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## Facile Synthetic Routes to Phenylene and Triazine Core Based Dendritic Cobaltabisdicarbollides<sup>§</sup>

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The synthesis and thermal properties of phenylene and triazine core based symmetrical macro-molecules containing three to six cobaltabis(dicarbollide) clusters are reported. The zwitterionic oxonium derivative of cobaltabis(dicarbollide), [3,3'-Co(8-C<sub>4</sub>H<sub>8</sub>O<sub>2</sub>-1,2-C<sub>2</sub>B<sub>9</sub>H<sub>10</sub>)(1',2'-C<sub>2</sub>B<sub>9</sub>H<sub>11</sub>)], has been used for the synthetic transformations, and silicon tetrachloride and triflic acid were used as the cyclotrimerization reagents. Compounds containing multiple cobaltabis(dicarbollide) clusters are found to be extremely thermally stable, and only a 10–30% mass loss occurred up to 700 °C.

### Introduction

Ever since the synthesis of the cobaltabis(dicarbollide) anion **1**, [3,3'-Co(1,2-C<sub>2</sub>B<sub>9</sub>H<sub>11</sub>)<sub>2</sub>]<sup>−</sup>, was reported by Hawthorne's research group,<sup>1</sup> its high thermal and chemical stability has made it one of the most widely used metallacarboranes<sup>2</sup> in synthetic chemistry (Figure 1).<sup>3</sup> A number of unique applications of the cobaltabis(dicarbollide) anion have also been reported. The cobaltabis(dicarbollide)–porphyrin conjugates have been evaluated as boron drug delivery platforms,<sup>4</sup> while derivatives of **1** have also been synthesized for the selective

removal of radionuclides.<sup>5</sup> Some other recent applications of **1** include its use in the synthesis of thermally stable conducting polymers,<sup>6</sup> coordination polymers and metal organic frameworks,<sup>7</sup> and ion selective electrodes and sensors.<sup>8</sup>

The synthesis of the zwitterionic oxonium derivative **2**, [3,3'-Co(8-C<sub>4</sub>H<sub>8</sub>O<sub>2</sub>-1,2-C<sub>2</sub>B<sub>9</sub>H<sub>10</sub>)(1',2'-C<sub>2</sub>B<sub>9</sub>H<sub>11</sub>)], ushered in a new area of research on the synthetic chemistry of mono-substituted cobaltacarborane complexes (Figure 1). Compound **2** was first prepared by the reaction of the parent metallacarborane with Me<sub>2</sub>SO<sub>4</sub> in 1,4-dioxane,<sup>9</sup> and later the same product was obtained using BF<sub>3</sub>·OEt<sub>2</sub>.<sup>10</sup> Compound **2** has been shown to undergo dioxane ring-opening reactions in the presence of a variety of nucleophilic reagents, such as fluoride, chloride, and hydroxide anions, imide, cyanide, and amines.<sup>11</sup> Recently there have been reports on the synthesis of dendritic macromolecules that contain multiple cobaltabis(dicarbollide) clusters. These dendritic molecules were synthesized by employing hydrosilylation reactions with the C<sub>6</sub>-silyl-substituted cobaltabis(dicarbollide) derivative Cs[1,1'-μ-SiMeH-3,3'-Co(1,2-C<sub>2</sub>B<sub>9</sub>H<sub>10</sub>)<sub>2</sub>].<sup>12</sup> For the above-mentioned metallacarborane dendrimers UV–vis absorption was found to be a good tool for estimating the number of cobaltabis(dicarbollide) moieties present in the molecule.<sup>12</sup> A few examples of symmetrical and dendritic compounds involving small

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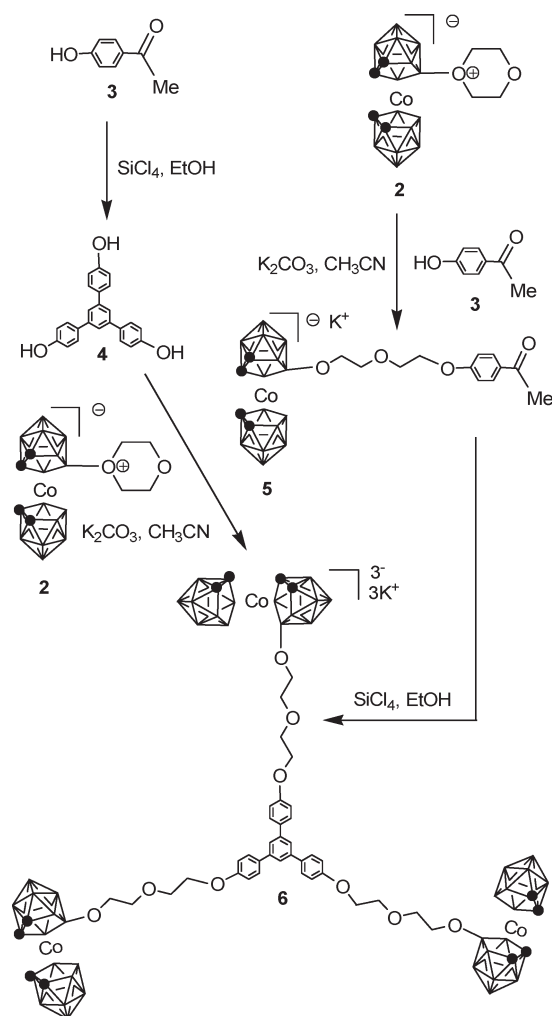
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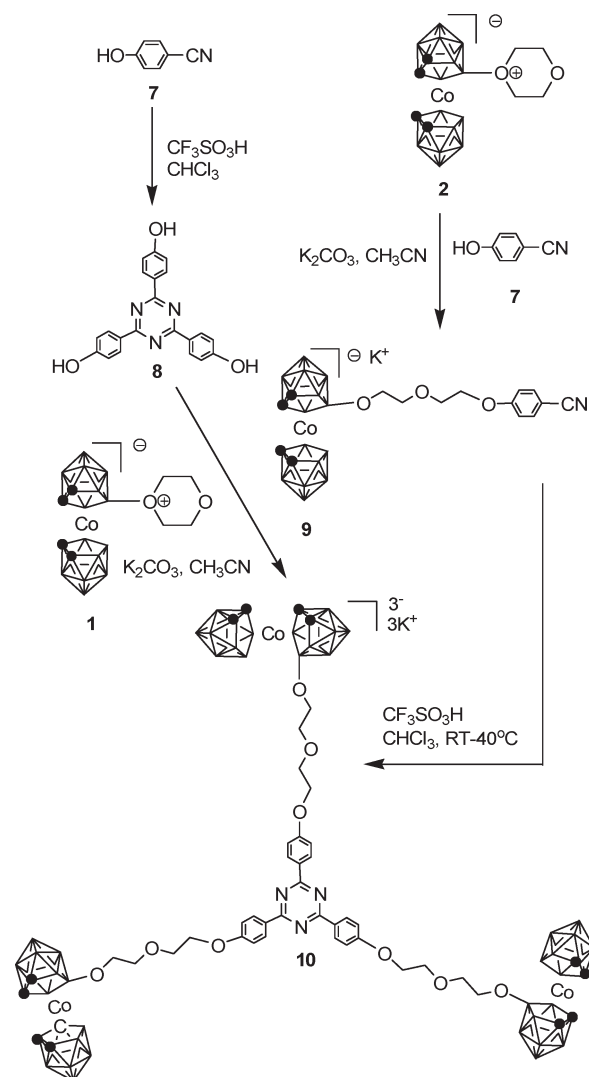
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Scheme 1. Synthesis of **6** via Trimerization of Keto Derivatives

synthesis of liquid crystalline and nonlinear optical materials as well as in a number of other areas.<sup>24</sup> The synthesis of the 1,3,5-triazine core based symmetrical compound **10**, containing three cobaltabis(dicarbollide) clusters, is shown in Scheme 2. Similar to the procedure as described in Scheme 1, the synthesis of **10** was carried out using two different methods. In the first method, 2,4,6-tris(*p*-hydroxyphenyl)-triazine **8** was synthesized from commercially available 4-cyanophenol via triflic acid-mediated cyclotrimerization, and then this was treated with **2**. The ring-opening reaction took place in the presence of potassium carbonate, which led to the formation of **10** in 95% yield. In the second approach, 4-cyanophenol was first treated with **2** in the presence of potassium carbonate, and then compound **9** was formed.

Scheme 2. Synthesis of **10** via Trimerization of Cyano Derivatives

This was then treated with triflic acid in chloroform to produce **10** in about 75% yield.

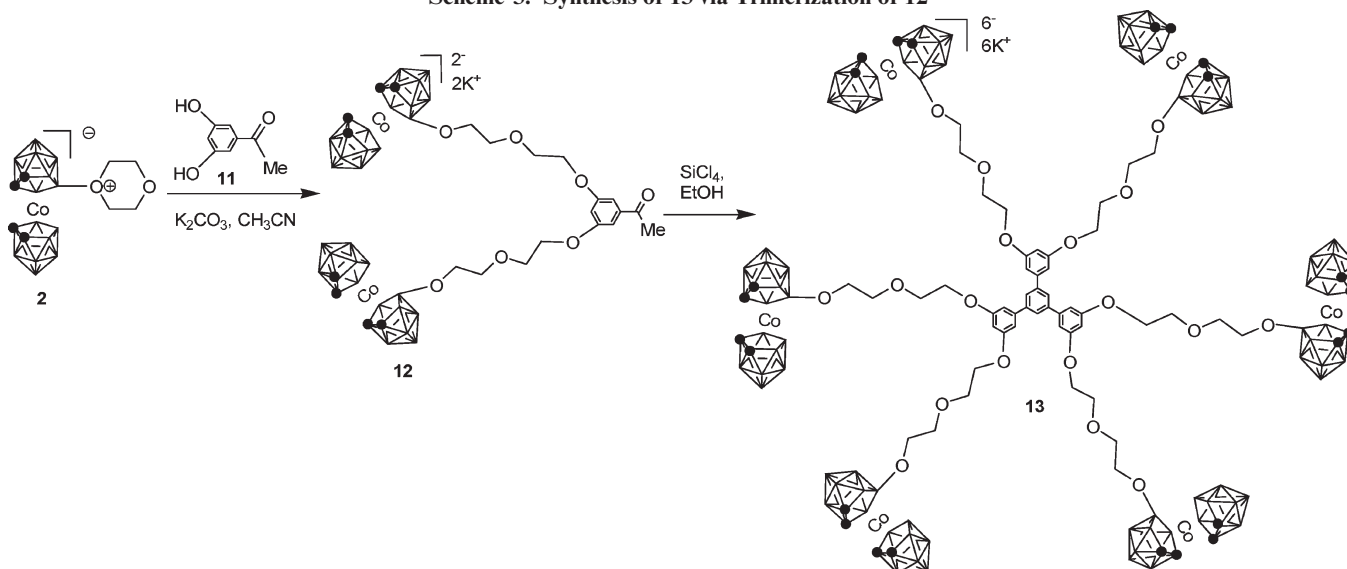
After the synthesis of phenylene and triazine core based trimers containing three peripheral cobaltabis(dicarbollide) clusters was successfully carried out, we extended the study to make a phenylene core based trimer containing additional peripheral cobaltabis(dicarbollide) clusters. The synthesis of such a trimer, containing six cobaltabis(dicarbollides), is outlined in Scheme 3. The synthesis of trimer **13** was started from the commercially available 3,5-dihydroxyacetophenone **11**. The nucleophilic ring-opening reaction of **2** in the presence of base and **11** led to the ketone **12** in quantitative yield. Then the ketone **12** underwent a silicon tetrachloride/ethanol-mediated trimerization reaction to form the trimer **13**, which contains six cobaltabis(dicarbollides).

All compounds were characterized by <sup>1</sup>H, <sup>13</sup>C, and <sup>11</sup>B NMR, IR, and elemental analysis. The IR spectra of compounds containing cobaltabis(dicarbollide) clusters showed strong bands between 2550 and 2570 cm<sup>-1</sup> corresponding to ν(B–H). For ketones **5** and **12** bands were observed at 1717 and 1737 cm<sup>-1</sup>, corresponding to ν(C=O). The aromatic nitrile **9** showed a moderate band at 2233 that corresponds to ν(C≡N). The presence of cobaltabis(dicarbollide) clusters was also evident from the <sup>1</sup>H, <sup>13</sup>C, and <sup>11</sup>B NMR spectra.

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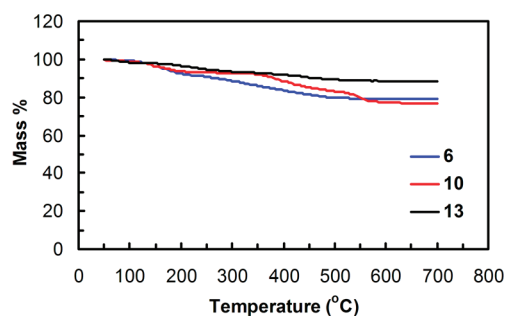


## Scheme 3. Synthesis of 13 via Trimerization of 12



Broad peaks between  $\delta$  3.5 and 4.3 ppm were observed in the  $^1\text{H}$  NMR spectra, which represent cluster C—H. Peaks observed at  $\delta$  46 and 53 ppm in the  $^{13}\text{C}$  NMR spectra are due to the cluster carbons. The proton-decoupled  $^{11}\text{B}$  NMR spectra also indicated the presence of cobaltabis(dicarbollides), and peaks were observed between  $\delta$  23 and  $-29$  ppm.<sup>9</sup> The NMR peak for the substituted B(8) boron atom of the cluster was observed around  $\delta$  23 ppm, which is in agreement with the literature.<sup>9</sup> The presence of aliphatic polyether chains was observed by the presence of resonances between  $\delta$  3.5 and 4.4 ppm in the  $^1\text{H}$  NMR, and peaks were also observed between  $\delta$  67 and 72 ppm in the  $^{13}\text{C}$  NMR spectra. Phenyl protons and carbons of phenylene and triazine cores also showed resonances in the appropriate region (see SI). Finally, the mass spectral data of all compounds confirmed their formation. The MALDI-TOF mass spectral data for trimers **6**, **10**, and **13** showed prominent peaks at  $m/z$  1661.63 [ $\text{M}^+ - \text{K}$ ], 1665.01 [ $\text{M}^+ - \text{K}$ ], and 2976.15 [ $\text{M}^+ - 3\text{K} + 1$ ] (see SI). The mass spectral data for compounds **6** and **10** were found to be identical for both synthetic approaches. Prominent peaks were observed for the molecular ion, indicating that the cyclic oxonium derivative **2** could be a useful synthetic building block for both convergent and divergent approaches of synthesizing symmetrical molecules. The MALDI-TOF spectra of compounds **6** and **10** are those obtained from the divergent synthetic approach, and they have been included in the SI. However, the yields of trimerization of keto and cyano derivatives, **5** and **9**, were found to be slightly lower than what was found in the divergent approach.

**Thermal Properties.** Some unique properties of boron clusters and weakly coordinating carborane anions have been exploited for the synthesis of a variety of polymeric materials. These include thermally stable polymeric materials and ceramics,<sup>25</sup> light-emitting luminescent polymers,<sup>26</sup>



**Figure 2.** TGA curves of cobaltabis(dicarbollides) trimers under argon.

conducting organic polymers (COPs),<sup>6</sup> and coordination polymers.<sup>7,27</sup> Over the past few decades several groups have reported the incorporation of carboranes into polymeric backbones, using various well-established polymer linking processes.<sup>28</sup> In addition, a few carborane-siloxane elastomers, bearing the commercial names Dexsil and Ucarsil, have found specialized applications.<sup>29</sup> Recent studies on the thermal properties of compounds containing multiple *ortho*-carborane clusters in our laboratory also led to the conclusion that incorporation of carborane units enhances thermal stability.<sup>19b,20</sup> Therefore, we were interested in the thermal properties of the trimers that contain multiple cobaltabis(dicarbollide) clusters. TGA curves of trimers **6**, **10**, and **13** are compared in Figure 2. As can be seen, the thermal decomposition is not simple; they all maintain a constant mass until about 150 °C and have finished their mass loss by about 550 °C. The temperatures at which 10% mass loss occurred for **6**, **10**, and **13** were found to be 270, 380, and 470 °C, respectively. The 270 °C reported for **6** is not all that

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different from that found for the unsubstituted phenylene core (257 °C)<sup>19b</sup> and much less than the carborane-substituted phenylene cores.<sup>19b</sup> However, for all these trimers a very high residue weight percent was maintained even at 700 °C, which is about 79%, 76%, and 88% of the mass for trimers **6**, **10**, and **13**, respectively. This is most likely due to the high inorganic cobaltabis(dicarbollide) component.

## Conclusion

Silicon tetrachloride- and triflic acid-mediated cyclotrimerization of cobaltabis(dicarbollide)-appended aromatic ketones and nitriles has been found to be an efficient method for the synthesis of phenylene and triazine core based thermally stable star-shaped molecules. The nucleophilic ring-opening reaction of zwitterionic [3,3'-Co(8-C<sub>4</sub>H<sub>8</sub>O<sub>2</sub>-1,2-C<sub>2</sub>B<sub>9</sub>H<sub>10</sub>)(1',2'-C<sub>2</sub>B<sub>9</sub>H<sub>11</sub>)] is also found to be suitable for both convergent and divergent approaches of making dendritic macromolecules. It is also found that compounds containing multiple cobaltabis(dicarbollides) exhibit only a 10–30% mass loss up to 700 °C. An increase in the number of cobaltabis(dicarbollides) in the molecule is found to enhance the thermal stability.

## Experimental Section

**General Methods and Instrumentation.** Reactions were generally performed under argon in oven-dried flasks. Solvents and reagents were added by syringes. Solvents were dried and distilled using standard procedures. Reagents were purchased and were used as received without further purification. All compounds were purified by column chromatography on silica gel (70–230 mesh, Aldrich). Yields of the products refer to analytically pure samples. <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded on a Bruker Fourier transform multinuclear NMR spectrometer at 500.13 and 125.75 MHz, respectively. Chemical shifts are reported relative to TMS (<sup>1</sup>H: δ = 0.00 ppm) and CDCl<sub>3</sub> (<sup>13</sup>C: δ = 77.0 ppm), and coupling constants are given in hertz. All <sup>13</sup>C spectra are proton-decoupled. <sup>11</sup>B NMR spectra were recorded at 64.2 and 160.5 MHz relative to BF<sub>3</sub>·Et<sub>2</sub>O. Infrared spectra were recorded on an ATI Mattson Genesis series FT-IR spectrophotometer. Elemental analyses were carried out with a Perkin-Elmer CHN analyzer 2400. Melting points were measured with a Mel-Temp II apparatus (Laboratory Devices, USA) and are uncorrected. Thermal gravimetric analysis (TGA) was performed on a Perkin-Elmer Pyris 1 analyzer at a heating rate of 5 °C/min under argon. Mass spectral analyses were performed with an Applied Biosystems Voyager-DE STR-MALDI-TOF spectrometer and a Waters Q-TOF Ultima ES spectrometer.

**Preparations and Analytical Data of Compounds.** **Ketone 5.** 4-Hydroxyacetophenone **3** (175 mg, 1.29 mmol) was dissolved in 20 mL of acetonitrile. Then K<sub>2</sub>CO<sub>3</sub> (1.25 g, 9.03 mmol) and **2** (530 mg, 1.29 mmol) were added, and it was refluxed at 90 °C for 6 h. Then the reaction mixture was filtered through a cotton plug. After evaporation of the solvent, the residue was purified by silica gel column chromatography with 50–70% ethyl acetate in hexanes as the eluent to obtain 574 mg of pure compound **5** as a yellow solid, yield 76%. Melting point: > 250 °C. <sup>1</sup>H NMR (CD<sub>3</sub>CN, 500 MHz): δ 7.97 (d, 2H, *J* = 7.0 Hz, Ar-*H*), 7.03 (d, 2H, *J* = 7.0 Hz, Ar-*H*), 4.21–4.20 (m, 4H, C<sub>cage</sub>-*H*, O-CH<sub>2</sub>), 4.16 (br s, 2H, O-CH<sub>2</sub>), 3.83–3.81 (m, 2H, O-CH<sub>2</sub>), 3.64–3.63 (m, 2H, O-CH<sub>2</sub>), 3.60–3.58 (m, 2H, O-CH<sub>2</sub>), 2.54 (s, 3H, CH<sub>3</sub>). <sup>13</sup>C NMR (CD<sub>3</sub>CN, 125 MHz): δ 196.5 (C=O), 162.7 (Ar-C), 130.4 (Ar-C), 114.2 (Ar-C), 72.0 (O-CH<sub>2</sub>), 69.0 (O-CH<sub>2</sub>), 68.4 (O-CH<sub>2</sub>), 67.9 (O-CH<sub>2</sub>), 53.5 (C<sub>cage</sub>), 46.7 (C<sub>cage</sub>), 25.7 (CH<sub>3</sub>). <sup>11</sup>B NMR (proton decoupled): δ 23.51 (1B), 4.59 (1B), 0.01 (1B), -2.70 (1B), -4.75 (2B), -7.66 (6B), -17.39 (2B),

-20.41 (3B), -28.48 (1B). IR (KBr): 3041, 2931, 2562 (B-H), 1717, 1671, 1600, 1254, 1097, 978, 836 cm<sup>-1</sup>. Anal. Calcd for C<sub>16</sub>H<sub>36</sub>B<sub>18</sub>CoK<sub>4</sub>O<sub>4</sub>: C 32.85, H 6.20. Found: C 32.80, H 6.19. MALDI-TOF-MS (*m/z*): calcd 585.08, found 547.23 (M<sup>+</sup> - K + 1, 100%).

**Ketone 12.** 3,5-Dihydroxyacetophenone **11** (161 mg, 1.05 mmol) was dissolved in 25 mL of acetonitrile. Then K<sub>2</sub>CO<sub>3</sub> (1.75 g, 12.69 mmol) and **2** (870 mg, 2.11 mmol) were added, and the mixture was refluxed at 90 °C for 6 h. Then the reaction mixture was filtered through a cotton plug. After evaporation of the solvent, the residue was purified by silica gel column chromatography with ethyl acetate to 5% methanol in ethyl acetate as the eluent to obtain 783 mg of pure compound **12** as a yellow solid, yield 71%. Melting point: > 250 °C. <sup>1</sup>H NMR (CD<sub>3</sub>CN, 500 MHz): δ 7.14 (d, 2H, *J* = 2.25 Hz, Ar-*H*), 6.79 (d, 1H, *J* = 2.15 Hz, Ar-*H*), 4.18–4.17 (m, 4H C<sub>cage</sub>, 4H O-CH<sub>2</sub>), 4.13 (br s, 4H, C<sub>cage</sub>-*H*), 3.83–3.81 (m, 4H, O-CH<sub>2</sub>), 3.68 (br s, 4H, O-CH<sub>2</sub>), 3.61–3.60 (m, 4H, O-CH<sub>2</sub>), 2.58 (s, 3H, CH<sub>3</sub>). <sup>13</sup>C NMR (CD<sub>3</sub>CN, 125 MHz): δ 197.8 (C=O), 160.0 (Ar-C), 139.2 (Ar-C), 107.1 (Ar-C), 106.0 (Ar-C), 71.9 (O-CH<sub>2</sub>), 69.1 (O-CH<sub>2</sub>), 68.5 (O-CH<sub>2</sub>), 67.9 (O-CH<sub>2</sub>), 53.3 (C<sub>cage</sub>), 46.8 (C<sub>cage</sub>), 26.3 (CH<sub>3</sub>). <sup>11</sup>B NMR (proton decoupled): δ 23.75 (2B), 4.95 (2B), 0.11 (2B), -2.66 (2B), -5.06 (4B), -7.47 (12B), -17.42 (4B), -20.33 (6B), -28.21 (2B). IR (KBr): 3044, 2929, 2569 (B-H), 1737, 1595, 1443, 1095, 968 cm<sup>-1</sup>. Anal. Calcd for C<sub>24</sub>H<sub>64</sub>B<sub>36</sub>Co<sub>2</sub>O<sub>7</sub>K<sub>2</sub>: C 27.45, H 6.14. Found: C 27.43, H 6.12. MALDI-TOF-MS (*m/z*): calcd 1050.01, found 1041.86 (M<sup>+</sup> - BH + 1, 100%).

**1,3,5-Tris(4-hydroxyphenyl)benzene, 4.** 4-Hydroxyacetophenone (**3**) (1.0 g, 7.34 mmol) was dissolved in 30 mL of dry ethanol. Then SiCl<sub>4</sub> (4.2 mL, 36.73 mmol) was added to it at 0 °C. The mixture was stirred at 0 °C for 10 min and then at room temperature for 16 h. The reaction mixture was quenched with water and extracted with dichloromethane. The combined organic layer was dried over MgSO<sub>4</sub>. After evaporation of the solvent the residue was purified by silica gel column chromatography with 40% ethyl acetate in hexane as eluent to obtain 620 mg of pure compound **4** as a colorless solid, yield 71%. Melting point: 230 °C. <sup>1</sup>H NMR (CD<sub>3</sub>CN, 500 MHz): δ 7.62 (s, 3H, Ar-*H*), 7.55 (d, 6H, *J* = 8.4 Hz, Ar-*H*), 6.92 (d, 6H, *J* = 8.4 Hz, Ar-*H*), 7.41 (br s, 3H, -OH). <sup>13</sup>C NMR (CD<sub>3</sub>CN, 125 MHz): δ 156.5 (Ar-C), 141.8 (Ar-C), 132.8 (Ar-C), 128.3 (Ar-C), 128.2 (Ar-C), 115.7 (Ar-C). Anal. Calcd for C<sub>24</sub>H<sub>18</sub>O<sub>3</sub>: C 81.34, H 5.12. Found: C 81.31, H 5.15. ES-MS (*m/z*): calcd 354.39, found 355.1 (M<sup>+</sup> + 1, 100%).

**Trimer 6. Method A:** 1,3,5-Tris(4-hydroxyphenyl)benzene (**4**) (100 mg, 0.282 mmol) was dissolved in 10 mL of acetonitrile. Then K<sub>2</sub>CO<sub>3</sub> (584 mg, 4.23 mmol) and **2** (383 mg, 0.93 mmol) were added, and the mixture was refluxed at 90 °C for 6 h. Then the reaction mixture was filtered through a cotton plug. After evaporation of the solvent, the residue was purified by silica gel column chromatography with ethyl acetate to 2% methanol in ethyl acetate as the eluent to obtain 422 mg of pure compound **6** as a yellow solid, yield 88%. **Method B:** Ketone **5** (460 mg, 0.84 mmol) was dissolved in 10 mL of dry ethanol. Then SiCl<sub>4</sub> (0.5 mL, 4.2 mmol) was added to it at 0 °C. It was stirred at 0 °C for 10 min and then stirred at room temperature for 24 h. The reaction mixture was quenched with water and extracted with ethyl acetate three times. The combined organic layer was dried over MgSO<sub>4</sub>. After evaporation of the solvent the residue was purified by silica gel column chromatography with ethyl acetate to 2% methanol in ethyl acetate as the eluent to obtain 350 mg of pure compound **6** as a yellow solid, yield 76%. Melting point: > 250 °C. <sup>1</sup>H NMR (CD<sub>3</sub>CN, 500 MHz): δ 7.78 (s, 3H, Ar-*H*), 7.76–7.73 (m, 6H, Ar-*H*), 7.01–7.05 (m, 6H, Ar-*H*), 4.23–4.19 (m, 12H C<sub>cage</sub>, 6H O-CH<sub>2</sub>), 3.72–3.59 (m, 18H, O-CH<sub>2</sub>). <sup>13</sup>C NMR (CD<sub>3</sub>CN, 125 MHz): δ 158.7 (Ar-C), 141.6 (Ar-C), 133.5 (Ar-C), 128.4 (Ar-C), 123.3 (Ar-C), 114.9 (Ar-C), 71.8 (O-CH<sub>2</sub>), 69.2 (O-CH<sub>2</sub>), 68.6 (O-CH<sub>2</sub>), 67.6 (O-CH<sub>2</sub>), 53.5 (C<sub>cage</sub>), 46.7 (C<sub>cage</sub>). <sup>11</sup>B NMR (proton decoupled): δ 23.6 (3B), 4.7 (3B),

0.03 (3B), -2.46 (3B), -4.82 (6B), -7.54 (18B), -17.30 (6B), -20.27 (9B), -28.45 (3B). IR (KBr): 3044, 2974, 2560 (B-H), 1604, 1509, 1399, 1244, 1095, 828  $\text{cm}^{-1}$ . Anal. Calcd for  $\text{C}_{48}\text{H}_{102}\text{B}_{54}\text{Co}_3\text{K}_3\text{O}_9$ : C 33.89, H 6.04. Found: C 33.84, H 6.01. MALDI-TOF-MS ( $m/z$ ): calcd 1701.20, found 1661.63 ( $\text{M}^+ - \text{K}$ , 100%), 1212.91 ( $\text{M}^+ - \text{C}_8\text{H}_{27}\text{B}_{18}\text{CoK}_2\text{O}_2 + 1$ ).

**Trimer 13.** Ketone **12** (450 mg, 0.426 mmol) was dissolved in 8 mL of dry ethanol. Then  $\text{SiCl}_4$  (0.5 mL, 4.26 mmol) was added to it at 0 °C. The mixture was stirred at 0 °C for 10 min and then at room temperature for 24 h. The reaction mixture was quenched with water and then extracted with ethyl acetate three times. The combined organic layer was dried over  $\text{MgSO}_4$ . After evaporation of the solvent the residue was purified by silica gel column chromatography with ethyl acetate to 10% methanol in ethyl acetate as eluent to obtain 250 mg of pure compound **13** as yellow solid, yield 56%. Melting point: > 250 °C.  $^1\text{H}$  NMR ( $\text{CD}_3\text{OD}$ , 500 MHz):  $\delta$  6.76 (s, 3H, Ar-H), 6.66 (br, 3H, Ar-H), 6.57 (br, 3H, Ar-H), 6.49 (br, 3H, Ar-H), 4.13 (br, 24H  $\text{C}_{\text{cage}}$ , 12H O- $\text{CH}_2$ ), 3.88–3.81 (m, 12H, O- $\text{CH}_2$ ), 3.73–3.67 (m, 24H, O- $\text{CH}_2$ ).  $^{13}\text{C}$  NMR ( $\text{CD}_3\text{OD}$ , 125 MHz):  $\delta$  158.8 (Ar-C), 149.1 (Ar-C), 140.4 (Ar-C), 125.6 (Ar-C), 124.1 (Ar-C), 107.6 (Ar-C), 71.7 (O- $\text{CH}_2$ ), 69.4 (O- $\text{CH}_2$ ), 68.7 (O- $\text{CH}_2$ ), 67.5 (O- $\text{CH}_2$ ), 53.1 ( $\text{C}_{\text{cage}}$ ), 46.3 ( $\text{C}_{\text{cage}}$ ).  $^{11}\text{B}$  NMR (proton decoupled):  $\delta$  23.0 (8B), 4.43 (6B), -7.18 (66B), -17.23 (30B). IR (KBr): 3044, 2930, 2563 (B-H), 1607, 1453, 1401, 1250, 1160  $\text{cm}^{-1}$ . Anal. Calcd for  $\text{C}_{72}\text{H}_{186}\text{B}_{108}\text{Co}_6\text{K}_6\text{O}_{18}$ : C 27.93, H 6.06. Found: C 27.91, H 6.05. MALDI-TOF-MS ( $m/z$ ): calcd 3096.01, found 2976.15 ( $\text{M}^+ - 3\text{K} + 1$ , 100%).

**Compound 9.** 4-Cyanophenol **7** (50 mg, 0.42 mmol) was dissolved in 10 mL of acetonitrile. Then  $\text{K}_2\text{CO}_3$  (405 mg, 2.94 mmol) and **2** (173 mg, 0.42 mmol) were added, and the mixture was refluxed at 90 °C for 5 h. Then the reaction mixture was filtered through a cotton plug. After evaporation of the solvent, the residue was purified by silica gel column chromatography with 50–70% ethyl acetate in hexane as the eluent to obtain 200 mg of pure compound **9** as a yellow solid, yield 84%. Melting point: > 250 °C.  $^1\text{H}$  NMR ( $\text{CD}_3\text{CN}$ , 500 MHz):  $\delta$  7.68 (d, 2H,  $J = 7.0$  Hz, Ar-H), 7.0 (d, 2H,  $J = 7.0$  Hz, Ar-H), 4.22 (br s, 2H,  $\text{C}_{\text{cage}}$ -H), 4.20–4.18 (m, 2H, O- $\text{CH}_2$ ), 4.15 (br s, 2H,  $\text{C}_{\text{cage}}$ -H), 3.83–3.81 (m, 2H, O- $\text{CH}_2$ ), 3.64–3.63 (m, 2H, O- $\text{CH}_2$ ), 3.59–3.58 (m, 2H, O- $\text{CH}_2$ ).  $^{13}\text{C}$  NMR ( $\text{CD}_3\text{CN}$ , 125 MHz):  $\delta$  162.3 (Ar-C), 134.1 (Ar-C), 119.0 (Ar-C), 115.4 ( $\text{C}\equiv\text{N}$ ), 103.5 (Ar-C), 72.0 (O- $\text{CH}_2$ ), 68.9 (O- $\text{CH}_2$ ), 68.5 (O- $\text{CH}_2$ ), 68.0 (O- $\text{CH}_2$ ), 53.5 ( $\text{C}_{\text{cage}}$ ), 46.7 ( $\text{C}_{\text{cage}}$ ).  $^{11}\text{B}$  NMR (proton decoupled, 160.5 MHz):  $\delta$  23.53 (1B), 4.52 (1B), 0.02 (1B), -2.65 (1B), -4.83 (2B), -7.48 (2B), -7.93 (2B), -8.76 (2B), -17.42 (2B), -20.38 (2B), -22.22 (1B), -28.60 (1B). IR (KBr): 3042, 2930, 2566 (B-H), 2233, 1604, 1507, 1209, 1097  $\text{cm}^{-1}$ . Anal. Calcd for  $\text{C}_{15}\text{H}_{33}\text{B}_{18}\text{CoK}_3\text{O}_3\text{N}$ : C 31.72, H 5.86. Found: C 31.70, H 5.84. MALDI-TOF-MS ( $m/z$ ): calcd 568.05, found 528.96 ( $\text{M}^+ - \text{K} + 1$ , 100%).

**2,4,6-Tris(*p*-hydroxyphenyl)triazine, 8.** 4-Cyanophenol (**7**) (500 mg, 4.197 mmol) was dissolved in 10 mL of dry chloroform. Then  $\text{CF}_3\text{SO}_3\text{H}$  (1.9 mL, 20.98 mmol) was added to it at 0 °C. The mixture was stirred at 0 °C for 10 min and then at room temperature for 24 h. The reaction mixture was quenched with water containing a small amount of  $\text{NH}_4\text{OH}$ . Then the reaction

mixture was filtered over a cotton plug, and the residue was dissolved in acetone and then recrystallized from acetone to obtain 400 mg of pure compound **8** as a colorless solid, yield 80%. Melting point: > 250 °C.  $^1\text{H}$  NMR (acetone- $d_6$ , 500 MHz):  $\delta$  8.67 (d, 6H,  $J = 7.0$  Hz, Ar-H), 7.07 (d, 6H,  $J = 7.0$  Hz, Ar-H), 7.67 (br s, 3H, -OH).  $^{13}\text{C}$  NMR (acetone- $d_6$ , 125 MHz):  $\delta$  170.6 ( $\text{C}\equiv\text{N}$ ), 161.6 (Ar-C), 130.7 (Ar-C), 127.7 (Ar-C), 115.4 (Ar-C). Anal. Calcd for  $\text{C}_{21}\text{H}_{15}\text{N}_3\text{O}_3$ : C 70.58, H 4.23, N 11.76. Found: C 70.53, H 4.21, N 11.79. ES-MS ( $m/z$ ): calcd. 357.36, found 358.2 ( $\text{M}^+ + 1$ , 100%).

**Compound 10.** *Method A:* Compound **8** (100 mg, 0.279 mmol) was dissolved in 10 mL of dry acetone. Then  $\text{K}_2\text{CO}_3$  (577.5 mg, 4.18 mmol) and **2** (378 mg, 0.92 mmol) were added, and the mixture was refluxed at 70 °C for 7 h. Then the reaction mixture was filtered through a cotton plug. After evaporation of the solvent, the residue was purified by silica gel column chromatography with 5% methanol in ethyl acetate as the eluent to obtain 452 mg of pure compound **10** as a yellow solid, yield 95%. *Method B:* Compound **9** (170 mg, 0.32 mmol) was dissolved in 5 mL of chloroform. Then  $\text{CF}_3\text{SO}_3\text{H}$  (0.3 mL, 3.4 mmol) was added to it. The mixture was then stirred at room temperature for 20 h and then at 40 °C for 2 h. The reaction mixture was quenched with water containing a small amount of  $\text{NH}_4\text{OH}$ . Then it was extracted with about 150 mL of dichloromethane three times. The combined organic layer was dried over  $\text{MgSO}_4$ . After evaporation of the solvent the residue was purified by silica gel column chromatography with ethyl acetate to 5% methanol in ethyl acetate as the eluent to obtain 118 mg of pure compound **10** as yellow solid, yield 76%. Melting point: > 250 °C.  $^1\text{H}$  NMR ( $\text{CD}_3\text{OD}$ , 500 MHz):  $\delta$  8.73 (d, 6H,  $J = 8.9$  Hz, Ar-H), 7.18 (d, 6H,  $J = 9.0$  Hz, Ar-H), 4.30–4.28 (br, 8H,  $\text{C}_{\text{cage}}$ -H, O- $\text{CH}_2$ ), 4.16 (br s, 6H,  $\text{C}_{\text{cage}}$ -H), 4.09–4.05 (m, 8H, O- $\text{CH}_2$ ), 3.94–3.92 (m, 8H, O- $\text{CH}_2$ ), 3.75–3.57 (m, 6H, O- $\text{CH}_2$ ).  $^{13}\text{C}$  NMR ( $\text{CD}_3\text{OD}$ , 125 MHz):  $\delta$  170.6 ( $\text{C}\equiv\text{N}$ ), 162.5 (Ar-C), 130.4 (Ar-C), 128.9 (Ar-C), 114.3 (Ar-C), 71.9 (O- $\text{CH}_2$ ), 69.2 (O- $\text{CH}_2$ ), 68.3 (O- $\text{CH}_2$ ), 67.5 (O- $\text{CH}_2$ ), 53.0 ( $\text{C}_{\text{cage}}$ ), 46.9 ( $\text{C}_{\text{cage}}$ ).  $^{11}\text{B}$  NMR (proton decoupled):  $\delta$  23.72 (3B), 5.43 (3B), 0.54 (6B), -6.99 (6B), -17.23 (24B), -19.97 (12B). IR (KBr): 3042, 2925, 2551 (B-H), 1605, 1508, 1367, 1255, 1206, 965  $\text{cm}^{-1}$ . Anal. Calcd for  $\text{C}_{45}\text{H}_{99}\text{B}_{54}\text{N}_3\text{Co}_3\text{K}_3\text{O}_9$ : C 31.72, H 5.86, N 2.47. Found: C 31.70, H 5.85, N 2.50. MALDI-TOF-MS ( $m/z$ ): calcd 1704.17, found 1665.01 ( $\text{M}^+ - \text{K}$ , 100%), 1324.13 ( $\text{M}^+ - \text{C}_4\text{H}_{21}\text{B}_{18}\text{CoK}_2\text{O}_2 - 1$ ).

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**Supporting Information Available:** NMR and MALDI-TOF mass spectra of the compounds prepared in this paper. This material is available free of charge via the Internet at <http://pubs.acs.org>.