# Tribenzotriquinacenes Bearing Six-Fold Benzofuran Extensions: Electron-Rich C<sub>3v</sub>-Symmetrical Hosts for C<sub>60</sub>

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#### S Supporting Information

**ABSTRACT:** New tribenzotriquinacene (TBTQ) hosts bearing six-fold peripheral benzofuran functionalization have been synthesized. The three polycondensed arene wings were shown to operate optically independently and to generate deeply bowl-shaped  $C_{3\nu}$ -symmetrical frameworks that act as relatively weak hosts toward  $C_{60\nu}$  as revealed by <sup>1</sup>H NMR spectroscopy.



### INTRODUCTION

The design and synthesis of preorganized bowl-shaped macrocyclic hosts which can have applications in supramolecular and material chemistry has been of considerable interest in recent years. In particular, calix[*n*] arenes, <sup>1–8</sup> resorcarenes, <sup>9–14</sup> cyclodextrins, <sup>15</sup> cyclotriveratrylenes, <sup>16–18</sup> corannulenes, <sup>19–21</sup> and similar macrocyclic frameworks have been studied, <sup>22</sup> all providing efficient shape complementarity to spherical, mostly C<sub>60</sub> fullerene, guests. From all of these investigations, it has become evident that a diversity of structures may be capable of associating with  $C_{60}$  at different abilities and in various organic solvents, such as benzene, toluene, or carbon disulfide. The solubilities of C<sub>60</sub> in these solvents are sufficiently high to enable the reliable determination of the binding constants of such host-guest complexes by spectroscopic titration experiments. UV-vis spectroscopy and <sup>1</sup>H NMR (complexation-induced chemical shift, "CIS")<sup>23</sup> measurements have commonly been used to confirm the binding constants. In some cases, C<sub>60</sub> was found to cocrystallize with a suitable guest in the solid state. Progress of the studies of  $C_{60}$ complexes in host-guest chemistry, separation science, and molecular electronics<sup>24,25</sup> has prompted synthetic chemists to construct well-designed host molecules possessing sizable bowl-, belt-, or cage-shaped cavities.

The molecular framework of the tribenzotriquinacenes (TBTQs) forms a unique conformationally rigid,  $C_{3\nu}$ -symmetrical, bowl-shaped structural motif consisting of three mutually fused indane units. Unidirectional and strictly parallel columnar stacking was found for single crystals of both **1a** and **1b** (Figure 1).<sup>26–28</sup> The concave molecular surface was found to exert a strongly negative electrostatic potential.<sup>29,30</sup> Various multiple functionalizations and sketetal extensions have already been reported by us and others.<sup>26–28,31–38</sup> Various applications have recently been suggested for the use of

the deep-cavity framework of the TBTQ core within the tristhianthrene **2** and novel TBTQ-based "sockets", such as **3**, with respect to their supramolecular interaction with fullerenes.<sup>35,36</sup> In the present report, we describe the synthesis of another set of rigid molecular building blocks based on the TBTQ structural motif. In the title compounds **12** and **13** (see below), six benzofuran groupings were either attached or annelated, respectively, to the outer periphery of the TBTQ skeleton. These strongly extended polycyclic TBTQ structures turned out to act as suitable supramolecular hosts for C<sub>60</sub> fullerene in solution. Because of the unique orthogonal orientation of the three electronically independent indane wings of the TBTQ core,<sup>26,27,37</sup> the optical properties of the three-fold chromophores **12** and **13**, as well as of their synthetic precursor, the TBTQ-based hexatolane **10**, were compared to those of the corresponding monomeric units, for example, the bisbenzofurans **16** and **17** and the ditolan **15**.

## RESULTS AND DISCUSSION

Our endeavors on the new benzofurano-annelated tribenzotriquinacenes has been based on the hexabromo derivative  $9^{26,33}$ and the protected ethynylphenol building block **8**. The latter compound was prepared in four steps with 44% overall yield from commercially available 4-*tert*-butylphenol according to the literature<sup>39–41</sup> (Scheme 1). Six-fold Sonogashira coupling of **9** with the terminal alkyne **8** ( $\geq$  25 equiv) gave the TBTQ-based hexatolane **10** in 82% yield, in analogy to previous results (Scheme 2).<sup>12</sup> The <sup>1</sup>H NMR spectrum of **10** exhibited four distinct resonances in the arene region, and the <sup>13</sup>C NMR spectrum showed exactly nine signals, which nicely reflect the

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Figure 1. Parent tribenzotriquinacenes 1 and the TBTQ derivatives 2 and 3 studied with respect to their association with fullerenes in the liquid and/or solid state.





molecular  $C_{3v}$ -symmetry of this compound. Its structure was further determined by X-ray single-crystal analysis (Figure 2a). As expected, the TBTQ framework of **10** was found to have the regular  $C_{3v}$ -symmetry, but the two tolane units within each wing adopt different angles about their acetylene axes. As a consequence, the *t*-butyl and acetoxy groups pending at the respective aryl groups are oriented in alternate directions, one to the concave and the other to the convex side of the TBTQ framework, giving rise to  $C_3$  molecular symmetry overall. Surprisingly, two molecules of **10** form a large cavity through a strong face-toface interaction by hydrogen bonding and  $\pi - \pi$  stacking (Figure 2b). In fact, the whole crystal structure of **10** shows very regular molecular stacking (Figure 2c), a frequently recurring feature of multiply functionalized TBTQ derivatives.

Benzofurans are important building blocks in organic chemistry and in the life sciences because of their presence in many natural products and their interesting chemical and physiological properties.<sup>42–47</sup> They have been the subject of extensive studies, and numerous synthetic methods in benzofuran chemistry have been developed.<sup>48–56</sup> Benzofurans can be synthesized via reaction of 2-halophenols with copper(I) acetylides<sup>57–59</sup> and via palladium-catalyzed heteroannulation of 2-halophenols with terminal or internal alkynes.<sup>60–64</sup> As compared to monobenzofurans, reports on the synthesis of dibenzofurans or higher congeners are very limited. Aiming at the synthesis of the TBTQ-based trisbenzofuran 13, we studied several strategies to generate six benzofuranyl residues in a single step by starting either from the precursor 10 or from its deprotected analogue 11. In particular, hexaphenol 11 was subjected to metal (Pd<sup>II</sup>, Au<sup>I</sup>, Zn<sup>II</sup>) catalysis by use of various bases, but different bases were also applied for the direct conversion of the hexaester 10 by concomitant saponification and cyclization. The best results were obtained with the sodium-hydroxide-promoted reaction of the latter compound in methanol under reflux, which afforded the desired six-fold benzofuranyl-substituted tribenzotriquinacene 12 in 46% yield. By contrast, hexaphenol 11 upon treatment with palladium(II) acetate and cesium carbonate in dimethylacetamide at 80 °C gave this product in 26% yield only. <sup>1</sup>H and <sup>13</sup>C NMR spectroscopy unequivocally confirmed the constitution of 12. Subsequent oxidation using ferric chloride (4 equiv per C-C bond) in nitromethane at 0  $^{\circ}$ C produced the target compound 13 in 85% yield. Remarkably, use of an excess of FeCl<sub>3</sub> gave rise to decomposition. The <sup>1</sup>H NMR spectrum of 13 reveals a downfield shift of all of the arene resonances due to the much better conjugated arene units. The pronounced vaulting of the convex-concave molecular structures of the new TBTQ derivatives and of the benzofuran derivatives 12 and 13, in particular, is illustrated in Figure 4 (see below).

In order to shed some light on the interaction of the three conjugated aromatic flaps attached to the TBTQ cores of 10-13 with their three mutually orthogonal arene units, the "monomers" 15-17 were synthesized for comparison (Scheme 3). The most efficient procedures that had led us to the TBTQ derivative 13 were successfully applied here, as well. Thus, Sonogashira coupling of dibromoxylene 14 with an excess of alkyne 8 gave the simple ditolane 15 in 87% yield. In further analogy, treatment of the latter compound with sodium hydroxide (6 equiv) in methanol afforded the di(benzofuranyl)xylene 16 and, finally, cyclodehydrogenation of 16 using ferric chloride (8 equiv) furnished the monomer 17 in 88% yield.

Scheme 2. Synthesis of the Six-fold Benzofurano-Annelated Trinaphthotriquinacene 13 via the TBTQ-Based Hexatolanes 10 and 11 and Hexa(benzofuranyl)tribenzotriquinacene 12



Compounds 10-13 and 15-17 represent new extended  $\pi$ -electron systems. Therefore, intramolecular interaction of two or more well-defined chromophores in these compounds opens a further manifold with respect to possible exciton effects<sup>65-69</sup> as well as energy<sup>70</sup> and electron transfer<sup>71</sup> processes that can take place between the chromophores. TBTQ derivatives bearing up to six mutually fused indane units<sup>27,72,73</sup> within their particularly rigid polycyclic molecular frameworks offer such suitable core scaffolds owing to their "Cartesian" geometry.<sup>26-28</sup> To assess the exciton interaction of three monomeric chromophores 15-17 when attached to the TBTQ scaffold, the relevant compounds were characterized by UV-vis and fluorescence spectroscopy. The band positions of the UV-vis and fluorescence spectra were found to be almost the same for the tris-chromophores 10, 12, and 13 and the respective monomers 15, 16, and 17, with the exception that the maximum absorption of the most highly annelated system, 13, is red-shifted by ca. 7 nm with respect to that of 17 (Table 1). The data suggest that operating three monomers 15-17 at the TBTQ core does not bring about significant changes of the optical properties, which proves that the three chromophores assembled at the TBTQ core are electronically independent. This finding is in accordance with our early studies of the centropolyindane family<sup>28</sup> and, in particular, with the report of Langhals et al. in 2008.<sup>37</sup> The quantum yields of the tris-chromophores 10, 12, and 13 degraded markedly with respect to corresponding monomers 15–17. This can be traced to the reduced efficiency of  $\pi$ – $\pi$  stacking due to the strongly bent TBTQ framework as compared to the planar chromophores 15–17.

The new tris-chromophores 12 and 13 with their characteristic  $C_{3\nu}$ -symmetrical, deep-bowl topography represent analogues of the TBTQ-based hosts 2 and 3, which were shown to associate with  $C_{60}$ in solution and in the solid state.<sup>35,36</sup> Therefore, <sup>1</sup>H NMR titration experiments of compounds 12 and 13 with  $C_{60}$  were carried out in toluene- $d_8$ . Figure 3 shows the changes of the chemical shifts of 12 and 13 observed as a function of the molar ratio with C<sub>60</sub> added. It is evident that, in the case of the fully condensed compound 13, the protons H<sup>b</sup> at the periphery of the TBTQ core are increasingly shielded by the guest molecule, whereas the benzofuran protons H<sup>c</sup> and H<sup>d</sup> and the methyl protons H<sup>a</sup> at the bridgeheads of the TBTQ core are increasingly deshielded. The changes by deshielding are somewhat smaller than that of the shielding effect. These observations are consistent with the formation of a complex in which the  $C_{60}$  guest is deeply embedded into the cavity of 13. The Benesi-Hildebrand treatment for the calculation of Kassoc determined for 298 K in toluene- $d_8$  for the complex C<sub>60</sub> $\subset$ 12 gave a value of







**Figure 2.** X-ray crystallographic structures of **10**: (a) molecular structure, (b) pairwise face-to-face aggregation, (c) crystal structure with a top view onto the face-to-face dimers (see also Supporting Information).

 $544 \pm 121 \text{ M}^{-1}$ , whereas the treatment for  $C_{60} \subset 13$  gave a value of  $321 \pm 47 \text{ M}^{-1}$ . The calculations were based upon the chemical shift changes observed for protons H<sup>c</sup> of hosts **12** and **13**. Job plots confirmed the 1:1 stoichiometry of the complexation in both cases.

In the case of host 12, almost all of the protons, and  $H^a$  and  $H^b$  in particular, were found to be increasingly deshielded upon complexation with increasing amounts of C<sub>60</sub>. By contrast, <sup>1</sup>H NMR

titration experiments with the hexatolan precursor 10 and C<sub>60</sub> gave no CIS changes at all. Therefore, we assume that steric hindance of the acetyl and *tert*-butyl groups prevents access to the cavity of the host in this case. The finding that host 13 forms a weaker complex with  $C_{60}$  and that its protons  $H^b$  are strongly shielded, rather than deshielded, by the guest molecule may indicate that the C<sub>60</sub> is positioned less deeply within the cavity of the host. This may be due to a stronger interaction with the rigid and planar diffurano [2,3:a,c]naphthalene unit of 13. Such extensive "face-to-face"  $\pi - \pi$  stacking is supported by the shortest distance of 3.18 Å of the C<sub>60</sub> molecule to the naphthalene plane of 13, as suggested by force-field (MM+) modeling.<sup>74</sup> Since suitable crystals for X-ray crystal structure analysis could not be obtained, molecular mechanics calculation using MM+ force field was performed for the complexes of C<sub>60</sub> with the hosts 10, 12, and 13. The distances from the centroids of the  $C_{60}$ guest to the apexes (C-12d) of the TBTQ hosts in  $10 \subset C_{60}$ ,  $12 \subset C_{60}$ , and  $13 \subset C_{60}$  were calculated to be markedly different, 13.11, 8.82, and 9.15 Å, respectively (Figure 4). These results are in accordance with the <sup>1</sup>H NMR titration experiments and thus supportive of the hypothesis that the depth of the nesting of  $C_{60}$ into the concave surface of a TBTQ host molecule is an important predictive criterion, as postulated previously.<sup>36</sup> It appears that the more flexible benzofuranyl-substituted tribenzotriquinacene 12 offers a tighter host-probably owing to an induced fitting of the six electron-rich pendants-as compared to the much more rigid annelated TBTQ analogue on 13.

# CONCLUSION

We have developed a new and efficient extension of the bowlshaped tribenzotriquinacene framework by introducing either six peripheral benzofuranyl residues or six annelated benzofurano groups in a  $C_{3\nu}$ -symmetrical orientation. Electron spectroscopy confirms that the three mutually orthogonal chromophores are electronically independent. These novel TBTQ-based trisbenzofurans provide strongly extended molecular cavities that are suitable albeit relatively weak—hosts for  $C_{60\nu}$  forming 1:1 complexes. We expect that the great chemical versatility of tribenzotriquinacene chemistry will increase the interest to study and apply TBTQ-based hosts in supramolecular chemistry.

# EXPERIMENTAL SECTION

General. All reactions that required anhydrous conditions were carried out by standard procedures under argon. Commercially available reagents were used as received. The solvents were dried by distillation over the appropriate drying reagents. Petroleum ether used had a bp range of 60-90 °C. Reactions were monitored by TLC. Column chromatography was generally performed through silica gel (200-300 mesh). IR spectra were reported in wavenumbers (cm<sup>-1</sup>). Melting points are uncorrected. <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra were recorded on a 400 or 600 MHz spectrometer, as were the DEPT 135 experiments. Chemical shifts ( $\delta$ ) are reported in parts per million relative to TMS ( $\delta$  0.00) for the <sup>1</sup>H NMR and to chloroform ( $\delta$  77.0) for the <sup>13</sup>C NMR measurements. EI mass spectra were recorded on a double focusing sector-field instrument; MALDI spectra were measured on a ToF instrument and ESI spectra were obtained with an ion trap mass spectrometer equipped with a standard nanoESI source. Accurate mass measurements were obtained on an FT-ICR mass spectrometer (ESI, MALDI) or on the double focusing sector-field instrument (EI).

**4-tert-Butyl-2-iodophenol (5).** A solution of 4-*tert*-butylphenol (4) (1.00 g, 6.67 mmol), potassium iodide (1.11 g, 6.69 mmol), and sulfuric acid (0.56 mL, 10 mmol) in methanol (100 mL) was stirred at 0 °C while hydrogen peroxide (30%) (1.38 mL, 13 mmol) was added dropwise.

# Scheme 3. Synthesis of the "Monomeric" Chromophores 15-17



Table 1. Electron Spectroscopic Properties of the Simple Chromophores 10, 12, and 13 and the Respective TBTQ-Based Tris-Chromophores 15, 16, and 17

compounds	10	15	12	16	13	17
$\lambda_{abs}{}^{a}$ (nm)	252	252	251	251	309	289
$\lambda_{\mathrm{ex}}{}^{a}$ (nm)	280	280	245	245	275	275
$\lambda_{\rm em}^{\ \ b}$ (nm)	374	374	378	376	399	392
$\Phi^{c}$ (%)	15.7	29.4	14.1	70.7	33.2	44.0
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<sup>*a*</sup> Only the largest absorption maxima are listed. <sup>*b*</sup> Wavelength of emission maximum when exicited at the absorption maximum. <sup>*c*</sup> Quantum yields obtained by using quinine sulfate (10  $\mu$ M) as a standard.

Stirring was continued for 2 h at ambient temperature. Then the solvent was removed under reduced pressure. The residue was diluted with concentrated sodium bisulfite (100 mL) and extracted with dichloromethane (3 × 100 mL). The combined organic layers were washed with brine, dried over sodium sulfate, filtered, and concentrated under reduced pressure. Flash chromatography of the residue over silica gel (petroleum ether/EtOAc, 100:1) afforded 5 (1.10 g, 60%) as an oil: IR (neat) 3487, 2960, 2866, 1494, 1465, 1398, 1364, 1264, 1179, 1032, 877, 819 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  1.27 (s, 9H, 3 × CH<sub>3</sub>), 5.15 (s, 1H, OH), 6.91 (d, <sup>3</sup>*J* = 8.8 Hz, 1H), 7.26 (dd, <sup>3</sup>*J* = 8.8 Hz, <sup>4</sup>*J* = 2.4 Hz, 1H), 7.62 (d, <sup>4</sup>*J* = 2.4 Hz, 1H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  31.4 (p), 34.0 (q), 85.6 (q), 114.5 (t), 127.3 (t), 134.9 (t), 145.6 (q), 152.5 (q); MS (EI, 70 eV) *m*/*z* 276 (34, M<sup>+•</sup>), 261 (100, [M - CH<sub>3</sub>]<sup>+</sup>).

4-tert-Butyl-2-iodophenyl acetate (6). A solution of iodophenol 5 (500 mg, 1.81 mmol) in pyridine (50 mL) was stirred while acetic anhydride (0.3 mL, 2.33 mmol) was added dropwise. Stirring was continued for 3 h at ambient temperature, then the mixture was neutralized by the addition of aqueous hydrogen chloride (10 mL, 1 M). The resulting mixture was extracted with dichloromethane  $(3 \times 50 \text{ mL})$ , dried over sodium sulfate, filtered, and concentrated under reduced pressure. Flash chromatography of the residue over silica gel (petroleum ether/EtOAc, 100:1) afforded 6 (547 mg, 95%) as oil: IR (neat) 2962, 1770, 1486, 1368, 1194, 1037, 909, 834 cm  $^{-1};\,^{1}\mathrm{H}$  NMR (400 MHz, CDCl3)  $\delta$  1.30 (s, 9H,  $3 \times CH_3$ , 2.36 (s, 3H, CH<sub>3</sub>), 7.01 (d, <sup>3</sup>J = 8.4 Hz, 1H), 7.37 (dd, <sup>3</sup>J = 8.4 Hz,  ${}^{4}J$  = 2.4 Hz, 1H), 7.80 (d,  ${}^{4}J$  = 2.4 Hz, 1H);  ${}^{13}C$  NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$ 21.2 (p), 31.3 (p), 34.4 (q), 90.2 (q), 122.2 (t), 126.6 (t), 136.4 (t), 148.8 (q), 150.9 (q), 168.8 (q); MS (EI, 70 eV) *m/z* 318 (18, M<sup>+•</sup>), 276 (57,  $[M - CH_2CO]^{+\bullet}$ ), 261 (100,  $[M - CH_2CO - CH_3]^+$ ), 43 (36); accurate mass (ESI-MS) m/z [M + NH<sub>4</sub>]<sup>+</sup>, calcd for C<sub>12</sub>H<sub>19</sub>NO<sub>2</sub>I 336.0455, found 336.0449.

4-tert-Butyl-2-(2-trimethylsilylethynyl)phenyl acetate (7). A solution of ester 6 (800 mg, 2.52 mmol), ethynyltrimethylsilane (0.50 mL, 3.54 mmol), PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> (172 mg, 0.25 mmol), and cuprous iodide (25 mg, 0.13 mmol) in dry triethylamine (15 mL) was stirred under argon at ambient temperature for 48 h. The reaction was quenched with water, the resulting mixture was extracted with dichloromethane, and the combined extracts were washed with brine, dried over sodium sulfate, filtered, and concentrated under reduced pressure. Flash chromatography of the residue over silica gel (petroleum ether/AcOEt, 30:1) afforded the product 7 (624 mg, 86%) as a colorless solid: mp 80-82 °C; IR (neat) 2958, 2161, 1766, 1493, 1368, 1250, 1206, 1187, 901, 845 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  0.25 (s, 9H, 3 × CH<sub>3</sub>), 1.30 (s, 9H, 3 × CH<sub>3</sub>), 2.32  $(s, 3H, CH_3), 6.99 (d, {}^{3}J = 8.8 Hz, 1H), 7.35 (dd, {}^{3}J = 8.8 Hz, {}^{4}J = 2.4 Hz,$ 1H), 7.50 (d,  ${}^{4}J$  = 2.4 Hz, 1H);  ${}^{13}C$  NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  0.1 (p), 20.8 (p), 31.2 (p), 34.5 (q), 98.8 (q), 100.2 (q), 116.4 (q), 121.5 (t), 127.0 (t), 130.2 (t), 148.7 (q), 149.7 (q), 168.9 (q); MS (EI, 70 eV) *m/z* 288 (3,  $M^{+\bullet}$ ), 246 (33,  $[M - CH_2CO]^{+\bullet}$ ), 231 (100,  $[M - CH_2CO - CH_3]^+$ ); accurate mass (ESI-MS) m/z [M + H]<sup>+</sup>, calcd for C<sub>17</sub>H<sub>25</sub>O<sub>2</sub>Si 289.1618, found 289.1616.

4-tert-Butyl-2-ethynylphenyl acetate (8). A solution of compound 7 (600 mg, 2.08 mmol) and acetic acid (1 mL) in tetrahydrofuran (40 mL) was stirred while tetrabutylammonium fluoride (1.02 g, 3.24 mmol) was added. Stirring was continued for 4 h at ambient temperature, and then the solvent was removed under reduced pressure. The mixture was quenched by addition of aqueous hydrogen chloride (25 mL, 1.2 M), and the product was extracted with dichloromethane  $(3 \times 30 \text{ mL})$ . The combined organic layers were washed with brine, dried over sodium sulfate, filtered, and concentrated under reduced pressure. Flash chromatography of the residue over silica gel (petroleum ether/CH<sub>2</sub>Cl<sub>2</sub>, 5:1) afforded the arylacetylene 8 (404 mg, 90%) as a colorless solid: mp 61-62 °C; IR (neat) 3284, 2964, 1763, 1493, 1368, 1206, 1183, 1123, 1011, 893, 842 cm $^{-1}$ ; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ 1.31 (s, 9H,  $3 \times CH_3$ ), 2.33 (s, 3H, CH<sub>3</sub>), 3.21 (s, 1H), 7.01 (d, <sup>3</sup>*J* = 8.8 Hz, 1H), 7.39 (dd,  ${}^{3}J = 8.8$  Hz,  ${}^{4}J = 2.4$  Hz, 1H), 7.54 (d,  ${}^{4}J = 2.4$  Hz, 1H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 20.9 (p), 31.2 (p), 34.5 (q), 79.2 (t), 81.2 (q), 115.4 (q), 121.7 (t), 127.3 (t), 130.6 (t), 148.8 (q), 149.8 (q), 169.1 (q); MS (EI, 70 eV) m/z 216 (4, M<sup>+•</sup>), 174 (41, [M - CH<sub>2</sub>CO]<sup>+•</sup>), 159 (100,  $[M - CH_2CO - CH_3]^+$ ); accurate mass (ESI-MS) m/z [M +NH<sub>4</sub>]<sup>+</sup>, calcd for C<sub>14</sub>H<sub>20</sub>NO<sub>2</sub> 234.1489, found 234.1484.

**2,3,6,7,10,11-Hexakis(5-***tert*-butyl-2-acetoxylphenylethynyl)-**4b,8b,12b,12d-tetramethyl-4b,8b,12b,12d-tetrahydrodibenzo-[2,3:4,5]pentaleno[1,6-***ab*]**indene (10).** A solution of hexabromotribenzotriquinacene 9<sup>26,33</sup> (113 mg, 0.14 mmol), 4-*tert*-butyl-2-ethynylphenyl acetate **8** (720 mg, 3.36 mmol), PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> (10 mg, 14 μmol), cuprous



Figure 3. Plot of the chemical shift changes ( $\Delta\delta$ ) versus the molar ratios for (left) [ $C_{60}$ ]/[12], protons H<sup>a</sup>-H<sup>e</sup>, and (right) [ $C_{60}$ ]/[13], protons H<sup>a</sup>-H<sup>d</sup>, in toluene- $d_8$ . For proton assignment, see Scheme 2.



Figure 4. Side views of the optimized structures of the 1:1 complexes (a)  $C_{60} \subset 10$ , (b)  $C_{60} \subset 12$ , and (c)  $C_{60} \subset 13$  (calculated by molecular mechanics method using MM+ force field).

iodide (5 mg, 26 µmol), and triphenylphosphine (7 mg, 27 µmol) in anhydrous triethylamine (15 mL) was heated to reflux under argon for 48 h. The reaction was quenched by addition of water, and the mixture was extracted with dichloromethane, washed with brine, dried over sodium sulfate, filtered, and concentrated under reduced pressure. Flash chromatography of the residue over silica gel (petroleum ether/CH2Cl2/AcOEt, 30:15:1) afforded the product 10 (185 mg, 82%) as a colorless solid: mp 269-271 °C; IR (neat) 3407, 2959, 2926, 2865, 1765, 1495, 1462, 1367, 1195, 1122, 1011, 897, 835 cm $^{-1}$ ; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  1.30 (s, 54H, 18 × CH<sub>3</sub>), 1.57 (s, 3H, CH<sub>3</sub>), 1.71 (s, 9H, 3 × CH<sub>3</sub>), 2.19 (s, 18H, 6  $\times$  CH<sub>3</sub>), 7.01 (d, <sup>3</sup>*J* = 8.8 Hz, 6H), 7.37 (dd, <sup>3</sup>*J* = 8.8 Hz, <sup>4</sup>*J* = 2.4 Hz, 6H), 7.55 (s, 6H), 7.67 (d,  ${}^{4}J$  = 2.4 Hz, 6H);  ${}^{13}C$  NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  14.2 (p), 20.8 (p), 25.6 (p), 31.3 (p), 34.5 (q), 62.6 (q), 70.8 (q), 88.9 (q), 92.2 (q), 116.5 (q), 121.7 (t), 125.4 (q), 126.7 (t), 126.9 (t), 130.2 (t), 148.6 (q), 148.8 (q), 149.5 (q), 169.2 (q); ESI(+)-MS (CH<sub>2</sub>Cl<sub>2</sub>/MeOH) m/z 1644.7  $(100, [M + Na]^+)$ , ESI(+)-CID/MS of  $[M + Na]^+ m/z$  1601.7 (100, [M $+ Na - CH_2CO]^+$ , 1559.6 (17,  $[M + Na - 2 CH_2CO]^+$ ); accurate mass  $[ESI(+)-MS] m/z [M + Na]^+$ , calcd for  $C_{110}H_{108}O_{12}Na$  1643.7733, found 1643.7705.

**2,3,6,7,10,11-Hexakis**(5-*tert*-butyl-2-hydroxyphenylethynyl)-**4b,8b,12b,12d-tetramethyl-4b,8b,12b,12d-tetrahydrodibenzo-[2,3:4,5]pentaleno[1,6-***ab***]indene (11). Hexaacetate 10 (20 mg, 12 \mumol) was dissolved in a mixture of methanol and tetrahydrofuran (1:1, 6 mL), and the solution was stirred at 0 °C while a portion of solid sodium hydroxide (5 mg, 125 \mumol) was added. The resulting solution was stirred at room temperature overnight. Then the mixture was neutralized with aqueous hydrogen chloride, extracted with ethyl ether, washed with brine, dried over magnesium sulfate, filtered, and concentrated under reduced pressure. Flash chromatography of the residue over silica gel (petroleum ether/CH<sub>2</sub>Cl<sub>2</sub>/MeOH, 30:20:1) afforded compound <b>11** (12 mg, 72%) as a colorless solid: mp 159–161 °C; IR (neat) 3477, 3405, 2960, 2929, 2868, 1710, 1496, 1463, 1365, 1258, 1239, 1182, 891, 823 cm<sup>-1</sup>; <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>)  $\delta$  1.29 (s, 54H, 18 × CH<sub>3</sub>), 1.48 (s, 3H, CH<sub>3</sub>), 1.73 (s, 9H, 3 × CH<sub>3</sub>), 6.06 (s, 6H, OH), 6.88 (d,  ${}^{3}J$  = 9.0 Hz, 6H), 7.29 (dd,  ${}^{3}J$  = 9.0 Hz,  ${}^{4}J$  = 2.4 Hz, 6H), 7.51 (d,  ${}^{4}J$  = 2.4 Hz, 6H), 7.65 (s, 6H);  ${}^{13}$ C NMR (125 MHz, CDCl<sub>3</sub>)  $\delta$  14.2 (p), 25.7 (p), 31.4 (p), 34.1 (q), 62.8 (q), 70.8 (q), 88.6 (q), 94.6 (q), 108.3 (q), 114.5 (t), 125.0 (q), 126.5 (t), 128.2 (t), 128.5 (t), 143.2 (q), 148.7 (q), 154.7 (q); MALDI(+)-MS (DCTB) *m*/*z* 1368.7 (100, M<sup>++</sup>); accurate mass (MALDI-MS, DCTB) *m*/*z* M<sup>++</sup>, calcd for C<sub>98</sub>H<sub>96</sub>O<sub>6</sub> 1368.7201, found 1368.7205.

2,3,6,7,10,11-Hexakis(5-tert-butylbenzofuran-2-yl)-4b,8b,12b, 12d-tetramethyl-4b,8b,12b,12d-tetrahydrodibenzo[2,3:4,5]pentaleno[1,6-*ab*]indene (12). *Procedure A*. A solution of compound 10 (30 mg, 18  $\mu$ mol) and powdered sodium hydroxide (23 mg, 0.57 mmol) in methanol (15 mL) was stirred under argon for 12 h. The solvent was evaporated, and the residue was carefully neutralized with dilute hydrochloric acid and then poured onto ethyl acetate. The separated layers were washed with brine, dried over magnesium sulfate, filtered, and concentrated under reduced pressure. Flash chromatography of the residue over silica gel (petroleum ether/ AcOEt, 30:1) afforded the product 12 (11 mg, 46%).

*Procedure B.* A solution of hexaphenol **11** (15 mg, 11 μmol) in dimethylacetamide (2.0 mL) was stirred while palladium(II) acetate (1 mg, 4 μmol) and cesium carbonate (43 mg, 0.13 mmol) were added under normal atmosphere. The reaction mixture was stirred for 8 h at 80 °C. The solvent was evaporated, and the residual mixture was carefully neutralized with dilute hydrochloric acid and then poured onto ethyl acetate. The separated layers were washed with brine, dried over MgSO<sub>4</sub>, filtered, and concentrated under reduced pressure. Flash chromatography of the residue over silica gel (petroleum ether/AcOEt, 30:1) afforded the product **12** (4 mg, 26%) as a colorless solid; mp 230–232 °C; IR (neat) 2960, 2926, 2860, 1741, 1465, 1263, 1085, 1028, 878, 804 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 1.36 (s, 54H, 18 × CH<sub>3</sub>), 1.56 (s, 3H, CH<sub>3</sub>), 1.86 (s, 9H, 3 × CH<sub>3</sub>), 6.49 (s, 6H), 7.35 (dd, <sup>3</sup>J = 8.8 Hz, <sup>4</sup>J = 2.0 Hz, 6H), 7.42 (d, <sup>3</sup>J = 8.8 Hz, 6H), 7.50

(d, <sup>4</sup>*J* = 2.0 Hz, 6H), 7.85 (s, 6H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  14.1 (p), 25.8 (p), 31.8 (p), 34.7 (q), 62.9 (q), 71.2 (q), 105.4 (t), 110.7 (t), 117.3 (t), 122.2 (t), 124.6 (t), 128.8 (q), 129.8 (q), 145.7 (q), 149.2 (q), 152.9 (q), 155.1 (q); MALDI(+)-MS (DCTB) *m*/*z* 1368.4 (100, M<sup>++</sup>); accurate mass [MALDI(+)-MS, DCTB] *m*/*z* M<sup>++</sup>, calcd for C<sub>98</sub>H<sub>96</sub>O<sub>6</sub> 1368.7201, found 1368.7197.

Hexakis(benzofurano)trinaphthotriguinacene 13. A solution of compound 12 (14 mg, 10  $\mu$ mol) in dichloromethane (10 mL) was stirred under argon at 0 °C, while a solution of ferric chloride (39 mg, 0.24 mmol) in dry nitromethane (2 mL) was added dropwise. Stirring was continued at 0 °C for 0.5 h, then the solvent was removed under reduced pressure. The residue was diluted with water (15 mL) and extracted with dichloromethane (3  $\times$  20 mL). The combined organic layers were washed with brine, dried over sodium sulfate, filtered, and concentrated under reduced pressure. Flash chromatography of the residue over silica gel (petroleum ether/ $CH_2Cl_2 = 10:1$ ) afforded 13 as amorphous colorless solid: mp >360 °C; IR (neat) 3421, 2958, 2924, 2855, 1651, 1461, 1385, 1261, 1110, 1025, 806  $\rm cm^{-1}; \ ^1H$  NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  1.55 (s, 54H, 18 × CH<sub>3</sub>), 1.68 (s, 3H, CH<sub>3</sub>), 2.20 (s, 9H, 3 × CH<sub>3</sub>), 7.63 (dd,  ${}^{3}J$  = 8.8 Hz,  ${}^{4}J$  = 1.6 Hz, 6H), 7.85 (d,  ${}^{3}J$  = 8.8 Hz, 6H), 8.57 (s, 6H), 8.88 (s, 6H);  $^{13}$ C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$ 16.7 (p), 27.8 (p), 32.0 (p), 35.0 (q), 63.2 (q), 71.1 (q), 111.4 (t), 113.6 (q), 116.0 (t), 118.7 (t), 121.1 (q), 123.9 (t), 124.7 (q), 145.8 (q), 149.3 (q), 149.4 (q), 154.3 (q); MALDI(+)-MS (DCTB) *m*/*z* 1362.7 (100, M<sup>+•</sup>); accurate mass [MALDI(+)-MS], DCTB) m/z M<sup>+•</sup>, calcd for C<sub>98</sub>H<sub>90</sub>O<sub>6</sub> 1362.6732, found 1362.6738.

**1,2-Di**(5-*tert*-**butyl**-2-acetoxylphenylethynyl)-4,5-dimethylbenzene (15). In analogy to the synthesis of compound **10**, this coupling reaction was carried out by starting from dibromoxylene **14**. Two hundred milligrams (0.76 mmol) of **14** gave **15** (354 mg, 87%) as an oil: IR (neat) 2961, 2869, 1767, 1499, 1366, 1193, 1123, 1010, 894, 837 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  1.29 (s, 18H,  $6 \times$  CH<sub>3</sub>), 2.24 (s, 6H,  $2 \times$  CH<sub>3</sub>), 2.28 (s, 6H,  $2 \times$  CH<sub>3</sub>), 7.03 (d, <sup>3</sup>*J* = 8.8 Hz, 2H), 7.32 (s, 2H), 7.36 (dd, <sup>3</sup>*J* = 8.8 Hz, <sup>4</sup>*J* = 2.4 Hz, 2H), 7.64 (d, <sup>4</sup>*J* = 2.4 Hz, 2H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  19.6 (p), 20.8 (p), 31.2 (p), 34.5 (q), 87.9 (q), 92.4 (q), 116.8 (q), 121.6 (t), 122.7 (q), 126.6 (t), 130.3 (t), 133.0 (t), 137.3 (q), 148.7 (q), 149.2 (q), 169.2 (q); MS (EI, 70 eV) *m*/*z* 534 (8, M<sup>++</sup>), 492 (18, [M - CH<sub>2</sub>CO]<sup>++</sup>), 450 (34, [M - 2 CH<sub>2</sub>CO]<sup>++</sup>), 43 (100); accurate mass (ESI-MS) *m*/*z* [M + NH<sub>4</sub>]<sup>+</sup>, calcd for C<sub>36</sub>H<sub>42</sub>NO<sub>4</sub> 552.3108, found 552.3112.

**1,2-Di(5-tert-butylbenzofuran-2-yl)-4,5-dimethylbenzene (16).** In analogy to the synthesis of compound **12**, this reaction was carried out by starting from ditolane **15**. From ditolan **15** (31 mg, 58  $\mu$ mol), compound **16** (17 mg, 65%) was obtained as a colorless solid: mp 65–67 °C; IR (neat) 2960, 2867, 1714, 1471, 1363, 1272, 1165, 879, 806 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  1.39 (s, 18H, 6 × CH<sub>3</sub>), 2.38 (s, 6H, 2 × CH<sub>3</sub>), 6.55 (s, 2H), 7.35 (dd, <sup>3</sup>*J* = 8.8 Hz, <sup>4</sup>*J* = 1.6 Hz, 2H), 7.41 (d, <sup>3</sup>*J* = 8.8 Hz, 2H), 7.52 (d, <sup>4</sup>*J* = 1.6 Hz, 2H), 7.59 (s, 2H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  19.6 (p), 31.9 (p), 34.7 (q), 105.0 (t), 110.5 (t), 117.2 (t), 122.1 (t), 126.9 (q), 128.9 (q), 131.0 (t), 137.6 (q), 145.7 (q), 152.8 (q), 155.3 (q); MS (EI, 70 eV) *m/z* 450 (100, M<sup>++</sup>), 435 (21, [M - CH<sub>3</sub>]<sup>+</sup>); accurate mass (EI-MS) *m/z* M<sup>++</sup>, calcd for C<sub>32</sub>H<sub>34</sub>O<sub>2</sub> 450.2559, found 450.2538.

**Bis(benzofurano]naphthalene 17.** In analogy to the synthesis of compound 13, this cyclodehydrogenation reaction was carried out by starting from di(benzofuranylxylene) 16. From di(benzofuranyl)xylene 16 (8 mg, 18  $\mu$ mol), compound 17 (7 mg, 88%) was obtained as a colorless solid: mp 267–269 °C; IR (neat) 2956, 2924, 2855, 1461, 1362, 1257, 1203, 1036, 808 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  1.57 (s, 18H, 6 × CH<sub>3</sub>), 2.56 (s, 6H, 2 × CH<sub>3</sub>), 7.60 (dd, <sup>3</sup>J = 8.8 Hz, <sup>4</sup>J = 1.6 Hz, 2H), 7.71 (d, <sup>3</sup>J = 8.8 Hz, 2H), 8.29 (s, 2H), 8.59 (d, <sup>4</sup>J = 1.6 Hz, 2H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  20.5 (p), 32.1 (p), 35.0 (q), 111.2 (t), 113.4 (q),118.6 (t), 119.1 (q), 121.4 (t), 123.8 (t), 124.7 (q), 136.4 (q), 145.8 (q), 149.0 (q), 154.2 (q); MS (EI, 70 eV) *m/z* 448 (100, M<sup>++</sup>), 433 (28, [M – CH<sub>3</sub>]<sup>+</sup>);

accurate mass (EI-MS)  $m/z \, \mathrm{M}^{+\bullet}$ , calcd for  $\mathrm{C}_{32}\mathrm{H}_{32}\mathrm{O}_2$  448.2402, found 448.2398.

# ASSOCIATED CONTENT

**Supporting Information.** Optical properties of compounds 10-13 and 15-17, crystal packing of 10 and its X-ray crystallographic file, complexation measurements of compounds 12 and 13 with C<sub>60</sub>, <sup>1</sup>H NMR, <sup>13</sup>C NMR, and DEPT 135 spectra of compounds 5-8, 10-13, and 15-17. This material is available free of charge via the Internet at http://pubs.acs.org.

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