

Synthesis and Characterization of Contorted Pentabenzofused Coronenes as Semiconducting Materials

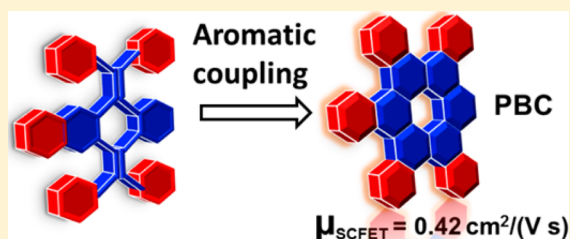
Yu-Tai Tao,^{*,†} Someshwar Pola,[‡] Sushil Kumar,[†] and M. Minarul Islam[†]

[†]Institute of Chemistry, Academia Sinica, Taipei, Taiwan, ROC, 11529

[‡]Department of Chemistry, Nizam College, Osmania University, Hyderabad, 500001, India

S Supporting Information

ABSTRACT: Here, we report the synthesis and characterization of a series of contorted, yet noncentrosymmetrical, polycyclic aromatic hydrocarbons with a pentabenzofused coronene as the core framework. The parent pentabenzofused coronene (PBC) compound is shown to exhibit a shifted and rotated type of π - π stacking interactions, which render this series a semiconducting material. Single-crystal-based field-effect transistor devices of PBC exhibited efficient charge transport behavior, giving a p-channel field-effect mobility of $0.42 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ and an on/off ratio of 10^5 .



INTRODUCTION

In recent years, there has been an enormous amount of effort on the design and synthesis of polyaromatic hydrocarbons (PAHs) due to their potential applications as semiconducting materials in the fast growing area of organic and flexible electronics.¹ The type and size of the core, the number of rings fused, and the geometry of the molecular framework all play vital roles on their packing arrangement in the solid state, which in turn determines their charge transporting properties among molecules.²

Design and synthesis of new PAHs for improved mobility and photo/chemical stability require a good understanding of the packing motif of these molecules. Significant progress has been made in using linear/planar aromatic compounds such as pentacene, rubrene, oligothiophenes, and their derivatives in fabricating organic field-effect transistors (OFETs).³ Nevertheless, attempts to reach a structure/property correlation is difficult since the mobility is related not only to the molecular structure but also to the crystal packing, film morphology, electrode contacts, etc., and the morphology factor more often than not overwrites the molecular structure factors. The morphology issue can be ignored by fabricating single-crystal field-effect transistors (SCFETs),⁴ which involve only one crystal arrangement, and the result may shed light on the correlation between intrinsic charge transport property and molecular structure. For example, a high carrier mobility over $15 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ was observed with rubrene^{2b} in a single-crystal transistor configuration, whereas very poor mobility was observed in thin film transistor mode due to poor crystallinity of thermally deposited films.⁵ Crystal packing of molecules is a complicated issue and relates to the electrostatic and steric interactions within the molecule. Several general categories of packing motifs have been proposed for pristine PAHs,⁶ although the actual packing details very much depend on the molecular shape and substituents.

Coronene-based PAHs have been interesting and potential candidates for their extensive π -conjugation and electron distribution for π -cloud overlap (electronic coupling).⁷ Planar *peri*-hexabenzocoronene (*peri*-HBC) and its derivatives have been used as active materials in OFETs.⁴ Nonplanar polyaromatics have been considered to have a high tendency to give co-facial packing due to the self-complementarity in shape, and thus a strong electronic coupling, which is beneficiary for charge transporting, might be expected.⁸ The Nuckolls group has also described spun-cast TFTs and solution-grown fibers transistors with contorted *cata*-hexabenzocoronene derivatives.⁹ Recently, we reported high-efficiency SCFETs using contorted pyreno[4,5-*a*]coronenes,¹⁰ tetrabenzofused coronenes,¹¹ and dibenzofused coronenes¹² as the channel materials. These compounds display exactly co-facial or shifted co-facial packing. These molecules are nevertheless more central-symmetrical in shape. For symmetrical molecules, regular and periodic packing arrangement in space is likely to be more easily achieved, whereas, for non-central-symmetrical molecules, the packing into a periodic array is more complicated and unpredictable.

In the present work, we report the synthesis and characterization of contorted pentabenzofused coronene (PBC) derivatives as semiconducting molecules. The pentabenzofused coronene derivative is twisted due to the steric repulsion between the hydrogens in the fjord regions.^{9d} In contrast to previous examples, these molecules are non-central-symmetrical. This may limit the way to give periodic crystal packing. As we demonstrated in this work, these molecules pack in a much shifted and rotated type of packing stacks, presumably due to their much distorted shape. The seemingly less π -overlap and thus less electronic coupling was

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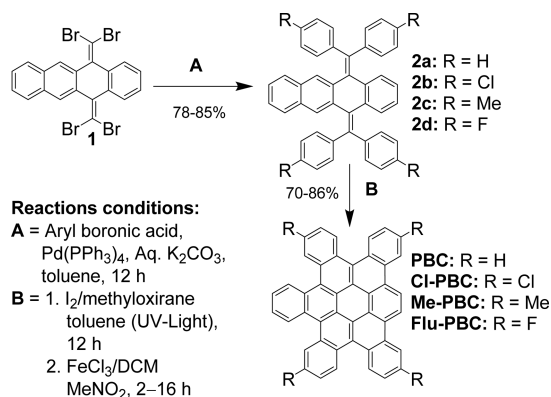
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compensated by the near one-dimensional stacking, and field-effect transistors based on the single crystal of the parent derivative are prepared to give a high hole mobility of $0.42 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, demonstrating the potential of these pentabenzocoronenes as a semiconductor.

RESULTS AND DISCUSSION

Synthesis. The PBC derivatives were synthesized via a two-step protocol following the steps shown in Scheme 1.¹³ The

Scheme 1. Synthesis of Pentabenzocoronene Derivatives (PBCs)



Suzuki coupling between the 5,12-bis(dibromomethylene)-5,12-dihydrotetracene (**1**) and aryl boronic acid resulted in the precursor olefins **2a–2d**, which, upon cyclization, yielded the desired products.

The iodine-mediated oxidative photocyclization¹⁴ and iron chloride-catalyzed oxidative cyclodehydrogenation¹⁵ showed a dependence on the functional group attached at the aryl olefins **2**. Thus, the olefin having *para*-methyl groups (**2c**) required shorter reaction time of the oxidative aromatic coupling to give the final derivative, whereas the coupling reactions of olefin **2b** were faster as compared to **2d**, presumably because the electron-donating ability in stabilizing the reaction intermediates involved. The molecular structures of final derivatives were established by ¹H NMR, high-resolution mass spectrometry, and, with the parent PBC, also by its single-crystal X-ray analysis, which will be described later.

Photophysical Studies. The UV–vis absorption spectra, as measured in dilute dichloromethane, are shown in Figure 1. These derivatives showed the characteristic absorption pattern

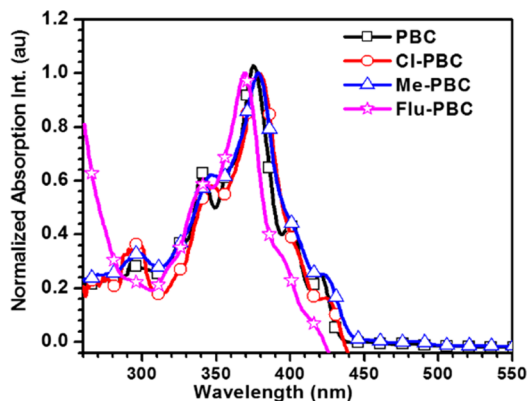


Figure 1. Absorption spectra of PBCs as recorded in dichloromethane.

of coronenes,¹⁶ with their absorption maxima confined in the region of 370–385 nm. A slight substituent effect on the λ_{max} can be observed in that the derivatives Me-PBC and Cl-PBC have a bathochromic shift of ~ 6 nm relative to the parent PBC, whereas Flu-PBC has a hypsochromic shift. The UV–visible absorption as a function of time is also measured, and no appreciable change was observed after irradiating the dilute solutions of PBCs for 2 h (Figure S21a–c, SI). Such photochemical stability was also observed for contorted tetrabenzocoronenes¹¹ and *cata*-hexabenzocoronenes.⁹

HOMO–LUMO Energies and Thermal Properties. The HOMO energy levels are measured by photoelectron spectrometry (AC2) of their solid samples. The resulting data are compiled in Table 1. The theoretically calculated HOMO

Table 1. Photophysical Properties, HOMO–LUMO Energies, and Thermal Data of PBCs

compd.	^a λ_{max} (nm)	^b E_{HOMO} (eV)	^c E_{LUMO} (eV)	^d E_{g} (eV)	^e T_{d} (°C)
PBC	375	5.52	2.98	2.54	446
Cl-PBC	381	5.89	3.47	2.42	519
Me-PBC	379	5.26	2.65	2.61	494
Flu-PBC	371	5.95	3.63	2.32	522

^aAbsorption maxima. ^b E_{HOMO} measured by photoelectron spectrometer (AC2). ^c $E_{\text{LUMO}} = E_{\text{HOMO}} - E_{\text{g}}$. ^dOptical band gap, E_{g} was obtained from the intersection of absorption and emission spectra. ^eThermal decomposition temperature measured at 5% weight loss.

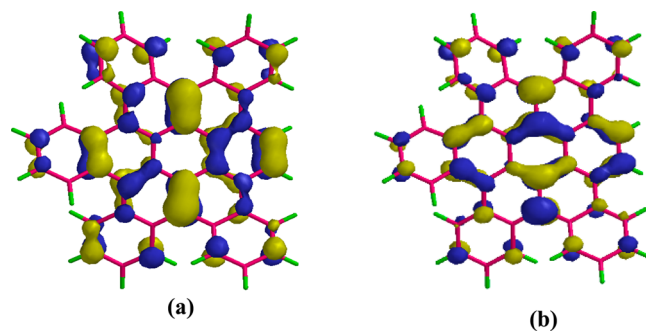


Figure 2. (a) HOMO and (b) LUMO plots for PBC, calculated by SPARTAN at the semi-empirical level.

plots for various PBCs are shown in Figure 2. As can be seen, the Me-PBC has a higher HOMO energy level relative to the parent PBC, whereas Cl-PBC has a lower one, with Flu-PBC having the lowest. However, all of these HOMO levels are lower than that of pentacene (5.2 eV). This may have to do with the twisting nature of the molecular framework so that the conjugation is less than that of planar pentacene, even though more rings are fused together. The lower HOMO levels suggest that all of these compounds are more stable against oxidation, as opposed to pentacene. The optical band gaps of these PBC derivatives were estimated from the absorption edges of their UV–visible spectra. LUMO energies are calculated by subtracting the optical band gap energies from HOMO energies. Again, a substituent effect is seen in the order of LUMO energy: Flu-PBC > Cl-PBC > PBC > Me-PBC, due to the electronic effects of the substituent.¹⁰

Thermal gravimetric plots of PBCs are shown in Figure S22a (SI), with the decomposition temperatures measured at 5%

weight loss (Table 1). These derivatives showed high thermal stability, decomposing at $>450\text{ }^{\circ}\text{C}$.¹¹ In the PBC series, the derivative Flu-PBC, embedded with four fluorine atoms, possesses the highest T_d .

Single-Crystal XRD Analysis. Single crystals were grown by using the physical vapor transport (PVT) technique¹⁷ in a stream of ultrapure argon. The parent derivative PBC gave rodlike crystals, whereas only very thin and wool-like crystals were obtained for other derivatives. Thus, single-crystal X-ray measurements can only be carried out on PBC (Figure 4). The

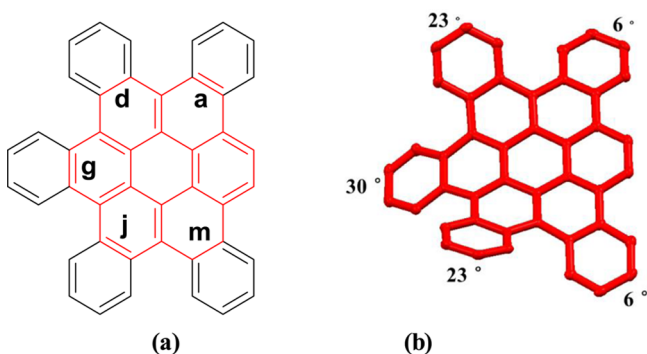


Figure 3. (a) Chemical structure of PBC showing positions of peripheral benzene rings fused with central coronene. (b) Molecular structure of PBC showing bent angles of peripheral benzenes with respect to central coronene.

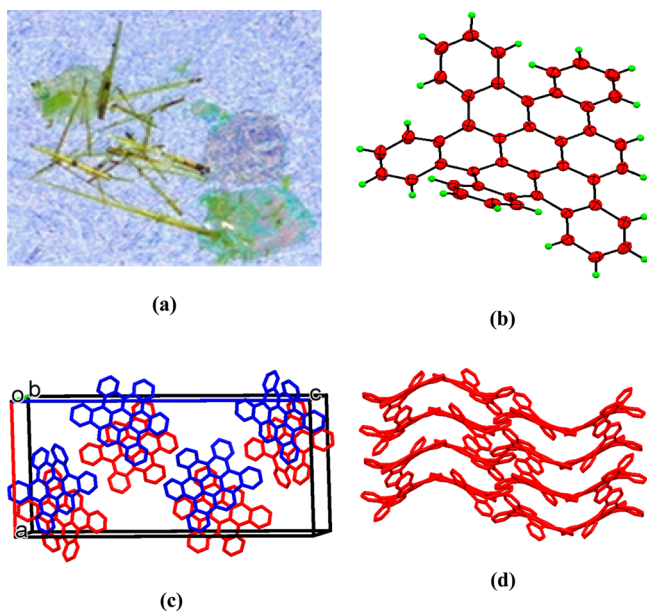


Figure 4. (a) Crystal image of PBC. (b) Thermal ellipsoids of PBC (65% probability). (c, d) Packing motif of PBC.

X-ray analysis revealed the contorted geometry for PBC. The three benzene rings (fused at *a*-, *g*-, and *m*-positions of coronene) bent downward (23° and 6° for *g*-ring and *a*-, *m*-rings, respectively) and the other two rings (fused at *d*-, *j*-positions) bent in the opposite direction ($\sim 30^{\circ}$); thus, only a mirror plane symmetry element (C_s) exists in the molecule (Figure 3 and Figure S23, SI).

The crystal growth direction is indexed to be along the *b*-axis, as shown in Figure S22b (SI). This derivative forms co-facial π -stacks, in which the second stacked molecular layer shifts and

rotates 90° with respect to the lower layer, along the *b*-axis. The interplanar distance between the two closer π -systems is $\sim 3.4\text{ \AA}$.

This packing feature is different from those highly symmetrical systems such as HBC^{9f} and TBC.^{11a} Although the co-facially stacked PBC molecules shift and rotate relative to each other, there is still significant in-phase overlap of their highest occupied molecular orbitals, leading to significant electronic coupling as demonstrated by the high mobility measured from the single-crystal FET (vide infra).

To examine the potential of these coronene-centered PAHs to serve as p-channel material, SCFETs were fabricated with crystals of PBC (Figure S24a,b). A top-contact, top-gate SCFET was fabricated by placing the crystal on a glass substrate, with painted colloidal graphite on both ends of the crystal as the source and drain electrodes. Parylene film was grown on the crystal as the dielectric layer and colloidal graphite on its top as the gate electrode.¹⁸ The channel length, width, and parylene thickness were 0.5–1.0 mm, 0.20–0.25 mm, and 1.8–2.5 μm , respectively. A high mobility of $0.42\text{ cm}^2\text{ V}^{-1}\text{ s}^{-1}$ was obtained with an on/off ratio of 10^5 , using PBC as channel material (Table S1, SI). This mobility is comparable to that of the symmetrical TBC series,¹¹ demonstrating the potential of this series as charge transporting material.

CONCLUSIONS

In conclusion, a new series of contorted and noncentrosymmetrical pentabenzocoronene derivatives are synthesized and characterized. The derivatives are chemically and thermally stable compared to pentacene. The crystal structure analysis shows that the much twisted molecule packs in a column with neighboring π -frameworks stacks shifted and rotated 90° relative to each other. The rodlike crystals of the parent PBC are used to fabricate SCFETs, which show a high hole mobility of $0.42\text{ cm}^2\text{ V}^{-1}\text{ s}^{-1}$ and a high on/off ratio of 10^5 .

EXPERIMENTAL SECTION

The starting materials were directly purchased from commercial sources. The solvents were distilled and dried before being used for spectrophotometric and spectrofluorimetric analyses. The C–C coupling reactions such as Suzuki coupling and iodine-mediated oxidative coupling reactions were carried out in a nitrogen atmosphere. The 5,12-bis(dibromomethylene)-5,12-dihydrotetracene (**1**)¹⁵ was prepared by the method reported in the literature. The compounds were purified through column chromatography by using silica gel of 60–230 mesh size. The UV-mediated photocyclization reactions were carried out in a PANCHUM PR-2000(M) photoreactor with a power of 128 W. Nuclear magnetic resonance spectra were recorded on a Bruker AMX400 O FT-NMR spectrometer in deuterated solvents, like chloroform-*d* and 1,1,2,2-tetrachloroethane-*d*₂ with tetramethylsilane (TMS) as the internal standard. A V-550JASCOUV/VIS spectrophotometer was used for UV-absorption measurements in dichloromethane solvent. The HOMO–LUMO plots of the final derivatives were obtained by using PC Spartan Pro software with semi-empirical methods at the AM1 level. The HOMO energies of the samples were measured by a photoelectron spectrometer AC-2 (Riken Keiki).

General Procedure for Preparation of Aryl Olefins (2a–2d). 5,12-Bis(dibromomethylene)-5,12-dihydrotetracene (**1**) (0.57 g, 1.0 mmol), arylboronic acid (4.1 mmol), Pd(PPh₃)₂Cl₂ (60 mg), PPh₃ (40 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 $110\text{ }^{\circ}\text{C}$ under a nitrogen atmosphere for 12 h. On completion of the reaction, the solution was cooled and the toluene layer was separated and collected. The toluene was removed under

vacuum, and the product was purified by column chromatography using dichloromethane/hexane as eluent.

5,12-Bis(diphenylmethylene)-5,12-dihydrotetracene (2a). According to the general procedure, 5,12-bis(dibromomethylene)-5,12-dihydrotetracene (**1**) (0.57 g, 1.0 mmol) and phenylboronic acid (0.50 g, 4.1 mmol) were reacted to give the product as a yellow solid. Yield: 0.45 g, 80%. Mp: 336–343 °C. ¹H NMR (CDCl₃, 400 MHz) δ: 7.48–7.46 (m, 10H), 7.36–7.14 (m, 16H), 7.04–7.02 (m, 2H) and 6.76–6.73 (m, 2H). ¹³C NMR (100 MHz, CDCl₃) δ: 142.4, 142.4, 140.4, 138.0, 135.7, 135.6, 131.3, 129.7, 129.6, 128.3, 128.1, 127.6, 126.9, 126.7, 126.6, 125.4. HRMS (MALDI-TOF) *m/z*: [C₄₄H₃₀]⁺ calcd for C₄₄H₃₀ 558.2347; found 558.2352.

5,12-Bis(bis(4-chlorophenyl)methylene)-5,12-dihydrotetracene (2b). According to the general procedure, 5,12-bis(dibromomethylene)-5,12-dihydrotetracene (**1**) (0.57 g, 1.0 mmol) and 4-chlorophenylboronic acid (0.64 g, 4.1 mmol) were reacted to give the product as a yellow solid. Yield: 0.54 g, 78%. Mp: 285–289 °C. ¹H NMR (CDCl₃, 400 MHz) δ: 7.46 (m, 2H), 7.43–7.40 (m, 2H), 7.32–7.24 (m, 18H), 7.02–6.99 (m, 2H), 6.83–6.81 (m, 2H). ¹³C NMR (100 MHz, CDCl₃) δ: 140.2, 137.9, 137.4, 136.5, 135.0, 133.1, 133.0, 131.3, 131.0, 128.7, 128.6, 128.1, 127.7, 127.1, 126.1, 126.1. HRMS (MALDI-TOF) *m/z*: [C₄₄H₂₆Cl₄]⁺ calcd for C₄₄H₂₆Cl₄ 694.0789; found 694.0775.

5,12-Bis(bis(4-methylphenyl)methylene)-5,12-dihydrotetracene (2c). According to the general procedure, 5,12-bis(dibromomethylene)-5,12-dihydrotetracene (**1**) (0.57 g, 1.0 mmol) and 4-methylphenylboronic acid (0.56 g, 4.1 mmol) were reacted to give the product as a yellow solid. Yield: 0.52 g, 85%. Mp: 351–356 °C. ¹H NMR (CDCl₃, 400 MHz) δ: 7.49 (s, 2H), 7.39–7.37 (m, 2H), 7.32 (d, 8H), 7.21–7.19 (m, 2H), 7.01–7.03 (m, 10H), 6.76–6.74 (m, 2H), 2.313 (s, 6H), 2.25 (s, 6H). ¹³C NMR (100 MHz, CDCl₃) δ: 140.2, 139.7, 139.7, 138.3, 136.2, 136.1, 136.0, 135.3, 131.2, 129.6, 129.5, 128.9, 128.8, 128.0, 127.6, 126.7, 125.3, 125.2. HRMS (MALDI-TOF) *m/z*: [C₄₈H₃₈]⁺ calculated for C₄₈H₃₈ 614.2974; found 614.2965.

5,12-Bis(bis(4-fluorophenyl)methylene)-5,12-dihydrotetracene (2d). According to the general procedure, 5,12-bis(dibromomethylene)-5,12-dihydrotetracene (**1**) (0.57 g, 1.0 mmol) and 4-fluorophenylboronic acid (0.57 g, 4.1 mmol) were reacted to give the product as a yellow solid. Yield: 0.53 g, 84%. Mp: 376–389 °C. ¹H NMR (CDCl₃, 400 MHz) δ: 7.47 (s, 2H), 7.43–7.34 (m, 10H), 7.29–7.26 (m, 2H), 7.04–6.97 (m, 10H), 6.82 (d, *J* = 9.2 Hz, 1.5 Hz, 2H). ¹³C NMR (100 MHz, CDCl₃) δ: 163.0, 162.9, 160.5, 160.4, 138.2, 138.0, 137.7, 136.3, 135.3, 131.3, 131.2, 128.1, 127.6, 127.0, 125.9, 115.5, 115.4, 115.3, 115.2. HRMS (MALDI-TOF) *m/z*: [C₄₄H₂₆F₄]⁺ calculated for C₄₄H₂₆F₄ 630.1971; found 630.1947.

General Method for the Preparation of Pentabenzocoronenes (PBCs). Aryl olefin (**2a–2d**) (1.0 mmol), iodine (2.1 mmol), and methyloxirane (10–20 mL) were taken in anhydrous toluene (30 mL). The reaction mixture was irradiated with UV light for 12 h under a nitrogen atmosphere. On completion of reaction, excessive iodine was neutralized by treatment with saturated sodium thiosulfate solution. The toluene layer was separated and solvent was removed under vacuum to afford a mixture of partially and completely fused products.

The mixed products were dissolved in anhydrous dichloromethane (60 mL). Iron chloride (3.24 g, 20.0 mmol) dissolved in nitromethane (10 mL) was added via syringe, and the mixture was further stirred for 2–16 h under a nitrogen atmosphere. The reaction mixture was then quenched by adding methanol. The precipitated solid was filtered and washed with methanol, hydrochloric acid, and water successively.

Pentabenzocoronene (PBC). Following the general procedure, 5,12-bis(diphenylmethylene)-5,12-dihydrotetracene (**2a**) (0.56 g, 1.0 mmol) and iodine (1.04 g, 4.1 mmol) were reacted for 12 h, yielding a mixture of partially and completely fused products. It was further treated with iron chloride for 6 h, to give the product as a yellow-brown solid. Yield: 0.46 g, 86%. The product was further purified by vacuum sublimation in a temperature gradient oven at 425 °C/380 °C/320 °C (5 × 10⁻⁵ Torr) to give 0.27 g (Yield: 45%). *R_f*: 0.52 (6:4, DCM/petroleum ether). Mp: > 300 °C. ¹H NMR (CDCl₃,

400 MHz) δ: 9.29 (d, *J* = 8.4 Hz, 2H), 9.27–9.18 (m, 8H), 9.02 (d, *J* = 7.6 Hz, 2H), 7.85–7.83 (m, 8H), 7.76 (t, *J* = 7.6 Hz, 2H). ¹³C NMR could not be recorded due to poor solubility. HRMS (MALDI-TOF) *m/z*: [C₄₄H₂₂]⁺ calculated for C₄₄H₂₂ 550.1716; found 550.1733.

2,7,14,19-Tetrachloropentabenzocoronene (Cl-PBC). Following the general procedure, 5,12-bis(bis(4-chlorophenyl)methylene)-5,12-dihydrotetracene (**2b**) (0.70 g, 1.0 mmol) and iodine (1.04 g, 4.1 mmol) were reacted for 12 h, yielding a mixture of partially and completely fused products. It was further treated with iron chloride for 10 h to give the product as a dark-yellow solid. Yield: 0.40 g, 70%. The product was further purified by vacuum sublimation in a temperature gradient oven at 510 °C/460 °C/410 °C (5 × 10⁻⁵ Torr) to give 0.32 g (Yield: 48%). *R_f*: 0.39 (6:4, DCM/petroleum ether). Mp: > 350 °C. ¹H NMR (C₂D₂Cl₄, 400 MHz) δ: 9.28 (s, 2H), 9.19–9.16 (m, 4H), 9.10 (d, *J* = 8.8 Hz, 2H), 9.06–9.04 (m, 4H), 7.96 (q, *J* = 9.6 Hz 3.2 Hz, 2H), 7.88 (dd, *J* = 10.8 Hz 2.0 Hz, 2H), 7.78 (dd, *J* = 11.2 Hz 2.4 Hz, 2H). ¹³C NMR could not be recorded due to poor solubility. HRMS (MALDI-TOF) *m/z*: [C₄₄H₁₈Cl₄]⁺ calculated for C₄₄H₁₈Cl₄ 686.0157; found 686.0154.

2,7,14,19-Tetramethylpentabenzocoronene (Me-PBC). Following the general procedure, 5,12-bis(di-*p*-tolylmethylene)-5,12-dihydrotetracene (**2c**) (0.61 g, 1.0 mmol) and iodine (1.04 g, 4.1 mmol) were reacted for 12 h, yielding a mixture of partially and completely fused products. It was further treated with iron chloride for 2 h, to give the product as a yellow solid. Yield: 0.47 g, 77%. The product was further purified by vacuum sublimation in a temperature gradient oven at 460 °C/410 °C/380 °C (5 × 10⁻⁵ Torr) to give 0.38 g (Yield: 51%). *R_f*: 0.62 (6:4, DCM/petroleum ether). Mp: > 350 °C. ¹H NMR (CDCl₃, 400 MHz) δ: 9.35 (s, 2H), 9.24–9.10 (m, 8H), 8.96 (s, 3H), 7.84 (s, 3H), 7.76 (d, *J* = 8.0 Hz, 2H), 7.60 (d, *J* = 7.2 Hz, 2H), 2.83 (s, 2H), 2.75 (s, 2H). HRMS (MALDI-TOF) *m/z*: [C₄₈H₃₀]⁺ calculated for C₄₈H₃₀ 606.2342; found 606.2336.

2,7,14,19-Tetrafluoropentabenzocoronene (Flu-PBC). Following the general procedure, 5,12-bis(bis(4-fluorophenyl)methylene)-5,12-dihydrotetracene (**2d**) (0.63 g, 1.0 mmol) and iodine (1.04 g, 4.1 mmol) were reacted for 16 h, yielding a mixture of partially and completely fused products. It was further treated with iron chloride for 16 h, to give the product as a yellow solid. Yield: 0.50 g, 81%. The product was further purified by vacuum sublimation in a temperature gradient oven at 480 °C/430 °C/380 °C (5 × 10⁻⁵ Torr) to give 0.35 g (Yield: 70%). *R_f*: 0.30 (6:4, DCM/petroleum ether). Mp: > 350 °C. ¹H NMR (C₂D₂Cl₄, 400 MHz) δ: 9.15–8.93 (m, 10H), 8.69–8.44 (m, 2H), 7.91–7.90 (m, 2H), 7.61–7.56 (m, 4H). ¹³C NMR could not be recorded due to poor solubility of the derivative. HRMS (MALDI-TOF) *m/z*: [C₄₄H₁₈F₄]⁺ calculated C₄₄H₁₈F₄ for 622.1339; found 622.1356.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.7b01328.

Complete spectroscopic analysis, single-crystal X-ray analysis, and computational details (PDF)

Crystallographic data for PBC (CIF)

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: ytt@chem.sinica.edu.tw. Fax: +886-2-27831237. Tel: +886-2-27898580.

ORCID

Yu-Tai Tao: 0000-0003-4507-0419

Notes

The authors declare no competing financial interest.

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