

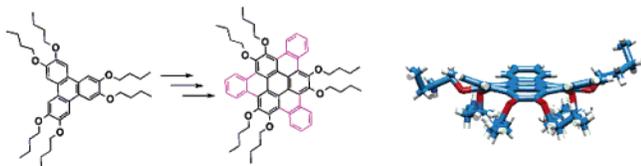
## Facile Synthesis of Janus “Double-Concave” Tribenzo[*a,g,m*]coronenes<sup>†</sup>

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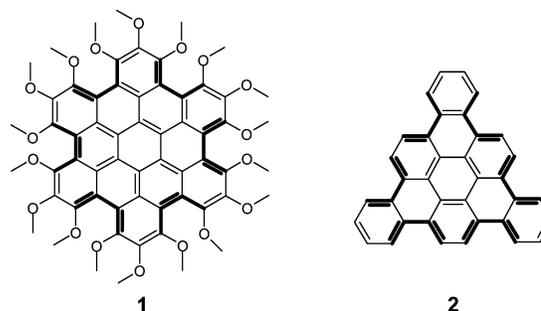
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Received January 17, 2007



Hexabutoxytribenzo[*a,g,m*]coronenes have been prepared in three steps from readily accessible hexabutoxytriphenylene. Single-crystal X-ray diffraction analysis reveals that these molecules can adopt an extraordinary “double-concave” conformation that makes them ideal hosts for the binding of different guest molecules at each face.

Polycyclic aromatic hydrocarbons (PAHs), which can be regarded as molecular subunits of graphite, have attracted increasing interest because of their potential application as functional materials.<sup>1</sup> Their planarity is often deemed to be their most significant geometric characteristic;<sup>2</sup> however, curved PAHs, which represent a fascinating class of molecules, have drawn persistent attention from many organic chemists,<sup>3</sup> in particular in view of the total synthesis of fullerenes.<sup>4</sup> Nonplanar PAHs may force aromatic rings to adopt unusual intermolecular contacts that are typically unavailable to planar molecules and



**FIGURE 1.** Structures of known highly symmetric large PAHs with different substituents in their bay regions.

which could form the basis for supramolecular self-assembled systems<sup>5</sup> and even self-healing electronic materials.<sup>6</sup>

To date, most highly nonplanar fused PAHs (e.g., spheres, bowls, tubes, onions) have been synthesized in extreme conditions such as flash vacuum pyrolysis (FVP). Difficulties in scale-up, low yields, and lack of functional group tolerance are the main problems that have been challenging to overcome, although a number of milder solution-phase synthetic routes have been investigated with some success.<sup>7</sup>

An extremely twisted graphene molecule, namely per-methoxylated hexa-*peri*-hexabenzocoronene **1** with a remarkable “double-concave” conformation, has recently been reported.<sup>5a</sup> The combination of a rigid “double-concave” aromatic core with 18 flexible methoxy groups at the periphery render **1** an ideal model compound for supramolecular host–guest chemistry. Herein we describe our endeavors to design a new series of Janus-type “double-concave” graphene molecules based on tribenzo[*a,g,m*]coronene **2** with lower symmetry compared with the  $D_{6h}$  hexa-*peri*-hexabenzocoronenes. Steric congestion in the bay regions is expected to induce a unique conformation with the likelihood of two different concave faces that can be further differentiated through appropriate functionalization.

A synthetic route toward 1,2,7,8,13,14-hexabutoxytribenzo[*a,g,m*]coronene **6a** is shown in Scheme 1. Readily available hexabutoxytriphenylene **3**<sup>8</sup> is brominated in dichloromethane at room temperature to give 1,4,8-tribromo-2,3,6,7,10,11-hexabutoxytriphenylene in moderate yield.<sup>9</sup> Palladium-catalyzed

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<sup>†</sup> Dedicated to Prof. Dr. Klaus Müllen on the occasion of his 60th birthday.

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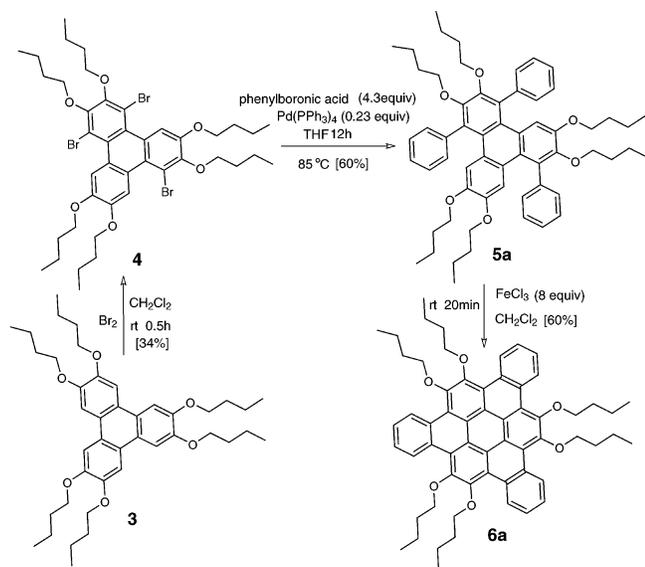
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## SCHEME 1



Suzuki–Miyaura cross-coupling<sup>10</sup> of **4** with phenylboronic acid affords the triphenyl-substituted hexabutoxytriphenylene **5a** as white solid in 60% yield. The key step in the synthesis is oxidative cyclodehydrogenation of **5a** with ferric chloride followed by reductive workup with methanol,<sup>11</sup> to give the desired product **6a** as a yellow solid in 60% yield.

Tribenzo[*a,g,m*]coronene **2** was first reported in 1968,<sup>12</sup> synthesized from *o,p,o,p,o,p*-hexaphenylene.<sup>13</sup> However, a poor yield, long synthetic route, and difficulties in selective modification limited its investigation further. In contrast to the vanishing solubility of parent molecule **2**, hexabutoxy-substituted tribenzo[*a,g,m*]coronene **6a** is soluble in common organic solvents such as THF and chloroform. The <sup>1</sup>H NMR spectrum of **6a** in CDCl<sub>3</sub> displays six signals, assigned to the two core proton environments and the three methylene and methyl proton environments of the butyl chains. A room temperature optical absorption spectrum of **6a** in chloroform is shown in Figure 2. The absorption spectrum of **6a** shows a maximum at 351 nm, which is bathochromically shifted about 72 nm compared to triphenylene **3** (279 nm) and consistent with a more extended  $\pi$ -system, albeit twisted. The relatively small change in absorption maximum in going from **3** to **6a**, despite the large increase in the size of the  $\pi$ -system, is typical of all-benzenoid PAHs.<sup>14</sup> The emission spectrum of **6a** in CHCl<sub>3</sub> exhibits a Stokes shift of 119 nm ( $\lambda_{\text{max}} = 470$  nm,  $\Phi_{\text{f}} = 0.06$ , see the Supporting Information).

Crystals of **6a** suitable for single-crystal X-ray diffraction structure analysis were obtained by slow evaporation of a solution of **6a** in acetone at room temperature. The molecular core is found to be markedly nonplanar as a consequence of the presence of pronounced peri-interactions (Figure 3). Further confirmation of the all-benzenoid character of **6a** is provided

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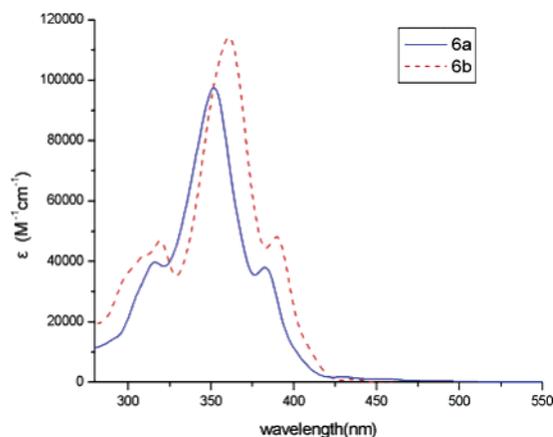


FIGURE 2. UV–vis absorption spectra of **6a** (solid line) and **6b** (dashed line) in chloroform ( $2.0 \times 10^{-6}$  M).

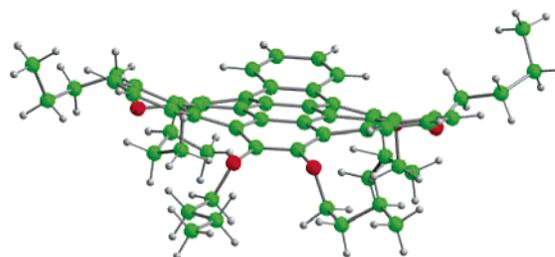


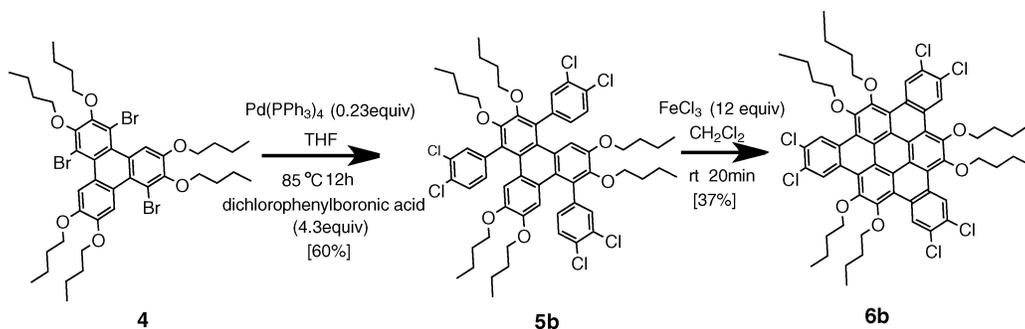
FIGURE 3. Molecular structure of **6a** as determined by single-crystal X-ray structure analysis.

through significantly longer interbenzenoid C–C bonds (1.44–1.48 Å) when compared with the intrabenzenoid C–C bonds (1.37–1.43 Å). The six carbon atoms of the central benzene ring (C31–C36) are coplanar to within 0.018 Å. Steric congestion between hydrogen atoms and oxygens in the bay positions forces the three unsubstituted benzene rings (C4–C9, C14–19, C24–C29) to bend 13.0–20.3° out of the plane of the central ring and all to the same side. Similarly, the three butoxy-substituted rings all bend toward the opposite side of the central ring by 8.6–9.6°, thereby giving **6a** a remarkable Janus-type “double-concave” conformation. The molecules pack as dimer pairs which exhibit close offset face-to-face contacts between one of the unsubstituted outer benzo rings (C14–C19) and its symmetry equivalent molecule; the inter-ring separation is 3.28 Å. This Janus-type conformation provides a large cavity on one side and a smaller cavity in the other side that are expected to be geometrically complementary to guest molecules of different size and shape.

As a further step toward the functionalization of this Janus-type “double-concave” graphene, analogues with 6-fold halogenation at the three outer benzene rings have been investigated. The introduction of six electron-withdrawing halogens is expected to not only have an influence on the electronic properties of the PAH, but also provide the possibility of nucleophilic substitution (such as hexasulfuration) of the aromatic core.

Hexachlorotribenzo[*a,g,m*]coronene **6b** has been prepared following the synthetic route shown in Scheme 2. Suzuki–Miyaura cross-coupling of commercially available 3,4-dichlorophenylboronic acid with **4** affords **5b** bearing six halogens (white solid, 60% yield). Following the critical final cyclode-

## SCHEME 2



hydrogenation step with ferric chloride, 1,2,7,8,13,14-hexabutoxy-4,5,10,11,16,17-hexachlorotribenzo[*a,g,m*]coronene **6b** was obtained as a yellow solid in 37% yield. It should be noted that oxidative cyclodehydrogenation with ferric chloride is sometimes limited by the electronic character of the substituents.<sup>16</sup> Typically, phenyl rings bearing electron-withdrawing groups are less active in the cyclodehydrogenation reaction.<sup>17</sup> Thus, the successful cyclodehydrogenation of **5b** to afford the desired product is particularly significant. The solution <sup>1</sup>H NMR spectrum displays five proton signals, one less than for **6a**, and is also consistent with the absence of conformational rigidity in solution (there is no change in the number of signals down to 233 K; see the Supporting Information). The 233 K <sup>1</sup>H NMR spectrum does, however, show broadening of the signals and a shift to lower frequency, indicative of greater face-to-face self-association at this lower temperature. The optical absorption maximum of **6b** (Figure 2) shows that incorporation of 6 chlorine atoms induces a small bathochromic shift of 10 nm compared with parent molecule **6a**. This red-shift is likely due to a combination of increased supramolecular interaction and a small degree of charge-transfer character between the donor and acceptor groups at the periphery. The emission spectrum of **6b** in CHCl<sub>3</sub> exhibits a Stokes shift of 112 nm ( $\lambda_{\text{max}} = 473 \text{ nm}$ ,  $\Phi_{\text{f}} = 0.045$ ; see the Supporting Information).

Crystals suitable for single-crystal X-ray structure analysis were obtained by slow evaporation of a solution of **6b** in cyclohexane at room temperature. The solid-state molecular structure of **6b** is somewhat different from that of **6a** as shown in Figure 4. The six carbon atoms (C31–C36) of the central benzene ring are coplanar to within 0.011 Å. However, in contrast to the alternating in- and out-of-plane twisting around the periphery of **6a**, the core of **6b** is saddle-shaped; two of the dichlorobenzo rings bend in the same direction (21.4° and 6.6° relative to the central ring), while the third dichlorobenzene ring bends in the opposite direction by 8.3°. The conformation of this third ring appears to be associated with a greater degree of  $\pi$ – $\pi$  interaction between PAH cores than is seen for the non-chlorinated analogue **6a** (Figure 5).

A view down the *b*-axis (Figure 5d) shows how the packing of **6b** is dominated by alternating stacked arrays of molecules tilted to the column axis. Overlap between intracolumn neighbors involves approximately 6 of the 10 fused rings that

constitute the core of the tribenzo[*a,g,m*]coronene (cf. only one ring overlap in the structure of **6a**). The chlorine atoms seem to play a significant role in supramolecular bonding interactions. Close intracolumn contacts between Cl4···C27/28 (3.38/3.31 Å) and Cl6···C32/33 (3.37/3.27 Å), and intercolumn hydrogen bonds between Cl2···H60C (2.936 Å) and Cl3···H40C (2.80 Å), leave only Cl1 and Cl5 without bonding roles. By contrast,

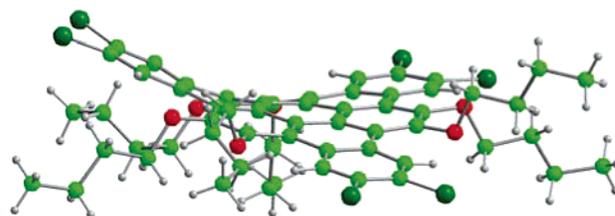


FIGURE 4. Molecular structure of **6b** as determined by single-crystal X-ray structure analysis.

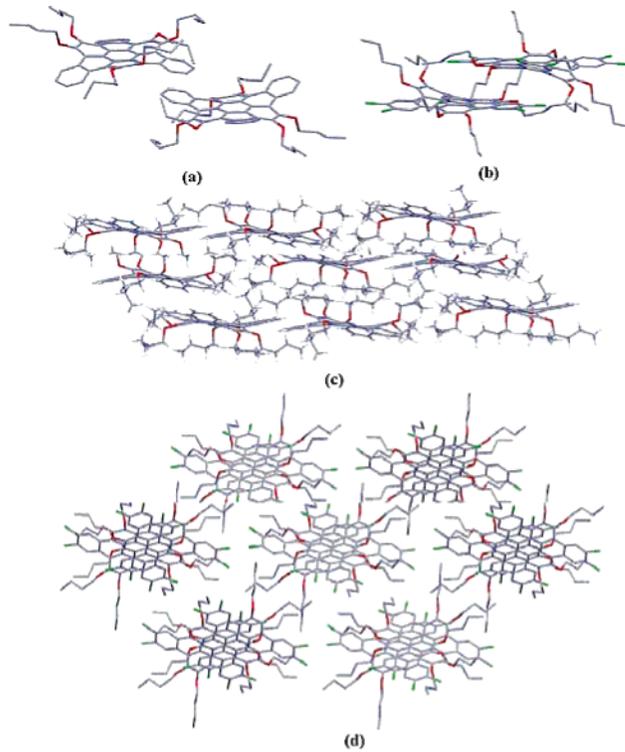


FIGURE 5. Crystal structures of (a) **6a**, a pair of  $\pi$ – $\pi$  interacting molecules, (b) **6b**, a pair of  $\pi$ – $\pi$  interacting molecules, (c) **6a**, molecular packing viewed down the *c*-axis, and (d) **6b**, molecular packing viewed down the *b*-axis.

(15) Data collection was carried out on a Rigaku diffractometer with a Saturn CCD area detector. The structure was solved by direct methods in SHELXS-97.

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only one of the oxygen atoms appears to stabilize the structure though intermolecular interactions, namely O1...H51B (2.54 Å).

In conclusion, we have presented a facile synthetic protocol to tribenzo[*a,g,m*]coronenes with a highly twisted core capable of adopting an extraordinary Janus-type “double-concave” conformation as revealed by X-ray single crystal analysis of **6a**. Symmetric incorporation of six chloro groups around the PAH periphery has the effect of enhancing  $\pi$ - $\pi$  interactions in the solid state, manifested by the molecules packing in columnar arrays with a desymmetrizing twisting of the aromatic core. Solution characterization reflects conformational flexibility of the core that would allow the tribenzo[*a,g,m*]coronenes **6** to strongly engage in host-guest interactions, potentially with facial selectivity. Significant face-to-face interaction in the solid-state structures is in agreement with increased aggregation at low temperatures in solution, as evidenced from variable-temperature NMR measurements. Further functionalization of this new class of twisted PAHs and an exploration of their supramolecular properties are currently underway.

## Experimental Section

**2,3,6,7,10,11-Hexabutoxy-1,4,8-triphenyltriphenylene 5a.** A Schlenk flask was charged with 1,4,8-tribromohexabutoxytriphenylene **4** (1.00 g, 1.15 mmol), tetrakis(triphenylphosphine)palladium(0) (300 mg, 0.260 mmol), THF (75 mL), and 2 M potassium carbonate solution (25 mL) under argon, then phenylboronic acid (600 mg, 4.91 mmol) was added. The mixture was heated to 85 °C with vigorous stirring for 12 h, then cooled to room temperature, and the organic phase was separated and washed twice with water. After drying over magnesium sulfate and filtering, the solvent was removed in vacuo. The residue was purified by column chromatography on silica (50% petroleum ether-dichloromethane) to give **5a** (0.6 g, 0.67 mmol, 60%) as a white solid. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz):  $\delta$  7.52 (d, *J* = 6.0 Hz, 4H), 7.44–7.29 (m, 11H), 7.29 (s, 1H), 7.01 (s, 1H), 6.87 (m, 1H), 3.70 (br t, *J* = 5.9 Hz, 4H), 3.49 (t, *J* = 6.2 Hz, 2H), 3.22 (t, *J* = 6.7 Hz, 2H), 3.17 (t, *J* = 6.7 Hz, 2H), 3.10 (t, *J* = 6.6 Hz, 2H), 1.63–1.56 (m, 6H), 1.43–1.35 (m, 12H), 1.08 (m, 6H), 0.96–0.83 (m, 9H), 0.71 (m, 9H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz):  $\delta$  149.5, 149.5, 149.1, 145.6, 145.4, 140.4, 139.9, 131.9, 131.9, 131.8, 131.2, 128.5, 128.4, 128.3, 126.7, 126.6, 126.4, 124.9, 124.3, 113.0, 112.4, 73.1, 72.3, 67.6, 67.4, 67.3, 32.2, 32.2, 31.2, 31.1, 19.00, 13.8. MALDI-TOF (*m/z*): calcd for C<sub>60</sub>H<sub>72</sub>O<sub>6</sub> 888.5, found 889.1. Elemental analysis calcd for C<sub>60</sub>H<sub>72</sub>O<sub>6</sub>: C, 81.04; H, 8.16. Found: C, 80.71; H, 8.16. Mp 42–44 °C.

**1,2,7,8,13,14-Hexabutoxytribenzo[*a,g,m*]coronene 6a.** To a solution of 2,3,6,7,10,11-hexabutoxy-1,4,8-triphenyltriphenylene **5a** (700 mg, 0.788 mmol) in dichloromethane (50 mL) was added ferric chloride (1.024 g, 6.3 mmol) in 2 mL of nitromethane. The mixture was stirred for 20 min at rt. To quench the reaction, methanol (20 mL) was added, then 30 mL of water. The organic layer was separated and the solvent removed in vacuo. The residue was purified by column chromatography on silica (50% petroleum ether-dichloromethane) and recrystallization of the major product from hexane afforded **6a** as green yellow needles (420 mg, 0.47 mmol, 60%). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz):  $\delta$  9.77 (dd, 6H), 7.74

(dd, 6H), 4.23 (t, *J* = 6.67 Hz, 12H), 2.01 (m, 12H), 1.64 (m, 12H), 1.03 (t, *J* = 7.3 Hz, 18H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz):  $\delta$  149.0, 128.7, 127.1, 126.4, 121.7, 120.6, 73.7, 32.2, 19.0, 13.6. MALDI-TOF (*m/z*): calcd for C<sub>60</sub>H<sub>66</sub>O<sub>6</sub> 882.5, found 883.1. Elemental analysis calcd for C<sub>60</sub>H<sub>66</sub>O<sub>6</sub>: C, 81.60; H, 7.53. Found: C, 81.82; H, 7.60. Mp 121–122 °C.

**2,3,6,7,10,11-Hexabutoxy-1,4,8-tris(3,4-dichlorophenyl)triphenylene 5b.** A Schlenk flask was charged with 1,4,8-tribromohexabutoxytriphenylene **4** (1.00 g, 1.15 mmol), tetrakis(triphenylphosphine)palladium(0) (300 mg, 0.260 mmol), THF (75 mL), and 2 M potassium carbonate solution (25 mL) under argon, then 3,4-dichlorophenylboronic acid (950 mg, 4.98 mmol) was added. The mixture was heated to 85 °C with vigorous stirring for 12h, then cooled to room temperature, and the organic phase was separated and washed twice with water. After drying over magnesium sulfate, the solvent was removed in vacuo. The residue was purified by column chromatography on silica (50% petroleum ether-dichloromethane) to give **5b** (760 mg, 0.695 mmol, 60%) as a pale yellow solid. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz):  $\delta$  7.83–7.39 (m, 7H), 7.24 (s, 1H), 7.16–7.06 (m, 2H), 6.90 (s, 1H), 6.81 (s, 1H), 4.05–3.11 (m, 12H), 1.64 (m, 6H), 1.41 (m, 12H), 1.18 (m, 6H), 1.01–0.94 (m, 9H), 0.77 (t, *J* = 7.2 Hz, 9H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz):  $\delta$  150.0, 149.8, 149.3, 146.6, 146.5, 145.9, 140.6, 140.4, 139.9, 132.9, 131.5, 131.2, 130.9, 130.6, 130.2, 129.6, 129.1, 127.9, 127.1, 124.6, 124.2, 112.8, 73.7, 73.0, 68.4, 68.2, 32.6, 32.4, 31.6, 31.5, 19.4, 14.3, 14.0. MALDI-TOF (*m/z*): calcd for C<sub>60</sub>H<sub>66</sub>Cl<sub>6</sub>O<sub>6</sub> 1092.3, found 1092.4. Elemental analysis calcd for C<sub>60</sub>H<sub>66</sub>Cl<sub>6</sub>O<sub>6</sub>: C, 65.75; H, 6.07. Found: C, 65.58; H, 6.32. Mp 76–78 °C.

**1,2,7,8,13,14-Hexabutoxy-4,5,10,11,16,17-hexachlorotribenzo[*a,g,m*]coronene 6b.** To a solution of **5b** (500 mg, 0.458 mmol) in dichloromethane (30 mL) was added ferric chloride (890 mg, 5.47 mmol) in 2 mL of nitromethane. The mixture was stirred for 20 min at room temperature, before being quenched with methanol (10 mL), then 30 mL of water. The organic layer was separated and the solvent removed in vacuo. The residue was purified by column chromatography on silica (50% petroleum ether-dichloromethane) and recrystallization of the major product from acetone afforded **6b** as yellow needles (180 mg, 0.173 mmol, 37%). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz):  $\delta$  9.97 (s, 6H), 4.16 (t, *J* = 6.5 Hz, 12H), 2.03 (m, 12 H), 1.72 (m, 12H), 1.09 (t, *J* = 7.3 Hz, 18H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz):  $\delta$  149.4, 131.3, 129.2, 128.4, 120.9, 120.6, 74.5, 33.0, 20.0, 14.6. MALDI-TOF (*m/z*): calcd for C<sub>60</sub>H<sub>60</sub>Cl<sub>6</sub>O<sub>6</sub> 1086.2, found 1086.2. Elemental analysis calcd for C<sub>60</sub>H<sub>60</sub>Cl<sub>6</sub>O<sub>6</sub>: C, 66.12; H, 5.54. Found: C, 65.91; H, 5.54. Mp 220–221 °C.

**Acknowledgment.** This work was supported by the “100 Talents” program of the Chinese Academy of Sciences, and the National Natural Science Foundation of China (20421101). The Australian Research Council is also thanked for financial support and the award of an Australian Postdoctoral Fellowship to N.T.L.

**Supporting Information Available:** Further experimental details, NMR spectra, and crystallographic data for compounds **6a** and **6b**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

JO0701029