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Facile Bottom-Up Synthesis of Coronene-based 3-Fold Symmetrical and Highly Substituted Nanographenes from Simple Aromatics

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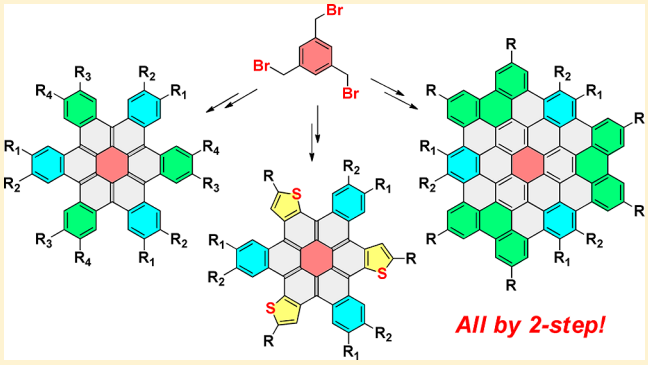
Supporting Information

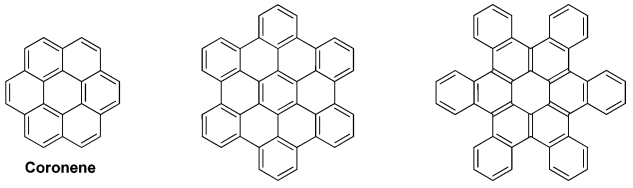
ABSTRACT: A facile and efficient self-sorting assemble (CSA) strategy has been paved for bottom-up construction of the 3-fold symmetrical and highly substituted hexa-*cata*-hexabenzocoronenes (*c*-HBCs), the trithieno analogues, and larger disc-shaped PAHs from simple chemicals using benzylic carbons as tenon joints and a novel $FeCl_3$-mediated AAA process as a key step. The structures of the as-prepared *c*-HBCs and related NGs were clearly identified by spectral analyses and X-ray crystallographic studies. Moreover, these can be envisaged to serve as new launching platforms for the construction of larger and more complex π-conjugated molecules and supramolecular architectures because of the modifiable and symmetrical decorations.



INTRODUCTION

Large polycyclic aromatic hydrocarbons (PAHs) or nanographenes (NGs) have kindled great excitement for their unique electronic and self-assembly properties in a variety of fields of scientific and technological applications.[1] Of particular interest should be coronene-based NGs, such as hexa-*peri*-hexabenzocoronene (planar HBC or *p*-HBC, also known as "superbenzene", Chart 1) and hexa-*cata*-hexabenzocoronene (contorted HBC, or *c*-HBC).[1a−d] Since the synthetic breakthrough of *p*-HBCs by Müllen et al.[2] in 1995, impressive progress has been achieved and a cornucopia of elegant *p*-HBC derivatives and more complex PAHs with different shape and size have been reported,[3] even a giant molecular graphene containing 222 carbon atoms[4] and structurally uniform graphene nanoribbons (GNRs) up to 12 nm in length.[5] Many of them have shown potential applications from next-generation electronic devices (e.g., field-effect transistors, light-emitting diodes, and solar cells) to bioimaging.[6] These works, taken together with numerous other works, make *p*-HBCs the most studied large disc-shaped PAHs.

Chart 1. Structures of Coronene, *p*-HBC, and *c*-HBC



In stark contrast with the prosperity of *p*-HBCs, however, *c*-HBC, the twin sister of *p*-HBC, remains relatively ignored, despite of its first synthesis by Clar and Stephen[7] near half a century ago. Recently, the Nuckolls group has reported the parent *c*-HBC and a variety of its substituted derivatives[8] and disclosed their unique nonplanar structure and intriguing electronic and self-assembly properties,[9] such as their strong tendency to self-assemble to nanowires[8a] and nanotubes[6d] and to form shape-complementary complexes with C_{60}.[8d,9h] Moreover, *c*-HBCs were found to be able to form bowls[9b] or hemisphere.[9k] Even with these striking properties and potentials, the *c*-HBC chemistry is far from being well-documented.[8a] We believe that the sluggish development of *c*-HBC chemistry can be ascribed mainly, if not purely, to the lack of a convenient and efficient approach for their synthesis. Although recent elegant work of Nuckolls et al. provided a quick access to the *c*-HBC scaffold from pentacene quinones,[8a,b,9b] the reported strategy give only mirror-symmetrically rather than C_3 symmetrically substituted *c*-HBC derivatives. Facile synthesis of substituted PAHs is the precondition for the development of superior organic materials, and the electronic optical, thermal, and morphological properties of organic materials are closely related to their aromatic structures and substitutional patterns. Clearly, a facile synthesis of *c*-HBCs with different pattern and degree of

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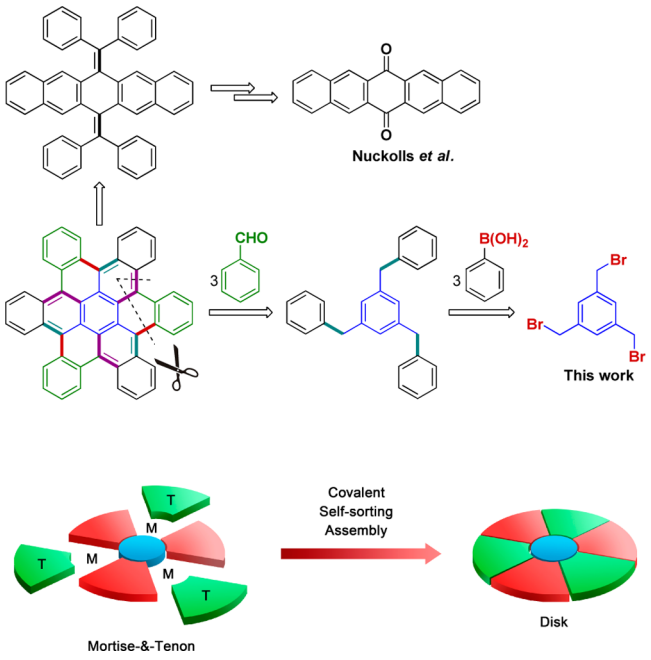
substitution from simple and readily available compounds is highly desired for creating prosperity for this family of PAHs and related compounds.

In planning a facile strategy that provides coronene-based NGs, for example, *c*-HBCs, we were attracted by their 3-fold symmetry and thus created our synthetic concept, the covalent self-sorting assembly (CSA) strategy, for construction of these NG cores based on the retrosynthesis shown in Chart 2. We

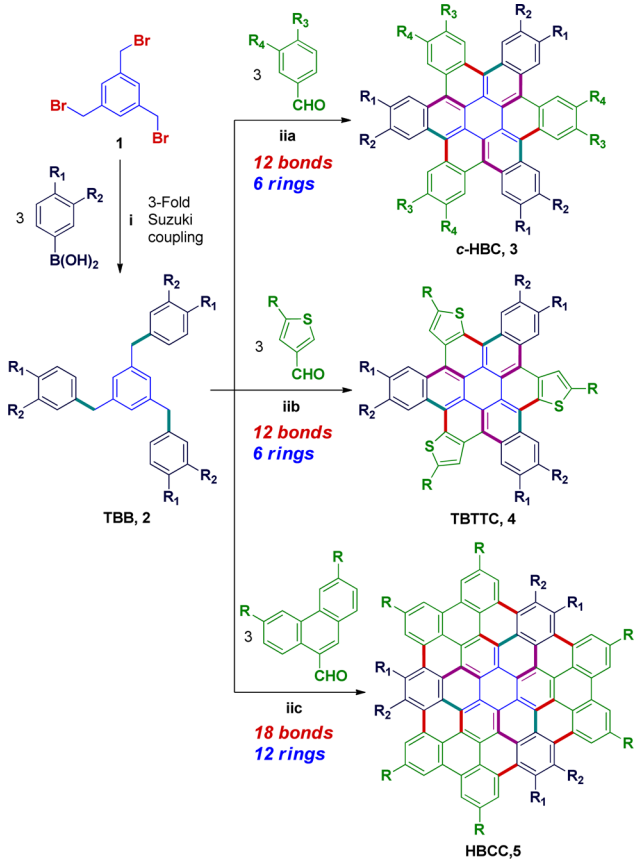
Chart 2. Retrosynthetic Analysis of the Contorted HBC (up) and Conceptual Illustration of the CSA Strategy for the Construction of 3-Fold Symmetric NGs (down)



assumed this CSA chemistry could be accomplished by means of mortise-and-tenon joints, that is, three benzyl tenons automatically were mated into three mortises that correspond to the "cove-regions" between the central ring and branched rings of an appropriate starburst dendritic aromatic molecule, for example, *sym*-tribenzylbenzene (TBBs **2**, Chart 2).

Total synthesis involving the CSA strategy for *c*-HBCs and large NGs is a concise two-step reaction sequence. As depicted in Scheme 1, TBB **2**, which can be readily accessed, for example, through Suzuki cross coupling reaction of 1,3,5-tri(bromomethyl)-benzene **1** and 3,4-dialkoxyphenyl boronic acid, is covalently self-sorting assembled with three arylaldehyde molecules into the polycyclic aromatic architectures. Far different from the reported strategies currently used for constructing *c*-HBCs and other NGs, the logic of our strategy derives from the recognition that 7 (i.e., the central ring and the 6 external rings) of the 13 rings necessary to constitute the entire aromatic scaffold of *c*-HBCs are provided directly by simple benzene building blocks, that is, *sym*-tri(bromomethyl)-benzene **1**, arylboronic acids and arylaldehydes, while the remaining 6 hexagonal grids, which are slotted in between the central and the peripheral rings, can be constructed by C−C bond formation reactions, that is, Friedel−Crafts[10] and Scholl reactions.[11] The feasibility of such a design should be enhanced by preinstalling appropriate ring-activating/directing/blocking groups, such as alkoxy groups, on the aromatic rings of the starting boronic acids and/or aldehydes.

Scheme 1. New Synthesis Involving the CSA Strategy for *c*-HBCs and Large NGs[a]



[a]Conditions: (i) $PdCl_2$, Na_2CO_3, Me_2CO/H_2O, rt 12 h, then 37-38 °C, 3 d, 64−83%; (ii) 10 mol % $FeCl_3$, Ac_2O, CH_2Cl_2, $MeNO_2$, Ar, rt; then excess $FeCl_3$. The newly formed bonds are highlighted in colored bold.

This approach, if successful, would conveniently provide not only *c*-HBCs having the pattern and degree of substitution different from the reported ones but also hetero analogs and even larger, more complex NGs with 3-fold symmetry. It should be noted that the rim decorations may serve as solubilizing groups. More significantly, they permit fine-tuning of the molecular and supramolecular properties and extending the aromatic π-systems via altering the reactants or functionalizing the final products. Also noteworthy is that our CSA strategy distinguishes itself from other protocols reported for access to NGs by dodging the preparation of corresponding oligophenylene precursors.

RESULT AND DISCUSSION

Synthesis of *c*-HBCs and the Heteroanalogues. The starburst mortise adaptors, TBB **2a−f**, were synthesized in good yields by a 3-fold Suzuki coupling reaction of 1,3,5-tri(bromomethyl)benzene **1** with 3,4-dialkoxyphenyl boronic acid by the method borrowed from B. P. Bandgar et al.[12] with some modifications. For realization of the CSA concept, we carried out the assembly of TBB **2a** and 3,4-dimethoxybenzaldehyde using $FeCl_3$ as catalyst/oxidant and acetic anhydride as dehydrator in a DCM/CH_3NO_2 solution at room temperature under argon atmosphere. To our delight, the TBB and the three arylaldehyde molecules covalently self-assemble into the requisite *c*-HBC **3a** in an excellent yield (entry 1, Table 1).

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Table 1. c-HBCs and Larger PAHs Synthesized by the CSA Method[a]

entry	R^1/R^2	R^3/R^4 or R	PAH	yield[b]
1	OCH_3/OCH_3	OCH_3/OCH_3	**3a**	90%
2		CH_3/CH_3	**3b**	93%
3		F/F	**3c**	95%[c]
4		Br/OCH_3	**3d**	97%
5		CH_3/H	**3e**	92%
6		$C(CH_3)_3$/H	**3f**	95%
7		F/H	**3g**	94%[c]
8		Cl/H	**3h**	82%
9		Br/H	**3i**	86%
10		CF_3/H	**3j**	39%
11		H/H	**3k**	88%[c]
12		OC_4H_9/OC_4H_9	**3l**	95%
13		OC_8H_{17}/OC_8H_{17}	**3m**	77%
14		$OC_{12}H_{25}/OC_{12}H_{25}$	**3n**	68%
15	OC_4H_9/OC_4H_9	OC_4H_9/OC_4H_9	**3o**	94%
16		CH_3/CH_3	**3p**	87%
17		F/F	**3q**	92%
18		Br/H	**3r**	90%
19		H/H	**3s**	81%
20	OC_6H_{13}/OC_6H_{13}	OC_6H_{13}/OC_6H_{13}	**3t**	91%
21	OC_8H_{17}/OC_8H_{17}	OC_8H_{17}/OC_8H_{17}	**3u**	80%
22	$OC_{12}H_{25}/OC_{12}H_{25}$	$OC_{12}H_{25}/OC_{12}H_{25}$	**3v**	51%
23	OC_4H_9/OCH_3	OC_4H_9/OCH_3	**3w**	86%
24		Br/OCH_3	**3x**	82%
25	OCH_3/OCH_3	H	**4a**	32%
26	OC_4H_9/OC_4H_9	H	**4b**	49%
27	OC_6H_{13}/OC_6H_{13}	H	**4c**	47%
28	OCH_3/OCH_3	t-Bu	**5a**	36%
29	OC_4H_9/OC_4H_9	t-Bu	**5b**	47%
30	OC_6H_{13}/OC_6H_{13}	t-Bu	**5c**	53%

[a]Conditions is the same as those shown in Scheme 1. [b]Isolated yields by column chromatography, unless otherwise noted. [c]Yields by filtration and washing with methanol, the product is pure enough for NMR analysis.

Such a one-step 6-fold self-sorting tenoning annulation is definitely highly efficient, especially if one considers that a total of 12 C−C bonds and 6 benzene rings are constructed in a single step. In this unprecedented process, four 3-fold transformations take place in tandem, that is, Friedel−Crafts hydroarylation and intramolecular alkylation, dehydrogenative aromatization and intramolecular Scholl reaction. So, this protocol may also be referred to as a direct annulation-aromatization-annulation (AAA) process.

The ^{1}H NMR spectrum of **3a** exhibits as being very simple and symmetrical; only two singlets appear at 8.78 and 4.20 ppm. The ^{13}C NMR spectrum showed six singles attributable to methoxy groups and five sets of the aromatic carbon atoms. These results are fully consistent with its 6-fold symmetry. In the MALDI-TOF spectrum, the molecular ion of m/z 960.3 was observed as a sole peak. The ultimate confirmation was provided by X-ray crystallography.

Pleased with these results, we applied this concept to the synthesis of *c*-HBCs with various substitution symmetries and peripheral decorations using different aryl boronic acids and arylaldehydes to explore the generality of our protocol. A series of *c*-HBCs was comfortably attained (Table 1). In most cases, the reaction was carried out with acetic anhydride and a catalytic amount of $FeCl_3$ in DCM/CH_3NO_2 solution, followed by dropwise addition of 15.6 equiv of the $FeCl_3/CH_3NO_2$ solution over ca. 1 h to the reaction mixture and stirring an additional 12 h before quenching by methanol.

As seen from Table 1, the desired *c*-HBCs were expediently achieved from the TBBs bearing different alkoxy groups and various benzaldehyde building blocks using this CSA protocol, most in high yields. Electron-rich aromatic aldehydes are favorable to give the hunted *c*-HBCs; while electron-poor ones hinder the assemble reaction (entries 8 and 10). These results suggest that our $FeCl_3$-mediated CSA chemistry follows a parallel trend as for electrophilic aromatic substitution and oxidative cyclodehydrogenation reactions. Yet, 3,4-difluorobenzaldehyde delivers the hexafluorinated *c*-HBC **3c** smoothly (entry 3). Owing to solubility issue, this compound was not further purified by columnar chromatography, but it was found to be sufficiently pure for spectral analysis after thoroughly rinsing with methanol. Noteworthy, **3c** has electron-rich and -poor rings alternately fused on the coronene core, providing a rare example of alternate push−pull structure.

The CSA method can also be comfortably applied to the mono- and nonsubstituted aldehydes (Table 1, entries 5−9, 11, 18 and 19) to deliver the related *c*-HBCs in good yields. This result indicates that the competing side reactions such as intermolecular Scholl chemistry on the bare positions of the rim are insignificant in this process. In the case of 4-(trifluoromethyl)benzaldehyde, the reaction afforded a low yield (entry 10), presumably because of the strong electron-withdrawing nature of the trifluoromethyl group which reduces the reactivity of the attached benzene ring toward Friedel−Crafts and Scholl reactions. Still, the reaction is quite effective considering that the 39% isolated yield of the product represents a 92% yield per C−C bond formed.

The *c*-HBCs decorated with phase-forming and solubilizing long-aliphatic chains were also accessible using this concept in satisfactory yields (entries 13, 14, and 20−22).

The TBB with the branched phenyl rings bearing two different groups contentedly affords the anticipated *c*-HBCs with mixed substitution of each peripheral benzo ring (entries 23 and 24). Such multisubstituted *c*-HBCs provide a promise to selective modification of the anellated benzo rings or extending their π-systems.

Switching benzaldehydes to thienaldehydes, we anticipated to attain a novel heteroversion of *c*-HBCs, *sym*-tribenzotetrathieno-coronenes (TBTTCs), wherein coronene core is alternately fused by thieno- and benzo-rings (Scheme 1, central raw), unlike Nuckolls' dibenzotetrathienocoronene (DBTTC)[9b] and Müllen's hexathienocoronene (HTC).[13] But unfortunately, exposure of 2-thienaldehyde to TBB **2b** under the same conditions led to TBTTC **4b** (m/z 1050.6) and a byproduct (m/z 970.6) that can be ascribed tentatively to excision of a thiophene ring. Similar results were found when using 5-methyl-2-thienaldehyde as the starting aldehyde (Figure S1 and Scheme S7 in the Supporting Information). We surmised the loss of thiophene units as a result of retro-Friedel−Crafts reaction during the CSA process (Figure S2 in the Supporting Information). Considering that the 3-isomer may be more robust toward this unwanted reaction, we tried to exploit 3-thienaldehyde instead of the 2-isomer and succeeded in assembling **4b** with 49% yield as a single regioisomer (entry 26). The simplicity of NMR spectra clearly elucidates its 3-fold symmetry in solution and thereby divulged the high regioselectivity of the Scholl cyclization. In analogy, TBB **2c** and **2a** with 3-thienaldehyde gave **4c** and **4a** in 47% and 32%

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yields (entries 27 and 25), respectively. The susceptibility of thiophene ring toward side reactions may be blamed for the low yields.

Synthesis of HBCCs. Spurred by the successful assembly of the *c*-HBCs, we turned to the construction of larger π-disks using our CSA concept. It can be foreseen that, upon installation of 9,10-phenanthro- moieties, the newly formed [5]helicene fjord regions of the intermediary *c*-HBC could be further stitched into hexagons via removing the fjord hydrogens with sufficient $FeCl_3$, thus elaborating a new NG species that has 72 aromatic carbon atoms, 25 fused benzene rings, 3-fold symmetric substitution and all-armchair periphery. This hitherto unknown disk may be formally viewed as a hexa-*peri*-hexabenzocircumcoronene (HBCC, 5). Markedly, HBCC 5 has the greatest number (12 rings) of aromatic sextets and no formal nonaromatic double bonds in the structure, being a full-benzenoid PAH according to the Clar's π-sextet rule.[15]

The hexahexoxy substituted TBB **2c** and 3,6-di-*tert*-butyl-9-phenanthraldehyde were chosen to avoid the solubility issue. The application of our CSA conditions, however, led to a mixture of incompletely dehydrogenated intermediates, of which the main MALDI ion is eight mass units higher than the molecular mass of the expected **5c**, meaning that eight hydrogen atoms were left unremoved or four fjords unclosed. Resubmitting this mixture, after simply wishing with water and drying with Na_2SO_4, to the Scholl reaction by adding fresh $FeCl_3/MeNO_2$ solution, we obtained the hunted **5c** smoothly in 56% yield. The MALDI molecular ion at *m*/*z* 1825.3 (hoped 1825.1) and unambiguous ^1H and ^{13}C NMR spectra were consistent with the expected structure. That HBCC **5c** was definitely in hand derived from X-ray crystal analysis.

Concurrently, we also tested the one-pot synthesis of the HBCC by increasing the dosage of $FeCl_3$ and found that, with 120 equiv $FeCl_3$ in the Scholl coupling, which is five times the stoichiometric requirement, dodeca-cyclized **5c** was accessed successfully in 53% yield (entry 30). It is striking that in this case 18 new C−C bonds (Scheme 1, colored bold red and purple) and 12 benzene rings are formed in one pot. The 53% isolated yield was not very high yet reasonable for access to such a large compact PAH via such a multifold reaction step, particularly in view of 96.5% average yield per bond or 94.8% per rings formed. In this regard, it further highlights the merit inherent to our CSA chemistry. The methoxy and *n*-butoxy analogues, **5a** and **5b**, were accessed in satisfactory yields following the same procedure (entries 28 and 29) and were identified by NMR and MS analyses. However, with 9-phenanthraldehyde, neither the one-pot synthesis nor resubmitting protocol succeeded in offering the desired product in pure form, instead a complex mixture contaminated by partially dehydrogenated species and chlorinated byproducts. Both **5b** and **5c** are readily soluble in common solvents while **5a** is less soluble. They all exhibit a red fluorescence on TLC plate or in DCM solution under 365 nm ultraviolet light, different from the *c*-HBCs derived from monocyclic arylaldehydes.

The successful synthesis of the *c*-HBCs and related PAHs exemplifies the application of our concept in rapid bottom-up construction of polyaromatic architectures and suggest its potential in the creation of new NG species with a variation in functional groups and aromatic frameworks since a wide range of aryl aldehydes and boronic acids are commercially available or preparatively accessible.

X-Ray Crystallographic Studies. Single crystals of *c*-HBCs **3a** and **3t** and TBTTC **4b** were obtained by slow evaporation of their solutions in different solvents (see the X-ray crystallographic analysis in the Supporting Information). We were also fortunate enough to obtain a crystal of **5c**, which, to the best of our knowledge, is hitherto the largest discoid NG molecule with all-hexagonal grids to be represented by X-ray crystal structure.

X-ray crystallographic outcomes unambiguously show that, in analogy to the unsubstituted *c*-HBC reported by Nuckolls et al.,[8a] the dodecaalkoxy substituted *c*-HBCs **3a** and **3t** (Figure 1A and B) have the as-expected nonplanar aromatic structure

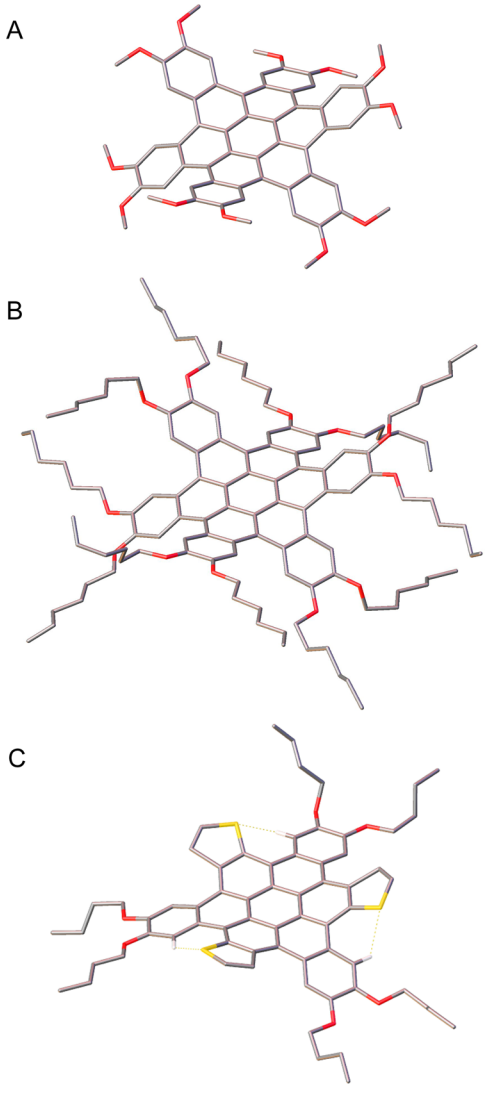

Figure 1. X-ray molecular structures of c-HBCs (A) **3a** and (B) **3t** and (C) TBTTC **4b** (**3a** and **3t** was measured at room temperature while **4b** at 105 K. Hydrogen atoms are omitted for clarity; oxygen is depicted in red and sulfur in yellow).

with a double-trefoil shape and an inversion center. The fused benzo-moieties are bent away from planarity in an alternate up and down arrangement because of the sterically congested cove-regions. The central and peripheral rings are essentially flat while the in-between benzofused rings adopt boat-conformations with a mean fold angle of 18.2° in **3a** and 18.1° in **3t** and the C−C bonds attached on the central ring are shorter than those on the exterior rings, as observed in the bare *c*-HBC.[8a] The average splay angle at cove-region is 41.6° in **3a**

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and 41.1° in **3t**, comparable to that of bare *c*-HBC (42.0°).[9c] Each ortho-methoxy group is almost coplanar with the attached benzo ring. In **3t**, two of the six hexoxys are out-of-plane with respect to the benzo-units while the others are coplanar and, notably, each two opposite oriented side-chains are inversion-related in conformation, forming a centrosymmetric pair. Introduction of the side chains has no marked effect on the shape of the aromatic core.

The hetero analogue, TBTTC **4b**, also adapts the up−down conformation (Figure 1C); three thieno-units bend to one side while three benzo-units bend to the opposite. The small size of thiophene ring leads to a noticeably flattening of the core in comparison with *c*-HBCs **3a** and **3t**. In the crystal, this twisted, chiral core molecule no longer holds the C_3 symmetry, unlike the case in solution. Neither splay angles at cove regions nor distortion of equivalent parts of the molecule are identical (Table S17 in the Supporting Information). Three intramolecular H-bonds were observed in the sulfur-containing bay regions. Each pair of enantiomeric molecules forms a cofacial, slipped, racemic dimer from their benzofused sides and in a centrosymmetric head-to-tail arrangement (Figure S8 in the Supporting Information). The interlayer distance in the dimer is 3.44 Å, slightly longer than that of DBTTC (3.3 Å)[9b] and HTC (3.37 Å).[13]

X-ray analysis of HBCC **5c** ascertained the devised structure and demonstrated its nonplanar and asymmetrical geometry in the crystalline state (Figure 2A). Both deplanarization and desymmetrization of the aromatic framework essentially stem from the alkoxyl substituents overcrowding at the bay regions: they force the neighboring benzene rings to deviate from planarity and concurrently are themselves compelled to bend out of the plane of the attached benzo-unit. The alkoxyl groups are twisted about C_{Ar}−O bonds with torsion angles of 68−82° and placed in an "up−up−down−up−down−up" pattern, leading to not only the curvature and asymmetry but also the inequivalent distortion of the molecule. In fact, only eight benzene rings, including the central ring, keep their own carbon atoms coplanar within 0.018 Å while the others are deplanarized ranging from 0.023 to 0.054 Å. Noteworthy is that the edge affixing the cisoid vicinal dialkoxyl groups is seriously lifted up; no torsional angles of the bays, including those unsubstituted, are alike.

Even so, the all-benzenoid nature of the core[3j,8a,16] is observed from the discrepancy between the discrepancy between inter- and intrabenzenoid C−C bonds (1.44−1.47 Å and 1.38−1.42 Å, respectively) (Table S21 in the Supporting Information). The *tert*-butyl groups keep in the same plane of the attached benzene rings and might trivially influence the distortion. In tramolecular H-bonds were observed between oxygen and hydrogen atoms.

Inspection of the crystal packing of **5c** (Figure 2B and C) illustrates that two molecules form a slipped cofacial dimer and are inversion related. In other words, the dimer is a racemate of two conformational enantiomers. Inside the dimer, two opposite conformers are stacked from the less crowded sides and slipped by 3.57 Å along a *p*-quaterphenyl unit, forming a concave-convex complementarity with a π-overlap of about 14 hexagons. The center−center distance is 4.87 Å and the separation between the mean planes of the central rings is 3.33 Å, close to the layer distance in graphite (3.35 Å). This is characteristic for a pronounced π−π interaction between two aromatic cores. The side-chains placed outside the dimers impede the interdimer π−π interactions but provide favored

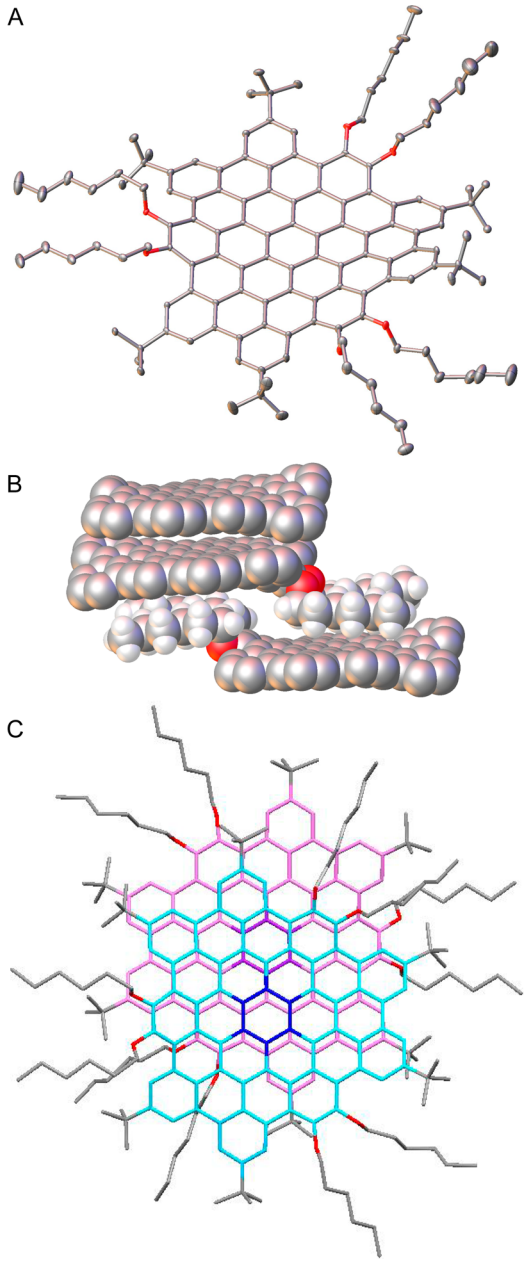

Figure 2. X-ray molecular structure of HBCC **5c** and the dimers in the crystal. (A) Overall view. (B) Side-view of the $\pi\cdots\pi$ and C−H$\cdots\pi$ dimers, looking along the slipping direction of the molecules (Sustituents and hydrogen atoms are omitted for clarity except for the ones shown). (C) Top-view of the $\pi\cdots\pi$ dimer, looking down the planes of two enantiomers (Measured at 100 K; Hydrogen atoms are omitted for clarity; oxygen is depicted in red).

aliphatic C−H$\cdots\pi$ interactions with the neighboring dimer. Interestingly, the hexoxyl chains adjust themselves with the topography of the nearest aromatic ring to facilitate the contact of the C−H bonds with the π-system. A series of 22 hydrogen atoms of four hexoxyl groups between two π−π dimers are involved in the cooperative interactions with atom-to-plane distances of 2.67−2.94 Å (Table S24, Figures S10 and S11 in the Supporting Information).

The size of the aromatic core, defined here as the mean distance of the *p*-quaterphenyl motifs, is 1.55 nm. It hence should serve as a new discogen possessing a π-system larger than both *p*- and *c*-HBCs.

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Spectral and Thermal Properties. The spectral properties of some *c*-HBCs, TBTTCs and HBCCs were summarized in the Supporting Information. The typical spectra of **3a**, **4b** and **5c** are shown in Figure 3.

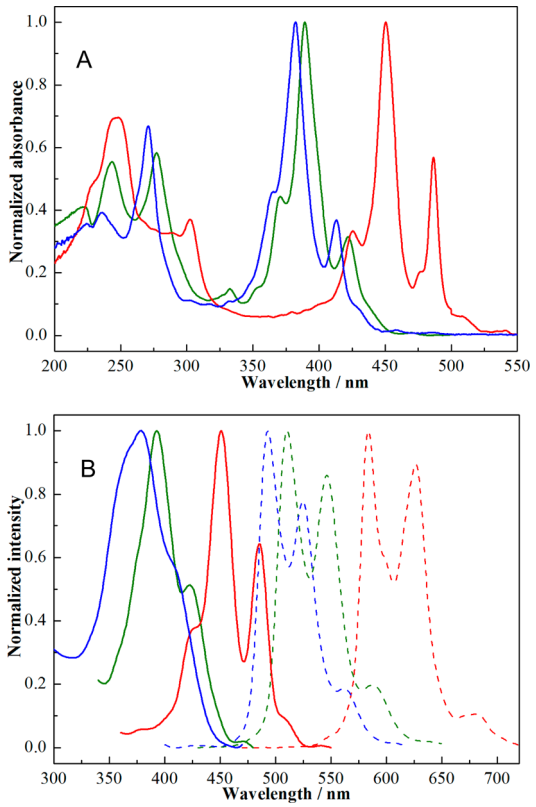

Figure 3. Normalized spectra of *c*-HBC **3a** (green) and TBTTC **4b** (blue) and HBCC **5c** (red profile). A: UV−visible spectra (4.00 μM for **3a** and **4b**; 2.00 μM for **5c**; all in DCM); B: emission and excitation (dashed line) spectra (rt., 0.40 μM in DCM).

c-HBC **3a** and its heteroversion TBTTC **4b** exhibit almost indistinguishable spectral natures in UV−visible and fluorescence spectra. They display three strong absorption bands around λ_{max} 250, 390, and 420 nm, similar to Clar's,[7] Nuckoll's,[9f] and Müllen's results.[13,14] For **3a**, the strongest absorption maximum is at wavelength of 390 nm with a molar extinction coefficient (ε_{max}) of 2.3 × 10^6 M^{-1} cm^{-1}, probably due to the conjugation of peripheral methoxy substituents. The emission spectra exhibit a strong green fluorescence with three maxima at λ_{max} 510, 550, and 580 nm with Stokes shifts near 120 nm (Figure 3B). The emission spectral features of **4b** resemble those of **3a**, except for slight blue-shifts.

HBCC **5c** shows three strong absorption bands around 250, 450, and 480 nm, typical of large aromatic molecules. Compared with those of *c*-HBCs, these bands are drastically red-shifted and the absorption coefficients at the maxima of ca. 450 nm are much higher (for **5c**, ε_{max} 3.2 × 10^6 $M^{-1}cm^{-1}$). Apparently, the extended size of the π-system contributes the red-shift and the enhanced intensity of the absorption bands. The HBCCs display a strong yellow fluorescence in DCM (Figure 3B). Two strong emission maxima of **5c** were observed at around 590 and 630 nm, respectively, with Stokes shifts in excess of 150 nm. The fluorescence quantum yield of **5c** in DCM is 24%, relative to a standard of Rhodamine B in 2.0 μM ethanol (Table S28 and Figure S13 in the Supporting Information). Both absorbance and emission maxima for the HBCCs are red-shifted by *ca.* 80 nm as compared to the *c*-HBCs.

The thermogravimetric analysis of several representatives reveals that they are stable to above 300 °C (Table S29 and Figure S14 in the Supporting Information), being thermally robust. Most of them exhibit sufficient solubility in ordinary organic solvents (e.g., DCM, chloroform, toluene, and THF) to consent usual spectroscopic analysis and chromatographical isolation.

CONCLUSION

We have paved a facile and efficient approach, based on the CSA strategy for access to 3-fold symmetrical and highly substituted *c*-HBCs from very simple chemicals using benzylic carbons as annulating partners, as an effective alternative to the reported approach. The total synthesis is composed of 2 steps of multifold transformations, both under mild conditions and in good to excellent yields. These merits make the *c*-HBCs one of the most accessible large polycyclic aromatic molecules and, more significantly, render the method a simple and versatile tool to be controlled in the hands of chemists and materials scientists. Also remarkable is that our method is amenable to creating the hetero-*c*-HBCs and large molecular graphenes. So it provides simple access to coronene-based PAHs that are substituted both in the periphery and at the aromatic core. X-ray analysis reveals their intriguing structural properties. Furthermore, the good accessibility and modifiable symmetric decorations of the synthesized PAHs allow them to serve as new launching platforms for going to even larger aromatic architectures with defined shape, size and periphery. We believe that this method will promote the development of *c*-HBC chemistry, along with the Nuckolls' approach. Further efforts to expand the synthetic diversification of this strategy and the synthetic uses of the as-prepared NGs are ongoing.

EXPERIMENT SECTION

General experimental details, synthesis and characterization for all compounds, X-ray crystallographic data for some products, and physicochemical data can be found in the Supporting Information. The synthetic details are exemplified by the synthesis of **2a**, **3a**, **4b**, and **5c** below.

General Synthesis of 1,3,5-Tri(3,4-dialkoxybenzyl)benzenes (TBBs). A mixture of arylboronic acid, Na_2CO_3 in 40 mL acetone−water (1:1) was stirred at room temperature until it became homogeneous. Then, it was cooled in an ice bath and degassed by bubbling Ar for 15 min. To this mixture was added 1,3,5-tris(bromomethyl)benzene **1** and $PdCl_2$ at 0 °C and it was stirred at rt for 12 h and 37−38 °C for 3 days under argon atmosphere. After completion of the reaction (monitored by TLC), acetone was removed under reduced pressure and the product was extracted with diethyl ether and dried with anhydrous Na_2SO_4. Removal of the ether on a rotary evaporator furnished the crude product, which was further purified by column chromatography (silica gel). 1,3,5-Tris(3,4-dimethoxybenzyl)-benzene (**TBB 2a**) was prepared from 3,4-dimethoxyphenylboronic acid and **1** and purified by column chromatography (silica gel, PE:EA = 2:1, v/v). White solid (yield 83%). Mp 112−114 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.85 (s, 3H), 6.79−6.76 (d, J = 9.0 Hz, 3H), 6.70−6.67 (d, J = 9.0 Hz, 3H), 6.65 (s, 3H), 3.84 (s, 18H), 3.78 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 148.8, 147.3, 141.5, 133.7, 127.1, 120.7, 112.2, 111.2, 55.8, 55.7, 41.3; HR-MS (ESI): m/z calcd for ($C_{33}H_{36}O_6$ + Na) 551.2410, found 551.2398.

General Procedures for the Synthesis of *c*-HBCs. To a solution of 3,4-dimethoxybenzaldehyde (100 mg, 1.65 mmol) and Ac_2O (0.47 mL, 5 mmol) in 350 mL DCM was added a solution of $FeCl_3$ (16.2

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mg, 0.1 mmol) in CH_3NO_2 (1 mL) while stirring at rt, followed by dropwise addition over 1 h of TBB **2a** (0.5 mmol, 264 mg) in DCM (50 mL). The resulting mixture was stirred at rt overnight and then degassed with Ar for 15 min. A second portion of $FeCl_3$ (1.26 g, 7.2 mmol, in 20 mL CH_3NO_2) solution was added dropwise over 1 h under Ar atmosphere and stirred for 12 h. Then, cold CH_3OH (100 mL) was added with stirring to quench the reaction and the mixture was poured into cold water (500 mL). The biphasic mixture was separated and the aqueous layer was extracted three times with DCM. The combined organic layers were washed with water, dried by Na_2SO_4, filtered, and rotoevaporated in vacuo. The residue was purified by chromatography (silica gel, DCM:EA = 10:1, v/v) to give **3a** as a yellow solid (432 mg, yield 90%). Mp > 300 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.78 (s, 12H), 4.20 (s, 24H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 148.4, 125.0, 123.7, 120.4, 109.0, 56.1; MS (MALDI-TOF) (CHCA): m/z calcd for $C_{60}H_{48}O_{12}$: 960.3 (M^+), found: 960.3.

General Procedures for the Synthesis of *c*-TBTTCs. To a solution of 3-thienaldehyde (0.9 mmol) and Ac_2O (0.2 mL, 2 mmol) in 350 mL DCM was added a solution of $FeCl_3$ (16.2 mg, 0.1 mmol) in CH_3NO_2 (1 mL) while stirring at rt, followed by dropwise addition over 1 h of TBB **2c** (0.20 mmol) in DCM (50 mL). The resulting mixture was stirred at rt overnight and then degassed with Ar for 15 min. A second portion of $FeCl_3$ (1.26 g, 7.2 mmol, in 20 mL CH_3NO_2) solution was added dropwise over 1 h under Ar atmosphere and stirred for 4 h. Then, cold CH_3OH (100 mL) was added with stirring to quench the reaction and the mixture was poured into cold water (500 mL). The biphasic mixture was separated and the aqueous layer was extracted three times with DCM. The combined organic layers were washed with water, dried by Na_2SO_4, filtered, and rotoevaporated in vacuo. The residue was purified by chromatography (silica gel, PE:DCM = 1:1, v/v) to give **4b** as a yellowish brown powder (99 mg, 49% yield). Mp > 300 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.12 (s, 3H), 8.67−8.66 (d, J = 5.6 Hz, 3H), 8.62(s, 3H), 7.77−7.76 (d, J = 5.6 Hz, 3H), 4.49−4.46 (t, J = 6.6 Hz, 6H), 4.39−4.36 (t, J = 6.6 Hz, 6H), 2.12−2.04 (m, 12H), 1.76−1.67 (m, 12H), 1.16−1.10 (m, 18H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 149.4, 148.7, 135.3, 134.0, 126.8, 125.0, 124.1, 123.7, 122.2, 121.0, 111.5, 108.3, 69.2, 69.1, 315, 31.4, 19.5, 19.4, 14.0; MS (MALDI-TOF) (CHCA): m/z calcd for $C_{66}H_{66}O_6S_3$: 1050.4 (M^+), found: 1050.6.

General Procedures for the Synthesis of HBCCs. To a solution of 3,6-di-*tert*-butyl-9-phenanthraldehyde (114.5 mg, 0.36 mmol) and Ac_2O (0.24 mL, 2.5 mmol) in 350 mL DCM was added a solution of $FeCl_3$ (8.1 mg, 0.05 mmol, 10 mol %) in CH_3NO_2 (1 mL) while stirring at rt, followed by dropwise addition of a solution of TBB **2c** (0.1 mmol, 94.8 mg) in 50 mL DCM. The resulting mixture was allowed to stir for 48 h at rt. Then it was degassed with Ar for 10 min and then added dropwise a second portion of $FeCl_3$ (1.92 g, 12 mmol) solution in 20 mL CH_3NO_2 over 1 h under Ar atmosphere. After being stirred at 0 °C for an additional 4 h, the mixture was added 100 mL CH_3OH with stirring and then poured into cold water. The biphasic mixture was separated and the aqueous layer was extracted three times with DCM. The combined organic layers were washed with water, dried by Na_2SO_4, filtered, and rotoevaporated in vacuo. The residue was purified by chromatography (silica gel, PE:DCM = 10:1) to give **5c** as a brick-red solid (97 mg, 53 % yield). Mp > 300 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.77 (s, 6H), 9.70 (s, 6H), 4.48−4.45 (t, J = 4.5 Hz, 12H), 2.40−1.98 (m, 12H), 1.94 (s, 54H), 1.60−1.37 (m, 36H), 0.95−0.91 (t, 18H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 151.0, 149.1, 130.1, 129.3, 124.6, 124.2, 123.4, 123.0, 120.8, 120.3, 119.4, 74.7, 36.2, 32.4, 31.9, 25.8, 22.7, 14.0; MS (MALDI-TOF) (CHCA): m/z calcd for $C_{132}H_{144}O_6$: 1825.1 (M^+), found: 1825.3.

■ ASSOCIATED CONTENT

Supporting Information

General experimental, synthetic details and characterization including the copies of NMR and MS spectra for all products and intermediate compounds, X-ray crystallographic data for products **3a**, **3t**, **4b** and **5c**, and physicochemical data. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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