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Synthesis and Properties of Carborane-Appended C_3-Symmetrical Extended π Systems

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Abstract: A series of C_3-symmetric π-conjugated compounds containing three to six *o*-carborane clusters have been synthesized by employing palladium-catalyzed Suzuki coupling reactions and palladium-catalyzed acetylation reactions, followed by silicon tetrachloride mediated trimerization reactions. Carborane-containing extended trimers were found to emit blue light. Incorporation of *o*-carborane clusters into extended π-conjugated systems led to 22−70% enhancement of their relative fluorescence quantum yields. Decapitation of *o*-carborane clusters made these extended trimers water soluble, and their aqueous solutions were also found to be fluorescent, but with a reduced fluorescence intensity. The carborane-appended π-conjugated compounds are found to be extremely thermally stable, and for some of these compounds only 10% mass loss occurred at temperatures close to 500 °C. The DSC thermograms of smaller C_{cage}-appended trimers indicate the occurrence of solid−solid phase transitions.

Introduction

The synthesis of dendritic and symmetrical star-shaped π-conjugated compounds and the study of their physical properties are of intense current scientific interest. These classes of compounds find a number of important applications,[1] including use as organic light-emitting materials,[2] liquid-crystalline materials,[3] effective drug delivery agents,[4] and highly efficient catalysts.[5] Some of the very exciting applications of such macromolecular compounds include their self-assembly and the aggregation leading to highly ordered nanostructured materials.[6] In a parallel development, it has been found that icosahedral carborane clusters are versatile synthetic building blocks and have been used in materials science, medicine, and catalysis.[7] Specifically, icosahedral carborane clusters are thermally very stable and easy to functionalize.[8] Current investigations in our laboratory to incorporate readily available *o*-carboranes into π-conjugated symmetrical structures have resulted in hybrid compounds of dramatically high thermal stability.[9] Metalated carborane-containing macrocycles show properties such as self-assembly which could make them useful in the promising field of nanoscience.[10] It has also been found that *o*-carborane clusters can readily be functionalized at both boron and carbon atoms of the cluster.[11] The electron-rich B_9

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(1) For reviews see: (a) Northrop, B. H.; Zheng, Y.-R.; Chi, K.-W.; Stang, P. J. *Acc. Chem. Res.* **2009**, *42*, 1554–1563. (b) Saragi, T. P. I.; Spehr, T.; Siebert, A.; Fuhrman-Lieker, T.; Salbeck, J. *Chem. Rev.* **2007**, *107*, 1011–1065. (c) Lo, S.-C.; Burn, P. L. *Chem. Rev.* **2007**, *107*, 1097–1116. (d) Hoeben, F. J. M.; Jonkheijm, P.; Meijer, E. W.; Schenning, A. P. H. J. *Chem. Rev.* **2005**, *105*, 1491–1546. (e) Grayson, S. M.; Frechet, J. M. J. *Chem. Rev.* **2001**, *101*, 3819–3867.

(2) (a) Laquai, F.; Mishra, A. K.; Ribas, M. R.; Petrozza, A.; Jacob, J.; Akcelrud, L.; Mullen, K.; Friend, R. H.; Wegner, G. *Adv. Funct. Mater.* **2007**, *17*, 3231–3240. (b) Watson, M. D.; Jackel, F.; Severin, N.; Rabe, J. P.; Mullen, K. *J. Am. Chem. Soc.* **2004**, *126*, 1402–1407. (c) Vijaylakshmi, N.; Maitra, U. *Org. Lett.* **2005**, *7*, 2727–2730. (d) Weil, T.; Reuther, E.; Mullen, K. *Angew. Chem., Int. Ed.* **2002**, *41*, 1900–1904.

(3) (a) Kumar, S. *Chem. Soc. Rev.* **2006**, *35*, 83–109. (b) Pisula, W.; Kastler, M.; Wasserfallen, D.; Pakula, T.; Mullen, K. *J. Am. Chem. Soc.* **2004**, *126*, 8074–8075. (c) Craats, A. M. V.; Warman, J. M.; Fechtenkotter, A.; Brand, J. D.; Harbison, M. A.; Mullen, K. *Adv. Mater.* **1999**, *11*, 1469–1472. (d) Muller, G. R. G.; Meiners, C.; Enkelmann, V.; Geerts, Y.; Mullen, K. *J. Mater. Chem.* **1998**, *1*, 61–64.

(4) (a) Fox, M. E.; Szoka, F. C.; Frechet, J. M. J. *Acc. Chem. Res.* **2009**, *42*, 1141–1151. (b) Almutairi, A.; Rossin, R.; Shokeen, M.; Hangooly, A.; Ananth, A.; Capoccia, B.; Guillaudeu, S.; Abendschein, D.; Welch, M. J.; Frechet, J. M. J. *Proc. Natl. Acad. Sci. U.S.A.* **2009**, 685–690. (c) Nishimaya, N.; Iriyama, A.; Jang, W.-D.; Miyata, K.; Itaka, K.; Inoue, Y.; Takahashi, H.; Yanagi, Y.; Tamaki, Y.; Koyama, H.; Kataoka, K. *Nat. Mater.* **2005**, 934–941.

(5) (a) Astruc, D.; Orneals, C.; Ruiz, J. *Acc. Chem. Res.* **2008**, *41*, 841–856. (b) Chi, Y.; Scroggins, S. T.; Boz, E.; Frechet, J. M. J. *J. Am. Chem. Soc.* **2008**, *130*, 17287–117289. (c) Lemo, J.; Heuze, K.; Astruc, D. *Chem. Commun.* **1999**, 4351–4353.

(6) (a) Kraft, M. L.; Moore, J. F. *Science* **2008**, *320*, 620–621. (b) Zang, L.; Che, Y.; Moore, J. F. *Acc. Chem. Res.* **2008**, *41*, 1596–1608. (c) Li, S. S.; Northrop, B. H.; Yuan, Q.-H.; Wan, L.-J.; Stang, P. J. *Acc. Chem. Res.* **2009**, *42*, 249–259. (d) Zheng, Y.-R.; Yang, H. B.; Ghosh, K.; Zhao, L.; Stang, P. J. *Chem. Eur. J.* **2009**, *15*, 7203–7214. (e) Northrop, B. H.; Yang, H.-B.; Stang, P. J. *Chem. Commun.* **2008**, 5896–5908. (f) Ghosh, K.; Hu, J.; White, H. S.; Stang, P. J. *J. Am. Chem. Soc.* **2009**, *131*, 6695–6697. (g) Lee, J.; Ghosh, K.; Stang, P. J. *J. Am. Chem. Soc.* **2009**, *131*, 12028–12029.

(7) For reviews see: (a) Zhu, Y.; Cheng, K. Y.; Maguire, J. A.; Hosmane, N. S. *Curr. Chem. Biol.* **2007**, *1*, 141–149. (b) Grimes, R. N. *J. Chem. Educ.* **2004**, *81*, 658–672. (c) Plesek, J. *Chem. Rev.* **1992**, *92*, 269–278. (d) Hawthorne, M. F.; Maderna, A. *Chem. Rev.* **1999**, *99*, 3421–3434. (e) Teixidor, F.; Vinas, C.; Demonceau, A.; Nunez, R. *Pure Appl. Chem.* **2003**, *75*, 1305–1313.

(8) Valliant, J. F.; Guenther, K. J.; Arienne, S.; King, S.; Morel, P.; Schaffer, P.; Sogbein, O. O.; Stephenson, K. A. *Coord. Chem. Rev.* **2002**, *232*, 173–230.

(9) Dash, B. P.; Satapathy, R.; Maguire, J. A.; Hosmane, N. S. *Chem. Commun.* **2009**, 3267–3269.

10.1021/ja101845m

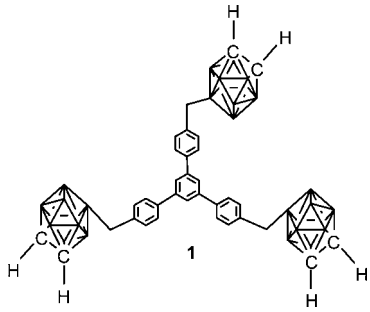


Figure 1. Structure of the B_{cage}-appended trimer.

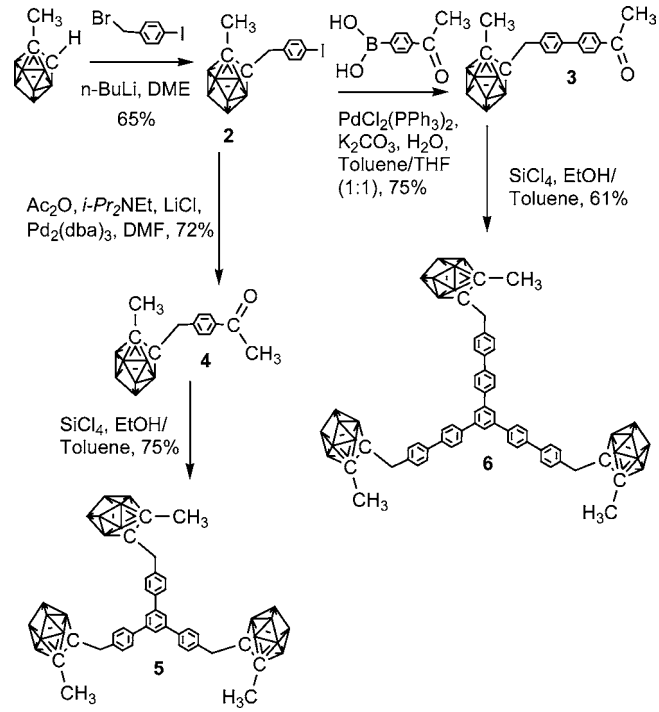
boron atom of the *o*-carborane clusters can undergo facile Friedel−Craft type electrophilic substitution reactions to generate B_9-substituted products. Carboranyl aromatic ketones attached to this boron atom of the cluster were synthesized and were found to undergo trimerization in the presence of a silicon tetrachloride/ethanol mediated reaction to generate C_3-symmetrical trimers having three carborane clusters in the periphery, as shown in Figure 1.[11] Because of the acidic nature of the cage hydrogens, these *o*-carborane clusters can also undergo facile functionalization at the cage carbon to produce C_{cage}-appended extended trimers. Herein we describe the syntheses of a number of C_{cage}-appended C_3-symmetrical trimers, incorporating *o*-carborane clusters. We also report on the relative thermal stabilities of B_{cage}- and C_{cage}-appended trimers, as well as the effect of carboranes on the photophysical properties of extended trimers. The deboronation of the attached *o*-carborane clusters led to the formation of the respective water-soluble compounds,[12] whose spectroscopic properties are also reported.

Results and Discussion

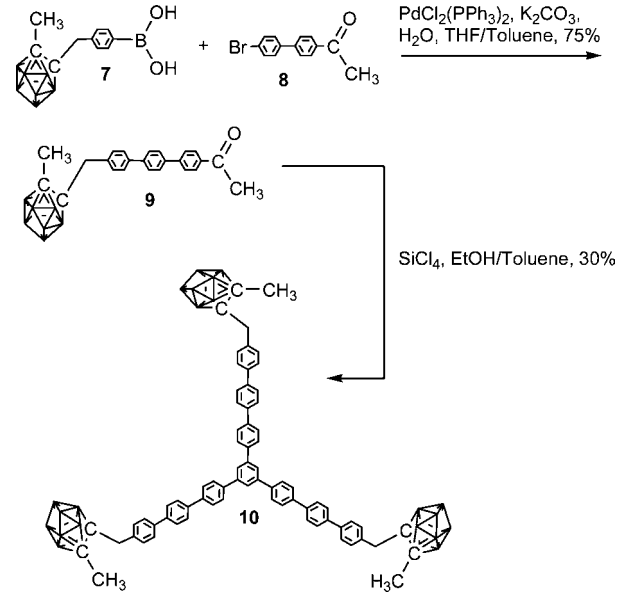
The carborane C_{cage}-appended C_3-symmetric trimers containing three to six *o*-carborane clusters were synthesized by employing Suzuki coupling reactions and palladium-catalyzed acetylation reactions,[13] followed by $SiCl_4$/ethanol mediated trimerizations[11,14] of the so formed carborane-appended aryl ketones, as shown in Schemes 1−3. Suzuki coupling reactions were generally carried out using the common palladium catalyst $PdCl_2(PPh_3)_2$ and K_2CO_3 as a base. Solubility difficulties of the aryl ketones in the trimerization reactions were solved by using as the solvent a mixture of toluene and ethanol in a 1:3 proportion. Smaller trimers could be obtained with room-temperature reactions, but for the extended trimers an elevated temperature of between 40−50 °C was required.

Synthesis of Trimers. The syntheses of the carborane C_{cage}-appended conjugated systems, containing three carborane

Scheme 1. Synthesis of C_{cage}-Appended Trimers Containing Three *o*-Carborane Clusters



Scheme 2. Synthesis of C_{cage}-Appended Extended Trimers Containing Three *o*-Carborane Clusters



clusters, are outlined in Schemes 1 and 2. Compound **2** was prepared from the lithiated 1-methyl-*o*-carborane and 4-iodobenzyl bromide in DME and was used as the starting compound.[15] A Suzuki coupling reaction of compound **2** with (4-acetylphenyl)boronic acid in the presence of catalytic amounts of water produced the desired carborane-appended aryl ketone **3** in good yield. Ketone **3** then underwent trimerization in the presence of $SiCl_4$/ethanol to produce the extended trimer **6**, in 61% yield. Palladium-catalyzed acetylation[13] of **2** worked well to produce the desired carborane-appended aryl ketone **4**, which

(10) (a) Jude, H.; Disteldorf, H.; Fischer, S.; Wedge, T.; Hawkridge, A. M.; Arif, A. M.; Hawthorne, F.; Muddiman, D. C.; Stang, P. J. *J. Am. Chem. Soc.* **2005**, *127*, 12131–12139. (b) Das, N.; Stang, P. J.; Arif, A. M.; Campana, C. F. *J. Org. Chem.* **2005**, *70*, 10440–10446.

(11) Dash, B. P.; Satapathy, R.; Maguire, J. A.; Hosmane, N. S. *Org. Lett.* **2008**, *10*, 2247–2250, and references therein.

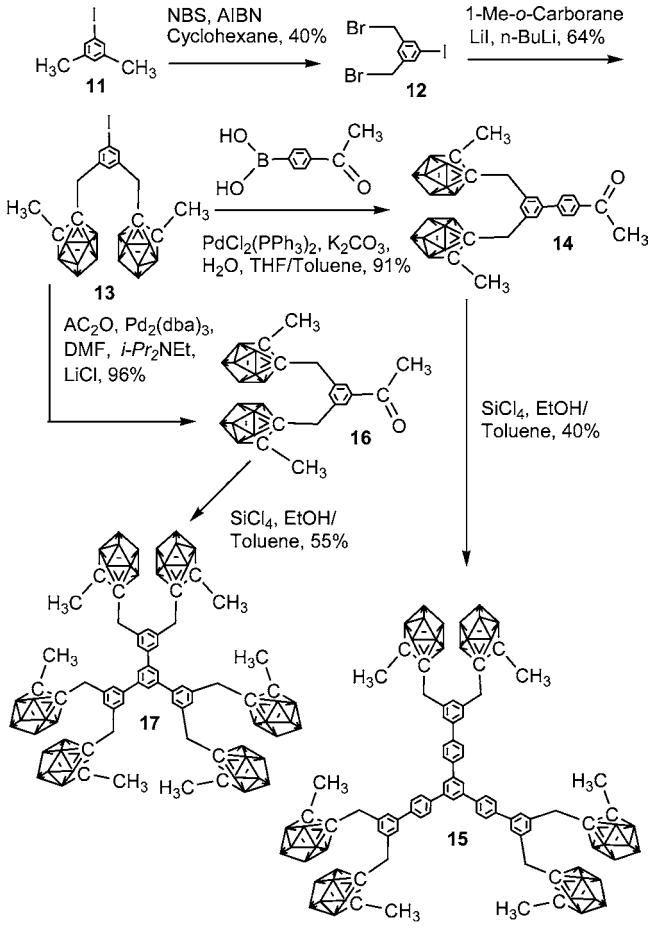
(12) (a) Vyakaranam, K.; Rana, G.; Ratanasuwan, A.; Hosmane, S. N.; Maguire, J. A.; Hosmane, N. S. *Organometallics* **2002**, *21*, 3905–3912. (b) Yoo, J.; Hwang, J.-W.; Do, Y. *Inorg. Chem.* **2001**, *40*, 568–570. (c) Gonzalez-Campo, A.; Vinas, C.; Teixidor, F.; Nunez, R.; Sillanpaa, R.; Kivekas, R. *Macromolecules* **2007**, *40*, 5644–5652.

(13) Cacchi, S.; Fabrizi, G.; Gavazza, F.; Goggiamani, A. *Org. Lett.* **2003**, *5*, 289–291.

(14) (a) Bao, C.; Lu, R.; Jin, M.; Xue, P.; Tan, C.; Xu, T.; Liu, G.; Zhao, Y. *Chem. Eur. J.* **2006**, *12*, 3287–3294. (b) Yang, J.-X.; Tao, X.-T.; Yuan, C. X.; Yan, Y. X.; Wang, L.; Liu, Z.; Ren, Y.; Jiang, M. H. *J. Am. Chem. Soc.* **2005**, *127*, 3278–3279. (c) Cao, X.-Y.; Liu, X.-H.; Zhou, X.-H.; Zhang, Y.; Jiang, Y.; Cao, Y.; Cui, Y.-X.; Pei, J. *J. Org. Chem.* **2004**, *69*, 6050–6058.

(15) Vicente, H.; Edwards, F.; Shetty, S. J.; Hou, Y.; Boggan, J. E. *Bioorg. Med. Chem.* **2002**, *10*, 481–492.

Scheme 3. Synthesis of C_{cage}-Appended Trimers Containing Six *o*-Carborane Clusters

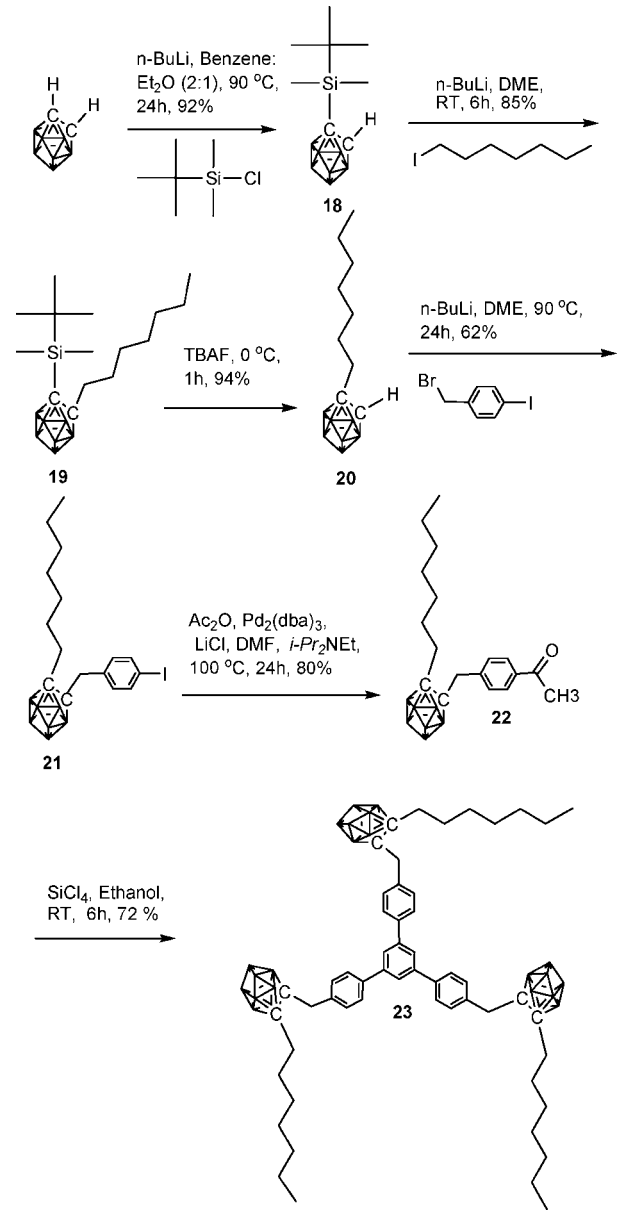


was then trimerized with $SiCl_4$/ethanol to produce trimer **5** (Scheme 1). A more extended version of the trimers, compound **10**, was prepared from the precursor ketone **9** via another $SiCl_4$/ethanol mediated trimerization reaction in about 30% yield. The intermediate ketone **9** was obtained via a Suzuki coupling between carborane-appended boronic acid **7**[16] and commercially available 4′-(4-bromophenyl)acetophenone **8** (Scheme 2).

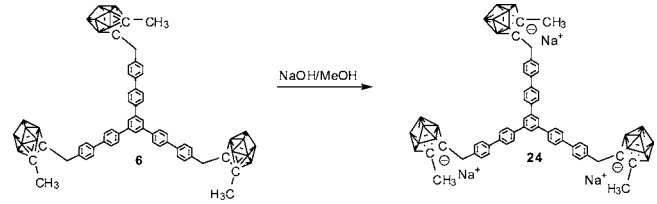
To further increase the number of carborane clusters around the 1,3,5-phenylene core, we started from the commercially available 3,5-dimethyl-1-iodobenzene (**11**), which underwent radical bromination in the presence of *N*-bromosuccinimide and the radical initiator AIBN to give compound **12** (Scheme 3). Two equivalents of lithiated 1-methyl-*o*-carborane in the presence of a catalytic amount of lithium iodide produced the key intermediate **13** in good yield, at room temperature. A Suzuki coupling of **13** with (4-acetylphenyl)boronic acid or a palladium-catalyzed acetylation produced the desired ketones **14** and **16**, respectively. Trimerizations of the ketones led to the respective products **15** and **17**, having six *o*-carborane clusters, as shown in Scheme 3.

A general synthetic route to functionalized C_{cage}-appended trimers is shown in Scheme 4. One of the acidic hydrogens on the *o*-carborane was protected by the bulky TBDMS group, following a literature procedure.[17] The TBDMS-protected *o*-carborane **18** could be lithiated and then treated with an iodo

Scheme 4. Synthesis of Substituted C_{cage}-Appended Trimers



Scheme 5. Deboronation of *o*-Carborane Clusters in Trimers



compound, in this case 1-iodoheptane, to produce the C_{cage}-heptyl-substituted carborane **19**. After deprotection of the TBDMS group with TBAF, the resulting compound **20** was then treated with 4-iodobenzyl bromide in the presence of BuLi in DME to give **21**, which upon palladium-catalyzed acetylation led to the desired heptyl-substituted carboranyl ketone **22**. Trimerization of this ketone led to the heptyl-substituted carboranyl trimer **23** in good yield (Scheme 4).

Water-Soluble Trimers. The decapitation reaction of *o*-carboranes by alcoholic NaOH leads to the removal of one of the vertex boron atoms to give monoanionic *nido*-carborane

(16) Hao, E.; Fabre, B.; Fronczeka, F. R.; Vicente, M. G. H. *Chem. Mater.* **2007**, *19*, 6195–6205.
(17) Gomez, F. A.; Hawthorne, M. F. *J. Org. Chem.* **1992**, *57*, 1384–1390.

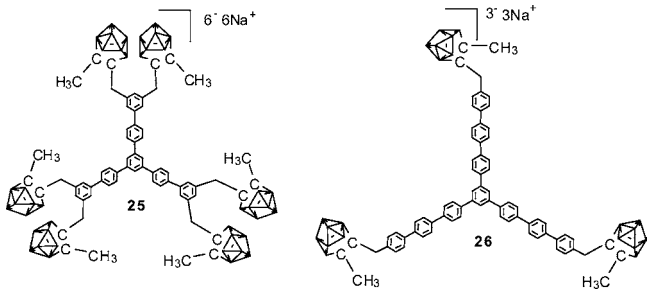


Figure 2. Water-soluble trimers.

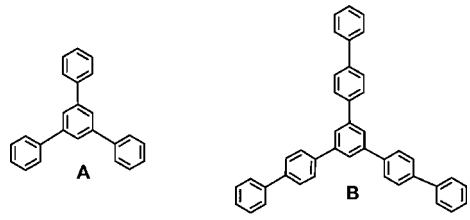


Figure 3. C_3-symmetric phenylene cores.

species. The monoanions can be further deprotonated to give dianions, which can act as ligands for different metals.[18] It was found that all of the carboranes of the trimers **5**, **6, 10**, **15**, and **17** could be decapitated to give the corresponding water-soluble compounds. Scheme 5 shows a typical decapitation reaction of **6** to give **24**. The two other extended trimers, **15** and **10**, underwent similar deboronation reactions that led to the corresponding water-soluble trimers **25** and **26**, respectively (Figure 2). The spectroscopic properties of these trimers were later evaluated in water.

Controls. The control trimers **A** and **B** (Figure 3) without any carboranes were also synthesized. Control **A** was prepared by the $SiCl_4$/ethanol mediated trimerization of acetophenone, whereas the extended control **B** was prepared via a Suzuki coupling reaction of commercially available 1,3,5-tris(4-iodophenyl)benzene with phenylboronic acid (see the Supporting Information).[19]

Photophysical Properties. Symmetrical 1,3,5-phenylenebenzene core based structures, shown in Figure 3, have been used as photostable chromophores for light-emitting materials.[20] Specifically, the extended versions such as 1,3,5-tris(*p*-oligophenylene)benzenes (**B**) were found to be blue-violet light emitting and therefore useful as hole-blocking molecular materials[21a] and UV-laser dyes.[21b] However, the low solubility of such symmetrical polycyclic aromatic compounds in polar solvents was considered as a primary drawback for their general use as laser dyes.[21b,22] The effect of carboranes on the photophysical properties of polycyclic compounds was studied by comparing the spectroscopic properties of dichloromethane solutions of the carborane-appended extended trimers **6**, **10**, and **15** with **B** (see

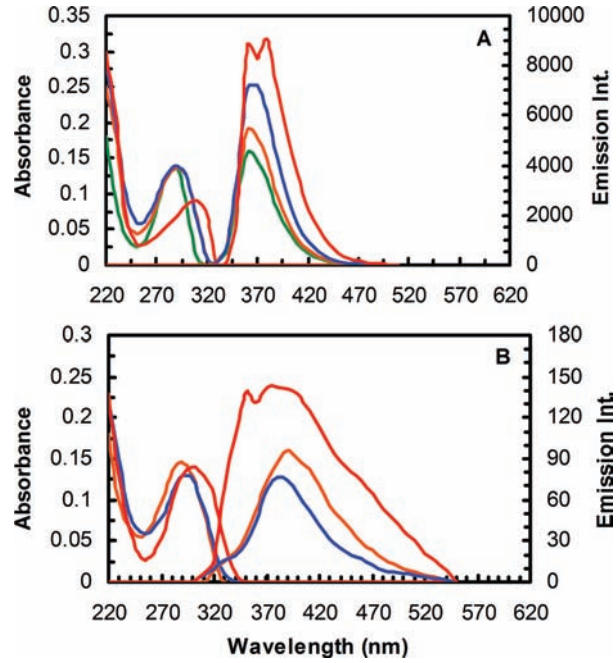


Figure 4. (A) Absorption and emission spectra of trimers in dichloromethane: (red) **10**; (blue) **15**; (orange) **6**; (green) control **B**. (B) Absorption and emission spectra of water-soluble trimers in water: (red) **26**; (orange) **24**; (blue) **25**. For compound **26** Raman scattering could not be completely suppressed.

Table 1. Spectroscopic Data of Carborane-Appended Trimers

trimer	solvent	absorption maximum (nm)	emission maximum (nm)	rel area	quantum yield (Φ_F)	λ_c (nm)	E (eV)
control **B**	CH_2Cl_2	290	360	1.0	0.27	330	3.75
6	CH_2Cl_2	290	360	1.22	0.33	335	3.70
15	CH_2Cl_2	294	370	1.70	0.46	335	3.70
10	CH_2Cl_2	307	360, 380	2.38	0.86[a]	340	3.64
24	H_2O	290	390	0.042	0.011	335	3.70
25	H_2O	294	380	0.030	0.008	340	3.64
26	H_2O	300	370	0.09	0.024	340	3.64

[a] Φ_F was calculated at $OD_{290} = 0.09$.

Figure 4A and Table 1). The aqueous solution spectra of the water-soluble trimers **24**−**26** are shown in Figure 4B. The UV absorption of all the trimers, irrespective of the solvents used, showed absorption maxima close to 290 nm, except for the extended trimers **10** and **26**, for which the absorbance maxima were red-shifted to 307 and 300 nm, respectively, due to the extended conjugation. Therefore, an excitation wavelength of 290 nm was chosen to measure emission intensities. A single emission maximum was observed for all trimers between 360 and 390 nm, except the extended trimer **10**, for which weak vibrational splitting was observed at 360 and 380 nm. Trimers **6**, **10**, and **15** showed sharp emission intensities between 320

(18) (a) Deng, L.; Xie, Z. *Organometallics* **2007**, *26*, 1832–1845. (b) Xie, Z. *Coord. Chem. Rev.* **2006**, *250*, 259–272. (c) Hosmane, N. S.; Maguire, J. A. *Organometallics* **2005**, *24*, 1356–1389. (d) Hawthorne, M. F.; Young, D. C.; Garrett, D. A.; Owen, D. A.; Schwerin, S. G.; Tebbe, F. N.; Wegner, P. A. *J. Am. Chem. Soc.* **1968**, *90*, 862–868. (e) Hawthorne, M. F.; Young, D. C.; Andrews, T. D.; Howe, D. V.; Pilling, R. L.; Pitts, A. D.; Reintjes, M.; Warren, L. F.; Wegner, P. A. *J. Am. Chem. Soc.* **1968**, *90*, 879–896.
(19) Kotha, S.; Kasinath, D.; Lahiri, K.; Sunoj, R.B. *Eur. J. Org. Chem.* **2004**, 4003–4013.
(20) (a) Finke, A. D.; Moore, J. F. *Org. Lett.* **2008**, *10*, 4851–4854. (b) He, Q.; Huang, H.; Yang, J.; Lin, H.; Bai, F. *J. Mater. Chem.* **2003**, *13*, 1085–1089. (c) Belser, P.; Zelewsky, A.; Frank, M.; Seel, C.; Vogtle, F.; Cola, L. D.; Barigelletti, F.; Balzani, V. *J. Am. Chem. Soc.* **1993**, *115*, 4076–4086. (d) Pang, J.; Marcotte, E. J.-P.; Seward, C.; Brown, R. S.; Wang, S. *Angew. Chem., Int. Ed.* **2001**, *40*, 4042–4045. (e) Miller, T. M.; Neenan, T. X.; Zayas, R.; Bair, H. E. *J. Am. Chem. Soc.* **1992**, *114*, 1018–1025.
(21) (a) Okumoto, K.; Shirota, Y. *Chem. Mater.* **2003**, *15*, 699–707. (b) Schmidt, B.; Rinke, M.; Gusten, H. *J. Photochem. Photobiol. A: Chem.* **1989**, *49*, 131–135.
(22) Muller, M.; Kubel, C.; Mullen, K. *Chem. Eur. J.* **1998**, *4*, 2099–2109.

and 470 nm (Figure 4A); less intense emissions were observed for the water-soluble trimers **24**−**26,** over a wider wavelength range, between 320 and 550 nm (Figure 4B). However, all the trimers emit in the blue-violet region of the spectrum, as seen in Figure 4. In order to measure the relative fluorescence quantum yields, the samples were excited at 290 nm and were all prepared with $OD_{290} = 0.13$. This allows for the emission intensities to be directly compared.[23]

Since the determination of absolute quantum yield is rather difficult, it is a common practice to determine the quantum yields of unknowns by comparing with a standard of known fluorescence quantum yield.[24] The quantum yield of control **B** is reported to be 0.27.[21b] From the relative area under the fluorescence band and the quantum yield of the control **B**, the relative quantum yields (Φ_F) of the carborane-appended trimers have also been calculated and are given in Table 1. The HOMO−LUMO gap energies were calculated using the Planck equation from the wavelengths where the absorbance and emission lines cross each other (λ_c) and are reported in electronvolts (eV) in Table 1. The incorporation of multiple *o*-carborane clusters in **6** and **15**, containing three and six *o*-carborane clusters, respectively, led to about a 22% and 70% increase in their quantum yields in comparison to the carborane-unsubstituted control **B**. The combination of extended conjugation and the inclusion of *o*-carborane, as found in **10**, resulted in a substantial enhancement (238%) of the quantum yield. Incorporation of *o*-carborane clusters also leads to a slight reduction of HOMO−LUMO gap energies (Table 1).

Icosahedral carboranes are pseudoaromatic, and they also possess electron-withdrawing properties.[7c,e] The increase in quantum yields on the introduction of the *o*-carboranes into control **B** (see Table 1) is in sharp contrast to the recent observations of Kokado and co-workers, who found that the introduction of *m*-carboranes into the backbones of the extended π systems of *p*-phenyleneethynyl-like polymers resulted in polymers having intense blue emission in solution, while the introduction of *o*-carboranes in the extended π systems showed no luminescence but only aggregation-induced emission (AIE).[25,26] An intensely blue emitting polymer was produced when *p*-carborane was introduced into the polymer backbone of a polyfluorene polymer.[27] However, in our studies the aromatic conjugated core and *o*-carborane clusters are separated by a methylene moiety which effectively blocks π interactions by the carborane. Therefore, shifts in the absorption and emission maxima due to the extension of the aromatic system on the introduction of the *o*-carborane clusters are not observed. It seems much more likely that the size and three-dimensional structure of the *o*-carborane moieties serve to prevent $\pi-\pi$ stacking interactions and also help to rigidify the system, minimizing nonradiative decay.[28] Therefore, higher emission intensity was observed in all *o*-carborane-appended extended trimers.

The aqueous solutions of the trimers **24** and **25**, containing three and six *nido*-carboranes, respectively, showed much lower quantum yields, which were only about 3.4% and 1.8% of the values for the corresponding *o*-carborane-containing trimers (**6** and **15**) in dichloromethane. Thus, we found that a small number of monoanionic *nido*-carborane clusters induce good water solubility to 1,3,5-oligophenylene chromophores. When we increased the number of water solubility inducing *nido*-carborane anions from three in trimer **24** to six in trimer **25**, we observed a decrease in Φ_F of about 29%. Therefore, increasing the number of water solubility inducing charged *nido*-carborane clusters close to the chromophore diminishes the fluorescence quantum yield. The Φ_F values of water-soluble trimers have been calculated by using the appropriate method, and only refractive index terms are considered during the calculation.[29]

Water-soluble fluorescent materials are used as fluorescent labels in biologically active probes.[30] Thus, a number of other water-soluble chromophores are also available. Such chromophores carry hydrophilizing substituents such as sulfonic acid moieties,[31] quaternary amine groups,[32] polyethylene glycols,[33] benzoate groups,[34] and peptide chains[35] attached to the aromatic chromophore scaffold. However, in most cases a very low fluorescence is observed in water.[36] A chromophore that meets all the criteria, such as water solubility, high fluorescence intensity, nontoxicity, and high photostability, is rather difficult to find.[36] The low fluorescence of chromophores in water may be attributed to a number of factors, such as the photoinduced electron transfer in polar solvents.[29b,37,38] In addition, significant hydrogen bonding in water reduces Φ_F by enhancing the nonradiative decay.[29,37] However, in our case degassing the solvents to get rid of the quenching due to dissolved oxygen did not result in any noticeable change in the fluorescence intensity.

Thermal Properties. Incorporation of carboranes enhances the thermal stability of the materials. Apart from a recent investigation in our laboratory,[9] there have also been a number of literature reports on the enhancement of thermal stability due to the presence of carboranes,[39] which motivated us to conduct a systematic thermal analysis of our trimers. TGA curves of

(23) Turro, N. J. *Modern Molecular Photochemistry*; Benjamin/Cummings: Menlo Park, CA, 1978.
(24) Birks, J. B. *Photophysics of Aromatic Molecules*; Wiley: London, 1970.
(25) (a) Kokado, K.; Tokoro, Y.; Chujo, Y. *Macromolecules* **2009**, *42*, 2925–2930. (b) Kokado, K.; Tokoro, Y.; Chujo, Y. *Macromolecules* **2009**, *42*, 9238–9242.
(26) Kokado, K.; Chujo, Y. *Macromolecules* **2009**, *42*, 1418–1420.
(27) Peterson, J. J.; Simon, Y. C.; Coughlin, B.; Carter, K. R. *Chem. Commun.* **2009**, 4950–4952.
(28) (a) Hong, Y.; Lam, J. W. Y.; Tang, B. Z. *Chem. Commun.* **2009**, 4332–4353. (b) We are also thankful to reviewers for valuable suggestions.
(29) (a) Bigger, S. W.; Ghiggino, K. P.; Meilak, G. A.; Verity, B. *J. Chem. Educ.* **1992**, *69*, 675–677. (b) Barghouthi, S. A.; Perrault, J.; Holmes, L. H., Jr. *Chem. Educ.* **1998**, *3*, 1–10.
(30) (a) Bastiaens, P. I. H.; Squire, A. *Trends Cell Biol.* **1999**, *9*, 48–52. (b) Nguyen, D. C.; Keller, R. A.; Jett, J. H.; Martin, J. C. *Anal. Chem.* **1987**, *59*, 2158–2161. (c) Peck, K.; Stryer, L.; Glazer, A. N.; Mathies, R. A. *Proc. Natl. Acad. Sci. U.S.A.* **1989**, *86*, 4087–4091.
(31) (a) Jose, J.; Burgess, K. *J. Org. Chem.* **2006**, *71*, 7835–7839. (b) Rivas, B. L.; Maureira, A. *Macromol. Symp.* **2008**, *270*, 143–152.
(32) (a) Schnurpfeil, G.; Stark, J.; Wohrle, D. *Dyes Pigm.* **1995**, *27*, 339–350. (b) Knaus, S.; Gruber, H. F. *J. Macromol. Sci. A, Pure Appl. Chem.* **1996**, *33*, 869–881.
(33) Patrick, M. J.; Ernst, L. A.; Waggoner, A. S.; Thai, D.; Tai, D.; Salama, G. *Org. Biomol. Chem.* **2007**, *5*, 3347–3353. Verma, S.; Padmawar, P. A.; Hauck, T.; Canteenwala, T.; Chiang, L. Y.; Pritzker, K. P. H. *J. Macromol. Sci. A, Pure Appl. Chem.* **2005**, *42*, 1497–1505.
(34) (a) Biosselier, E.; Orneals, Catia.; Pianet, I.; Aranzaes, R. J.; Astruc, D. *Chem. Eur. J.* **2008**, *14*, 5577–5587.
(35) (a) Klok, H.-A.; Hernandez, J. R.; Becker, S.; Mullen, K. *J. Polym. Sci., Part A: Polym. Chem.* **2001**, *39*, 1572–1583. (b) Stafforst, T.; Diederichsen, U. *Eur. J. Org. Chem.* **2007**, 899–911. (c) Hempel, K.; Heinze, K. *Chem. Eur. J.* **2009**, *15*, 1346–1358.
(36) (a) Kohl, C.; Weil, T.; Qu, J.; Mullen, K. *Chem. Eur. J.* **2004**, *10*, 5297–5310. (b) Quante, H.; Schlichting, P.; Rohr, U.; Geerts, Y.; Mullen, K. *Macromol. Chem. Phys.* **1996**, *197*, 4029–4044.
(37) Lakowicz, J. R. *Principles of Fluorescence Spectroscopy*; Plenum Press: New York, 1986.
(38) Lor, M.; Thielemans, J.; Viaene, L.; Cotlet, M.; Hofkens, J.; Weil, T.; Hampel, C.; Mullen, K.; Verhoeven, J. W.; Auweraer, M. V.; De Schryver, F. C. *J. Am. Chem. Soc.* **2002**, *124*, 9918–9925.

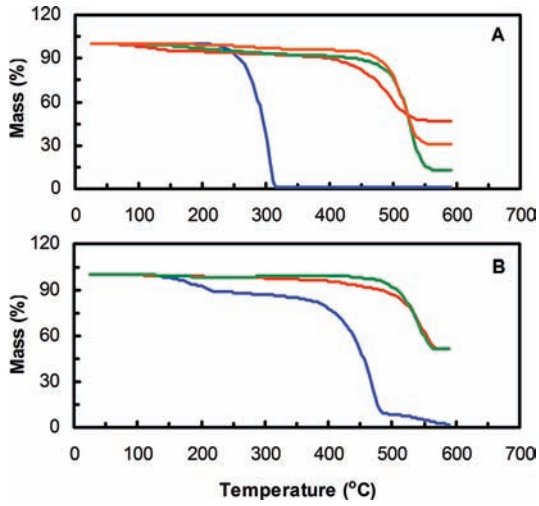


Figure 5. (A) TGA curves of small trimers under nitrogen: (orange) **17**; (green) **5**; (red) **1**; (blue) control **A**. (B) TGA curves of extended trimers under nitrogen: (green) **15**; (red) **6**; (blue) control **B**.

Table 2. 10% Mass Loss Temperatures from TG Analysis

trimer	temp (°C)
control A	257
1	385
5	420
17	475
control B	210
6	475
15	505

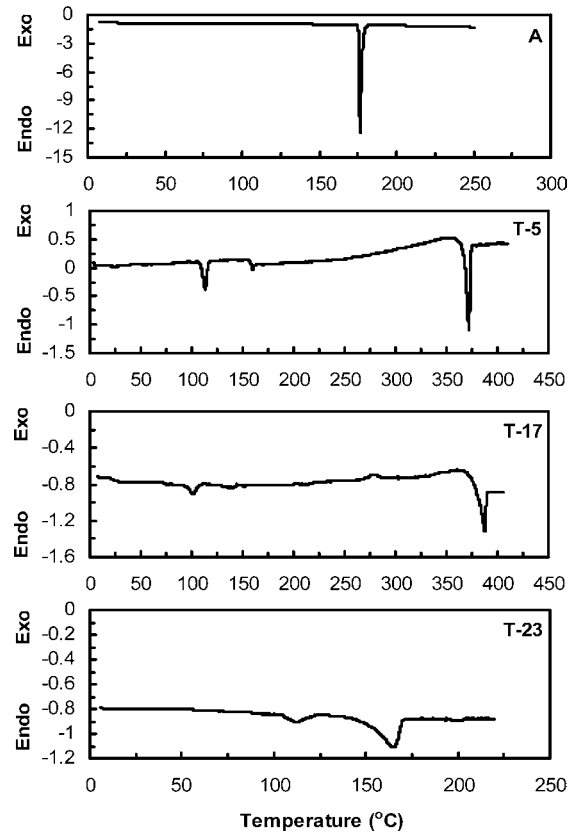


Figure 6. DSC analysis of small trimers at a heating rate of 5 K min^{-1}: (A) control **A**; (T-5) **5**; (T-17) **17**; (T-23) **23**.

small trimers are compared with that of control **A** (Figure 5A), and those of the extended trimers are compared with that of control **B** (Figure 5B). The temperatures at which 10% mass loss of all the trimers occurred have been summarized in Table 2. In general, for both the B_{cage} -and C_{cage}-appended trimers there was a dramatic enhancement of the thermal stability on incorporating the carborane. By analyzing the TGA plot shown in Figure 5A, we observe that the temperature at which 10% mass loss occurs for the control **A** is 257 °C, and then rapid decomposition of the compound was observed until complete degradation of the compound happened at about 320 °C. However, for **1**, which contains three B_{cage}-appended *o*-carborane clusters, the point where 10% mass loss occurred is found to be 385 °C and finally about 47 wt % of the residue is maintained at 600 °C, whereas for **5**, which contains three C_{cage}-appended *o*-carboranes, the 10% mass loss occurs at 420 °C and about 13 wt % of the residue is maintained at 600 °C. However, for **17**, which has six C_{cage}-appended *o*-carboranes, the 10% mass loss observed at 475 °C and about 30 wt % of the residue is maintained at 600 °C. This was found to be the most stable compound in the smaller trimer series. A similar trend was observed for extended trimers, and these are even found to be more thermally stable than the smaller ones. For the extended control **B** the thermal degradation occurs in two successive steps. The first step, which occurs between 155 and 220 °C, accounts for about 10% of the mass loss. This could be due to the decomposition of the peripheral phenyl ring. Then, in the second step rapid decomposition of the molecule was observed in the temperature range 380−500 °C and leads to almost 0 wt % residue. Such stepwise degradation is commonly observed in macromolecular and branched polymeric materials, where degradation starts from the branching units and loss of small molecular fragments also occurs.[40] However, in the presence of peripheral *o*-carboranes such stepwise mass loss is not observed, and for both **6** and **15**, about 51 wt % residue is maintained at 600 °C. The 10% mass loss temperature for **6** and **15** is also found to be high, occurring at 475 and 505 °C, respectively. Thus, we consistently found that increasing the number of *o*-carborane clusters increases the thermal stability of compounds.

Another property of small C_{cage}-appended trimers was seen in their DSC thermograms (Figure 6). The phase transition temperatures of those trimers that have shown such mesomorphic behavior are summarized in Table 3. Only one endothermic peak is seen for the control **A** at 176.6 °C, whereas for **5**, which contains three *o*-carborane clusters, we observe three endothermic peaks at 113.9, 160.3, and 372.5 °C, respectively. Similarly for **17**, which contains six *o*-carborane clusters, endothermic peaks at 103.8, 146.3, and 388 °C were found. However, for the heptyl-substituted trimer

(39) (a) Hao, E.; Fabre, B.; Fronczeka, F. R.; Vicente, M. G. H. *Chem. Commun.* **2007**, 4387–4389. (b) Benhabbour, S. R.; Parrott, M. C.; Gratton, S. E. A.; Adronov, A. *Macromolecules* **2007**, *40*, 5678–5688. (c) Farha, O. K.; Spokoyny, A. M.; Mulfort, K. L.; Hawthorne, M. F.; Mirkin, C. A.; Hupp, J. T. *J. Am. Chem. Soc.* **2007**, *129*, 12680–12681.

(40) (a) Wriedt, M.; Sellmer, S.; Nather, C. *Dalton Trans.* **2009**, 7975–7984. (b) Kostler, S.; Zechner, B.; Trathnigg, B.; Fasl, H.; Kern, W.; Ribitsch, V. *J. Polym. Sci., Part A: Polym. Chem.* **2009**, *47*, 1499–1509. (c) Duquesne, S.; Bras, M. L.; Bourbogot, S.; Delobel, R.; Camino, G.; Eling, B.; Lindsay, C.; Roels, T.; Vezin, H. *J. Appl. Polym. Sci.* **2001**, *82*, 3262–3274.

Table 3. DSC Data of Trimers

trimer	peak (°C)
control A	176.6
5	113.9, 160.3, 372.5
17	103.8, 146.3, 388
23	115.3, 166.7

23 only two peaks at 115.3 and 166.7 °C are observed. The peaks observed at 372.5, 388, and 166.7 °C represent the melting of the respective trimers; the other peaks reflect solid−solid phase transitions. Substituted polycyclic aromatic hydrocarbons are known to form liquid-crystalline phases[3,41] and in some cases such thermally induced solid-state phase transitions that are associated with the conformational reorganization of the bulky side groups.[42] Unique properties such as molecular symmetry, conformational mobility, and their role in stabilizing liquid-crystalline phases make *closo*-carborane clusters ideal choices for use in the synthesis of liquid-crystalline materials,[43] and so the combination of π-conjugated systems and *closo*-carboranes therefore could be useful in making hybrid materials possessing such characteristics.

Conclusion

In summary, we have demonstrated a silicon tetrachloride mediated facile synthetic route to symmetrical conjugated π systems containing multiple *o*-carborane clusters. The properties of carborane-containing π-conjugated compounds are found to be unique and significantly different from those of carborane-unsubstituted species. Presence of *o*-carborane clusters in π-conjugated systems prevents $\pi-\pi$ stacking interactions and enhances the rigidity of such molecules. Thus, *o*-carborane-appended extended trimers show enhanced fluorescent intensity. Deboronation of *o*-carboranes led to the water-soluble compounds that are also found to be fluorescent in water but with a lower relative fluorescence quantum yield. The presence of *o*-carborane clusters also made these compounds highly thermally stable. An increase in the number of *o*-carborane clusters led to more thermally stable products. Thermally induced solid−solid phase transitions are observed in smaller C_{cage}-appended trimers.

Experimental Section

General Methods. 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. ^{1}H and ^{13}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 (^{1}H, δ 0.00 ppm), and $CDCl_3$ (^{13}C, δ 77.0 ppm), and coupling constants are given in Hz. All ^{13}C spectra are proton-decoupled. ^{11}B NMR spectra were recorded at 64.2 MHz relative to $BF_3\cdot Et_2O$. Infrared spectra were recorded on an ATI Mattson Genesis series FT-IR spectrophotometer. Elemental analyses were carried out with a CHN-Analyzer 2400 (Perkin-Elmer). Melting points were measured with a Mel-Temp II apparatus (Laboratory Devices) and are uncorrected. Differential scanning calorimetry (DSC) and thermal gravimetric analysis (TGA) were performed on DSC 220C and TG/DTA 320 instrument (Seiko Instruments), respectively. UV absorption and emission spectra were measured with a Perkin-Elmer Lambda 19 UV−vis spectrometer and Hitachi F-2500 fluorescence spectrophotometer, respectively. Mass spectral analyses were performed with a Applied Biosystems Voyager-DE STR-MALDI-TOF spectrometer and Waters Q-TOF Ultima ES spectrometer.

Preparations and Analytical Data of Compounds. Ketone 3. Compound **2** (710 mg, 1.89 mmol) was dissolved in 20 mL of solvent (THF/toluene, 1/1). Then 4-(acetylphenyl)boronic acid (622.1 mg, 3.79 mmol), $PdCl_2(PPh_3)_2$ (53.26 mg, 4 mol %), and a solution of K_2CO_3 (785.35 mg, 5.69 mmol) in 5 mL of distilled water were added to the solution. The mixture was refluxed at 100 °C for 24 h and then extracted three times with dichloromethane, and the combined organic layers were dried over $MgSO_4$. After evaporation of the solvent, the residue was purified by silica gel column chromatography with 5−25% ethyl acetate in hexanes as the eluent to obtain 520 mg of pure compound **3** as a colorless solid, yield 75%. Mp: 165 °C. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.0 (d, 2H, J = 7.96 Hz), 7.71 (d, 2H, J = 7.98 Hz), 7.63 (d, 2H, J = 7.75 Hz), 7.31 (d, 2H, J = 7.79 Hz), 3.54 (s, 2H), 2.67 (s, 3H), 2.21 (s, 3H, cluster-CH_3). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 197.5, 144.8, 139.6, 136.1, 135.0, 130.9, 128.9, 127.4, 127.1, 77.3 (C_{cage}), 74.8 (C_{cage}), 40.7, 26.6, 23.6. ^{11}B NMR (proton decoupled): −4.08, −5.47, −10.0. IR (KBr): 3034, 2589, 1678, 1602, 1365, 1266, 958, 817 cm^{-1}. Anal. Calcd for $C_{18}H_{26}B_{10}O$: C, 58.99; H, 7.15. Found: C, 59.08; H, 7.03. ES-MS (*m*/*z*): calcd 366.5, found 365.1 (M − 1, 100%).

Ketone 4. Compound **2** (450 mg, 1.2 mmol) was dissolved in 10 mL of dry DMF. Then acetic anhydride (0.57 mL, 6 mmol), *i*-Pr_2NEt (0.42 mL, 2.4 mmol), LiCl (255 mg, 6 mmol), and $Pd_2(dba)_3$ (22 mg, 2 mol %) were added to this solution. The mixture was then heated at 100 °C for 20 h, quenched with water, and extracted three times with diethyl ether. The combined organic layer was dried over $MgSO_4$. After evaporation of the solvent the residue was purified by silica gel column chromatography with 5−15% ethyl acetate in hexane as eluent to obtain 250 mg of pure compound **4** as a colorless solid, yield 72%. Mp: 90 °C. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.95 (d, 2H, J = 6.85 Hz), 7.31 (d, 2H, J = 6.85 Hz), 3.53 (s, 2H), 2.62 (s, 3H), 2.19 (s, 3H, cluster-CH_3). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 197.4, 139.9, 136.7, 130.6, 128.6, 76.6 (C_{cage}), 74.9 (C_{cage}), 40.9, 26.6, 23.6. ^{11}B NMR (proton decoupled): −3.89, −5.50, −10.0. IR (KBr): 3005, 2944, 2599, 1673, 1608, 1417, 1359, 1271, 1020 cm^{-1}. Anal. Calcd for $C_{12}H_{22}B_{10}O$: C, 49.63; H, 7.64. Found: C, 49.61; H, 7.58. ES-MS (*m*/*z*): calcd 290.2, found 290.3 (M^+).

Ketone 9. Commercially available 4-(4-bromophenyl)acetophenone (**8**; 370.7 mg, 1.34 mmol) was dissolved in 40 mL of solvent (THF/toluene, 1/1). Then the carborane-appended boronic acid **7**[16] (750 mg, 2.56 mmol), $PdCl_2(PPh_3)_2$ (38 mg, 4 mol %), and a solution of K_2CO_3 (557.6 mg, 4.04 mmol) in 4 mL of distilled water were added to this solution. The reaction mixture was refluxed at 100 °C for 24 h and then quenched with water and extracted three times with dichloromethane. The combined organic layer was then dried over $MgSO_4$. After evaporation of solvent the crude product was purified by silica gel column chromatography with 5−40% ethyl acetate in hexanes as the eluent to obtain 450 mg of the pure product **9** as a colorless solid, yield 75%. Mp: 240 °C. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.0 (d, 2H, J = 8.24 Hz), 7.77−7.72 (m, 6H), 7.65 (d, 2H, J = 8.0 Hz), 7.31 (d, 2H, J = 8.0 Hz), 3.54 (s, 2H), 2.67 (s, 3H), 2.22 (s, 3H, cluster-CH_3). ^{13}C NMR ($CDCl_3$,

(41) (a) Rohr, U.; Schlichting, P.; Bohm, A.; Gross, M.; Meerholz, K.; Brauchhle, C.; Mullen, K. *Angew. Chem., Int. Ed.* **1998**, *37*, 1434–1437. (b) Ito, S.; Wehmeier, M.; Brand, J. D.; Kubel, C.; Epsch, R.; Rabe, J. P.; Mullen, K. *Chem. Eur. J.* **2000**, *6*, 4327–4342.

(42) Chen, J.; Anthony, J.; Martin, D. C. *J. Phys. Chem. B* **2006**, *110*, 16397–16403.

(43) (a) Kaszynski, P.; Pakhomov, S.; Tesh, K. F.; Young, V. G., Jr. *Inorg. Chem.* **2001**, *40*, 6622–6631. (b) Nagamine, T.; Januszko, A.; Kaszynski, P.; Ohta, K.; Yasuyuki, E. *J. Mater. Chem.* **2006**, *6*, 3836–3843. (c) Januszko, A.; Kaszynski, P.; Gruner, B. *Inorg. Chem.* **2007**, *46*, 6078–6082. (d) Kaszynski, P.; Douglas, A. G. *J. Organomet. Chem.* **1999**, *581*, 28–38.

125 MHz): δ 197.6, 145.1, 140.2,140.1, 138.9, 136.0, 134.3, 130.8, 128.9, 127.7, 127.6, 127.1, 127.0, 77.5 (C_{cage}), 74.8 (C_{cage}), 40.9, 26.6, 23.7. ^{11}B NMR (proton decoupled): −5.37, −9.99. IR (KBr): 3191, 2588, 1683, 1600, 1260, 1128, 809 cm^{-1}. Anal. Calcd for $C_{24}H_{30}B_{10}O$: C, 65.13; H, 6.83. Found: C, 65.0; H, 7.01. ES-MS (*m*/*z*): calcd 442.6, found 441.3 (M − 1, 100%).

Carboranyl Adduct 13. 1-Methyl-*o*-carborane (2.49, 15.80 mmol) was dissolved in 120 mL of dry THF. This solution was cooled to 0 °C, and BuLi (10.36 mL, 1.6 M solution in hexane) was added dropwise to it. Then it was stirred at 0 °C for 1 h and then cooled to −10 °C. At −10 °C, LiI (307.5 mg, 2.29 mmol) and compound **12** (2.8 g, 7.18 mmol) in 10 mL of dry THF were added dropwise to the reaction mixture. Then the reaction mixture was stirred for 30 min at same temperature and warmed to room temperature for 24 h. After completion of the reaction, the reaction mixture was filtered off through a silica gel pad and concentrated. After evaporation of the solvent, the residue was purified by silica gel column chromatography with 5−10% ethyl acetate in hexanes as the eluent to obtain 2.5 mg of pure compound **13** as a colorless solid, yield 64%. Mp: 165 °C. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.53 (s, 2H), 7.01 (s, 1H), 3.42 (s, 4H), 2.18 (s, 6H, cluster-CH_3). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 138.8, 137.3, 131.4, 94.1, 76.5 (C_{cage}), 74.8 (C_{cage}), 40.3, 23.6. ^{11}B NMR (proton decoupled): −5.39, −9.96. IR (KBr): 2944, 2584, 1567, 1437, 1020 cm^{-1}. Anal. Calcd for $C_{14}H_{33}B_{20}I$: C, 30.88; H, 6.11. Found: C, 30.69; H, 6.08.

Ketone 14. Compound **13** (300 mg, 0.55 mmol) was dissolved in 12 mL of solvent (THF/toluene, 1/1). Then 4-(acetylphenyl)boronic acid (180.6 mg, 1.101 mmol), $PdCl_2(PPh_3)_2$ (15.4 mg, 4 mol %), and a solution of K_2CO_3 (228 mg, 1.65 mmol) in 2 mL of distilled water were added to the solution. The mixture was refluxed at 100 °C for 24 h and then extracted three times with dichloromethane, and the combined organic layer was dried over $MgSO_4$. After evaporation of the solvent, the residue was purified by silica gel column chromatography with 40% ethyl acetate in hexanes as the eluent to obtain 270 mg of pure compound **14** as a colorless solid, yield 91%. Mp: 240 °C. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.0 (d, 2H, J = 7.8 Hz), 7.67 (d, 2H, J = 7.8 Hz), 7.41 (s, 2H), 7.06 (s, 1H), 3.56 (s, 4H), 2.68 (s, 3H), 2.23 (s, 6H, cluster-CH_3). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 197.3, 144.3, 140.9, 136.5, 136.2, 131.6, 129.0, 128.9, 127.3, 74.9 (C_{cage}), 60.3 (C_{cage}), 41.1, 26.6, 23.6. ^{11}B NMR (proton decoupled): −5.40, −9.94. IR (KBr): 2941, 2586, 1733, 1675, 1603, 1435, 1359, 1270, 1025, 957, 840 cm^{-1}. Anal. Calcd for $C_{22}H_{40}B_{20}O$: C, 49.23; H, 7.51. Found: C, 49.31; H, 7.54. ES-MS (*m*/*z*): calcd. 536.7, found: 536.6 (M^+, 100%).

Ketone 16. Compound **13** (490 mg, 0.9 mmol) was dissolved in 10 mL of dry DMF. Then acetic anhydride (0.43 mL, 4.5 mmol), *i*-Pr_2NEt (0.32 mL, 1.8 mmol), LiCl (191 mg, 4.5 mmol), and $Pd_2(dba)_3$ (16.5 mg, 2 mol %) were added to the solution. It was heated at 100 °C for 20 h and then quenched with water, and the reaction mixture was extracted three times with diethyl ether. The combined organic layer was dried over $MgSO_4$. After evaporation of the solvent the residue was purified by silica gel column chromatography with 30% ethyl acetate in hexane as eluent to obtain 400 mg of pure compound **16** as a colorless solid, yield 96%. Mp: 185 °C. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.76 (s, 2H), 7.25 (s, 1H), 3.56 (s, 4H), 2.66 (s, 3H), 2.12 (s, 6H, cluster-CH_3). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 196.8, 137.8, 136.3, 136.2, 129.7, 76.5 (C_{cage}), 74.9 (C_{cage}), 40.8, 26.6, 23.7. ^{11}B NMR (proton decoupled): −4.34, −8.93, −11.10. IR (KBr): 2944, 2585, 2351, 1703, 1603, 1448, 1360, 1293, 1210 cm^{-1}. Anal. Calcd for $C_{16}H_{36}B_{20}O$: C, 41.72; H, 7.88. Found: C, 41.67; H, 7.89. ES-MS (*m*/*z*): calcd 460.6764, found 461.5 (M^+ + 1).

Ketone 22. The TBDMS-protected *o*-carborane **18** was prepared as per the reported procedure.[17] A solution of **18** (4 g, 15.48 mmol) in 60 mL of dry THF at 0 °C was treated with *n*-BuLi (1.6 M solution in hexane, 10.2 mL, 16.25 mmol). The solution was stirred at 0 °C for 30 min at room temperature. Then a solution of 1-iodoheptane (3.67 g, 16.25 mmol) in 5 mL of THF was added at 0 °C and the resulting reaction mixture was stirred at room temperature for 2 h and refluxed for 3 h. After removal of solvent the product was purified by silica gel column chromatography with 5−10% ethyl acetate in hexanes as the eluent to obtain a quantitative 5.5 g of pure compound **19** as an oil. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 2.20−2.17 (m, 2H), 1.56−1.53 (m, 2H), 1.27 (br, s, 8H), 1.08 (s, 9H), 0.90 (br, s, 3H), 0.34 (s, 6H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 81.8, 76.2, 38.0, 31.5, 30.17, 29.16, 28.8, 27.57, 22.5, 20.3, 13.9, −2.4. Compound **19** (5.5 g, 15.42 mmol) was then solubilized in 40 mL of THF. It was cooled to −78 °C, and a 1 M solution of tetrabutylammonium fluoride in THF (32 mL, 32 mmol) was added to it at the same temperature over 10 min; this mixture was then warmed to room temperature and stirred at room temperature for 30 min. Water was added, and the reaction mixture was extracted with diethyl ether. Removal of the solvent and purification by column chromatography using hexane gave 3.5 g of the pure product **20** as a colorless oil, yield 94%. Compound **20** (600 mg, 2.475 mmol) was dissolved in 25 mL of DME, and to this solution was added *n*-BuLi (1.6 M solution in hexane, 1.7 mL, 2.72 mmol) at 0 °C. This mixture was then stirred at 0 °C for 1 h, and a solution of 4-iodobenzyl bromide (598 mg, 1.98 mmol) in 5 mL of dry DME was added to it at 0 °C; then it was refluxed at 90 °C for 24 h, after which the reaction mixture was cooled to room temperature and filtered over a silica gel pad. Removal of solvent and purification of the compound by silica gel column chromatography using hexane as the eluent resulted in 705 mg of pure compound **21** as an oily liquid, yield 62%. ^{1}H NMR ($CDCl_3$, 200 MHz): δ 7.72 (d, 2H, J = 8.17), 6.97 (d, 2H, J = 8.17), 3.41 (s, 2H), 2.29−2.19 (m, 2H), 1.59−1.48 (m, 2H), 1.29 (br, s, 8H), 0.94 (t, 3H). Compound **21** (130 mg, 0.282 mmol), $Pd_2(dba)_3$ (5.16 mg, 2 mol %), and LiCl (60 mg) were dissolved in 2 mL of dry DMF. Then acetic anhydride (0.13 mL, 1.414 mmol) and *i*-Pr_2NEt (0.098 mL, 0.564 mmol) were added to this solution. The mixture was then stirred at 100 °C for 20 h. After this mixture was cooled to room temperature, it was filtered over a silica gel pad and then water was added. This mixture was then extracted with diethyl ether. The combined organic layer was dried with $MgSO_4$. After evaporation of the solvent the residue was purified by column chromatography with 30% ethyl acetate in hexane to obtain 80 mg of pure product **22** as a colorless oil, yield 76%. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.96 (d, 2H, J = 8.15 Hz), 7.31 (d, 2H, J = 8.15 Hz), 3.51 (s, 2H), 2.63 (s, 3H), 2.36−2.32 (m, 2H), 1.64−1.62 (m, 2H), 1.36−1.32 (m, 8H), 0.92 (t, 3H, J = 7.0 Hz). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 197.3, 140.0, 136.7, 130.6, 128.5, 80.1, 78.1, 40.6, 35.6, 31.6, 29.8, 29.2, 28.8, 26.6, 22.5, 14.0. ^{11}B NMR (proton decoupled): −4.49, −10.25. IR (neat): 2957, 2928, 2856, 2580, 1685, 1609, 1264, 1012 cm^{-1}. Anal. Calcd for $C_{18}H_{34}B_{10}O$: C, 57.52; H, 9.15. Found: C, 57.50; H, 9.11. ES-MS (*m*/*z*): calcd 374.57, found 375.37 (M^+ + 1).

General Procedure for Trimerization of Ketones. Carborane-appended aryl ketones were dissolved in the required amounts of solvent (dry absolute ethanol/toluene, 1/1). Then $SiCl_4$ was added to the solution and the reaction mixture was stirred at room temperature to 50 °C for 10−24 h. The reaction mixture was quenched with water and extracted three times with dichloromethane. The combined organic layer was dried with $MgSO_4$. After evaporation of the solvent the crude product was purified by silica gel column chromatography.

Trimer 5. Ketone **4** (170 mg, 0.58 mmol) was solubilized in 5 mL of solvent (absolute ethanol/toluene 3/1). Then $SiCl_4$ (0.67 mL, 5.8 mmol) of was added to the solution at room temperature, and this mixture was then stirred at room temperature for 10 h. Purification of the compound with silica gel column chromatography with 5 −15% ethyl acetate in hexanes as eluent resulted in 120 mg of the pure product **5** as a colorless solid, yield 75%. Mp: >260 °C. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.81 (s, 3H), 7.70 (d, 6H, J = 8.0 Hz), 7.33 (d, 6H, J = 8.0 Hz), 3.56 (s, 6H), 2.23 (s, 9H, cluster-CH_3). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 141.6, 140.7, 134.4, 130.8, 127.5, 125.2, 77.5 (C_{cage}), 74.8 (C_{cage}), 40.9, 23.7. ^{11}B NMR (proton decoupled): −5.43, −10.0. IR (KBr): 3033, 2925, 2853, 2581, 1598,

1512, 1261, 1020, 810 cm^{-1}. Anal. Calcd for $C_{36}H_{60}B_{30}$: C, 52.91; H, 7.40. Found: C, 53.03; H, 7.33. MALDI-TOF-MS (*m*/*z*): calcd 817.19, found 817.78 (M^+, 100%).

Trimer 6. Ketone **3** (480 mg, 1.31 mmol) was dissolved in 24 mL of solvent (absolute ethanol/toluene, 3/1). Then $SiCl_4$ (4.5 mL, 39.29 mmol) was added to the solution at room temperature, and this mixture was then stirred at 40 °C for 24 h. Purification of the compound with silica gel column chromatography with 5 −20% ethyl acetate in hexanes as eluent resulted in 280 mg of the pure product **6** as a colorless solid, yield 61%. Mp: >260 °C. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.92 (s, 3H), 7.85 (d, 6H, J = 8.10 Hz), 7.76 (d, 6H, J = 8.10 Hz), 7.68 (d, 6H, J = 8.0 Hz), 7.32 (d, 6H, J = 8.0 Hz), 3.55 (s, 6H), 2.23 (s, 9H, cluster-CH_3). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 141.9, 140.3, 140.2, 139.6, 134.2, 130.8, 127.8, 127.5, 127.1, 125.0, 77.5 (C_{cage}), 74.8 (C_{cage}), 40.9, 23.7. ^{11}B NMR (proton decoupled): −5.45, −10.1. IR (KBr): 3029, 2580, 1589, 1504, 1387, 812 cm^{-1}. Anal. Calcd for $C_{54}H_{72}B_{30}$: C, 62.04; H, 6.94. Found: C, 62.11; H, 7.03. MALDI-TOF-MS (*m*/*z*): calcd 1045.47, found 1044.48 (M − 1, 100%).

Trimer 10. Ketone **9** (410 mg, 0.926 mmol) was dissolved in 50 mL of solvent (absolute ethanol/toluene 3/1). Then $SiCl_4$ (10.6 mL, 92.6 mmol) was added to the solution at room temperature, and this mixture was then stirred at 50 °C for 24 h. Purification of the compound with silica gel column chromatography with 5 −30% ethyl acetate in hexanes as eluent resulted in 118 mg of the pure product **10** as a colorless solid, yield 30%. Mp: >260 °C. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.94 (s, 3H), 7.86 (d, 6H, J = 8.0 Hz), 7.83−7.78 (m, 12H), 7.74 (d, 6H, J = 8.0 Hz), 7.66 (d, 6H, J = 7.7 Hz), 7.31 (d, 6H, J = 7.7 Hz), 3.55 (s, 6H), 2.22 (s, 9H, cluster-CH_3). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 141.9, 140.3, 140.1, 139.8, 139.7, 139.3, 134.1, 130.8, 127.8, 127.5, 127.1, 125.0, 77.5 (C_{cage}), 74.8 (C_{cage}), 40.9, 23.7. ^{11}B NMR (proton decoupled): −9.0, −11.25. IR (KBr): 3028, 2924, 2583, 1906, 1595, 1492, 819 cm^{-1}. Anal. Calcd for $C_{72}H_{84}B_{30}$: C, 67.89; H, 6.65. Found: C, 67.92; H, 6.63. MALDI-TOF-MS (*m*/*z*): calcd 1273.76, found 1273.48 (M^+, 100%).

Trimer 15. Ketone **14** (260 mg, 0.484 mmol) was solubilized in 15 mL of solvent (absolute ethanol/toluene, 3/1). Then $SiCl_4$ (2.8 mL, 24.2 mmol) was added to the solution at room temperature, and this mixture was then stirred at 45 °C for 24 h. Purification of the compound with silica gel column chromatography with 50% ethyl acetate in hexanes as eluent resulted in 100 mg of the pure product **15** as a colorless solid, yield 40%. Mp: >260 °C. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.93 (s, 3H), 7.87 (d, 6H, J = 7.2 Hz), 7.73 (d, 6H, J = 7.2 Hz), 7.47 (s, 6H), 7.0 (s, 3H), 3.59 (s, 12H), 2.24 (s, 18H, cluster-CH_3). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 141.9, 141.6, 140.6, 139.3, 136.1, 130.9, 128.8, 127.9, 127.7, 125.2, 77.1 (C_{cage}), 74.9 (C_{cage}), 41.2, 23.7. ^{11}B NMR (proton decoupled): −5.59, −9.95. IR (KBr): 3026, 2942, 2585, 1601, 1518, 1455, 1386, 1035, 830 cm^{-1}. Anal. Calcd for $C_{66}H_{114}B_{60}$: C, 50.94; H, 7.38. Found: C, 50.82; H, 7.20. MALDI-TOF-MS (*m*/*z*): calcd 1556.27, found 1555.46 (M^+ − 1, 100%).

Trimer 17. Ketone **16** (470 mg, 1.02 mmol) was dissolved in 40 mL of solvent (absolute ethanol/toluene, 3/1). Then $SiCl_4$ (9.3 mL, 81.6 mmol) was added to the solution at room temperature, and this mixture was then stirred at 40 °C for 24 h. Purification of the compound with silica gel column chromatography with 20−25% ethyl acetate in hexanes as eluent resulted in 250 mg of the pure product **17** as a colorless solid, yield 55%. Mp: >260 °C. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.74 (s, 3H), 7.52 (s, 6H), 7.11 (s, 3H), 3.60 (s, 12H), 2.24 (s, 18H, cluster-CH_3). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 141.4, 136.4, 131.4, 128.8, 125.5, 76.4 (C_{cage}), 75.0 (C_{cage}), 41.1, 23.7. ^{11}B NMR (proton decoupled): −0.81, −5.21. IR (KBr): 2994, 2942, 2857, 2593 1593, 1449, 1387, 1328, 1027, 867 cm^{-1}. Anal. Calcd for $C_{48}H_{102}B_{60}$: C, 43.41; H, 7.74. Found: C, 43.46; H, 7.61. MALDI-TOF-MS (*m*/*z*): calcd 1327.98, found 1328.5 (M^+ + 1, 100%).

Trimer 23. Ketone **22** (80 mg, 0.213 mmol) was dissolved in 4 mL of dry absolute ethanol. The solution was cooled to 0 °C, and then $SiCl_4$ (0.49 mL, 4.27 mmol) was added to it. This mixture was then stirred at room temperature for 5 h. Then the reaction was quenched with water and the mixture extracted three times with dichloromethane. The combined organic layer was dried with $MgSO_4$. After evaporation of the solvent the residue was purified by silica gel column chromatography using 20−25% ethyl acetate in hexane to obtain 40 mg of the pure product **23** as a colorless solid, yield 50%. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.80 (s, 3H), 7.70 (d, 6H, J = 8.0 Hz), 7.32 (d, 6H, J = 8.0 Hz), 3.53 (s, 6H), 2.39−2.36 (m, 6H), 1.65−1.56 (m, 6H), 1.38−1.28 (m, 24H), 0.92 (t, 9H, J = 7.0 Hz). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 141.6, 140.6, 134.4, 130.8, 127.4, 125.2, 80.1, 79.0, 40.6, 35.6, 31.6, 29.8, 29.3, 28.9, 22.5, 14.0. ^{11}B NMR (proton decoupled): −4.76, −10.0. IR (KBr): 2925, 2859, 2591, 1511, 1397, 1023, 808 cm^{-1}. Anal. Calcd for $C_{54}H_{96}B_{30}$: C, 60.63; H, 9.05. Found: C, 60.58; H, 9.11. MALDI-TOF-MS (*m*/*z*): calcd 1069.67, found 1069.68 (M^+, 100%).

General Procedure for Deboronation (Decapitation) of *o*-Carborane Clusters Present in Trimers. NaOH was solubilized by stirring it in 5−10 mL of dry methanol. Then a solution of trimers in about 3−5 mL of THF was added to the solution and the reaction mixture was refluxed at 90 °C for 20 h. After that time the excess NaOH was neutralized by adding a few pieces of dry ice, and then the precipitate was filtered off over a frit. Evaporation of the solvent led to a white solid which was characterized without further purification.

Decapitated Ttrimer 24. Trimer **6** (150 mg, 0.143 mmol) and NaOH (274 mg, 6.86 mmol) gave 140 mg of the colorless solid **24**, which was water-soluble. Yield: 90%. Mp: > 260 °C. ^{1}H NMR (CD_3CN, 500 MHz): δ 8.05 (s, 3H), 7.98 (d, 6H, J = 8.0 Hz), 7.85 (d, 6H, J = 8.1 Hz), 7.7 (d, 6H, J = 8.0 Hz), 7.45 (d, 6H, J = 7.85 Hz), 3.31 (s, 6H), 2.18 (s, 9H, cluster-CH_3), −2.4 (br, cluster-bridge 3H). ^{13}C NMR (CD_3CN, 125 MHz): δ 142.5, 142.0, 140.5, 139.4, 137.2, 129.2, 127.2, 126.9, 125.7, 124.0, 62.0 (br, C_{cage}), 54.6 (br, C_{cage}), 41.7, 21.8.^{11}B NMR (proton decoupled): −9.4, −16.4, −19.8, −34.6, −36.7. IR (KBr): 2984, 2950, 2862, 2516 (B−H), 2014 (B−H−B), 1627, 1473, 1371, 1099, 825 cm^{-1}. Anal. Calcd for $C_{54}H_{72}B_{27}Na_3$: C, 59.94; H, 6.71. Found: C, 59.89; H, 6.70. MALDI-TOF-MS (*m*/*z*): calcd 1082.01, found 1010.76 (M^+ − 3Na − 3H).

Decapitated Trimer 25. Trimer **15** (100 mg, 0.064 mmol) and NaOH (139 mg, 3.47 mmol) gave 90 mg of the colorless solid **25**, which was water-soluble. Yield: 86%. Mp: > 260 °C. ^{1}H NMR (CD_3CN, 200 MHz): δ 8.13 (s, 3H), 8.07 (d, 2H, J = 8.21), 7.91 (d, 2H, J = 8.16), 7.59 (s, 3H), 7.17(s, 2H), 3.21 (s, 12H), 2.22 (s, 18H, cluster-CH_3), −2.28 (br, cluster-bridge 6H). ^{13}C NMR (CD_3CN, 125 MHz): δ 143.5, 141.8, 141.2, 139.5, 139.1, 129.0, 127.9, 127.3, 124.7, 62.3 (br, C_{cage}), 54.8 (br, C_{cage}), 41.9, 22.3. ^{11}B NMR (proton decoupled): −9.4, −16.4, −19.7, −34.5, −36.7. IR (KBr): 3015, 2951, 2862, 2517 (B−H), 2013 (B−H−B), 1631, 1473, 1376, 1099 cm^{-1}. Anal. Calcd for $C_{66}H_{114}B_{54}Na_6$: C, 48.65; H, 7.05. Found: C, 48.43; H, 7.22. MALDI-TOF-MS (*m*/*z*): calcd 1629.34, found 1537.62 (M^+ − 4Na).

Decapitated Trimer 26. Trimer **10** (140 mg, 0.11 mmol) and NaOH (211 mg, 5.2 mmol) gave 120 mg of the colorless solid **26**, which was water-soluble. Yield: 83%. Mp: > 260 °C. ^{1}H NMR (CD_3CN, 500 MHz): δ 8.08 (s, 3H), 8.03−7.99 (m, 6H), 7.92−7.82 (m, 12H), 7.78−7.76 (m, 6H), 7.69−7.64 (m, 6H), 7.45−7.44 (m, 6H), 3.19 (s, 6H), 2.20 (s, 9H, cluster-CH_3), −2.4 (br, cluster-bridge 3H). ^{13}C NMR (CD_3CN, 125 MHz): δ 142.8, 141.7, 140.1, 139.6, 138.6, 137.0, 129.3, 129.2, 127.3, 126.8, 125.6, 124.7, 61.4 (br, C_{cage}), 54.6 (br, C_{cage}), 41.7, 21.8. ^{11}B NMR (proton decoupled): −9.7, −16.5, −19.8, −34.4, −36.4. IR (KBr): 2984, 2952, 2863, 2520 (B−H), 2002 (B−H−B), 1632, 1472, 1376, 1192, 1099 cm^{-1}. Anal. Calcd for $C_{72}H_{84}B_{27}Na_3$: C, 66.00; H, 6.46. Found: C, 65.94; H, 6.42. MALDI-TOF-MS (*m*/*z*): calcd 1310.30, found 1216.62 (M^+ − 3Na − 3BH).

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Supporting Information Available: Text and figures giving synthetic procedures and characterization data for controls **A** and **B** and NMR spectra of the compounds prepared in this paper. This material is available free of charge via the Internet at http://pubs.acs.org.

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