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J. Org. Chem., Just Accepted Manuscript • DOI: 10.1021/acs.joc.9b00802 • Publication Date (Web): 10 Jun 2019

Downloaded from http://pubs.acs.org on June 10, 2019

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is published by the American Chemical Society. 1155 Sixteenth Street N.W., Washington, DC 20036

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Polysubstituted Hexa-*cata*-Hexabenzocoronenes: Syntheses, Characterization and Their Potential as Semiconducting Materials in Transistor Application Sushil Kumar,^a Someshwar Pola,^a Chih-Wei Huang,^a Md. Minarul Islam,^{b,c} Samala Venkateswarlu,^{b,d} and Yu-Tai Tao^{*,a} ^aInstitute of Chemistry, Academia Sinica, Taipei, Taiwan, 115 ^bTaiwan International Graduate Program, Academia Sinica, Taipei, Taiwan, 115 ^cDepartment of Chemistry, National Tsing Hua University, Hsinchu, Taiwan, 300 ^dDepartment of Applied Chemistry, National Chiao Tung University, Hsinchu 300, Taiwan

Supporting Information (SI) Placeholder



Abstract

A series of tetra- and octa-substituted hexa-*cata*-hexabenzocoronenes (*cata*-HBCs) were synthesized from tetraryl olefins via iodine- and iron chloride-catalyzed oxidative cyclodehydrogenation reactions. The substitutions on the periphery of the parent HBC serve to modify the photophysical properties, HOMO–LUMO gaps and thermal stabilities of the respective derivatives. The crystal structures were determined to display multiple twists in the framework, resulting different packing motifs depending on the position, type and the number of functional groups on the hexabenzocoronene framework. Nearly perfect cofacial packing to marginally or extensively shifted cofacial stacks were obtained due to substitution. The single-crystals of parent HBC was used to fabricate single crystal field-

effect transistor, from which a highest p-channel mobility of $0.51 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$ was measured. Thin film transistors of selected HBCs were also prepared and $0.61 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$ was obtained for MeHBC-2. These results attest the potential of these materials as semiconducting materials.

Introduction

The cyclic π -conjugated organics composed of fused benzene moieties in different shapes and sizes have been considered as useful semiconducting materials in organic electronics, which owes its advancement to the the availability of numerous aromatic compounds through the diligent efforts of synthetic chemists.¹ Being the ubiquitous component of electronic devices, field-effect transistors(OFETs) based on organic semiconducting materials are particularly important.² Much progress has been gained in improving the field-effect mobility of OFETs through new molecular designs and device structure modulations over the past decade, so that devices with properties surpassing that of amorphous silicon are not uncommon.³ However, more is to learn about the structure/property correlation in designing new materials. Efforts to understand the structure/property correlation are nevertheless complicated by the various grain sizes and morphologies always involved in a deposited thin film.⁴ These complications might be avoided by using single cryatals to fabricate transistor devices.

The contorted polyaromatics are of particular interest for their tendency to form co-facial π - π stackings due to self-complementarity in molecular shape or geometry.⁵ The direct π face overlap in a co-facial packing is considered beneficial to the electronic coupling, which is a required property allowing for efficient charge transport between organic molecules.⁶ Nuckolls' group unraveled the framework of hexa-*cata*-hexabenzocoronene (*cata*-HBC) as a potential transistor material, although the measured mobility was rather limited (~0.02 cm²V⁻¹s⁻¹) for the thin film-based devices.⁷ A number of coronene-cored

non-planar derivatives have also been studied (**Chart 1**), with the effect of substitutents on the crystal packing and thus mobility examined.⁸ Yet the effect of substituents on the packing of *cata*-HBC has not been reported.



Chart 1. Coronene and its benzo analogues.

In this report, we present the syntheses and characterizations of a series of tetra- and octasubstituted hexa-*cata*-hexabenzocoronenes (**Chart 2**). These are synthesized from tetra and octaaryl olefins via oxidative cyclodehydrogenation reactions catalyzed by iodine and iron chloride. The packing motifs of these HBCs were much influenced by the substituents attached to the main aromatic core. Although, they had twisted polyfused frameworks, they formed strong π -aggregates, affecting the self-assembly behavior of these molecules. The potential of these derivatives as transistor materials were exemplified by single crystal field-effect transistor fabricated from the parent HBC, which gave a high mobility of 0.51 cm²V⁻¹s⁻¹ and an on-off ratio of 10⁴ ~10⁷.



Chart 2. Chemical structures of synthesized HBCs.

Results and Discussion

Syntheses

The syntheses of substituted **HBC**s are illustrated in Schemes **1**, **2**, and **3**. The 6,13bis(dibromomethylene)-6,13-dihydropentacene (**1**) was prepared via known synthetic protocol.⁹ Multifold Suzuki coupling reactions were carried out on **1** to afford polyaryl olefins (**2–8**). These polyaryl olefins were subjected to oxidative cyclodehydrogenation reactions by first irradiating the solutions of polyaryl olefins and iodine with UV-light,¹⁰ and then treating the resulted partially annulated derivatives with iron chloride¹¹ to furnish the substituted **HBC**s in high yields (**Table 1**, entries 1–6).



Scheme 1. Preparation of 3,10,15,22-tetrasubstituted hexabenzo[a,d,g,j,m,p]coronenes (HBC, Flu-

HBC, Cl-HBC, Met-HBC and Me-HBC1).









 $\mathbf{B} = 1.1_2$ /methyloxirane toluene (UV-Light), rt, 36 h

Scheme 3. Preparation of 2,4,9,11,14,16,21,23-octafluorohexabenzo[*a*,*d*,*g*,*j*,*m*,*p*]

coronene (OFlu-HBC).

It is noted that the reactivity of the tetraaryl olefin toward oxidative cyclodehydrogenation¹² depended on the functional groups attached to polyaryl olefin, as manifested by the diverse reaction times and reaction yields of the final *cata*-HBCs (Table 1, entries 1–7). Presumably because the functional groups stabilize the reaction

intermediates¹³ to different extent during their conversion to the final products. Interestingly, the octafluoro-substituted tetraaryl olefin **8** led to complete annulation product via iodine-mediated oxidative cyclodehydrogenation reaction, forming **OFlu-HBC**, although this reaction took the longest reaction time of 36 h compared to the iodine reactions of other derivatives (**Table 1**, entry 7).

Table 1. conversions o	f aryl	olefins	to the	HBCs.
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entry	olefin	product	reactio ()	reaction vield ^b	
			Iodine- catalyzed reaction	Iron chloride- catalyzed reaction	(%)
1	2	HBC	10	4	88
2	3	Flu-HBC	24	8	81
3	4	Cl-HBC	24	8	90
4	5	Met-HBC	10	2	94
5	6	Me-HBC1	10	4	88
6	7	Me-HBC2	12	4	90
7	8	OFlu-HBC	36	_ c	76 ^d

^areaction time for iodine and iron chloride-catalyzed oxidative cyclodehydrogenation reactions. ^breaction yields for iron chloride-catalyzed reactions. ^ciron chloride was not used in this case, as the iodine reaction led to complete annulation. ^dreaction yield for iodinecatalyzed reaction.

Single-crystal X-ray analyses

The single crystals of various *cata*-**HBC**s were obtained by using physical vapor transfer technique (PVT) at the temperature range of 400–500 °C. The **HBC**s gave needle-like or platellet-like crystals in the PVT process.¹⁴

The single-crystal X–ray analyses (**Figure S23**, **SI**, showing thermal ellipsoid plots) revealed the packing motifs of **HBC**s as well as detailed features including geometry of their frameworks, twisting angles, plane-to-plane and centroid-to-centroid distances, which were parameters related to the electronic coupling.^{8c,15} As can be seen from their molecular structures, these derivatives showed multiple twists at the periphery, where six benzene

rings bent up and down alternately with respect to the central coronene part, with contortion angles varying from 22.2° to 28.5° (**Figure 1**). Among the six peripheral benzenes, the four benzenes substituted by different groups (fused at a-, d-, j-, and m-positions at the coronene moiety) displayed different contortion angles with respect to the other two benzenes (fused at g- and p-positions), presumably due to the electronic and steric effects exerted by different functional groups.



Figure 1. (a) molecular structure of **Me-HBC2**, showing positions (a-, d-, g-, j-, m- and p-) of six benzene rings fused with the central coronene. **(b)**-**(g)** twist angles of **HBC**s measured for the peripheral benzenes (red-colored) with respect to central benzene (black-colored).

In terms of packing, the severely twisted molecuels pack in several modes, depending on the substituent. The CI-HBC is the only one adopting exactly co-facial packing, presumably the Cl...Cl interaction¹⁶ plays the role to bring the molecules to on-top arrangement (Figure 2e,f). For HBC, Flu-HBC, OFlu-HBC, and Me-HBC2, similar shifted packing mode with one molecule inserted nearly halfway between two co-facially aligned molecules (Figure 2) was obtained. The Me-HBC1 and Met-HBC adopt different packing with much tilted moleculear orientation. Interestingly, molecules Cl-HBC, Me-HBC1, Met-HBC, and OFlu-HBC were found to be chiral, exhibiting two mirror image forms (enantiomers). The π - π stacking distance (measured from the closest distance from two overlapping π rings, shown in Figures 2a, c, e, i, k, and m) and centroid-to-centroid distances for HBCs (measured from the centers of two cofacially stacked molecules shown in Figure S24, SI) are given in the Table 2. These derivatives gave $\pi - \pi$ stacking distance of 3.274 Å to 3.367 Å, with the four fluorine- and eight fluorine-funtionalized HBCs having the smallest and the largest coupling distance of 3.4 Å and 4.1 Å, respectively. Although, the derivatives **Me-HBC1** and **Me-HBC2** are different in the positions of methyl groups on the parent **HBC**, they display closer stacking distance of 3.284 Å and 3.293 Å. **Table 2.** Cell parameters, π - π stacking and centroid-to-centroid distances for the single crystals of HBCs.

Cell	Flu-HBC	Cl-HBC	Met-HBC	Me-HBC1	Me-HBC2	OFlu-
Parameters						HBC
a (Å)	12.59	4.10	9.95	10.95	15.32	26.54
b (Å)	7.89	14.23	13.09	14.40	12.95	8.06
c (Å)	14.17	27.38	14.46	11.15	16.53	14.58
α (°)	90	94.4	113.9	90	90	90
β (°)	90.1	90.7	103.3	115.1	90.4	103.9
γ (°)	90	97.7	92.3	90	90	90
Point group	P_1/c	P-1	P-1	$P2_1/c$	$P2_1/n$	<i>P</i> 1 21/c 1
$^{a}d_{\pi-\pi}(\text{\AA})$	3.274	3.341	3.309	3.284	3.293	3.367
$^{b}d_{c-c}(\text{\AA})$	7.737	3.341	8.301	14.717	10.130	7.804

 $a\pi - \pi$ coupling distance. ^bcentroid-to-centroid distance.





Figure 2. Packing motifs of **HBCs**: (a)–(b) **HBC**, (c)–(d) **Flu-HBC**, (e)–(f) **Cl-HBC**, (g)– (h) **Met-HBC**, (i)–(j) **Me-HBC1**, (k)–(l) **Me-HBC2** and (m)-(n) **OFlu-HBC** As shown in **Figure 3**, **Flu-HBC**, **Cl-HBC** and **Met-HBC** were able to develop strong contacts¹⁷ CF...HC, CCl...HC, CO...HC at the interatomic distances of 2.45 Å to 2.92 Å. These interactions were able to hold nearby molecules providing a regular packing motifs to these polyaromatics.



Figure 3. Packing motifs of HBCs showing CF...HC, CC1...HC and CO...HC interactions.

Since the molecular arrangement in polyaromatics has important impact on electronic coupling, which in turn affect the charge transporting properties of single-crystals. The twisted geometry and attached functional groups of these **HBC**s were considered to be effective features in affecting their electro-optical properties.

Photophysical, HOMO-LUMO, and Thermogravimetric studies

The **HBC**s displayed yellow to yellow-orange colors in their solid states. The electronic absorption spectra of the benzocoronenes are displayed in the **Figure 4** and **S24** (**SI**), while the related data are listed in the Table **3**. The parent coronene exhibited three absorption bands located at the 220 nm, 340 nm and 350 nm.¹⁸ The absorption profiles of the tetrasubstituted coronenes stemmed from the central coronene as suggested by the spatial distribution of their HOMOs. Functional groups such as chlorine, methyl and methoxy groups slightly shifted the absorption toward longer wavelength, whereas fluorine groups shifted it to shorter wavelength. As expected, **HBC**s showed red-shifted absorption with respect to less extended systems of **TBC** and **DBC** derivatives.^{8a, 8b}



Figure 4. UV-Visible spectra of HBCs as recorded in dichloromethane.

Due to poor solubility of **HBCs** in organic solvents, the cyclic voltammetric measurements were not successful. The HOMO energies of these derivatives were thereby obtained using photoelectron spectrometer (AC–2) (**Table 3**). Theoretically calculated HOMOs of these **HBCs** were mainly centralized on coronene unit, which possibly affected the oxidation potentials of designed coronenes (**Figure 5**). Substituting parent **HBC** by the electron donors and electron acceptors affected their HOMO energies. For example, **Met-HBC** and **OFlu-HBC** have the highest-lying and lowest-lying HOMO energies respectively in this **HBC** series (**Table 3**). The weak donor methyl groups at different positions of **HBC** framework cause the HOMO values to fall in between. The optical band gaps of these benzocoronenes were estimated from their absorption band edges, which on substrating from E_{HOMO} provided the E_{LUMO} values. Similar to the HOMO energies, the LUMO energies were also perturbed by the attached functional groups. Therefore, the introduction of fluorine or chlorine atoms lowered the LUMO energy levels in **HBC**s.



Figure 5. Forntier molecular orbitals and respective measured energies for **HBC**s: HOMO (bottom), LUMO (top).

Table 3. Energy of HOMO, LUMO, band gap and thermogravimetric data of HBCs.

Compd.	$a \lambda_{abs}$	${}^{\mathrm{b}}E_{\mathrm{HOMO}}$	^с ELUMO	${}^{\mathrm{d}}E_{\mathrm{g}}$	^e T _d
	(nm)	(eV)	(eV)	(eV)	(°C)
HBC	371	5.22	2.72	2.50	516
	(max),				
	265				
Flu-HBC	370	5.63	3.18	2.45	488
	(max),				
	263				
Cl-HBC	375	5.53	3.09	2.44	532
	(max),				
	268				
Met-HBC	380	5.06	2.48	2.58	498
	(max),				
	266				
Me-HBC1	372	5.12	2.50	2.62	469
	(max),				
	268				
Me-HBC2	374,	5.16	2.52	2.64	528
	271				
	(max)				
OFlu-HBC	378,	5.76	2.78	2.98	486
	262				
	(max)				

^aAbsorption wavelengths. ^b E_{HOMO} measured by photoelectron spectrometer (AC-2). ^c $E_{LUMO} = E_{HOMO} - E_{g}$. ^dOptical bandgap, E_{g} , was obtained from the absorption edge. ^eThermal decomposition temperature measured at 5% weight loss.

Thermal stability of these **HBC**s is evaluated by their thermogravimetric analyses, whose results are given in Figure **S25–S26**, (**SI**), while their values are compiled in Table **3**. The

thermal decomposition temperatures of these **HBC**s were obtained at 5% weight loss. The thermal decomposition temperatures of these polyaromatics were as high as 516 °C and were not lower than 469 °C. Thus, stable transistor devices could be prepared from these derivatives.¹⁹

SCFET performance

To evaluate the potential of this series of compounds as channel material for field-effect transistor, single crystal field-effect transistors (SCFETs) were fabricated with the parent HBC crystals, as it generated crystals of adequate sizes. A heavily n-doped silicon substrate covered with 300 nm SiO₂ on top was used as the gate and the dielectric insulator. A selfassembled monolayer (SAM) of octadecyltricholorosilane (ODTS) was formed on the SiO₂ surface to remove the trapping sites due to hydroxyl groups. Previous report showed that pre-rubbing of the SAM would improve the performance of the transistor.²⁰ Thus single crystals of HBC were laminated on the surfaces of bare SiO₂, ODTS/SiO₂ and rubbed ODTS/SiO₂ substrates and gold was deposited through a mask to serve as the source and drain electrodes. The output and transfer characteristics of SCFETs on bare SiO₂, unrubbed-ODTS/SiO₂, and rubbed-ODTS/SiO₂ substrates are shown in Figure 6. The related data is given in Table 4. A typical p-type behaviour was observed. The carrier mobilities, as calculated from the saturation regime of current-voltage curves, showed that a highest mobility of 0.51 cm²V⁻¹s⁻¹ was observed for device on rubbed ODTS/SiO₂, while 0.27 and 0.084 cm²V⁻¹s⁻¹ were observed for devices on un-rubbed ODTS/SiO₂ and bare SiO₂ respectively. Thin film field-effect transistors were also prepared for selected HBCs such as CI-HBC and Me-HBC2 on ODTS-modified SiO₂ surfaces in a top-contact, bottom-gate configuration. Again a better performance was in general obtained on rubbed ODTS/SiO₂ surface. As shown in **Table 5**, a high mobility of 0.61 cm²V⁻¹s⁻¹ was obtained for MeHBC-2 deposited at 70 °C, whereas for Cl-HBC, the value of mobility was recorded to be 0.24 cm²V⁻¹s⁻¹, even though an exact cofacial packing is found for Cl-HBC.

The morphology/grain size will play a major role in the case of thin film devices. The data nevertheless also demonstrate the potential of these molecules as transistor materials.



Figure 6. (a)-(c) Output SCFET characteristics of compound HBC. (d) transfer characteristics on bare SiO_{2} , unrubbed ODTS/SiO₂ and rubbed ODTS/SiO₂.

Table 4. SCFET data of HBC at the SiO₂, unrubbed-ODTS and rubbed-ODTS surfaces

SAM	Mobility	On/off ratio	V _{th}	
	$(cm^2 V^{-1} s^{-1})$		(V)	
SiO ₂	0.028 - 0.084	$10^5 - 10^6$	-10 - (-17)	
ODTS	0.16 - 0.27	$10^5 - 10^8$	-21 - (-32)	
rub-ODTS	0.34 - 0.51	$10^5 - 10^7$	-12 - (-20)	

Table	5.	Thin-film	transistors	characteristics	for	HBCs	deposited	on	rubbed-ODTS
surfaces	at '	70°C.							

Compd	Mobility	On/off ratio	V _{th}	
	(cm ² V ⁻¹ s ⁻¹)		(V)	
HBC	0.38 - 0.42	105	-21 - (-23)	
CI-HBC	0.22 - 0.24	106	-23 - (-24)	
MeHBC-2	0.59 – 0.61	106	-12 - (-14)	

Conclusions

In conclusion, we have successfully synthesized and characterized a series of substituted hexa-*cata*-hexabenzocoronenes **HBC**s. The substitution affects the physical properties such as oxidation potential and UV absorption to a small extent but affects the crystal packing to a larger extent. Single-crystal X–ray analyses showed different extents of twist angle for the peripheral benzene rings aound the coronene core, depending on the substitutent. Although, peripheral addition of functional groups at hexabenzocoronene did not affect much the distortions at the fjords, they changed the packing pattern, due to the size, dipole and/or heteroatom interactions. The parent **HBC** afforded a p–type field-effect mobility in the range of $0.34\sim0.51$ cm²V⁻¹s⁻¹, with an on/off ratio of 10^5 – 10^7 . Thin film transistors based on **MeHBC-2** gave a highest mobility of 0.61 cm²V⁻¹s⁻¹ and an on/off ratio of 10^6 . These characteristics demonstrate the potential of HBC derivatives as conducting channel for transistor application.

Experimental Section

The required starting materials were commercially available and used without further purification. The Suzuki coupling, iodine- and iron chloride-mediated oxidative cyclodehydrogenation reactions were conducted under nitrogen atmosphere. The prefinal

tetraaryl olefins were purified by column chromatography using silica gel with 60–230 mesh size. ¹H and ¹³C NMR spectra were recorded on a Bruker AMX400 O FT-NMR spectrometer in deuterated solvents like chloroform-d and benzene-d₆, using tetramethylsilane (TMS) as the internal standard. V-550 JASCO UV/VIS spectrophotometer was used to perform absorption studies in dried and distilled dichloromethane. The HOMO–LUMO energy levels of selected **HBC**s samples were measured using photoelectron spectrometer (AC-2) (Riken Keiki) in ambient. A temperature-gradient copper tube, equipped with argon flow as the carrier gas, was used to grow single crystals of HBC samples. The single-crystal X-ray diffractions were obtained on a Bruker X8APEX X-ray diffractometer with Mo K α radiation (λ = 0.710 73 Å), and the structures of **HBC** samples were solved by the SHELX 97 program. To get HOMO–LUMO plots, theoretical calculations were performed for **HBC**s by using PC Spartan Pro software with semi-empirical methods at the AM1 level.

General reaction procedure for the preparation of polyaryl olefins 2–8 through Suzuki C–C cross coupling reactions. 6,13-Bis(dibromomethylene)-6,13dihydropentacene (0.62 g, 1.0 mmol) (1), arylboronic acid (4.1 mmol), Pd(PPh₃)₂Cl₂ (72 mg), PPh₃ (52 mg) and potassium carbonate (1.38 g, 10.0 mmol) were taken in a mixture of toluene (30 ml) and water (15 ml). The reaction mixture was heated at 110 °C for 12 h under nitrogen atmosphere. On completion of reaction, the mixture was cooled and toluene layer was extracted. On removal of toluene, the product was purified by column chromatography using dichloromethane/hexane as eluent.

6,13-Bis(diphenylmethylene)-6,13-dihydropentacene (2)⁷ Following the general reaction procedure, a Suzuki C–C cross coupling reaction on 6,13-bis(dibromomethylene)-6,13-dihydropentacene (1) using phenylboronic acid (0.50 g, 4.1 mmol) gave the title product as white solid. Yield: 0.49 g, 80%.

6,13-Bis(bis(4-fluorophenyl)methylene)-6,13-dihydropentacene (3) Following the general reaction procedure, a Suzuki C–C cross coupling reaction on 6,13-bis(dibromomethylene)-6,13-dihydropentacene (1) using (4-fluorophenyl)boronic acid (0.57 g, 4.1 mmol) gave the title product as white solid. Yield: 0.53 g, 78%. mp > 350 °C. ¹H NMR (CDCl₃, 400 MHz) δ 7.50 (s, 4H), 7.44-7.39 (m, 12H), 7.29-7.28 (m, 4H), 6.99 (t, *J* = 8.4 Hz, 8H). ¹³C NMR (CDCl₃, 400 MHz) δ 162.9, 160.4, 138.7, 138.0, 136.4, 135.5, 131.5, 131.3, 131.2, 127.7, 127.1, 125.9, 115.5, 115.3. HRMS (MALDI-TOF) m/z [M]+ calcd for C₄₈H₂₈F₄ 680.2127, found 680.2137.

6,13-Bis(bis(4-chlorophenyl)methylene)-6,13-dihydropentacene (4) Following the general reaction procedure, a Suzuki C–C cross coupling reaction on 6,13-bis(dibromomethylene)-6,13-dihydropentacene **(1)** using (4-chlorophenyl)boronic acid (0.64 g, 4.1 mmol) gave the title product as white solid. Yield: 0.63 g, 84%. mp 326–330 °C. ¹H NMR (CDCl₃, 400 MHz) δ 7.52 (s, 4H), 7.46-7.45 (m, 4H), 7.36-7.45 (d, *J* = 7.2 Hz, 8H), 7.31-7.29 (m, 8H), 7.19 (d, *J* = 6.8 Hz, 4H). ¹³C NMR (CDCl₃, 400 MHz) δ 140.2, 138.4, 136.6, 135.2, 133.0, 131.5, 131.0, 129.0, 128.2, 127.7, 127.2, 126.1, 125.3. HRMS (MALDI-TOF) m/z [M]+ calcd for C₄₈H₂₈Cl₄ 744.0945, found 744.0934.

6,13-Bis(bis(4-methoxyphenyl)methylene)-6,13-dihydropentacene (5) Following the general reaction procedure, a Suzuki C–C cross coupling reaction on 6,13-bis(dibromomethylene)-6,13-dihydropentacene **(1)** using 4-methoxyboronic acid (0.62 g, 4.1 mmol) gave the title product as white solid. Yield: 0.64 g, 88%. mp 266–270 °C. ¹H NMR (CDCl₃, 400 MHz) δ 7.56 (s, 4H), 7.44-7.42 (m, 4H), 7.36 (d, *J* = 8.4 Hz, 8H), 7.24-7.21 (m, 4H), 6.81 (d, *J* = 8.8 Hz, 8H), 3.75 (s, 12H). ¹³C NMR (CDCl₃, 400 MHz) δ 158.2, 139.9, 136.6, 135.4, 135.0, 131.5, 130.9, 127.7, 126.8, 125.3, 113.7, 55.2. HRMS (MALDI-TOF) m/z [M]+ calcd for C₅₂H₄₀O₄ 728.2927, found 728.2934.

6,13-bis(di-*p*-tolylmethylene)-6,13-dihydropentacene (6) Following the general reaction procedure, a Suzuki C–C cross coupling reaction on 6,13-bis(dibromomethylene)-6,13-dihydropentacene (1) using *p*-tolylboronic acid (0.56 g, 4.1 mmol) gave the title product as white solid. Yield: 0.55 g, 82%. mp 296–300 °C. ¹H NMR (CDCl₃, 400 MHz) δ 7.55 (s, 4H), 7.42 (dd, *J* = 9.6 Hz 3.6 Hz, 4H), 7.37 (d, *J* = 7.6 Hz, 8H), 7.24-7.21 (m, 4H), 7.08 (d, *J* = 8.0 Hz, 8H), 2.28 (s, 12H). ¹³C NMR (CDCl₃, 400 MHz) δ 140.8, 139.6, 136.4, 136.0, 135.4, 131.5, 129.6, 129.0, 128.9, 128.2, 127.7, 126.8, 125.3, 21.1. HRMS (MALDI-TOF) m/z [M]+ calcd for C₅₂H₄₀ 664.3130, found 664.3134.

6,13-Bis(di-*m***-tolylmethylene)-6,13-dihydropentacene (7)** Following the general reaction procedure, a Suzuki C–C cross coupling reaction on 6,13-bis(dibromomethylene)-6,13-dihydropentacene **(1)** using *m*-tolylboronic acid (0.56 g, 4.1 mmol) gave the title product as white crystalline solid. Yield: 0.57 g, 86%. mp 268–272 °C. ¹H NMR (CDCl₃, 400 MHz) δ 7.59 (s, 4H), 7.45-7.38 (m, 12H), 7.28-7.22 (m, 8H), 7.06 (d, *J* = 7.6 Hz, 4H), 2.34 (s, 12H). ¹³C NMR (CDCl₃, 400 MHz) δ 142.5, 141.4, 137.9, 136.2, 135.3, 131.4, 130.2, 128.0, 127.4, 127.3, 126.7, 125.5. HRMS (MALDI-TOF) m/z [M]+ calcd for C₅₂H₄₀ 664.3130, found 664.3133.

6,13-Bis(bis(3,5-difluorophenyl)methylene)-6,13-dihydropentacene (8) Following the general reaction procedure, a cross Suzuki C–C coupling reaction on 6,13-bis(dibromomethylene)-6,13-dihydropentacene **(1)** using 3,5-difluorophenylboronic acid (0.65 g, 4.1 mmol) gave the title product as white crystalline solid. Yield: 0.65 g, 87%. mp 297–301 °C. ¹H NMR (CDCl₃, 400 MHz) δ 7.54 (s, 4H), 7.52-7.50 (m, 4H), 7.37-7.34 (m, 4H), 6.98-6.95 (m, 8H), 6.70 (d, *J* = 8.8 Hz, 4H). ¹³C NMR (CDCl₃, 400 MHz) δ 164.3, 164.2, 161.8, 161.7, 144.1, 144.0, 143.9, 137.5, 136.5, 133.9, 131.7, 127.8, 127.1, 126.6, 112.8, 112.6, 103.3, 102.8 . HRMS (MALDI-TOF) m/z [M]+ calcd for C₄₈H₂₄F₈ 752.1750, found 752.1754.

General procedure for the preparations of HBCs through oxidative cyclodehydrogenation reactions on aryl olefins Polyaryl olefin (2-8) (1.0 mmol), iodine (2.03 g, 4.1 mmol) and methyloxirane (10 ml) were taken in toluene (30 ml). This reaction mixture was irradiated under UV-light for 6–24 h under nitrogen atmosphere. On completion of the reaction, excessive iodine was neutralized by treating with saturated sodium thiosulphate solution. Removing toluene led to a mixture of partially and completely annulated products (except polyaryl olefin 8). In case of polyaryl olefin 8, iodine (2.03 g, 4.1 mmol) reaction led to the complete annulation.

A mixture of differently annulated products, obtained from polyaryl olefins 2–7, was dissolved in anhydrous dichloromethane (60 ml). To this, a solution of iron chloride (3.24 g, 20.0 mmol) in nitromethane (10 ml) was added via a syringe. This reaction mixture was stirred for 2–16 h under nitrogen atmosphere. On completion of reaction, the product was precipitated on addition of methanol. The precipitated solid was filtered, washed with methanol, hydrochloric acid, and water successively. Product was dried to give yellow to yellow-orange solid.

Hexabenzo[*a,d,g,j,m,p*]**coronene (HBC)**⁷ Following the general reaction procedure, two consecutive oxidative cyclodehydrogenation reactions on 6,13-bis(diphenylmethylene)-6,13-dihydropentacene (2) (0.61 g, 1.0 mmol), using iodine (10 h) and iron chloride (4 h), afforded **HBC** as yellow solid. Yield: 0.53 g, 88%.

3,10,15,22-Tetrafluorohexabenzo[*a,d,g,j,m,p*]**coronene (Flu-HBC)** Following the general reaction procedure, two consecutive oxidative cyclodehydrogenation reactions on 6,13-bis(bis(4-fluorophenyl)methylene)-6,13-dihydropentacene **(3)** (0.68 g, 1.0 mmol), using iodine (24 h) and iron chloride (8 h), afforded **Flu-HBC** as yellow solid. Yield: 0.54 g, 81%. mp > 350 °C. ¹H NMR and ¹³C NMR could not be recorded due to poor solubility of this derivative. HRMS (MALDI-TOF) m/z [M]+ calcd for C₄₈H₂₀F₄ 672.1501, found 672.1506. The crystal structure was solved by X-ray diffraction.

3,10,15,22-Tetrachlorohexabenzo[*a,d,g,j,m,p*]**coronene (CI-HBC)** Following the general reaction procedure, two consecutive oxidative cyclodehydrogenation reactions on 6,13-bis(bis(4-chlorophenyl)methylene)-6,13-dihydropentacene (**4**) (0.75 g, 1.0 mmol), using iodine (24 h) and iron chloride (8 h), afforded **CI-HBC** as yellow solid. Yield: 0.66 g, 90%. mp > 350 °C. ¹H NMR (CDCl₃, 400 MHz) δ 9.22-9.20 (m, 8H), 9.10 (d, *J* = 8.8 Hz, 4H), 7.94-7.92 (m, 4H), 7.82-7.80 (m, 4H). ¹³C NMR could not be recorded due to poor solubility of this derivative. HRMS (MALDI-TOF) m/z [M]+ calcd for C₄₈H₂₀Cl₄ 736.0314, found 736.0294. The crystal structure was solved by X-ray diffraction.

3,10,15,22-Tetramethoxylhexabenzo[*a,d,g,j,m,p*]coronene (Met-HBC) Following the general reaction procedure, two consecutive oxidative cyclodehydrogenation reactions on 6,13-bis(4-methoxyphenylmethylene)-6,13-dihydropentacene (6) (0.73 g, 1.0 mmol), using iodine (10 h) and iron chloride (2 h), afforded **Met-HBC** as yellow solid. Yield: 0.68 g, 94%. mp > 350 °C. ¹H NMR (CDCl₃, 400 MHz) δ 9.34 (s, 4H), 9.11 (d, *J* = 8.8 Hz, 4H), 8.72 (s, 4H), 7.79 (s, 4H), 7.45-7.44 (m, 4H), 4.11 (m, 12H). ¹³C NMR could not be recorded due to poor solubility of this derivative. HRMS (MALDI-TOF) m/z [M]+ calcd for C₅₂H₃₂O₄ 720.2301, found 720.2305. The crystal structure was solved by X-ray diffraction.

3,10,15,22-Tetramethylhexabenzo[*a,d,g,j,m,p*]coronene (Me-HBC1) Following the general reaction procedure, two consecutive oxidative cyclodehydrogenation reactions on 6,13-bis(di-*para*-tolylmethylene)-6,13-dihydropentacene (**6**) (0.66 g, 1.0 mmol), using iodine (10 h) and iron chloride (4 h), afforded the **Me-HBC1** as yellow solid. Yield: 0.58 g, 88%. mp > 350 °C. ¹H NMR (CDCl₃, 400 MHz) δ 9.28-9.26 (m, 4H), 9.14 (d, *J* = 8.4 Hz, 4H), 9.06 (s, 4H), 7.83-7.81 (m, 4H), 7.65 (d, *J* = 8.4 Hz, 4H), 2.75 (m, 12H). ¹³C NMR could not be recorded due to poor solubility of this derivative. HRMS (MALDI-TOF) m/z [M]+ calcd for C₅₂H₃₂ 656.2499, found 656.2502. The crystal structure was solved by X-ray diffraction.

2,11,14,23-Tetramethylhexabenzo[*a,d,g,j,m,p*]coronene (Me-HBC2) Following the general reaction procedure, two consecutive oxidative cyclodehydrogenation reactions on 6,13-bis(di-*meta*-tolylmethylene)-6,13-dihydropentacene (6) (0.66 g, 1.0 mmol), using iodine (12 h) and iron chloride (4 h), afforded the Me-HBC2 as yellow solid. Yield: 0.59 g, 90%. mp > 350 °C. ¹H NMR (CDCl₃, 400 MHz) δ 9.22 (s, 4H), 9.14 (d, *J* = 8.8 Hz, 4H), 9.07 (s, 4H), 7.81 (m, 4H), 7.64 (d, *J* = 7.6 Hz, 4H), 2.74 (m, 12H). ¹³C NMR could not be recorded due to poor solubility of this derivative. HRMS (MALDI-TOF) m/z [M]+ calcd for C₅₂H₃₂ 656.2499, found 656.2510. The crystal structure was solved by X-ray diffraction.

2,4,9,11,14,16,21,23-Octafluorohexabenzo[*a,d,g,j,m,p*]coronene (OFlu-HBC)

Following the general reaction procedure, an oxidative cyclodehydrogenation reaction on 6,13-bis(bis(3,5-difluorophenyl)methylene)-6,13-dihydropentacene **(6)** (0.75 g, 1.0 mmol), using iodine (36 h), afforded the **OFlu-HBC** as yellow-orange solid. Yield: 0.57 g, 76%. mp > 350 °C. ¹H NMR (C₆D₆, 400 MHz) δ 8.52-8.46 (m, 8H), 7.55-7.52 (m, 4H), 6.91-6.89 (m, 4H). ¹³C NMR could not be recorded due to poor solubility of this derivative. HRMS (MALDI-TOF) m/z [M]+ calcd for C₄₈H₁₆F₈ 744.1124, found 744.1135. The crystal structure was solved by X-ray diffraction.

ASSOCIATED CONTENT

Supporting Information

The Supporting information is available free of charge on the ACS Publications website. ¹H and ¹³C NMR spectra, thermal ellipsoids, additional absorption spectra, thermogravimetric plots, theoretical calculation data, additional single-crystal field-effect transistor data and X-ray crystallography data for the complete spectroscopic analysis (PDF).

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ACKNOWLEDGMENT

Financial support from Ministry of Science and Technology, Taiwan (Grant Number: 103-2120-M-009-003-CC1) is gratefully acknowledged.

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