxidative cyclodehydrogenation (Scholl) route from hexaphenylbenzene starting materials by Müllen and coworkers.<sup>11</sup> The copper(II) salts and aluminium trichloride were initially used as reagents for the oxidative cyclodehydrogenation. The use of iron trichloride (FeCl<sub>3</sub>) gave improved functional group tolerance as a result of milder reaction conditions. However, the iron trichloride route often led to chlorination of products and left undesirable iron residues. The development of dichlorodicyano-p-benzoquinone (DDQ) as an oxidant in the presence of acids gave cleaner products without chlorination or iron contamination.<sup>12</sup> As the success of the reaction is highly dependent on the oxidation of the arene starting materials, most Scholl reaction substrates predominantly contain electron rich arenes that are relatively easy to oxidise. Electron poor arenes are much less reactive in oxidative cyclo-dehydrogenations and often led to incomplete cyclisations.<sup>6b,13</sup> The starting point of this study is to determine the scope of the oxidative cyclodehydrogenation for electron poor arene substrates.

Interestingly, the successful synthesis of 2,11-dibromo-HBC **3** and hexabromo-HBC **4** has not been reported in the literature (Fig. 1). One study by Müllen and coworkers reported attempts to synthesise hexabromo-HBC **4** by cyclo-dehydrogenation of the hexaphenylbenzene precursor with



Fig. 1 Hexa-peri-hexabenzocoronenes with electron withdrawing substituents.

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Scheme 1 Synthesis of a series of HBC derivatives containing Br, F and CF<sub>3</sub> substituents. (a) Ph<sub>2</sub>O, 250 °C; (b) oxidative cyclo-dehydrogenation with DDQ–CF<sub>3</sub>SO<sub>3</sub>H; (c) Pd(PPh<sub>3</sub>)<sub>4</sub>, 9,9-dioctyl-fluorene-2-boronic acid pinacol ester, toluene, Et<sub>4</sub>NOH (aq.), 90 °C, 14 h.

FeCl<sub>3</sub> which resulted in a mixture of chlorinated products and starting material.<sup>13</sup> In contrast, less electronegative iodo analogue **5** has been used as a precursor to ethynyl substituted HBCs.<sup>14</sup> We began our investigations with the oxidative cyclodehydrogenation of a dibromo derivative of hexaphenylbenzene **8a** (Scheme 1). Precursor **8a** was synthesised from the Diels– Alder addition of diphenylacetylene **6a** to cyclopentadienone **7a** followed by CO extrusion/aromatisation (Scheme 1).

The reactivity of hexaphenylbenzene 8a was investigated using a range of oxidative cyclodehydrogenation conditions. Firstly, treatment of 8a with nitromethane solution of FeCl<sub>3</sub> (6 equiv.) in dichloromethane with nitrogen purge gave only trace amounts of dibromo-HBC 3 (see ESI<sup>‡</sup> for experimental details). It is of interest to note that there are two proposed reaction mechanisms for the oxidative cyclodehydrogenation (Scholl) reaction, an arenium-ion or a radical-cation.<sup>15</sup> In both pathways, acids play a vital role in the progress of the reaction. With this in mind, trifluoromethanesulfonic acid (CF<sub>3</sub>SO<sub>3</sub>H, 6 equiv.) was added with FeCl<sub>3</sub> to precursor 8a. Matrix assisted laser desorption ionisation mass spectrometry (MALDI-MS) analysis of the reaction mixture revealed the formation of the desired dibromo-HBC 3 along with some chlorinated derivatives (Fig. S23, ESI<sup>‡</sup>). In the quest to develop cleaner Scholl reaction conditions, DDQ was used as oxidant instead of FeCl<sub>3</sub>. Interestingly, neither methanesulfonic acid (CH<sub>3</sub>SO<sub>3</sub>H) nor trifluoroacetic acid (CF<sub>3</sub>COOH) promoted the oxidative cyclodehydrogenation of 8a with DDQ (see ESI<sup>‡</sup> for experimental details). However, the combination of DDQ and CF<sub>3</sub>SO<sub>3</sub>H gave HBC **3** in 94% yield with the MALDI-MS analysis revealing a clean product (Fig. S24, ESI<sup>‡</sup>). In addition, multi-gram scale synthesis of HBC 3 was demonstrated using this oxidative cyclodehydrogenation condition (see ESI<sup>‡</sup>).

With the reaction conditions optimised for the electronpoor bromo derivatives, we were interested in the scope of this strong acid-mediated oxidative cyclodehydrogenation for substrates bearing additional electron withdrawing groups such as

fluoro and trifluoromethyl. Both literature examples of fluorinated HBC compounds 1 and 2 were synthesized using iron trichloride in 47% and 20% yield respectively.<sup>8,9</sup> The reactivity of a series of hexaphenylbenzene derivatives 8b-d, with Br, F and CF<sub>3</sub>, groups towards the DDQ-CF<sub>3</sub>SO<sub>3</sub>H system was examined (Scheme 1). The hexaphenylbenzene precursors 8b-d were synthesised from the Diels-Alder addition of acetylenes 6b-d to cyclo-pentadienones 7b-d followed by CO extrusion and aromatisation (Scheme 1). HBC compounds 9b and 9c were obtained from hexaphenylbenzenes 8b and 8c in high yields of 82% and 81% respectively. The solubility of HBC derivatives 9b-d was too low for general analysis. In MALDI-MS analysis, the parent molecular cations for compounds 9b and 9c were clearly observed while a mixture of partially cyclodehydrogenated products was observed for 9d. The use of additional CF<sub>3</sub>SO<sub>3</sub>H, longer reaction time and elevated reaction temperature did not improve the product distribution for 9d.

In order to obtain a more detailed analysis of these novel electron-poor HBC derivatives, solution processable fluorenyl HBC compounds 10b and 10c were synthesised by Suzuki-Miyaura coupling of 9,9-dioctylfluorene-2-boronic acid pinacol ester with 9b and 9c respectively (Scheme 1). HBC derivative 10a, which has been reported by our group using a different synthetic route, <sup>4a</sup> was obtained from dibromo-HBC **3** in 89% vield. It is also noteworthy that multi-gram scale synthesis of compound 10a was demonstrated using this improved route (see ESI<sup>†</sup>). Fluorenvl HBC compounds 10a and 10b showed high thermal stability with decomposition temperature  $(T_{\rm d}, 5\%$  weight loss) of 409 °C and 404 °C respectively. The  $T_{\rm d}$  of compound **10c** was 286 °C which could be a result of the decomposition of the CF<sub>3</sub> groups. All three derivatives 10a-c showed no significant thermal transitions in differential scanning calorimetry analysis. The HBC compounds 10a-c showed strong association behaviour in solution. As reported previously, the aromatic proton resonances in the <sup>1</sup>H NMR spectrum of 10a shifted upfield with increasing concentration.<sup>4a</sup> This is indicative of strong  $\pi - \pi$  interactions in solution. Compounds 10b and 10c showed broadened resonances in their NMR spectrum (Fig. S19-S22, ESI<sup>‡</sup>). This is a result of strong aggregation behaviour in chloroform solution. Unlike compound 10a, no significant concentration dependent aggregation behaviour was observed in NMR experiments for the fluorinated HBC compounds 10b and 10c.



Fig. 2 Normalised UV-vis and PL spectra of compounds 10a-c in chloroform solution.

Table 1 Photophysical and electrochemical data for HBC compounds 10a-c

	UV-vis		PL						
	$\lambda_{\max}$ (nm), solution <sup><i>a</i></sup>	$\lambda_{\max}$ (nm), film <sup>b</sup>	$\lambda_{\max}$ (nm), solution <sup>c</sup>	$\lambda_{\max}$ (nm), film <sup>b</sup>	Optical energy gap <sup>d</sup> (eV)	$E_{ox} onset^e$ (V)	$E_{\rm red}  {\rm onset}^e$ (V)	$E_{\rm HOMO}^{f}$ (eV)	$E_{\text{LUMO}}^{g}$ (eV)
10a	365 (1.8)	374	490	550	2.79	0.33	-2.20	-5.43	-2.64
10b	365 (0.9)	365	502	532	2.73	0.64	-2.07	-5.74	-3.01
10c	370 (0.4)	373	502	582	2.70	0.62	-2.00	-5.71	-3.01

glass slides by spin coating from chlorobenzene solution (25 mg mL<sup>-1</sup>). <sup>e</sup> Photoluminescence (PL) measured in CHCl<sub>3</sub>,  $1 \times 10^{-5}$  M, 295 K, excitation wavelength = 365 nm. <sup>d</sup> Determined from the onset of absorption. <sup>e</sup> Cyclic voltammogram measured in chlorobenzene–MeCN 10 : 1,  $1 \times 10^{-3}$  M, Bu<sub>4</sub>NPF<sub>6</sub> (0.1 M), 295 K, scan rate = 50 mV s<sup>-1</sup>, versus Fc/Fc<sup>+</sup>. <sup>f</sup> Determined from  $E_{HOMO} = -(E_{ox}^{onset} + 5.10)$  (eV). <sup>g</sup> Calculated from  $E_{LUMO} = E_{HOMO}$  + optical energy gap.

The normalised UV-vis and photoluminescence (PL) spectra of compounds **10a–c** in chloroform solution are shown in Fig. 2. All three compounds have UV-vis absorption bands at 285 nm and 365 nm with vibrational broadening of the 365 nm band for **10b** and **10c** (Fig. 2). The absorption onset for **10b** and **10c** is slightly red-shifted compared to that for **10a**. The optical energy gap of compounds **10a–c** was calculated to be 2.79, 2.73 and 2.70 eV respectively (Table 1). The PL spectrum of **10b** and **10c** is also red shifted compared to that of **10a** (Fig. 2). The PL intensity decreased from **10a** to **10c**. UV-vis and PL spectrum of thin films of **10a–c** showed broadened and red-shifted signals. This is an expected outcome for HBC systems which have a tendency to aggregate through  $\pi$ - $\pi$  interactions.

Cyclic voltammogram (CV) of 10a-c in chlorobenzene-MeCN 10 : 1 with 0.1 M Bu<sub>4</sub>N PF<sub>6</sub> electrolyte was recorded with a glassy carbon working electrode, an Ag/AgCl reference electrode and a platinum counter electrode (see ESI<sup>‡</sup> for details). The oxidation onset in the CV was used to estimate the highest occupied molecular orbital (HOMO) energy of the compounds (Table 1). The corresponding lowest unoccupied molecular orbital (LUMO) energies were calculated from the HOMO energies and the optical band gap. The electron withdrawing effect of the F and CF<sub>3</sub> groups is reflected in the lowering of the HOMO and LUMO energies for 10b and **10c** (Table 1). Density functional theory calculations on simplified structures of 10a-c gave frontier orbital energies that agree with experimental values (Fig. S35, ESI<sup>‡</sup>). It is expected that both HBC compounds 10b and 10c will display electron transport behaviour in organic electronic devices. The performance of these materials in OFET devices is currently under investigation.

A new set of reaction conditions for the oxidative cyclodehydrogenation of electron-poor arenes has been developed. Bromo- and fluoro-HBC derivatives, which were difficult to obtain previously, can be prepared from hexaphenylbenzene precursors by treatment with a combination of DDQ and  $CF_3SO_3H$ . In addition, the introduction of electron withdrawing F and  $CF_3$  groups has a significant influence on the frontier orbital energies of the HBC core paving the way for the use of these compounds as electron transport materials. Future studies are focussed on the role of strong acids in oxidative cyclodehydrogenation of electron-poor arenes and the application of the products in organic electronics. This work was supported by the Australian Solar Institute (fellowship and project grant), the Australian Research Council (DP0877325), the Victorian Organic Solar Cell Consortium (www.vicosc.unimelb.edu.au), Victorian State Government (DBI-VSA and DPI-ETIS) and the University of Melbourne.

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